KINETIC AND OTHER STUDIES OF DI- AND TRI-ARYLMETHYL COMPOUNDS.

by

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Bedford College is thanked for the provision of research facilities and of a Tutorial Research Studentship.
To my parents........
Abstract.

The steric requirements of the three aromatic rings in the triphenylmethyl radical impose non-planarity upon the system, and a three-bladed propeller shape, where the blades are slightly feathered out of plane is thought to be a good approximation to the actual structure. Such a species, in appropriate circumstances could in principle exist in two geometric modifications, termed a symmetrical helix and an unsymmetrical helix.

The isolation of a triarylmethyl derivative in an optically active modification, which possesses two identical aromatic rings, and retains its optical properties upon conversion to a free radical, would provide support for this conception.

Accordingly, tri-1,1',1''-naphthylmethanol, some 4-substituted tri-1,1',1''-naphthylmethanols and 5-dimethylamino-tri-2,2',2''-tolylmethanol were prepared.

With the objective of preparing triarylmethyl chlorides from which a radical should be accessible, the behaviour of these alcohols with some acid chlorides was studied. However, triarylmethyl chlorides were not isolated as dehydration processes seemed to predominate.

The publication of evidence against the hexaphenylethane formulation for the triphenylmethyl radical dimer, suggested that a quantitative investigation of the effects of crowding upon polyarylmethyl systems would be of interest. The measurement of rate coefficients for formation of polyarylmethyl carbonium ions from their respective chlorides is a convenient way to achieve this.

The diphenylmethyl skeleton was studied, and variations in the extent of crowding of the central carbon atom were achieved by the successive replacement of the four ortho- hydrogen atoms by methyl groups.
The preparation and measurement of rates of ethanolyis of

diphenylmethyl, 2-methylidiphenylmethyl, 2,2'-dimethylidiphenylmethyl
2,6-dimethyldiphenylmethyl, 2,2',6-trimethyldiphenylmethyl and
2,2',6,6'-tetramethyldiphenylmethyl chlorides were carried out.
The results showed the intervention of a large steric acceleration
to ethanolyis with the two most highly substituted molecules.

The mode of transmission of electronic effects through aromatic
systems with different dihedral angles was also studied by
investigating the stabilisation imparted by 4-methyl and
4-t-butyl groups in the systems diphenylmethyl, 2,6-dimethyldiphenylmethyl and 2,2',6-trimethyldiphenylmethyl. The results
indicate that the predominant contributor to the activation
produced by these groups is $\pi$-electron-transmitted, probably a
hyperconjugative interaction. Steric inhibition of the
hyperconjugation is also demonstrated.
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References
A.1. Homolysis and heterolysis.

In 1916 G.N. Lewis introduced the concept of the electron pair or covalent bond. It had been clear for some years that simple electrostatics could yield only a portion of the valence picture. The Lewis proposal was that "one or more electron pairs shared by two atoms could bind them together". Such a covalent bond is formed by the pairing of electrons with opposite spins, and it can be shown by wave mechanical calculations that such an electron pair is a stable arrangement, its formation being accompanied by a decrease in energy of the system. In order to break such a bond, energy in the form of heat, light or other forms of electromagnetic radiation must be supplied to the system.

In 1938 Ingold\(^1\) distinguished two general modes of fission of covalent bonds, referred to as 'homolysis' and 'heterolysis'.

\[
\begin{align*}
\text{Homolysis} & \quad A:B \rightarrow A^* + B^* \\
\text{Heterolysis} & \quad A:B \rightarrow A^+ + B^{-}
\end{align*}
\]

From estimates of the energetics of the two processes, it is deduced that homolysis is the more favoured mechanism since the separation of the ions formed by heterolysis requires the provision of additional energy in order to overcome coulombic forces. Free radicals which possess unpaired electrons are formally uncharged and require no such additional energy. This simple argument ignores the possible interaction of the molecules comprising the reaction environment with the reactant molecules. For reactions conducted in the gas phase these interactions are unimportant due to the large intermolecular
distances, and under these conditions homolysis is the more common mode of fission. When a reaction is carried out in solution in a good ionising solvent, however, ions formed by heterolysis become associated with solvent molecules, a process (solvation) which increases the stability of the system and often more than compensates for the coulombic attraction of the ions. In solution therefore, heterolysis can and commonly does compete successfully with homolysis.

A.2. Free radicals.

A.2.(a). Definition.

A free radical may be defined as a species possessing one or more unpaired electrons. This definition includes such inorganic species as nitric oxide and the halogen atoms. Transition metal ions like Cr$^{3+}$ although possessing unpaired electrons are not generally referred to as free radicals, although they do possess some properties in common with free radicals, like their ability to catalyse the conversion of para-hydrogen to ortho-hydrogen.

A.2.(b). Short lived and long lived free radicals.

It is convenient to divide free radicals into two categories, long lived radicals and short lived radicals. This division is completely arbitrary and is based upon the concept of stability outlined below.

The stability of a free radical depends upon the chemical circumstances. For example, the methyl radical can be kept almost indefinitely in an argon matrix at very low temperature, although it reacts irreversibly with some species upon warming the matrix. In the gas phase hydroperoxyl radicals are 'stable' compared with hydroxyl radicals. On the other hand diphenylpicrylhydrazyl (DPPH) is capable of existing permanently
in the solid state as a free radical: it can be crystallised, isolated and treated as a normal organic compound, although in the presence of other organic radicals it usually reacts rapidly with them.

In order to define stability, it is necessary to define not only the time scale but also the environment of a radical, and a long lived radical is defined as one which can be prepared by conventional methods and will exist long enough to be used in subsequent chemical reactions, or be examined in a static system by the normal methods of spectroscopy. This limitation prescribes a lifetime of the order of a few minutes. In terms of environment, the radicals must be in contact with one another, either by the normal processes of collision in the liquid phase or in the solid state. The medium surrounding the radicals must be inert; this refers to solvent if the radical is in solution and to the atmosphere.

Examples of long lived radicals are triarylmethyl radicals, oxygen radicals such as the tri-t-butylphenoxy- radical, and nitrogen radicals such as diphenylpicrylhydrazyl which has no associated dimer and is used as a radical scavenger.

Examples of short lived radicals are phenyl and methyl radicals which are not stabilised by delocalisation of the unpaired electron.

This thesis will be concerned with long lived radicals of the di- and tri-arylmethyl type.

A.2.(c). Evidence for the existence of free radicals.

The existence of free radicals was first demonstrated by Gomberg\textsuperscript{2,3} by his work on the dissociation of the dimers of triarylmethyl radicals. The presence of long lived radicals may be demonstrated in several ways.

1) Magnetic methods.
Ordinary organic compounds are diamagnetic; when they are
placed in a magnetic field, small currents are set up in the
filled molecular orbitals. These currents are associated with
induced magnetic fields opposite in direction to the applied
field. As a result, the sample tends to be pushed out of the
applied field. Paramagnetic materials, like free radicals
which possess unpaired electrons, are pulled into the applied
field, despite a push deriving from the diamagnetic filled
orbitals which is generally small in comparison to the para-
magnetic contribution.

2) Electron spin resonance (ESR) spectroscopy.

A magnetic moment which can be expressed by a quantum number
of +1/2 or -1/2 is associated with the spin of an electron.
According to the Pauli exclusion principle, the two electrons
in a filled molecular orbital must possess opposite spins, i.e.,
possess different spin quantum numbers, so that the total
magnetic moment is zero for any two electrons occupying the
same region of space. In the presence of an applied magnetic
field, the unpaired electron of a paramagnetic material may
align its spin so that it either reinforces or opposes the
applied field. These two orientations differ in energy by
an amount proportional to the applied field, and if energy is
applied to the system, translation from one orientation to the
other may occur with the absorption of energy. The observed
absorption bands have fine structure, that is they are composed
of two or more thin bands lying very close together. This
splitting arises from interactions between the spin of the
unpaired electron and the spins of one or more nuclei. Analysis
of fine structure can yield information about the extent to
which an electron is localised on a particular atom.

3) Miscellaneous methods.

The degrees of dissociation of some hydrocarbons have been
evaluated by cryoscopic measurements of their apparent molecular weights. These results are usually very approximate in nature.

For systems in which the free radicals are coloured, colorimetric methods have been applied.\(^4,5\)

Evidence for the existence of short lived radicals was first indicated by Paneth, who studied the thermal decompositions of certain volatile organometallic compounds like tetramethyl-lead in an inert gas stream through a glass tube, a small portion of which had been coated with a mirror of zinc, antimony or lead. No appreciable reaction occurred in the absence of heat, but if a small area of the tube was vigorously heated so the molecules of the substrate passed through the hot zone before reaching the mirror, a new metallic mirror was deposited upon the inside of the tube at the point of heating. More significantly, the gaseous decomposition products were found to remove the original mirror as they passed over it, although neither the carrier gas nor the stable final decomposition products could do this. Moreover, this mirror disappeared most rapidly when it was situated very close to the point of heating. It was thus inferred that the decomposition of the organometallic compound yielded the parent metal and free alkyl radicals, and that these radicals reacted with the original mirror converting it to a volatile organometallic compound, which could be isolated by condensing the emergent gases.

However, if the mirror was removed far from the site of heating most of the radicals produced dimerised before reaching the mirror, and removal was slow.

The Paneth technique is not applied to reactions in solution, but there are many substances known which react with short lived radicals in solution. Among these is diphenylpicryl-
hydrazyl, whose consumption may be followed by the fading of its characteristic violet colour, and ferric chloride, which often transfers chlorine atoms to active free radicals yielding the readily titratable ferrous ions.

Chemical detection is of course only possible if the test reaction proceeds at a faster, or at least comparable rate to that of the alternative reaction of the radicals (e.g. dimerisation).

E.S.R. is perhaps the most generally applicable technique for the detection of short lived free radicals. Radical concentrations as small as $10^{-7}$ molar have been detected.

For reactions in which short lived free radicals are generated as transient intermediates, their participation in the reaction can sometimes be deduced from the complex kinetics displayed by the process, and by detailed analysis of the reaction products.?

A.2.(d). General factors which contribute to the stabilities of free radicals.

These are most easily discussed by reference to a particular system, for example, the dissociation of the hydrocarbon $R\rightarrow R'$.

It is theoretically possible to calculate the thermodynamic properties of such a system using statistical thermodynamics if the rotational and vibrational partition functions are known.

$$
\frac{k_1}{k^{-1}} \quad R \rightarrow R' \quad R^* + R'^* \quad \text{-----}(1)
$$

This requires a complete vibrational analysis of the molecule using spectral data, a task which is clearly impossible for complex molecules. The thermodynamics of the dissociation must be obtained from experimental measurements.
When equilibrium has been reached in reaction (1), the free energy change of the system at constant pressure \((\Delta G)\) is zero, but the extent of the reaction or the degree of dissociation of the hydrocarbon, depends upon the enthalpy and the entropy changes of the reaction. \(\Delta H\) is the difference between the activation energies for the forward and backward reactions and 
\[
\Delta S = R \ln\left(\frac{A_1}{A_{-1}}\right),
\]
where \(A_1\) and \(A_{-1}\) are the pre-exponential factors of the rate equations (1) and (-1).

With the usual assumption that the activation energy for the radical recombination reaction is zero, the heat of reaction (1) is to a first approximation, the dissociation energy of the carbon-carbon bond, and is thus an important factor in determining the stability of the radical. The value \(\Delta H\) can be obtained by measurement of the equilibrium constant for a reaction at two different temperatures \(T_\beta\) and \(T_\alpha\).

\[
-\Delta H = R(\frac{1}{T_\beta} - \frac{1}{T_\alpha})^{-1} \ln\left(\frac{K_\beta}{K_\alpha}\right).
\]

The lower the value of \(\Delta H\), the further the equilibrium lies to the right, and the more stable the radical towards dimerisation.

The expected value for the pre-exponential factor 'A' in a unimolecular decomposition is about \(10^{13}\) sec.\(^{-1}\), i.e., approximately the stretching frequency of the bond being broken, and the total entropy change corresponding to the equilibrium (1) can be readily calculated, and thus the 'A' factor for the reverse reaction. Occasionally the 'A' factors in unimolecular decompositions are abnormally high and then, by the principle of microscopic reversibility, so are the 'A' factors for the radical recombination reaction. This state is usually ascribed to a loosening of the molecule in the transition state, allowing the two parts to rotate and vibrate about the bond being broken.
These high 'A' factors are found in the decomposition of certain symmetrical tetraphenylalkylalkanes.8

Several factors contribute to the strengths of covalent bonds which are formed by the pairing of two electrons in the overlap of two singly occupied orbitals. If the atoms being joined have different electronegativities, then the bond strength may be increased by electrostatic attraction. The wide differences in the strengths of carbon-carbon bonds, where the bond polarity is usually small, indicate that other factors are involved.

One such factor is the change in hybridisation that usually occurs on the rupture of a carbon-carbon bond: for example, in the dissociation of n-butane to ethyl radicals the bond which is broken is formed by the overlap of two sp\(^3\) hybrids, but in the ethyl radical the unpaired electron is in a \('p'\ orbital, and the carbon atom has changed its hybridisation to sp\(^2\).\(^9\) This results in a small increase in the energy of the bond between the carbon atoms of the ethyl radical compared to the energy of the bond between these two atoms in n-butane. This energy is released during the breaking of the bond and contributes to the dissociation energy of the central carbon-carbon bond in n-butane. It should be noted however, that hybridisation changes do not always occur upon carbon-carbon bond rupture, for example, in the dissociation of the following, the unpaired electron of the radical remains in a sigma orbital.

\[
\begin{align*}
\text{Ar} & \quad \text{Ar} \\
\text{CH}_2=\text{CH}-\text{CH}=\text{CH}_2 & \quad \rightarrow \quad 2\text{Ar}^* \\
\text{CH}_2=\text{CH}-\text{CH}=\text{CH}_2 & \quad \rightarrow \quad 2\text{CH}_2=\text{CH}^*
\end{align*}
\]

These are known as sigma radicals in contrast to the more common pi radicals, where the unpaired electron is situated in an orbital possessing pi symmetry.

The energy involved in the rearrangement of the bonding of
the radical is small, but a much larger effect occurs if the 'p' orbital containing the unpaired electron can overlap with a pi system in the remainder of the radical allowing delocalisation of the free electron. The bond dissociation energy $D$ of ethylbenzene is 72 kcal.mole$^{-1}$, a reduction of 16 kcal.mole$^{-1}$ compared to that of the carbon-carbon bond in ethane. The delocalisation energy of the benzyl radical compared to the methyl radical is thus 16 kcal.mole$^{-1}$.10

The delocalisation of an electron in a molecule is usually described in terms of mesomeric structures: for example, the benzyl radical can be formally represented in the following mesomeric or canonical structures which illustrate the delocalisation of the unpaired spin density over the radical. This reduces the free spin density at the side chain carbon atom and increases the stability of the radical in the sense that it is less likely than the methyl radical, for example, to abstract a hydrogen atom from another molecule. Increasing the possibility of delocalisation of the unpaired electron increases

1) the number of canonical structures, and hence
2) the resonance energy,
and so decreases the carbon-carbon bond dissociation energy.

A further factor which determines the strength of a chemical bond and hence the stability of the radicals obtained by its rupture, is the size and shape of the two parts of the molecule.
Much of the information on this steric effect has been obtained from studies of the dimers arising from polyarylmethyl radicals. These will be discussed in the next section (A.3.). Bulky groups not only weaken the central bond, making dissociation easier, but they also place an activation energy barrier in the way of radical recombination, which shifts the position of the equilibrium towards the monomer.

The work described in this thesis provides some quantitative results relating to the weakening of the carbon-chlorine bond produced by bulky ortho- substituents in diphenylmethy]l chlorides.

A.3. Dimers of triphenylmethyl radicals.

The discovery of the first stable free radical, triphenylmethyl, was reported by Gomberg\(^2,3\) in 1900. It was found that the triphenylmethyl radical dimer, a colourless solid, gave a yellow solution in various solvents. This coloration intensified upon heating a solution, and rapidly disappeared when contact was made between the solution and oxygen or halogens. It became evident that a reversible dissociation was taking place, and the formation of radicals which was originally deduced from chemical properties and molecular weight determinations, was later proved by magnetic susceptibility measurements and by E.S.R. spectroscopy.


As nearly all of these radicals exist in equilibrium with their dimers,

\[ 2\text{Ar}_3\text{C}^- \xrightarrow{\text{dimer}} \]

the preparations described below are actually procedures for preparing the dimers, which dissociate to varying degrees in
solution.

1) The reaction of a triarylmethyl halide with a metal, e.g., Zn, Mg or Ag.

\[ \text{Ar}_3\text{CCl} + \text{M}^+ \longrightarrow \text{Ar}_3\text{C}^- + \text{M}^+\text{Cl}^- \]

The reaction proceeds rapidly at room temperature upon shaking in a dry solvent (commonly benzene, although petrol, ether, acetone and ethyl acetate have been used). A variation on this method is the reaction of triphenylacetyl chloride with silver to give triphenylmethyl radicals and carbon monoxide.\(^{11}\)

\[ \text{Ph}_3\text{COCl} + \text{Ag} \longrightarrow \text{Ph}_3\text{C}^- + \text{CO} \]

2) Oxidation of a triarylmethyl carbanion with a triarylmethyl chloride or silver nitrate.\(^{12,13}\) e.g.,

\[ \text{Ar}_3\text{C}^- + \text{AgNO}_3 \longrightarrow \text{Ar}_3\text{C}^- + \text{Ag} + \text{NO}_3^- \]

3) Reduction of triarylmethyl halides and related carbonium salts, including the reduction of carbinols in acid media by the action of vanadous, titanous or chromous ions.\(^{14,15,16,17}\) e.g.

\[ \text{Ar}_3\text{COH} + \text{H}^+ \longrightarrow \text{Ar}_3\text{C}^+ \longrightarrow \text{Ar}_3\text{C}^- + \text{V}^{2+} \]

Recent examples are the preparation of perfluorotriphenylmethyl by the reduction of the carbinol with titanous chloride in acid solution\(^{18}\), and the synthesis of the radical (2)\(^{19}\) by reduction of the chloride (1) with chromous chloride in acetic acid-hydrochloric acid.
In the latter case the Gomberg method failed because of the insolubility of the starting materials in the usual solvents.

4) Miscellaneous methods.

Grignard reagents\textsuperscript{20,21}, and other organometallic reagents and carbenions\textsuperscript{22} have been used to reduce triarylmethyl halides and related perchlorates\textsuperscript{23}, but the reactions are complex as other radicals are formed in the process and the triarylmethyls tend to act as scavengers for the rest. These complications do not arise when the Grignard reagent is a triphenylmethylmagnesium halide.\textsuperscript{24}

\[
\text{Ar}_3\text{CCl} + \text{Ar}_3\text{MgBr} \longrightarrow \text{Ar}_3\text{C}^- + \text{Ar}_3\text{C}^- + \text{MgBrCl}
\]

Similar difficulties attend the Arbusov method\textsuperscript{25} which employs sodium diethyolphosphite as the reducing agent.

\[
\text{Ar}_3\text{CBr} + (\text{EtO})_2\text{PO}^-\text{Na}^+ \longrightarrow \text{Ar}_3\text{C}^- + (\text{EtO})_2\text{P}=\text{O} + \text{Na}^+\text{Br}^-
\]

Although good yields of triarylmethyl (isolated as the dimer or peroxide) have been reported, the method is not a reliable preparative route as on occasion exclusive formation of diethyl
triarylphosphonate may result.

The formation of triarylmethyls by physical methods has been frequently observed. In general, these reactions are not of preparative value. They commonly take the form of a homolytic dissociation into stable free radicals and a stable molecule.\textsuperscript{26,27,28,29.}

\begin{align*}
\text{Ph}_3\text{C.CO.O.CPh}_3 & \rightarrow 2\text{Ph}_3\text{C}^* + \text{CO}_2 \\
\text{Ph}_3\text{C-N=N-CPh}_3 & \rightarrow 2\text{Ph}_3\text{C}^* + \text{N}_2 \\
\text{Ph}_3\text{C.CO.O.}^\circ\text{Bu}^t & \rightarrow \text{Ph}_3\text{C}^* + \text{CO}_2 + \cdot\text{OBu}^t
\end{align*}

The tri-1,1',1''-naphthylmethyl free radical has not previously been prepared.

The tri-2,2',2''-tolylmethyl free radical has been obtained by classical methods\textsuperscript{33} but its optical resolution has not been accomplished.

A.3.(b). Chemical properties of triarylmethyls.

As might be expected, triarylmethyls are extremely reactive species. Only two reactions, dimerisation and disproportionation, will be considered here as they are particularly relevant to this thesis.

1) Dimerisation.

Triarylmethyl radicals exist in equilibrium with their dimers. The position of equilibrium or degree of dissociation of the dimer is governed chiefly by structural features, the principal contributing factors being steric strain in the dimer and mesomeric stabilisation of the monomer, both of which may be influenced by substitution. The relative importance of these two factors has been the subject of much discussion for a number of years, and attempts have been made\textsuperscript{30} to quantify the position
for the triphenylmethyl radical dimer. Such estimates are generally obtained from thermochemical data, and involve comparison between the heats of hydrogenation of ethane to methane and of hexaphenylethane to two molecules of triphenylmethane, which can give a measure of the importance of the steric strain factor in the dimer. Alternatively, comparison of the heats of dissociation of ethane and hexaphenylethane might give a measure of the contribution of resonance stabilisation of the monomer to the position of equilibrium. It has been shown recently that the substance obtained by evaporation of the solvent from a triphenylmethyl radical solution, does not in fact possess a hexaphenylethane structure. In the absence of an authentic sample of hexaphenylethane, the quantitative contributions of strain in the dimer and stabilisation of the monomer to the equilibrium is uncertain. However, qualitatively the operation of the two factors is illustrated in the examples given below.

Substitution of groups in ortho- positions in polyarylmethyl radicals reduces the extent of association markedly in comparison to the effect of meta- or para- substituents. For example, the dissociation constant for the 2-methyltriphenylmethyl dimer (in benzene at 25°) is 0.033 mole,1.1 whereas the figures for the corresponding 3- and 4-methyl isomers are 0.0018 and 0.0011 mole1.1 respectively. The tri-2,2',2''-tolylmethyl dimer is 87% dissociated (0.1M in benzene at 19°). Replacement of a phenyl group by a 2-naphthyl group, or better a 1-naphthyl group, promotes dissociation of the dimer even more. Conversely in diphenylmethyl radical dimers or in diphenylbifluorenyl (where two pairs of phenyl rings are held coplanar), steric repulsion is markedly reduced and the ease of dissociation rapidly falls off. In solution pentaphenylethane does not dissociate into radicals below 100° and 1,1,2,2-tetraphenylethane only
A solution of the dimesityl radical dimer in benzene on heating turns red and gives an E.S.R. spectrum consisting of two sets of lines separated by 24 gauss, showing splitting by the proton on the central carbon atom. Both the colour and the E.S.R. spectrum disappear upon cooling. Recent measurements on the absolute radical concentrations indicate that the 2,2',6,6'-tetramethyldiphenylmethyl radical dimer dissociates slightly in dilute solutions at room temperature, whilst the corresponding isopropyl compound is fully dissociated in meta-xylene above -60°. At room temperature these radicals rapidly disproportionate. In addition, one ortho-t-butyl group per benzene ring is sufficient to produce slight dissociation of the dimer. The dimer of 2,2',5,5'-tetra-t-butyldiphenylmethyl radical is completely dissociated in benzene at room temperature.

Substituents in the para-position also increase the degree of dissociation of radical dimers, an effect which can scarcely be attributed to their steric influences. For example, the degree of dissociation of the tri-4,4',4''-tolylmethyl radical dimer (0.1M in benzene at 25°) is 16%, whilst tri-4,4',4''-nitrotriphenylmethyl and tri-4,4',4''-phenyltriphenylmethyl radicals can be obtained as dark green crystals, and are largely, if not entirely, monomeric even in the solid state.

Irrespective of the structures of the radical dimers it is clear that the ability to delocalise the lone electron of the radical over the whole molecule is a major factor in promoting dissociation of dimers, and thermodynamic calculations support this view. The maximum possible mesomeric stabilisation will be obtained when the pi orbitals of the aromatic rings are coplanar with the 'p'orbital of the central
carbon atom. In reality in the triphenylmethyl system, non-bonded interactions between ortho-hydrogen atoms inhibit planar geometry and the maximum stabilisation is not achieved. The question of the configuration of the monomer will be discussed in section (A.3. (d)(3)). Increasing the sizes of the ortho-substituents increases deviations from complete planarity, and accordingly reduces even further the possibility of stabilisation for the radical. This statement is strikingly illustrated by reference to the tri-(2,6-dimethoxyphenyl)methyl system (3) which is completely dissociated even in the solid state, the angle of twist being about 50°. At the other extreme, the sesquixanthrydryl dimer (4) dissociates into radicals only to the extent of 1-2% upon heating (10^{-3}M in xylene at 140°C), and clearly, in this case the enhanced mesomeric stabilisation of the latter arising from planar geometry is more than offset by the decrease in steric interactions in the dimer.

\[ X = \text{OMe} \]

In contrast, the dimer of the radical (5), which cannot attain a completely planar structure because of steric interactions between the two remaining ortho-hydrogen atoms, appears to be largely dissociated both in solution and in the solid state.
2) Disproportionation.

Upon heating or exposure to visible light, triarylmethyls tend to disproportionate. This is particularly true of radicals containing primary or secondary alkyl groups. Triphenylmethyl itself undergoes an intramolecular cyclisation leading to fluorene derivatives.\(^{43,44}\) Upon exposure to visible light in non-polar solvents fairly rapid decolorisation is observed, and diphenylbifluorenyle (6) separates out, the other product being triphenylmethane. If the reaction is carried out in an alkaline dioxan solution 9-phenylfluorene (7) is obtained\(^ {45}\), and both the latter and its dehydrodimer (6) are found on photolysis of triphenylmethyl chloride.\(^ {46}\) The cyclic structure (8) seems to be a likely intermediate in these reactions, from which the dimer can be obtained via hydrogen abstraction, and the monomer (7) by an allylic shift especially in alkaline solution.
Methylated triarylmethyls are particularly prone to disproportionation. Because of the instability of the phenyl-di-2,2'-tolylmethyl radical it is necessary to handle it at temperatures below 10°. The tri-4,4',4''-tolylmethyl radical dimer gives an initial orange colour in benzene solution.
where fades over a period of a few hours at room temperature,
and magnetic susceptibility measurements indicate that radicals
are no longer present. The solution then contains tri-4,4',4''-tolylmethane and polymeric material very similar to that
obtained by treating tri-4,4',4''-tolylmethyl chloride with
pyridine, and suggests that disproportionation proceeds as
follows.\(^4\)

\[
\begin{align*}
\text{CH}_3 & \rightarrow (\text{p-tolyl})_3\text{CH} + \text{POLYMER} \\
\text{p-tolyl} & \quad \text{p-tolyl} \\
\text{p-tolyl} & \quad \text{p-tolyl}
\end{align*}
\]

A.2.(c). Structure of triphenylmethyl radical dimers.

The delocalisation depicted above in the triphenylmethyl
radical suggests that radical dimerisation might take place
at ortho- or para- positions. In principle therefore, a
variety of isomeric dimers might be expected to arise. For
example, representing the central carbon atom as C\(\alpha\) and the
ortho- and para- ring carbon atoms as C\(\alpha\), C\(\sigma\), and C\(\rho\), respectively,

\[
\underline{C_{\alpha} - C_{\alpha}}; \underline{C_{\alpha} - C_{\sigma}}; \underline{C_{\alpha} - C_{\rho}}; \underline{C_{\rho} - C_{\rho}} \quad \text{etc.}
\]

Furthermore, as the equilibrium process is being considered,
the amount of each dimer formed will be in relation to its
thermodynamic stability. On this basis dimers arising from
ortho- coupling would be expected to comprise only a small amount
of the total product, but coupling at para- positions might be
expected to occur to a significant extent, particularly if the
stability of a $C\alpha-C\alpha$ dimer became comparable to that of a $C\alpha-C\beta$ dimer. Such a situation could arise if, for example, crowding was extensive around the $C\alpha$ atom, which in addition to straining the molecule would create a large barrier to $C\alpha-C\alpha$ bond formation.

Prior to 1968 the vast majority of dimers which had been isolated were considered to be derivatives of ethane, i.e., arising from $C\alpha-C\alpha$ bond formation. However, the anomalous behaviour of several substituted triphenylmethyl chlorides had been known for some time. Some illustrative examples are given below.

When 4-bromotriphenylmethyl chloride is shaken with an excess of silver, the rapid loss of the chlorine atom from the molecule is followed by the slower abstraction of the nuclear bromine atom. This phenomenon can be interpreted in terms of the coupling of the primary radical (9) to form the reactive allyl bromide (10). This in turn reacts with silver to give the secondary radical (11) which can be identified by the isolation of its peroxide.

\begin{align*}
\text{(9)} & \quad \leftrightarrow \quad \text{(10)}
\end{align*}
The removal of fluorine from 4-fluorotriphenylmethyl chloride takes place much more slowly (less than 20% in 10 days, whereas bromine is removed to the extent of 50% in 3 days), but evidently fluorine attached to the allyl system of the analogue of (10) with fluorine instead of bromine is more reactive than in triphenylmethy fluoride, which is inert to silver.

Certain triarylmethlys are prone to dimerise unsymmetrically in the presence of a trace of acid. Upon treating triphenylmethyl radicals with hydrogen chloride, the predominant product is the dimer (13), and smaller amounts of triphenylmethyl chloride and triphenylmethane can be isolated. The reaction appears to be an electrophilic tritylation, as formulated below, and initiated by the formation of the stabilised radical cation (12). The hydrocarbon (13) was first prepared by the direct reduction of triphenylmethyl chloride under acidic conditions, and was naturally confused with the triphenylmethy radical dimer.
In addition the ethane formulation for the dimers failed to explain other important experimental observations, for example,

1) The stability of the tri(4-t-butylphenyl)methyl radical (14)\textsuperscript{55} and of the di(2,5-di-t-butylphenyl)methyl radical (15).\textsuperscript{56}

2) The effect of para-alkyl substituents in the di(2,6-dimethylphenyl)methyl radical (16): the introduction of one para-alkyl group being without effect, whereas, two para-alkyl groups cause almost complete inhibition of dimerisation.\textsuperscript{57}
In 1968 N.M.R. and ultra-violet spectral investigations showed that dimers, derived from substituted diphenylmethyl radicals and which exist in equilibrium with the monomers in solution, are not true ethanes at all, but are derivatives of methylenecyclohexadiene. Such structures would arise by \( C_\alpha - C_2 \) bond formation.
In contrast to these dimers, which were prepared by treatment of the corresponding chlorides with silver, the isomeric true tetraphenylethanes were prepared by reduction of the corresponding carbonium ions in acetone-hydrochloric acid solution, with \( \text{Ru}^{2+} \) or \( \text{Cr}^{2+} \) (structures (17')-(20')).

Unlike the unsymmetrical dimers these were found to be high melting and to dissociate only with difficulty into radicals. Isomerisation to the unsymmetrical dimers took place upon heating in an inert solvent.

The dimer obtained by shaking triphenylmethyl chloride with molecular silver in carbon tetrachloride, also appeared to be 1-diphenylmethylene-4-triphenylmethyl-2,5-cyclohexadiene (21) rather than hexaphenylethane.

In support of this assignment of an unsymmetrical structure for the triphenylmethyl radical dimer is the observation that

\[
\begin{align*}
R_1 &= R_2 = \text{Me}; R_3 = R_4 = \text{H} \\
R_1 &= R_2 = R_3 = R_4 = \text{Me} \\
R_1 &= R_2 = R_3 = R_4 = \text{H}
\end{align*}
\]
treatment of a solution of triphenylmethyl radicals in benzene with 0.5M potassium t-butoxide in t-butanol at room temperature for 24 hours, gave \( \alpha, \alpha, \alpha, \alpha', \alpha'' \)-pentaphenyl-\( \pi \)-xylene (22) (71\% after two recrystallisations). The formation of (22) under these conditions requires the intermediacy of (21).

\[
2 \text{Ph}_3 \text{C}^* \rightarrow \begin{array}{c}
\text{Ph}_3 \text{C} \\
\text{Ph}_2 \text{C} \\
\text{H}
\end{array} \xrightarrow{\text{K}^+ \text{O}^- \text{t-Bu}} \begin{array}{c}
\text{Ph}_3 \text{C} \\
\text{Ph}_3 \text{C} \\
\text{CH}_3
\end{array}
\]

(21) (22)

A.3.(d). Structure of triphenylmethyl radicals.

1) Hybridisation.

There are two possible basic structures for simple alkyl radicals. They might be described as \( sp^2 \) hybrids, in which case the structure is trigonal planar, with the lone electron in a 'p' atomic orbital, or they might be described as \( sp^3 \) hybrids, which would confer pyramidal geometry, with the lone electron situated in an \( sp^3 \) hybrid orbital.

Evidence from E.S.R measurements on \( ^{13}\text{CH}_3^* \) indicates that the lone electron is in a 'p' orbital.\(^59,60\) This observation is in accordance with the known loss of optical activity when a free radical is generated at an asymmetric carbon atom. Kinetic evidence obtained from iodine exchange reactions also suggests that simple alkyl radicals are planar.\(^61\) In addition, the electronic spectra of the \( \text{CH}_3^* \) and the \( \text{CD}_3^* \) radicals, generated by flash photolysis in the gas phase, have definitely established that under these conditions the radicals are planar or very
nearly planar. 62

On the other hand the ease of formation of radicals at bridgehead positions indicates that a pyramidal structure is not energetically impossible, and some radical reactions have been found to proceed with some retention of optical activity, 63 although these results can be rationalised without recourse to the postulation of free radical intermediates. At any rate, it seems that the energy difference between the planar and the pyramidal structures is not great in comparison to the energy of formation of the radicals. 64

The two modes of hybridisation outlined above are also possible for triarylmethyl radicals. The absence of a dipole moment for triphenylmethyl and tri(biphenylyl)methyl radicals, 65 would seem to indicate $sp^2$ arrangement.

2) Resonance stabilisation of triphenylmethyl radicals.

Assuming for the moment that a triarylmethyl radical is planar with a three-fold axis of symmetry, quantum mechanics predicts that delocalisation of the unpaired electron will stabilise the radical. The resonance method of approximation to the true nature of the molecule represents the delocalisation of the unpaired electron in the triphenylmethyl radical (23) in the following manner.
In order to attain maximum stabilisation of the radical, all of the benzene rings are required to be coplanar. The molecular orbital method of approximation makes the same condition. The unpaired electron may be thought of as occupying a 'p' orbital of the central carbon atom, perpendicular to the plane of the three bonding $sp^2$ orbitals. If this central 'p' orbital is to overlap with the $\pi$ orbitals of the adjacent benzene ring carbon atoms to form a molecular orbital, then for maximum effect all orbitals must be parallel. Since the $\pi$ orbitals of the benzene rings are perpendicular to the planes of the rings, the rings have to be coplanar.

A structure that prevents coplanarity inhibits resonance stabilisation to a corresponding degree. Thus, the triptyceny}
radical (24), where the benzene rings are tied back in a position with the very maximum deviation from coplanarity, has none of the stability of triphenylmethyl.

Substituents in ortho- or para-positions of the aromatic rings can stabilise the radicals, if their stabilising capability is transmitted by the \( \pi \) orbitals of the rings. However, substituents in ortho- positions also tend to increase deviations from planarity, thus reducing the effective stabilisation.

3) Configuration of triphenylmethyl radicals.

Although resonance stabilisation is at its greatest only when the radical is completely planar, such an arrangement involves repulsions between the six hydrogen atoms occupying the ortho-positions of the rings.
Because of these non-bonded interactions, the radicals are not likely to be completely planar under normal conditions. It has been suggested that the departure from planarity which appears to be necessary takes the form of rotation of each of the phenyl groups about the axis of the bond joining them to the extranuclear carbon atom. The structure is then analogous to that of a three bladed propeller, in which the blades are slightly feathered out of plane. This type of structure was also advocated by Lewis and Calvin. Molecular orbital calculations of the interaction energy between the nearest hydrogen atoms in the triphenylmethyl radical, have shown that the aromatic rings should lie at an angle of about 30° to the plane of the three central bonds, thus affording theoretical justification for the propeller configuration.

It was also predicted that molecules of this type should exist in two isomeric forms, which were termed 'symmetrical helix' and 'unsymmetrical helix'. The former is strictly analogous to a three bladed propeller, and the latter is analogous to a propeller in which the direction of inclination of one of the blades to the plane of the structure, is opposite to that of
the other two.

In order to demonstrate the existence of the two isomeric forms, carbonium ions possessing a triphenylmethyl skeleton were studied. The spectrum of the crystal violet cation was measured in a number of solvents.\textsuperscript{70,71}

All of the spectra showed two particular absorption bands which were called A and B. In ethanolic solution it was found that the relative heights changed with change of temperature, and thus it was concluded that the two bands belonged to the two isomers of the crystal violet cation (26) and (27), of which the distorted helix (26) has the higher energy by $580\text{cal.mole}^{-1}$.

The necessary restriction to the rotation of the aromatic rings, which, if free, would allow interconversion was considered to be due to steric interference by the adjacent ortho- hydrogen atoms.

![Diagram of isomers](image)

The force of repulsion arising from this interference was thought to be balanced by the forces opposing free rotation, which in turn, may arise from the partial double bond character of the bonds joining the rings to the extranuclear carbon atom. These two isomers are diastereoisomeric, although each form,
given the necessary conditions for asymmetry, should exist in enantiomeric modifications. The activation energy for interconversion of these forms was thought to be only of the order of 2 or 3 kcal.mole\(^{-1}\), since interconversion was rapid in ethanol even at \(-159^\circ\).

The phenomenon was also observed with the cation of malachite green, but investigation of the absorption of the triphenylmethyl radical did not yield any evidence for isomerism.

A.4. The addition of organometallic reagents to unsaturated systems.

Of the limited number of ways by which triarylmethanols may be prepared unambiguously, the addition of organometallics to diaryl ketones appeared the most promising. Even this, however, has not always given unequivocal results, and so a review of the types of anomalous reactions encountered will follow.

A.4.(a). Organomagnesium compounds.

The constitution of solutions of organometallic reagents is complex and largely speculative. Solutions of Grignard reagents have been perhaps the most studied, and evidence for the existence in solution of RMgX, R\(_2\)Mg, MgX\(_2\), MgX\(^+\), R\(_2\)MgX\(^-\) and polymeric species has been obtained.\(^{72,73,74,75}\) The uncertainty of the identity of the reacting species makes the establishment of definite mechanistic pathways for these reactions impossible. However, it is often appropriate to consider the effective reactants as RMgX, RLi, RNa etc., polarised in the sense R--MgX, R--Li, R--Na.

It is evident that whilst Grignard reagents possess moderately polar carbon-magnesium bonds, extensive ionisation to R\(^-\) does not occur, because the anion so formed would rapidly attack ether in the manner associated with the highly polar alkylsodium compounds.
Although Grignard reagents as prepared in ethereal solution do not attack the solvent, they are highly associated with it. Not all of the ether can be removed even under reduced pressure at moderate temperatures, and the solid contains one or more moles of ether for every mole of reagent. The ether molecules appear to be coordinated through the unshared electron pairs to magnesium. This type of coordination accounts for the high solubility of Grignard reagents in ether.

A.4.(b). The synthesis of tertiary alcohols by the addition of organometallic reagents to carbonyl compounds.

One of the most important uses of organometallic reagents is for the formation of new carbon-carbon bonds by addition to multiple bonds, particularly of carbonyl compounds. In each case the metal is transferred from carbon to a more electronegative element. An example is the addition of methylmagnesium iodide to acetone.

\[
\text{CH}_3\text{MgI} + (\text{CH}_3)_2\text{C}=\text{O} \rightarrow (\text{CH}_3)_2\text{C}=\text{O}\text{MgX} \xrightarrow{\text{H}_2\text{O}} (\text{CH}_3)_2\text{COH} + \text{MgXOH}
\]

The product is a complex magnesium salt from which the organic product t-butyl alcohol, is freed by acid hydrolysis. If the organic product is sensitive to strong acids, hydrolysis may be conveniently carried out using a saturated solution of ammonium chloride. Acid chlorides, \(\text{RCOCl}\), and esters, \(\text{RCOOR'}\), usually combine with two moles of reagent to give a tertiary alcohol, whilst phosgene, \(\text{COCl}_2\), ethyl chloroformate, \(\text{ClCOOEt}\), and diethyl carbonate, \((\text{EtO})_2\text{C}=\text{O}\), combine with three moles of reagent. The first step in these reactions is presumably addition to the carbonyl bond, the product of which might decompose into
magnesium halide and another carbonyl compound which undergoes further attack.

\[
\text{RCOCl} + \text{R'MgX} \rightarrow \text{R-C-OMgX} \rightarrow \text{RR'C}=\text{O} \rightarrow \text{RR'OH}
\]

The number of reagent molecules taking part in these reactions is uncertain. There are a number of instances known where careful admixture of equivalent quantities of ketone and Grignard reagent yields a precipitate, which, upon treatment with water yields the ketone once more. Generally in such cases the addition takes place in the usual manner if excess of reagent is employed.

A.4.(c). The addition of organometallic reagents to conjugated systems.

The addition of organometallic reagents to carbon-carbon double bonds would not be expected to take place as readily as additions to carbonyl groups. Not only is the carbon-carbon double bond less susceptible to nucleophilic attack by \( \text{R}^- \) from \( \text{RMgX} \), but is also less readily attacked by the electrophile \( \text{MgX}^+ \).

\[
\begin{align*}
\text{C=C} & + \text{R.....MgX} \rightarrow \text{C-MgX} \\
\text{C=O} & + \text{R.....MgX} \rightarrow \text{O-OMgX}
\end{align*}
\]

The difference in reactivity is probably due to the greater electronegativity of oxygen relative to carbon, which makes the carbonyl group considerably more polar than a carbon-carbon double bond. However, formal additions to carbon-carbon double bonds especially, when the double bond is activated by the proximity of electron attracting groups do occur. In the following example of reaction of a Grignard reagent with an \( \alpha,\beta \)-unsaturated ester,
1,4-addition takes place leading ultimately to a saturated ester (28).

\[
\text{C=C} - \text{C}=\text{O} + \text{R...MgX} \rightarrow \text{C=C} - \text{C}=\text{OMgX}.
\]

(28) unstable enol form of ester

Such additions can also occur with \(\alpha,\beta\)-unsaturated aldehydes and ketones, although usually in competition with the normal 1,2-addition. Thus, with pent-3-en-2-one, (29), the ratio of 1,4-product to 1,2-product is 3:1.

\[
\text{CH}_3 \quad \text{EtMgX,} \\
\text{CH} = \text{CH} - \text{C}=\text{O} \quad \text{Et} \\
\text{CH}_2 - \text{CH}=\text{CH} - \text{C}=\text{O} \quad \text{CH}_3
\]

(29) unstable enol form of ester

The balance between 1,2- and 1,4-addition is found in general to be sensitive to two factors:

1) The steric environment of the site of attack of the substrate.

2) The reactivity of the organometallic reagent.

In contrast with the behaviour of pent-3-en-2-one (29), the amount of 1,4-addition of ethylmagnesium bromide to crotonaldehyde (30) drops to zero. Substitution of a second \(\beta\)-methyl group, as in 2-methylpent-2-en-4-one (31), has the same effect.
Examination of the reactions of chalkone (32) with a series of metal phenyls indicates that the mode of addition is influenced markedly by the relative reactivity of the organometallic reagent. The less reactive phenyl derivatives of beryllium, manganese, zinc, aluminium and magnesium show predominantly, if not exclusively, 1,4-addition. The more highly reactive compounds of potassium and calcium show predominantly 1,2-addition. Organometallic reagents derived from lithium and sodium, appear to be of more intermediate reactivity and give products arising from both 1,2- and 1,4-addition.
More extensive conjugated systems can give rise to products resulting from 1,6-addition of reagent.

On this basis therefore, if tertiary alcohol formation is desired (which requires 1,2-addition of reagent to a carbonyl group), organolithium reagents are to be preferred to Grignard reagents.

A.4.(d). The addition of arylmagnesium halides and aryl-lithium reagents to aromatic ketones.

Aromatic ketones possess a bond arrangement analogous to that of the 1,2-unsaturated ketones discussed above. They are cyclic conjugated systems, and as such might be expected to undergo the types of reaction discussed above.

The 'anomalous' addition of Grignard reagents to aromatic systems was first described by Gilman who observed that treatment of benzophenone anil (33) with excess phenylmagnesium bromide, gave N((α-2biphenyl)benzylaniline (34) as the major product, and not the expected N-triphenylmethylaniline (35).

\[ \text{PhMe}_2C=\text{NPh} \xrightarrow{\text{PhMgBr}} \text{PhNH-CHPh} \]

(33)

\[ \begin{align*}
\text{PhMgBr} & \quad \text{PhMe}_2C=\text{NPh} \\
\text{PhMgBr} & \quad \text{Ph}_2\text{C}-\text{NHPh}
\end{align*} \]

(35)

Since then, many such examples have been demonstrated, particularly in the reactions of certain aromatic ketones. In this particular case, experimentally, two situations may be
distinguished:

1) Where the predominant mode of addition is 1,2-, leading to preferential formation of a tertiary alcohol.

2) Where the predominant mode of reaction is 1,4- or 1,6-addition of reagent leading to the formation of nuclear alkylated or arylated ketones.

Reactions falling into category (1) are strictly analogous to additions of organometallic reagents to isolated double bonds, and are the rule for simple alkylaryl ketones and for simple diaryl ketones (for example, benzophenone) where there is not much hindrance to the approach of the reagent to the site of reaction. These 'normal' additions will not be discussed further.

One of the first aromatic ketones observed to show 'anomalous' addition of Grignard reagents was benzanthrone, which upon reaction with an excess of phenylmagnesium bromide, gave 4-phenylbenzanthrone in 42% yield. The Grignard reagents derived from n-heptyl and cyclohexyl bromides gave 61% and 15% yields of the 4-alkyl (1,4-addition) product respectively. With t-butyilmagnesium chloride the predominant product was the carbinol arising from 1,2-addition of reagent (20%).
In contrast neither fluorenone nor anthraquinone have been observed to give products arising from 1,4-addition of reagent.

Similar behaviour is displayed by naphthacenequinone (39). The addition of an excess of phenylmagnesium bromide gives a mixture of the two stereoisomeric tetrahydroquinones (40), which in alkaline solution are both oxidised by atmospheric oxygen to give 6,11-diphenyl-5,12-naphthacenequinone (41).
Interestingly, (41) is not further attacked by phenylmagnesium bromide, even after heating on a steam bath for 24 hours, but addition of excess phenyl-lithium gave the diol (42).

\[
\text{(41)}
\]

A similar type of reaction has been shown to occur with simpler aromatic ketones containing a 2,6-dimethylbenzophenone system, for example, mesityl phenyl ketone (benzoylmesitylene). Treatment of benzoylmesitylene with phenylmagnesium bromide gives 2-phenylbenzoylmesitylene (43) as the predominant product. Similarly, mesityl 4-tolyl ketone and 4-tolylmagnesium bromide give 2-mesitoyl-4',5-dimethylbiphenyl (44).

\[
\text{(43)}
\]
The compounds (43) and (44) presumably arise as oxidation products of the enols (45) and (46), which would be expected to be formed as the first products of the 1,4-addition of reagent.

The enols were not isolated, but evidence for their participation in the reaction was gained from a study of additions to other ketones. For example, addition of phenylmagnesium bromide to 1-mesitoylnaphthalene (47) gave an oil from which mesitoic acid and 2-phenylnaph-1-ol were obtained by exposure to air. These are both products expected to be formed by cleavage of the enol (48).
The reactions discussed above are illustrative of additions of organometallic reagents to aromatic ketones where the major product isolated was that corresponding to 1,4-addition of reagent. If 1,2- or 1,6 addition took place, the products arising from these modes of reaction were not isolated.

The first example where all three modes of addition took place simultaneously was demonstrated by Fuson, who obtained 1,1-durylphenylethylene (49), 2-methylphenyl duryl ketone (50) and 4-methylphenyl duryl ketone (51) as products of the reaction of duryl phenyl ketone with an excess of methylmagnesium iodide, the first arising by dehydration of durylmethylphenylmethanol, the product of 1,2-addition of reagent.
These six examples are illustrative of situations in which aromatic ketones have not reacted with Grignard reagents by simple 1,2-addition. It was noted that in studies of additions of various organometallic reagents to open-chain conjugated compounds, phenyl-lithium reagents were more likely to add in a 1,2-manner, owing in part presumably to their greater reactivity and more compact nature compared with the corresponding Grignard reagents.

Experiments with phenyl-, mesityl- and duryl-lithiums have made possible the synthesis of a number of carbinols containing one mesityl- or duryl- function. Duryl- and mesityl-lithium combine with benzophenone to yield diphenylidencyl- and diphenylmesityl-carbinols respectively. The addition of the corresponding Grignard reagents to benzophenone under the same conditions produces ortho-phenylation. Phenyl-lithium reacts with mesityl-3,4-dimethoxyphenyl ketone and with mesityl-2-methoxy-5-tolyl ketone to give 3,4-dimethoxyphenyl-mesitylphenylcarbinol (54) and mesityl-2-methoxy-5-methylphenylphenylcarbinol (55) in 18% and 57% yields respectively.
These are examples where phenyl-lithium has added in a 1,2-manner, whereas, under similar conditions phenylmagnesium bromide gives 1,4-addition of reagent.

There are many instances where phenyl-lithium itself adds predominantly in the 1,4-manner. For example, duryl 4-methoxyphenyl ketone (56) and mesityl 3-methoxyphenyl ketone (58) are phenylated at ortho-positions by phenyl-lithium, giving the dihydro-derivatives of (57) and (59) in 52% and 7% yields, respectively.

In a similar way duryl phenyl ketone reacts with phenyl-lithium to give duryl 2-phenylphenyl ketone (60)(28%), and with duryl-lithium to give duryl 2-durylphenyl ketone (61)(40%).
Where the ortho-positions in the unsubstituted aromatic ring are blocked by alkyl groups, as for example in dimesityl ketone (62), reaction with phenyl-lithium gives rise to complex products, presumably arising from a side-chain metallation reaction.84,85

A.4.4(e). Cyclisation reactions of triarylmethanols

So far we have considered the possible modes of addition of organometallic reagents to aromatic ketones, with a view to being in a position to predict some of the products that might be isolable from reactions of this type.
The expectation of isolating a tertiary alcohol from the reaction mixture if 1,2-addition of reagent has occurred, involves an assumption that the tertiary alcohol, or its immediate precursor (a metal complex), will be stable in its chemical environment. Empirically, this assumption is found to be valid in many cases, but there are many examples where it apparently does not hold. For example, treatment of phenanthrene-9-aldehyde with 1-naphthylmagnesium bromide gives 9-phenanthryl-1-naphthyl-methane (63) and 1,2,3,4,7,8-tribenzfluorene (64), but no 1-naphthyl-9-phenanthryl-methanol (65).
In the preparation of 1-naphthyl-9-phenanthryl-phenyl-methanol (66)\textsuperscript{86}, by the interaction of 9-phenanthrylmagnesium bromide with 1-benzoylnaphthalene, the carbinol was obtained in 6\% yield and the cyclised product 9-phenyl-1,2,3,4,7,8-tri- benzofluorene in 15\% yield.

\[
\begin{array}{c}
\text{15\%} \\
\end{array}
\]
The additional formation of condensed ring hydrocarbons like (64) as apparently primary products of the reactions, is perhaps most easily ascribed to a cyclo-dehydration reaction, a type of change that many triarylmethanols undergo, particularly those containing bulky aromatic groups like 1-naphthyl or 9-phenanthryl. This dehydration generally takes place by the influence of electrophilic reagents, particularly in acidic media, and would seem to involve the participation of carbonium ions. The products of such reactions are usually considered to be fluorene derivatives. For example, 1-naphthyldiphenylmethanol (67) is converted into 9-phenyl-1,2-benzofluorene (68), 2-naphthyldiphenylmethanol (69) is converted into 9-phenyl-3,4-benzofluorene (70) and di-2-naphthylphenylmethanol (71) is converted into 9-phenyl-3,4,5,6-dibenzofluorene (72).

\[
\text{Ph}_2\text{C—OH} \quad 1-\text{C}_10\text{H}_7 \quad \xrightarrow{\text{H}^+} \quad \text{Ph}^\text{CH—OH} \quad 1-\text{C}_10\text{H}_7
\]
To optimise the yield of triarylmethanol in a particular synthesis, it is necessary to reduce to a minimum the extent of cyclodehydration.
A.5. The stabilisation of polyarylmethyl carbonium ions and of polyarylmethyl carbonium ion-like intermediates.

The formation of free radicals by homolysis, and the formation of ions by heterolysis has been discussed in section A.1. The ease with which such processes take place is directly proportional to the free energy difference between the ground state and the transition state of the reaction. Factors which can lower the intrinsic free energy of the transition state, or alternatively increase the intrinsic free energy of the ground state, would be expected to facilitate the reaction.

Wave mechanical calculations show that the delocalisation of electric charge over a number of atoms is energetically more favourable than localisation of charge on one particular atom. A system which permits delocalisation is therefore a more stable arrangement than if no delocalisation takes place.

Delocalisation of charge, or charge dispersal, in general may be achieved in two ways:

1) Internally, within a molecule, by electrical induction, conjugation and related phenomena.
2) Externally, by solvation, ion association and charge transfer.

To simplify the discussion, only the first set of factors will be considered.

Substituent groups within a molecule which facilitate delocalisation of charge therefore have the capacity to stabilise carbonium ions, free radicals or carbanions. The stabilisation of triphenylmethyl radicals has been discussed in section A.3(d), and the observation made there hold by and large for the analogous carbonium ions.

The delocalisation of charge within a molecule can in general be achieved in two ways:

1) By inductive or field effects.
2) By resonance or conjugation effects.
A.5.(a). Inductive and field effects.

Inductive effects are generally understood to be electrostatic in origin, and to be transmitted by the bonding electrons through a chain of atoms, whereas, electrostatic forces which are transmitted through empty space or through solvent molecules are referred to as field effects.

Inductive and field effects may arise not only from ionic charges, but also from the action of dipoles within the reacting molecules. Atoms like nitrogen, oxygen and the lighter halogens, are, because of their greater measure of unscreened nuclear charge, better electron attractors, i.e., more electronegative than the carbon or hydrogen atoms. When a more electronegative atom is substituted for hydrogen within a molecule, electron density moves towards this atom and away from nearby atoms, and those atoms nearest to the position of substitution will suffer the greatest induced polarisation. Such effects are short range in their action, obeying an inverse square law and therefore rapidly diminishing with increasing distance.

A.5.(b). Resonance or conjugation effects.

In contrast to simple inductive effects which are transmitted by the sigma electrons of a molecule, charge can be transmitted by the $\pi$ orbitals of unsaturated molecules. This mode of transmission is particularly important in the study of aromatic systems, and particularly where a substituent is orientated para- to the reaction centre. In such a situation simple inductive effects would be expected to be small due to the large separation (4 carbon atoms) of the substituent from the reaction centre. Unlike inductive transmission, conjugation effects are capable of operating over large distances; a disturbance of $\pi$ electron density at one atom in a conjugated system may become distributed over the $\pi$ electron orbitals.
associated with the whole system, with those atoms far from the source of the disturbance being just as much affected as those close to it. This mode of transmission is readily described by the resonance method. For example, two resonance structures for nitrobenzene (73) and (74) indicate that the substitution of a nitro-group in benzene brings about the withdrawal of π electron density from the ring, especially from the ortho- and para-positions. In the same way the structures (75) and (76) for the phenoxide ion indicate that the negative charge is not localised on the oxygen atom but also resides partially on the ring, again at the ortho- and para- positions.

\[ \text{[Chemical structures]} \]
Resonance forms analogous to (73), (74), (75) and (76) which place positive or negative charges in the meta-position would be relatively high energy structures, and as such would be expected to contribute very little to the resonance hybrid. The interactions depicted above operate to a maximum extent when the 'p' orbitals of the substituent can overlap most effectively with the π orbitals associated with the unsaturated carbon atoms. In general conjugation is more important for substituents involving first row elements (-F, -OH, -NH₂) than for substituents involving the heavier elements (-Cl, -Br, -SH). The outer (2p) orbitals of the first row elements are roughly the same size as the π orbitals of the unsaturated carbon atoms, but the outer (3p) orbitals of the heavier elements are considerably larger, and orbital overlap which is the basis for bonding action is less effective.

Structures analogous to (73)-(76) can be drawn for ortho-substituents, although in this case inductive effects may operate strongly.

In addition to the substituents discussed above which all possess lone pairs of electrons which can be involved in the delocalisation process, it is observed that methyl and alkyl groups generally situated para- to a reaction site can influence the rate of reaction. For example, reactions which are known to be accelerated by electron donating groups are similarly promoted by the presence of a methyl group situated para- to the reaction centre. The absorption bands associated with π-π* transitions, are moved to longer wavelength by the substitution of alkyl groups (bathochromic shifts). Such phenomena are usually attributed to hyperconjugation represented by the structures (77), (78), (79) and (80).
A.5.(c). The steric inhibition of conjugation.

Molecular orbital calculations show that if effective combination of atomic orbitals is to occur, three conditions in general must be fulfilled:

1) The combining orbitals should represent states of similar energy.

2) Overlap must occur to a considerable extent.

3) The orbitals should possess the same symmetry with respect to the molecular axis.

Interactions of the type described in section A.5.(b). involve the \( p \) orbital of the substituent with the \( \pi \) molecular orbitals of the aromatic rings. These interactions therefore fulfill condition (3). The effect of energy inequalities becomes important with substituents containing heavier elements, for example, bromine or iodine, where \( \{4p\} \) and \( \{5p\} \) orbitals are
involved. In addition to the greater energies of these orbitals, their sizes also reduce their effective overlap with the smaller π orbitals of the rings.

The fulfillment of condition (2) is sensitive to the geometry of a molecule. The overlap of two orbitals with π symmetry is likely to be most effective when the orbitals lie in a common plane, as in case (a) below.

(a) (b) (c)

Case (c) represents a state where the interacting orbitals are orthogonally arranged, when no overlap and hence no interaction occurs. Between the two extremes (a) and (c) there must be intermediate states like (b) where a degree of interaction occurs.

In real molecules steric factors can bring about deviations from complete planarity, thus reducing the capability of a substituent to interact with a site of electric perturbation in another part of the molecule. Some examples are given below.

A nitro— group substituted para— to a phenolic hydroxide group greatly increases its acidity. The substitution of bulky groups ortho— to the nitro— group might be expected to reduce the acidity of the phenol, as they would not allow the nitro— group to attain complete coplanarity with the ring. Thus of the two nitro-m—xylenols (81) and (82), the latter is the weaker acid⁹⁰, even though the methyl groups ( whose inductive effect would tend to weaken the acidity) are closer to the hydroxyl group in (81).
Similarly, N,N-dimethylpicramide (83) is a far stronger base than picramide itself (84), since the ortho-nitro groups in the former compound force the dimethylamino-group out of the plane of the benzene ring, insulating the nitrogen atom of the amino-group from the electron-withdrawing resonance effects of all three nitro-groups. In picramide itself, however, there is little interference between the smaller amino-group and the nitro-groups ortho-to it; departures from coplanarity are slight and considerable n-electron density is drained off from the amino-group to the nitro-group.

Similar effects are observed in respect to reaction rates. Aromatic substitution reactions are generally accelerated by substituents which allow the charge originally associated with
the attacking reagent to be spread over a large area, either in
the activated complex or in a high energy intermediate. The
benzene ring in dimethylaniline is attacked by electrophilic
reagents such as the benzenediazonium ion PhN$_2^+$ far more rapidly
than is benzene itself, largely because the 'p' electron density
of the amino- nitrogen atom can shift into the $\pi$ orbitals of the
benzene ring in the intermediate (85) to help accommodate the
added positive charge. Thus, the dimethylamino- group has
activated the benzene ring towards electrophilic substitution.

This is a conjugative effect whose magnitude can be reduced
by the substitution of bulky groups ortho- to the activating
group, since the latter will be pushed far out of the plane of
the benzene ring.

On this basis, it can be seen why the hindered amine (86) does
not react with diazonium compounds under conditions in which
dimethylaniline reacts readily.$^{91}$

Similarly, bromination of the amine (87) is much faster than
of the amine (88).$^{92}$
The situation described here is quite different from classical steric hindrance, since there is no direct interference between the hindering methyl groups and the attacking reagent.

A.5.(d). The steric inhibition of hyperconjugation.

The question as to whether hyperconjugation is subject to steric hindrance is not easy to answer. Suppose for example, that two methyl groups are substituted ortho- to a substituent like a methyl group participating in hyperconjugation. Since hyperconjugation effects are relatively small, it would be difficult to disentangle effects supposedly due to the inhibition of hyperconjugation from the inductive effects of the two methyl groups themselves.

It has been one of the aims of this research to investigate this question, as it was felt that difficulties in the interpretation of data could be eliminated by the use of a suitable system.

The chloride (89) in hydrolysed in aqueous acetone almost twice as rapidly as is the chloride (90). Both hydrolyses are thought to proceed via carbonium ions, the ion derived from (89) presumably being stabilised by hyperconjugation. Using molecular models it is possible to show that although both the five membered ring in the compound (89) and the seven membered ring in the molecule (90) are puckered, the latter is much more so.
The bond from $C_\alpha$ to the benzene ring lies more nearly in the plane of the ring in (89) than in (90). It might then be argued that hyperconjugation in the carbonium ion derived from (90) should be considerably less important than in the carbonium ion derived from (89), and to the extent that the stability of the intermediate carbonium ion governs the rate of solvolysis, (89) should react more rapidly than (90).

A.6. Free energy relationships.

A.6.(a). The Hammett equation.

There exist a number of quantitative or semi-quantitative relationships which can be used to predict rate constants and equilibrium constants for many reactions on the basis of the ability of a group or substituent either to withdraw or to supply electron density to the reaction site. One of the oldest of these is the Hammett equation, which relates structure to both rate and equilibrium constants for the reactions of meta- and para- substituted benzene derivatives.

Consider a series of aromatic compounds, each with the same
reaction centre present in a side chain, but each having in addition, a different substituent situated meta- or para- to that reaction centre; for example, a series of substituted benzyl chlorides. The Hammett relationship stipulates that the rate or equilibrium constant associated with any of these compounds may be determined from the rate constant for the parent molecule (benzyl chloride itself), if two parameters are known.

The first parameter (\( \sigma \)) is characteristic of the substituent only, and represents the ability of the group to attract or to repel electrons by a combination of its resonance and inductive effects.

The second parameter (\( \eta \)), characteristic of the reaction series at hand, is a measure of the sensitivity of the reaction in question to substituent effects.

If \( k \) and \( k_0 \) are the rate constants for the reaction of the substituted and the unsubstituted molecules, respectively, the Hammett equation may be written:

\[
\log \left( \frac{k}{k_0} \right) = \sigma \eta
\]

The \( \sigma' \) value for a substituent is defined in terms of the effect of that substituent upon the ionisation constant of benzoic acid in water at 25°.

\[
\sigma' = \log \left( \frac{K_{X-C_6H_4-CO_2H}}{K_{C_6H_5CO_2H}} \right)
\]

where \( K_{X-C_6H_4-CO_2H} \) and \( K_{C_6H_5CO_2H} \) are the ionisation constants for the substituted and unsubstituted benzoic acids, respectively.

In effect, the ionisation of benzoic acids has been chosen arbitrarily as a standard reaction type (for which \( \eta \) is defined at unity), and \( \sigma' \) is defined on the basis of this standard. A positive \( \sigma' \) value for a substituent indicates that the substituent
is a stronger electron attractor than hydrogen; substituents with negative \( \sigma' \) values are weaker electron attractors than hydrogen.

To obtain \( \rho \) for a given reaction series, it is necessary to measure the rate or equilibrium constants for a number of compounds, each having the reaction centre under consideration and each having a ring substituent with a different known \( \sigma' \) value. The logarithms of the measured constants are plotted against the appropriate \( \sigma' \) values, and the slope of the best straight line through the points on such a graph is the \( \rho \) value for the series at hand. Reactions with positive \( \rho \) values are aided by electron withdrawal from the benzene ring, whereas, those with negative \( \rho \) values are hindered by electron withdrawal.

A.6.(b). The applicability of the Hammett equation.

It will be recalled that the logarithm of the equilibrium constant for a reaction is proportional to the standard free energy change, \( \Delta G^\circ \), and that the logarithm of the rate constant for a reaction is proportional to the free energy of activation for the process, \( \Delta G^\ast \).

Considering equilibrium constants only, the Hammett equation may be written as:

\[
\log K = \sigma' \rho + \log K_0
\]

or in terms of free energy changes,

\[
-\Delta G^\circ = (RT \rho) \sigma' - \Delta G_0^\circ
\]

Similar relationships may be written using rate constants. For a given reaction series at a given temperature, \( T \), \( \rho \), and \( \Delta G_0^\circ \) are constants, the equation is thus of the form \( y = mx + c \).
The free energy change associated with the reactions of members of the series are thus linearly related to the respective $\sigma$ values.

In meta- and para- substituted benzene derivatives, the substituents are relatively rigid and it is reasonable to assume that since their separation from the reaction centre is large, steric interaction between the substituent and the reaction centre is negligible. It appears that in most cases, substituents may affect reactivity, directly or indirectly, solely by their ability to withdraw or to supply electron density from or to the reaction site. The Hammett equation in its simple form, is not generally applicable to ortho- substituents, because these lie close to the reaction site and may influence the reaction both by their electron attracting ability and their steric interaction. For a valid relationship to hold for ortho- substituents, each substituent must possess what may be described as a steric interaction capacity, which, like its electron attracting ability, is independent of the reaction at hand. In some cases this has been shown to be true.

Secondly, the sensitivity of the reaction to steric effects must quantitatively parallel its sensitivity to electron withdrawal or supply (generally this is not true).

It is tempting to assume that changes in $\Delta G^0$ or $\Delta G^+$ resulting from the introduction of a substituent, merely reflect a change in the electrostatic energy gap that separates the reactants from the products or transition state. Such a change is presumably proportional to the electronic effects of the substituent, as represented by its $\sigma$ value. However, substituents may also introduce kinetic energy effects: they may affect the speed of molecular vibrations and may thereby alter the degree and mode of solvation of the species involved in the reaction. In order that the Hammett equation be applicable, it is necessary that these kinetic energy effects be negligible or that they be proportional to the potential energy effects.
A.6.(c). $\sigma^+$ values.

The simple Hammett equation involves the two parameters $\sigma$ and $\rho$. Experimentally, it has been found necessary to abandon the view that a single substituent constant is adequate for all reactions, and a number of modified sets of substituent constants have been proposed to deal with specific classes of reactions. Of particular relevance to this research is a substituent constant $\sigma^+$ applicable to reactions where a large amount of charge is developed during the course of the reaction.

For such reactions, the simple Hammett equation is modified in the following way:\(^{95}\)

$$\log\left(\frac{k}{k_0}\right) = \sigma^+ \rho$$

$\sigma^+$ is obtained by comparing the solvolysis rates, in 90% aqueous acetone at 25°C, of $\alpha$-cumyl chlorides (91) with different substituents $Y$ in the aromatic ring.

$$\text{(91)}$$

Under such conditions, the influence of the substituent $Y$ in stabilising the transition state of a structure strongly disposed towards unimolecular reaction can be measured. The $\sigma^+$ factors derived in this way are a set of parameters considered applicable for the correlation of equilibrium constants of carbonium ion equilibria, and rate constants of reactions with carbonium ion-like
transition states.

The value of the reaction constant $\rho (= -4.54$ in 90% acetone–water at 25°) is chosen so as to connect the $\sigma^+$ values to the $\sigma$ values proposed by Hammett for the general correlation of substituent effects in different types of organic reactions.

A.7. The kinetic determination of the stabilities of polyarylmethylic carbonium ions.

Arguments about the stabilities of carbonium ions as determined from rate measurements fall into two broad categories. The first type of argument is concerned with the rates of reactions of carbonium ions, and generally amounts to the proposition that for analogous modes of reaction a less stable carbonium ion will be destroyed more rapidly. This implies that the transition state, whatever the cause of its instability relative to the reactant carbonium ion, has substantially lost the carbonium ion character of the reactant, and that the energy of the transition state is less influenced by structural variations than is the energy of the carbonium ion. The situation is shown below, illustrating the difference in the reaction rates of the two carbonium ions A and B on this supposition.

![Diagram](Figure 1)
The second kind of argument, and the one with which this thesis will be concerned, considers the rates of formation of carbonium ions, and is equivalent to the idea that a more stable ion will be formed more rapidly from a given type of parent molecule. The rate comparison now measures the free energy difference between the transition state leading to the carbonium ion and the parent molecule, and is a measure of carbonium ion stability if the energies of the related transition states parallel the respective energies of the carbonium ions. The more the transition states resemble the carbonium ions the closer will be the correspondence, as indicated below.

![Diagram of carbonium ion-like transition states](image)

**Figure 2.**

In a reaction conforming to the potential energy profile of figure 2, the reaction velocity is determined by the rate of the ionisation step, i.e., the energies of the transition states for any processes after the ionisation are lower than the supposedly carbonium ion-like transition state.

Both figure 1. and figure 2. also show the reference mark with
respect to which the energy of the carbonium ion (or carbonium ion-like transition state) is measured. A statement that of two carbonium ions $R^+$ and $R'^+$, $R^+$ is the more stable on the grounds that the ionisation $R \rightarrow X \rightarrow R^+ + X^-$ is more rapid than the corresponding ionisation of $R'^+$, thus means that the stability of the transition state $R^{\delta^+} \rightarrow X^\delta$ relative to its parent molecule $RX$ is greater than the stability of the transition state $R'^{\delta^+} \rightarrow X^\delta$ relative to its parent compound.

It is evident from these considerations that kinetic arguments about carbonium ion stabilities can be criticized on the grounds that they involve approximations. However, it is found experimentally that in many cases these assumptions are valid. The correct prediction of relative reaction rates, and of the composition of products formed by reaction with competing reagents, from known relative stabilities of carbonium ions is clearly useful. Naturally the approximations involved are more appropriate in some cases than in others.

A.7.(a). Rate laws.

Consider a reaction in which a free carbonium ion is formed by a reversible process, viz.;

$$
RX_1 \xrightleftharpoons[k_1]^{k_2} R^+ + X_1
$$

$$
R^+ + X_2 \xrightarrow[k_2]{} P_2
$$

$$
R^+ + X_1 \xrightarrow[k_4]{} P_1 \text{ etc.}
$$

The parallel routes for the destruction of the carbonium ion are written as involving a series of competing nucleophilic reagents $X_1, X_2, X_3, \ldots, X_4$ with respective rate constants $k_1$. 
$k_1, k_2, \ldots, k_i$. The first of these, $X_1$, is the anion of the group originally combined with the carbonium ion in the species $RX_1$. Assuming that the concentration of $R^+$ is always small compared with the concentration of other species, and applying the steady state hypothesis,

$$-\frac{d[RX_1]}{dt} = \frac{d[I]}{dt} = \frac{k_d[RX_1] \sum_{i=2}^i k_i[X_i]}{k_1[X_1] + \sum_{i=2}^i k_i[X_i]}$$

Dividing top and bottom by $\sum_{i=2}^i k_i[X_i]$

$$-\frac{d[RX_1]}{dt} = \frac{k_d[RX_1]}{k_1[X_1] / \sum_{i=2}^i k_i[X_i] + 1}$$

Writing the dimensionless quantity

$$k_1[X_1] / \sum_{i=2}^i k_i[X_i] = S$$

$$-\frac{d[RX_1]}{dt} = \frac{k_d[RX_1]}{1 + S}$$

Three experimentally distinguishable situations may arise.

1) Where $S \ll 1$ throughout the reaction,

$$-\frac{d[RX_1]}{dt} = k_d[RX_1]$$
Carbonium ion formation alone is rate limiting, a simple first order rate law is obeyed.

2) Where $S \gg 1$ throughout the reaction,

$$-rac{d[RX_1]}{dt} = \frac{k_d[RX_1] \sum k_i[X_i]}{k_1[X_1]}$$

Carbonium ion destruction as well as formation is now kinetically important. The concentration of nucleophile involved now enters the kinetic equation and the rate limiting step is a bimolecular reaction between the carbonium ion and the nucleophiles.

3) Where $S$ varies during the course of the reaction.

If the value of $k_1$ is sufficiently large and the reaction medium contains little or no $X_1$ initially, then the size of $k_1[X_1]$ and hence of $S$ varies appreciably during the course of the disappearance of $RX_1$. Should $S$ become comparable with, or much greater than unity, then the simple first order law (case 1) will no longer be obeyed: the reaction rate will decrease more rapidly than expected on the basis of case 1.

As we have seen, the equation of the stability of a carbonium ion with its rate of formation can only be made for a system undergoing a unimolecular solvolysis. This research is therefore concerned only with decompositions which fall into the first category, i.e., reactions that obey the simple first order rate law.

A.8. Scope of the present work.

The supposed configuration of triarylmethyl free radicals has been discussed in section A.3.(d).(3). The steric constraints imposed by the dimensions of the aromatic rings render the
radicals non-planar, and a 'three-bladed propeller' shape, where the blades are slightly feathered out of plane, is thought to be a good approximation to the actual structure. Such a species, given the imposition of restricted movement of the aromatic rings about the central carbon atom, could exist in the two geometric modifications, termed the symmetrical and the unsymmetrical helices: and each of the geometric modifications themselves could exist in optically active modifications.

The first part of this research is therefore concerned with the attempted preparation of these radicals and their precursors. Radical syntheses were not achieved because of rearrangements of the tri-1,1',1''-naphthylmethyl skeletons, and so some of the reactions undergone by these structures were investigated.

To test the 'three-bladed propeller' model it was considered of interest to:

1) construct a system of the type Ar$_3$OH, which could exist in optically active modifications and which could retain asymmetry upon conversion to a free radical of the type Ar$_3$C$^\cdot$.

2) resolve the system Ar$_3$COH into optical isomers.

3) show that the retention of optical properties persisted in the free radical.

For convenience in handling of the materials it was considered desirable to obtain two properties:

1) as large as possible an energy barrier to interconversion of the enantiomers. This in effect meant that the aryl groups used were:

   a) as large as could be accommodated around the central carbon atom.

   b) of large crowding capacity, for example, the α-naphthyl group is the same size as the β-naphthyl group but the constraints that it imposes are much greater.
2) A considerable resistance to further reaction. This in effect meant maximum stability towards dimerization, which can of course be achieved by using a very crowded system where a large barrier to dimerization exists, and also by providing the possibility for resonance stabilization of the radical. Also the maximum resistance to intramolecular reaction, for example, disproportionation was desirable.

The ideal system would be the one in which all of these tendencies were maximized. In practice this is difficult, if not impossible, to achieve, as alterations to the skeleton for the purpose of maximizing one property very often at the same time reduce the system's ability to maximize another. For example, increasing the capacity of the system to stabilize the radical by resonance, by using a more extensive aromatic system, may increase the departure from planarity (the position of maximum resonance stabilization) and therefore the same amount of stabilization might be achieved by using an aromatic system with a smaller crowding capacity. Increasing the resistance of the radical to dimerization by using a very crowded system (this weakens the carbon-carbon bond that would be formed upon dimerization, and at the same time increases the activation energy for dimerization) often markedly increases the tendency to disproportionation. For example, the necessity to handle the phenyldi-(2-tolyl)methyl free radical at temperatures below 10° must be handled with care.

The decision to use a particular system is therefore very much a compromise.

Two systems were considered for study: a tri-1,1',1''-naphthylmethyl and a tri-2,2',2''-tolylmethyl skeleton. The real objects of study, the free radicals derived from these skeletons were to be prepared from the corresponding triarylmethanols.
Optical resolution of the triarylmethanols was to be attempted by separation of a mixture of diastereoisomeric salts, for which purpose a 'handle' (either an acidic or a basic function) was built into the skeletons. The method of synthesis of the molecules (use of organometallic reagents) restricted the choice of such groups to methyl— (which upon oxidation is converted into a carboxylic function) and dimethylamino—.

The orientation of these groups in the aromatic rings was governed in the first instance by the accessibility of starting materials, and for this reason a 4-dimethylamino— and a 4-methyl group were used in the trinaphthylmethyl series, and a 5-dimethylamino— group was used in the tritolylmethyl system. The use of a methyl group as a precursor of the carboxylic function in the tritolylmethyl system was precluded because selective oxidation of the methyl groups was considered improbable. The compounds (92) to (95) were synthesised.

\[
\begin{align*}
X = H & \quad (92) \\
X = \text{Me} & \quad (93) \\
X = \text{NMe}_2 & \quad (94)
\end{align*}
\]

In addition 4,4'-dimethyl-tri-1,1',1''-naphthylmethanol (93A) and 4,4',4''-trimethyl-tri-1,1',1''-naphthylmethanol (93B) were prepared.

\[
\begin{align*}
(2\text{-tolyl})_2 & \quad \text{C} \quad \text{OH} \\
(95)
\end{align*}
\]
The publication by Lankamp and Nauta in 1968\textsuperscript{37} of evidence against the hexaphenylethane formulation for the species which arises by dimerisation of triphenylmethyl radicals suggested that a quantitative investigation of the effects of crowding upon polyarylmethyl systems would be of interest since steric influences upon the normal mode of dimerisation seemed to be responsible for the anomalous behaviour. The second part of this research is concerned with such an investigation.

A convenient approach to this objective is to measure the rates of formation of polyarylmethyl carbonium ions from the respective chlorides, quantities which for unimolecular reactions are a measure of the thermodynamic stabilities of the ions.

The choice of system for study was dictated by the ease of measurement of the rate of ionisation, very fast or very slow processes being undesirable. The solvolysis of diphenylmethyl chloride in a 90\% ethanol-acetone mixture was found to be suitable.

Variation in the extent of crowding of the central carbon atom was achieved by the use of substituent groups situated in ortho- positions. For simplicity it was decided to use one such group only, and for convenience the methyl- group was selected.

Accordingly, the preparation and rates of solvolysis of diphenylmethyl- (96), 2-methyldiphenylmethyl- (97), 2,2'-dimethyldiphenylmethyl- (98), 2,6-dimethyldiphenylmethyl- (99), 2,2',6-trimethyldiphenylmethyl- (100) and 2,2',6,6'-tetramethyldiphenylmethyl- (101) chlorides were undertaken and measured. The series reflects increasing crowding of the central carbon atom.
The aromatic rings of the diphenylmethyl system twist out of plane to accommodate the ortho- substituents, and therefore the compounds shown above all possess different dihedral angles. This property seemed particularly desirable, as the transmission of substituent, effects through the aromatic rings could be studied in systems possessing different dihedral angles. Information about the mode of transmission of electronic effects could thus be gained, as influences transmitted by electrons in \( \sigma \) orbitals should be unaffected by angular variations, whereas, effects relayed by \( \pi \)-electrons would be expected to be reduced with increasing departure from planarity.

The two groups, 4-methyl- and 4-t-butyl-, seemed of particular interest and were particularly amenable for investigation using this variable dihedral angle technique.

The preparation and solvolyses of 4-substituted diphenylmethyl, 4-substituted 2,6- dimethyldiphenylmethyl, 4-substituted
2,2',6-trimethyldiphenylmethyl and some 4-substituted 2,2',6,6'-tetramethyldiphenylmethyl chlorides were therefore undertaken and studied.
Discussion.

B.1. Preparations of tri-1,1',1''-naphthylmethanol (92).

B.1.(a). Historical.

The synthesis of (92) has been reported by several authors.

1) Elbs\textsuperscript{89} obtained a brown solid after a reaction between a chloropicrin-naphthalene mixture and anhydrous aluminium chloride.

2) Gomberg\textsuperscript{96} obtained a crude product considered to be (92) from the reaction of naphthalene, carbon tetrachloride and aluminium chloride in carbon disulphide.

3) Chichibabin\textsuperscript{97} added 1-naphthylmagnesium bromide to di-1(naphthyl) ketone in dry ether. A product which possessed the following properties was obtained.

a) It gave an orange-red solution in concentrated sulphuric acid.

b) It absorbed oxygen at ordinary temperatures.

c) It decolourised potassium permanganate solution at ordinary temperatures, being oxidised to 9-(1-naphthyl)-1,2:7,8-dibenzofluoren-9-ol (102).

d) It formed a dihydro- derivative.

e) On treatment with iodine it gave an 'iodide', which
could not be converted back to the carbinol nor into a free radical.

4) Schmidlin and co-workers\(^98,99\) reacted 1-naphthoyl chloride with excess of 1-naphthylmagnesium bromide in dry ether. The colourless product possessed the following properties.

a) It gave an orange-red solution in concentrated sulphuric acid

b) It contained no 'active hydrogen atoms.

c) The reagents which normally convert tertiary alcohols into their respective chlorides had no action on it.

d) It did not undergo reactions (3b) and (3c) above.

Both the Schmidlin product and the Chichibabin product gave satisfactory combustion analyses.

**B.1.(b). Discussion of historical methods and results.**

Any synthesis of tri-1,1',1\(^\text{"}\)-naphthylmethanol (92) must involve at some stage the joining together of a di-1,1\(^\text{"}\)-naphthylmethyl system with a 1-naphthyl moiety. These two relatively bulky groups must approach one another in relatively precise orientations (a process which would be expected to have a very large negative entropy of activation, and consequently to be slower than the corresponding reaction with less crowded systems) forming a three-bladed propeller structure, which is expected to display large deviations from planarity and to possess a very crowded central carbon atom.

Historically, two distinct approaches to the synthesis have been adopted:

1) The employment of a Friedel-Crafts method involving the replacement of the three chlorine atoms in a molecule of the type \(X-\text{Cl}_3\) (\(X = \text{H}, \text{NO}_2, \text{Cl}\) etc.) by three 1-naphthyl groups.
2) A Grignard synthesis involving the addition of 1-naphthylmagnesium bromide to a carbonyl compound.

The Friedel-Crafts method seems to be beset with difficulties. Firstly, the reversible alkylation reaction would be subject to thermodynamic control, as a result of which it would be anticipated that the more thermodynamically stable isomers of (92), viz., 1,1',2-, 1,2,2'- and 2,2',2'-trinaphthylmethanols would be formed preferentially, or at least in very significant quantities. The separation of one particular isomer from the mixture would therefore be difficult, and it is doubtful whether the Elbs or the Gomberg products were even moderately pure (92). Moreover, the precursors of the final products (the trinaphthylmethanols) are expected to be species like \((\text{C}_9\text{H}_7)_3\text{AlCl}_4\) which in addition to being probably more crowded than the carbinols themselves would be expected to be especially prone to intramolecular cyclisation.

On the other hand, a synthesis using organometallic reagents has the advantage that if addition of the reagent takes place in a 1,2- manner to di-(1-naphthyl) ketone (or its precursor), the final product must possess a 1,1',1"- orientation of the naphthyl rings to the central carbon atom.

The Chichibabin product and the Schmidlin product, on the basis of their differing chemical properties, are evidently different compounds, and this is one point of agreement between the respective authors. However, which one, if either, was in fact (92), was a point of profound disagreement.

The absorption of oxygen and the decolourisation of permanganate solution at ordinary temperatures are not properties shared with any known simple triarylmethanols. On the other hand, the unreactivity of the 'iodide' said to be formed by reaction of the carbinol with iodine, the failure to prepare the triarylmethyl chlorides by normal methods and the apparent unreactivity of
the hydroxyl group with methylmagnesium iodide and contrary to
the behaviour of other triarylmethyl halides and other
triarylmethanols, particularly diphenyl-1-naphthylmethanol and
phenyl-di-1,1'-naphthylmethanol.

The evidence presented by Chichibabin that his product had
structure (92) rests upon its oxidation product 9-(1-naphthyl)-
1,2,7,8-dibenzofluoren-9-ol (102). This is a circular argument
since (102) has not been prepared by any other route. Therefore
the supposition that the triarylmethanol product possessed the
structure (92) was not justified.

The combustion analysis figures presented for all of these
compounds, serve only to indicate that the products, whichever
they are, contain three naphthyl systems and not two, i.e.,
addition of 1-naphthylmagnesium bromide to a dinaphthyl system
has occurred. Distinction between molecular weights of 408,
410 and 412 is clearly beyond the limits of accuracy of
gravimetric analysis.

It therefore appears unlikely that (92) has ever been prepared
in a pure state.

The true identity of the products described above is worthy
of speculation.

It would seem likely that products isolated from reactions
based upon the Friedel-Crafts method are, if alcohols, mixtures
of isomers.

The products obtained by the action of 1-naphthylmagnesium
bromide upon carbonyl compounds of the type described above
are evidently non-alcoholic in nature. It has been shown in
section A.4.(d) that reaction of Grignard reagents with some
carbonyl compounds, especially aromatic ketones possessing bulky
aromatic groups, does not always lead to tertiary alcohol
formation. If, as seems likely, the observed pattern of 1,4-
and 1,6- addition of reagent to such carbonyl systems is due to
the restricted accessibility of the carbonyl group to the reagent, the effect would be accentuated by the use of Grignard reagents which themselves possessed relatively large steric requirements, for example, 1-naphthylmagnesium bromide. It might therefore be expected that reaction of di-(1-naphthyl) ketone (or its precursor) with 1-naphthylmagnesium bromide would lead to 1,4- or possibly 1,6- addition of reagent, resulting in the formation of ring arylated ketones. As has been observed, in some cases it has proved possible to isolate the intermediate enol. The overall reaction can then be envisaged as follows:

In regard to the experimental techniques employed by Schmidlin and by Chichibabin: apart from the use of 1-naphthyl chloride by the former and of di-(1-naphthyl) ketone by the latter, the
synthetic methods differed in one important aspect. Schmidlin conducted his reaction and work-up without the exclusion of atmospheric oxygen, whereas Chichibabin's reaction was at all stages conducted under carbon dioxide. The latter product when left standing in air absorbed oxygen.

As has been already noted, enols of the type (103) are very easily oxidised by air to ketones like (104). On this basis, it might be predicted that the Schmidlin product was a ketone (104), and the Chichibabin product was the enol (103). This interpretation appears to be consistent with all of the available experimental evidence. For example, structure (103) would:

a) be expected to give a red colouration in concentrated sulphuric acid, as it is effectively a dinaphthyl system. Di-(1-naphthyl) ketone itself is red in sulphuric acid.
b) be expected to be easily oxidised.
c) possibly be expected to form a dihydro- derivative.
d) certainly react with iodine, and could ultimately give a nuclear-iodo product, which would not behave like a triarylmethyl iodide.

On the other hand structure (104) would:

a) react with concentrated sulphuric acid like (103), and for the same reason.
b) not evolve methane upon treatment with methylmagnesium iodide, since it is a non-enolisable ketone.
c) not be converted to a triarylmethyl halide by reaction with acetyl chloride, thionyl chloride or phosphorous pentachloride, since it is not an alcohol.
d) not be readily oxidised under the conditions in which (103) is oxidised.

B.1.(c). The synthesis of tri-1,1',1''-naphthylmethanol (92).

Since the reaction between 1-naphthylmagnesium bromide and
Figure 3.

N.M.R. spectrum of tri-1,1',1''-naphthylmethanol (92) in deuterochloroform.

Instrument: Varian HA-100.
di-(1-naphthyl) ketone has been shown not to lead to the formation of the desired product, attention was directed towards the use of a more compact and more reactive organometallic reagent.

The reaction of 1-naphthyl-lithium in large excess with diethyl carbonate gave a white solid m.p. 278°.

B.1.(d). Evidence for the assignment of the structure tri-1,1',1"-naphthylmethanol to the reaction product.

The strongest evidence for designating the reaction product as tri-1,1',1"-naphthylmethanol was obtained from mass spectral and N.M.R. investigations.

The N.M.R. spectrum of the product dissolved in deuterochloroform is shown in figure 3.

Qualitatively, the presence of two proton magnetic environments (an aromatic band and a hydroxylic band) are to be anticipated. In practice this pattern was observed, a complex 21H absorption between 1.6 and 3.0τ and a singlet 1H absorption at 5.9τ were found, the latter disappearing upon equilibration with heavy water. The positions of these resonances are in reasonable accord with the structure (92). The positions of resonance are very sensitive to the geometry of the molecule and so comparisons with other systems (in this case) are not really very meaningful.

However, triphenylmethanol and tri-2,2',2"-tolylmethanol under the same conditions show a 15H multiplet (2.7-2.9τ) with a 1H singlet (7.2τ), and a 12H multiplet (2.6-3.3τ) with a 1H singlet (5.3τ) and a 9H singlet (7.8τ) respectively.

The mass spectrum of the product shows several interesting characteristics. A molecular weight of 410 (consistent with (92)) is indicated, and the intensity of the molecular ion peak (94%) would seem to indicate stabilisation by the aromatic groups. Similarly, the size of the (M-17) peak (74%), corresponding to loss of a hydroxyl radical, is as anticipated.
Triarylmethanols might be expected to fragment by successive loss of the aryl groups, i.e., triarylmethyl system → diarylmethyl system → monoarylmethyl system. This type of fragmentation occurs with triphenylmethanol and also occurs in the spectrum of (92), the peaks at 410, 283 and 155 being explicable on this basis. However, in the spectrum of (92) there are also two large peaks at 392(48%) and 265(59%) mass numbers which have no counterparts in the spectrum of triphenylmethanol. Similar peaks also occur in the spectrum of tri-2,2',2''-tolylmethanol, i.e. at 284(11%)(M-18) and 193(4%)(M-18-2-tolyl) mass numbers. These cannot arise from the main fragmentation route as they are of intermediate mass, and so it must be concluded that they arise from a separate mode of fragmentation.

A clue to the nature of this process is afforded by the peak at 392 mass numbers in the spectrum of (92). In section A.4.(e), the cyclodehydration reactions that some triarylmethanols possessing bulky aromatic groups undergo were discussed. It was noted that this process was brought about by treating the carbinols with electrophilic reagents, and it seems likely that the hydrocarbon products of such reactions can arise from the triarylmethyl carbonium ions. If this is so, it seems reasonable to attribute the peak at 392 mass numbers to the presence of the molecular ion of a hydrocarbon residue. The situation is illustrated in figure 4.

For clarity, this hydrocarbon product will be referred to as (92*), the superscript indicating its derivation from tri-1,1',1''-naphthylmethanol (92).
In addition, as will be shown later, the hydrocarbon residue is expected to fragment further by loss of a 1-naphthyl group, giving rise to a peak at 265 mass numbers. This is observed.

Evidence for the derivation of this 265 mass number fragment from a hydrocarbon is provided by its occurrence to a significant extent in the mass spectrum of \( (92') \), which was, as will be described, obtained by treating \( (92) \) with electrophilic reagents.

The fact that triphenylmethanol displays little evidence of the cyclodehydration process taking place in the spectrometer, follows from the observation that more severe conditions \( (400^\circ) \) are needed to form the fluorene derivative in significant quantities. On the other hand, tri-\( 2,2',2'' \)-tolymethanol can...
be cyclodehydrated by boiling in aqueous acid.

These mass spectral observations:

1) confirm the order of reactivity of triphenylmethanol and tri-2,2',2''-tolylmethanol towards cyclisation, and order which had been deduced using normal chemical procedures.

2) support the view that steric effects contribute considerably to this type of reactivity.

3) adumbrate the possibility that tri-1,1',1''-naphthylmethanol in normal chemical circumstances might be greatly susceptible to cyclodehydration.

In addition to this physico-chemical evidence, a number of other observations were made which are consistent with the tri-naphthylmethanol formulation. For example, the product gave a blue colouration in concentrated sulphuric acid (cf. the red colouration given by both the Schmidlin and the Chichibabin products) and also gave a hydrocarbon (92') upon boiling in acidic media. This hydrocarbon (92') was also formed when the product was treated with acetyl and thionyl chlorides. This behaviour, as will be shown in section B.2.(a), is consistent with the trinaphthylmethanol structure. In addition, stable addition compounds were formed with some solvents, particularly aromatic solvents, and the product gave an absorption at 3,550 cm^{-1} indicative of a hydroxyl compound. The combustion analysis results are also consistent with such a structure.

It seems evident that the reaction product is a triarylmethanol, whereas considerable doubt exists as to whether the Schmidlin or Chichibabin products were triarylmethanols. The results also indicate that (92) is a stable yet very reactive molecule.

B.2. Properties of tri-1,1',1''-naphthylmethanol (92).

B.2.(a). Rationalisation of the behaviour of tri-1,1',1''-naphthylmethanol in acidic media.

In acidic media, many triarylmethanols exist in equilibrium with their respective carbonium ions. The position of the
equilibrium is a function of the structure of the triarylmethanol and of the acidity of the medium.

\[
\text{Ar}_3\text{COH} + \text{H}^+ \rightleftharpoons \text{Ar}_3\text{C}^+ + \text{H}_2\text{O}
\]

Upon boiling (92) in glacial acetic acid a hydrocarbon (92') was formed and structural considerations indicate that this product arises by a cyclodehydration process.

The motivation for such a process can be understood in terms of a favourable free energy change, which in turn can be achieved by a reduction in the potential energy function. Within a series of triarylmethyl carbonium ions in which the aromatic rings are increasingly feathered out of plane, the potential energies of the ions are expected to increase with increasing departure from planarity, the conformation where the maximum resonance stabilisation is conferred. Cyclisation of the triarylmethyl carbonium ion produces a flattening of the propeller shaped ion, and it is anticipated that the more twisted a system is, the more advantageous the energy change resulting from cyclisation. A tri-1,1',1''-naphthylmethyl carbonium ion should be more disposed towards cyclisation than either triphenylmethyl or tri-2,2',2''-tolylmethyl carbonium ions.

The ease or rate at which such a process takes place is governed by the free energy difference between the ground state carbonium ion and the transition state leading to the cyclised product—the free energy of activation for the process. The smaller the latter is, the faster the reaction. This quantity can be advantageously affected by either increasing the energy of the reactant molecule or lowering the energy of the transition state. As the more twisted a carbonium ion is, the higher its intrinsic energy, it is evident that the less bond deformation a molecule has to undergo to arrive at the transition state, the
more accessible that state will be. It can then be anticipated that if analogous modes of cyclisation (for example, between 2- and 2'- positions) are being considered, from consideration of ground state energies tri-1,1',1"-naphthylmethyl carbonium ions should be faster than triphenylmethyl carbonium ions. If on the other hand pathways other than by 2,2'- bond formation are viable, and which require less total bond deformation, these should speed the dehydration process.

Experimentally, the propensity for rearrangement of triaryl­methyl carbonium ions and radicals has been shown to increase with increasing size of the aromatic group, to such an extent that di-1,1'-naphthylphenylmethanol cyclises within minutes upon boiling in glacial acetic acid (a weakly acid medium). The putative tri-1,1',1"-naphthylmethanol shows similar behaviour.

The products of these dehydration reactions have been considered to be fluorene derivatives. It is possible however, that where the triarylmethanol contains a 1-naphthyl residue or a similar structure, for example, 9-phenanthryl, cyclisation might not only occur by condensation between two ortho- positions of two aromatic rings forming fluorene derivatives like (105) but also between an ortho- position of one ring and a peri- position of another, to give a six-membered ring anthracene derivative like (106).

The situation in the context of a cyclodehydration reaction upon tri-1,1',1"-naphthylmethanol (92) is illustrated below. The problem then arises, and will be discussed in section B.2.(c), as to which, if either of the structures (105) or (106), is the product that is actually isolated i.e. (92')?
Examination of molecular models of the structures (105) and (106) reveals that the six-membered ring in (106) is a far less strained structure than the fluorene-like five-membered of (105), and on this basis would seem not only a more stable arrangement but also to possess a more accessible transition state.

The possibility that six-membered rings might be formed from triarylmethanols of suitable structure seemed a promising idea, particularly as only one example was found in the literature where the identity of the dehydration product was established by independent synthesis.\textsuperscript{101} Products were designated as fluorene derivatives on the basis of their absorption spectra and of their combustion analyses.

The dehydrated product obtained from (92) was, as far as could be ascertained from a melting point, a pure product and not a
mixture of isomers.

A discussion of the attempts that were made to distinguish between (105) and (106) follows in section B.2.(c).

The hydrolysis of triarylmethyl halides in polar solvents is known to proceed by an $S_N^1$ mechanism.$^{100}$ By the principle of microscopic reversibility, the formation of the halides under similar conditions must proceed by the same mechanism, involving an intermediate carbonium ion. With a very crowded ion like the tri-1,1',1"-naphthylmethyl carbonium ion, a significant activation energy for the formation of the chloride from the carbonium ion and chloride ion might exist. This barrier would be expected to slow down chloride formation relative to less crowded systems, and cyclisation of such carbonium ions being much faster than for less crowded systems, may result in the latter reaction becoming predominant. The chloride itself would be expected to possess a very polar carbon-chlorine bond and therefore by its very nature be liable to decomposition.

The isolation of tri-1,1',1"-naphthylmethyl chloride therefore depends upon slowing down the decomposition reaction more extensively than was found possible with techniques developed for the synthesis of other crowded systems.

B.2.(b). Influence of the properties observed for (92) upon the ease of preparation of a tri-1,1',1"-naphthylmethyl radical.

Two routes were considered as possibilities for the preparation of this free radical.

1) From the triarylmethyl chloride by reaction with a metal (Gomberg method).

2) By reduction of the corresponding carbonium ion with a transition metal ion.

The failure to isolate a trinaphthylmethyl chloride, and the observation that the blue colouration obtained by treating the
carbinol with concentrated sulphuric acid rapidly disappeared when the acid concentration was reduced from 97%, indicating low stability of the carbonium ion in aqueous media (the environment usually used for transition metal ion reductions) ruled out both of these routes to the free radical.

Other routes to the radical were ruled out because of the inaccessibility of the starting materials. It was therefore impossible to proceed further with the synthesis of the radical.

B.2.(c). Attempts to identify the hydrocarbon (92') obtained by treating tri-1,1',1''-naphthylmethanol (92) with electrophilic reagents.

The sharp melting point unchanged by further recrystallisation suggested the presence of a pure substance rather than a mixture of isomers. N.M.R. and combustion analyses were, as far as was ascertainable, consistent with either structure (105) or structure (106). The mass spectrum indicated a molecular weight of 392, also in accord with either structure.

Since a distinction between the two is very difficult to make on the basis of physical evidence alone, the syntheses of the two hydrocarbons (105) and (106) was attempted.

The only potentially viable route to these compounds seemed to be by 1,2- addition of 1-naphthyl-lithium to the ketones (107) and (108), to form the tertiary alcohols (109) and (110), followed by reduction of the alcohols.
The ketones (107) and (108) were prepared by previously reported procedures \textsuperscript{103,104}; the alcohols (109) and (110) and the hydrocarbons (105) and (106) have not previously been prepared.

Mixtures of 1-naphthyl-lithium with the ketone (107) using
various reaction conditions always gave intractable oils.

Reaction of 1-naphthyl-lithium with a benzene solution of the ketone (108) (the use of benzene as a solvent medium might be expected to reduce the extent of solvation of the organometallic reagent and therefore perhaps the size of the attacking species—a factor of crucial importance if 1,2-addition of reagent is required) gave an oil which on one occasion yielded two solid components (111) and (112) in 2% and 15% yields respectively. Both species melted at the same temperature, but the former appeared to be an alcohol whereas the latter appeared to be a ketone, although different from the starting material (108). Subsequent experiments aimed at preparing more of the product (111) were unsuccessful—this product was never again separated from the reaction mixture despite many attempts using various reaction conditions and times. The only solid product that was isolated on these occasions was (112).

The product (111) whose properties seemed consistent with the structure (110) was dissolved in glacial acetic acid and heated under reflux with zinc and hydrochloric acid for 1 week (the method used to reduce 9-phenyl-1,2:7,8-dibenzfluoren-9-ol to 9-phenyl-1,2:7,8-dibenzfluorene) after which time reduction had not taken place. Other attempts were made at the reduction using sodium borohydride and phosphorus/iodine.

All attempts to convert the alcohol (111) into a hydrocarbon having failed, it was decided to try to convert the hydrocarbon (92') to a tertiary halide which could then be hydrolysed to an alcohol which could be compared with the product (111). N-Bromosuccinimide was without action on (92'), but bromination in carbon tetrachloride whilst resulting in the evolution of hydrogen bromide did not lead to identifiable products, but only to a tar. Alcohols can be prepared by reaction of the corresponding anion with molecular oxygen. However, the hydrocarbon
(92') was recovered unchanged after treatment with phenyl-lithium and phenylsodium, and treatment with n-butyl-lithium gave a tar.

B.2.(d). Rationalisation of the results of attempts to prepare the hydrocarbons (105) and (106).

The formation of the alcohols (109) and (110) must arise through 1,2- addition of 1-naphthyl-lithium to the appropriate ketones. It has already been noted that α,β- unsaturated ketones can add reagent in two distinct ways (1,2- or 1,4- and 1,6- addition, and that the more complex situations arise when the geometry of the ketone is such that the approach of the attacking species to the carbonyl group is impeded. This would seem to be the case with the ketones (107) and (108), since structurally they possess many features in common with benzanthrone and the hindered benzophenones.

The problem therefore reduces to the question of whether 1,2- addition of reagent to the ketones (107) and (108) was achieved.

In the case of the ketone (107) it was not found possible to isolate the product of such an addition (or indeed any product or reactant) from this reaction.

On the other hand a low yield (2%) of a species which on the available evidence appeared to be (110) was once obtained. The stability of the product (111) towards air seemed to rule out the possibility of it being the enol precursor of a ring arylated ketone which would result from 1,4- or 1,6- addition of reagent.

The isolation of (112) in greater yield than (111) indicates that 1,2- addition competed unsuccessfully with other processes, and the information available suggests that the product (112) was a 1-naphthyl derivative of (108). By analogy with benzanthrone it would seem likely to be a 4-(1-naphthyl) derivative, for example,
The reaction of an alcohol of the type of (109) or (110) would be expected to proceed via a carbonium ionic species (by any method), and for the reduction to proceed the reducing species must have access to the reaction site. The reduction of this type of molecule is thus more likely to occur where the reducing species is a very compact reagent, for example, hydride ion. In practice this condition is very difficult to fulfil, although the very reactive reducing agents like lithium aluminium hydride or sodium borohydride effectively transfer $\text{H}^-$ to a species, it is doubtful if the true reagent is hydride ion itself. Similarly catalytic hydrogenations and dissolving metal reductions are thought to involve hydrogen in some way associated with, but not necessarily in a sterically compact form, the metal surface. It is conceivable that a molecule may exist that will not undergo reduction because of steric hindrance to the approach of the reducing species.

Similar difficulties arise in attempting bromination at the tertiary position of hydrocarbons like (105) or (106), for example, the conversion (106) to (113).
Such a reaction must involve the removal of the tertiary hydrogen atom followed by carbon-halogen bond formation. It might be anticipated that N-bromosuccinimide, whether it reacts as such or as a source of bromine atoms in low concentration, might extract the hydrogen atom less easily than from a less crowded molecule, and that the activation energy for tertiary halide formation from the tertiary radical might be prohibitively large. For example, N- Bromosuccinimide is without action on 2,2',4,4',6,6'-hexachlorodiphenylmethane (114).  

More interestingly the hydrocarbon (115) said to be obtained from 9-phenanthryl-(1-naphthyl)phenylmethanol (116) by treatment with acid, is not converted by molecular bromine (in carbon tetrachloride) into a tertiary halide (117).  

Hydrogen bromide is evolved from the reaction mixture but the product is unaffected by treatment with sodium ethoxide, a property not
shared with tertiary bromides. Apparently nuclear bromination takes place, and the observation of reaction between the hydrocarbon (92') and bromine would also suggest this.

It seems apparent that the rate of bromination at the allylic positions of hydrocarbons like (92') and (115) can be slowed to such an extent that other processes, particularly nuclear bromination, can successfully compete with, and even overtake it.

The inability of phenyl-lithium and phenylsodium to metallate the hydrocarbon (92') demonstrates further the inertness of the tertiary hydrogen atom. n-Butyl-lithium, possibly a more compact species in solution than the phenyl derivatives, did give some reaction but led to complex products, metallation probably occurring at several sites.

B.3. Substituted tri-1,1',1''-naphthylmethanols.
The preparation of substituted tri-1,1',1''-naphthylmethanols.

The syntheses of the substituted compounds were undertaken for the purpose of providing a 'handle' through which optical resolution of the systems might be achieved. The limitations of the method of synthesis and of the availability of the starting materials restricted the choice of substituent groups to the 4-methyl- and the 4-dimethylamino- groups. Four new compounds were prepared, namely

(93) 4-methyl-tri-1,1',1''-naphthylmethanol,
(93A) 4,4'-dimethyl-tri-1,1',1''-naphthylmethanol,
(93B) 4,4',4''-trimethyl-tri-1,1',1''-naphthylmethanol,
(94) 4-dimethylamino-tri-1,1',1''-naphthylmethanol,

The compounds (93), (93A), (93B) and (94) were prepared by
reaction of the corresponding aryl-lithium with di-(1-naphthyl) ketone, ethyl naphthoate, diethyl carbonate and di-(1-naphthyl) ketone, respectively. In each case the aryl-lithium was prepared by a transmetallation reaction using n-butyl-lithium.


All of the compounds were thermally unstable, particularly 4-methyl-tri-1,1',1''-naphthylmethanol (93) and 4-dimethylamino-tri-1,1',1''-naphthylmethanol (94). Heating the crude product (93) above 50° resulted in decomposition leading to the formation of a violet oil. This process was probably promoted by the presence in the crude product of traces of Lewis acids, which would facilitate the removal of the hydroxyl group.

The three methyl- derivatives (93), (93A) and (93B), upon warming in acidic media (for example, with a few drops of glacial acetic acid), all gave violet products which were never obtained crystalline, and were therefore never properly purified. However, interaction of these crude products with bromine gas resulted in the formation of blue coloured species, similar in appearance to those obtained when the carbinols (92), (93), (93A) and (93B) were treated with 97% sulphuric acid. Each of the blue species was very unstable, changing rapidly to a violet product.

On the other hand the dimethylamino- derivative (94) in acidic media firstly gave a blue species, but unlike the other carbinols this decomposed to give a permanently red solution.

Each of the carbinols formed stable crystalline complexes with ether and with aromatic solvents. In the case of 4-methyl-tri-1,1',1''-naphthylmethanol (93), it was found impossible to prepare the unsolvated carbinol in a pure state, as it rapidly reddened. Analysis of this product was therefore performed on the ether adduct which N.M.R. evidence suggested
Figure 5.

N.M.R. spectrum of the ether solvate of 4-methyl-tri-1,1',1''-naphthylmethanol (93) in deuterochloroform.

Instrument: Varian HA-60.
Figure 6.

N.M.R. spectrum of the dehydration product of the ether adduct of 4-methyl-tri-1,1',1''-naphthyl-methanol superimposed upon the spectrum of the undecomposed carbinol.

Instrument: Varian HA-60.
was a 1:1 mixture.

The N.M.R. spectrum of 4-methyl-tri-1,1',1''-naphthylmethanol (93) as the ether solvate is shown in figure 5. It consists of an aromatic band (1.8-3.4%), a hydroxyl resonance (6.0%) and bands arising from the bound ether (6.6% and 8.8%). The resonance from the 4-methyl- group is at 7.4%.

Interestingly, upon warming the specimen, water was eliminated giving rise to the violet oil mentioned above. The N.M.R. spectrum of this species superimposed upon the spectrum of the undecomposed carbinol is illustrated in figure 6. The spectrum indicates that the ether of crystallisation is lost whilst the hydroxyl resonance disappears completely, and the absorption from the 4-methyl- group changes both in intensity and structure.

The mass spectra of the methyl substituted derivatives (93) (93A) and (93B) all show large (M-17 and (M-18) peaks. The figures are (40% and 50%) (32% and 40%) and (33% and 48%) respectively. The dimethylamino- derivative (94) shows a substantial (26%) (M-17) peak.

B.3.(c). Rationalisation of the observed properties of the substituted trimethylmethanols.

Carbonium ions possessing a tri-1,1',1''-naphthylmethyl skeleton are evidently very reactive species. This reactivity can be understood in terms of the electronic repulsions within the molecules which are accentuated by their geometries. These interactions lower the thermodynamic stabilities of the systems so disposing them towards reaction. The type of reaction undergone is a function of the structure of the individual molecule.

The four substituted trimethylmethanols prepared (93)-(94) all possess substituent groups which are capable of interacting with electron deficient sites within the molecules: furthermore,
the orientations of these groups are such that their stabilising influences on the carbonium ions are maximised. The enhanced stabilities of such 4-substituted ions relative to the unsubstituted ion is usually attributed to resonance interactions of the types:
In principle, two main possibilities arise for the mode or modes of decomposition of the carbinols. The resonance hybrid (119) of the 4-methyl-tri-1,1',1''-naphthylmethyl carbonium ion (118) might give rise to a cyclised product, for example (121), directly analogous to the behaviour of the tri-1,1',1''-naphthylmethyl carbonium ion in forming the hydrocarbon (92'), or another hybrid (120) might give rise to a hydrocarbon of the type (122) and polymeric material, where one hydrogen atom of the water molecule eliminated is provided by the 4-methyl group.

The N.M.R. spectra of the decomposition products, the violet oils, indicate participation of the 4-methyl group in a dehydration reaction (as evidenced by the disappearance of the hydroxyl resonance, and the modification to the 4-methyl resonance).

The mass spectral data does not permit that a distinction be made between the two routes, since both result in the formation of dehydrated products, although of different structures.
In the case of the 4-dimethylamino-carbinol (94), loss of a hydrogen atom from the side chain, analogous to the transformation (120) to (122) is not possible. The large (M-17) fragment (26%) with no trace of a (M-18) fragment, suggests the initial formation of a stabilised triarylmethyl carbonium ion, and indicates the absence of a significant cyclodehydration reaction. It might reasonably be inferred that the methyl-substituted tri-naphthylmethanols (93), (93A) and (93B) in similar circumstances also do not undergo significant cyclodehydration reactions, implying that their primary mode of decomposition is along the lines of (120) → (122).

The behaviour of 4-dimethylamino-tri-1,1',l"-naphthylmethanol (94) in acidic media might be expected to be analogous to that of a crystal-violet type indicator because of the structural similarities. However indicator behaviour was not observed, perhaps on account of the very much greater crowding of the central carbon atom.


The instability of the tri-1,1',l"-naphthylmethyl carbonium ion and its 4-substituted analogues suggested the need to study an alternative system. A possibility, from the point of view of stability towards cyclisation, was a tri-2,2',2"-tolylmethyl skeleton, with a dimethylamino-group as a 'handle' for eventual optical resolution, situated in a position where its interaction with a free radical or carbonium ion generated at the α-carbon would be minimal.
Synthetically, the title compound was easily accessible although previously unreported. It was obtained as an oil which was not crystallised, but upon treatment with methyl iodide gave a crystalline quaternary salt.

B.5. Consequences of the new formulation for the triphenylmethyl radical dimer.

The three bladed propeller configuration with the aromatic rings feathered out of plane allows for two geometric isomers, the symmetrical and the unsymmetrical helices. If this picture is correct then optical activity could in principle be observed under certain conditions. The situation may be represented in the following way, where each of the capital letters refers to the sense of the orientation of one of the three rings comprising the triarylmethyl system.

\[
\begin{align*}
\text{R R R} & \quad \text{symmetrical helix} \\
\text{R L L} & \quad \text{unsymmetrical helix}
\end{align*}
\]

These two forms are diastereoisomers but not enantiomers, although each form possesses an enantiomer.

The racemisation of a symmetrical form, for example, of the isomer with an \textit{R R R} configuration, can be envisaged as involving
an inversion of one of the aromatic rings, i.e.,

\[
\begin{array}{cc}
R R R & \rightarrow & R L L \\
\text{stage (1)} & & \text{stage (2)}
\end{array}
\]

The isomer at stage (2) is of course the diastereoisomeric unsymmetrical helix. Further inversion of one of the right-handed rings,

\[
\begin{array}{cc}
R R L & \rightarrow & R L L \\
\text{stage (2)} & & \text{stage (3)}
\end{array}
\]

gives rise to the mirror image of the diastereoisomer obtained at stage (2), the isomer of stage (3). Further inversion leads to the enantiomer of the stage (1) isomer, the isomer of stage (4).

\[
\begin{array}{cc}
R L L & \rightarrow & L L L \\
\text{stage (3)} & & \text{stage (4)}
\end{array}
\]

Consider the transition from stage (1) to stage (2).
Irrespective of the mechanism, the net result is a change in the dihedral angle (the angle at which the aromatic ring is inclined to a plane containing the carbon atoms $C^\alpha$, $C^1$, $C^1_1$, and $C^1_1$) from say $+x^\circ$ to $-x^\circ$, during the course of which a state must exist (although not necessarily as an intermediate) in which the dihedral angle is $0^\circ$. Assuming this condition is reached, two possibilities arise:

1) The ring can revert to its original orientation.
2) The ring can invert its configuration.

Both courses are possible.

The anomalous dimer represents a state which for one ring fulfils the condition $\Theta = 0^\circ$. It might therefore be considered as an intermediate state in the overall racemisation sequence.
Dissociation of the dimer can lead to either retention or inversion of configuration. Anomalous dimer formation thus constitutes a mechanism whereby racemisation could take place, and which energetically may be more favourable than a mechanism which involves C—C bond stretching followed by rotation.

Ultimately what is important is the overall rate of racemisation, which conceivably might become so large that optical activity may not be detectable.

Assuming that racemisation could take place by a series of mechanisms, 1,2,3...n, each proceeding with a rate coefficient \( k_1, k_2, k_3, \ldots, k_n \),

\[
\text{the total rate of racemisation} = \sum_{k=n}^{k=n} k.
\]

Therefore any factor which can reduce the number of possible racemisation mechanisms, will tend to reduce the overall racemisation rate. Inhibition of anomalous dimer formation would be a step in the right direction.

As anomalous dimer formation occurs by C—C or C—C bond formation, inhibition to such processes would be achieved by the incorporation into a molecule of bulky groups in the 3- or 4- positions. Alkyl groups could be used for this purpose but the need for substituent groups in the aromatic rings themselves is obviated by using a tri-1,1',1''-naphthylmethyl skeleton. The three 1-naphthyl groups around the \( \alpha \)-carbon atom provide considerable steric hindrance to any new bond formation at the \( \alpha \)-carbon atom.

The optical resolution of a triaryl methyl system is therefore totally dependent upon the magnitudes of the rate coefficients for the individual racemisation routes, which may or may not combine to make the resolution possible.
B.6. The solvolysis of substituted diphenylmethyl chlorides.

B.6.(a). Objectives of the present work.

Since one of the factors contributing to the stabilities of triarylmethyl free radicals is resonance stabilisation, and as little is known quantitatively of the effects produced by alterations in the dihedral angles (the angles between the planes defined by the carbon atoms which comprise the aromatic rings and axis of the singly occupied p-orbital of the central carbon atom) upon the stabilisation of polyarylmethyl systems, the rates of solvolysis of some ortho- substituted diphenylmethyl chlorides were measured. Reaction conditions were chosen such that a carbonium ion or carbonium ion-like intermediate was formed, and hence changes in the stability of the ion would be reflected in corresponding changes in the free energy function.

The rapidity of the solvolysis of triphenylmethyl chloride itself, under the chosen reaction conditions ($k_1 = 0.343 \text{ sec.}^{-1} \text{ at } 0^\circ$)\(^{106}\) necessitates measurement at low temperatures ($-60^\circ$), with the attendant experimental difficulties.

On the other hand diphenylmethyl chloride is much less rapidly solvolysed and can be conveniently studied near room temperatures.

The methyl group was selected as the ortho- substituent for several reasons. Of prime importance was the size of the rate increment produced by the ortho- substituent both singly and severally: this ideally should be large enough to produce experimentally significant changes in the thermodynamic functions for the reaction, yet be not so large that the rate coefficients for the series of compounds under study have to be measured over different ranges of temperatures. The rate coefficients for solvolysis of a series of compounds were ultimately to be compared at one specific temperature (say $25^\circ$), and it was advantageous if all of the members of the series of compounds could be studied near this temperature. The methyl group satisfied this condition well.
The effects of replacing ortho hydrogen atoms in diphenylmethyl chloride by methyl groups were studied from two viewpoints.

1) The effect produced upon the rate coefficients and thermodynamic parameters (and hence stabilities) by progressively increasing the number of ortho methyl groups from none (in diphenylmethyl chloride) to the maximum of four (in 2,2',6,6'-tetramethyldiphenylmethyl chloride).

2) The size of the activating effects of 4-methyl and 4-t-butyl groups were observed in three systems, each possessing different dihedral angles, namely diphenylmethyl, 2,6-dimethyl diphenylmethyl and 2,2',6-trimethyldiphenylmethyl chlorides.

B.6. (b). Solvolysis conditions and method of rate measurement.

The free energy of activation for a unimolecular solvolysis is a measure of the kinetic stability of the carbonium ion-like transition state relative to the ground state molecule. Since the transition state for a bimolecular or more complex reaction cannot reasonably approximate to a diphenylmethyl carbonium ion, reaction conditions were chosen such that the solvolyses proceeded by an entirely unimolecular process and displayed first order kinetics.

This was achieved by using a polar, good solvating medium for the reaction: a mixture of absolute ethanol (90 ml.) and acetone (10 ml.) was found to be satisfactory. In this solvent medium the rate determining stage in the solvolysis was shown to be the ionisation of the halide (as required by a unimolecular solvolysis), the subsequent destruction of the carbonium ion occurring at a very much faster rate.

The solvolyses were followed by an adaption of Swain's method for following 'fast' reactions. This method has the advantage of checking the solvolysis mechanism of each run with each compound (this is essential if parameters for different
compounds are to be meaningfully compared), since it measures the reaction velocity in the presence of varying amounts of sodium ethoxide.

A plot of $\log \frac{a}{a-x}$ against time on every occasion gave a good straight line, showing first order kinetics for the solvolyses but not necessarily unimolecular solvolyses. However, if carbonium ion destruction were contributing to the rate expression to any significant extent, the rate of the overall reaction would involve ethanol and ethoxide ion concentrations. If the concentration of ethanol were involved in the rate expression, because of its presence in large excess the reaction would display pseudo-first order kinetics; however, the much stronger nucleophile ethoxide ion is present in a continuously varying concentration (although not in excess) and, if it were participating in the rate expression, would produce deviations in the plot of $\log \frac{a}{a-x}$ against time. Such deviations were not observed, and the good straight line plots under these conditions proved the unimolecularity of the processes.

Two of the more highly substituted diphenylmethyl chlorides (dimesitylmethyl and didurylmethyl chlorides) were solvolysed far too rapidly for the rates to be measured accurately in 9/1 v/v alcohol-acetone, and were therefore studied in a 1/1 v/v mixture. To obtain an approximate factor which could be used to predict a rate for the 9/1 mixture, the solvolyses of some halides were measured in both solvents. It was found that the mechanisms of the solvolyses were unchanged by changing to the new solvent.

B.7. Results of the measurements and a discussion of the rate coefficients obtained.

B.7.(a). General comments on the results obtained.

All compounds gave satisfactory first order plots up to at
least 70% reaction, many to 95% reaction. The correlation coefficients $r$ (a factor which for points lying exactly on a straight line is equal to 1.0000) were frequently 0.9995 or better, demonstrating the quality of the relationship between the individual points.

A slight trend towards a decreased rate coefficient beyond 80% reaction was sometimes observed - an observation also reported by Eaborn\textsuperscript{108} when studying the solvolyses of 9-chloro-9-phenylfluorene derivatives in 95% aqueous acetone. Such a trend is typical of the $S_N^1$ process and can be ascribed to the kinetically effective intervention of chloride ion at, and beyond, this point in the solvolysis, which effectively reduces the rate of the initial ionisation step.

E.7.(b). Results of the solvolyses of ortho-substituted diphenylmethyl chlorides

The rate coefficients for the ethanolyses and the derived transition state parameters are shown in tables 1, 2 and 3.
Table 1.

Rate coefficients, $k \times 10^4$ (sec$^{-1}$), for solvolysis of substituted diphenylmethyl chlorides in ethanol-acetone (9:1 v/v), temperatures in parentheses.

<table>
<thead>
<tr>
<th>Substituents</th>
<th>$k \times 10^4$ (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>None</td>
<td>0.0567(10.3) : 0.211(20.4) : 0.772(29.4) : 1.13(34.4)</td>
</tr>
<tr>
<td>2-Me</td>
<td>5.37(39.9) : 6.89(41.7) : 7.99(43.9) : 10.1(46.8) : 13.3(50.1) : 16.7(52.4)</td>
</tr>
<tr>
<td>2,2'-Me$_2$</td>
<td>0.70(22.5) : 1.91(30.4) : 3.65(36.4) : 4.60(39.9) : 9.72(46.8) : 15.0(52.5)</td>
</tr>
<tr>
<td>2,6-Me$_2$</td>
<td>0.190(25.3) : 0.407(35.2) : 0.851(40.0) : 1.48(45.0) : 2.29(49.4) : 3.63(53.7)</td>
</tr>
<tr>
<td>2,2',6-Me$_3$</td>
<td>2.36(30.4) : 4.23(35.4) : 6.77(39.9) : 10.6(44.1) : 14.5(47.8) : 20.8(51.7)</td>
</tr>
<tr>
<td>2,2',6,6'-Me$_4$</td>
<td>39.2(0.5) : 71.5(6.3) : 114(11.2) : 129(12.5) : 221(17.6) : 400(24.5)</td>
</tr>
</tbody>
</table>
### Table 2.

**Arrhenius parameters and transition state parameters, at 25° for solvolysis of substituted diphenylmethyl chlorides in ethanol-acetone (9:1 v/v).**

<table>
<thead>
<tr>
<th>Substituents</th>
<th>$E_\text{a}$ (kcal. mole$^{-1}$)</th>
<th>$\Delta H^\ddagger$ (kcal. mole$^{-1}$)</th>
<th>$\Delta G^\ddagger - \Delta H^\ddagger$ (kcal. mole$^{-1}$)</th>
<th>$\Delta S^\ddagger$ (e.u.)</th>
<th>$10^4k$ (sec$^{-1}$)</th>
<th>$\Delta G^*$ (kcal. mole$^{-1}$)</th>
<th>$k_{rel}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>None</td>
<td>22.1</td>
<td>21.5</td>
<td>2.1</td>
<td>7.0</td>
<td>0.38</td>
<td>23.6</td>
<td>1.00</td>
</tr>
<tr>
<td>2-Me</td>
<td>17.5</td>
<td>16.9</td>
<td>6.0</td>
<td>20.1</td>
<td>1.31</td>
<td>22.9</td>
<td>3.4</td>
</tr>
<tr>
<td>2,2'-Me$_2$</td>
<td>19.5</td>
<td>18.9</td>
<td>4.2</td>
<td>14.1</td>
<td>0.963</td>
<td>23.1</td>
<td>2.51</td>
</tr>
<tr>
<td>2,6-Me$_2$</td>
<td>19.4</td>
<td>20.8</td>
<td>3.3</td>
<td>11.1</td>
<td>0.184</td>
<td>24.1</td>
<td>0.48</td>
</tr>
<tr>
<td>2,2',6-Me$_3$</td>
<td>19.7</td>
<td>19.1</td>
<td>3.8</td>
<td>12.7</td>
<td>1.33</td>
<td>22.9</td>
<td>3.5</td>
</tr>
<tr>
<td>2,2',6,6'-Me$_4$</td>
<td>15.7</td>
<td>15.1</td>
<td>4.4</td>
<td>14.8</td>
<td>408</td>
<td>19.5</td>
<td>1074.00</td>
</tr>
</tbody>
</table>

Values of $E$, $\Delta H^\ddagger$ are accurate to ±200 cal. mole$^{-1}$, and $\Delta S^\ddagger$ to ±1 e.u.
Table 3.

Transition-state parameters and deviations from the maximum values of each set, at 25° for solvolysis of substituted diphenylmethyl chlorides in ethanol-acetone (9:1 v/v).

| Substituents | \( \Delta H^\dagger \) (kcal. mole\(^{-1}\)) | \( |\Delta H_{\text{max}}^\dagger - \Delta H^\dagger| \) (kcal. mole\(^{-1}\)) | \( \frac{\Delta G^\dagger - \Delta H^\dagger}{T \Delta S.} \) (kcal. mole\(^{-1}\)) | \( |(T \Delta S)_{\text{max}} - T \Delta S.| \) (kcal. mole\(^{-1}\)) | \( \Delta G^\dagger \) (kcal. mole\(^{-1}\)) | \( |\Delta G_{\text{max}}^\dagger - \Delta G^\dagger| \) (kcal. mole\(^{-1}\)) |
|--------------|---------------------------------|---------------------------------|---------------------------------|---------------------------------|---------------------------------|---------------------------------|
| None         | 21.5                            | 0.0                             | 2.1                             | 3.9                             | 23.6                             | 0.5                             |
| 2-Me         | 16.9                            | 4.6                             | 6.0                             | 0.0                             | 22.9                             | 1.2                             |
| 2,2'-Me\(_2\) | 18.9                            | 2.6                             | 4.2                             | 1.8                             | 23.1                             | 1.0                             |
| 2,6-Me\(_2\) | 20.8                            | 0.7                             | 3.3                             | 2.7                             | 24.1                             | 0.0                             |
| 2,2',6-Me\(_3\) | 19.1                            | 2.4                             | 3.8                             | 2.2                             | 22.9                             | 1.2                             |
| 2,2',6,6'-Me\(_4\) | 15.1                            | 6.4                             | 4.4                             | 1.6                             | 19.5                             | 4.6                             |

*Values of \( \Delta H \) are accurate to ±200 cal. mole\(^{-1}\) and \( \Delta S \) to ±1 e.u.*
Graph 1.

Transition-state functions, relative to the maximum value in each set, for the series of ortho-methyl substituted diphenylmethyl chlorides.
116. General observations.

In table 3, the transition state parameters shown in table 2 are expressed relative to the largest value of each set, i.e.

\[ \Delta H_{\text{max}}^* - \Delta H^*, \Delta G_{\text{max}}^* - \Delta G^* \text{ etc.} \]

These relative values are used in graph 1 to show the trends in the transition state parameters as the diphenylmethyl system is progressively substituted by ortho-methyl groups. The signs of these relative energy changes were chosen so that an ascending line represents a rate enhancing energy change, whereas a descending line represents a rate diminishing change.

Graph 1 reveals two interesting features:

1) The trend in the entropy term \( T \Delta S \) always opposes the trend in the enthalpy term \( \Delta H^* \).

2) The trend in the free energy of activation \( \Delta G \) is mirrored by the trend in the activation enthalpy \( \Delta H^* \).

These two observations indicate that the predominant contributor to the observed rate coefficients is always the appropriate activation enthalpy change, rather than the activation entropy change. Trends in rate coefficients within the series can therefore be meaningfully discussed either in terms of the free energies or the activation enthalpies for the solvolyses.

The size of the activation enthalpy for a unimolecular solvolysis of this type is, as expected, generally found to be very susceptible to the degree of charge delocalisation and solvation possible in the ground and transition states— an isolated localised charge is a less stable configuration than a solvated or dispersed charge.

The extent of participation of both of these potential stabilising factors in the reactions of a molecule is sensitive to the geometries of the ground and transition states of the reactant molecule, as will be shown. In rationalising the activation enthalpy parameters in table 2, or the trends revealed in graph 1, the changing geometries of the ground and
transition states are of primary importance.

The series of diphenylmethyl chlorides (96) $\rightarrow$ (101) represents a situation where the number of ortho- methyl substituents progressively increases from zero in diphenylmethyl chloride (96) to four, the maximum, in 2,2',6,6'-tetramethyldiphenylmethyl chloride (101). The introduction of ortho- substituents (with a van-der-Waals radius greater than that of hydrogen) into (96) modifies the geometries of the chloride and of the derived carbonium ion in much the same way as ortho- substituents modify the shapes of triphenylmethyl chlorides, carbonium ions and free radicals (section A.3(d)). Unlike species derived from triphenylmethyl systems, where interactions between ortho-substituents inhibit coplanarity of the aromatic rings (resulting in a propeller shape for the molecule), molecular models suggest that the diphenylmethyl carbonium ion is planar or very nearly planar. However, replacement of the four ortho- hydrogen atoms by methyl groups increases the sizes of the interactions between the ortho- substituents to such an extent that the most stable conformation of the molecule is one in which the aromatic rings are no longer coplanar, but are feathered as in the triphenylmethyl system. The geometries of the ground states of the chlorides (96) $\rightarrow$ (101), and of the carbonium ions derived therefrom, therefore reflect a regular increase in the interactions between ortho-substituents from the minimum in (96) to the maximum (for a given substituent) in (101). The dihedral angles tend to increase in the direction (96) $\rightarrow$ (101). This trend is expected to have two obvious consequences.

1) Increasing buckling of a system is expected to reduce the extent of solvation of the ground and transition states. Access to the primary site of charge localisation in the transition state (the α-carbon atom) is inhibited by rotation of the aromatic rings away from planarity.
2) Since the maximum transmission of \(\pi\)-electron-transmitted effects (for example, resonance and hyperconjugative interactions) is achieved when the dihedral angle is \(0^\circ\), increasing departure from planarity is expected to result in decreased stabilisation by this mechanism.

The systems (100) and (101) are therefore expected to derive less stabilisation by solvation of their transition states than are the systems (96) or (97), where access of solvent molecules to the centre of charge density is less restricted.

On the other hand the ground states of the chlorides (100) and (101) are expected to possess more highly polar carbon-chlorine bonds, i.e., nearer along the reaction coordinate to the transition state for the reaction (due to the greater crowding of the \(\alpha\)-carbon atom) than either (96) or (97), which in a good solvating medium will render them more amenable to solvent stabilisation than either (96) or (97).

These two factors, reduced solvation of the transition state and increased polarity of the ground state, operating in isolation from other effects, would make the solvolyses of the more crowded chlorides faster than the less crowded chlorides.

Increasing dihedral angle (as represented by the transition from (96) to (99)) presumably has the effect of increasing the energy of the ground state chlorides by virtue of reducing the extent of ground state \(\pi\)-electron-propagated stabilisation. However, because the transition state of the reaction is assumed to be close to the carbonium ion along the reaction coordinate, i.e., very similar in nature to the carbonium ion, it is much more polar than the ground state and is therefore very considerably more involved in \(\pi\)-electron-transmitted interactions than is the ground state. Changes in the stabilities of the transition states therefore greatly overshadow whatever changes occur in the energy contents of the ground states on this basis. As the
activating effect of ortho-methyl groups is relatively small, on the basis of change in the dihedral alone, the more crowded chlorides should be solvolysed more slowly than the less crowded ones.*

Solvation effects and π-electron-transmitted interactions are therefore expected to operate so as to lower the rate of solvolysis with increasing substitution. However, the operation of a further two factors might be anticipated acting to encourage solvolysis with increasing substitution.

The methyl group exerts a positive inductive effect which classically is transmitted by the bonding σ electrons. Electron density should thus be increased by each methyl group present in the molecule, and the activation arising from this release of charge should be undiminished by any change that might occur in the dihedral angle. The groups should always assist the reaction as the effect upon the more polar transition state should be much greater than upon the ground state.

An additional consequence of incorporating a number of bulky groups into ortho-positions within molecules like diphenylmethyl chloride is the invocation of what might be termed a 'steric strain factor'. Non-bonded interactions within a molecule are increased to such an extent due to restrictions imposed by the sheer physical dimensions of the system, that the intrinsic energy of the molecule becomes very high. These unfavourable interactions can be partially reduced by twisting of the aromatic rings. This method of accommodating the imposed stress over the molecule as a whole does not absorb or take up all of the strain. The ground state energy of the molecule thus rises, thus facilitating the attainment of any less crowded transition state, particularly the attainment of a transition state which is close in hybridisation to \( sp^2 \) (where the angle between the bonds from the central carbon atom approaches \( 120^\circ \) - as opposed to the tetrahedral angle of
about 109°. A change in hybridisation from sp³ to sp² in these circumstances can therefore be a very favourable transition.

The individual rate coefficients and transition state parameters for the solvolyses of the chlorides (96) → (101) will now be discussed in terms of the factors enumerated above.

(ii). Diphenylmethyl chloride (96).

\[ \Delta H = 21.5 \text{ kcal.mole}^{-1} : \quad 10^4 k = 0.38 \text{ sec}^{-1} : \quad k_{rel} = 1.00 \]

(iii). 2-Methyldiphenylmethyl chloride (97).

\[ \Delta H = 16.9 \text{ kcal.mole}^{-1} : \quad 10^4 k = 1.31 \text{ sec}^{-1} : \quad k_{rel} = 3.4 \]

A reduction in activation enthalpy from 21.5 to 16.9 kcal.mole⁻¹ implies considerable stabilisation by the substituent. Internal distribution of charge can be achieved by several mechanisms, hyperconjugation with the methyl group and σ-electron transmission of the inductive effect of the methyl group being particularly important.

The transition state in the solvolysis is not expected to be much different (in dihedral angle) from that in the corresponding reaction of diphenylmethyl chloride. While two extreme conformations (97A) and (97B) are possible for the carbonium ion, the latter is expected to be a much higher energy state than the former as it involves one methyl-hydrogen interaction which must modify the dihedral angle, whereas this type of interaction is avoided by the conformation (97A).
In the conformation (97A), the methyl group can exert almost its maximum possible activation upon the solvolysis. The virtual planarity of the ion means that all \( \pi \)-electron-transmitted interactions are maximised, and the ortho- positioning of the methyl group maximises the inductive stabilisation.

It is interesting to compare activation enthalpies for the solvolyses of the 2-methyl and 4-methyl isomers: the value for the latter being 17.4 kcal.mole\(^{-1}\) (see next section). The difference between the two values (0.5 kcal.mole\(^{-1}\)), although only just outside experimental error, indicates the 2-methyl solvolysis to be the more activated.

If it were assumed that the \( \pi \)-electron-transmitted activations of the two groups were comparable, then the greater proximity of the 2-methyl group to the reaction centre, on the basis of its larger inductive effect alone, could account for the difference in stability. However, if the 2-methyl group altered the dihedral angle to any great extent away from 0\(^\circ\), then the \( \pi \)-electron-transmitted activation of the 4-methyl group must exceed that of the 2-methyl group. It seems likely that the similarity of the two figures can be ascribed to a similarity in the two dihedral angles.

A similar result has been observed in the activation enthalpy
parameters for the solvolyses of 2- and 4-methoxyphenyl-9-chloro-fluorenes (129) and (130) (16.9 and 17.5 kcal.mole\(^{-1}\) respectively). In contrast the figures for 2- and 4-methyl compounds (131) and (132) are 18.3 and 17.2 kcal.mole\(^{-1}\), and the figures for the 2- and 4-chloro compounds (133) and (134) are 20.2 and 18.6 kcal.mole\(^{-1}\) respectively. The results for the 2- and 4-chloro compounds can in part be rationalised in terms of the greater inductive deactivating influence of the 2-chloro group.

\[
\begin{align*}
X &= 2-\text{MeO} \quad (129) \\
X &= 4-\text{MeO} \quad (130) \\
X &= 2-\text{Me} \quad (131) \\
X &= 4-\text{Me} \quad (132) \\
X &= 2-\text{Cl} \quad (133) \\
X &= 4-\text{Cl} \quad (134)
\end{align*}
\]

The experimental errors involved in these figures are similar in magnitude to those in our own results. It is particularly noticeable that the 2- and 4-methyl compounds (131) and (132) differ by 1.1 kcal.mole\(^{-1}\) in their activation enthalpies, a figure well outside the range of experimental error, and inexplicably opposite in direction to our own.

The lower values for the activation enthalpies of the ortho-substituted molecules (where they occur) cannot be attributed to a release of steric strain, as this factor would operate in all cases being perhaps of greater dimensions in the cases of the 9-phenylfluorenes.

(iv) 2,2'-Dimethyldiphenylmethyl chloride (98).

\[\Delta H^\ddagger = 18.9 \text{ kcal.mole}^{-1}; \quad 10^4 k = 0.963 \text{ sec}^{-1}; \quad k_{rel} = 2.5\]
The presence of a further methyl group provides extra inductive stabilisation and the possibility of extra \( \pi \)-electron-transmitted stabilisation. However, as the activation enthalpy for solvolysis rises from 16.9 (for 2-methyl) to 18.9 kcal.mole\(^{-1} \) for (98), it must be concluded that one or both of the following has occurred.

1) An increase in the dihedral angle of the transition state (relative to the 2-methyl transition state) which effectively reduces the amount of \( \pi \)-electron stabilisation available (from the maximum).

2) The effect of the extra group has been to provide relatively more steric inhibition to solvation of the transition state than occurs with the 2-methyl compound (97).

As with (97), the carbonium ion can exist in two possible extreme conformations (98A) and (98B), the former with a cis relationship of the methyl groups, the latter with a trans relationship.

\[ \text{(98A)} \]

\[ \text{(98B)} \]

Of the two, (98A) would seem to be the more stable, as it is the more nearly planar conformation and hence more resonance stabilised. No unfavourable methyl-hydrogen interaction is involved.

If this assumption is correct it must be concluded that the
2 kcal.mole\(^{-1}\) difference from (97) in activation enthalpy is due to steric inhibition to solvation of the transition state, brought about by the positioning of the methyl groups. If on the other hand the conformation (98B) is an important contributor to the ground state of the molecule, the difference in stability can be rationalised in terms of the different dihedral angles.

In terms of the relative rates, if the extra methyl group was identical in effect to the first methyl group, the rate of solvolysis (relative to diphenylmethyl chloride) would be 11.6 instead of the observed value of 2.5.

(v). 2,6-Dimethyldiphenylmethyl chloride (99).

\[ \Delta H = 20.8 \text{ kcal.mole}^{-1} : \quad 10^4 k = 0.184 \text{ sec.}^{-1} : \quad k_{rel} = 0.48 \]

The trend towards increasing activation enthalpy for the solvolyses, first apparent with the 2,2'-dimethyl compound (98), is maintained. However, unlike the latter which can adopt the nearly planar conformation (98A), (99) cannot avoid an ortho-methyl-ortho-hydrogen interaction, and the carbonium ion must possess a somewhat buckled conformation (99A).
As a result all $\pi$-electron-transmitted stabilisation is reduced (increasing the enthalpy of activation), and as predicted for (98), there must be a contribution to the enthalpy term arising from steric inhibition of solvation (also tending to increase the activation enthalpy).

The net effect of two methyl groups is to place an energy barrier to reaction, exceeded only in this series of compounds, by diphenylmethyl chloride itself. Moreover, the size of the relative rate factor (0.48) suggests that the assumption that structures (97B) and (98B) are minor contributors to the overall situation in regard to the molecules (97) and (98), is reasonable. The entropic requirements of the reaction impose restraint to reaction (additional to that in the diphenylmethyl system), which results in a larger free energy of activation (24.1 kcal.mole$^{-1}$ as opposed to 23.6 kcal.mole$^{-1}$ for the diphenylmethyl system) and consequently a relative rate factor of 0.48.

(vi). 2,2',6-Trimethyldiphenylmethyl chloride (100).

$\Delta H = 19.1$ kcal.mole$^{-1}$ : $10^4 k = 1.33$ sec.$^{-1}$ : $k_{rel} = 3.5$

The introduction of a further ortho- methyl group might be expected to increase the activation enthalpy by further buckling the molecule, with attendant reduction in resonance and solvation stabilisation. As with (98), of the two extreme conformations available to the carbonium ion (100A) and (100B), (100A) is expected to be the more stable: and similarly like (98), the main effect of the additional methyl group is expected to result from steric inhibition to solvation, rather than decreased conjugation.
On this simple analysis an activation enthalpy in excess of 20.8 kcal.mole\(^{-1}\) would be expected.

On the contrary, a movement in the opposite direction is in fact observed, to 19.1 kcal.mole\(^{-1}\). Clearly an additional factor or factors, of sufficient magnitude to compensate for the expected rise in activation enthalpy above 20.8 kcal.mole\(^{-1}\), and moreover to reduce the enthalpy barrier to 19.1 kcal.mole\(^{-1}\) (a 1.7 kcal.mole\(^{-1}\) reduction) must now be operating.

It has already been observed that the more buckled is a chloride, the more favourable and easy is the change from the \(\text{sp}^3\) hybrid state to the less crowded \(\text{sp}^2\) state, in which the system is better able to accommodate non-bonded interactions. It follows that all of the chlorides (96) to (101) will be predisposed towards solvolysis for this reason alone, but the magnitude of the effect will be greatest in the more buckled molecules (99), (100) and (101). The activation enthalpy figures suggest that this effect becomes appreciable first with (100), although logically it might be expected to make a significant contribution to the value for the 2,6-dimethyl compound (99).

The more crowded chlorides (99), (100) and (101) might be expected to possess more highly polar carbon-chlorine bonds (because of steric effects) and would thus be more susceptible to ground state solvation stabilisation than the earlier members of
the series (96), (97) and (98). On an enthalpy basis this factor is expected to retard the solvolyses of (99), (100) and (101), and so any accelerating influence will appear to be lessened.

It can therefore be concluded that the reduction (by 1.7 kcal.mole \(^{-1}\) in activation enthalpy achieved by the introduction of the third methyl group is a minimum value for the size of any accelerating phenomena.

The relative rate of 3.5 thus indicates the counterbalancing of rate reducing factors by the rate enhancing release of steric strain. If this interpretation is correct, it can be predicted that further crowding should be characterised by acceleration of the rate of solvolysis.

(vii). 2,2',6,6'-tetramethyldiphenylmethyl chloride (101).

\[ \Delta H = 15.1 \text{ kcal.mole}^{-1} ; \quad 10^4 k = 408 \text{ M}^{-1} \cdot \text{s}^{-1} ; \quad k_{rel} = 1074 \]

The addition of the fourth methyl group produces a further reduction in activation enthalpy (as predicted) of 4.0 kcal.mole \(^{-1}\) to 15.1 kcal.mole \(^{-1}\). It is concluded that this is directly and unambiguously attributable to the participation of a very sizeable steric acceleration, which has completely overwhelmed the three rate reducing tendencies that are known to operate and which, for the sake of clarity, are enumerated below.

1) A reduction in transition state stabilisation by \(\pi\)-electron-transmitted interactions. The dihedral angle in this molecule is expected to be the greatest encountered in the series, as for the first time an ortho-methyl-ortho-methyl repulsion is unavoidable.

2) A reduction, greatest with greatest extent of ortho-substitution, in solvation of the transition and ground states due to increased buckling of the system.
3) The possibility (also greatest with increasing ortho-substitution) of increased solvent stabilisation of the ground state, due to the polarity of the carbon-chlorine bond.

(viii). Summary.

The replacement of the four ortho-hydrogen atoms of diphenylmethyl chloride by four methyl groups has reduced the activation enthalpy for ethanolysis by 30%. This figure can be thought of as a minimum measure of a weakening of the carbon-chlorine bond brought about by steric effects.

The magnitude of the steric effect of course depends upon the crowding present within a system, which in turn is a function of the geometry of the system and the sizes of the interacting groups. As diphenylmethyl chloride can be induced to display a large effect by the use of the relatively small methyl group, triphenylmethyl chloride would be expected to show even more dramatic rate changes upon ortho-substitution. The activation enthalpy for solvolysis of triphenylmethyl chloride under the same conditions as our solvolyses has been shown to be 12.3 kcal.mole\(^{-1}\) as opposed to 22.1 kcal.mole\(^{-1}\) for diphenylmethyl chloride. This reduction is undoubtedly due in part to an increased contribution from resonance stabilisation in the transition state, but the relative importance
of this interaction and of the increased steric strain within the molecule are uncertain.

The greater steric requirements of triphenylmethyl radicals (compared to chlorine) would suggest that in triphenylmethyl radical equilibria the steric effect is very substantial indeed.

B.7.(c). Results of the ethanoly ses of \textit{meta-} and \textit{para-}
substituted diphenylmethyl chlorides.

The rate coefficients for ethanolysis and the derived transition state parameters are shown in tables 4, 5 and 6. The Hammett functions are shown in table 7.
**Table 4.**

Rate coefficients, $k \times 10^4$ (sec.$^{-1}$), for solvolysis of *meta-* and *para-* substituted diphenylmethyl chlorides in ethanol-acetone (9:1 v/v), temperatures in parentheses.

<table>
<thead>
<tr>
<th>Substituents</th>
<th>None</th>
<th>4-Me</th>
<th>4,4'-Me$_2$</th>
<th>4-t-Bu</th>
<th>4,4'-t-Bu$_2$</th>
<th>3-Me</th>
<th>3,3'-Me$_2$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>0.0567(10.3) : 0.211(20.4) : 0.772(29.4) : 1.15(34.4)</td>
<td>10.1(26.1) : 14.8(29.7) : 26.6(35.4) : 39.3(39.9) : 63.0(44.9) : 92.1(49.8)</td>
<td>9.12(1.0) : 43.7(14.5) : 73.9(19.6) : 83.5(22.5) : 121.0(24.7) : 180.0(29.5)</td>
<td>7.91(26.1) : 1.9(29.7) : 20.9(35.4) : 32.8(39.9) : 51.4(44.9) : 75.8(49.8)</td>
<td>29.4(14.5) : 43.2(19.4) : 58.2(20.9) : 80.5(24.5) : 122.0(29.5) : 174.0(32.9)</td>
<td>1.43(30.1) : 2.44(35.0) : 4.59(41.2) : 8.56(47.1) : 11.0(49.8) : 14.0(52.5)</td>
<td>2.81(30.1) : 4.88(35.0) : 9.08(41.2) : 15.9(47.1) : 24.2(52.1)</td>
</tr>
</tbody>
</table>
Table 5a

Arrhenius parameters and transition state parameters, at 25° for solvolysis of substituted diphenylmethyl chlorides in ethanol-acetone (9:1 v/v).

<table>
<thead>
<tr>
<th>Substituents</th>
<th>$E_*$ (kcal. mole$^{-1}$)</th>
<th>$\Delta H^*$ (kcal. mole$^{-1}$)</th>
<th>$\Delta G^* - \Delta H^*$ (kcal. mole$^{-1}$)</th>
<th>$\Delta S^*$ (e.u.)</th>
<th>$10^9 k$ (sec$^{-1}$)</th>
<th>$\Delta G^*$ (kcal. mole$^{-1}$)</th>
<th>$k_{rel}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>None</td>
<td>22.1</td>
<td>21.5</td>
<td>2.1</td>
<td>7.0</td>
<td>0.38</td>
<td>23.6</td>
<td>1.0</td>
</tr>
<tr>
<td>3-Me</td>
<td>20.3</td>
<td>19.7</td>
<td>3.5</td>
<td>11.7</td>
<td>0.769</td>
<td>23.2</td>
<td>2.0</td>
</tr>
<tr>
<td>3,3'-Me$_2$</td>
<td>19.2</td>
<td>18.6</td>
<td>4.2</td>
<td>14.1</td>
<td>1.61</td>
<td>22.8</td>
<td>4.2</td>
</tr>
<tr>
<td>4-Me</td>
<td>18.0</td>
<td>17.4</td>
<td>4.3</td>
<td>14.4</td>
<td>8.93</td>
<td>21.7</td>
<td>23.5</td>
</tr>
<tr>
<td>4,4'-Me$_2$</td>
<td>17.2</td>
<td>16.6</td>
<td>3.6</td>
<td>12.1</td>
<td>115</td>
<td>20.2</td>
<td>302</td>
</tr>
<tr>
<td>4-t-Bu</td>
<td>18.4</td>
<td>17.8</td>
<td>4.1</td>
<td>13.8</td>
<td>7.01</td>
<td>21.9</td>
<td>18.4</td>
</tr>
<tr>
<td>4,4'-t-Bu$_2$</td>
<td>17.0</td>
<td>16.4</td>
<td>4.0</td>
<td>13.4</td>
<td>79.2</td>
<td>20.4</td>
<td>208</td>
</tr>
</tbody>
</table>

Values of $E$ and $\Delta H^*$ are accurate to ± 200 kcal. mole$^{-1}$, and $\Delta S$ to ± 1 e.u.
Table 6.

Transition-state parameters and deviations from the maximum values of each set, at 25° for solvolysis of substituted diphenylmethyl chlorides in ethanol-acetone (9:1 v/v).

| Substituents | \( \Delta H^* \) kcal. mole\(^{-1} \) | \( |\Delta H_{\text{max}}^* - \Delta H^*| \) kcal. mole\(^{-1} \) | \( |\Delta G^* - \Delta H^*| \) kcal. mole\(^{-1} \) | \( |(TAS)_{\text{max}}^* - TAS^*| \) kcal. mole\(^{-1} \) | \( \Delta S^* \) kcal. mole\(^{-1} \) | \( |\Delta G_{\text{max}}^* - \Delta G^*| \) kcal. mole\(^{-1} \) |
|--------------|---------------------------------------|--------------------------------------|--------------------------------------|--------------------------------------|---------------------------------------|--------------------------------------|
| None         | 21.5                                  | 0.0                                  | 2.1                                  | 2.2                                  | 23.6                                  | 0.0                                  |
| 3-Me         | 19.7                                  | 1.8                                  | 3.5                                  | 0.8                                  | 23.2                                  | 0.4                                  |
| 3,3'-Me\(_2\)| 18.6                                  | 2.9                                  | 4.2                                  | 0.1                                  | 22.8                                  | 0.8                                  |
| 4-Me         | 17.4                                  | 4.1                                  | 4.3                                  | 0.0                                  | 21.7                                  | 1.9                                  |
| 4,4'-Me\(_2\)| 16.6                                  | 4.9                                  | 3.6                                  | 0.7                                  | 20.2                                  | 3.4                                  |
| 4-t-Bu       | 17.8                                  | 3.7                                  | 4.1                                  | 0.2                                  | 21.9                                  | 1.7                                  |
| 4,4'-t-Bu\(_2\)| 16.4                                  | 5.1                                  | 4.0                                  | 0.3                                  | 20.4                                  | 3.2                                  |

Values of \( \Delta H^* \) are accurate to ±200 cal. mole\(^{-1} \) and \( \Delta S^* \) to ±1 e.u.
Table 7.

Hammett treatment (graph of log $k_{rel}$ against $\sigma^+$) for meta- and para- substituents.

<table>
<thead>
<tr>
<th>Substituents</th>
<th>$k_{rel}$</th>
<th>log $k_{rel}$</th>
<th>$\sigma^+$</th>
</tr>
</thead>
<tbody>
<tr>
<td>None</td>
<td>1.0</td>
<td>0.000</td>
<td>-0.000</td>
</tr>
<tr>
<td>3-Me</td>
<td>2.0</td>
<td>0.501</td>
<td>-0.069</td>
</tr>
<tr>
<td>3,3'-Me₂</td>
<td>4.2</td>
<td>0.627</td>
<td>-0.138</td>
</tr>
<tr>
<td>4-t-Bu</td>
<td>18.4</td>
<td>1.263</td>
<td>-0.256</td>
</tr>
<tr>
<td>4-Me</td>
<td>23.5</td>
<td>1.371</td>
<td>-0.311</td>
</tr>
<tr>
<td>4,4'-t-Bu₂</td>
<td>208</td>
<td>2.319</td>
<td>-0.512</td>
</tr>
<tr>
<td>4,4'-Me₂</td>
<td>302</td>
<td>2.481</td>
<td>-0.622</td>
</tr>
</tbody>
</table>
Graph 2.
Transition-state functions, relative to the largest value in each set, for the ethanlyses of meta- and para- substituted diphenylmethyl chlorides.

\[
\Delta H^\circ_{\text{max}} - \Delta H^\circ \\
\Delta G^\circ_{\text{max}} - \Delta G^\circ \\
\Delta S^\circ_{\text{max}} - \Delta S^\circ
\]
Graph 3.

Hammett treatment of the effects of meta- and para-substituents in the diphenylmethyl system.
B.7.(c)(i). Discussion of results.

The compounds shown in table 4 comprise a series of mono-alkyl- and symmetrically substituted di-alkyl- diphenylmethyl chlorides. As before, a graph (2) was constructed to illustrate changes in the transition state parameters produced by each substituent. The graph reveals two main features.

1) With each compound, the change in the enthalpy of activation considerably exceeds the corresponding entropy of activation change, thus demonstrating the relevance of the activation enthalpy parameter to a discussion of relative rates of solvolysis.

2) The maximum observed change in the $\Delta S$ term is $2.2 \text{kcal.mole}^{-1}$, found by introducing a 4-methyl group into diphenylmethyl chloride, and the maximum difference between any two substituted compounds is only $0.8 \text{kcal.mole}^{-1}$ (between 4- methyl and 3-methyl diphenylmethyl chlorides).

The rate enhancing effect of the three substituent groups is in the order 4-methyl > 4-t-butyl > 3-methyl, and this is also the order of the stabilising effect as measured by the enthalpy of activation. This relation between a 4-methyl and a 4-t-butyl group is the so-called Baker-Nathan or hyperconjugative order of activation. A Baker-Nathan order of activation has also been observed for the solvolyses of $\alpha$-cumyl chlorides at $25^\circ$ in 90% aqueous acetone and in ethanol at $25^\circ$, and also for the solvolyses of triphenylmethyl chlorides in 40% ethanol-ether at $60^\circ$. The figures from this research show that the relative rate-enhancing effect of the 4-methyl group to the 4-t-butyl group is 1.13 corresponding to a free energy of activation difference of only $0.2 \text{kcal.mole}^{-1}$. Such a small energy difference is very difficult to account for as many factors could produce such a small change.

The rate coefficients for the di-alkylated series are in the order 4,4'-dimethyl > 4,4'-di-t-butyl > 3,3'-dimethyl, but the order
of activation enthalpies is 4,4'-di-t-butyl > 4,4'-dimethyl > 3,3'-di-methyl. This unexpected result may not be significant in view of the experimental error associated with the measurement of these quantities (0.3 kcal.mole⁻¹, represented by the vertical lines on graph 2).

Interestingly, even after taking into account possible experimental errors, it appears that on an enthalpy basis, introduction of the second substituent stabilises the systems less than did the introduction of the first (the deviation from additivity is more discernible with the more potent activating substituents 4-methyl and 4-t-butyl). Using the figures plotted on the graph, the 3'-methyl group imparts only 60% of the stabilisation resulting from the 3-methyl group. The corresponding figures for the 4-methyl and 4-t-butyl groups are 20% and 38% respectively. Without placing too much emphasis on these percentages, the underlying trend can be discerned. It seems likely that the unequal effects of the two substituents can be rationalised in terms of unequal electron demand upon each.

The almost isoentropic behaviour of the solvolyses of the substituted compounds confirms the relevance of the activation enthalpy parameter to a discussion of the relative rates of solvolysis, as it implies that, in addition to the enthalpy term predominating over the entropy term (deduced from the relative magnitudes of the ΔH and TΔS terms), changes in rate within the series can be attributed almost entirely to changes in activation enthalpy. The entropy of a system depends in a complex way upon the modes of vibration and rotation of all of the molecules, and from reactions in solution there are contributions from solvation which cannot be estimated at all. Small changes in the entropy requirements of reactions are thus very difficult to account for.

A Hammett-type treatment was applied to the series (the 4,4'-di-alkylated compounds with methyl and t-butyl groups were excluded
from the calculation of the $Q$ value because of the lack of additivity of substituent effects. Least squares analysis gave a $Q$ value of $-4.6 \pm 0.24$. The quality of this line (graph 3) through the five points demonstrates the applicability of the $\sigma^+$ function to this reaction.

This representation of the results also indicates that the effects of the second methyl and t-butyl groups is less than that of the first, so that the disubstituted derivatives would lie on a line of lesser slope. In this context it is useful to treat the magnitude of the $Q$ value as a measure of the electron demand upon the substituents. On this basis the second substituents in the molecules have a lesser electron demand made upon them than the first.

This measured value of the reaction constant is consistent with values obtained for similar systems under similar reaction conditions. Some of these results appear in table 8.

<table>
<thead>
<tr>
<th>Reaction</th>
<th>Solvent</th>
<th>$Q$</th>
<th>Temp. ($^\circ$C)</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>$X-C_6H_4-CMe_2^+ + H_2O$</td>
<td>90% acetone-H$_2$O</td>
<td>$-4.54$</td>
<td>25</td>
<td>95</td>
</tr>
<tr>
<td>$X-C_6H_4-CMe_2^+ + EtOH$</td>
<td>EtOH</td>
<td>$-4.67$</td>
<td>25</td>
<td>95</td>
</tr>
<tr>
<td>$Ar^tCHCl$</td>
<td>MeOH</td>
<td>$MeOH$</td>
<td>$-4.07$</td>
<td>25</td>
</tr>
<tr>
<td>$ar^tCHCl$</td>
<td>EtOH</td>
<td>$EtOH$</td>
<td>$-5.09$</td>
<td>25</td>
</tr>
<tr>
<td>$Ar^tCHCl$</td>
<td>i-ProH</td>
<td>i-ProH</td>
<td>$-2.76$</td>
<td>25</td>
</tr>
<tr>
<td>$Ar^tCl$</td>
<td>EtOH</td>
<td>60% ether-EtOH</td>
<td>$-2.92$</td>
<td>0</td>
</tr>
<tr>
<td>9-$Ar^t-C_7H_5-OH-9-Cl + EtOH$</td>
<td>90% EtOH-Me$_2$CO</td>
<td>$-4.40$</td>
<td>25</td>
<td>106</td>
</tr>
</tbody>
</table>
B.7.(d). Results of the ethanolyses of substituted 2,6-dimethyl-diphenylmethyl chlorides.

The rate coefficients for ethanolysis and the derived transition state parameters appear in tables 9, 10 and 11. The Hammett functions appear in table 12.
Table 9.

Rate coefficients, $k \times 10^4$ (sec.$^{-1}$), for solvolysis of 2,6-dimethyldiphenylmethyl chlorides in ethanol-acetone (9:1 v/v), temperatures in parentheses.

<table>
<thead>
<tr>
<th>Substituents</th>
<th>0.190(25.3)</th>
<th>0.407(35.5)</th>
<th>0.851(40.0)</th>
<th>1.49(45.0)</th>
<th>2.29(49.9)</th>
<th>3.63(53.7)</th>
</tr>
</thead>
<tbody>
<tr>
<td>None</td>
<td>2.08(20.8)</td>
<td>6.02(29.5)</td>
<td>8.07(32.5)</td>
<td>13.1(36.5)</td>
<td>24.1(42.9)</td>
<td></td>
</tr>
<tr>
<td>4-Me</td>
<td>2.71(25.4)</td>
<td>4.03(30.5)</td>
<td>5.37(33.2)</td>
<td>9.55(39.6)</td>
<td>17.1(45.8)</td>
<td>33.9(52.4)</td>
</tr>
<tr>
<td>4-t-Bu</td>
<td>35.1(-7.9)</td>
<td>56.3(-4.2)</td>
<td>80.2(-0.7)</td>
<td>123(3.8)</td>
<td>209(9.1)</td>
<td>289(13.3)</td>
</tr>
<tr>
<td>4-MeO</td>
<td>3.00(26.1)</td>
<td>4.97(30.3)</td>
<td>8.36(35.1)</td>
<td>14.8(40.9)</td>
<td>24.5(45.8)</td>
<td>35.7(50.1)</td>
</tr>
<tr>
<td>3,5-Me$_2$</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
Table 10.

Arrhenius parameters and transition-state parameters, at 25° for solvolysis of substituted 2,6-dimethyldiphenylmethyl chlorides in ethanol-acetone (9:1 v/v).

<table>
<thead>
<tr>
<th>Substituents</th>
<th>E (kcal. mole⁻¹)</th>
<th>ΔH⁺ (kcal. mole⁻¹)</th>
<th>ΔG - ΔH⁺ (kcal. mole⁻¹)</th>
<th>ΔS⁺ (e.u.)</th>
<th>10⁴ k (sec⁻¹)</th>
<th>ΔG* (kcal. mole⁻¹)</th>
<th>krel</th>
</tr>
</thead>
<tbody>
<tr>
<td>None</td>
<td>21.4</td>
<td>20.8</td>
<td>3.3</td>
<td>11.1</td>
<td>0.184</td>
<td>24.1</td>
<td>1.0</td>
</tr>
<tr>
<td>4-He</td>
<td>20.7</td>
<td>20.1</td>
<td>2.2</td>
<td>7.3</td>
<td>3.36</td>
<td>22.3</td>
<td>18.3</td>
</tr>
<tr>
<td>4-t-Bu</td>
<td>19.4</td>
<td>18.8</td>
<td>3.7</td>
<td>12.4</td>
<td>2.60</td>
<td>22.5</td>
<td>14.1</td>
</tr>
<tr>
<td>4-MeO</td>
<td>14.9</td>
<td>14.3</td>
<td>4.8</td>
<td>16.1</td>
<td>819</td>
<td>19.1</td>
<td>44.51</td>
</tr>
<tr>
<td>3,5-Me₂</td>
<td>19.8</td>
<td>19.2</td>
<td>3.3</td>
<td>11.1</td>
<td>2.62</td>
<td>22.5</td>
<td>14.2</td>
</tr>
</tbody>
</table>

*Values of E and ΔH are accurate to ±200 cal. mole⁻¹, and ΔS to ±1 e.u.*
Table 11.

Transition-state parameters and deviations from the maximum values of each set, at 25° for solvolysis of substituted 2,6-dimethyldiphenylmethyl chlorides in ethanol-acetone (9:1 v/v).

| Substituents | $\Delta H^*$ | $|\Delta H_{max}^* - \Delta H^*|$ | $\Delta G^* - \Delta H^* = \Delta S^*$ | $|(TAS)_{max}^* - (TAS)^*$ | $\Delta G^*$ | $|\Delta G_{max}^* - \Delta G^*|$ |
|--------------|--------------|---------------------------------|-----------------------------------|----------------------------|-------------|---------------------------------|
|              | (kcal. mole$^{-1}$) | (kcal. mole$^{-1}$) | (kcal. mole$^{-1}$) | (kcal. mole$^{-1}$) | (kcal. mole$^{-1}$) | (kcal. mole$^{-1}$) |
| None         | 20.8         | 0.0                            | 3.3                               | 1.5                       | 24.1        | 0.0                             |
| 4-Me         | 20.1         | 0.7                            | 2.2                               | 2.6                       | 22.3        | 1.8                             |
| 4-t-Bu       | 18.8         | 2.0                            | 3.7                               | 1.1                       | 22.5        | 1.6                             |
| 4-NO          | 14.3         | 6.5                            | 4.8                               | 0.0                       | 19.1        | 5.0                             |
| 3,5-Me$_2$    | 19.2         | 1.6                            | 3.3                               | 1.5                       | 22.5        | 1.6                             |

Values of $\Delta H^*$ are accurate to $\pm 200$ kcal. mole$^{-1}$ and $\Delta S^*$ to $\pm 1$ e.u.
<table>
<thead>
<tr>
<th>Substituents</th>
<th>$k_{rel}$</th>
<th>$\log k_{rel}$</th>
<th>$\sigma^+$</th>
</tr>
</thead>
<tbody>
<tr>
<td>None</td>
<td>0.000</td>
<td>0.000</td>
<td>-0.000</td>
</tr>
<tr>
<td>4-Me</td>
<td>10.0</td>
<td>1.262</td>
<td>-0.311</td>
</tr>
<tr>
<td>4-t-Bu</td>
<td>14.1</td>
<td>1.149</td>
<td>-0.256</td>
</tr>
<tr>
<td>3,5-Me$_2$</td>
<td>14.2</td>
<td>1.152</td>
<td>-0.138</td>
</tr>
<tr>
<td>4-Me$_2$</td>
<td>44.51</td>
<td>3.648</td>
<td>-0.705</td>
</tr>
</tbody>
</table>

Table 12: Hammett treatment (graph of $\log k_{rel}$ against $\sigma^+$) for meta- and para-substituted 2,6-dimethylphenylmethy
Graph 4.
Transition-state functions, each relative to the largest value in each set, for the ethanolyzes of substituted 2,6-dimethyldiphenylmethy1 chlorides.
B.7.(d).(i). Discussion of results.

The graph (4) which illustrates changes in the transition state parameters within the series, shows several interesting features.

Firstly, that the overwhelming contribution to the observed increases in the rates of solvolysis of the 4-t-butyl- and 4-methoxy- chlorides comes from the reduction in the activation enthalpy term, which presumably is brought about by transition state stabilisation. The enthalpy changes are 2.0 kcal.mole\(^{-1}\) and 6.5 kcal.mole\(^{-1}\) respectively, and the free energy changes are 1.6 kcal.mole\(^{-1}\) and 5.0 kcal.mole\(^{-1}\) respectively.

Secondly, the insertion of two meta- methyl groups into 2,6-dimethyldiphenylmethyl chloride, giving the 2,3,5,6-tetramethyl analogue, does not change the entropy of activation but lowers the activation enthalpy difference between the two reactions by the surprisingly large value of 1.6 kcal.mole\(^{-1}\). This result can be attributed to the effect of interactions between the methyl groups situated in the 2- and 3- positions, and similar interactions between the methyl groups situated at the 5- and 6- positions.

![Diagram](144)

This buttressing effect of the two adjacent methyl groups can produce a distortion of the bond angle between the carbon atoms A, B and C (ABC), from 120°. This effectively increases the
crowding around the α-carbon atom, one effect of which is a steric acceleration of solvolysis. This acceleration has been observed in the solvolyses of 2,2',6-trimethyl- and 2,2',6,6'-tetramethyl-
diphenylmethyl chlorides (100) and (101).

The thermodynamic parameters observed for the solvolysis of the 4-methyl chloride (141) are also suprising. This compound is observed to solvolyse marginally faster than the analogous 4-t-butyl chloride (142) by a factor of 1.30 (table 10) (a Baker-Nathan order of reactivity), yet this relationship of the two rates appears to be brought about predominantly by the more favourable entropy requirement of the solvolysis of (141). The order of activation enthalpies is in fact an anti-Baker-Nathan order, the transition state in the solvolysis of (141) being only 0.7 kcal.mole⁻¹ more stable than the parent molecule, whereas the transition state in the solvolysis of the 4-t-butyl compound (142) is 2.0 kcal.mole⁻¹ more stable than its parent molecule.

A Hammett treatment was applied to the series, the 3,5-dimethyl-
chloride (144) being excluded from the calculation of the reaction constant θ, because of the probable intervention of the buttressing effect which would alter the geometry about the reaction site. Least squares analysis gave θ = -5.22±0.39. A line with this slope is the full line on graph (5). The broken lines most rationally illustrate the probable limits of error involved. However, on consideration of the graph, it can be seen that a line of lesser slope (θ = -4.2) could be drawn, taking into account only the points for the 4-methyl, 4-t-butyl and hydrogen groups. This procedure could be justified by the argument that the point corresponding to the 4-methoxy group is possibly in much greater error than the other points, as the individual rate coefficients for this compound were measured over a different temperature range (-7°C - +13.3°C), as opposed to +25°C - +50°C, the extrapolations to 25°C producing disproportionate errors.
In view of this observation, it does not seem sensible to attribute great significance to the rather unusually high derived $\psi$ (-5.2; cf. Table 8).

Even taking into account the uncertainty in the value of the reaction constant in this series, the point corresponding to the 3,5-dimethyl derivative (144) is inconsistent with other values obtained in the series. This discrepancy is understandable in terms of a steric acceleration to solvolysis, arising from a buttressing effect due to the presence of the two meta- methyl groups.

B.7.(e). Results of the ethanolyse of substituted 2,2',6-
trimethylidiphenylmethyldichlorides.

The rate coefficients for ethanolyse and the derived transition state parameters appear in tables 13, 14 and 15. The appropriate Hammett functions appear in table 16.
Table 13.

Rate coefficients, $k \times 10^4$ (sec.$^{-1}$), for solvolysis of para-substituted 2,2',6-trimethyldiphenylmethyl chlorides in ethanol-acetone (9:1 v/v), temperatures in parentheses.

<table>
<thead>
<tr>
<th>Substituents</th>
<th>2.36(30.4)</th>
<th>4.23(35.4)</th>
<th>6.77(39.9)</th>
<th>10.6(44.1)</th>
<th>14.5(47.8)</th>
<th>20.8(51.7)</th>
</tr>
</thead>
<tbody>
<tr>
<td>None</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>4-t-Bu</td>
<td>13.5(24.7)</td>
<td>23.0(29.5)</td>
<td>34.7(33.9)</td>
<td>53.8(38.4)</td>
<td>78.3(43.0)</td>
<td></td>
</tr>
<tr>
<td>4-Me</td>
<td>9.39(19.4)</td>
<td>18.8(25.4)</td>
<td>29.4(30.5)</td>
<td>42.4(33.5)</td>
<td>72.1(38.9)</td>
<td></td>
</tr>
</tbody>
</table>
Table 14.

Arrhenius parameters and transition-state parameters, at 25° for solvolysis of substituted 2,2',6-trimethyl-diphenylmethyl chlorides in ethanol-acetone (9:1 v/v).

<table>
<thead>
<tr>
<th>Substituents</th>
<th>E*</th>
<th>ΔH*</th>
<th>ΔG - ΔH*</th>
<th>ΔS*</th>
<th>10^b k</th>
<th>ΔG‡</th>
<th>k_rel</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>(kcal. mole⁻¹)</td>
<td>(kcal. mole⁻¹)</td>
<td>(kcal. mole⁻¹)</td>
<td>(e.u.)</td>
<td>(sec⁻¹)</td>
<td>(kcal. mole⁻¹)</td>
<td></td>
</tr>
<tr>
<td>None</td>
<td>19.7</td>
<td>19.1</td>
<td>3.8</td>
<td>12.7</td>
<td>1.33</td>
<td>22.9</td>
<td>1.0</td>
</tr>
<tr>
<td>4-t-Bu</td>
<td>18.0</td>
<td>17.4</td>
<td>4.1</td>
<td>13.8</td>
<td>13.8</td>
<td>21.5</td>
<td>10.4</td>
</tr>
<tr>
<td>4-Me</td>
<td>18.8</td>
<td>18.2</td>
<td>3.2</td>
<td>10.7</td>
<td>16.7</td>
<td>21.4</td>
<td>12.5</td>
</tr>
</tbody>
</table>

Values of E and ΔH are accurate to ±200 cal. mole⁻¹, and ΔS to ±1 e.u.
Table 15.

Transition-state parameters and deviations from the maximum values of each set, at 25° for solvolysis of substituted 2,2',6-trimethyldiphenylmethyl chlorides in ethanol-acetone (9:1 v/v).

<table>
<thead>
<tr>
<th>Substituents</th>
<th>$\Delta H^\ddagger$</th>
<th>$\Delta H_{\text{max}}-\Delta H^\ddagger$</th>
<th>$\Delta G^\ddagger - \Delta H^\ddagger$</th>
<th>$(T\Delta S)^<em>_{\text{max}}-T\Delta S^</em>$</th>
<th>$\Delta G^\ddagger$</th>
<th>$\Delta G_{\text{max}}-\Delta G^\ddagger$</th>
</tr>
</thead>
<tbody>
<tr>
<td>None</td>
<td>19.1</td>
<td>0.0</td>
<td>3.8</td>
<td>0.3</td>
<td>22.9</td>
<td>0.0</td>
</tr>
<tr>
<td>4-t-Bu</td>
<td>17.4</td>
<td>1.7</td>
<td>4.1</td>
<td>0.0</td>
<td>21.5</td>
<td>1.4</td>
</tr>
<tr>
<td>4-Me</td>
<td>18.2</td>
<td>0.9</td>
<td>3.2</td>
<td>0.9</td>
<td>21.4</td>
<td>1.5</td>
</tr>
</tbody>
</table>

Values of $\Delta H^\ddagger$ are accurate to ±200 cal. mole$^{-1}$ and $\Delta S$ to ±1 e.u.
Table 16.

Hammett treatment (graph of log $k_{rel}$ against $\sigma^+$) for para-substituted 2,2',6-trimethyldiphenylmethyl chlorides.

<table>
<thead>
<tr>
<th>Substituents</th>
<th>$k_{rel}$</th>
<th>log $k_{rel}$</th>
<th>$\sigma^+$</th>
</tr>
</thead>
<tbody>
<tr>
<td>None</td>
<td>1.0</td>
<td>0.000</td>
<td>-0.000</td>
</tr>
<tr>
<td>4-t-Bu</td>
<td>10.4</td>
<td>1.016</td>
<td>-0.256</td>
</tr>
<tr>
<td>4-Me</td>
<td>12.5</td>
<td>1.099</td>
<td>-0.311</td>
</tr>
</tbody>
</table>
Graph 6.

Transition-state functions, each relative to the largest value in each set, for the ethanoylation of substituted 2,2',6-trimethyl2-phenylmethyl chlorides.
B.7.(e).(i). Discussion of results.

The order of reactivity towards solvolysis in this series is still 4-methyl > 4-t-butyl- (the Baker-Nathan order). However, it is again noticeable that the order of activation enthalpies is the reverse of this, and that it is the entropy effect which brings about the observed Baker-Nathan order of reactivity.

The Hammett plot indicates a $\rho$ value of $3.67 \pm 0.36$, but this is derived from three points only, covering a small range of $\sigma^+$ values, one of which (the 4-methyl) is suspected of displaying anomalous behaviour (section B.7.(d).(i). compound (141)).

More detailed discussion of the results of these experiments and of the derived reaction constant is probably not very fruitful because of the paucity of experimental information available and the several incalculable factors which must influence them.

B.7.(f). Results of the ethanolyses of substituted 2,2',6,6'-tetramethyldiphenylmethyl chlorides.

Rate coefficients for ethanolysis and the derived transition state parameters are shown in tables 17, 18 and 19. The results for three reference compounds are also shown.
Table 17.
Rate coefficients, $k \times 10^k \text{ (sec.}^{-1})$, for solvolysis of substituted diphenylmethyl chlorides in ethanol-acetone (1:1 v/v) and of three reference compounds in the same solvent mixture, temperature in parentheses.

<table>
<thead>
<tr>
<th>Substituents</th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>2,2',4,4',6,6'-Me$_6$</td>
<td>8.63(-36.5)</td>
<td>19.1(-30.7)</td>
<td>30.8(-25.7)</td>
<td>40.2(-21.2)</td>
<td>90.5(-14.0)*</td>
</tr>
<tr>
<td>2,2',3,3',5,5',6,6'-Me$_8$</td>
<td>4.41(-39.3)</td>
<td>8.76(-31.7)</td>
<td>20.8(-24.1)</td>
<td>83.3(-13.0)</td>
<td>108(-7.3)*</td>
</tr>
<tr>
<td>4-Me</td>
<td>4.85(35.0)</td>
<td>9.38(41.5)</td>
<td>14.7(46.4)</td>
<td>19.4(49.7)*</td>
<td></td>
</tr>
<tr>
<td>4-t-Bu</td>
<td>2.08(30.0)</td>
<td>3.82(36.0)</td>
<td>5.27(40.1)</td>
<td>9.44(45.0)*</td>
<td></td>
</tr>
<tr>
<td>2,4,6-Me$_3$</td>
<td>2.03(33.2)</td>
<td>2.88(37.4)</td>
<td>3.62(40.9)</td>
<td>5.58(43.3)</td>
<td>7.44(45.8)*</td>
</tr>
</tbody>
</table>
### Table 18

Arrhenius parameters and transition-state parameters, at 25° for solvolysis of substituted 2,2',6,6'-tetramethyl-diphenylmethyl chlorides in ethanol-acetone (1:1 v/v).

<table>
<thead>
<tr>
<th>Substituents</th>
<th>$E_0$ ($\text{kcal. mole}^{-1}$)</th>
<th>$\Delta H^+$ ($\text{kcal. mole}^{-1}$)</th>
<th>$\Delta G^+-\Delta H^+$ ($\text{kcal. mole}^{-1}$)</th>
<th>$\Delta S^+$ (e.u.)</th>
<th>$10^6 k$ (sec$^{-1}$)</th>
<th>$\Delta G^+$ ($\text{kcal. mole}^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>4,4'-Me$_2$</td>
<td>12.2</td>
<td>11.6</td>
<td>6.9</td>
<td>23.1</td>
<td>1940</td>
<td>18.5</td>
</tr>
<tr>
<td>3,3',5,5'-Me$_4$</td>
<td>13.0</td>
<td>12.4</td>
<td>6.2</td>
<td>20.8</td>
<td>1670</td>
<td>18.6</td>
</tr>
</tbody>
</table>

Values of $E$ and $\Delta H$ are accurate to ±200 cal. mole$^{-1}$, and $\Delta S$ to ±1 e.u.
Table 19.

Arrhenius parameters and transition-state parameters, at 25° for solvolysis of substituted diphenylmethyl chlorides in ethanol-acetone (1:1 v/v).

<table>
<thead>
<tr>
<th>Substituents</th>
<th>$E_*$ (kcal. mole$^{-1}$)</th>
<th>$\Delta H^*$ (kcal. mole$^{-1}$)</th>
<th>$\Delta G^* - \Delta H^*$ (kcal. mole$^{-1}$)</th>
<th>$\Delta S^*$ (e.u.)</th>
<th>$10^k$ (sec$^{-1}$)</th>
<th>$\Delta G^*$ (kcal. mole$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>4-Me</td>
<td>18.7</td>
<td>18.1</td>
<td>4.6</td>
<td>15.4</td>
<td>1.70</td>
<td>22.7</td>
</tr>
<tr>
<td>4-t-Bu</td>
<td>19.0</td>
<td>18.4</td>
<td>4.5</td>
<td>15.1</td>
<td>1.16</td>
<td>22.9</td>
</tr>
<tr>
<td>2,4,6-Me$_3$</td>
<td>20.1</td>
<td>19.5</td>
<td>3.7</td>
<td>12.4</td>
<td>0.511</td>
<td>23.2</td>
</tr>
</tbody>
</table>

Values of $E$ and $\Delta H^*$ are accurate to ± 200 cal. mole$^{-1}$, and $\Delta S^*$ to ± 1 e.u.
B.7.(f).(i). Discussion of results.

The rates of solvolysis of dimesitylmethyl- and didurylelmethyl
clorides were found to be too fast to follow in the ethanol-
acetone mixture (9:1 v/v) even at temperatures around $-45^\circ$. Two
alternative means of measurement suggested themselves. Either
the same solvent mixture could be used when the temperature range
over which the solvolyses were to be studied would have to be
reduced dramatically below $-45^\circ$, or, a different solvent medium
could be used which allowed the solvolyses to be studied at more
accessible temperatures. Both methods at best give only very
approximate values for the rate coefficients in the 9:1 mixture
at $25^\circ$.

The former method suffers from the practical difficulty of the
substantial viscosity of the reaction medium at the low temperature
necessary, and the fact that the slope of the Arrhenius graph must
be extrapolated back over a large temperature range with
consequent errors.

On the other hand, the use of the latter method presents
difficulties in as much as the new reaction medium must be such as
to slow down the reaction appreciably yet leave the mechanism
unchanged. Fortunately the method of measurement of the rate
coefficients allowed a check on the mechanism of the reaction.
Secondly, and perhaps of paramount importance, its success depends
upon the existence of a definite relationship between the rates
of solvolysis in the two media. On balance the second approach
seemed more promising.

The medium acetone-ethanol (1:1) satisfied the mechanistic
and kinetic requirements. The rates of solvolysis of three
compounds, 4-tert-butyl-, 4-methyl- and 2,4,6-trimethylidiphenylmethyl
clorides were measured in the new solvent medium and the rate
coefficients at $25^\circ$ for these solvolyses were found to be
reduced (compared with those in ethanol-acetone(9:1)) by factors
of 0.166, 0.191 and 0.152 respectively. Using the average of these three figures as an approximate conversion factor, the rate coefficient at 25° in acetone-ethanol (1:9 v/v) for the solvolyses of dimesitylmethyl and didurylmethyl chlorides are predicted to be $11,400 \times 10^{-4}$ sec$^{-1}$ and $9,850 \times 10^{-4}$ sec$^{-1}$ respectively. The rate coefficient for the solvolysis of the parent molecule of the series 2,2',6,6'-tetramethylidiphenylmethyl chloride (101), under these conditions was measured to be $408 \times 10^{-4}$ sec$^{-1}$. 
B.8. Summary and conclusions.

A Hammett treatment to ascertain whether linear free energy relationships apply to effects of substituents in the three systems diphenylmethyl (section B.7.(c). graph (3)), 2,6-dimethyl-diphenylmethyl (section B.7.(d). graph (5)) and 2,2',6-trimethyl-diphenylmethyl (section B.7.(e). graph (7)) has been applied using \( \sigma^+ \) values. The reaction constants thus evaluated, particularly the values for the 2,6-dimethyl diphenylmethyl and the 2,2',6-trimethyl diphenylmethyl series, were obtained using only a relatively small range of \( \sigma^+ \) values (0.706 units and 0.311 units respectively) and also were obtained from a relatively small number of experimental points. However, the results afford a fairly definite indication that a trend to smaller susceptibilities occurs with increasing dihedral angle.

The demonstration of a linear free energy relationship by means of a Hammett-type graph depends upon the existence of such a valid relationship, and also upon the suitability to the reaction under consideration, of the \( \sigma^+ \) values chosen to represent the substituent constants. As indicated above, the reaction constants (the Hammett parameters) derived from our results must be accepted only with some reservations.

However, the question of whether a linear free energy relationship holds for the effect of the 4-methyl and 4-t-butyl groups in the three systems studied in this work, can be approached in an alternative way using only the rate coefficients actually measured to define the free energy changes. This is illustrated in the treatment below.

The equations (2), (3) and (4) represent the application of the Hammett equation to the three systems diphenylmethyl, 2,6-dimethyl-diphenylmethyl and 2,2',6-trimethyl diphenylmethyl, and show the effect of one substituent (the 4-methyl group) upon each of the systems.
Diphenylmethyl system. \[ \log k_{\text{rel}} = \sigma^+ \varphi = 1.3711 (2) \]

2,6-Dimethyldiphenylmethyl system. \[ \log k_{\text{rel}} = \sigma^+ \varphi' = 1.2615 (3) \]

2,2',6-Trimethyldiphenylmethyl system. \[ \log k_{\text{rel}} = \sigma^+ \varphi'' = 1.0987 (4) \]

\( \sigma^+ \) is the substituent constant for the 4-methyl substituent and \( \varphi, \varphi' \) and \( \varphi'' \) are the reaction constants for the three series (not individually calculated in this treatment).

\[
k_{\text{rel}} = \frac{k_{4-\text{Me}}}{k_{4-\text{H}}} \quad \text{in the diphenylmethyl series, and } k'_{\text{rel}} = \frac{k'_{4-\text{Me}}}{k'_{4-\text{H}}}
\]
in the 2,6-dimethyldiphenylmethyl system etc. These values were obtained from the rate coefficients measured and which appear in tables 7, 12 and 16.

Since \(-\Delta G = RT \log k\), \( \log k_{\text{rel}}, \log k'_{\text{rel}} \) and \( \log k''_{\text{rel}} \) are proportional to the changes in the activation free energy requirements brought about by the substitution of the 4-methyl groups in the three series (\( \Delta \Delta G_{4-\text{Me}} \)).

Dividing equations (2), (3) and (4) by equation (2),

\[
\frac{\log k_{\text{rel}}}{\log k_{\text{rel}}} = \frac{\varphi}{\varphi} = 1.00 = \Delta \Delta G \text{ relative to } Ph_2CH \quad (2')
\]

\[
\frac{\log k'_{\text{rel}}}{\log k_{\text{rel}}} = \frac{\varphi'}{\varphi} = 0.92 = \Delta \Delta G \text{ relative to } Ph_2CH \quad (3')
\]

\[
\frac{\log k''_{\text{rel}}}{\log k_{\text{rel}}} = \frac{\varphi''}{\varphi} = 0.80 = \Delta \Delta G \text{ relative to } Ph_2CH \quad (4')
\]

Similarly for the effect of the 4-t-butyl group,

Diphenylmethyl system. \[ \log k_{\text{rel}} = \sigma^+ \varphi = 1.2660 (5) \]

2,6-Dimethyldiphenylmethyl system. \[ \log k'_{\text{rel}} = \sigma^+ \varphi' = 1.1501 (6) \]

2,2',6-Trimethyldiphenylmethyl system. \[ \log k''_{\text{rel}} = \sigma^+ \varphi'' = 1.0162 (7) \]
Dividing equations (5), (6) and (7) by equation (5),

\[
\frac{\log k_{rel}}{\log k'_{rel}} = \frac{\rho}{\rho'} = 1.00 = \Delta AG \text{ relative to Ph}_2\text{CH} \quad (5')
\]

\[
\frac{\log k''_{rel}}{\log k'_{rel}} = \frac{\rho''}{\rho} = 0.91 = \Delta AG \text{ relative to Ph}_2\text{CH} \quad (6')
\]

This treatment of the results obviates the assumption of particular values for substituent constants. Only the rate coefficients are used to define the changes in the free energy parameters.

Two conclusions can be drawn from the close correspondence of the free energy ratios for the two substituents.

1) A free energy relationship does apply for the effect of the 4-methyl and 4-t-butyl groups upon all three systems.

2) The reaction—facilitating effects of the two groups (as measured by the free energy changes) are reduced by identical amounts upon changing their associated reaction systems.

This second conclusion is of particular interest since the ability of a substituent group which conjugates with the reaction site, to influence the reaction rate, is related to the extent of orbital overlap that can be achieved. In the cases above, the degree of overlap is governed by the dihedral angle. Several examples of such steric inhibition of resonance have been cited in sections A.5.(c) and A.5.(d). Now the remoteness of the para— substituents from the reaction site suggests that \(\pi\)-electron-transmitted interactions from this position make only a minor contribution to the total rate increment (4-methyldiphenylmethyl
chloride is solvolysed 12 times faster than is 3-methyl diphenylmethyl chloride (table 7)), and so it may be concluded that the predominant contributor to the activation is a conjugative interaction, which is expected to decrease with increasing dihedral angle. In such circumstances, the stabilising influences of substituent groups are expected to decrease.

The fact that the stabilities of the transition states in the solvolyses are observed to decrease (in the ratios 1.0 : 0.91 : 0.80) is in harmony with this interpretation. Moreover, the observation that the same proportion (1.0 : 0.91 : 0.80) of the available stabilisation is lost by systems containing both groups, implies that the predominant mode of activation by both groups is a π-electron-transmitted effect. This conclusion incidentally confirms the assertion that π-electron-transmitted interactions from the para- position are of minor significance in determining the total rate of the process (at least in the substituents studied), since if they were predominant, little change would be observed upon increasing the dihedral angle.

If activation by para- alkyl groups is attributed to hyper-conjugation as our results for the 4-methyl and 4-t-butyl groups suggest, then the decreasing stabilities of the transition states with increasing dihedral angle, clearly indicates the intervention of steric inhibition of hyperconjugation in the 2,6-dimethyl- diphenylmethyl and 2,2',6-trimethyldiphenylmethyl systems.

The effects of conjugative interactions are expected to be apparent in the activation enthalpy as well as the activation free energy parameters. Interestingly, while the trends in the activation enthalpy parameter mirrors the trend in the activation free energy parameter in the progressively ortho- methyl substituted diphenylmethyl chlorides (graph 1), this is not always found to be the case, particularly in regard to the operation of the 4-methyl group in other systems (graphs 2, 4 and 6). In these
situations, the reason for the greater activation by the 4-methyl group compared to the effect of the 4-t-butyl group appears to be attributable to the more favourable activation entropy changes. This parameter is not expected to change in simple relationship to changes in the dihedral angle.

The position may be summarised in the following way. If the magnitude of the free energy parameter is taken as the criterion of transition state stability, then the stabilising influences of the two alkyl groups are decreased by identical amounts upon increasing the dihedral angle, however, upon reference to table 21 which is assembled from the relevant data in tables 6, 11 and 15, it can be seen that this relationship does not hold if the activation enthalpy (a potential energy function which is expected to be very sensitive to the extent of conjugative stabilisation) is taken as the criterion of transition state stability.

Table 20.

Activation enthalpies and activation free energies (in kcal.mole⁻¹) for the solvolyses of 4-methyl and 4-t-butyl substituted diphenylmethyl and substituted-diphenylmethyl chlorides (each relative to the parent molecule of its series (the appropriate 4-H derivative)) in ethanol-acetone (9:1 v/v) at 25°.

<table>
<thead>
<tr>
<th>System</th>
<th>4-Methyl</th>
<th>4-t-Butyl</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>ΔG⁺</td>
<td>ΔH⁺</td>
</tr>
<tr>
<td>Diphenylmethyl.</td>
<td>1.9</td>
<td>4.1</td>
</tr>
<tr>
<td>2,6-dimethyldiphenylmethyl.</td>
<td>1.8</td>
<td>0.7</td>
</tr>
<tr>
<td>2,2',6-trimethyldiphenylmethyl.</td>
<td>1.5</td>
<td>0.9</td>
</tr>
</tbody>
</table>

These conflicting conclusions do not necessarily detract from the usefulness of the activation enthalpy function in interpreting
potential energy changes within molecules, but suggests that perhaps the division of the free energy parameter into enthalpy and entropy contributions defined by the quantities $\Delta H$ and $T \Delta S$ is not applicable per se to all reactions.

Interestingly, and perhaps suprisingly, the 4-t-butyl group rather than the 4-methyl group appears to be 'well behaved' in respect to both the free energy and the enthalpy parameters. Table 20 indicates that both parameters decrease with increasing dihedral angle for this group, whereas the activation enthalpy term for the 4-methyl group displays irregular behaviour. We are unable to account for this irregular behaviour on the basis of the present experimental evidence.
Section C.  Experimental.

Infra-red spectra were measured in liquid suspension (Nujol, or hexachlorobutadiene) using a Perkin-Elmer 427 or a Unicam SP 200 instrument.

Melting points are uncorrected.

N.M.R. spectra were measured using a Varian HA-100 or a Varian HA-60 instrument.

Mass spectra were recorded using an A.E.I. MS.9 instrument.

Microanalyses were carried out at the University of Cambridge Chemical Laboratory, Lensfield Road, Cambridge.
C.1. Tri-1,1',1''-naphthylmethanol (92).

C.1.(a). Preparation.

1-Naphthyl-lithium \[ \text{from 1-bromonaphthalene (104 g., 0.5 mole) and lithium wire (7.7 g., 1.1 moles)} \] in dry ether (100 ml.) was added dropwise to a stirred solution of diethyl carbonate (11.8 g., 0.1 mole) in dry ether (100 ml.). After the addition, the mixture was heated on a steam bath for 2 hours and then decomposed by pouring on a mixture of ice and ammonium chloride, in sufficient quantity to bring all solid materials into solution. The ether layer was separated, washed with sodium carbonate solution (10%, 2 x 50 ml.) and water, and finally dried by the addition of anhydrous sodium sulphate. Removal of the solvent under reduced pressure (the solution temperature being kept below 50°) gave a transparent oil from which a yellowish solid mp. 250-260° was isolated in 40-45% yield (16.5-18.5 g.). Recrystallisation from ethyl acetate raised the melting point to 278-9°.

C_{31}H_{22}O requires C. 90.70%, H. 5.40%; Found C. 90.57%, H. 5.39%.

C.1.(b). N.M.R. spectrum in deuterochloroform \[ \text{also see section B.1.(d)} \].

21 H multiplet (aromatic band) 1.6-3.0τ, 1 H singlet (hydroxylic proton) 5.9τ which disappeared upon equilibration with D_{2}C.

When benzene and toluene were used as recrystallising solvents (the crystals being dried to constant weight in vacuo), adducts with the solvent were found with apparent composition Ar_{3}COH_{.} 1.5 C_{6}H_{6} and Ar_{3}COH 1.5 C_{7}H_{8} respectively. Adducts were not isolated with acetone or ethyl acetate. The N.M.R. spectra consisted of a 30 H multiplet 1.6-3.0τ with a 1 H singlet 5.9τ and a 57 H multiple 1.6-3.0τ, 2 H singlet 5.9τ and a 9 H singlet 7.7τ respectively. After heating to 100° in vacuo for several hours, the solvates
still retained some of the solvent of crystallisation, as evidenced by the N.M.R. spectra.

C.1.(c). Mass spectrum [see also section B.1.(d)].
410(M)(94%), 393(11%), 392(48%), 283(70%), 282(49%), 265(59%), 155(100%), 127(64%).

C.1.(d). Infrared spectrum [see also section B.1.(d)].
3550(w), 1600(m), 1510(m), 1300(m), 1160(m), 1050(m), 1010(m), 985(m), 903(m), 865(m), 810(s), 780(s), 760(m).

C.1.(e). The treatment of tri-1,1',1''-naphthylmethanol with acid.

Upon dissolving tri-1,1',1''-naphthylmethanol (92) in 98% sulphuric acid, a blue solution was produced, which, over a period of hours changed to red. This colour transition was greatly accelerated by any changes to the sulphuric acid medium, for example, the addition of a few drops of water or acetic acid. Such solutions became red in a matter of minutes.

C.1.(f). The attempted preparation of tri-1,1',1''-naphthylmethyl chloride.

The alcohol (1 g.) was dissolved in dry benzene (50 ml.) containing a few lumps of anhydrous calcium chloride. The solution was cooled to 10° and dry hydrogen chloride gas was passed through the solution for 1 hour. The crude reaction product was obtained by filtration of the calcium chloride in a dry atmosphere, followed by evaporation of volatile species under reduced pressure. The solution temperature was kept at 10° throughout. The tarry residue gave a small quantity of (92') on extraction with a mixture of equal volumes of petrol (60-80°) and chloroform. The remainder was taken up in chloroform and this solution shaken with water. The aqueous layer gave an almost insignificant
precipitate with acidified silver nitrate solution.

The solution of the alcohol in benzene initially took on a blue colouration (characteristic of the reaction with sulphuric acid) when hydrogen chloride gas was introduced. A succession of colour changes then followed quite rapidly, the solution ending up red (apparently identical to the behaviour in concentrated sulphuric acid, except much faster). Similar results were obtained when acetyl chloride and thionyl chloride in benzene were used as the chlorinating agents.

C.2. The tri-1,1',1''-naphthylmethanol rearrangement product, the hydrocarbon (92').

C.2.(a). Preparation.

A solution of tri-1,1',1''-naphthylmethanol (92) in glacial acetic acid was boiled for 0.5 hour. Upon cooling, a pale yellow solid separated in almost quantitative yield. This was filtered off and washed with petrol (bp. 60-80°), and then purified by column chromatography (alumina as stationary phase, 2% chloroform-petrol (bp. 60-80°) as eluent). A white solid melting at 251-252° was obtained which gave no colouration upon dissolving in concentrated sulphuric acid. A small amount of tar was also obtained. Repeated chromatography of the solid product thus obtained failed to improve the sharp melting point.

C_{31}H_{20} requires C. 94.86%, H. 5.14%; Found C. 94.80%, H. 5.15%.

C.2.(b). N.M.R. spectrum in deuterobenzene [also see section B.2.(c)].

Multiplet (aromatic band) 1.5-3.5τ, singlet 3.9τ.

The spectrum was not further interpreted because of the large errors involved in comparing peak areas of such different magnitudes (the ratio of aromatic to non-aromatic protons in this
molecule is 19:1).

C.2.(c). Mass spectrum [also see section B.2.(c).]
392(M)(100%), 265(20%).

C.3. 4-Methyl-tri-1,1',1''-naphthylmethanol (93) [also see section B.3.(b) and section B.3.(c)].

C.3.(a). Preparation.

1-Naphthyl-lithium [from 1-bromonaphthalene (82.8 g., 0.4 mole) and lithium wire (5.1 g., 0.88 mole)] in dry ether (200 ml.) was added dropwise to a stirred solution of ethyl 4-methyl-naphthoate (21.4 g., 0.1 mole) in dry ether (100 ml.). After working up in the usual manner (as described for (92)), a white solid melting at 100-120° with decomposition was obtained (yield 30-35% as the tertiary alcohol). It was not possible to obtain the alcohol pure in an unsolvated form: warming a solvate in vacuo resulted in extensive decomposition. Physical measurements were therefore conducted on the 1:1 adduct formed with diethyl ether.

C.3H30O requires C. 86.77%, H. 6.43%: Found C. 86.70%, H. 6.40%.

C.3.(b). N.M.R. spectrum in deuterochloroform [also see sections B.3.(b) and B.3.(c)].

20H multiplet (aromatic band) 1.8-3.2, 1H singlet (hydroxyllic proton) 6.0, 4H quartet (aliphatic -CH2-) 6.6, 3H singlet (side-chain methyl protons) 7.4, 6H triplet (aliphatic methyl protons) 8.85.

C.3.(c). Mass spectrum [also see sections B.3.(b) and B.3.(c)].
424(M)(100%), 407(40%), 406(50%), 297(70%), 283(25%), 282(30%), 127(46%).

C.3.(d). Infrared spectrum.
The absorption at 3630 cm\(^{-1}\) is indicative of a hydroxylic compound.

C.3.(e). The preparation and properties of the dehydration product of 4-methyl-tri-1,1',1''-naphthylmethanol (93) [also see section B.3.(b)].

A benzene solution of the carbinol (93) was boiled for 1 hour and then dried by the addition of anhydrous sodium sulphate. When the solvent was removed a purple oil remained which could not be obtained in a crystalline state. This was purified by column chromatography (alumina stationary phase, petrol (bp. 60-80\(^\circ\)) as eluent. The purple oil was recovered in almost quantitative yield and appeared to consist of one component only.

The N.M.R. spectrum of this oil (in deuterochloroform) gave a 20 H multiplet (aromatic band) 2.0-4.0\(\alpha\) and a 2 H unsymmetrical triplet (side-chain protons) 7.3-7.6\(\alpha\). Evidently the solvent of crystallisation and water was lost in the boiling process.

Upon warming the carbinol-etherate in a test tube, water, as evidenced by the colouration of anhydrous copper sulphate, condensed in the cool parts of the tube. The N.M.R. spectrum of the residue was identical to the above.

C.4. 4,4'-Dimethyl-tri-1,1',1''-naphthylmethanol (93A).

C.4.(a). Preparation.

4-Methyl-1-naphthyl-lithium [from 1-bromo-4-methylnaphthalene (66.3 g., 0.3 mole) and lithium wire (4.7 g., 0.66 mole)] in dry ether (100 ml.) was added dropwise to a stirred solution of ethyl naphthoate (20 g., 0.1 mole) in dry ether (100 ml.). Working up in the usual manner gave a white solid melting at
250-5° dec., (yield 20% as the carbinol).

C_{34}H_{28}O requires C 90.37%, H 5.97%; Found C 90.40%, H 5.98%.


19 H multiplet (aromatic band) 1.8-3.2ß, 1 H singlet (hydroxylic proton) 6.0ß, 6 H singlet (side-chain methyl protons) 7.4ß.

After dehydration in the manner described in section C.3.(e), the N.M.R. spectrum showed a collapse of the singlet at 6.0ß, and the singlet at 7.4ß became an unsymmetrical triplet of diminished intensity, indicating participation of the methyl group in the dehydration.

C.4.(c). Mass spectrum [see also sections B.3.(b) and B.3.(c)].

438(40%) (M), 421(28%), 419(4%), 311(28%), 295(20%), 277(40%), 169(100%), 155(64%), 141(52%), 127(36%).


3630(w), 1600(m), 1520(m), 1010(m), 990(m), 830(s), 800(s), 780(m), 760(m). The absorption at 3630 cm.⁻¹ indicates a hydroxyl group.

C.5. 4,4',4''-Trimethyl-tri-1,1',1''-naphthylmethanol (93B).

C.5.(a). Preparation.

4-Methyl-1-naphthyl-lithium [from 1-bromo-4-methylnaphthalene (11g., 0.5 mole) and lithium wire (7.7 g., 1.1 moles)] in dry ether (200 ml.) was added dropwise to a stirred solution of diethyl carbonate (11.8 g., 0.1 mole) in dry ether (100 ml.). After working up in the usual manner, a white solid melting at 280-5° dec. was obtained.

C_{34}H_{28}O requires C 90.23%, H 6.24%; Found C 90.17%, H 6.23%.

18 H multiplet (aromatic band) 1.8-3.3, 1 H singlet (hydroxylic proton) 6.0, 9 H singlet (side-chain methyl protons) 7.4.

C.5.(c). Mass spectrum [also see sections B.3.(b) and B.3.(c)].
452(M)(18%), 435(33%), 434(48%), 293(36%), 292(9%), 169(100%), 141(45%), 91(27%).

C.5.(d). Infra-red spectrum.
3640(w), 1600(s), 1520(m), 1010(s), 990(m), 830(s), 800(s), 780(s), 760(m).

The absorption at 3640 cm$^{-1}$ is characteristic of a hydroxyl compound.

C.6. 4-Dimethylamino-tri-1,1',1''-naphthylmethanol (94).
C.6.(a). Preparation.

4-Dimethylamino-1-naphthyl-lithium [from 1-bromo-4-dimethylamino-naphthalene (50 g., 0.2 mole) and n-butyl-lithium (12.8 g., 0.2 mole) in dry ether (100 ml.) was added dropwise to a stirred solution of di-(1-naphthyl) ketone (28.2 g., 0.1 mole) in dry ether (200 ml.). When the addition was complete the mixture was heated on a steam bath for 2 hours and then decomposed by pouring on a mixture of ice and ammonium chloride. After separation of the ether layer and washing with hydrochloric acid (3N, 3 x 50 ml.), the aqueous portion and washings were made alkaline to litmus by the addition of sodium carbonate (10%) and the liberated base was extracted with ether. After drying by the addition of anhydrous sodium sulphate, and solvent removal under reduced pressure, a white solid melting at 250-9° dec. was obtained. Recrystallisation from benzene raised the melting point to 264-8° dec.

C$_{33}$H$_{27}$ON requires C. 87.38%, H. 6.00%, N. 3.09%; Found C. 87.35%, H. 5.99%, N. 3.10%.

20 H multiplet (aromatic band) 1.4-3.7%, 1 H singlet (hydroxylic proton) 6.1%, 6 H singlet (the dimethylamino group protons) 7.4%.

C.6.(c). Mass spectrum [also see section B.3.(c)].

453(M)(10%), 436(26%), 326(15%), 172(16%), 171(100%), 155(25%), 127(22%).


3500(w), 1610(w), 1590(s), 1520(m), 1060(s), 1018(s), 920(m), 850(m), 810(m), 785(s), 777(s).

The absorption at 3500 cm.⁻¹ is indicative of a hydroxyl compound.

C.7. The attempted preparation of triarylmethyl chlorides derived from the carbinols (93), (93A), (93B) and (94).

The general methods adopted for the synthesis of tri-1,1',1"-naphthylmethyl chloride were again applied, but unsuccessfully.

The 4-methyl-substituted carbinols (93), (93A) and (93B) all gave purple oils, suggesting dehydration products upon treatment with chlorinating agents, whereas the carbinol (94) gave a red solution from which no crystalline product could be isolated.

C.8. The attempted preparation of 9-(1-naphthyl)-1,2:7,8-dibenzofluoren-9-ol (109) [also see section B.2.(c)].

1-Naphthyl-lithium [from 1-bromonaphthalene (4.1 g., 0.02 mole) and lithium wire (0.31 g., 0.045 mole)] in dry ether (25 ml.) was added dropwise to a stirred solution of 1,2:7,8-dibenzofluoren-one (2.8 g., 0.01 mole) in benzene (100 ml.). The mixture was heated on a steam bath for 2 hours and then decomposed and worked up in the usual way. A dark coloured oil was obtained
which was purified by column chromatography (alumina as stationary phase, petrol (bp. 60-80°), followed by 2% chloroform-petrol (bp. 60-80°) as eluent). No hydroxylic compound was found in the reaction products but a small quantity of the starting material (the ketone) (250 mg.) was recovered in company with a large amount of intractable material. The reaction conditions and procedures were then modified in the following ways.

1) The organo-lithium solution was added to a benzene solution of the ketone (107) maintained at 7° and the mixture was stirred at this temperature for 8 hours.

2) The organo-lithium solution was added to the benzene solution of (107) maintained at 70° and the mixture was stirred for a further 8 hours at this temperature.

3) The order of addition of the reagents was reversed.

4) The organo-lithium solution was added to an ethereal suspension of (107).

No crystalline material other than the starting ketone was isolated from these reactions, moreover, the infra-red spectra of fractions taken from the columns at regular intervals never indicated the presence of a hydroxylic component.

C.9. The attempted preparation of 9-(1-naphthyl)-1,2:5,10-dibenzo-anthran-9-ol (110) [also see section B.2.(c)].

1-Naphthyl-lithium [from 1-bromonaphthalene (4.1 g., 0.02 mole) and lithium wire (0.31 g., 0.045 mole)] in dry ether (25 ml.) was added dropwise to a stirred solution of 1,2:5,10-dibenzo-anthr-9-one 104 (108) (2.8 g., 0.01 mole) in dry benzene (100 ml.), at room temperature. The mixture was allowed to stand for two hours and was then heated on a steam bath for four hours. It was worked up in the usual manner. A dark oil was obtained which was purified by column chromatography (alumina as stationary phase, petrol (bp. 60-80°), followed by diethyl ether as eluents).
On one occasion only, a yellow solid (111) was isolated (100 mg., 2%) in company with another yellow solid (112) (750 mg., 15%) and a large amount of intractable material. On subsequent occasions only (112) was isolated, and variation of the reaction conditions as described above failed to give further quantities of (111).

The product (111) possessed the following properties.
1) mp. 278° (sharp).
2) Mass spectrum 408(100%)(M), 391(5%).
3) Infra-red spectrum 3550(w), 1597(m), 1563(m), 1320(w), 1250(w), 1180(m), 1160(m), 1140(m), 1118(m), 900(m), 808(s), 790(s), 710(m). The 3550 cm.\(^{-1}\) peak indicates a hydroxyl group.
4) Red colour in concentrated sulphuric acid.

The product (112) possessed the following properties.
1) mp. 276-8°. Mixed melting point with 1,2:5,10-dibenzoanthr-9-one (108) 245-50°.
2) Mass spectrum 406(M).
3) Infra-red spectrum 1640(m), 1615(w), 1600(w), 1575(w), 1270(m), 1202(m), 1102(m), 1160(w), 820(m), 800(m), 770(m), 740(m), 720(m). The 1640 cm.\(^{-1}\) absorption indicates a carbonyl group being present.
4) Red colour in concentrated sulphuric acid.

C.10. The attempted reduction of the unidentified product (111) to a hydrocarbon [also see section B.2.(c)].

Method 1.

A few milligrams of solid were dissolved in glacial acetic acid and heated under reflux with granulated zinc (2 g.) for 1 week (with the periodic addition of a drop of concentrated hydrochloric acid). At the end of this time, a test portion of the solution still gave a red colouration on the addition of a few drops of concentrated sulphuric acid. It was concluded that reduction had not taken place.
Method 2.

The use of phosphorus (2 g.) and hydriodic acid (57%, 5 ml.) in glacial acetic acid (10 ml.) at reflux for 12 hours did not reduce the product (111), nor did pouring the sulphuric acid solution of (111) into ice-cold aqueous sodium borohydride.

C.11. Attempted modifications to the rearrangement product of tri-1,1',1''-naphthylmethanol, the hydrocarbon (92') [also see sections B.2.(c). and B.2.(d)].

Method 1.

The hydrocarbon (92')(2.0 g., 0.005 mole) was dissolved in carbon tetrachloride (50 ml.) and the solution cooled was cooled to 0°. A solution of bromine (0.72 g., 0.0045 mole) in carbon tetrachloride was added dropwise and the mixture was stirred at 0° until the evolution of hydrogen bromide had ceased (3 hours). The solvent and volatile products were removed by evaporation under reduced pressure leaving an intractable tar.

Method 2.

The hydrocarbon (2.0 g., 0.005 mole) and N-bromosuccinimide (0.9 g., 0.005 mole) were heated with carbon tetrachloride (50 ml.) under reflux for 12 hours. The precipitate of succinimide was filtered off from the hot solution, which gave only unreacted starting material upon removal of the solvent.

Method 3.

A solution of phenyl-lithium in dry ether was added to a solution of (92') in dry benzene (equivalent proportions). Oxygen was passed through the solution for 4 hours and the mixture was then hydrolysed and worked up in the usual way. The resulting oily product was chromatographed (alumina stationary phase, 2% chloroform-petrol (bp.60-80°) as eluent), but no hydroxylic component was detected. Unchanged starting material was recovered in 80% yield. Metallation with phenylsodium in dry
benzene gave a similar result but when n-butyl-lithium was used, an intractable material resulted suggesting complex reaction.
C.12. The preparation of starting materials for tri-1,1',1''-naphthylmethanol syntheses.

As direct bromination of 1-methylnaphthalene leads to the formation of a mixture of isomers and of polybromo-derivatives, 1-bromo-4-methylnaphthalene (bp. 135°/4 mm., lit. 146°/8 mm.¹¹¹) was prepared by treating 4-methylnaphthalene-sulphonic acid with a solution of bromine in sodium bromide, following the procedure of Fieser and Seligman.¹¹¹ The sulphonic acid was prepared by direct sulphonation of 1-methylnaphthalene (which was the commercial product).

4-Methyl-naphthoic acid (mp. 174-175°, lit. 175°¹¹²) was prepared by pouring an ethereal solution of 4-methyl-naphthylmagnesium bromide on a slurry of 'Drikold' and dry ether, extracting the acid from the reaction mixture as the sodium salt. It was esterified by the basic procedure of heating under reflux with an excess of ethanol, in the presence of a small quantity of concentrated sulphuric acid.¹¹³ The boiling point of the ester was 182-5°/3 mm., lit. 203°/12 mm..¹¹² Ethyl naphthoate was also prepared in this way and boiled at 143-145°/3mm (lit. 143-145°/3mm.¹¹³).

1-Naphthonitrile (bp. 299°, lit. 165-170°/20 mm.¹¹⁴) was prepared by the method of Cook and De Worms¹⁰⁴, and was converted into di-(1-naphthyl) ketone (mp. 99°, lit. 99-100°¹¹⁵) by reaction with 1-naphthylmagnesium bromide, followed by hydrolysis of the resulting imine.¹¹⁵

Di-(1-naphthyl) ketone was reduced to di-1,1'-naphthylmethanol (mp. 145°, lit. 144°¹¹⁶) by the action of zinc and ethanolic sodium hydroxide.¹¹⁷ Di-1,1'-naphthylmethanol was converted into 1,2:7,8-dibenzofluorene (mp. 238-240°, lit. 236°⁹⁸) using the method of Schmidlin and Massini.⁹⁸ Oxidation with chromic acid in glacial acetic acid gave 1,2:7,8-dibenzofluorenone (mp. 255-6°, lit. 255°¹⁰³)¹⁰³.
Di-(1-naphthyl) ketone was cyclised to 1,2:5,10-dibenzo-
anthrone (mp. 184-185°, lit. 184-185°) by treatment with a
mixture of aluminium chloride and sodium chloride. 104

1-Bromo-4-dimethylaminonaphthalene (bp. 115-120°/1.5 mm., lit.
115-130°/1 mm. 118) was prepared by direct bromination of
1-dimethylaminonaphthalene (the commercial product). 118

C.13.(a) 2-Bromo-4-nitrotoluene.

Bromine (100 ml., 1.9 moles) was added during 3 hours to a stirred mixture of 4-nitrotoluene (280 g., 2.1 moles) and iron powder (10 g., 0.18 mole) maintained at 95-100°. The mixture was heated for a further hour when it was poured into hot water and the oil obtained was washed with sodium thiosulphate solution (10%), hydrochloric acid (3N) and finally water. The oil which solidified upon cooling melted at 73-76°. It was reduced without further purification.

C.13.(b) 4-Amino-2-bromotoluene.

The nitro-compound (107 g., 0.3 mole) was dissolved in the minimum of hot ethanol, and a solution of stannous chloride (380 g., 2.0 moles) in concentrated hydrochloric acid (750 ml.) was added slowly. Reaction was vigorous, and after the addition the solution was heated on a steam-bath until no oily drops of the nitro-compound were seen in the condenser and the solution was clear. The majority of the ethanol was removed by distillation and the remaining solution cooled, whereupon crystals of the amine stannichloride were deposited. These were filtered off and the free base liberated by the addition of the salt to a well cooled solution of sodium hydroxide (300 ml., 8N). The amine was extracted with ether, washed with water, dried with sodium sulphate and distilled under reduced pressure. The yield was 74.5 grammes (85%) bp. 96-100°/2 mm, mp. 25° (lit. 26-27° 119)

Potentiometric titration with 0.1N perchloric acid in glacial acetic acid indicated a purity of 99.7%.

C.13.(c) 2-Bromo-4-dimethylaminotoluene.
4-Amino-2-bromotoluene (93 g., 0.5 mole) was dissolved in dimethylformamide (50 ml.) and the solution was cooled to 0°C. A mixture of methyl iodide (135 g., 0.95 mole) and dimethylformamide (25 ml.) was added during 1 hour to the stirred solution, the temperature of which was maintained below 10°C throughout. After the addition the mixture was stirred for a further hour at room temperature and then poured into sodium hydroxide (1 l., 3N). The liberated amine was worked up as described above. Yield 70% (75 g.) bp. 98°/1 mm., mp. 32°C (lit. 33°C 120°C).

Potentiometric titration with 0.1N perchloric acid in glacial acetic acid showed a purity of 99.8%.

3 H multiplet (aromatic band) 3.0-3.7τ, 6 H singlet (dimethylamino-group protons) 7.2τ, 3 H singlet (side-chain methyl protons) 7.8τ.

214(M)(85%), 213(100%), 212(77%), 198(10%), 134(12%), 118(22%), 91(23%), 42(20%).

C.14. Quaternary methiodide of 2-bromo-4-dimethylaminotoluene.

The addition of a mixture of methyl iodide (more than one equivalent) and dimethylformamide to 2-bromo-4-dimethylaminotoluene gave a crystalline solid which was filtered off and recrystallised from ethanol.

C.14.(b). N.M.R. spectrum in heavy water (t-butyl alcohol as internal standard).
3 H multiplet (aromatic band) 3.1-4.0τ, 9 H singlet (trimethyl-
ammonium protons) 6.5\text{t}, 3 H singlet (side-chain methyl protons 7.6t.


214(76\%), 142(100\%), 127(20\%).

The elements of methyl iodide are lost and the highest molecular weight peak observed (at 214 mass numbers) corresponds to the molecular ion of 2-bromo-4-dimethylaminotoluene.

C.15. 5-N,N,N-Dimethylamino-tri-2,2',2''-tolylmethanol (128).


5-Dimethylamino-2-methylphenyl-lithium \textit{[from} 2-bromo-4-dimethylaminotoluene (21.4 g., 0.1 mole) and n-butyl-lithium (6.4 g., 0.1 mole)\textit{]} in dry ether (100 ml.) was added to a stirred solution of di-(2-tolyl) ketone (21 g., 0.1 mole) in dry ether (100 ml.). After the addition, the mixture was heated on a steam bath for 2 hours and then decomposed by pouring on a mixture of ice and glacial acetic acid. The ether layer was separated washed with hydrochloric acid (3N, 3 x 50 ml.), and the aqueous washings were then made alkaline to litmus by the addition of sodium carbonate (10%). The liberated bases were extracted into chloroform and this extract was steam distilled until the distillate contained no oily drops. The remaining oil was taken up in ether, the ether layer separated, dried and concentrated, under reduced pressure. A brown transparent oil remained from which crystals were not isolated. The infra-red spectrum of this product showed a weak absorption at 3550 cm.\textsuperscript{-1}. Yield of crude material 50\% (17.3 g.).

Reaction of 5-N,N-dimethylamino-tri-2,2',2''-tolylmethanol (128) with an excess of methyl iodide containing a few drops of dimethylformamide gave a crystalline solid which was recrystallised from ethanol.

The molecular weight of this salt was determined by potentiometric titration using the following procedure.

Approximately 100 milligrammes of the salt were accurately weighed and then dissolved in glacial acetic acid (75 ml.). Ten millilitres of a solution of AnalaR mercuric acetate (6 g. in 100 ml. of glacial acetic acid) were added. The solution was titrated against 0.01N perchloric acid in glacial acetic acid. The apparent molecular weight for the salt was found to be 485 mass units (calculated value 487.1).

N.M.R. spectrum in heavy water using tertiary butyl alcohol as internal standard.

11 H multiplet (aromatic band), 3.2-4.6 ppm, 9 H singlet (trimethylammonium protons) 6.5 ppm, 9 H singlet (side-chain methyl protons) 7.6 ppm.

Mass spectrum.

345 (10%), 344 (27%), 142 (90%), 141 (50%), 119 (20%), 91 (12%), 85 (90%), 49 (100%).
C.17. Diarylmethyl chlorides.

C.17.(a). Preparation.

The chlorides were prepared by treatment of the corresponding diarylmethanols with thionyl chloride.

To a stirred and cooled solution of the diarylmethanol (0.1 mole) in dry benzene (50 ml.) was added dropwise a solution of thionyl chloride (0.3 mole) in dry benzene (25 ml.). The mixture was allowed to stand at room temperature for 0.5 hours when unchanged thionyl chloride and other volatile products were removed by distillation at 15 mm. The crude product was recrystallised from petrol (bp. 40-60°) containing 5% thionyl chloride, and finally from dry acetone at -70° in the case of solid products: liquid products were distilled under reduced pressure. Where distillation was used for purification, the resulting product was hydrolysed and oxidised and compared with the starting ketone or diarylmethanol to assess whether decomposition or isomerisation had occurred as a result of distillation. The purity of the compounds was determined by titrimetric measurement of the hydrogen ion concentration produced by complete hydrolysis. On the whole the observed melting points agreed with those recorded in the literature, and where this was not so, the purity of the chloro-compound obtained was determined by the analysis described above.


Melting points are given in table 21 and the results of the analyses in table 22.
<table>
<thead>
<tr>
<th>Substituents</th>
<th>Lit. b.p.</th>
<th>Lit. mp.</th>
</tr>
</thead>
<tbody>
<tr>
<td>4-Me</td>
<td>169-70 / 0.4 mm.</td>
<td>136/1 mm.</td>
</tr>
<tr>
<td>4-4-Me 2</td>
<td>169-70 / 0.4 mm.</td>
<td>136/1 mm.</td>
</tr>
<tr>
<td>4-t-Bu</td>
<td>169-70 / 0.4 mm.</td>
<td>136/1 mm.</td>
</tr>
<tr>
<td>4,4-t-Bu 2</td>
<td>169-70 / 0.4 mm.</td>
<td>136/1 mm.</td>
</tr>
<tr>
<td>3-Me</td>
<td>109-11 / 1 mm.</td>
<td>136/1 mm.</td>
</tr>
<tr>
<td>3,5,6-Me 3</td>
<td>109-11 / 1 mm.</td>
<td>136/1 mm.</td>
</tr>
<tr>
<td>2,2,6,6-Me 4</td>
<td>189-85 / 2 mm.</td>
<td>136/1 mm.</td>
</tr>
<tr>
<td>2-Me</td>
<td>230-51 / 3 mm.</td>
<td>136/1 mm.</td>
</tr>
<tr>
<td>2,6-Me 2</td>
<td>230-51 / 3 mm.</td>
<td>136/1 mm.</td>
</tr>
<tr>
<td>4-t-NO 2,6-Me 2</td>
<td>230-51 / 3 mm.</td>
<td>136/1 mm.</td>
</tr>
</tbody>
</table>

Table 21: Diarylmethyl chlorides.
Table 21 (continued).

<table>
<thead>
<tr>
<th>Substituents</th>
<th>mp</th>
<th>bp</th>
<th>Lit. mp</th>
<th>Lit. bp</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>4-t-Bu-2,6-Me₂</td>
<td>-</td>
<td>188°/1 mm.</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>2,4,6-Me₃</td>
<td>-</td>
<td>160-62°/4 mm.</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>2,2',6-Me₃</td>
<td>74-75°</td>
<td>-</td>
<td>75°</td>
<td>-</td>
<td>121</td>
</tr>
<tr>
<td>4-t-Bu-2,2',6-Me₃</td>
<td>68-69°</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>2,2',4,6-Me₄</td>
<td>95-97°</td>
<td>-</td>
<td>96°</td>
<td>-</td>
<td>121</td>
</tr>
<tr>
<td>2,2',6,6'-Me₄</td>
<td>95-96°</td>
<td>-</td>
<td>93°</td>
<td>-</td>
<td>121</td>
</tr>
<tr>
<td>2,2',4,4',6,6'-Me₆</td>
<td>104-105°</td>
<td>-</td>
<td>105°</td>
<td>-</td>
<td>121</td>
</tr>
<tr>
<td>2,2',3,3',5,5',6,6'-Me₈</td>
<td>99-100°</td>
<td>-</td>
<td>98°</td>
<td>-</td>
<td>121</td>
</tr>
</tbody>
</table>
Molecular weights of diarylmethyl chlorides by hydrogen ion titration.

<table>
<thead>
<tr>
<th>Substituents</th>
<th>Formula</th>
<th>Molecular weight</th>
<th>By H⁺ titre</th>
<th>Calculated value</th>
</tr>
</thead>
<tbody>
<tr>
<td>4-Me</td>
<td>C(<em>{14})H(</em>{13})Cl</td>
<td>216.7</td>
<td>216.7</td>
<td></td>
</tr>
<tr>
<td>4,4'-Me(_2)</td>
<td>C(<em>{15})H(</em>{15})Cl</td>
<td>230.8</td>
<td>230.7</td>
<td></td>
</tr>
<tr>
<td>4-t-Bu</td>
<td>C(<em>{17})H(</em>{21})Cl</td>
<td>260.6</td>
<td>260.8</td>
<td></td>
</tr>
<tr>
<td>4,4'-t-Bu(_2)</td>
<td>C(<em>{21})H(</em>{29})Cl</td>
<td>316.7</td>
<td>316.9</td>
<td></td>
</tr>
<tr>
<td>3-Me</td>
<td>C(<em>{14})H(</em>{13})Cl</td>
<td>216.8</td>
<td>216.7</td>
<td></td>
</tr>
<tr>
<td>3,3'-Me(_2)</td>
<td>C(<em>{15})H(</em>{15})Cl</td>
<td>230.9</td>
<td>230.7</td>
<td></td>
</tr>
<tr>
<td>2,3,5,6-Me(_4)</td>
<td>C(<em>{17})H(</em>{19})Cl</td>
<td>259.0</td>
<td>258.8</td>
<td></td>
</tr>
<tr>
<td>2-Me</td>
<td>C(<em>{14})H(</em>{13})Cl</td>
<td>216.9</td>
<td>216.7</td>
<td></td>
</tr>
<tr>
<td>2,2'-Me(_2)</td>
<td>C(<em>{15})H(</em>{15})Cl</td>
<td>230.8</td>
<td>230.7</td>
<td></td>
</tr>
<tr>
<td>2,6-Me(_2)</td>
<td>C(<em>{15})H(</em>{15})Cl</td>
<td>230.5</td>
<td>230.7</td>
<td></td>
</tr>
<tr>
<td>4-Me0-2,6-Me(_2)</td>
<td>C(<em>{16})H(</em>{17})Cl(_{10})</td>
<td>261.0</td>
<td>260.9</td>
<td></td>
</tr>
<tr>
<td>4-t-Bu-2,6-Me(_2)</td>
<td>C(<em>{19})H(</em>{23})Cl</td>
<td>287.0</td>
<td>286.6</td>
<td></td>
</tr>
<tr>
<td>2,4,6-Me(_3)</td>
<td>C(<em>{16})H(</em>{17})Cl</td>
<td>244.5</td>
<td>244.8</td>
<td></td>
</tr>
<tr>
<td>2,2',6-Me(_3)</td>
<td>C(<em>{16})H(</em>{17})Cl</td>
<td>244.6</td>
<td>244.8</td>
<td></td>
</tr>
<tr>
<td>4-t-Bu-2,2',6-Me(_3)</td>
<td>C(<em>{20})H(</em>{25})Cl</td>
<td>300.6</td>
<td>300.9</td>
<td></td>
</tr>
<tr>
<td>2,2',4,6-Me(_4)</td>
<td>C(<em>{17})H(</em>{19})Cl</td>
<td>259.1</td>
<td>258.8</td>
<td></td>
</tr>
<tr>
<td>2,2',6,6'-Me(_4)</td>
<td>C(<em>{17})H(</em>{19})Cl</td>
<td>258.9</td>
<td>258.8</td>
<td></td>
</tr>
<tr>
<td>2,2',4,6,6'-Me(_6)</td>
<td>C(<em>{19})H(</em>{23})Cl</td>
<td>287.1</td>
<td>286.8</td>
<td></td>
</tr>
<tr>
<td>2,2',3,3',5,5',6,6'-Me(_8)</td>
<td>C(<em>{21})H(</em>{27})Cl</td>
<td>314.7</td>
<td>314.4</td>
<td></td>
</tr>
</tbody>
</table>
Diarylmethanols were prepared by three general methods:

**Method A.**

By reduction of a diaryl ketone with lithium aluminium hydride.

**Method B.**

By reaction of ethyl formate with an excess of an arylmagnesium halide.

**Method C.**

By reaction of benzaldehyde with an excess of an arylmagnesium halide.

**Method A.**

To a suspension of lithium aluminium hydride (3.8 g., 0.1 mole) in dry ether was added dropwise a solution of the diaryl ketone (0.2 mole) in dry ether. The mixture was heated on a steam-bath for 0.5 hour and then cautiously decomposed by pouring on ice. The ether layer was separated, washed with dilute hydrochloric acid and water, and finally dried by the addition of anhydrous sodium sulphate. Liquid products were distilled under reduced pressure and solid products crystallised from ethanol.

**Method B.**

A solution of the arylmagnesium bromide (0.25 mole) in dry ether was added dropwise to a stirred solution of ethyl formate (7.4 g., 0.1 mole) in dry ether. The mixture was heated on a steam-bath for 2 hours and then decomposed by pouring on a mixture of ice and ammonium chloride (in sufficient quantity to bring all solid materials into solution). The ether layer was separated, washed with sodium hydroxide (5%) and water, and finally dried by the addition of anhydrous sodium sulphate. Liquid products were distilled under reduced pressure while solid products were recrystallised from ethanol.
Method C.

The procedure described for method B was modified by using benzaldehyde (10.6 g., 0.1 mole) (instead of ethyl formate) and the arylmagnesium bromide (0.15 mole).

C.18. (b). Physical measurements.

Melting points or boiling points are given in table 23.
### Table 23.

**Diaryl methane, s**

<table>
<thead>
<tr>
<th>Substituents</th>
<th>mp$^\circ$</th>
<th>bp$^\circ$</th>
<th>Lit. mp$^\circ$</th>
<th>Lit. bp$^\circ$</th>
<th>Ref.</th>
<th>Method of preparation</th>
</tr>
</thead>
<tbody>
<tr>
<td>4-Me</td>
<td>51-53$^\circ$</td>
<td>-</td>
<td>51-53$^\circ$</td>
<td>-</td>
<td>124</td>
<td>A</td>
</tr>
<tr>
<td>4,4$'$-Me$_2$</td>
<td>59-60$^\circ$</td>
<td>-</td>
<td>61$^\circ$</td>
<td>-</td>
<td>121</td>
<td>A</td>
</tr>
<tr>
<td>4-t-Bu</td>
<td>83-84$^\circ$</td>
<td>-</td>
<td>81.5-82$^\circ$</td>
<td>-</td>
<td>125</td>
<td>A</td>
</tr>
<tr>
<td>4,4$'$-t-Bu$_2$</td>
<td>220-222$^\circ$</td>
<td>-</td>
<td>220-221$^\circ$</td>
<td>-</td>
<td>126</td>
<td>A</td>
</tr>
<tr>
<td>3-Me</td>
<td>59-60$^\circ$</td>
<td>-</td>
<td>52$^\circ$</td>
<td>-</td>
<td>123</td>
<td>A</td>
</tr>
<tr>
<td>3,3$'$-Me$_2$</td>
<td>-</td>
<td>155$^\circ$/1 mm</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>B</td>
</tr>
<tr>
<td>2,3,5,6-Me$_4$</td>
<td>70-71$^\circ$</td>
<td>-</td>
<td>66-69$^\circ$</td>
<td>-</td>
<td>82</td>
<td>A</td>
</tr>
<tr>
<td>2-Me</td>
<td>92-95$^\circ$</td>
<td>-</td>
<td>87.5-90$^\circ$</td>
<td>-</td>
<td>127</td>
<td>A</td>
</tr>
<tr>
<td>2,2$'$-Me$_2$</td>
<td>120$^\circ$</td>
<td>-</td>
<td>119$^\circ$</td>
<td>-</td>
<td>121</td>
<td>B</td>
</tr>
<tr>
<td>2,6-Me$_2$</td>
<td>57-58$^\circ$</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>A</td>
</tr>
<tr>
<td>4-MeO-2,6-Me$_2$</td>
<td>-</td>
<td>180-181$^\circ$/1 mm</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>C</td>
</tr>
<tr>
<td>-----------------------</td>
<td>-------</td>
<td>------</td>
<td>-----------</td>
<td>-----------</td>
<td>------</td>
<td>-----------------------</td>
</tr>
<tr>
<td>4-t-Bu-2,6-Me₂</td>
<td>119-120°</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>A</td>
</tr>
<tr>
<td>2,2',4,6-Me₄</td>
<td>127-129°</td>
<td>-</td>
<td>127°</td>
<td>-</td>
<td>121</td>
<td>A</td>
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<td>2,2',6,6'-Me₄</td>
<td>133-134°</td>
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<td>135°</td>
<td>-</td>
<td>121</td>
<td>A</td>
</tr>
<tr>
<td>2,2',4,4',6,6'-Me₆</td>
<td>149-150°</td>
<td>-</td>
<td>150°</td>
<td>-</td>
<td>121</td>
<td>A</td>
</tr>
<tr>
<td>2,2',3,3',5,5',6,6'-Me₈</td>
<td>163-164°</td>
<td>-</td>
<td>162°</td>
<td>-</td>
<td>121</td>
<td>A</td>
</tr>
</tbody>
</table>


Three general methods were used to prepare the diaryl ketones. Method D.

By reaction of an aromatic hydrocarbon with an aroyl chloride in the presence of anhydrous aluminium chloride.

Method E.

By reaction of an arylmagnesium halide with an aroyl chloride in dry ether.

Method F.

By reaction of an aromatic hydrocarbon with oxalyl chloride in the presence of anhydrous aluminium chloride.

Method D.

To a suspension of anhydrous aluminium chloride (133.5 g., 1.0 mole) in methylene chloride (250 ml.) was added a mixture of the hydrocarbon (1.0 mole) and the acid chloride (1.0 mole). The reaction mixture was stirred and the temperature of the solution was kept at 5-10° during the addition. The mixture was then allowed to warm to room temperature when it was heated on a steam-bath for 0.5 hour. After cooling it was poured on a mixture of ice (750 g.) and hydrochloric acid (150 ml., 38%), the organic layer was separated and washed once with water, twice with 250 ml. portions of sodium hydroxide (5%), and finally with water. It was dried by the addition of anhydrous calcium chloride and distilled under reduced pressure.

For the preparation of ketones possessing a t-butyl group, nitrobenzene was used as the solvent medium. When the addition was complete the reaction mixture was stirred for 5 hours at 30-40°, and then left at room temperature overnight.

Débutylations. 127

A mixture of the butylated benzophenone (1.0 mole), anhydrous
aluminium chloride (400 g., 3.0 moles) and benzene (1 l.) was stirred for 8 hours at 65°. The resulting mixture was worked up as described above.

Method E.

A solution of the arylmagnesium bromide (0.1 mole) in dry ether (50 ml.) was added over a period of 2 hours to a stirred solution of the aroyl chloride (0.1 mole) in dry ether (10 ml.). When the addition was complete the mixture was heated on a steam-bath for 0.5 hour, after which it was decomposed by pouring on a mixture of ice and ammonium chloride. The whole was exhaustively steam distilled and the residue was taken up in ether. The organic layer was separated and washed with sodium carbonate (100 ml., 10%) and water, and was dried with anhydrous sodium sulphate. The solvent was removed and the solid ketone crystallised from ethanol.

Method F.

A mixture of oxalyl chloride (79.5 g., 0.5 mole) and carbon disulphide (150 ml.) was added during 1 hour to a stirred mixture of anhydrous aluminium chloride (133 g., 1.0 mole), the hydrocarbon (1.0 mole) and carbon disulphide (300 ml.) at 0-5°. The mixture was allowed to warm to room temperature and it was then heated on a steam-bath for 3 hours. After the addition of hydrochloric acid (1 l., 6N), the carbon disulphide layer was washed with water and extracted with sodium carbonate (10%). It was filtered and dried with anhydrous sodium sulphate. Evaporation of the solvent gave oily crystals which were washed with petrol (bp. 40-60°) and finally recrystallised from ethanol.


Physical data for the ketones are given in table 24.
<table>
<thead>
<tr>
<th>Substituents</th>
<th>Mp</th>
<th>bp</th>
<th>Lit. mp</th>
<th>Lit. bp</th>
<th>Ref.</th>
<th>Method of preparation</th>
</tr>
</thead>
<tbody>
<tr>
<td>4-Me</td>
<td>59°</td>
<td>314-15°/760 mm.</td>
<td>59.5°</td>
<td>-</td>
<td>124</td>
<td>D</td>
</tr>
<tr>
<td>4,4'-Me₂</td>
<td>90-91°</td>
<td>-</td>
<td>95°</td>
<td>-</td>
<td>121</td>
<td>D</td>
</tr>
<tr>
<td>4-t-Bu</td>
<td>-</td>
<td>170-71°/2 mm.</td>
<td>-</td>
<td>205-15°/15 mm.</td>
<td>110</td>
<td>D</td>
</tr>
<tr>
<td>4,4'-t-Bu₂</td>
<td>-</td>
<td>155-58°/1 mm.</td>
<td>-</td>
<td>-</td>
<td></td>
<td>D</td>
</tr>
<tr>
<td>3-Me</td>
<td>-</td>
<td>315-17°/760 mm.</td>
<td>-</td>
<td>311-13°/720 mm.</td>
<td>128</td>
<td>D</td>
</tr>
<tr>
<td>2,3,5,6-Me₄</td>
<td>118-20°</td>
<td>-</td>
<td>119-20°</td>
<td>-</td>
<td>129</td>
<td>D</td>
</tr>
<tr>
<td>2-Me</td>
<td>-</td>
<td>140-41°/2 mm.</td>
<td>-</td>
<td>128-30°/2 mm.</td>
<td>127</td>
<td>D</td>
</tr>
<tr>
<td>2,6-Me₂</td>
<td>64-65°</td>
<td>-</td>
<td>64-65°</td>
<td>-</td>
<td>127</td>
<td>D</td>
</tr>
<tr>
<td>4-t-Bu-2,6-Me₂</td>
<td>-</td>
<td>138-40°/2 mm.</td>
<td>-</td>
<td>140-43°/2 mm.</td>
<td>127</td>
<td>D</td>
</tr>
<tr>
<td>2,4,6-Me₃</td>
<td>-</td>
<td>318-20°/760 mm.</td>
<td>-</td>
<td>174°/12 mm.</td>
<td>130</td>
<td>D</td>
</tr>
<tr>
<td>2,2',6-Me₃</td>
<td>69°</td>
<td>-</td>
<td>69°</td>
<td>-</td>
<td>121</td>
<td>D</td>
</tr>
</tbody>
</table>
### Table 24 (continued).

**Diaryl ketones.**

<table>
<thead>
<tr>
<th>Substituents</th>
<th>mp</th>
<th>bp</th>
<th>Lit. mp</th>
<th>Lit. bp</th>
<th>Ref</th>
<th>Method of preparation</th>
</tr>
</thead>
<tbody>
<tr>
<td>4-t-Bu-2,2',6-Me₃</td>
<td>-</td>
<td>170°/2 mm</td>
<td>-</td>
<td>157-65°/2 mm</td>
<td>127</td>
<td>D</td>
</tr>
<tr>
<td>2,2',4,6-Me₄</td>
<td>110-111°</td>
<td>-</td>
<td>111°</td>
<td>-</td>
<td>121</td>
<td>D</td>
</tr>
<tr>
<td>2,2',6,6'-Me₄</td>
<td>132-134°</td>
<td>-</td>
<td>134°</td>
<td>-</td>
<td>121</td>
<td>E</td>
</tr>
<tr>
<td>2,2',4,4',6,6'-Me₆</td>
<td>138-139°</td>
<td>-</td>
<td>139°</td>
<td>-</td>
<td>121</td>
<td>F</td>
</tr>
<tr>
<td>2,2',3,3',5,5',6,6'-Me₈</td>
<td>114°</td>
<td>-</td>
<td>115°</td>
<td>-</td>
<td>121</td>
<td>F</td>
</tr>
</tbody>
</table>
C.20. The solvolysis of diarylmethyl chlorides.

C.20.(a). General procedure.

A conventional thermostat was used for the temperature range 0° to 55°, the temperature usually being controlled to 0.05° or better. For the range -45° to 0° a bath containing calcium chloride solution was cooled externally by a Drikold-acetone bath, which with adequate stirring allowed a temperature control of 0.1°. The thermometers used were calibrated against the melting or boiling-points of purified solvents.

A 100 ml. three-necked flask was fitted with a stirrer, thermometer and 5-ml. burette containing standard sodium ethoxide (ethanolic, approximately 0.05M). Absolute ethanol (90 ml.) containing a crystal of methyl-red indicator was placed in the flask, which was immersed in the thermostat bath. A standard solution (0.05-0.1M) of the given chloride was brought to the temperature of the thermostat bath and the ethanolysis was started by adding 10.0 ml. of this solution to the ethanol contained in the flask, the time of half-addition being taken as zero.

Hydrogen chloride was generated by the ethanolysis, turning the indicator red, and the rate of acid production was measured in the following way.

A measured volume of the ethoxide solution, sufficient to change the colour of the indicator from red to yellow, was immediately run in from the burette and the time at which the indicator reverted to the red colour was noted. Successive measured volumes of ethoxide were added in this way until the ethanolysis was complete (shown by the persistent yellow colouration of the solution).

The solvolysis generates acid according to the stoichiometric equation,

\[
\text{ArCl} + \text{EtOH} \rightarrow \text{ArOEt} + \text{HCl}.
\]
Thus, from the ethoxide titre, the amount of chloride consumed could be calculated for a series of time intervals, and the purity of the starting chloride could be ascertained from the infinity titre.

Reactions were followed usually to 99% completion with an accuracy greater than that given by the usual sampling technique. As explained in section 6.6.(b), the method depends upon the reaction pursuing the $S_N^1$ mechanism (i.e. its rate is unaffected by the added ethoxide), and on keeping the total volume of titrant small in relation to the initial volume of the reaction solution. In all reactions the 'infinity titre' gave a satisfactory check with the concentration of the solution of the chloride determined by weighing the chloride.

With the very extensively ortho-methyl substituted chlorides the possibility of a rearrangement of the intermediate carbonium ion exists, which conceivably could modify the observed kinetics of the process. This rearrangement was shown to be unimportant by comparing the N.M.R. spectra of the starting chlorides with the spectra of the reactions products (the diarylmethyl ethers). The molecular skeletons were apparently identical in all cases.

The results of a typical solvolysis experiment are shown in table 25 and also appear in graph 8.
C.20.(b). Results in a typical solvolysis experiment.

Table 25.

The ethanolysis of 2,3,5,6-tetramethyldiphenylmethyl chloride (0.06M) in ethanol-acetone (9:1 v/v) at 30.3°: titrant ethanolic sodium ethoxide (0.0100M).

<table>
<thead>
<tr>
<th>Time (sec.)</th>
<th>Volume of titrant (ml.)</th>
<th>log $a/a-x$</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>0.00</td>
<td>0.0000</td>
</tr>
<tr>
<td>33</td>
<td>0.10</td>
<td>0.0171</td>
</tr>
<tr>
<td>46</td>
<td>0.13</td>
<td>0.0223</td>
</tr>
<tr>
<td>63</td>
<td>0.18</td>
<td>0.0310</td>
</tr>
<tr>
<td>87</td>
<td>0.24</td>
<td>0.0415</td>
</tr>
<tr>
<td>101</td>
<td>0.28</td>
<td>0.0486</td>
</tr>
<tr>
<td>125</td>
<td>0.34</td>
<td>0.0594</td>
</tr>
<tr>
<td>148</td>
<td>0.40</td>
<td>0.0702</td>
</tr>
<tr>
<td>170</td>
<td>0.46</td>
<td>0.0812</td>
</tr>
<tr>
<td>207</td>
<td>0.56</td>
<td>0.0997</td>
</tr>
<tr>
<td>225</td>
<td>0.62</td>
<td>0.1110</td>
</tr>
<tr>
<td>248</td>
<td>0.67</td>
<td>0.1205</td>
</tr>
<tr>
<td>276</td>
<td>0.75</td>
<td>0.1360</td>
</tr>
<tr>
<td>298</td>
<td>0.80</td>
<td>0.1457</td>
</tr>
<tr>
<td>330</td>
<td>0.88</td>
<td>0.1615</td>
</tr>
<tr>
<td>350</td>
<td>0.94</td>
<td>0.1735</td>
</tr>
<tr>
<td>379</td>
<td>1.00</td>
<td>0.1857</td>
</tr>
<tr>
<td>406</td>
<td>1.07</td>
<td>0.2001</td>
</tr>
<tr>
<td>431</td>
<td>1.13</td>
<td>0.2126</td>
</tr>
<tr>
<td>456</td>
<td>1.19</td>
<td>0.2253</td>
</tr>
<tr>
<td>495</td>
<td>1.28</td>
<td>0.2446</td>
</tr>
<tr>
<td>516</td>
<td>1.33</td>
<td>0.2554</td>
</tr>
<tr>
<td>536</td>
<td>1.37</td>
<td>0.2642</td>
</tr>
<tr>
<td>566</td>
<td>1.44</td>
<td>0.2798</td>
</tr>
<tr>
<td>593</td>
<td>1.50</td>
<td>0.2933</td>
</tr>
</tbody>
</table>
Graph of $\log \frac{a}{a-x}$ against time for the ethanolyis of 2,3,5,6-tetramethylphenylmethyl chloride at 30.5°C.

$10^4 k = 4.97 \pm 0.008 \text{ sec}^{-1}$
<table>
<thead>
<tr>
<th>Time (sec.)</th>
<th>Volume of titrant (ml.)</th>
<th>$\log \frac{a}{a-x}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>626</td>
<td>1.57</td>
<td>0.3094</td>
</tr>
<tr>
<td>658</td>
<td>1.64</td>
<td>0.3257</td>
</tr>
<tr>
<td>688</td>
<td>1.70</td>
<td>0.3399</td>
</tr>
<tr>
<td>735</td>
<td>1.80</td>
<td>0.3640</td>
</tr>
<tr>
<td>785</td>
<td>1.90</td>
<td>0.3887</td>
</tr>
<tr>
<td>845</td>
<td>2.02</td>
<td>0.4191</td>
</tr>
<tr>
<td>infinity</td>
<td>5.90</td>
<td></td>
</tr>
</tbody>
</table>

Rate coefficient calculated on all 30 points, $10^k = 4.97 \pm 0.008 \text{sec}^{-1}$, correlation coefficient $r' = 0.999966$

C.20. (c). Treatment of results.

Rate coefficients were calculated from the equation $kt = 2.303 \log \frac{a}{a-x}$ by plotting $\log \frac{a}{a-x}$ against time for all 30 points. The slopes of the graphs were calculated by the method of least squares.

First order rate coefficients were generally measured at six temperatures covering a temperature range of usually about 30°.

Arrhenius graphs were constructed and the slopes of the graphs were calculated by the method of least squares. From these were derived the rate coefficients (at 25°) and the activation energies for the solvolyses. These quantities were used to derive the transition state parameters at 25° for the solvolyses.

The modified Hammett equation $\log \frac{k}{k_o} = \sigma^+$, using the $\sigma^+$ values derived by Brown for the phenyldimethylcarbinyl system, was applied to the effects of meta- and para- substituents.

C.21.(a). Acid chlorides.

Acid chlorides were prepared by treating the corresponding acids with thionyl chloride.

A mixture of the acid (1.0 mole) and thionyl chloride (3.0 moles) was allowed to stand overnight. The excess thionyl chloride and other volatile products were removed by distillation at 15mm., and the acid chloride itself was purified by distillation at lower pressure.

In this way 2,6-dimethylbenzoyl chloride (bp. 88-90°/10mm., lit. 217°/752mm.\(^{131}\)) and 2-methylbenzoyl (bp. 206-208°, lit. 206-208° \(^{121}\)) were prepared. The benzoyl chloride used was the commercial product.

Oxalyl chloride was prepared by the method of Staudinger \(^{132}\) (bp. 63-64°, lit. 63.5-64°/763mm.\(^{132}\)).


2,6-Dimethylbenzoic acid was prepared by treating 2,6-dimethylphenylmagnesium iodide with a 'Drikold'-ether slurry (mp. 115°, lit. 115° \(^{133}\)). Other acids were commercially available.

C.21.(c). Aryl halides.

2-Bromo-5-methoxy-\(\text{m}\)-xylene was prepared by bromination of 3,5-dimethylanisole (bp. 194°, lit. 193° \(^{134}\)) (prepared by methylation of 3,5-dimethylphenol using dimethyl sulphate, following the procedure of Edwards and Cashaw \(^{135}\)). The boiling point was 99°/3mm., lit. 98.5°/2.75mm\(^{135}\).

3-Iodotoluene (bp. 213°, lit. 213° \(^{136}\)) and 2-iodo-\(\text{m}\)-xylene (bp. 66-67°/1mm., lit. 58-59°/0.5mm.\(^{137}\)) were prepared by diazotisation of the corresponding amines followed by reaction with potassium iodide.
The amine (1.0 mole) was dissolved in hydrochloric acid (500 ml., 5N) and diazotised at 5-7° by the slow addition of sodium nitrite solution (1.04 moles). Upon completion of diazotisation the solution was freed from undissolved solids by filtration and slowly poured into a well stirred solution of potassium iodide (166 g., 1.0 mole) in water (200 ml.) at room temperature. During vigorous decomposition, oxides of nitrogen were evolved; iodine was liberated and a brown unstable precipitate formed. The reaction mixture was allowed to stand for 15 minutes at room temperature and then warmed on a steam bath until gas evolution had ceased. The cooled solution was shaken with ether (500 ml.) and the ether layer separated and washed with sodium hydroxide (2N), sodium thiosulphate (2N) and water. It was dried by the addition of sodium sulphate and purified by distillation under reduced pressure.
References.

2. M. Gomberg, Ber., 1900, 33, 3150.
11. J. Schmidlin, Ber., 1910, 42, 1140.
12. W. Schlenk and E. Marcus, Ber., 1914, 47, 1664.
23. K. Ziegler and C. Ochs, Ber., 1922, 55, 2257.


27. H. Wieland, E. Popper, and H. Seefried, Ber., 1922, 55, 1816.


43. M. Gomberg and L. H. Cone, Ber., 1904, 37, 3545.


51. M. Gomberg, Ber., 1902, 35, 3914.
52. A. E. Chichibabin, Ber., 1908, 41, 2421.
1950, 15, 1155.


87. F. Ullman and A. Mourawiew-Winigradoff, Ber., 1905, 38, 2213.

88. T. Wagner-Jauregg, Ber., 1930, 63, 3213.

89. K. Elbs, Ber., 1883, 16, 1275.


91. E. Friedlander, Monatsch, 1898, 12, 627.


96. M. Gomberg, Ber., 1904, 37, 1638.


102. A. Kliegl, Ber., 1905, 38, 284.

103. J. Schmidlin and M. Huber, Ber., 1910, 43, 2833.


112. F. Mayer and A. Sieglitz, Ber., 1922, 55, 1835.


128. H. Goldtschmidt and H. Stocker, Ber., 1891, 24, 2807.
132. H. Staudinger, Ber., 1908, 41, 3563.
134. K von Auwers, Annalen, 1921, 422, 133.