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SYNTHETIC STUDIES IN THE BIPHENYL SERIES

A Thesis submitted to the University of London
for the Degree of Doctor of Philosophy
in the Faculty of Science.

By

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November 1963

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ABSTRACT

2,2'-Di(1-hydroxy-1-methylethyl)biphenyl has been prepared in poor yield from 2,2'-dilithiobiphenyl and acetone. Attempts to resolve it or to activate it optically have failed.

The use of the Wittig olefin synthesis in the biphenyl series has been studied. 2,2'-Bis(triphenylphosphoniomethyl)biphenyl dibromide has been prepared in a pure state and converted into the corresponding phosphorane by the action of n-butyllithium. The phosphorane, although not isolated, reacts readily with aldehydes but has failed to react with the ketones acetone and cyclohexanone, indicating that it is rather stable. With benzaldehyde, the phosphorane condenses to give 2,2'-distyrylbiphenyl wich, on hydrogenation for different periods of time, gives 2,2'-diphenethylbiphenyl and 2,2'-bis(β -cyclohexylethyl) biphenyl. The geometrical structure of 2,2'-distyrylbiphenyl was discussed.

As an alternative approach carbomethoxymethylenetriphenylphosphorane has been treated with carbonyl compounds in the biphenyl series. It fails to react with ketones under ordinary conditions (confirming the recently published findings of Trippett and Walker) but reacts readily with aldehydes. From its condensation with biphenyl-2,2'-dialdehyde, prepared by an improved route from phenanthraquinone, two isomeric 2,2'-bis (β -carbomethoxyvinylene)biphenyls have been obtained, and their stereochemistry is discussed.

Attempts to synthesise 2,2'-bridged biphenyls with 8- or 9-membered bridging rings by the reaction of biphenyl-2,2'-dialdehyde with Wittig reagents from ethylenebis(triphenylphosphonium) dibromide and trimethylene-1,3-bis(triphenylphosphonium) dibromide have been unsuccessful. Heterocyclic bridged compounds have been obtained from the condensation of the dialdehyde with o-phenylenediamine but the exact structure of the products is still uncertain. From the condensation of ethyl 3,4-diaminobenzoate with the dialdehyde, 3"-carbethoxy-5,10-dihydro-2,3:6,7:8,9-tribenzo-1,4-diazecine has been obtained. If this condensation is carried out at room temperature, and not at 150°, 3"-carbethoxy-phenanthrene-9',10':2,3-quinoxaline is obtained as a by-product.

It has not so far proved possible to demonstrate optical activity in either 2,2'-bis(triphenylphosphoniomethyl)biphenyl dibromide or in its 6-nitro derivative, although steric hindrance to rotation round the 1,1'-bond in the latter compound must be considerable.

ACKNOWLEDGMENTS

The author is indebted to Dr. D.M. Hall for her constant advice and encouragement. She wishes to thank Professor P.B.D. de la Mare and all the Chemistry Department of Bedford College for their help and interest. She also wishes to thank the Government of Thailand for a scholarship.

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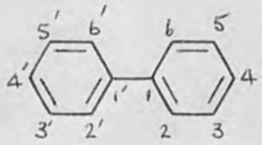
INTRODUCTION

I *2,2'-Disubstituted biphenyls and related compounds*

The biphenyl molecule (1) is collinear and the two benzene rings can rotate about the 1,1'-bond, through a flat coplanar state, with only a small energy barrier, e.g. Howlett (*J.*, 1960, 1055) calculated this activation energy for inversion to be 3.9k cal. mole^{-1}.



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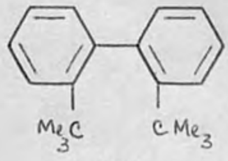
In the crystalline state the molecule is shown by x-ray crystal analysis (Dhar, *Indian J. Phys.*, 1932, *7*, 43) to be coplanar, with the 1,1'-bond length of 1.48A^{o}. Trotter (*Acta Cryst.*, 1961, *14*, 1135), and Hargreaves and Rizvi (*Acta Cryst.*, 1962, *15*, 365) have recently confirmed the above coplanar structure of biphenyl in the crystalline state. The hydrogen atoms were shown to be in the plane of the carbon atoms, but there were small in-plane displacements of the *ortho* hydrogen atoms from idealised positions, which reduced steric strain. However, their length of central C-C bond was 1.507A^{o}.

In the gaseous phase the biphenyl molecule deviates from coplanarity of the two rings by about 45^{o} ($\pm$ 10^{o}), as determined by the electron diffraction method (Bastiansen, *Acta Chem. Scand.*, 1949, *3*, 408).

In solution the interplanar angle between the two rings will presumably have an intermediate value between 0 and 45° (Braude, *Ann. Reports*, 1945,**42**,105). One method of determining the molecular structure of a compound in solution is to determine its ultraviolet absorption spectrum. Empirical correlation between ultraviolet light absorption and molecular structure depends on the fact that ultraviolet light absorption is characteristic of certain groups or chromophores rather than that of molecule as a whole. When two or more chromophores are present in the same molecule, their absorption is usually additive as long as they are separated by two or more single bonds. Two chromophores in conjugation, i.e. separated by only one single bond, give rise to a new type of absorption with increased λ max (wavelength of the maximum) and ε max (extinction coefficient of the maximum). This "conjugation band" is normally observed in the region 230 and 260 mμ. The ultraviolet absorption spectrum of biphenyl is quite different from that of benzene which has a band of low intensity between 230 and 270 mμ with some fine structure, and a more intense band at 210 mμ. Biphenyl exhibits an intense band at 246 mμ, ε max 20,000 in *n*-hexane (Gillam & Hey, *J.*, 1939, 1170), indicating pronounced conjugation between the two phenyl groups and that the internuclear bond has some of the properties of a double bond. However, two chromophores can still produce a strong conjugation band when the angle between their planes is greater than zero. (Suzuki, Bull. Chem. Soc. Japan, 1954, 27, 597).

The introduction of ortho-substituents into the biphenyl molecule in the 2,2'-positions makes it more difficult for the two aromatic rings to rotate about the 1,1'-bond. This is illustrated in the ultraviolet absorption spectrum by the shift to a shorter wavelength and reduction in intensity of the conjugation band. In addition, fine structure may appear at longer wavelengths. If the substitutents are large enough in size so that the two rings are prevented from becoming coplanar, the compound will exist in two stereo-isomeric forms, one being the mirror image of the other. Such compounds can be resolved into their optically active enantiomers, provided that a) each benzene ring is unsymmetrically substituted, b) a resolving group is present, and c) the restriction in rotation is large enough for the enantiomers to be comparatively stable optically under the experimental conditions. As one isomer will be converted into the other isomer simply by passing through the coplanar configuration, the optical stability of any such compound will depend on the ease with which the molecule can attain coplanarity.

A few 2,2'-disubstituted biphenyls, without substituents in other positions, have been obtained optically active; some of them are sufficiently optically stable to be resolvable [(2)-(4)], some are optically labile and undergo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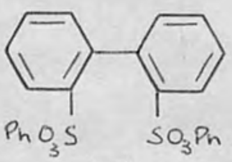
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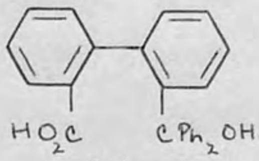
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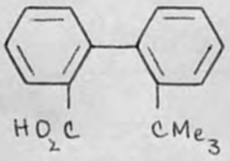
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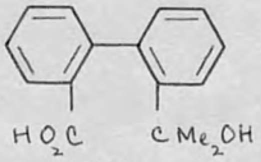
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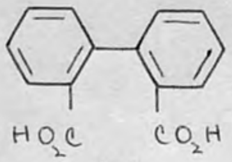

(7)

(2) Lesslie and Mayer, J., 1962, 1401.

(3) Lesslie and Turner, J., 1932, 2394.

(4) Corbellini and Pizzi, Atti. accad.Lincei, 1932, 15, 287.

(5) Lesslie and Mayer, J., 1961, 611.

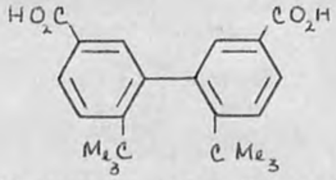
(6) Corbellini and Angeletti, Atti. accad. Lincei, 1932, 15, 968.

Jamison and Turner, J., 1942, 437.

(7) Lesslie, Turner and Winton, J., 1941, 257.

asymmetric transformation [(5)-(7)]; all, with the exception of (3), have the substituents in the form of AX_3.

2,2'-Di-t-butylbiphenyl (2) was obtained in both (+)- and (-)-forms from the optically active 6,6'-di-t-butylbiphenyl-3,3'-dicarboxylic acid (8) [Lesslie and Mayer, J., 1962, 1401] through the Schmidt reaction. This acid had



(8)

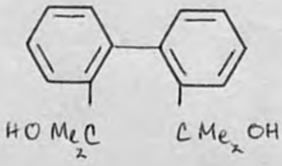
been resolved through the brucine salt and both (2) and (8) are optically stable. Scale models based on atomic radii show that in the di-_t_-butyl acids the two benzene rings cannot become coplanar since, owing to their volume, the two tertiary butyl groups cannot pass the hydrogens in the 2,2'-positions. Interconversion of the (+)- and (-)- forms is therefore inhibited.

Biphenyl-2,2'-disulphonic acid (3) was resolved through its monobrucine salt by successive addition of 0.25 mole of strychnine hydrochloride to the sodium salt. The aqueous solution of its ammonium salt racemises rapidly at 100°. 2-(Diphenyl-hydroxymethyl)-2'-biphenylcarboxylic acid (4), resolved by fractional crystallisation of the brucine salt, racemises gradually at room temperature.

2'-_t_-Butylbiphenyl-2-carboxylic acid (5) undergoes second-order asymmetric transformation with strychnine and brucine from methanol and ethanol. Its half life period of racemisation in ethanol was determined at 57° (35 min.), 67° (14.1 min.), and 79° (5.6 min.); by plotting $\log_{10} k$ against $\frac{1}{T}$ and extrapolating, the half life period of racemisation at 25° was found to be 14.1 hours.

2-(Dimethylhydroxymethyl)-2'-biphenylcarboxylic acid (6) undergoes second-order asymmetric transformation with brucine from ethanol and chloroform, and also first-order asymmetric transformation in chloroform. Its half life period of racemisation at 25.15° was 12.4 hrs. This compound (6) reverted to the racemic form more readily than (4), showing the reduced spatial interference of the methyl group compared to the phenyl group. Diphenic acid (7) is optically highly unstable and mutarotates rapidly with nor-(+)-ephedrine at -30° in chloroform.

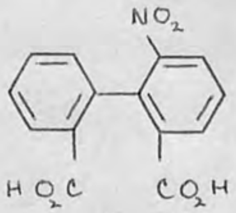
It will be noted that these compounds have been dealt with in the order of decreasing optical stability. Compounds (2), (5) and (6) are of particular interest in connection with the present work. It was shown that, at 25°, compounds (5) and (6) had similar order of optical stability. They have one carboxyl group in common. As the compound with t-butyl group in both 2,2'-positions (2) is very stable optically, it was thought that one with both dimethylhydroxymethyl group in the 2,2'-positions (9) should be comparatively optically stable too. It was then proposed to resolve or activate



(9)

optically the compound (9).

Ortho-substituents in the 6-position, as well as those in the 2,2'-positions, help to increase the optical stability of the molecule. For example, 6-nitrodiphenic acid (10) can be readily resolved through the normal quinine or morphine salt (Bell and Robinson, *J.*, 1927, 1695, 2234) and the solution of acid left at room temperature had practically the same rotation after 6 months. Brooks, Harris, and Howlett (*J.*, 1957, 1934) redetermined racemisation rates of this acid, together with those for two other 6-nitrodiphenic acids, and from their data at 57°, 67.55°, 80.6° and 87.6° the half life period of racemisation at 25° was obtained (by extrapolation) as approx. 164 hrs. This showed that the acid (10) is fairly stable optically. When compared with diphenic acid (7) it is clear that the presence of the nitro group in position 6 is essential to prevent the interchange of enantiomorphs. For the present work, in connection with the Wittig reaction, 2,2'-bis(triphenylphosphoniomethyl)biphenyl dibromide (11) has been



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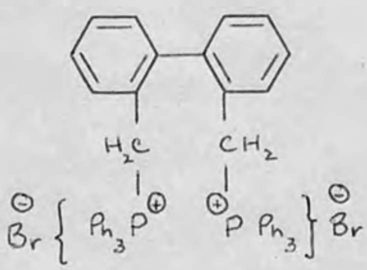

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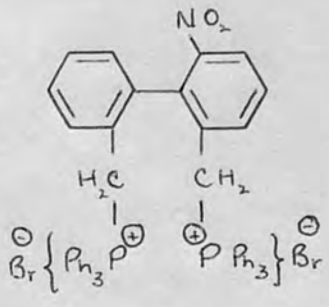
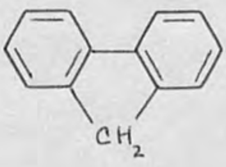


(12)

prepared. The 2,2'-substituents here are also of the type AX_3, but the fact that two of the X's are hydrogen atoms (compared with the more bulky methyl group or oxygen atom) and the C-P bond length is 1.87A° (against C-C bond length of 1.54A° or C-N bond length of 1.47A°) make it less likely that any optical activity will be detectable in compound (11). However, the presence of a nitro group in the 6-position would render the compound potentially optically active. It was then proposed to prepare 2,2'-bis(triphenylphosphoniomethyl)-6-nitrobiphenyl dibromide (12) and examine it for optical activity.

Restricted rotation about the 1,1'-bond can also be brought about by joining the 2,2'-positions with a bridge consisting of two or more atoms.

In the case of the compound containing a 2,2'-bridge of one carbon atom, i.e. fluorene (13), there can be no possibility of optical isomerism as the molecule is planar and strained, and the rings are no longer coaxial (Brown and Bortner, Acta Cryst., 1954, **7**, 139; Burns and Iball, Nature, 1954, 173, 635). This is also true for compounds in which the bridging chain is composed of two atoms, and without ortho substituents. For example, benzo [3,4-c] cinnoline (14) and phenanthrene (15) are both planar.



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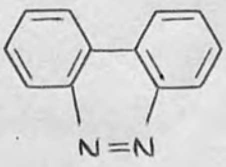

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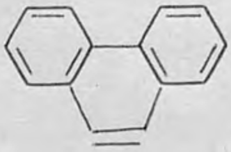
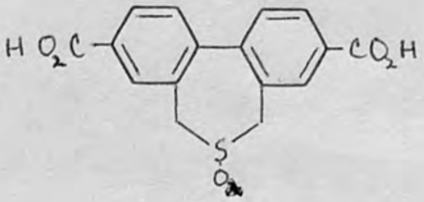


(15)

On increasing the number of atoms in the bridging chain to three, in order to accommodate these three atoms, one benzene ring has to twist from the planar position, and hence asymmetry can arise owing to the twisted conformation. The formation of seven-membered ring is particularly easy (Kenner and E.G.Turner, J., 1911, 99, 2101; Beaven, Hall, Lesslie and Turner, J., 1952, 854) but only two compounds without *ortho*-substituents have been obtained optically active. They both have low optical stability and low optical rotation. 2,7-Dihydro-3,4:5,6-dibenzothiepin-1-oxide-2',3"-dicarboxylic acid (16) was said to owe its asymmetry to the presence of a large hetero atom (Truce and Emrick, J. Amer. Chem. Soc., 1956, 78, 6130), $[\alpha]_D^{25^\circ} + 3.1^\circ$. 6,6-Dicarbethoxy-1,2:3,4-dibenzo[1,3]-cycloheptadiene (17) is optically stable in crystalline state and had a



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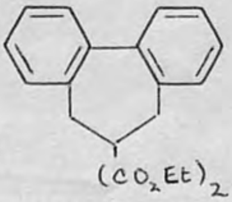
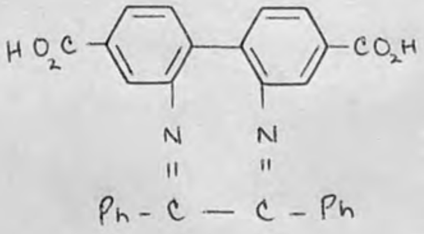


(17)

half life period of racemisation in cyclohexane at 31.5° of 80 min. (Iffland and Siegel, J. Amer. Chem. Soc., 1958, 80, 1947).

Three optically active bridged biphenyls with eight-membered bridging ring have been reported. 2,3-Diphenyl-5,6:7,8-dibenzo-1,4-diazocine-2',3"-dicarboxylic acid (18) was resolved by crystallisation of its brucine salt from ethanol [Bell, J., 1952, 1527]. 1,2:3,4-Dibenz-1,3-cyclo-octadiene-6,7-di-carboxylic acid (19) was obtained in two optically active forms, one form being cis-acid and the other one of the two possible trans-acids [Dvorken, Smyth, and Mislow, J. Amer. Chem. Soc., 1958, 80, 486]. The cis-acid was resolved through its morphine salt from acetone, and it has a half life period of racemisation of 85 min. at 31.5° and of 630 min. at 16.5° (both in ethanol). The trans-acid was resolved through its brucine salt from acetone, and has a half life period of mutarotation of 12 min. at 31.5° in ethanol. 1,2,7,8-Tetrahydro-3,4:5,6-dibenzazocine-1-spiro-1'-piperidinium picrate (20) was obtained in optically active forms by



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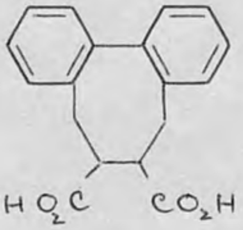

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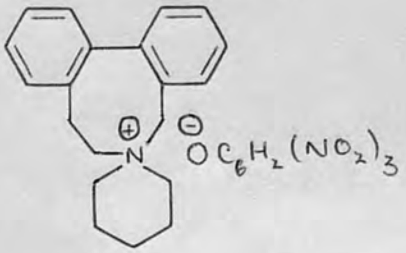
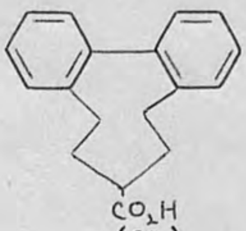


(20)

crystallisation of the (+)- and (-)-α- bromocamphor-π-sulphonates. It is optically highly labile and has a half life period of racemisation of 3.5 min. at 16° in acetone. It is less optically stable than (19) and the replacement of the carbon atom by the small nitrogen may be partly responsible for this [Ahmed and Hall, J., 1959, 3383].

2,2'-Bridged biphenyls with a nine-membered bridging ring are rather difficult to synthesize. But Mislow, Hyden, and Schaefer [J. Amer. Chem. Soc., 1962, 84, 1449] had obtained optically active 1,2,3,4-dibenzcyclonona-1,3-diene-7-carboxylic acid (21). It was optically activated by second-order asymmetric transformation of its quinidine salt from acetone; subsequent decomposition of the salt gave the (-)-acid, $[\alpha]_D$-48.4° in benzene. It was optically stable at room temperature but heating under reflux in benzene for one hour resulted in complete racemization.



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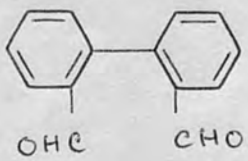
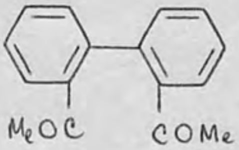


(22)

Not much work has been done on compounds with a longer bridging chain. For the present work biphenyl-2,2'-dialdehyde (22) was prepared for use in the Wittig reaction.

It was thought that if (22) was condensed with _o_-phenylenediamine a 2,2'-bridged biphenyl with ten-membered bridging ring would be obtained, and if a carboxy group was introduced into the diamine molecule, the condensation product would be ready for resolution.

Previous condensation reaction with (22) to give 2,2'-bridged biphenyl was carried out by Bacon and Lindsay [_J_., 1958, 1375] who condensed both (22) and 2,2'-diacetylbiphenyl (23) with hydrazine. Biphenyl-2,2'-dialdehyde (22) in polar solvents, at 0° to > 100°, and under acidic and alkaline conditions, gave only phenanthrene in yields up to 100%. By contrast, the cyclisation with (23) readily gave cyclic azines containing a central eight-membered (1,2-diazocine) ring, the best yield being obtained at 0° (Bacon & Lindsay, _ibid_., 1382). It was proposed to condense (22) with ethyl 3,4-diaminobenzoate and hydrolyse the resulting condensation product to give a compound containing a central ten-membered (1,4-diazecine) ring with a resolving group. A certain amount of difficulty is to be expected in the synthesis, but when once it is made the double bonds and the benzene ring present may



(23)

help to stabilise the effect of free movement of atoms in the long chain of the bridge.

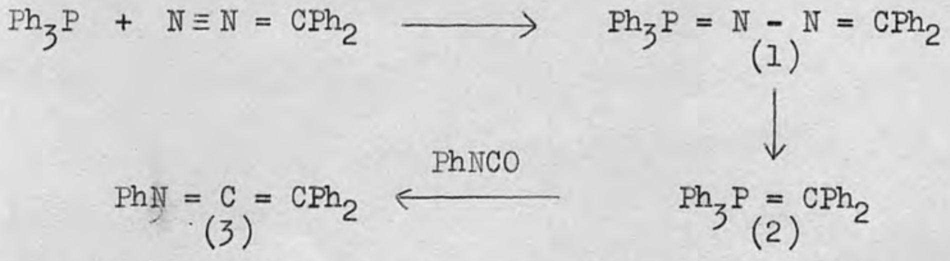
II. The Wittig reaction

1. Introduction

Wittig reaction is a method for replacement of carbonyl oxygen atom by a methylene group. This is effected by the reaction of methylene-triphenylphosphorane, and its substituted derivatives in the methylene group, with a carbonyl compound, resulting in triphenylphosphine oxide and the corresponding olefin.

$$Ph_3P = CR_1R_2 + O = CR_3R_4 \longrightarrow Ph_3P = O + R_1R_2C = CR_3R_4$$

The first substituted methylenetriphenyl-phosphorane had been prepared by Staudinger and Meyer (Helv. Chim. Acta, 1919, 2, 619) who were trying to obtain quinquevalent compounds of phosphorus. From triphenylphosphine and diphenyldiazomethane they obtained the phosphazine (1) which, on heating, lost nitrogen to give diphenylmethylenetriphenyl-phosphorane (2), a red crystalline compound, which was stable to ordinary carbonyl compounds



$$Ph_3P + N \equiv N = CPh_2 \longrightarrow \underset{(1)}{Ph_3P = N - N = CPh_2}$$

$$\underset{(3)}{PhN = C = CPh_2} \xleftarrow{PhNCO} \underset{(2)}{Ph_3P = CPh_2}$$

but with phenylisocyanate gave the keteneimide (3).

Other methylenetriphenylphosphoranes have been reported. Coffman and Marvel [J. Amer. Chem. Soc., 1929, 51, 3496] found that triphenylalkylphosphonium halides reacted with alkali metal alkyls to give coloured products, apparently identical with the methylenetriphenylphosphoranes of Staudinger. Kröhnke [Chem. Ber., 1950, 83, 291] treated p-nitro-benzyl-triphenylphosphonium bromide with alkali and obtained deeply coloured product in the zwitter-ionic form. However, the use of these compounds in the exchange reaction was discovered by Wittig and the reaction is justly named after him.

In the usual procedure of converting C:O to C:C a Grignard reagent is attached to a carbonyl group and a molecule of water is eliminated from the resulting carbinol. But this classical method does not give the exact position of the double bonds introduced from aldehydes and ketones into the olefins. With tertiary or secondary alcohols the splitting of water may take place in two or three directions giving more than one product. In such cases, Wittig's method is employed. The advantage of this method is that the double bond formed remains in the same position as that in the carbonyl group, even when it occupies an energetically unfavourable position. This new method is based on the work of Wittig and Geissler (Annalen, 1953, 580, 44) who found that triphenylmethylphosphonium bromide (4) was easily obtained from triphenylphosphine and methyl bromide, and when treated with phenyl-lithium afforded methylenetriphenylphosphorane (5). The reaction with benzophenone yielded almost quantitative amount of asymmetric diphenylethylene and triphenylphosphine oxide.

$$\left[Ph_3\overset{\oplus}{P}\,CH_3\right]\overset{\ominus}{Br} + PhLi \longrightarrow Ph_3P = CH_2 + PhH + LiBr$$

(4) (5)

$$Ph_3P = CH_2 + O = CPh_2 \longrightarrow Ph_3P = O + Ph_2C = CH_2$$

In connection with this Wittig and Schöllkopf (<u>Chem. Ber.</u>, 1954, <u>87</u>, 1318) and Wittig and Haag (<u>Chem. Ber.</u>, 1955, <u>88</u>, 1654) showed that other alkylidene- and arylidene-triphenylphosphoranes undergo exchange reactions with carbonyl compounds, giving the best yield of olefins. It was then proposed that methylenetriphenylphosphoranes should be used for the conversion of $C=O$ to $C=C$. Experimentally the exchange takes place in an alkaline medium, and most readily in the cold or at a slightly raised temperature.

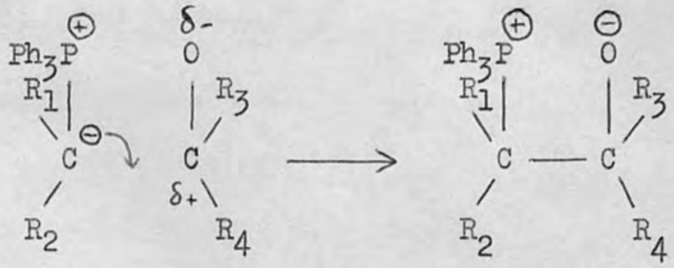
2. <u>Mechanism</u>

An alkylidene triphenylphosphorane may be represented as a resonance hybrid of contributing structures such as (6) and (7). Wittig and Schöllkopf [<u>Chem. Ber.</u>, 1954, <u>87</u>, 1318]

$$Ph_3P = CR_1R_2 \qquad\qquad Ph_3\overset{\oplus}{P} - \overset{\ominus}{C}R_1R_2$$

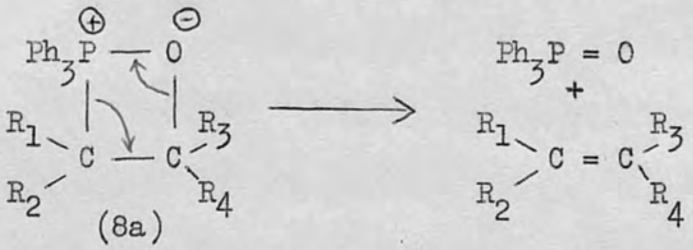
YLENE (6) YLIDE (7)

proposed that reaction with a carbonyl compound involved attack by the nucleophilic carbon of the phosphorane (in its ylide form) on the polarised carbonyl group to give a phosphobetaine (8).



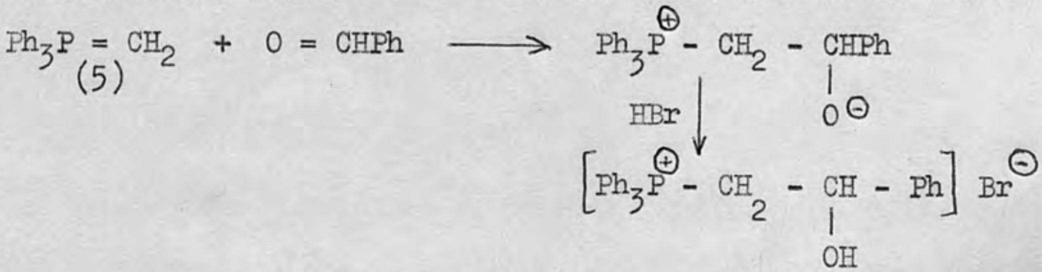
(8)

The tendency of phosphorus to coordinate with oxygen, and the free doublet on oxygen, result in the decomposition of (8) into triphenylphosphine oxide and olefin, probably via a four-membered cyclic transition state (8)a. The formation of the zwitterion (8) in the first step is



(8a)

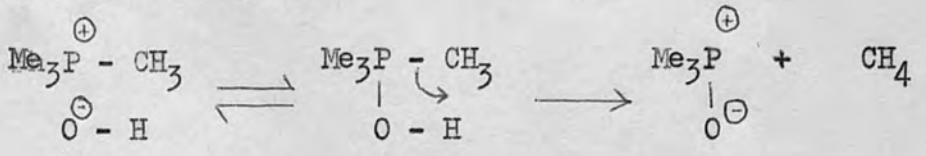
proved in the reaction between benzaldehyde and methylenetriphenylphosphorane. The zwitterion (9) was isolated



(10)

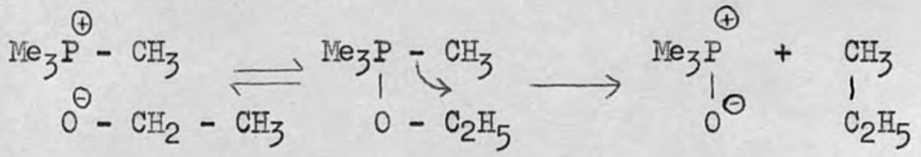
and characterised as its hydrobromide (10) [U. Schöllkopf, Thesis, Tubingen, 1955; quoted by Schöllkopf in his review *Angew. Chem.*, 1959, *71*, 260].

Wittig and Haag [Chem. Ber., 1955, 88, 1654] pointed out the analogy between the elimination of triphenylphosphine oxide from the betaine (8) and the thermal decomposition of quaternary phosphonium hydroxide (11) and alcoholates (12).



(11)

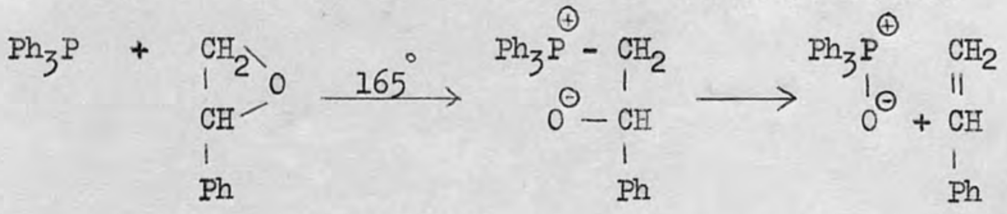
[Fenton & Ingold, J., 1929, 2342]



(12)

[Hey & Ingold, J., 1933, 531]

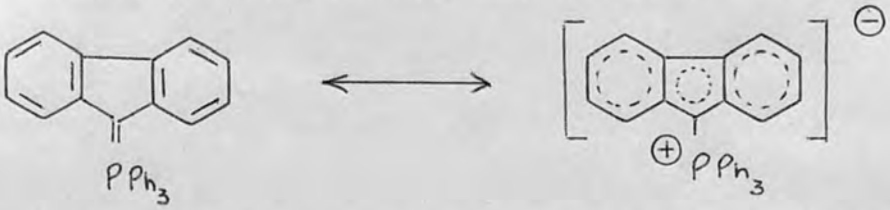
Zwitterions of type (8) are probable intermediates in the action of triphenyl-phosphine on epoxides to give olefins. Triphenylphosphine and styrene oxide on heating together at 165° gave triphenylphosphine oxide (86%) and styrene (50%) [Wittig and Haag, loc. cit.]



Similarly, triphenylphosphine and β-phenylglycidic ester at 170° gave a mixture of cis-(48%) and trans-(52%) cinnamic esters.

McDonald and Campbell [J. Org. Chem., 1959, 24, 1969] report, in support of the Zwitterion intermediate, that when the Wittig reaction is carried out in an ether solvent a temperature of about 65° is required to decompose the intermediate to products. However, using ethanol-ethoxide system the reactions proceed rapidly in about 30-60 sec. at room temperature. They conclude that the rapidity of reaction in ethanol is in line with the polar nature of reaction intermediate.

Johnson [J. Org. Chem., 1959, 24, 282] investigated the reaction of fluorenyltriphenylphosphorane, one of the stable phosphoranes (stabilised by resonance shown), with carbonyl compounds, and found evidence supporting



the nucleophilic attack on the carbonyl carbon.

Fluorenylene-triphenylphosphorane reacted with benzaldehyde to give the conversion product in 84% yield, and rapidly with p-nitrobenzaldehyde giving the corresponding p-nitro-conversion product in 96% yield. It failed to react with fluorenone, but with 2,4,7-trinitrofluorenone it reacted in 100% yield. p-Dimethylamino-benzaldehyde did not react at all. It thus seems that substitution by a group (e.g., nitro group) which increases the polarization of the carbonyl group in benzaldehyde or fluorenone facilitates the reaction, and the attack of a negative carbon at the positive carbonyl carbon must be the controlling step in the

Wittig reaction.

Speziale and Ratts [J. Amer. Chem. Soc., 1962, 84, 854] first put forward the possibility of prior co-ordination of phosphorus with the carbonyl oxygen in the initial step of the reaction. But they decided against it from the result of the competitive reaction of dichloromethylenetriphenylphosphorane with p-nitrobenzaldehyde and p-dimethylaminobenzaldehyde giving exclusively β,β-dichloro-4-nitrostyrene. Again, the p-nitrobenzaldehyde was demonstrated to be more reactive than the corresponding dimethylamino derivative, and only a nucleophilic attack at the carbonyl carbon would explain the difference. However, this possibility of nucleophilic attack by the carbonyl oxygen will be dealt with later in connection with stereochemistry of the product.

3. Scope and limitation

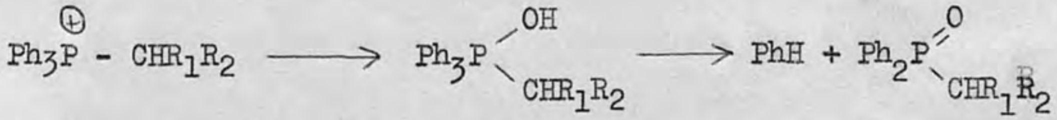
a. The triphenylphosphorane

Wittig reagents of the general formula $Ph_3 P = CR_1R_2$ are prepared by the action of a suitable base on the corresponding phosphonium halide. Ordinarily they are not isolated as they are unstable. They are yellow to red crystalline compounds. The formation reaction depends on the proton-releasing effect of the positively charged central P atom, which is able to stabilise the inductive and mesomeric effect of the negative charge produced on the neighbouring carbon atom. As an element in the second row, P is capable of extending its valency shell of d-orbitals to a decet~~t~~ [Wittig and Rieber, Annalen, 1949, 562, 187, had prepared pentaphenylphosphorus successfully] so that it can pull the free electron pair towards itself, with the formation of a P-C bond. Methylenetriphenylphosphorane can thus be written as two resonance hybrids, the ylene form (6), and the ylide form (7).

The semipolar nature of the ylide structure gives methylenetriphenylphosphoranes their nucleophilic character and makes them capable of reacting with carbonyl compounds or undergoing polar additions. With halogen acids the corresponding phosphonium halides are

$$Ph_3\overset{\oplus}{P} - \overset{\ominus}{C}R_1R_2 \quad + \quad HX \longrightarrow \left[Ph_3\overset{\oplus}{P} - CHR_1R_2\right]X^{\ominus}$$

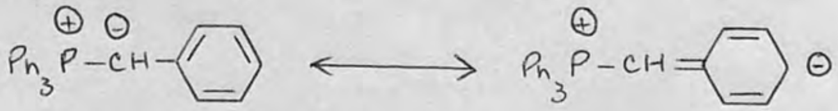
formed and with water the corresponding hydroxides



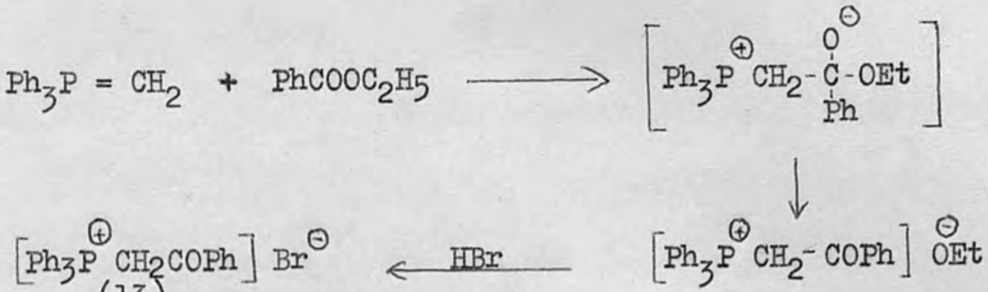
$$Ph_3\overset{\oplus}{P} - CHR_1R_2 \longrightarrow Ph_3P\begin{matrix} OH \\ CHR_1R_2 \end{matrix} \longrightarrow PhH + Ph_2P\begin{matrix} O \\ CHR_1R_2 \end{matrix}$$

Although the hydrolysis is a reversible reaction, in practice it proceeds only in one direction as the resulting phosphonium hydroxides are most unstable and decompose irreversibly to the diphenylalkylphosphine oxide and benzene. This is why reactions with methylenetriphenylphosphoranes must exclude moisture and why the hydroxyl ions, in general, are not suitable for the HX-splitting.

The yellow alkylidenetriphenylphosphoranes (6; R_1,R_2=H or alkyl) are highly reactive; they rapidly absorb oxygen and, besides adding to aldehydes and ketones, react with water, halogen acids, alcohols, and other carbonyl compounds, e.g. esters (see below). The red-orange arylmethylenetriphenyl-phosphorane (6;R_1=H;R_2=aryl) are somewhat less reactive, e.g. benzylidenetriphenylphosphorane does not react with Michler's ketone [Wittig and Haag, loc.cit.], and the red diarylmethylene-triphenylphosphorane (R_1,R_2=aryl) are stable to oxygen and ordinary carbonyl compounds, but are decolorized by water, alcohols, and acids [Staudinger and Meyer, Helv. Chim. Acta, 1919, 2, 635]. This increasing stability and colour is associated with increasing delocalization of the negative charge on the methylene carbon atom, e.g.



Alkylidenetriphenylphosphoranes add rapidly to esters [Wittig and Schöllkopf, loc.cit.], and treatment of the intermediates with halogen acids gives β-ketoalkyltriphenylphosphonium halides, e.g. (13)

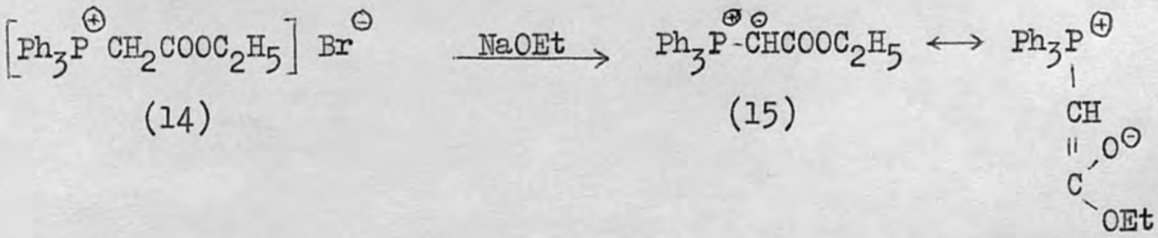


$$Ph_3P=CH_2 + PhCOOC_2H_5 \longrightarrow \left[Ph_3\overset{\oplus}{P}CH_2-\underset{Ph}{\overset{O^{\ominus}}{C}}-OEt\right]$$

$$\left[Ph_3\overset{\oplus}{P}CH_2COPh\right]Br^{\ominus} \xleftarrow{HBr} \left[Ph_3\overset{\oplus}{P}CH_2-COPh\right]\overset{\ominus}{O}Et$$

(13)

This reaction precludes the use of Wittig reagents containing an ester group in the same molecule, except in the special case of the reagents derived from α-bromoesters, e.g. (15), where resonance of the type depicted stabilizes the phosphorane and deactivates the ester group.

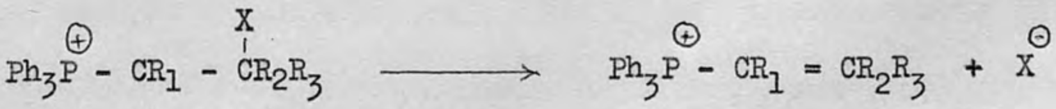


$$\left[Ph_3\overset{\oplus}{P}CH_2COOC_2H_5\right]Br^{\ominus} \xrightarrow{NaOEt} Ph_3\overset{\oplus}{P}-\overset{\ominus}{C}HCOOC_2H_5 \longleftrightarrow Ph_3P^{\oplus}-CH=C(O^{\ominus})OEt$$

(14) (15)

Thus, the phosphonium bromide (14) with sodium ethoxide in ethanol gave with benzaldehyde a 77% yield of ethyl cinnamate [Wittig and Haag, loc. cit.] which subsequently gave 86% trans-cinnamic acid. In fact, (15) is so stable that it can be prepared in an aqueous solution [Isler, Gutmann, Montavon, Rüegg, Ryser, and Zeller, Helv. Chim. Acta, 1957, 40, 1242].

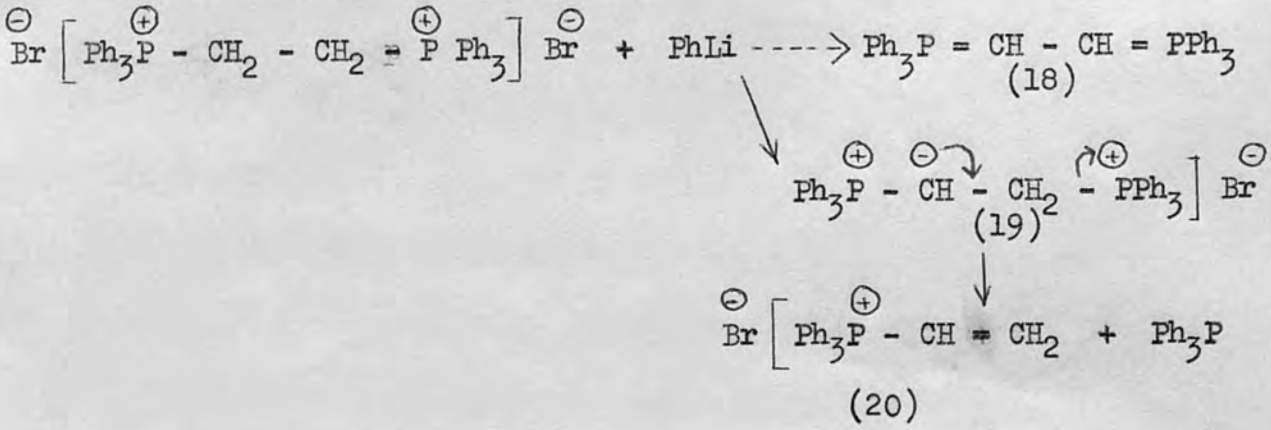
The stability of phosphoranes is markedly affected by certain structural features. Generally systems of



$$Ph_3\overset{\oplus}{P}-CR_1-\overset{X}{\overset{|}{C}}R_2R_3 \longrightarrow Ph_3\overset{\oplus}{P}-CR_1=CR_2R_3 + X^{\ominus}$$

(16)

the type (16) appear to be unstable if X is an easily removable anion, e.g. alkoxide, halogen, etc. [Schöllkopf, Angew. Chem., 1959, 71, 260]. In such cases the molecule is capable of β-elimination. The easily obtainable bisphosphonium salt (17) from 1,2-dibromoethane and triphenylphosphine [Stilz, Thesis, 1955, Univ. of Tubingen, quoted by Wittig, Eggers, and Duffner, Annalen, 1958, 619, 10] does not give the expected bifunctional phosphorane (18) by the action of phenyl-lithium, but gives triphenylphosphine and triphenylvinylphosphonium bromide (20), (19) being a probable intermediate.



$$\overset{\ominus}{Br}\left[Ph_3\overset{\oplus}{P}-CH_2-CH_2-\overset{\oplus}{P}Ph_3\right]\overset{\ominus}{Br} + PhLi \dashrightarrow Ph_3P=CH-CH=PPh_3$$

(18)

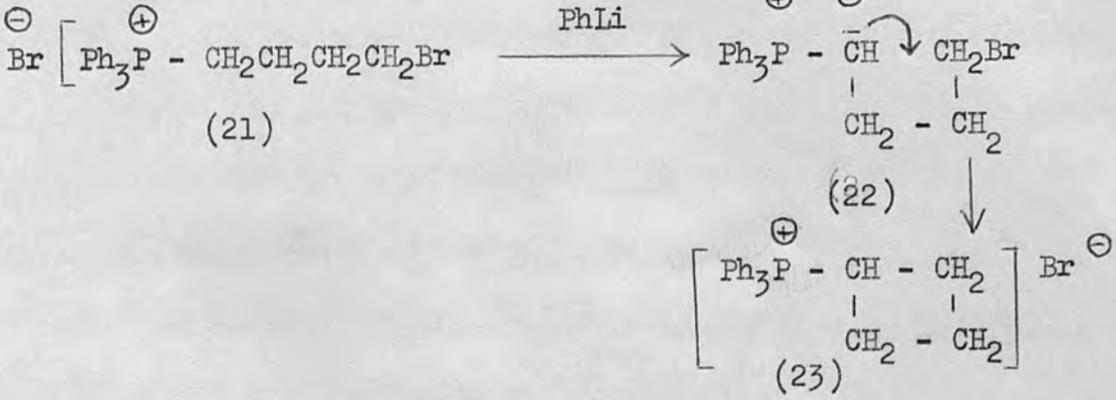
$$Ph_3\overset{\oplus}{P}-\overset{\ominus}{C}H-CH_2-\overset{\oplus}{P}Ph_3\left.\right]\overset{\ominus}{Br}$$

(19)

$$\overset{\ominus}{Br}\left[Ph_3\overset{\oplus}{P}-CH=CH_2\right. + Ph_3P$$

(20)

In special cases, decomposition of phosphoranes can lead to cyclic products as noted by Mondon [Annalen, 1957, 603, 115]. Tetramethylenetriphenylphosphonium bromide (21) gives a deep red ylide (22) with phenyl-lithium in ether. This is then converted slowly into a new phosphonium salt which is probably triphenylcyclobutylphosphonium bromide (23).



b. The aldehydes or ketones

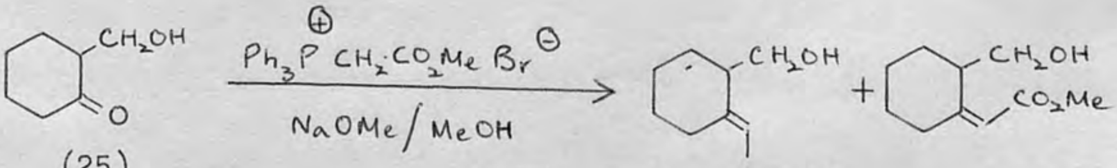
The Wittig reaction proceeds without complication with saturated and unsaturated aliphatic and alicyclic aldehydes and ketones, with alkylaryl and diaryl ketones, and with aromatic aldehydes. Some of the carbonyl compounds used by Wittig and his co-workers are : benzaldehyde, benzophenone, acetophenone, cyclohexanone, cinnamaldehyde, p-nitrobenzophenone, p,p'-dimethylaminobenzophenone, fluorenone, glyoxal, o-phthalaldehyde, 2,2'-dibenzoylbiphenyl, ethyl benzoate and N-methylformanilide.

c. Stereochemistry of the resulting olefin

The formation of a mixture of cis- and trans-isomers in the Wittig reaction was first noted by Wittig and Schöllkopf [loc. cit.] in the reaction of allylidenetriphenylphosphorane with benzaldehyde to give a 1:1 mixture of cis- and trans-1-phenylbutadiene. The ratio of cis- to trans-isomer isolated may vary with the direction of coupling, the base used, and the temperature of the reaction. Thus benzyltriphenylphosphonium bromide with butyl-lithium and benzaldehyde gave 30% of cis- and 70% of trans- stilbenes [Wittig and Haag, loc. cit.], but, with sodium ethoxide as the base in ethanol, 53% of cis- and 47% of trans-stilbenes were obtained. Temperature of reaction influenced the ratio of isomers isolated in the reaction of benzaldehyde with the biphosphorane (24): at room temperature a mixture of the three cis-trans isomers was obtained, but heating under reflux in ether for 1 hr. gave only the trans-trans isomer [Mondon, loc. cit.]

$$\underset{(24)}{Ph_3P = CHCH_2CH_2CH = PPh_3} \xrightarrow{PhCHO} PhCH = CHCH_2CH_2CH = CHPh$$

In many Wittig reactions, only one of the possible isomers is formed, probably for steric reasons, e.g. 2-hydroxymethylcyclohexanone (25) with carbomethoxymethyltriphenylphosphonium bromide and sodium methoxide in methanol gave a product containing only 0.5% of cis-isomer (26), detected by its ready lactone formation [Harrison & Lythgoe, unpublished, quoted by Trippett, Advances in Organic Chemistry, Vol. 1, 1960, Interscience Publishers, New York].



(25)

(26)

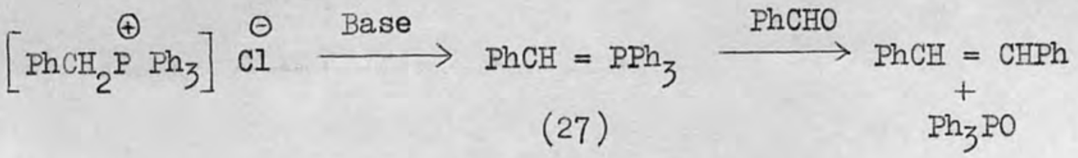
Thus, up to 1960, it was generally accepted that the Wittig reaction normally yielded mixed stereoisomeric olefins, with the predominance of the _trans_-forms. Consequently products obtained as mixtures of _cis_-and _trans_-isomers were isomerized to the all _trans_ configuration by digesting in the boiling xylene containing a trace of iodine, or by crystallizing from dimethylformamide. [McDonald and Campbell, _J. Org. Chem._, 1959, _24_, 1969]

In 1961, Bergelson, Vaver, and Shemyakin [_Izvest. Akad. Nauk S.S.S.R., Otdel. Khim. Nauk_, 1961, 729] reported the effect of the solvent on steric orientation of the Wittig reaction. They showed that when run in cold dimethylformamide the reaction yielded mainly the _cis_-isomer. Thus, benzylidene-triphenylphosphorane (27) with benzaldehyde in dimethylformamide gave 3:1 mixture of _cis_- and _trans_-stilbene, whereas the corresponding ratio of the product in ether was 3:7 [same as Wittig and Haag's]. Shemyakin _et_. _al_. then proceeded to investigate the effect of external factors on the mechanism and stereodirection of the Wittig reaction. Bergelson and Shemyakin [_Tetrahedron_, 1963, _19_, 149] showed that in the presence of Lewis bases, _cis_-olefin was formed in optimal yield. Thus in the reaction between benzylidenetriphenylphosphorane (27) and benzaldehyde in dimethylformamide, and with the addition

$$Ph_3P = CHPh + PhCHO \longrightarrow PhCH = CHPh + Ph_3PO$$

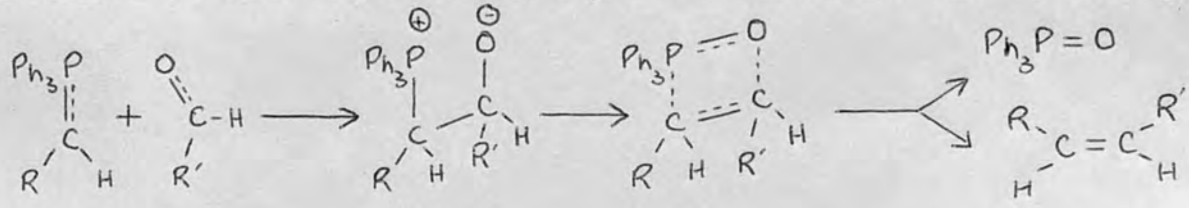
(27)

of LiBr or LiI as Lewis base, the ratio of *cis*-:*trans*-stilbene is increased to 81:19. In another series of reaction between benzylidenetriphenylphosphorane (27) and propionaldehyde [Bergelson, Vaver, Barsukov, and Shemyakin, *Dokl. Akad. Nauk S.S.S.R.*, 1962, *143*, 111] it was confirmed

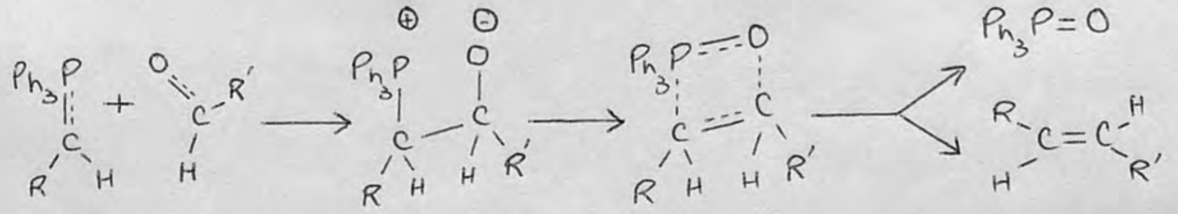


$$\left[PhCH_2\overset{\oplus}{P}Ph_3\right]\overset{\ominus}{Cl} \xrightarrow{Base} \underset{(27)}{PhCH = PPh_3} \xrightarrow{PhCHO} \begin{array}{c} PhCH = CHPh \\ + \\ Ph_3PO \end{array}$$

that the greatest effect on the steric course of the reaction was exerted by lithium bromide or iodide (prepared by neutralizing a benzene solution of butyl-lithium with dry hydrogen bromide or iodide). In the presence of these salts the reaction becomes selective, i.e. giving mainly the *cis*-isomer, even in benzene. In dimethylformamide it gives practically only *cis*-β-ethylstyrene. They found that phosphorus of (27), with its tendency to enlarge its electronic octet to a decett, interacted with the Lewis base. Such interaction was evidenced by the change in infrared spectrum of (27), and by the total or partial decolorising of its deep red solution on adding lithium bromide or lithium iodide, the colourless products not losing their capacity for reaction with aldehydes to form olefins. They explained this by way of schematic representations. If the reaction between the phosphorane and the aldehyde begins with electrophilic attack upon the ylide carbon [Wittig and Schöllkopf, loc. cit.], a mixture of cis- and trans-olefins should result, depending on the orientation of the reactants in the initial attack (scheme 1a and 1b). However, it seems that the electrophilic

Ia


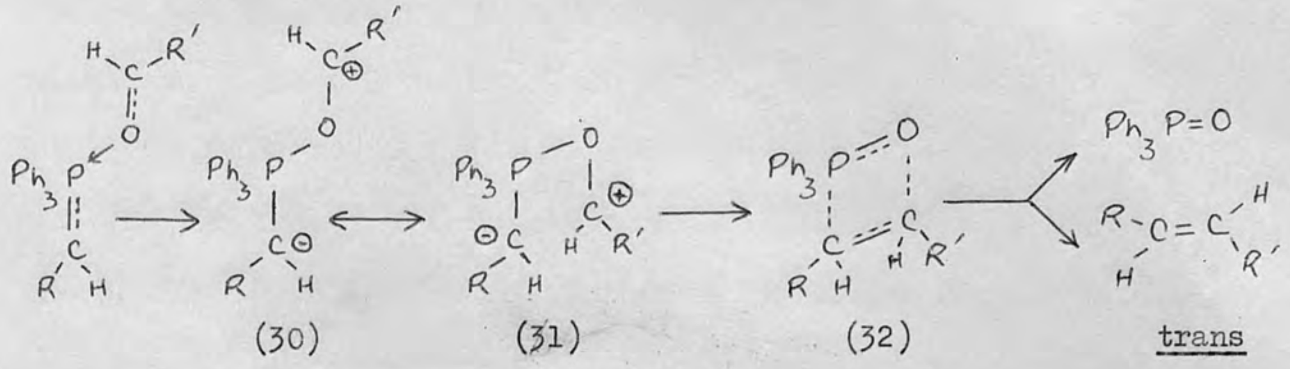
(28)
cis

Ib


(29)
trans

attack of the ylide carbon by the carbonyl carbon is not the only route. An alternate pathway [already pointed out by Speziale and Ratts, loc. cit., but without positive evidence], involving nucleophilic attack on the phosphorus, would result in the trans-olefin, regardless of the initial orientation of the reactants (scheme II). The first intermediate may be the bipolar ion (30) which retains its freedom of rotation about the P-O and C-O bonds. The

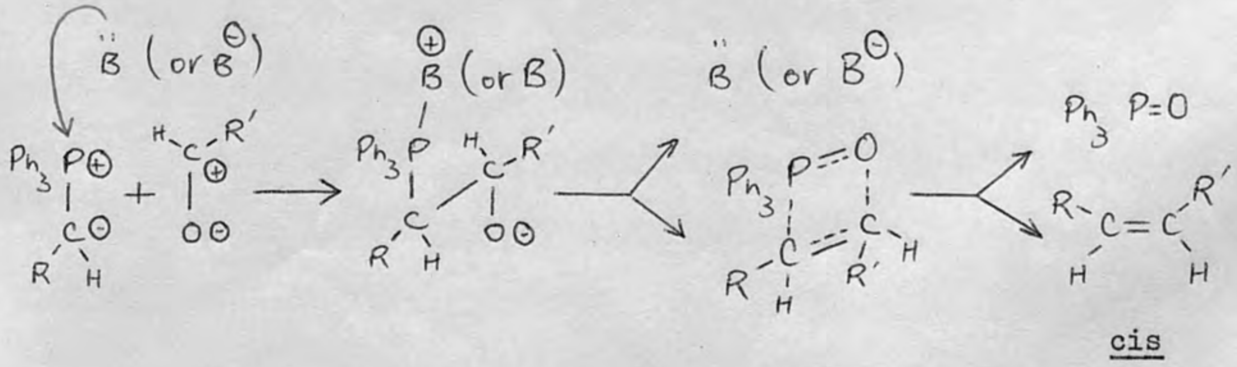
II



turn about the P-O bond necessary for the formation of the four-membered ring (32) can be accompanied by the turn about the C-O bond, leading to the conformation (31) most advantageous for the subsequent cyclisation.

As a result of interaction with the Lewis base the ylide phosphorus becomes less electrophilic and at the same time less accessible. Hence the reaction in the presence of Lewis bases cannot begin with nucleophilic attack on the phosphorus according to scheme II, but should take place via electrophilic attack by the carbonyl carbon on the ylide carbon (scheme III, where B is the Lewis base). The fact that Lewis bases selectively lead

III



to cis-olefins shows that under such conditions betaine

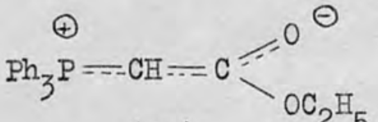
(28) forms more readily than its diastereo-isomer (29; see scheme 1a and 1b). This is obviously due to the mutual inaccessibility of the phosphorus and oxygen in the pre-reaction complex. In polar medium this may be the result of the screening effect of solvate sheaths about the P and O atoms whereas in the case of ylide phosphorus-halide interaction it is due to electrostatic repulsion between the halide and oxygen electronic shells. The selective formation of <u>cis</u>-olefins shows that this effect is considerable.

The influence of similar species of Lewis bases on the relative yield of the <u>cis</u>-isomer increases with their nucleophility in the order chloride, bromide, iodide. The effect of amines, as Lewis bases, on the relative yield of <u>cis</u>-isomer is greatly dependent upon steric factors, falling sharply in the order butylamine, diethylamine, triethylamine. The strong effect of the weakly basic dimethylformamide may be due to possible interaction between the ylide phosphorus and the strongly polarised oxygen rather than the nitrogen. The effect of oxygen-containing compounds on the relative yield of the <u>cis</u>-isomer also depends upon their nucleophility, increasing in the order ether, tetrahydrofuran, alcohol (ethoxide ion).

An important implement for controlling the steric course of the Wittig reaction (namely, external influences on the availability of electrons in the ylide, and hence the position of attack by the carbonyl containing molecule) may also be applied to the structure of the ylide so that the reaction becomes selective. For instance, the stereoselective synthesis of <u>trans</u>-olefins can be achieved when the ylide molecule carries an electron acceptor group at the ylide carbon. Thus the reaction of carbethoxymethylenetriphenylphosphorane (33) with benzaldehyde yields practically only <u>trans</u>-cinnamic ester, regardless of the presence of halide ions or of the solvent used [Bergelson <u>et al</u>., <u>Doklady Akad. Nauk S.S.S.R.</u>, 1962, <u>143</u>, 111; Wittig and Haag, <u>Chem. Ber.</u>, 1955, <u>88</u>, 1654].

$$PhCHO + \underset{(33)}{Ph_3P = CHCOOC_2H_5} \longrightarrow PhCH = CHCOOC_2H_5 + Ph_3PO$$

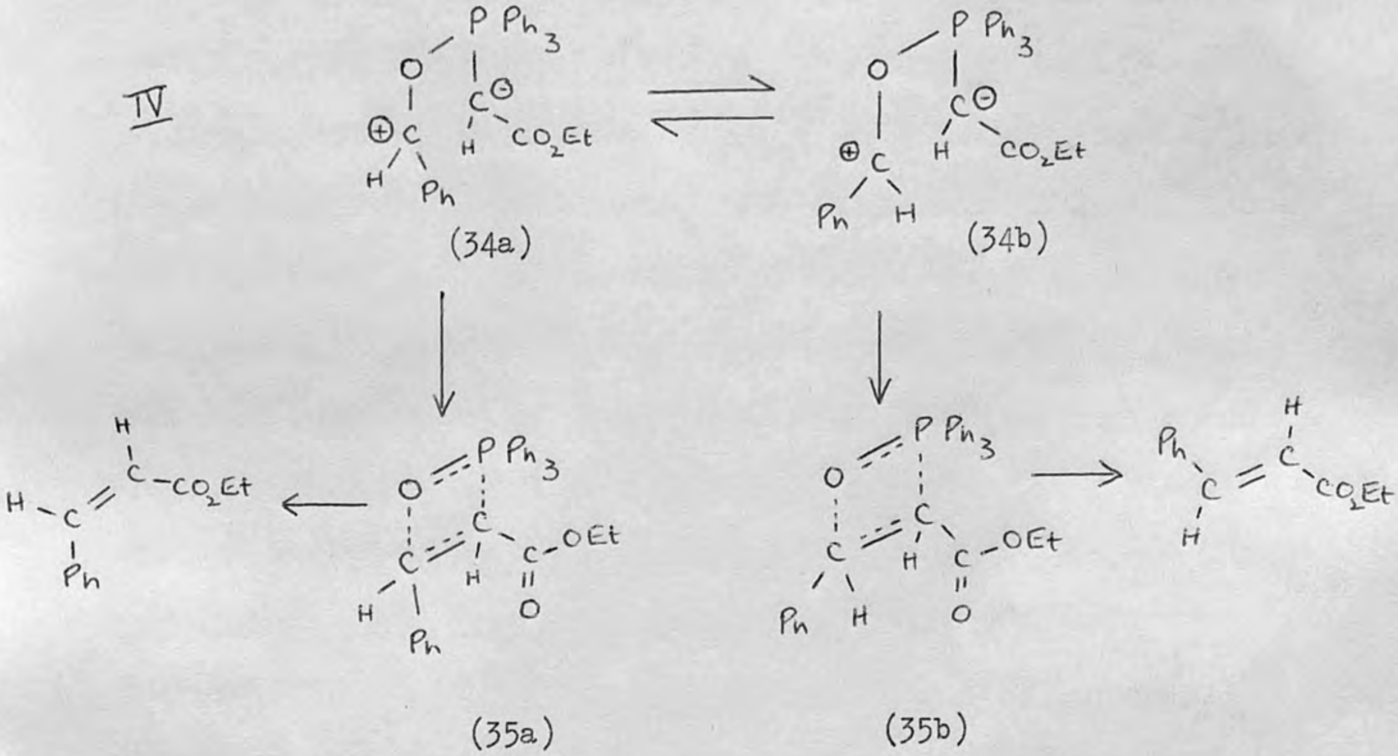
The specifically <u>trans</u> directed reaction of the ylide (33) with benzaldehyde may be explained by the electron density distribution in the ylide. The deficiency in



(33)

electron density at the ylide C-atom hinders electrophilic attack by the carbonyl carbon so that nucleophilic attack on the ylide phosphorus by the carbonyl oxygen becomes more probable. Of the two possible conformation for the resultant dipolar ion (34) that preferred is (34b), leading to the more stable four-membered ring (35b) and thence to the <u>trans</u>-isomers (Scheme IV). The lower energy

IV



of the transition state (35b) as compared with (35a) is due on the one hand to less steric interaction of the substituents (phenyl and carbethoxyl) and on the other, to the circumstance that only in the case of (35b) can there be maximum overlap of the π-electrons of the carbethoxyl and phenyl groups and the developing ethylenic bond (coplanarity factor).

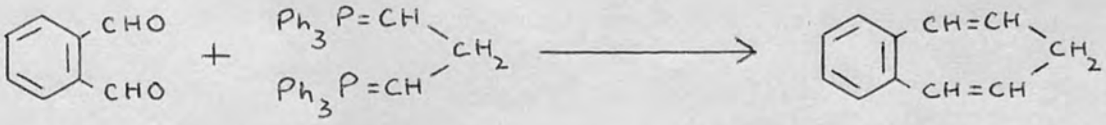
4. <u>Scope of the present work</u>

Isler, <u>et</u> <u>al</u>. [<u>Helv.</u> <u>Chim.</u> <u>Acta</u>, 1957, <u>40</u>, 1242] had prepared both carbethoxy- and carbomethoxymethylenetriphenylphosphorane (33 and 36) $Ph_3P = CHCO_2Me$ (36)

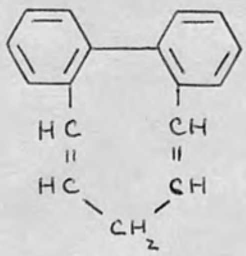
and used them in the preparation of ethyl- and methyl-esters of bixin and crocetin by reaction with corresponding dialdehydes. The ethyl ester as originally prepared by Wittig and Haag (*loc.cit.*) had been treated with benzaldehyde to give a 77% yield of ethyl cinnamate, which subsequently gave 86% of *trans*-cinnamic acid.

Simple reactions of (36) had not been reported and it was proposed to treat it with acetone, benzaldehyde, acetophenone and then with biphenyl-2,2'-dialdehyde and 2,2'-diacetyl-biphenyl. The ultimate aim was to prepare biphenyl derivatives in which the substituents in the 2,2'-positions were unsaturated. These olefinic products would be interesting stereochemically and spectroscopically. Only one ketone in the 2,2'-biphenyl series had been used in the Wittig reaction. Wittig and Stilz (*Annalen*, 1956, *598*, 93) treated methylenetriphenylphosphorane with 2,2'-dibenzoylbiphenyl, and obtained 2,2'-di(β-phenylvinyl)-biphenyl in 85% yield.

Wittig, Eggers, and Duffner [*Annalen*, 1958, *619*, 10] had prepared a number of benzocyclopolyene compounds using phthaldehyde and various bifunctional Wittig reagents, mainly those from polyalkylene dibromides; e.g. phthaldehyde had been treated with trimethylene-bis(triphenylphosphonium) dibromide in phenyl-lithium and benzocyclohepta-1,3,5-triene was obtained in 22% yield. It was proposed to introduce a central homocyclic ring into biphenyl-2,2'-dialdehyde using bifunctional Wittig reagents from ethylene dibromide and trimethylene dibromide.



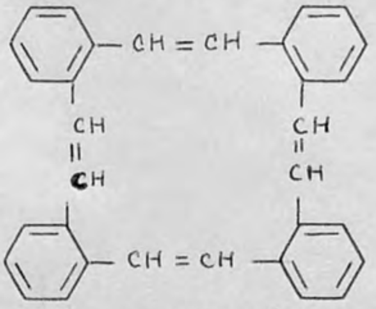
The bisphosphonium salt (17) prepared by Stilz from ethylene dibromide had not been treated with n-butyl-lithium; this reagent has been found to be more effective than phenyl-lithium in the preparation of phosphoranes. The products such as (37), would be very interesting synthetically. 2,2'-Bridged biphenyls with nine-membered



(37)

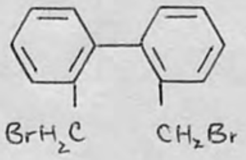
bridging ring would thus be obtained via a shorter route (see e.g. Mislow et al., J. Amer. Chem. Soc., 1962, 84, 1449). Systems such as this, when saturated in the bridging chain, will be twisted and dissymmetric and there is a possibility of optical isomerism.

The use of bifunctional Wittig reagent together with a dialdehyde had also been employed by Griffin, Martin, and Douglas [J. Org. Chem., 1962, 27, 1627] in a synthesis of the macrocycle 1,2,5,6,9,10,13,14-tetrabenzocyclohexadeca-1,3,5,7,9,11,13,15-octaene (38). It is of stereochemical interest that this compound possesses an all-trans configuration.



(38)

No Wittig reagent in the biphenyl series had been reported. It was proposed to obtain a new bifunctional Wittig reagent by preparing a new diphosphonium salt from 2,2'-dibromomethylbiphenyl (39), and then subject it to the Wittig reaction with acetone,acetaldehyde, benzaldehyde and cyclohexanone. The last two reagents had been commonly used in the Wittig reaction, but there had been no report in the literature of the use of acetaldehyde and acetone. Again the products would contain unsaturated substituents in the 2,2'-positions.

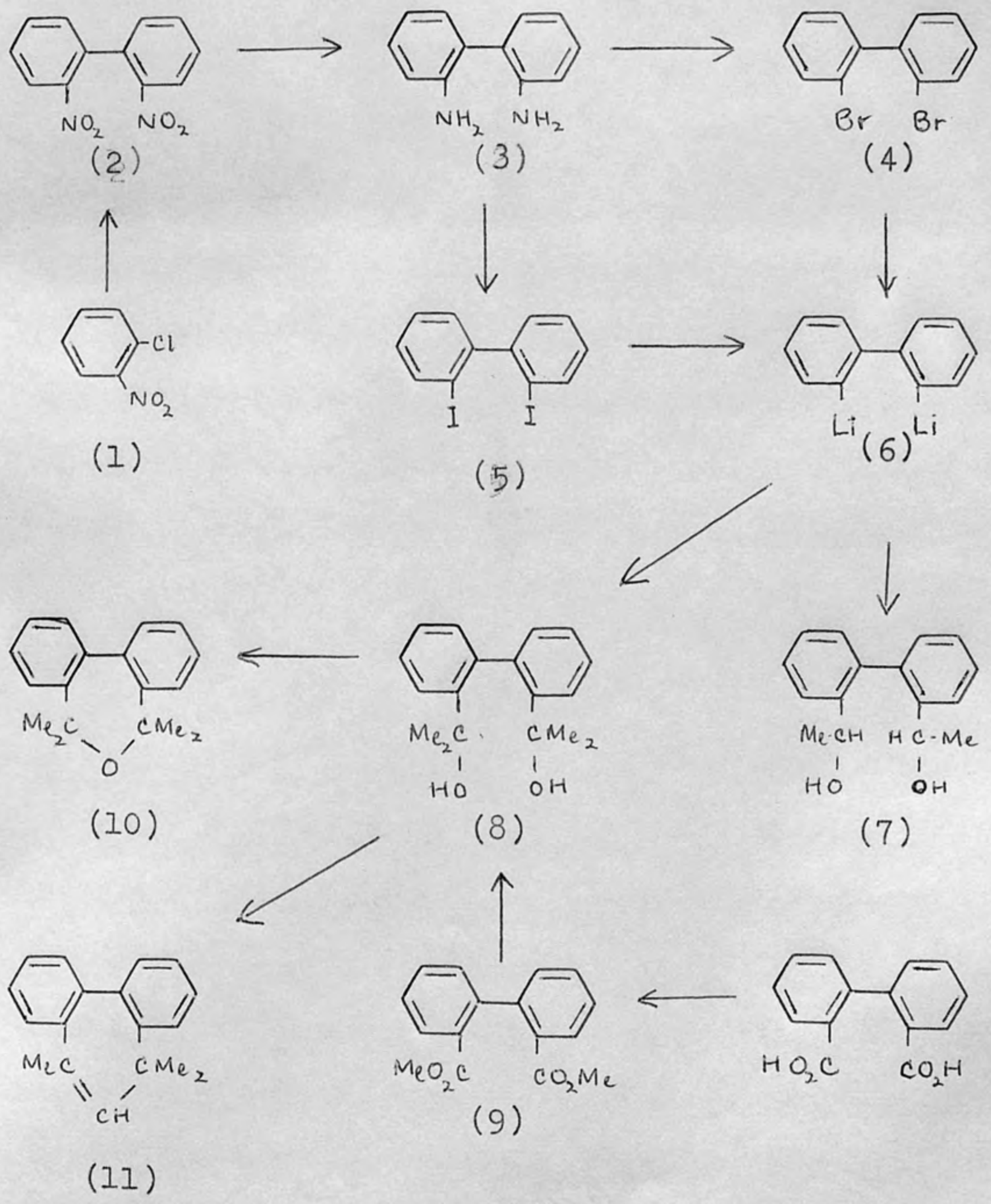


(39)

DISCUSSION

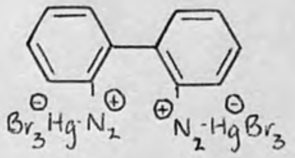
I. 2,2'-Di-(1-hydroxy-1-methylethyl)biphenyl

This compound was obtained according to the following syntheses :



2,2'-Dinitrobiphenyl (2) was prepared from *o*-chloronitrobenzene (1) in 67% yield [Shaw and Turner, *J.*, 1933, 135] and was crystallised from glacial acetic acid [Macrae and Tucker, *J.*, 1933, 1520]. It was reduced with stannous chloride in boiling hydrochloric acid, giving 2,2'-diaminobiphenyl (3) in 81% yield. A similar yield was obtained using catalytic hydrogenation [Ross, Kahan, and Leach, *J.Amer.Chem.Soc.*, 1952, *74*, 4122] in a 1:3 mixture of ethyl alcohol and ethyl acetate, although these authors reported 96% yield under similar conditions.

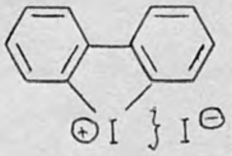
2,2'-Dibromobiphenyl (4) was prepared via a complex salt of the tetrazotised diamino compound and mercuric bromide [Schwechten, *Ber.*, 1932, *65B*, 1605]. It was found that the complex salt (12)



(12)

could be obtained in 98% yield if mercuric bromide was carefully prepared first from the theoretical amount of hydrobromic acid and mercuric nitrate. An excess of hydrobromic acid tended to produce brown fumes and lower the yield of (12); and a mixture of mercuric nitrate and potassium bromide produced a dark brown precipitate. Schwechten found that by mixing the salt (12) with a suitable diluent, in this case potassium bromide, it could be decomposed smoothly giving generally pure product in good yield and without undesirable by-products. However, it was found that by heating the mixture in a long thin-walled tube, only a small yield was obtained as the sublimate. A method modified by Littlejohn [Ph.D. Thesis, London, 1952] was followed. The decomposition temperature of (12) was determined, and the salt mixture was decomposed in a flask in an oil-bath maintained at 185° (10° above the decomposition temperature). The mixture was then steam-distilled and crude product was filtered off from the distillate, giving 64% yield of crystalline 2,2'-dibromobiphenyl.

2,2'-Di-iodobiphenyl (5) was obtained in a similar manner in 60% yield, the intermediate being the diphenyleneiodonium iodide (13)



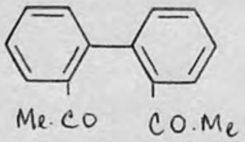
(13)

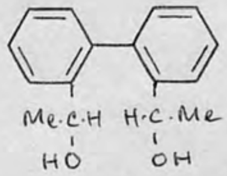
obtained from the tetrazotised diamino compound and potassium iodide in 72% yield [Lothrop, J.Amer.Chem.Soc., 1941, 63, 1187; a procedure originally described by Mascarelli and Benati, Gazzetta, 1908, 38 (11), 624]. The iodonium iodide decomposed on heating to give (5), which was extracted with ether and purified on an alumina column [Heaney, Heinekey, Mann, and Millar, J., 1958, 3838].

The preparative methods for organolithium reagents derived from dihalogen compounds have been reviewed by Millar and Heaney [Quart. Rev., 1957, 11, 109]. 2,2'-Dilithiobiphenyl (6) can be prepared from either (4) [Heinekey and Millar, J., 1959, 3101] or (5) [Heaney, Heinekey, Mann, and Millar, J., 1958, 3838]. The dihalogenobiphenyl in sodium-dried ether was added to the lithium in dried ether, and when the reaction had finished the product was decanted into a similar three-necked flask, under nitrogen, ready to be treated with aldehyde or ketone.

2,2'-Di(1-hydroxyethyl)biphenyl (7) was prepared by the action of acetaldehyde on the dilithio compound (6). The mixture was decomposed by acid and water and the ethereal layer gave one of the isomeric diols (7), m.p. 144-146.5°, in only 10% yield. Hall, Ladbury, Lesslie, and Turner [J., 1956, 3475] had previously obtained two isomeric forms of (7) by reduction of 2,2'-diacetylbiphenyl (14)

(14)





(7)

with lithium aluminium hydride, and separated them by tedious fractional crystallisation into diol A, m.p. 147.5 - 149°, and diol B, m.p. 153-155°. These were presumably the two diastereoisomeric (racemic and <u>meso</u>) forms resulting from the presence of two asymmetric carbon atoms. It thus seemed that the solid obtained was impure diol A. This was confirmed by the evidence that mixed m.p. of diol obtained and diol A was 145-148°, and that for diol obtained and diol B was 127-132°. There was also a small quantity of second crop, m.p. 140-142°. The remainder was a brown gum which would not crystallise when seeded with either

A or B form, and hence must have been a mixture of several products.

2,2'-Di(1-hydroxy-1-methylethyl)biphenyl (8) was prepared from the dilithio compound (6) by action of acetone. The residue from the ethereal extract gave a mixture of solid and liquid. The solid part, on crystallising from light petroleum (b.p. 60-80°) afforded the required product (8), m.p. 138-139°%, in 23% yield; and a second crop m.p. 120-135°. The liquid part, on distilling, gave biphenyl (b.p. 180-190°/68 m.m.; mixed m.p. with pure specimen 65-68°), and a second fraction b.p. 180-190°/13m.m. which remained liquid. Bromine was detected in this fraction. This probably contained some 2-bromobiphenyl (b.p. 296-298°/760m.m. or 165°/13m.m., Schultz, Schmidt and Strasser, <u>Annalen</u>, 1881, <u>207</u>, 353).

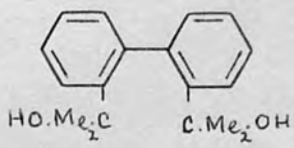
As it seemed that the diol (8) could not be obtained satisfactorily via the dilithio compound (6), another route to it was attempted [Cook and Turner, <u>J.</u>, 1937, 117]. Dimethyl diphenate (9) was allowed to react with methylmagnesium bromide and the diol (8) m.p. 139-141°, was obtained in 60% yield. Attempts were then made to activate it optically.

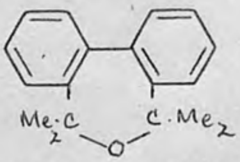
In 2,2'-di(1-hydroxy-1-methylethyl)biphenyl (8) there is no asymmetric carbon atom, and any optical isomerism present must be due to restricted rotation of the biphenyl skeleton.

The standard method for resolving a racemic alcohol is to convert it into the acid ester derivative using phthalic anhydride [Pickard and Kenyon, *J.*, 1912, 620; Doering and Zeiss, *J.Amer.Chem.Soc.*, 1950, *72*, 147]. The acid ester, consisting of equimolecular amounts of the (+)- and (-)-forms, may now be resolved as for acids, i.e. they are treated with optically active bases, mainly alkaloids, e.g. brucine, quinine, etc., and the diastereoisomers thereby produced are separated by fractional crystallisation.

A pyridine solution of the diol (8) was mixed with one equivalent of phthalic anhydride. After $\frac{1}{2}$ hr. at room temperature and 1 hr. on a water bath, the mixture was poured into hydrochloric acid. The solid obtained has m.p. 87-130° after three crystallisations from aqueous acetone; mixed m.p. with 2,7-dihydro-2,2:7,7-tetramethyl-3,4:5,6-dibenzoxepin (10) [m.p. 92-94°, obtained by dehydration of the diol in 4N sulphuric acid] was 85-122°. It was concluded to be the mixture of the diol and the oxepin. However, when the experiment was repeated, less oxepin was formed and the diol was recovered pure after two crystallisations. The reaction was then repeated using two equivalents of phthalic anhydride. This time the product was entirely the oxepin. An attempt was also made to prepare the hydrogen phthalate of the diol via its potassium salt and two equivalents of phthalic anhydride

(8)





(10)

(rendered free from phthalic acid by dissolving in cold chloroform, the acid being insoluble), but the oxepin was again obtained.

Another method for obtaining optically active esters from racemic alcohols is to employ (-)-menthoxyacetyl chloride [Wilson and Read, J., 1935, 1269]. However, an attempt was first made to prepare a simple acetate of the diol (8), using acetyl chloride in pyridine solution. But only the oxepin (10) was obtained (mixed m.p.). An attempt to prepare the diol acetate via its potassium salt also failed, the oxepin (10) being the entire product (mixed m.p. and infrared spectrum). This meant that the same results would be obtained in trying to make the menthoxyacetate.

The chromatographic resolution of the diol by adsorption on a cellulose column also failed.

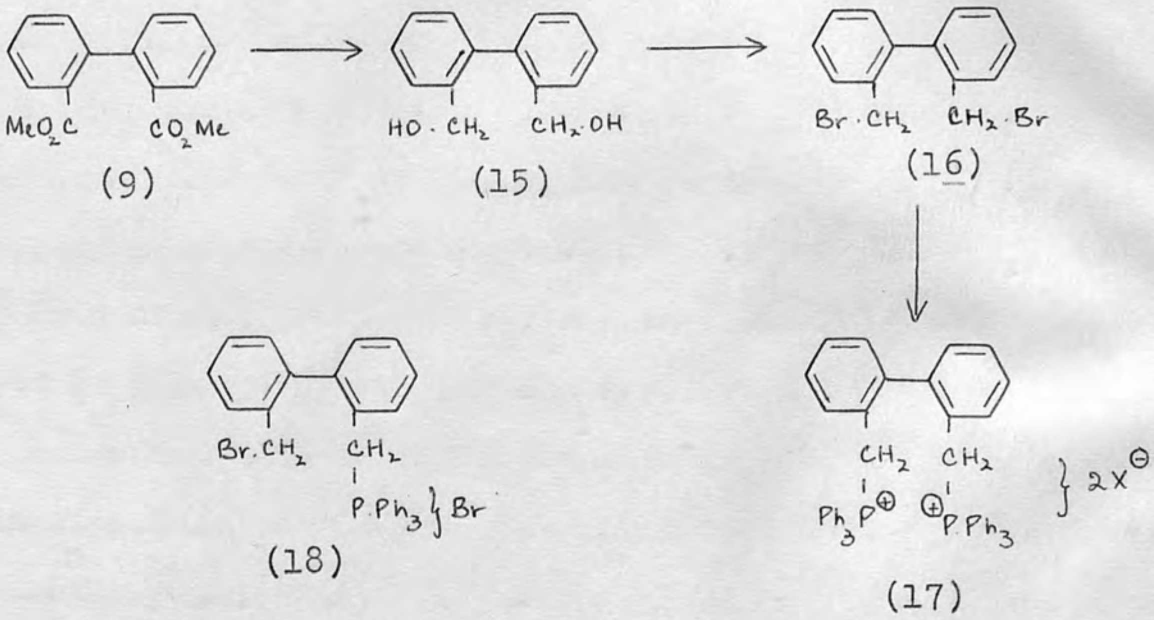
A method of resolution which has been applied to compounds which lack a salt-forming group and so cannot be resolved by the normal means is optical activation by asymmetric solvent action. Buchanan and Graham [J., 1950, 500] found that asymmetric transformations occurred when potentially optically active, but optically unstable, compounds were dissolved in an optically active solvent. The compounds so obtained had a sufficiently high rotation in an inactive solvent. The asymmetric solvent employed most generally was ethyl-(+)-tartrate, which, apart from its ready availability, possessed several advantages. It is a most powerful solvent, soluble in water and can be removed easily from solid materials, while water-soluble compounds can be freed from it by extraction with ether. A typical procedure by Glazer, Harris and Turner [J., 1950, 1753] was followed. The diol (1 g.) was dissolved in ethyl-(+)-tartrate (20 c.c.) at 60°. It was cooled to 25° and kept at this temperature for 1 hr. Iced water was added and the precipitate obtained (0.8665 g.), when washed and dried, had m.p. 91-92°. This was shown to be the oxepin (10) by mixed m.p. and infrared spectrum. Activation at 50° for 1 hr. also gave the same results.

The diol (8), when treated with hydrobromic acid (d 1.49), also underwent cyclisation into 2,7,7-trimethyl-3,4:5,6-dibenzocyclohepta-1,3,5-triene (11).

In view of the facile cyclisation of the diol, no further attempts were made to effect optical resolution or activation. It was concluded that the failure to resolve or activate the diol (8) was due to the fact that no esters, either racemic or optically active, could be prepared from it.

II. 2,2'-Bis(triphenylphosphoniomethyl)biphenyl Dibromide

This compound was prepared according to the following reaction scheme:



2,2'-Bishydroxymethylbiphenyl (15) was obtained in 95% yield from dimethyl diphenate (9) by reduction with lithium aluminium hydride [Hall, Lesslie, and Turner, J., 1950, 711]. This diol was then boiled with hydrobromic acid (48-50%) to give 2,2'-bisbromomethylbiphenyl (16) in 88% yield [Hall, Lesslie, and Turner, loc. cit.].

The preparation of 2,2'-Bis(triphenylphosphoniomethyl)biphenyl dibromide (17, X= Br) from triphenylphosphine and 2,2'-bisbromomethylbiphenyl (16) was first attempted in benzene at room temperature (a general method quoted by Trippett in his review "The Wittig Reaction", Advances in Organic Chemistry, Vol. 1, Interscience Publishers, New York, 1960). The two reactants were dissolved separately in dry benzene, and then mixed at room temperature and stirred. The solid obtained had m.p. 238°, when crude and also after purifying by dissolving in chloroform and precipitating with ether [general method quoted by Friedrich and Henning, Chem.Ber., 1959, 92, 2756]. Its infrared absorption spectrum showed a weak broad band at 604cm^{-1} [see Fig. 1], which was concluded to be the C-Br band. [Bellamy, The Infrared Spectra of Complex Molecules, Methuen, London, 1958, gives C-Br band as 500-600cm^{-1}; C-Br absorption frequency in 2,2'-bisbromomethylbiphenyl is 601cm^{-1}; in bromobenzene it is 678cm^{-1} and in benzylbromide it is 550cm^{-1}, given by Mortimer, Blodgett and Daniels, J.Amer.Chem.Soc., 1947, 69, 822]. In addition, it showed the characteristic bands of triphenylphosphonium salts, i.e. two strong bands at 1110 and 722cm^{-1} [Sheldon and Tyree, J.Amer.Chem.Soc., 1958, 80, 2117], and the P-Phband at 1437cm^{-1} [Bellamy, loc.cit. gave 1435-1450cm^{-1} for P-Ph]. Its empirical formula was $C_{32}H_{28}Br_3P$. From the evidence of the infrared spectrum and the product of subsequent reaction on it, it was concluded that this solid was 2-bromomethyl-2'-triphenylphosphoniomethylbiphenyl bromide (18), empirical formula $C_{32}H_{27}Br_2P$.

As the product was not satisfactory, it was decided to carry out the reaction between triphenylphosphine and the dibromo compound (16) in boiling benzene. The solid obtained now had m.p.

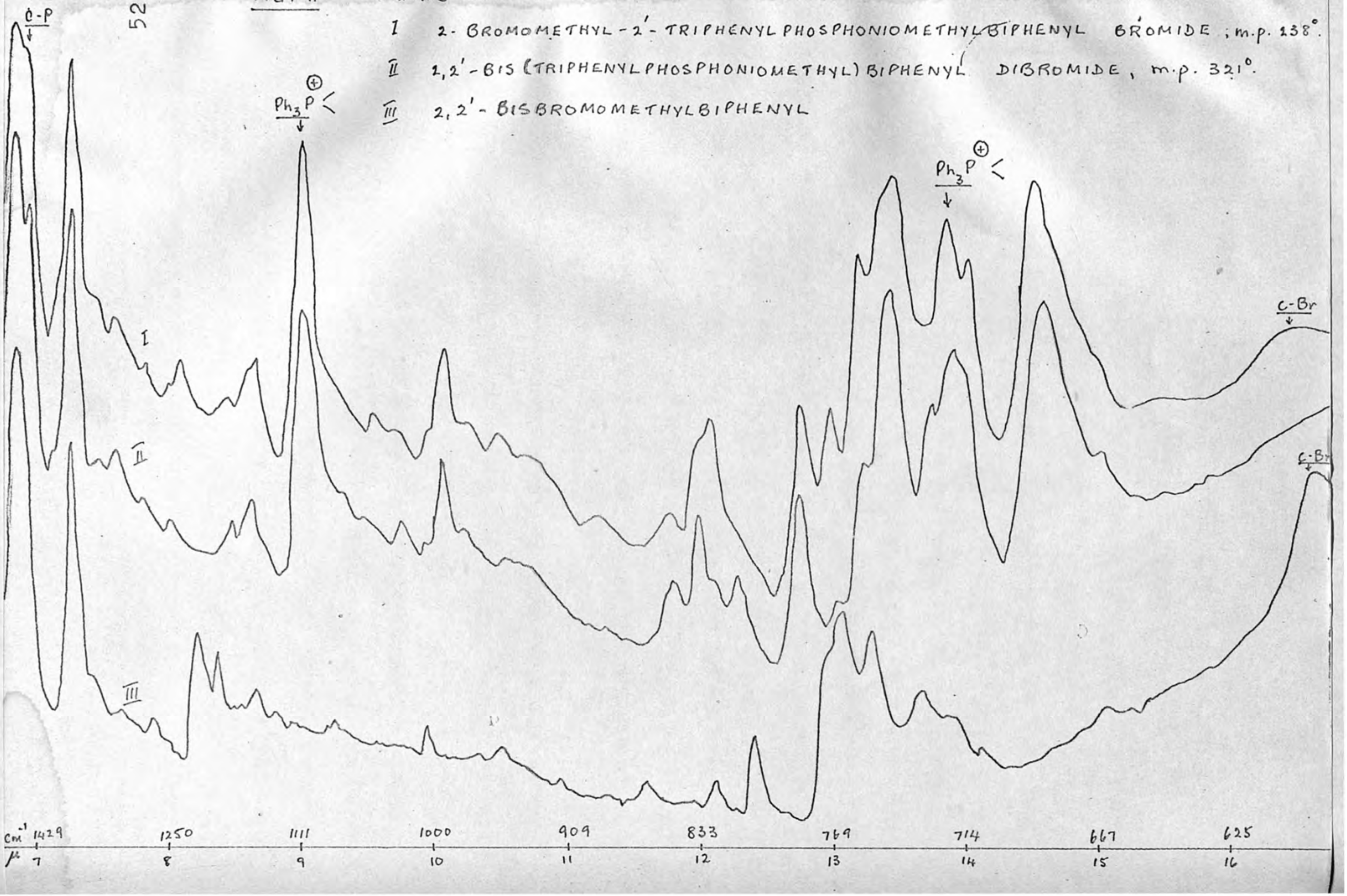


FIG. 1. INFRARED SPECTRA IN NUJOL OF

I 2-BROMOMETHYL-2'-TRIPHENYLPHOSPHONIOMETHYLBIPHENYL BROMIDE; m.p. 238°.

II 2,2'-BIS(TRIPHENYLPHOSPHONIOMETHYL)BIPHENYL DIBROMIDE, m.p. 321°.

III 2,2'-BISBROMOMETHYLBIPHENYL

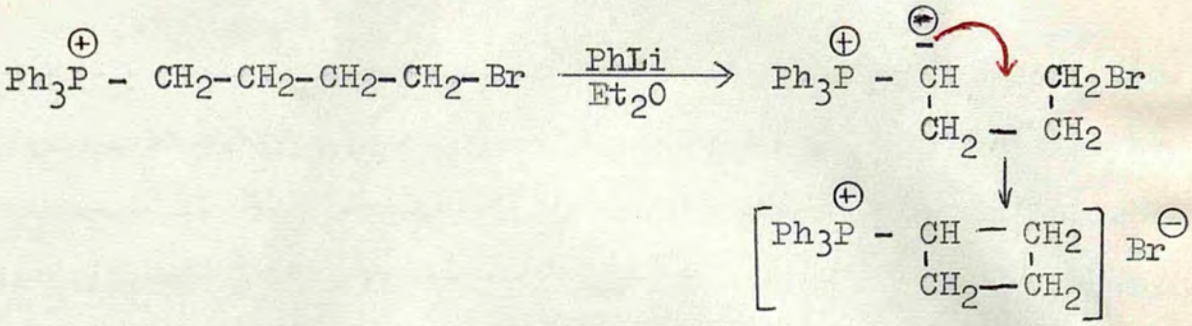
277-280° when crude and also when crystallised from a mixture of alcohol and ether. The infrared spectrum was not quite identical with that of the previous product, m.p. 238°. It showed a weak broad band of C-Br (613cm^{-1}), a P-Ph band (1435cm^{-1}) and two strong bands of triphenylphosphonium salt (1109 and 719cm^{-1}). Whereas the previous product gave phenanthrene in the reaction with acetone in the presence of sodium ethoxide, this solid gave a liquid, as well as phenanthrene, in its reaction. It was subsequently crystallised repeatedly from a mixture of alcohol and ethyl acetate until the m.p. was constant at 323-324°. This was subsequently shown to be 2,2'-bis(triphenylphosphoniomethyl)biphenyl dibromide (17,X = Br). The solid m.p. 280° was concluded to be a mixture of the mono- and di-phosphonium salts.

It seemed that the proportion of diphosphonium salt could be increased if the preparation was done at higher temperature. Boiling xylene was then used as the solvent and 2,2'-bistriphenylphosphoniomethylbiphenyl dibromide (17 X = Br) was obtained in 81% yield, crystallising from ethyl alcohol/ethyl acetate mixture with two molecules of water. Its infrared absorption spectrum showed the P-Ph band (1443cm^{-1}), two phosphonium salt bands (1109 and 719 cm^{-1}) and none in the C-Br region.

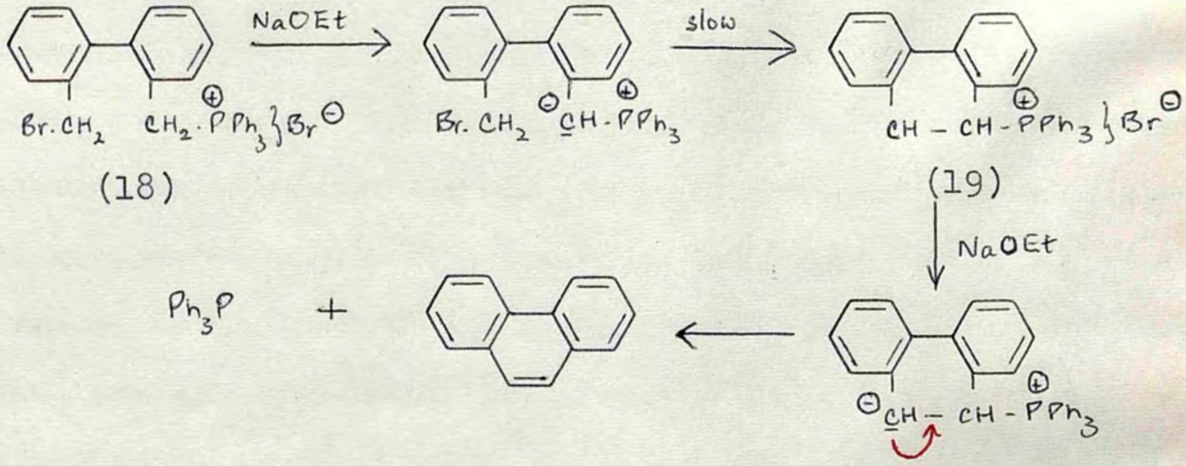
2,2'-Bis(triphenylphosphoniomethyl)biphenyl dipicrate (17,X = $C_6H_2N_3O_7$), m.p. 209-210°, was easily obtained from the corresponding dibromide. 2,2'-Bis(triphenylphosphoniomethyl) biphenyl dicamphorsulphonate (17,X = $C_{10}H_{15}O_4S$), m.p. 70° (decomp.) obtained from the corresponding dibromide, solidifed under ether and the solid contained three molecules of water, but it could not be crystallised. It showed no mutarotation in 95% ethanol at room temperature, the first reading being taken $1\frac{1}{2}$ min. after wetting with solvent, $[\alpha]^{22^\circ}_{5461}$ + 21.5° (c,0.500).

2,2'-Bis(triphenylphosphoniomethyl)biphenyl dibromide (17,X = Br) was used in the Wittig reaction without isolating the corresponding phosphorane. The first solid obtained in the preparation, m.p. 238°, was used without its true identity being realised. An alcoholic solution of the phosphonium salt was allowed to react with acetone in the presence of sodium ethoxide for 3 days at room temperature. The residue from the ethereal extract was digested with light petroleum (any triphenylphosphine oxide present would be insoluble and could be filtered off). The solid obtained from the filtrate had m.p. 97.5-98°. This solid was found to be phenanthrene by its infrared and ultraviolet absorption spectra, and also by m.p. and mixed m.p. with pure specimen.

Bestmann and Häberlein [*Z. Naturforsch.*, 1962, 176, 787], in trying to prove Mondon's assumption [Mondon, *Annalen*, 1957, 603, 115] that treatment of $\overset{-}{Br}\{Ph_3P\,CH_2(CH_2)_nCH_2Br$ (n = 2) (from Ph_3P



and $Br(CH_2)_4Br$) with 1 mol. phenyl-lithium gave triphenylcyclobutylphosphonium bromide by intramolecular C-alkylation of the intermediate ylide $Ph_3P = CH. \smile (CH_2)_nCH_2Br(n = 2)$, treated the monophosphonium salt (18) with 1 mol. sodium ethoxide and obtained the cyclised product (19), m.p. 240°. Unfortunately



they did not give the m.p. of the starting material. However the cyclisation product underwent a Hofmann Degradation with a second mol. of sodium ethoxide to give phenanthrene and triphenylphosphine.

It was thus confirmed that the starting material (m.p. 238°) in the present reaction was the monophosphonium salt (18), a conclusion supported by the spectral evidence described above.

If the salt, sodium ethoxide and acetone were heated under reflux, a liquid, b.p. 66°/4m.m., as well as phenanthrene, was obtained. It was unsaturated (bromine water). Its infrared absorption spectrum showed a conjugated carbonyl peak (1695 cm^{-1}), a very strong peak probably belonging to C=C (1658cm^{-1}), C=C conjugated (1626cm^{-1}), aromatic C=C (1590, 1570 and 1493cm^{-1}), no biphenyl peak [at 1010cm^{-1}, see Beaven and Johnson, Proceedings on the Conference of Molecular Spectroscopy, 1959, 78], but aromatic substitution peaks were present (738, 719 and 694cm^{-1}). A peak at 1372 cm^{-1} probably belonged to $C-(CH_3)_2$ absorption. There was also a trace of P-Phband (1431cm^{-1}) of triphenylphosphine, byproduct of the Hofmann degradation. It thus seems that this liquid was a mixture of the product of aldol and related reactions on acetone, and traces of triphenylphosphine; the presence of the former would account for the conjugated carbonyl peak, and the latter for the aromatic substitution peaks. As no triphenylphosphine oxide was obtained, the Wittig reaction could not have taken place.

Meanwhile, another solid, m.p. 278-280°, was obtained in the preparation of the phosphonium salt. This was subjected to the Wittig reaction with acetone in the presence of boiling sodium ethoxide. After a similar working up as above, a liquid, b.p. 114°/6 m.m., was obtained. It had an empirical formula $C_{29}H_{34}O_2$. It was also unsaturated to bromine water. Its infrared absorption spectrum [see Fig.2] showed a conjugated C = O peak (1698cm^{-1}), C=C conjugated with aromatic ring (1634 cm^{-1}), aromatic C=C peaks (1575, 1477 and 1451cm^{-1}), two strong peaks probably belonging to C-CH_3 (1435 and 1379cm^{-1}) [the ones belonging to C-$(CH_3)_2$ in mesityl oxide are 1380 and 1360cm^{-1}, given by Thompson and Torkington, _J._, 1945, 640], and aromatic substitution peaks (755 and 730cm^{-1}). However, this liquid, unlike the previous one, contained a biphenyl peak (1008cm^{-1}) in its spectrum.

This yellow liquid, when hydrogenated for 3 hrs. at room temperature, gave an infrared spectrum showing that its carbonyl group was no longer in conjugation (1704cm^{-1}). The biphenyl and the substitution peaks were still present. In addition, spectra of the compound both before and after the hydrogenation showed an OH peak (3484 and 3436cm^{-1} respectively), indicating that it contained traces of aldol reaction product.

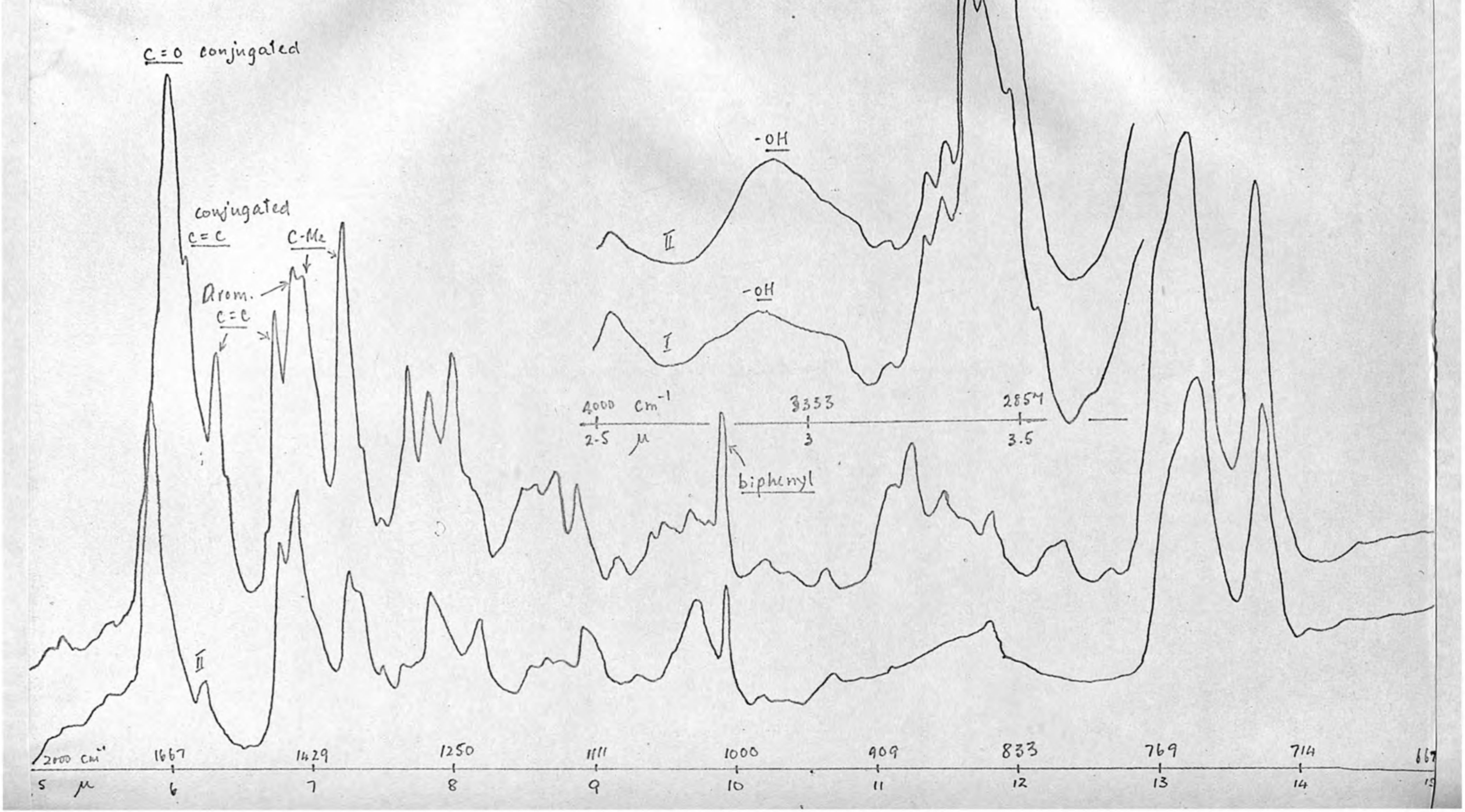
It thus seems that the product of this reaction was a biphenyl derivative containing carbonyl and unsaturation groups. Again no triphenylphosphine oxide was obtained and hence no Wittig reaction could have taken place. It was concluded that the starting material, m.p. 278-280°, was a mixture of the monophosphonium salt (giving phenanthrene) and the impure diphosphonium salt.

The Wittig reaction on the purified diphosphonium salt

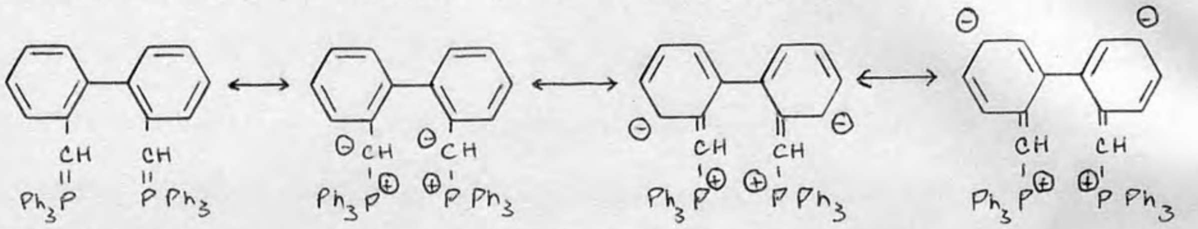
FIG. 2. INFRARED SPECTRA IN NUJOL OF

I PALE YELLOW LIQUID, b.p. 114°/6 m.m.

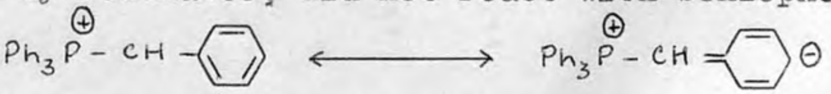
II ITS HYDROGENATION PRODUCT.



(17,X=Br) and acetone was not carried out because, at that time, Trippett and Walker [J., 1961, 1266] reported that stable phosphoranes are generally unreactive towards ketones (see p. 85). It is probable that the corresponding bisphosphorane is highly stal stabilised by resonance (see illustration).

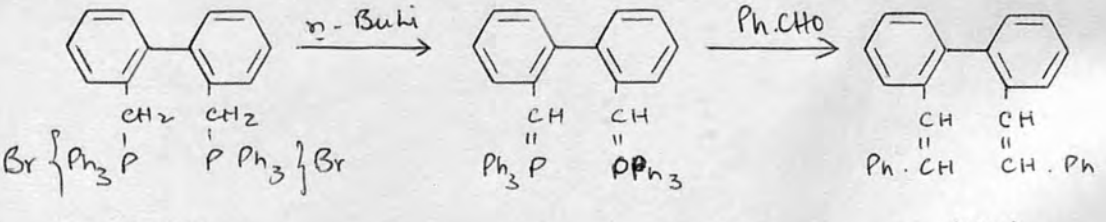


The analogous phosphorane, benzylidenetriphenylphosphorane, also stabilised by resonance, did not react with benzophenone.



[Wittig and Haag, Chem.Ber., 1955, 88, 1654]. It was decided to attempt the Wittig reaction on the purified salt with an aldehyde which is more reactive than a ketone.

The reaction between (17,X=Br) and benzaldehyde proved unsuccessful in boiling sodium ethoxide; the dark red residue obtained, when chromatographed on a silica-gel column, gave only brown viscous substances, presumably macromolecules. In the presence of ethereal phenyl-lithium, prepared from lithium and bromobenzene under an atmosphere of nitrogen and used at once, the corresponding phosphorane appeared to have been formed as shown by the orange-red mixture. This colour faded when benzaldehyde was added. But when the reaction mixture was worked up, 78% of the diphosphonium salt (m.p. and infrared spectrum) was recovered together with benzaldehyde. It was decided to use n-butyl-lithium prepared from n-butyl chloride and lithium, as a base. A calculated amount of n-butyl-lithium was decanted into a reaction flask before the phosphonium salt was added. Orange-red solid of the phosphorane was again obtained. After the addition of benzaldehyde the colour went pale yellow. Triphenylphosphine oxide was filtered off in the form of ether-insoluble complex with lithium bromide, and when ether was removed from the filtrate, 2,2'-distyrylbiphenyl (20) (1.54g., 29%) was obtained.

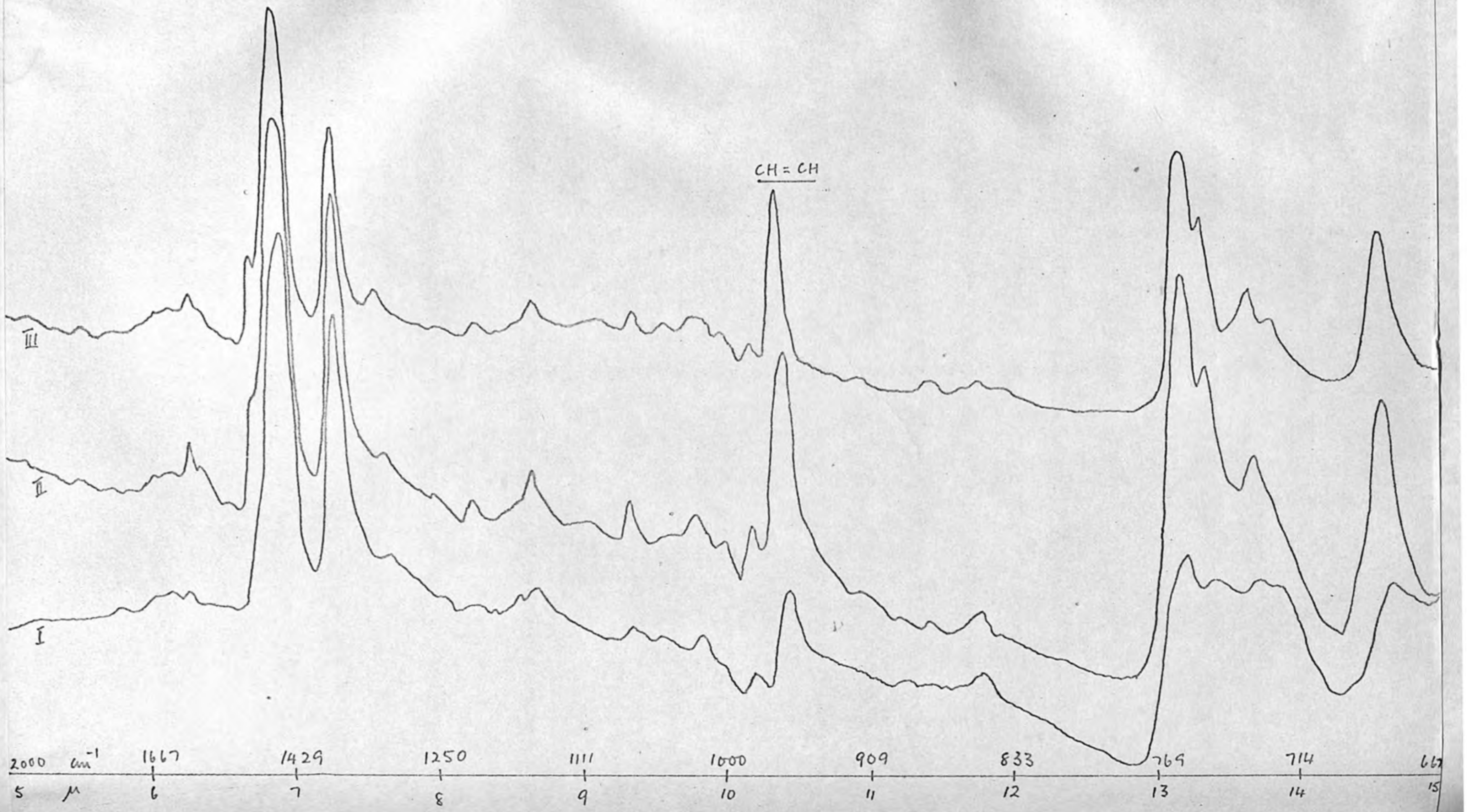


(17) (20)

When crystallised from n-hexane, with an addition of charcoal, the first crop (0.75g., 15%) had m.p. 123°. The second crop, m.p. 119°, when recrystallised from light petroleum (b.p. 60-80°) it had m.p. 147°; mixed m.p. with the first crop was 145-146°. On repeating the experiment the first two crops obtained had m.p. 144-146°. On investigating these melting points, by recrystallising from n-hexane and seeding with appropriate crops and taking the m.p.'s of the solids obtained, it was found that only the high melting solid was present; the low melting one originally obtained in the first experiment now had m.p. 147°. Thus the low melting solid, m.p. 123°, was a metastable form of 2,2'-distyrylbiphenyl (20). The infrared spectra of all crops were identical [see Fig. 3].

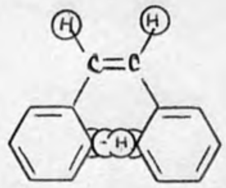
FIG. 3. INFRARED SPECTRA OF 2,2'-DISTYRYLBIPHENYL IN NUJOL

I m.p. 121-123°
II m.p. 147°
III m.p. 123° originally, 147° on standing.

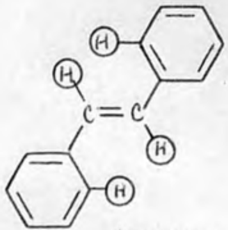


From the infrared spectra, there was only one prominent unsaturation peak (960cm^{-1}) indicating a *trans*-configuration in conjugation [see e.g. Wittig, Koenig and Clauss, *Annalen*, 1955, *593*, 127; Inhoffen, Quinkert, Hess and Erdmann, *Chem. Ber.*, 1956, *89*, 2273; Isler, *et.al.*, *Helv.Chim.Acta*, 1957, *40*, 1256; Thompson, *et.al.*, *J.*, 1950, 214.] The ultraviolet absorption spectrum in cyclohexane gave λ_{max} 300 and 230 mμ with the corresponding ε_{max} 44,000 and 65,000, i.e. the intensity of the shorter-wavelength band is higher than that of the longer-wavelength band. This situation also exists in, for example, *cis*-stilbene and *cis*-cinnamic acid. In the case of *cis*-stilbene the figures are λ_{max} 280, 224; ε_{max} 10500, 24400 [Beale and Roe, *J. Amer.Chem.Soc.*, 1952, *74*, 2302; *J.*, 1953, 2755], while in the *trans*-isomer [λ_{max} 295, 228; ε_{max} 29000, 16400] the longer-wavelength band has higher intensity. Thus, there is an evidence for a *cis*-configuration for compound (20).

The longer-wavelength band of stilbenes was ascribed by Braude & Waight [Progress in stereochemistry, Vol. 1, Ed. Klyne, Butterworths, 1954, Chap. IV] to electronic oscillations over the whole length of the molecule, or, to transition from ground states to excited states in which dipolar structures e.g. Ph^{+}=CH-CH=Ph^{-} make larger contributions. In the case of *cis*-stilbene, steric hindrance to a coplanar arrangement of the conjugate system (see diagram) will result in an equilibrium configuration in which



cis-stilbene



trans-stilbene

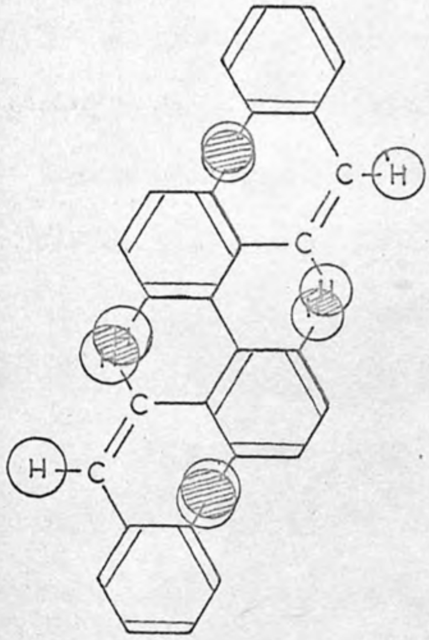
the planes of the phenyl rings are rotated to an appreciable extent with respect to the plane of the ethylenic double bond; this will raise the potential energy of the excited state more than that of the ground state and the transition energy will be increased i.e. λ_{max} will be decreased compared with that of the *trans*-isomer. The shorter-wavelength band was ascribed by the same authors to the "partial" styryl (Ph-C=C-) chromophore.

In the case of 2,2'-distyrylbiphenyl (20), the shorter-wavelength band may thus be ascribed to the styryl chromophore the intensity of which far exceeds that of *cis*- or *trans*-stilbene, as is to be expected. The longer-wavelength band is at a higher wavelength than either *cis*- or *trans*-stilbene, showing that there is little steric hindrance in the molecule. This would seem to support a *trans-trans* configuration, but the evidence supporting a *cis*-configuration cannot be ignored.

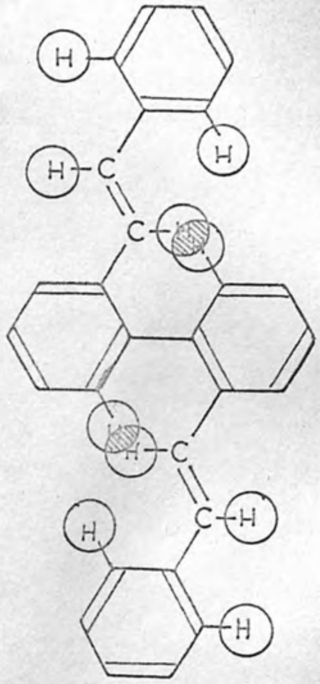
In the diagram, p. 64, figure a, the steric hindrance between hydrogen on the biphenyl skeleton and that on the ethylenic carbon can be easily relieved by a twist in the biphenyl 1,1'-bond. In figure b., in addition to a twist in this 1,1'-bond, some twist in the bond joining the terminal benzene ring of the *cis*-part

2,2'-DISTYRYLBIPHENYL

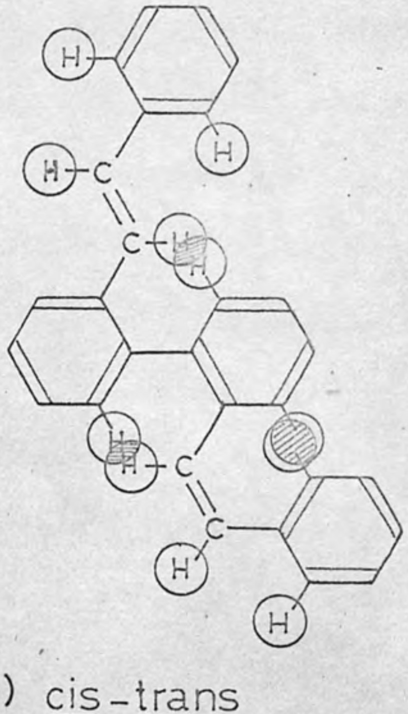
[showing hydrogen interference]



(c) cis-cis



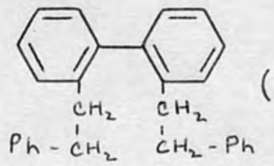
(a) trans-trans



(b) cis-trans

would be necessary to relieve the strain. But in figure c, the molecule is heavily restricted, even with maximum twisting there will still be an interference between various hydrogen atoms, and it seems feasible that this form was not obtained. Thus, the only form that fits in with the evidence from both the long- and short-wave band is figure b, and it is proposed that 2,2'-distyrylbiphenyl obtained has a cis-trans configuration. The evidence for the cis-configuration in the infrared spectrum, a medium to weak band at 690cm^{-1}, might have been masked by the stronger band of monosubstituted aromatic ring at 686cm^{-1} [see Fig. 3].

When 2,2'-distylrylbiphenyl was hydrogenated for 12½ hrs. at room temperature, 65 lb./in.^{2} pressure, in the presence of platinum oxide catalyst, 2,2'-diphenethylbiphenyl (21) was obtained in 93% yield. The infrared absorption spectrum showed



(21)

the CH_2 peaks at 2915, 2849 and 1449cm^{-1} with no unsaturation peaks, the biphenyl peak at 1008cm^{-1} and the aromatic substitution peaks at 754 and 696cm^{-1} [see Fig. 4]. The ultraviolet absorption spectrum in cyclohexane showed λ_{max} 300, ε_{max} 3400, i.e. there was neither biphenyl conjugation nor stilbene conjugation.

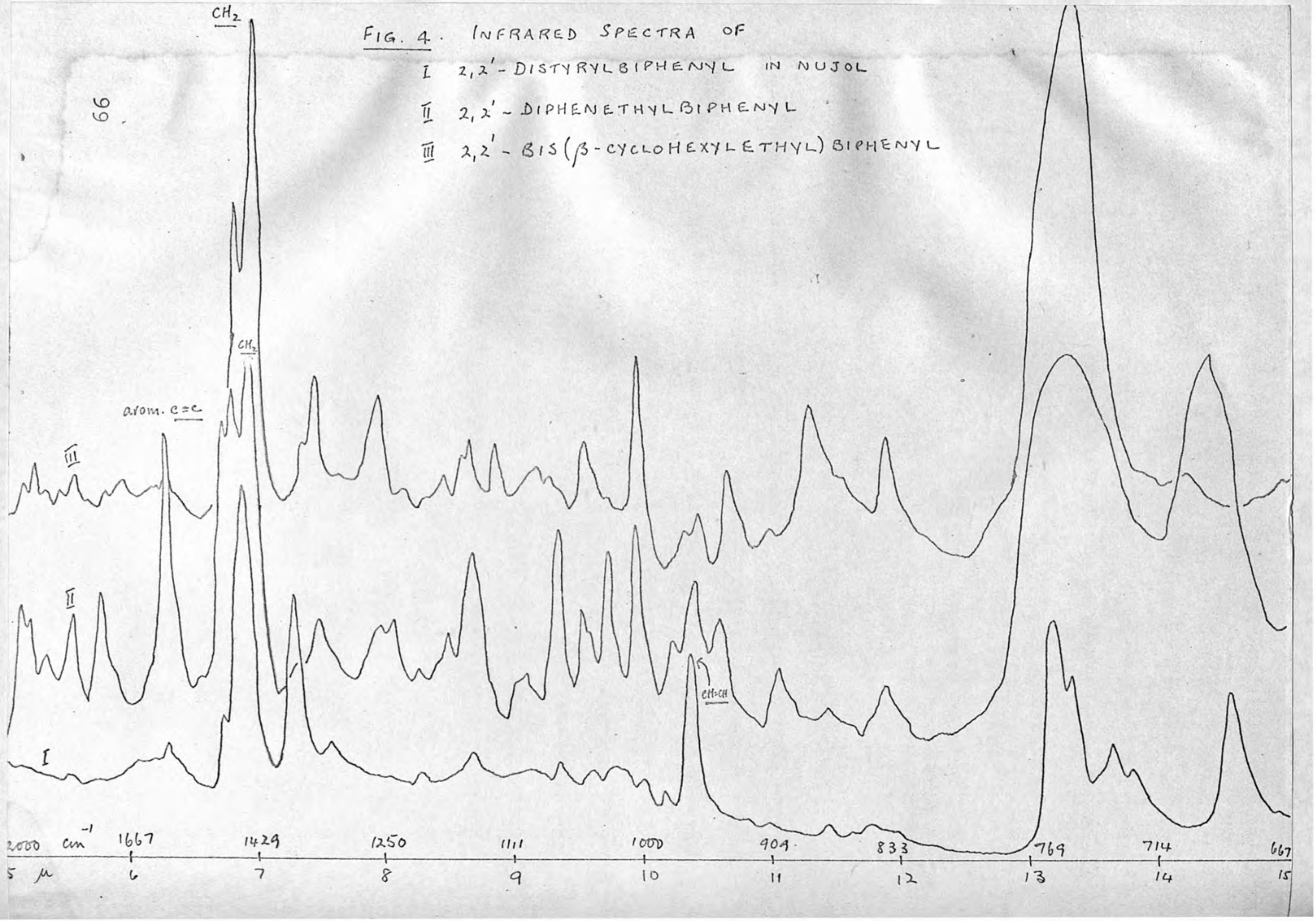


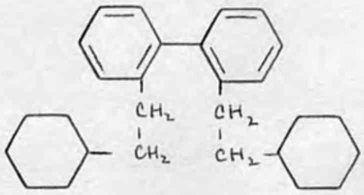
FIG. 4. INFRARED SPECTRA OF

I 2,2'-DISTYRYLBIPHENYL IN NUJOL

II 2,2'-DIPHENETHYLBIPHENYL

III 2,2'-BIS(β-CYCLOHEXYLETHYL) BIPHENYL

When the hydrogenation was repeated (to find the b.p. of the product) for $21\frac{1}{2}$ hrs. 2,2'-bis(β-cyclohexylthyl)biphenyl (22) was obtained. This was confirmed by the analysis and the



(22)

infrared spectrum which showed the CH_2 peaks at 2907, 2841 and $1445cm^{-1}$, the biphenyl peak at $1006cm^{-1}$, and the aromatic substitution peak at $750cm^{-1}$ only. The 2000-$1600cm^{-1}$ region gave a different absorption pattern from that of the previous product (21), and the aromatic C=C peaks at 1597 and $3018cm^{-1}$ were also weaker in intensity [Fig. 4]. It was concluded that during the extra 9 hrs. the benzene rings at the end of the chain of 2,2'-substituents had been hydrogenated as well as the ethylenic double bond.

It is apparent that the phosphonium dibromide (17,X=Br) reacted satisfactorily, in the presence of strong base like n-butyl-lithium with benzaldehyde, giving 29% yield of the desired product. It was decided to attempt the reaction with acetaldehyde. At the time, there had been no report in the literature of simple aliphatic aldehydes being used in the Wittig method of olefin synthesis. It was not apparent whether this absence of literature reports on the use of such compounds as intermediates in the Wittig reaction was due to failure of these compounds to function normally, or to the fact that such experiments had not been carried out.

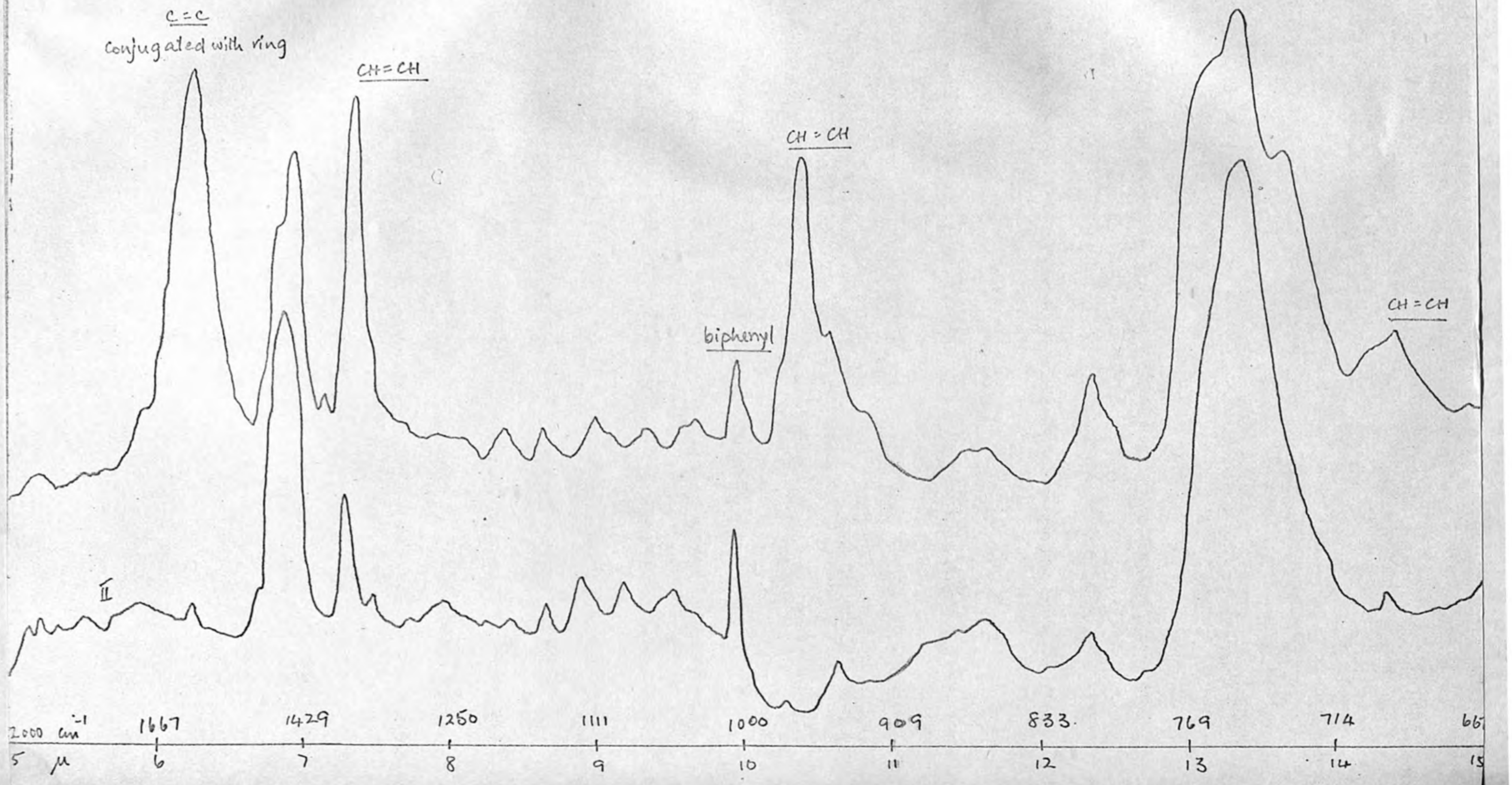
When acetaldehyde was added to the bright red phosphorane a cream-coloured solution was obtained. Yellow solid (presumably a triphenylphosphine oxide - lithium bromide complex) was filtered off and the filtrate, after removing excess of aldehyde and then ether, afforded yellow liquid which was unsaturated to tetranitromethane. When a benzene solution of this was chromatographed on a silica-gel column and eluted with light petroleum, three fractions were collected. The last two fractions were viscous liquids and their infrared spectra in nujol were very complex. However, C=O and OH peaks were present, which suggested that they must be the products of aldol and related reactions which acetaldehyde underwent in the presence of strong bases such as n-butyl-lithium (it is possible that butyl-lithium was present especially as some diphosphonium salt was recovered as was proved later).

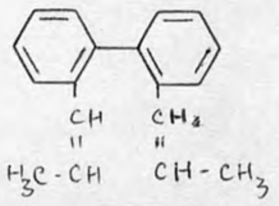
The first fraction of the chromatogram (0.242g.) was unsaturated to tetranitromethane. Its infrared spectrum showed the phenyl conjugated C=C at 1592cm^{-1} [see Fig. 5], CH=CH at 1357 (rather high frequency), 693 and 962cm^{-1}, indicating a mixture of cis- and trans-isomer of a compound containing ethylenic double bond, all of which disappeared on hydrogenation. The biphenyl (1005cm^{-1}) and aromatic substitution (750cm^{-1}) peaks were present both before and after the hydrogenation. The product which was thought to be 2,2'-di(prop-1-enyl)biphenyl (23), obtained in 7% yield, was

FIG. 5. INFRARED SPECTRA OF

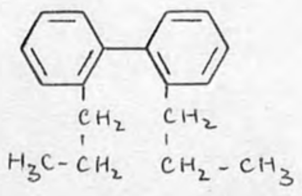
I 2,2'-DI (PROP-1-ENYL) BIPHENYL

II 2,2'-DIPROPYLBIPHENYL

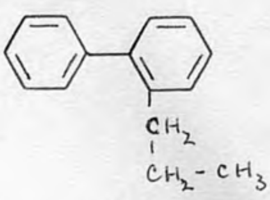




(23)



(24)



(25)

hydrogenated. The infrared spectrum of the hydrogenation product, thought to be 2,2'-dipropylbiphenyl (24), was compared with those of compound (23) and 2-propylbiphenyl (25) [API Research Project 44, Serial Number 2094] (see Table 1). According to the spectral evidence, compounds (23) and (24) seemed to have been obtained in this reaction, although analysis of the hydrogenated compound gave an empirical formula of $C_{18}H_{26}$ instead of $C_{18}H_{22}$. However, this could have been due to the fact that the product was not distilled owing to the small quantity obtained.

The yellow solid (believed to be the complex with lithium bromide) filtered off at the beginning, gave 0.5g. (6%) of triphenylphosphine oxide, and a yellow solid m.p. 220-250°. This solid could not be crystallised. Its infrared spectrum showed peaks characteristic of triphenylphosphonium salt at 1110 and 717cm^{-1} [Sheldon and Tyree, J.Amer.Chem.Soc., 1958, 80, 2117], as well as other indefinite, poorly resolved bands. It thus seems that this solid was a mixture of the starting diphosphonium bromide and some other unknown product or products.

TABLE 1

Infrared Spectra of compounds (23), (24), and (25).

(2000 - 667 cm^{-1})

(23)	(24)	(25)	ASSIGNMENT
1597 (sh)	1597	1603	C = C aromatic
1592			C = C
	1475	1481	$-CH_2-$
1441	1453	1449	CH_3- asym.
1376 (sh)	1376	1377	CH_3- sym.
1357			CH = CH
1005	1007	1000	biphenyl
962			CH = CH <u>trans</u>
750	749	750	1,2-disubstituted ring
		701	monosubstituted ring
693			CH = CH <u>cis</u>

The experiment was not repeated because of the possible competing aldol reaction of the aldehyde in the presence of such a strong base. Other conditions would have to be sought to improve the yield of the product. However, in 1963, Hauser, Brooks, Miles, Raymond and Butler [*J.Org.Chem.*, 1963, *28*, 372] reported a comprehensive use of certain aliphatic aldehydes as intermediates in the Wittig reaction. These aldehydes included both gaseous and paraformaldehyde, acetaldehyde, and acrolein. They showed that reactions involving these compounds tended to be rapid and therefore were carried out under very mild thermal conditions by the use of aqueous quenching solutions. For example in a typical reaction with acetaldehyde, the resulting deep red solution of the phosphorane, liberated from the corresponding phosphonium bromide in dry ether in the presence of butyl-lithium under a nitrogen atmosphere, was cooled to 10°, and a solution of acetaldehyde (twice as much) in dry ether was added while maintaining the bath temperature at 10°. They immediately obtained a heavy, cream-coloured suspension which was then decomposed by the addition of water. From the ethereal layer, after precipitating triphenylphosphine oxide with light petroleum, they obtained a mixture of isomeric olefins by fractional distillation, the *cis*-form being predominant from qualitative gas-liquid chromatography analyses. This would seem to confirm results by Bergelson, *et.al.* [*Tetrahedron Letters*, 1963, *19*, 149] that in the presence of a

Lewis base like lithium bromide, a cis-isomer was predominant.

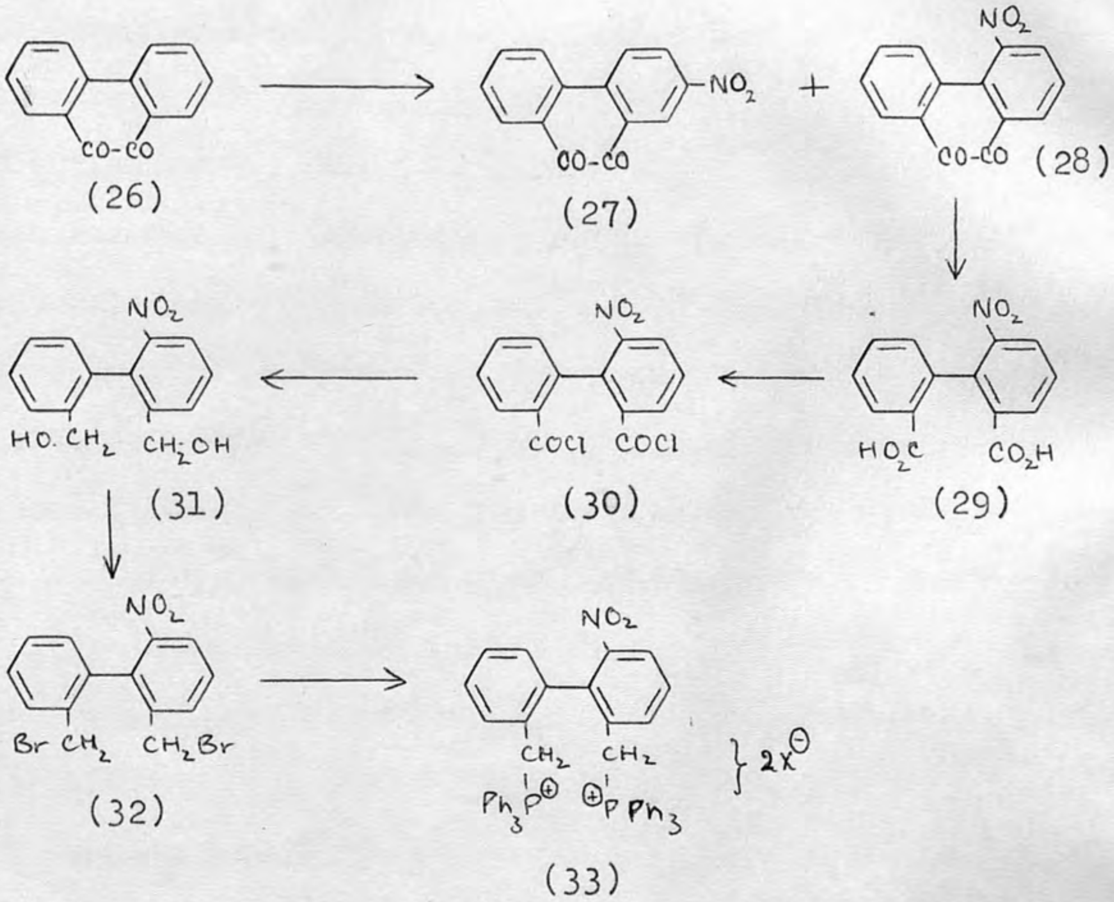
However, in the course of the present work, predominance of either isomer was estimated solely by absorption spectra. Another point against using water to decompose the reaction mixture was that triphenylphosphine oxide conveniently forms an ether-insoluble complex with lithium bromide and was thus filtered off, leaving the desired product uncontaminated. Normally it is rather difficult to separate triphenylphosphine oxide from the resulting oelfin; light petroleum does not always precipitate all of the oxide which shows a tendency to leak slowly through all but the most carefully conducted chromatographic columns.

It is thus possible to improve the yield of the olefins in the reaction between the phosphonium dibromide (17,X=Br) and simple aliphatic aldehydes. This would perhaps apply also to ketones that were liable to undergo aldol reaction, such as acetone the use of which had not been reported in the literature either. One of the ketones commonly reported in the literature as an intermediate in the Wittig reaction is cyclohexanone. The reaction between 2,2'-bis(triphenylphosphoniomethyl)biphenyl dibromide (17,X=Br), in the presence of butyl-lithium, and cyclohexanone, was rather unsatisfactory. The solid filtered from the reaction mixture gave 60% of the starting dibromide, identified by its m.p. and infrared spectrum, and 26% of triphenylphosphine oxide. Some cyclohexanone was also recovered together with a liquid, the infrared spectrum of which showed that it contained carbonyl and CH_2 groups. There was nothing in the regions 1660 and 800-650cm^{-1} to indicate an aromatic substance. The residue of this fraction was chromatographed on a silica-gel column and the first fraction obtained seemed to be unsaturated. Its infrared spectrum showed two very strong bands at 1597cm^{-1} (phenyl conjugated C=C) and 1357cm^{-1} (probably CH=CH, as in the reaction of the dibromide with acetaldehyde), and a doublet at 2907 and 2841cm^{-1} (CH_2 stretching). There were two medium bands at 1460 and 770cm^{-1}, and two weak ones at 746 and 718cm^{-1}. Hydrogenation of this fraction gave a product with poor infrared spectrum in the 2000 to 650cm^{-1} region, containing weak bands at 1706, 1447, 1376, 1120 and 747cm^{-1}; the two medium peaks at 2912 and 2849cm^{-1} were similar to those of the unsaturated material

It was concluded that the phosphorane derived from the phosphonium dibromide (17,X=Br) was rather stable. It would perhaps react quite easily with an aldehyde, but with a ketone, it appears to be sterically hindered in some way. Successful reactions with cyclohexanone that had been reported by Wittig and his co-workers involved simpler phosphoranes like $Ph_3P=CH_2$ [giving 52% yield of the product, Wittig and Schöllkopf, Chem. Ber., 1954, 87, 1318] and $Ph_3P=CH.Ph$ which is less reactive [giving 60% yield on the reacted salt, together with 34% unreacted phosphonium salt, Wittig and Haag, Chem. Ber., 1955, 88, 1654]. As was pointed out earlier benzylidenetriphenylphosphorane ($Ph_3P=CH.Ph$) did not react with benzophenone, which made it feasible that the phosphorane obtained in the present work did not react with cyclohexanone.

III. 2,2'-Bis(triphenylphosphoniomethyl)-6-nitrobiphenyl dibromide

This compound was prepared according to the following synthesis:



Phenanthraquinone (26) was nitrated [Schmidt and Spoun, Ber., 1922, 55, 1194] and a mixture of 2-nitro- (27) (47%) and 4-nitrophenanthraquinone (28) (25%) was obtained. To prepare a 6-substituted 2,2'-biphenyl derivative, only the 4-nitro compound was required. It was oxidised with potassium dichromate in sulphuric acid [Moore and Huntress, J.Amer.Chem.Soc., 1927, 49, 1324; modified from Schmidt and Kämpf, Ber., 1903, 36, 3737] giving 6-nitrodiphenic acid (29) in 71% yield.

It was found [T.M. Poole, Ph.D. Thesis, London, 1963] that to obtain the corresponding diol (31) from the acid (29) by reducing the ester, without reduction of the nitro group present, was unsatisfactory. A better route was found via the acid chloride. The acid (29) was heated under reflux with an excess of thionyl chloride [Bell and Robinson, J., 1927, 1695] which was then removed by distillation under reduced pressure. The crude acid chloride (30) was fairly easily hydrolysed in air and was therefore used directly in the reduction without being purified. The condition of reduction of 6-nitrobiphenoyl chloride (30) with lithium borohydride had been worked out by Poole, and this was strictly followed. 2,2'-Bishydroxymethyl-6-nitrobiphenyl (31) was then obtained in 86% yield. The standard method of converting a bishydroxymethyl compound to a bisbromomethyl compound was followed [see Hall, Lesslie and Turner, J., 1950, 711] and 2,2'-bisbromomethyl-6-nitrobiphenyl (32) was obtained in 70% yield.

The preparation of 2,2'-bis(triphenylphosphoniomethyl)-6-nitrobiphenyl dibromide (33,X=Br) proved very interesting. The usual method of preparing a phosphonium salt from a solid halogen compound and triphenylphosphine is to dissolve the two starting materials in a common solvent. It was decided to use xylene in this case because it had proved successful in the case of 2,2'-bis(triphenylphosphoniomethyl)biphenyl dibromide (17,X=Br). The bisbromomethyl compound (32) and triphenylphosphine were then dissolved separately in sodium-dried xylene, stirred together, and then heated on a heating mantle. Some brown solid as well as gum was obtained. In an attempt to crystallise it, all the solid was dissolved in chloroform, but addition of acetone produced no crystals. Solid could be obtained in ethereal suspension and in solution only. A mixture of ethyl alcohol and ethyl acetate was tried, and after a few times with gum as a result, crystalline solid (m.p. 200°) was obtained when the slightly cloudy mixture was left in the refrigerator. After three crystallisations from the same solvent, 2,2'-bis(triphenylphosphoniomethyl)-6-nitrobiphenyl dibromide (33,X=Br), m.p. 212°, was obtained in 10% yield, crystallising with three molecules of water. The infrared spectrum showed an OH peak (3400 cm^{-1}), triphenylphosphonium salt peaks (1109 and 717 cm^{-1}), nitro peaks (1520 and 1366cm^{-1}) and P-Ph peak (1441cm^{-1}) [see Fig. 6 a and b].

When the experiment was repeated with 50% more of the bis-bromomethyl compound (32) in half as much as xylene, only gum was obtained and could not be crystallised from the same solvent. However, after boiling the alcoholic solution twice with charcoal and using a mixture of ethyl alcohol and ether, crystals m.p. 206° were obtained in 12.5% yield.

If the mixture was heated in an oil bath at a controlled temperature (140°), the yield of the diphosphonium salt was increased (20%), but the monophosphonium salt, probably (34) rather

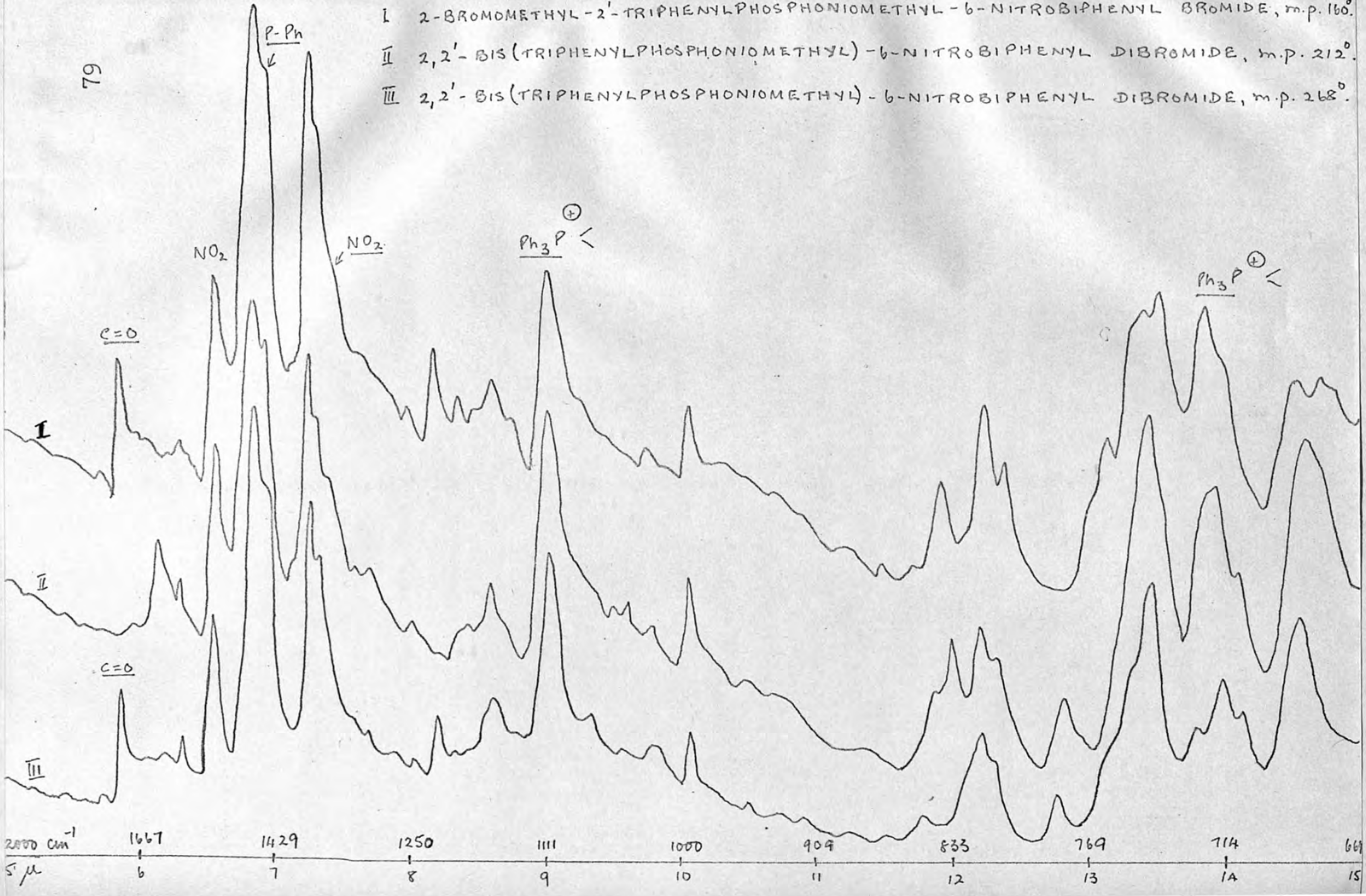


FIG. 6a. INFRARED SPECTRA IN NUJOL OF

I 2-BROMOMETHYL-2'-TRIPHENYLPHOSPHONIOMETHYL-6-NITROBIPHENYL BROMIDE, m.p. 160°.

II 2,2'-BIS(TRIPHENYLPHOSPHONIOMETHYL)-6-NITROBIPHENYL DIBROMIDE, m.p. 212°.

III 2,2'-BIS(TRIPHENYLPHOSPHONIOMETHYL)-6-NITROBIPHENYL DIBROMIDE, m.p. 268°.

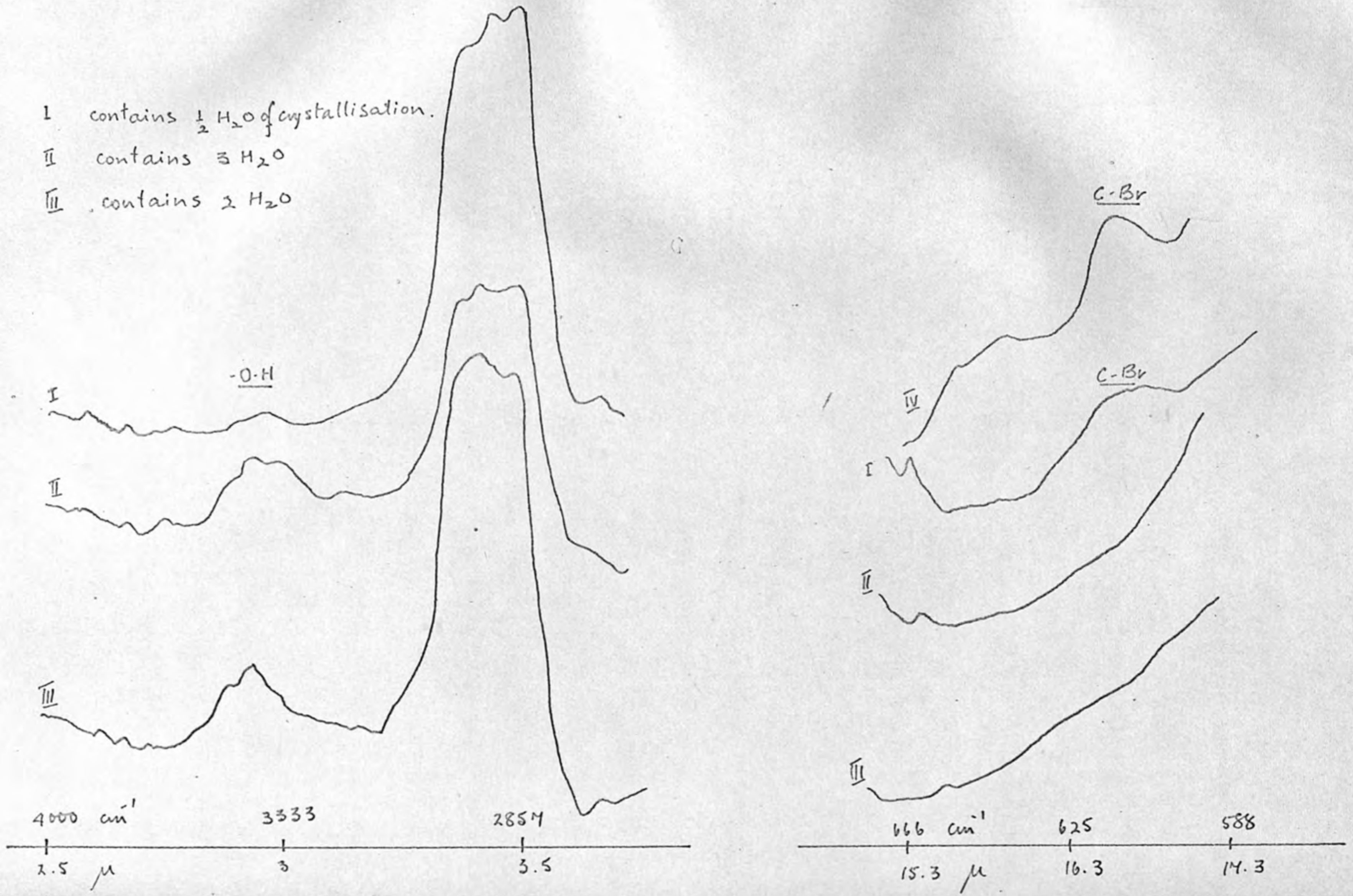
FIG. 6b.

IV 2,2'-BISBROMOMETHYL-6-NITROBIPHENYL.

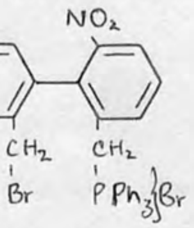
I contains $\frac{1}{2}$ H_2O of crystallisation.

II contains 3 H_2O

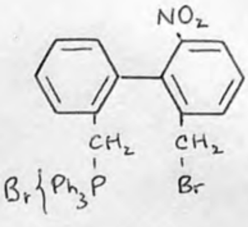
III contains 2 H_2O



than (34 A), was obtained as well (14%). Separation was effected by fractional crystallisation from acetone, the diphosphonium salt being less soluble.



(34)



(34A)

The diphosphonium salt (33,X=Br) crystallised from acetone with two molecules of water and one molecule of acetone and had m.p. 266-268°. Its infrared spectrum showed an OH peak (3400cm^{-1}) triphenylphosphonium salt peaks (1109 and 716 cm^{-1}), P-Ph (1435cm^{-1}), NO_2 (1527, 1364cm^{-1}) and C=O (1701 cm^{-1}).

2-Bromomethyl-2'(triphenylphosphoniomethyl)-6-nitrobiphenyl bromide i.e. the monophosphonium salt (34), crystallised from acetone with half a molecule of water and half a molecule of acetone and had m.p. 157-160°. Its infrared spectrum showed an OH peak (3348cm^{-1}), triphenylphosphonium salt peaks (1107, 716cm^{-1}) P-Ph peak (1445cm^{-1}), NO_2 peaks (1522 and 1404cm^{-1}), C=O peak (1704cm^{-1}) and C-Br peak (610cm^{-1}) indicating a mono-phosphonium salt.

To get to the dibromide, the monobromide must be soluble and the dibromide insoluble in the solvent of preparation (triphenylphosphine is soluble in most organic solvents). But it was found that both the mono- and dibromide had similar solubility (e.g. in nitrobenzene, alcohol) and insolubility (e.g. in xylene, acetone and ether).

Friedrich and Henning [Chem.Ber., 1959, 92, 2756], in their paper on the general methods of preparation of phosphonium salts, and in particular diphosphonium dibromides, stated that a mixture of mono- and diphosphonium salts was obtained in chloroform, but the diphosphonium salt only was obtained from nitrobenzene and dimethylformamide. It thus seems that higher temperature is needed to obtain the pure dibromide. Similarly, Mondon [Annalen, 1957, 603, 115] could get only the monophosphonium bromide by heating triphenylphosphine and 1,4-dibromobutane in benzene in an oil bath at 130°. However, Horner and Lingnau [Annalen, 1955, 591, 135] had prepared diphenylmethyltriphenylphosphonium bromide by melting triphenylphosphine and diphenylmethyl bromide together in a porcelain dish on a water bath for 3/4 hrs. This reaction had proved very slow in benzene. The solid cake was cooled, powdered and crystallised in 50% yield. It was then decided to prepare the diphosphonium salt (33,X=Br) without solvent.

Triphenylphosphine and 2,2'-bisbromomethyl-6-nitrobiphenyl (32), in finely powdered form, were stirred together in a flask immersed in a previously heated oil-bath at 180° (higher than the m.p. of the monobromide so that any of the mono salt formed would stay liquid and could react further with triphenylphosphine). After 5 min. at bath temperature, the mixture was cooled, washed and ground well with xylene, and crystallised from acetone. A

68% yield was obtained, the first crop having m.p. 265-266° and the ~~further~~ fourth crop m.p. 250°. It was found that longer reaction time did not improve the yield, only worsened it. This method seems to be the best one for preparing the phosphonium dibromide (33,X=Br), giving pure product in fairly good yield.

The preparation of the dibromide (33) from the monobromide (34) [adapted from method by Mondon, loc.cit. who obtain 1,4-tetramethylene-bis-triphenylphosphonium bromide from the monobromide] by melting the monobromide with triphenylphosphine was also attempted. A 1:1 mixture was stirred for 1 hr. (strictly following Mondon) at 200° (half-way between the m.p.'s of the mono- and the dibromide). However, the yield of the dibromide was only 17%. It was thought that the reaction time might have been too long. At 200°, any solid present must have been the dibromide. The hard mess formed in the first 5 min. seemed to go soft again if left too long (as was also the case when triphenylphosphine and the bisbromomethyl compound were melted together).

2,2'-Bis(triphenylphosphoniomethyl)-6-nitrobiphenyl dicamphorsulphonate (33,X=$C_{10}H_{15}O_4S$), prepared from the corresponding dibromide, was examined polarimetrically at 22° and at 50° (in 95% ethanol) and showed no mutarotation or change of rotation with temperature. It had $[\alpha]_{5461} + 21^\circ$ at both temperatures.

2,2'-Bis(triphenylphosphoniomethyl)-6-nitrobiphenyl di-α-bromocamphor-π-sulphonate (33,X=$C_{10}H_{14}BrO_4S$) was prepared from the corresponding iodide, and its optical activity is still being investigated.

IV. Carbomethoxymethylenetriphenylphosphorane and its use in the Wittig reaction

The phosphorane (37) was prepared as follows:

$$\begin{array}{ccc}
\mathrm{Ph_3P} + \underset{(35)}{\mathrm{BrCH_2\text{-}CO_2Me}} & \longrightarrow & \mathrm{Br}\left\{\underset{(36)}{\mathrm{Ph_3P\text{-}CH_2\text{-}CO_2Me}}\right. \\
 & & \downarrow \\
\mathrm{Ph_3P=O}\quad(38) & & \mathrm{Ph_3P=CH\text{-}CO_2Me}\quad(37)
\end{array}$$

Carbomethoxymethyltriphenylphosphonium bromide (35) was prepared by mixing methyl bromoacetate (35) and triphenylphosphine in benzene according to the method of Isler, Gutmann, Montavon, Rüegg, Ryser and Zeller [Helv.Chim.Acta., 1957, 40, 1242]. Carbomethoxymethylenetriphenylphosphorane was then obtained in aqueous solution by adding sodium hydroxide solution (10%) to an aqueous solution of (36) [Isler, et.al., loc.cit.]. It was crystallised from hot ethyl acetate and light petroleum (b.p. 40-60°). However, it was found that if the phosphorane (37) was boiled too long in ethyl acetate, for example, when trying to dissolve it in a minimum amount of the solvent before the addition of light petroleum, part of it was decomposed to give triphenylphosphine oxide (38) m.p. 154-155° [Michaelis and Soden, Annalen, 1885, 229, 295].

An attempted reaction between the phosphorane (37) and acetone was unsuccessful. The phosphorane in alcohol was heated under reflux with acetone for 10 hrs. No volatile product was isolated (the expected product, methyl β,β-dimethylacrylate, has b.p. 135-138°) although triphenylphosphine oxide was obtained in 50% yield.

Similar reaction with acetophenone was equally unsatisfactory. In benzene, under an atmosphere of nitrogen, the phosphorane was recovered after 9 hrs. heating under reflux. In alcohol, acetophenone was recovered, and triphenylphosphine oxide was obtained in 75% yield with no other product. Even when the phosphorane was freshly obtained from the phosphonium bromide (36) in sodium ethoxide and acetoph~~ane~~enone was added at once, only alcohol was obtained in the distillate.

At this time, Trippett and Walker [J., 1961, 1266] reported that carbethoxymethylenetriphenylphosphorane (39) did not react

$$Ph_3P = CH\text{-}CO_2Et \quad (39)$$

with ketones in boiling benzene. This is in common with similar stable phosphorane, $Ph_3P{=}CH.CO\,R$, R=Me, Ph, H, NH_2, none of which reacts with ketones [see also Ramirez and Dershowitz, J.Org.Chem. 1957, 22, 41]. They thought this was due to failure in the first step of the Wittig reaction, viz. nucleophilic attack on carbon, and not in the subsequent elimination of phosphine oxide. However, Sugasawa and Matsuo [Chem. and Pharm. Bull. (Japan), 1960 8, 819] reported a successful reaction between carbethoxymethyltriphenylphosphonium bromide (corresponding phosphonium salt of 39) and cyclohexanones in methanol at room temperature in the presence of sodium methoxide. Accordingly, in another paper [Chem.and Ind. 1961, 990] Trippett and Walker reinvestigated the reaction of ketones with the phosphorane (39) and found that although the phosphorane reacted with cyclohexanone, in boiling benzene or toluene, to give 25% yield of cyclohexylidene acetic ester, it did not react with 2-methylcyclohexanone, diethyl ketone, methyl nonyl ketone, acetophenone and benzophenone, under these conditions or under the ones used by the Japanese workers. Apparently, they thought the reactivity of the ketone is critical, cyclohexanone and the pyridyl ketones are among those ketones most susceptible to nucleophilic attack. They also found that a solution of the ester phosphorane (39) in ethanol gave the same results as were obtained with the corresponding phosphonium bromide plus sodium ethoxide, the competing reaction in each case being decomposition to triphenylphosphine oxide.

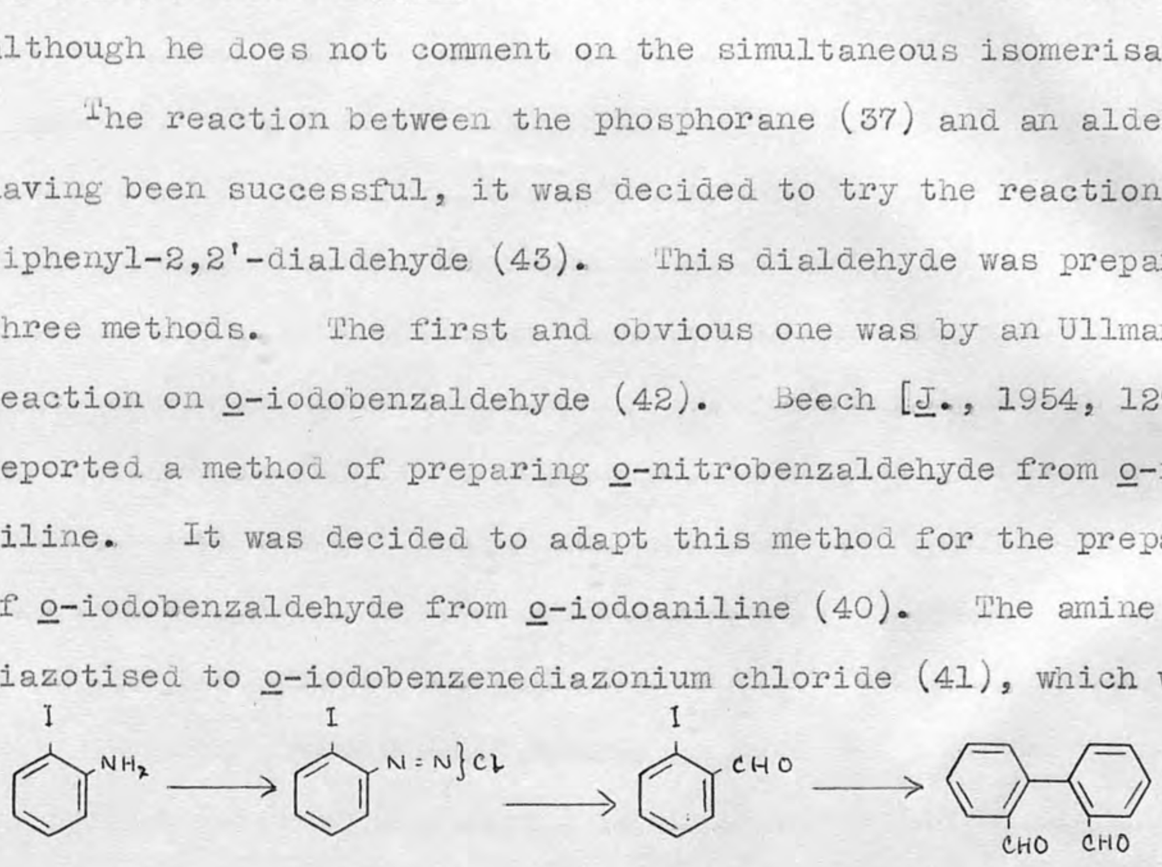
All this agrees with the result of the present work, which was carried out before the above results came into print, and included the work on the reaction between 2,2'-bis(triphenylphosphoniomethyl)biphenyl dibromide and ketones, in the presence of sodium ethoxide. It was then decided not to investigate any further the reaction between the respective phosphoranes with ketones.

Work on these two ester phosphoranes (37 and 39) was published again some months later by Fodor and Tömösközi [Tetra-hedron Letters, 1961, 579] who maintained that the phosphoranes reacted with ketones of rather different character when the components were heated in a sealed tube for 10-24 hrs. at 100°, or for a short time at 170°. The yields seemed to be practically unaffected by the excess of ketone present above the molar ratio 2:1, when the components were heated at 100° for 10 hrs. Products from the two "mixed" ketones, methyl ethyl ketone and acetophenone, consisted of <u>cis</u>- and <u>trans</u>-isomers as evidenced by m.p. determinations, but there was more of the <u>trans</u>-isomer in the former reaction than in the latter, which furnished a comparable quantity of both isomers. However, in the course of the present work, it was decided to pursue the investigation with aldehydes which have been used successfully in the Wittig reaction in almost all the cases reported.

Carbomethoxymethylenetriphenylphosphorane (37) reacted with benzaldehyde, in alcohol, giving 69% yield of isomeric methyl cinnamates and 94% of triphenylphosphine oxide. This is comparable to the reaction between the ethyl phosphorane (39) and benzaldehyde [Wittig and Haag, <u>Chem</u>. <u>Ber</u>., 1955, <u>88</u>, 1654] in which 77% of ethyl cinnamate and 88% of triphenylphosphine oxide were obtained. Methyl <u>trans</u>-cinnamate solidified, was separated from the <u>cis</u>-cinnamate, and identified by its m.p. and infrared absorption spectrum (CH=CH absorption at 1312 and 979cm^{-1}, with absence of 694cm^{-1} band). The <u>cis</u>-isomer was identified by the presence of 694cm^{-1} band in its infrared spectrum [Bellamy, Infrared Spectra of Complex Molecules, Methuen, London, 1958]. Both <u>cis</u>- and <u>trans</u>-esters, on hydrolysis with alcoholic potash, gave <u>trans</u>-

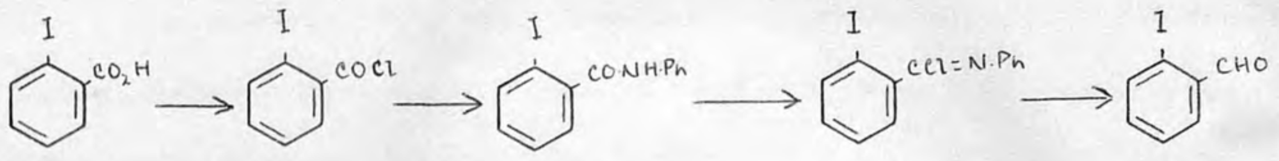
cinnamic acid. The ethyl esters were also reported by Wittig (*loc.cit.*) to give *trans*-acid m.p. 131-131.5° on hydrolysis although he does not comment on the simultaneous isomerisation.

The reaction between the phosphorane (37) and an aldehyde having been successful, it was decided to try the reaction with biphenyl-2,2'-dialdehyde (43). This dialdehyde was prepared by three methods. The first and obvious one was by an Ullmann reaction on *o*-iodobenzaldehyde (42). Beech [*J.*, 1954, 1297] had reported a method of preparing *o*-nitrobenzaldehyde from *o*-nitraniline. It was decided to adapt this method for the preparation of *o*-iodobenzaldehyde from *o*-iodoaniline (40). The amine was diazotised to *o*-iodobenzenediazonium chloride (41), which was treated with a formaldoxime solution prepared from paraformaldehyde and hydroxylamine hydrochloride. The mixture was then treated with iron alum and then steam-distilled. The aldehyde obtained was purified by making it into bisulphite compound. The overall yield was only 14%, compared with 33% for the corresponding nitro-compound.



(40) (41) (42) (43)

It was then decided to prepare *o*-iodobenzaldehyde from *o*-iodobenzoic acid (44) according to a method by Rapson and

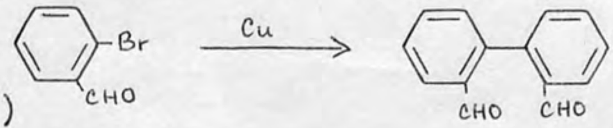


(44) (45) (46) (47) (42)

Shuttleworth [*J.* 1941, 487] who reported a yield of 80%. *o*-Iodobenzoyl chloride (45) was obtained from the acid (44) and then treated with aniline. The resulting anilide (46) was treated with phosphorus pentachloride to give the corresponding anilide-imino chloride (47). An ethereal solution of (47) was then treated with anhydrous stannous chloride and the resulting mixture was steam-distilled. The aldehyde (42) was collected from the distillate in 19% yield.

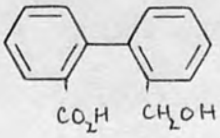
The Ullmann reaction on the aldehyde (42) in the presence of copper bronze was carried out in an atmosphere of nitrogen. The mixture was heated slowly in a metal-bath as control of temperature was important. A suitable reaction temperature was found to be 190°. The reaction time and the working up were cut down to a minimum so as to avoid long contact with air. The toluene extract was distilled and biphenyl-2,2'-dialdehyde (43) was obtained in 69% yield. It was crystallised from a mixture of dry ether and light petroleum according to the method of Bailey and Erickson [*Org.Synth.*, 1961, *41*, 41] who prepared the dialdehyde (43) from phenanthrene by ozonolysis. A second recrystallisation was made from 70% aqueous ethanol.

Although the yield of the Ullamnn reaction was reasonable the yields of the starting material (42) were too low, so it was decided to use o-bromobenzaldehyde (48) which was available.

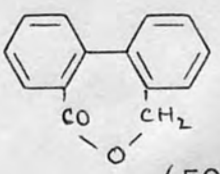


(48) (43)

After 8 hrs. in boiling dimethylformamide [adapted from method by Kornblum and Kendall, J.Amer.Chem.Soc., 1952, 74, 5782] half of the starting material (48) was recovered together with 4% of the product (43). But when the experiment was repeated with half as much solvent and three times longer heating, the same yield of the dialdehyde was obtained, as well as an ε-lactone (50) of the corresponding hydroxy acid [2-hydroxymethyl-2'-carboxybiphenyl (44), see Kenner and Turner, J., 1911, 2101] identified by its m.p. and the C=O band (1724cm^{-1}), =C-O- band (1274cm^{-1}) and -C-O- band (1110cm^{-1}) in the infrared absorption spectrum.



(49)

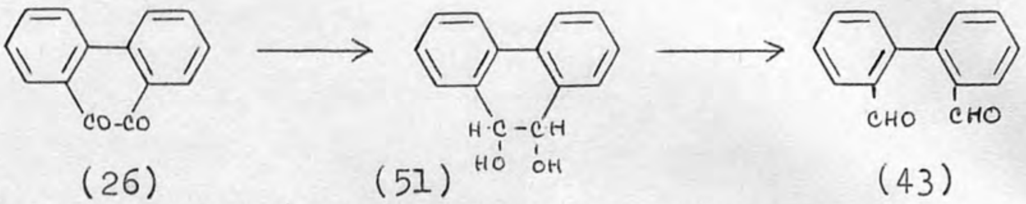


(50)

The final residue was an unidentified intense yellow oil.

If the reaction was done without solvent, i.e. as for the iodo compound (42), the reaction temperature being 200°, the yield of the dialdehyde was still poor (17%) compared with that from the reaction on the iodo compound, and the residual intense yellow oil was again obtained, as well as 5% of the starting material (48).

Another route to the dialdehyde was attempted. <u>trans</u>-9,10-Dihydroxy-9,10-dihydrophenanthrene (51) was prepared by reducing



(26) (51) (43)

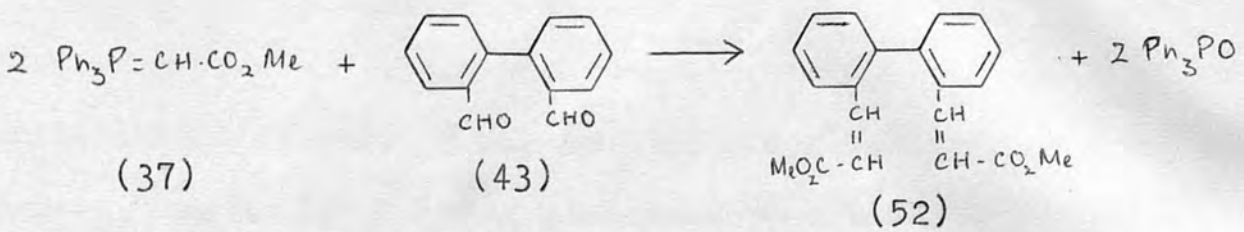
phenanthraquinone (26) with lithium aluminium hydride. If the reduction was done in tetrahydrofuran (as the quinone is sparingly soluble in ether) only 15% yield of the diol (51) was obtained and 24% of the quinone was recovered. The reduction in half as much solvent and with twice as much lithium aluminium hydride did not go at all and the quinone was recovered almost quantitatively.

The reduction in ether [Booth, Boyland and Turner, <u>J.</u>, 1950, 1188] was then attempted. Using a Soxhlet apparatus, only 5% of the product was obtained, and 75% of the quinone was recovered. The quinone was then added to the lithium aluminium hydride, in ether, in solid form. When the mixture was heated under reflux for 4½ hrs. and worked up in the usual manner, the diol (51) was obtained crystalline in 59% yield.

The diol (51) was then oxidised with lead tetracetate [Criegee, Marchand and Wannowius, <u>Annalen</u>, 1942, <u>550</u>, 99] to give the dialdehyde (43) in 50% yield.

This last method was the shortest and gave the best overall yield of the dialdehyde.

The reaction between carbomethoxymethylenetriphenylphosphorane (37) and biphenyl-2,2'-dialdehyde (43) was carried out in boiling toluene. A 2:1 mixture of the reactants was heated under reflux for 16 hrs. The solid obtained was separated by chromatographing on a silica-gel column, eluting with a 1:1 mixture of toluene and methanol, and finally methanol. The residue of the first eluate had to be chromatographed again on an alumina column. Finally three products were obtained.



1. Solid m.p. $148-149^{\circ}$ or $152-153^{\circ}$, found to be triphenylphosphine oxide by m.p., mixed m.p. and infrared absorption spectra. Total yield 65%.

2. Solid m.p. $106-107^{\circ}$, found to be the <u>cis</u>-<u>trans</u>-isomer of 2,2'-bis(β-carbomethoxyvinylene)biphenyl (52). The infrared spectrum contained unsaturation peaks at 1314, 973 and 693cm^{-1}. Total yield 43%.

3. Solid m.p. $118-119^{\circ}$, found to be the <u>trans</u>-<u>trans</u>-isomer of 2,2'-bis(β-carbomethoxyvinylene)biphenyl (52). The infrared spectrum contained unsaturation peaks at 1316 and 974cm^{-1}. Total yield 24%.

<u>Evidence for assigning the configuration</u> of the two geometrical isomers obtained:

[For convenience, solid m.p. 106° will be called isomer A, and solid m.p. 118-119°, isomer B.]

1. Melting point and solubility

A has lower m.p. than B. Since the trans-isomer has, in general, greater symmetry than the cis-isomer, it fits into the crystal lattice more easily and therefore usually has a higher m.p.; e.g. cinnamic acid, cis, m.p. 68°, trans, m.p. 133°; stilbene, cis, m.p. 6°, trans, m.p. 124°. Hence A is the cis-isomer and B is the trans-isomer.

Along with this goes the higher solubility of the cis-isomer. In the process of crystallisation where both isomers were obtained from the same fraction, isomer B was obtained first, indicating that B is the trans-isomer.

2. Ultraviolet spectra (Fig. 7)

Readily observable differences between cis- and trans-isomers are found in olefins of the type abC=Cbc where the substituents a and c may enter into resonance interaction with the olefinic system. The resonance interaction may be of the polyene type, C=C-C=C, of the styrene type, C=C-Ph, or of the α,β -unsaturated carbonyl type, C=C-C=O. In most cases the cis-isomer has its absorption maximum at a slightly shorter wavelength and its extinction coefficient is in all cases considerably smaller than that of the trans-isomer. The major contributing factor to this situation seems to be steric inhibition of resonance [Braude, Determination of Organic Structures by Physical Methods, Braude

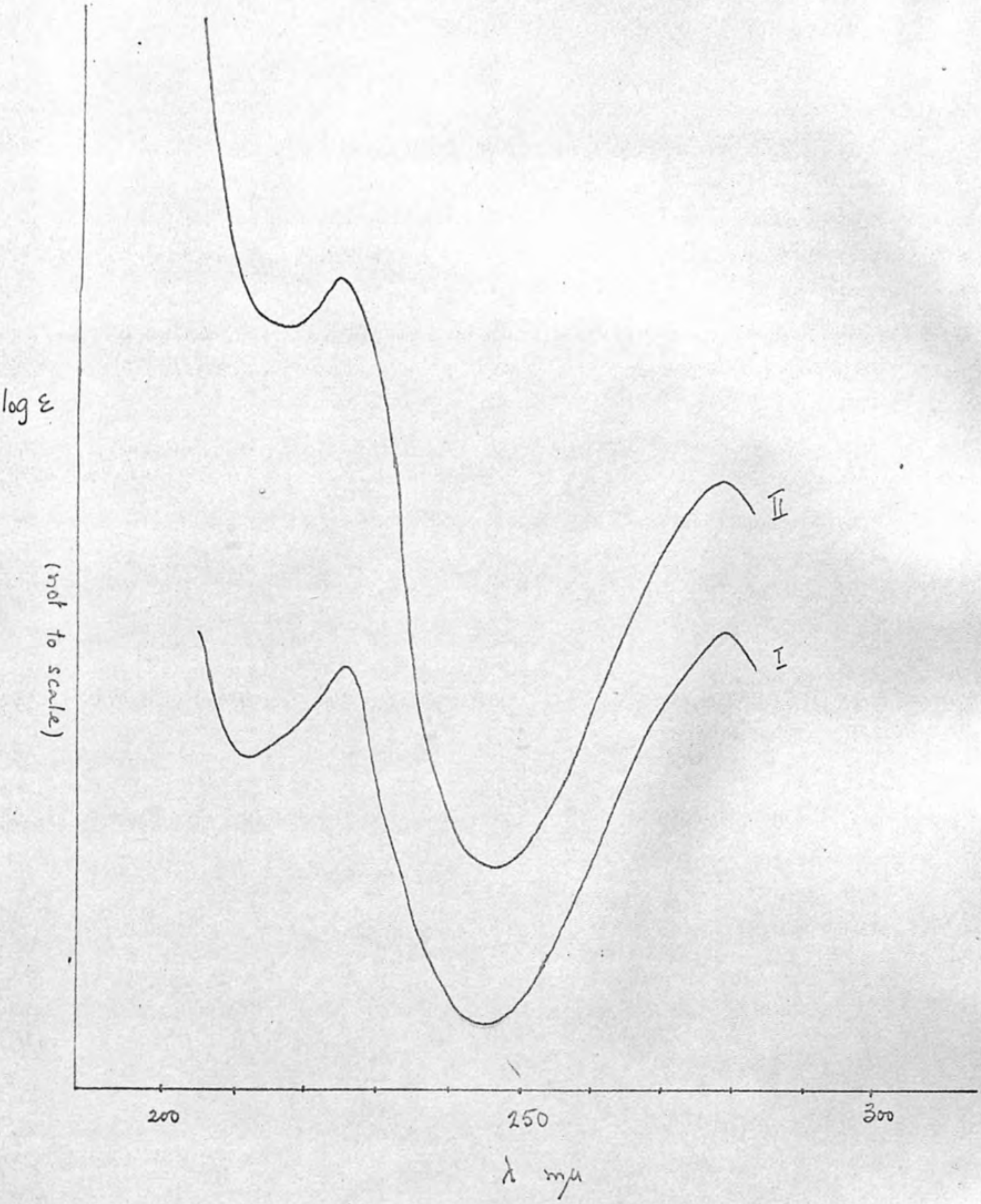


FIG. 7 ULTRAVIOLET ABSORPTION SPECTRA IN 95% ETHANOL OF ISOMERIC 2,2'-BIS(β-CARBOMETHOXYVINYLENE) BIPHENYL

I ESTER m.p. 118-119°.	λmax	278	225	mμ
	εmax	26,000	24,000	
II ESTER m.p. 106°.	λmax	274	224	mμ
	εmax	19,000	27,000	

and Nachod Eds., Academic Press, New York, 1955, Chap. IV; Braude and Waight, Progress in Stereochemistry, Vol. 1, Klyne, Ed., Butterworth, London, 1954, Chap. IV].

Isomer A has its absorption maxima at 274 and 224 mμ which are at slightly shorter wavelengths than those for isomer B, at 278 and 225. The extinction coefficient (19,000) of the long-wave band (274 mμ) is also smaller than the corresponding figure for isomer B (26,000). Thus A is the cis-isomer and B is the trans-isomer.

Also, the spectral patterns of A and B follow those for cis- and trans-isomer respectively, i.e. the short-wave band (224 mμ) of the cis-isomer has a larger extinction coefficient than the long-wave band, whereas the opposite is true for the trans-isomer. This is also true for isomeric stilbenes and cinnamic acids [see Braude, Ann. Reports, 1945, 42, 105].

3. Infrared spectra [Fig. 8, Table 2]

Differences in the infrared spectra of geometrical isomers of olefins are found in the 1650cm^{-1} region (C=C stretching) and in the 970 and 690cm^{-1} regions (=CH out-of-plane vibration). As a comparison, in an α,β-unsaturated ketone, the C=C stretching band is helpful in olefins of the type aCH=CHb. cis-Isomers show higher intensity of the C=C stretching vibration (near 1625cm^{-1}) and lower intensity of the C=O stretching (near 1700cm^{-1}) than the trans-compound [Erskine and Waight, J., 1960, 3425].

FIG. 8. INFRARED SPECTRA IN NUJOL OF ISOMERIC 2,2'-BIS (β-CARBOMETHOXYVINYLENE) BIPHENYL

I m.p. 118-119°.

II m.p. 106°.

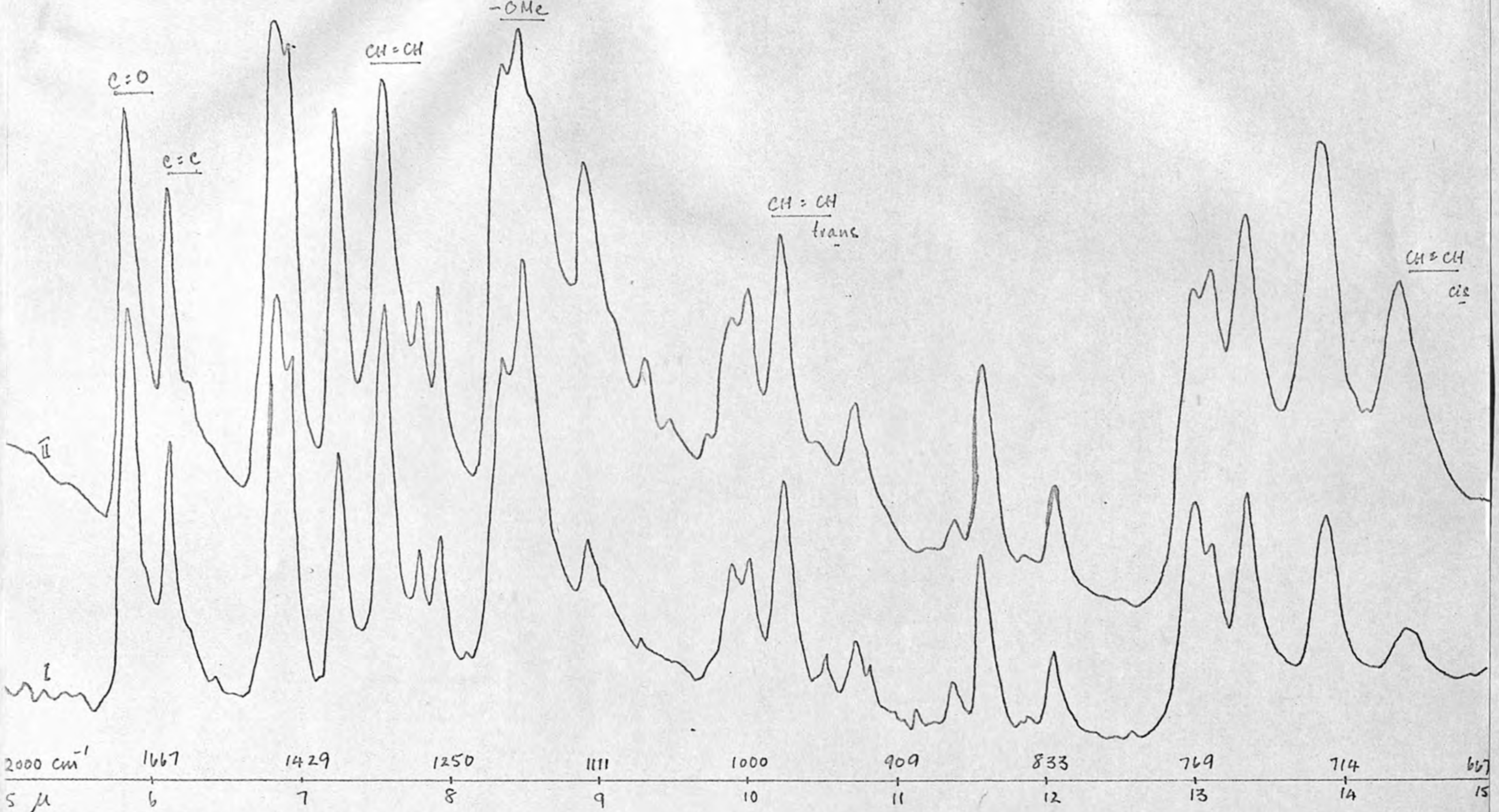


TABLE 2

Infrared Spectra of isomeric 2,2'-bis(β-carbomethoxyvinylene)biphenyl.

(and comparative intensities)

CIS-TRANS ESTER	TRANS-TRANS ESTER	ASSIGNMENT
1709 s (100)	1709 s (100)	C = O
1631 s (84)	1631 m-s (69)	C = C conjugated
1440 s	1443 s	CH_3
1314 s (106)	1314 s (100)	CH = CH
1279 1256 } w	1279 1259 } w	
1190 1170 } s	1193 1172 } s	methoxy group
1117 s	1121 w	
1066 w		
1009 w-m	1007 w	biphenyl
985 m	980 w	
973 m-s (74)	973 m-s (59)	CH = CH trans
932 w	933 w	
861 m	861 m	
828 w	828 w	
768 m	768 m	
761 m	764 m	
746 719 } m-s	746 720 } m-s	1,2-disubstituted ring
691 m-s (63)	692 w (24)	CH = CH cis

From Table 2, using C=O intensity as a standard, it is clear that A has a higher intensity of C=C than B, indicating that A is a _cis_-isomer.

The C=H out-of-plane vibration is also useful in distinguishing _cis_- and _trans_- 1,2-disubstituted olefins. The _trans_-isomer almost invariably absorb at 895-990cm^{-1}. The _cis_-isomers are usually free or almost free of absorption in this region and often show, instead, a band at 675 to 730cm^{-1}. For example:

trans-2-butene	964cm^{-1}	_cis_	675cm^{-1}
1-chloro-1-propene	930		675
1,2-dichloroethylene	895		697

[Eliel, Stereochemistry of Carbon Compounds, McGraw-Hill, New York, 1962, Chap. XII].

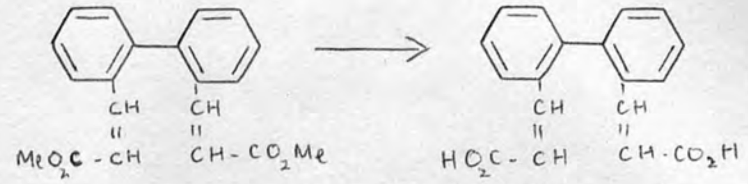
Further evidence that _trans_-isomers absorb at 965 cm^{-1} with complete absence of 690cm^{-1} band came from Rasmussen and Brattain, _J.Chem.Phys._, 1947, _15_, 135; Wittig, Koenig and Clauss, _Annalen_, 1955, _593_, 127; Inhoffen, Quinkert, Hess and Erdmann, _Chem.Ber._ 1956, _89_, 2273; Isler, _et.al._, _Helv.Chim.Acta_, 1957, _40_, 1256; Griffin, Martin and Douglas, _J.Org.Chem._, 1962, _27_, 1627.

Infrared spectrum of A shows quite a strong band at 694cm^{-1}, whereas that of B shows only a weak band, indicating that A is the _cis_-isomer and B is the _trans_-isomer. However, the 976cm^{-1} band, almost exclusive to the _trans_-isomer is present in both A and B. It is then proposed that A is the _cis_,_trans_-isomer of compound (52) and B is the _trans_,_trans_-isomer of the same compound.

According to a Leybold model, the *trans*-*trans*-isomer is nearly flat and maximum conjugation can be expected. In the *cis*-*trans*-isomer, the *trans*-half is still nearly flat, but the *cis*-half is somewhat restricted. A *cis*-*cis*-model is very restricted indeed. To attain this configuration, the two benzene rings of the biphenyl skeleton must be nearly at 90° to each other, and then there can be little movement of the 2,2'-substituents. Hence for steric reason, the *cis*-*cis*-isomer of compound (52) had not been obtained. It is not clear why the *cis*-*trans*-isomer has been obtained in a bigger yield than the *trans*-*trans*-isomer. In previous reports on preparation of diolefins using bifunctional Wittig reagents and dialdehydes, mostly *trans*-*trans*-forms were obtained. For example, Mondon [*Annalen*, 1957, *603*, 115] prepared 1,6-diphenylhexadiene from the 1,4-tetramethylene-bis-triphenylphosphonium bromide and benzaldehyde, in the presence of phenyl lithium, and obtained 14% yield of *trans*-*trans*-isomer (m.p. 82°) and 12.7% yield of *cis*-*trans*- or *cis*-*cis*-isomer (m.p. 37°). But in the presence of sodium ethoxide, 75% of crude product gave crystalline *trans*-*trans*-isomer on crystallisation. There was no spectral or other evidence to support this assignment. Hauser *et*.*al*. [*J*.*Org*.*Chem*., 1963, **28**, 372] obtained 1,6-heptadiene from pentamethylene-bis-triphenylphosphonium bromide and formaldehyde, in the presence of *n*-butyl-lithium in hexane, in 45% yield. He gave the characteristic infrared absorption bands of the diene as

1640, 990 and 910cm^{-1}, indicating that it was a trans-trans-isomer.

(52)



(53)

Each of the isomeric esters (52) was hydrolysed with alcoholic potash, and it was found that both gave the same acid (53)[m.p. and mixed m.p.]. Their infrared spectra were also identical [see Fig. 9]. It is proposed that the acid has a trans-trans configuration. The unsaturation peak for a trans-isomer at 976cm^{-1} [Table 3], although not strong compared with that in the ester series [compare Table 2] is stronger than the peak for a cis-isomer at 698cm^{-1}. This last peak is very weak, even weaker than the one in the trans-trans ester. The assignment is supported by the ultraviolet spectral evidence [Fig. 10]. The spectra of the two acids obtained from the esters are identical, and they follow the same pattern, i.e. the conjugation band has a larger extinction coefficient than the shortwave band, indicating a maximum conjugation, and hence a trans-trans-configuration.

The two acids, although identical, were esterified separately in methanolic hydrogen chloride. The two esters obtained both had m.p. 118-119^{o} (and mixed m.p. also). The infrared spectra were also identical [Fig. 11], and these showed that the esters had a trans-trans-configuration. The unsaturation peaks at 972cm^{-1} were

FIG. 9. INFRARED SPECTRA IN NUJOL OF 2,2'-BIS (β-CARBOXYVINYLENE) BIPHENYL

I FROM HYDROLYSIS OF ESTER m.p. 106° ; m.p. 291-293°

II FROM HYDROLYSIS OF ESTER m.p. 118-119° , m.p. 289-290°

[mixed m.p. of I and II , 289-290°].

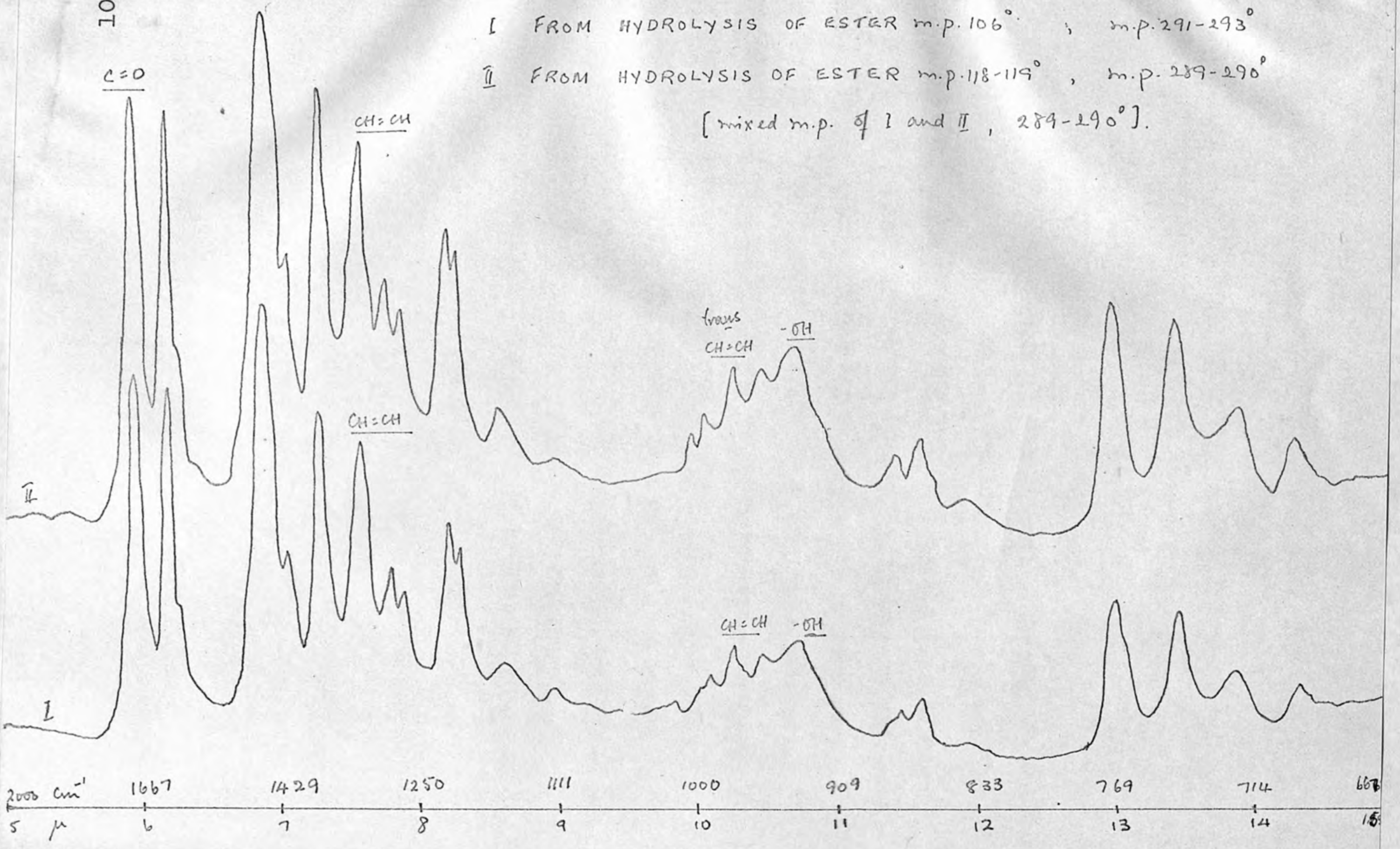


TABLE 3

Infrared Spectra of 2,2' - Bis (β-carboxyvinylene) biphenyl.
(and comparative intensities)

Acid from cis-trans ester	Acid from trans-trans ester	Assignment
1686 s (100)	1686 s (100)	C=O
1618 s (96)	1618 s (97)	C = C Conjugated
1605 w-m 1414 m	1605 w-m 1414 m	$-C\begin{smallmatrix}\nearrow O\\ \searrow O^-\end{smallmatrix}$
1319 s (82)	1319 s (90)	CH=CH
1285 m	1285 m	
1267 m	1267 m	
1218 m-s 1208 m-s	1218 m-s 1208 m-s	
1166 w	1166 w	
1004 w	1003 w	biphenyl
936 w	945 w	
976 m-w (29)	976 m-w (38)	CH = CH trans
954 m-w	954 m-w	
934 m	934 m	-OH of acid
875 w	874 w	
861 w	862 w	
769 m 744 m	769 m 742 m	1,2-disubstituted ring
720 w	720 w	
698 w (18)	699 w (19)	CH = CH cis

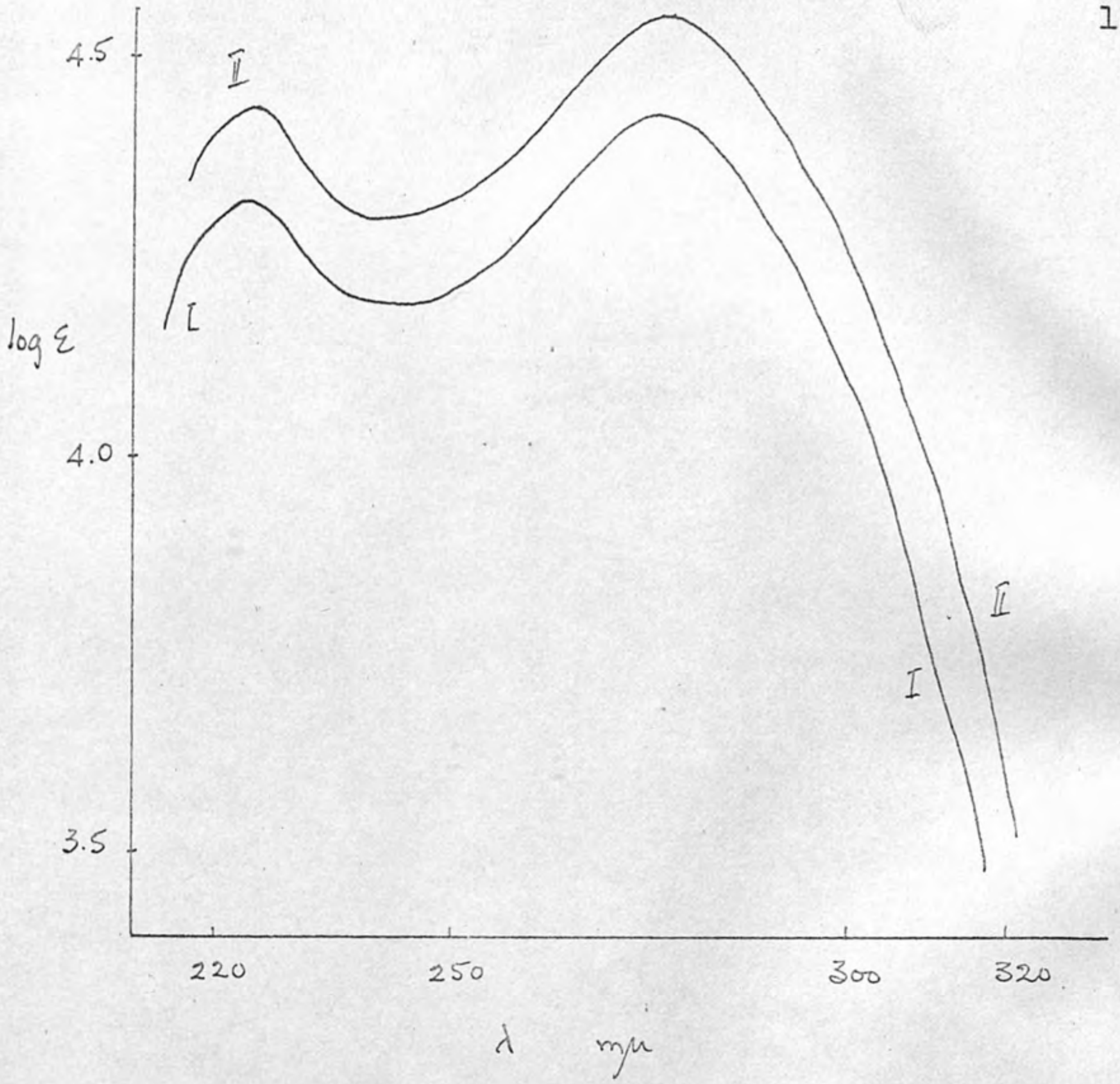


FIG. 10. ULTRAVIOLET ABSORPTION SPECTRA IN 95 % ETHANOL OF 2,2′-BIS (β-CARBOXYVINYLENE) BIPHENYL FROM HYDROLYSIS OF ISOMERIC ESTERS (FIG. 8)

I ACID FROM CIS-TRANS ESTER

λ max	275	225	mμ
ε max	26,500	21,000	

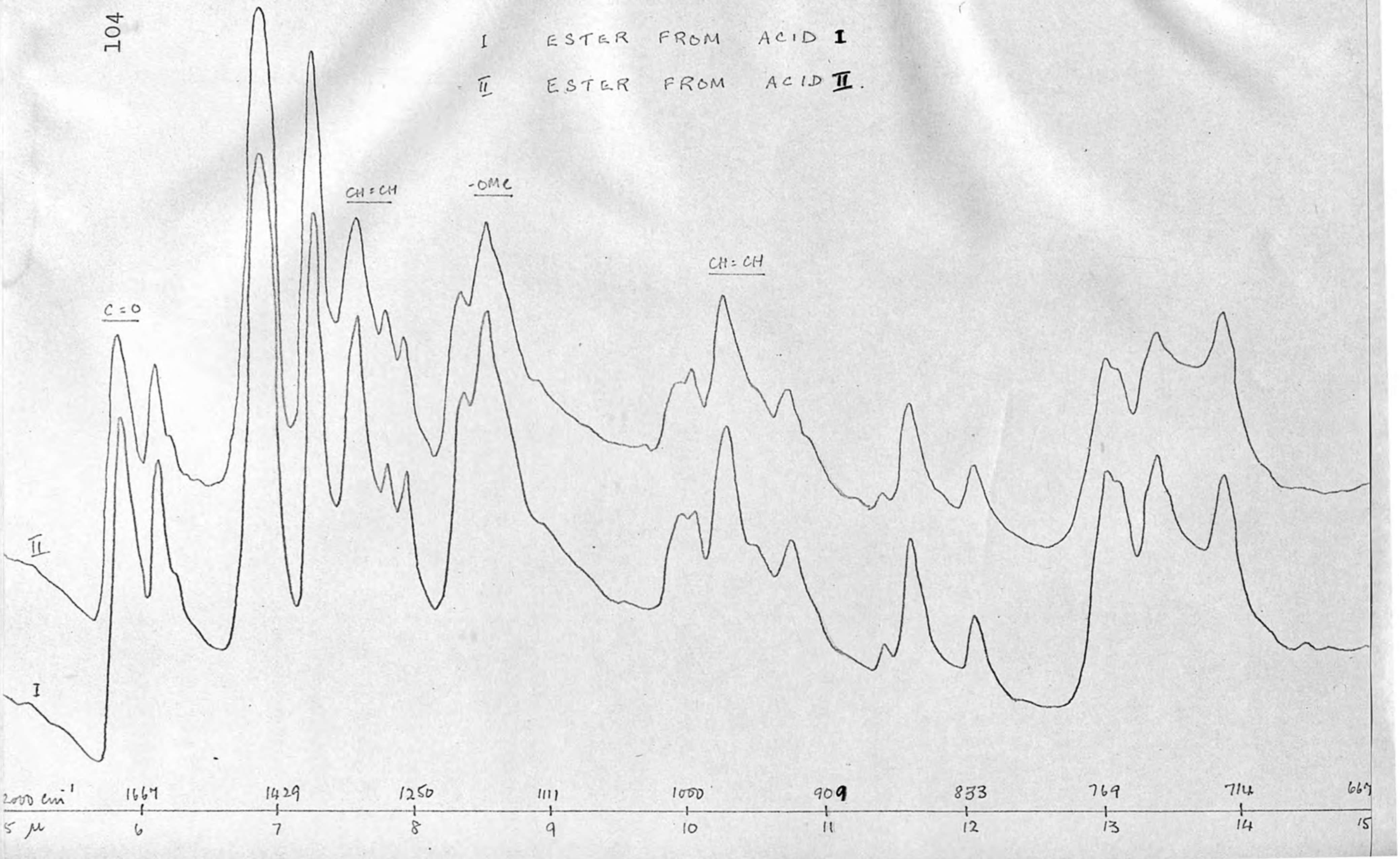
II ACID FROM TRANS-TRANS ESTER

λ max	279	225	mμ
ε max	35,000	27,000	

FIG. 11. INFRARED SPECTRA ON NUJOL OF $2,2'$- BIS (β - CARBOMETHOXYVINYLENE)- BIPHENYL OBTAINED BY ESTERIFICATION OF ACIDS (SEE FIG. 9).

I ESTER FROM ACID **I**

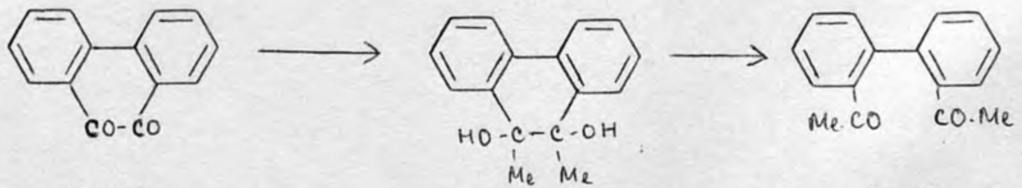
II ESTER FROM ACID **II**.



very strong, and there was complete absence of the 690cm^{-1} band.

Thus, in the reaction between carbomethoxymethylenetriphenylphosphorane and biphenyl-2,2'-dialdehyde, isomeric 2,2'-bis (β-carbomethoxyvinylene)biphenyls were obtained, one with a _cis-trans_ configuration, the other with a _trans_-_trans_ configuration. However, when the esters were hydrolysed, only the _trans_-_trans_ acid was obtained. Again when the acids were esterified, the _trans_-_trans_ ester, the most stable configuration, was found.

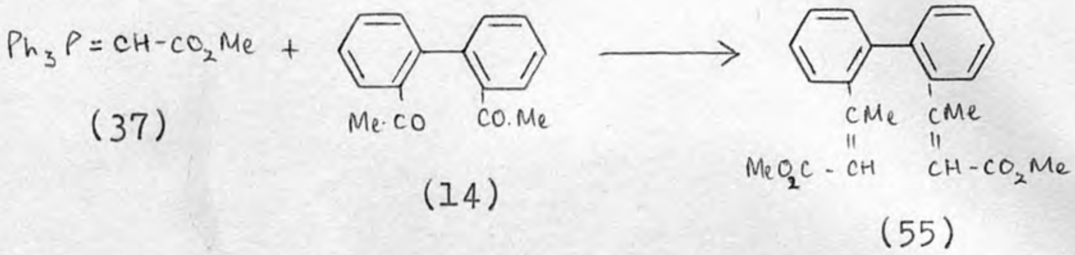
The reaction between the phosphorane and 2,2'-diacetylbiphenyl (14) was also investigated. This compound was prepared from phenanthraquinone according to the following scheme:



(26) (54) (14)

A Grignard reagent was prepared from methyl iodide and magnesium, and was then allowed to react with phenanthraquinone; 9,10-dihydro-9,10-dihydroxy-9,10-dimethylphenanthrene (54) was then obtained in 54% yield [Hall, Ladbury, Lesslie and Turner, _J._, 1956, 3475]. This diol was then oxidised with chromic anhydride, in glacial acetic acid, and diacetylbiphenyl (14) was then obtained in 60% yield [Hall, _et.al._, _loc.cit._].

The reaction between the phosphorane (37) and the ketone (14) in absolute alcohol gave a liquid b.p. 218°/9m.m.-228°/7m.m.



(37) (14) (55)

which would not solidify completely, and when crystallisation was attempted only gum resulted. A separation on a chromatographic column was also tried, but the fractions could not be obtained pure, and the only sign that the reaction had gone at all was the cinnamate-like smell.

When the experiment was repeated in toluene, which had been used successfully in the reaction with the dialdehyde (43), a mixture of solids (m.p. partly 75°, partly 125°) was obtained in the distillate. When fractional crystallisation was attempted only triphenylphosphine oxide was obtained (m.p. and infrared spectrum). Some of the oxide had been obtained earlier in the cool reaction mixture.

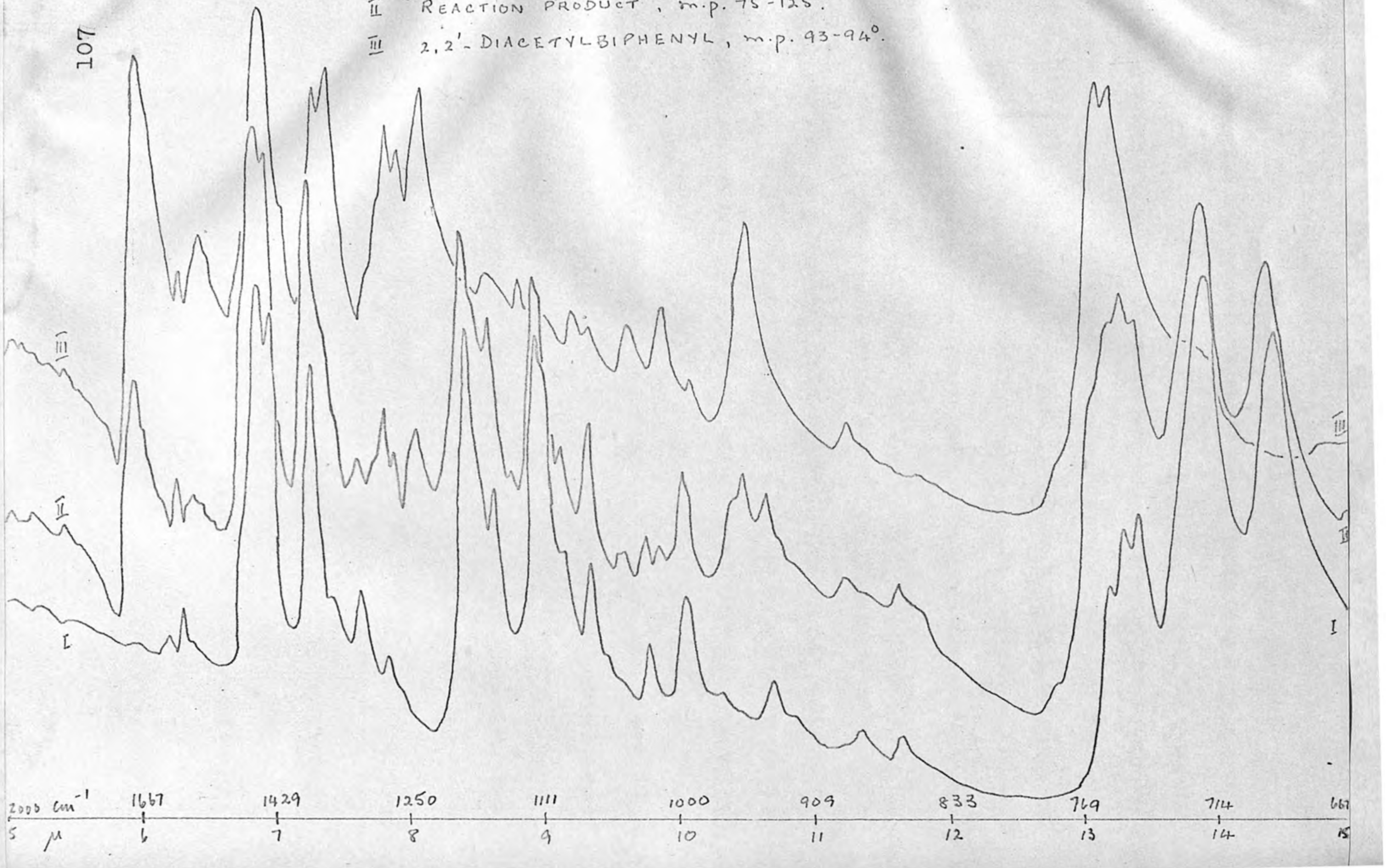
The solid, m.p. partly 75° and partly 125°, certainly contained some triphenylphosphine oxide, as shown by the infrared spectrum [Fig. 12]. The presence of C=O peak suggested that it probably was a mixture of the unreacted diacetyl compound and the oxide. A mixture of the diacetyl compound and triphenylphosphine oxide melted completely at 90° (soft 80°). The reaction was not investigated any further in view of the general lack of reactivity of the phosphorane (37) towards ketones. [See p. 85].

FIG. 12. INFRARED SPECTRA IN NUJOL OF

I TRIPHENYLPHOSPHINE OXIDE, m.p. 155-157°.

II REACTION PRODUCT, m.p. 75-125°.

III 2,2'-DIACETYLBIPHENYL, m.p. 93-94°.



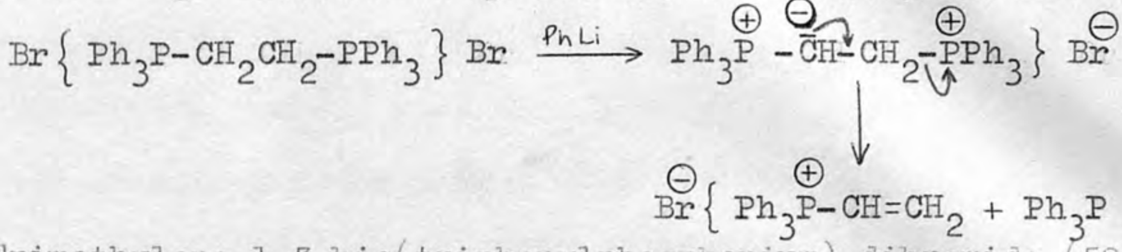
V. Polyalkylene dibromide series

Ethylenebis (triphenylphosphonium) dibromide (57) was obtained in 91% yield by boiling triphenylphosphine with ethylene dibromide (56) [Wittig, Eggers, and Duffner, Annalen, 1958, 619, 10] and crystallising from chloroform and cyclohexane.

$$Ph_3P + \underset{(56)}{BrCH_2CH_2Br} \longrightarrow Br\left\{ \underset{(57)}{Ph_3P\text{-}CH_2CH_2\text{-}PPh_3} \right\}Br$$

The corresponding diphosphorane was prepared from it by the action of n-butyl-lithium, but this did not seem satisfactory. The resulting solution was dark brown instead of orange or red, and it became darker on heating. Biphenyl-2,2'-dialdehyde (43) was added when the Colour Test (Gilman and Schulze, J. Amer. Chem. Soc., 1925, 47, 2002) was negative, indicating absence of butyl-lithium, and when the mixture had cooled down. It was observed that at the point of contact the mixture was green. This seems to suggest the decomposition of the dialdehyde. However, when the mixture was stirred the colour became pale. When worked up, only triphenylphosphine was obtained (m.p. and mixed m.p.).

Wittig et. al. (loc. cit.) had tried to obtain the corresponding diphosphorane by treating the dibromide with phenyl-lithium, sodium ethoxide and lithium piperidide. In each case, a brown solution resulted and triphenylphosphine was finally obtained. It is clear that a stronger base like n-butyl-lithium still had the same effect on the dibromide (unlike 2,2'-bistriphenylphosphonio-methyl)biphenyl dibromide) which was stable to phenyl-lithium and sodium ethoxide, but gave the corresponding phosphorane with n-butyllithium). Wittig suggested that what happened was analogous to the Hofmann degradation of a quaternary ammonium hydroxide.



$$\text{Br}\left\{\text{Ph}_3\text{P-CH}_2\text{CH}_2\text{-PPh}_3\right\}\text{Br} \xrightarrow{\text{PhLi}} \text{Ph}_3\overset{\oplus}{\text{P}}-\overset{\ominus}{\text{C}}\text{H-CH}_2-\overset{\oplus}{\text{P}}\text{Ph}_3\}\overset{\ominus}{\text{Br}}$$

$$\downarrow$$

$$\overset{\ominus}{\text{Br}}\left\{\text{Ph}_3\overset{\oplus}{\text{P}}\text{-CH=CH}_2 + \text{Ph}_3\text{P}\right.$$

Trimethylene-1,3-bis(triphenylphosphonium) dibromide (59) was prepared in 75% yield by warming triphenylphosphine slowly with 1,3-dibromopropane (58), with stirring. The solid mass was purified by boiling the chloroform solution in charcoal, filtering, and adding acetone [Wittig, et.al., loc.cit.].

The preparation of the corresponding diphosphorane seemed successful as the mixture was obviously bright red. The addition of biphenyl-2,2'-dialdehyde did not seem satisfactory, the heat of the reaction which had been observed in previous successful reactions (e.g. one resulting in 2,2'-distyrylbiphenyl) was not apparent, and the green colour at the point of contact was again observed. When the reaction mixture was worked up in the usual manner, the solid part gave the starting phosphonium dibromide instead of the expected triphenylphosphine oxide. A little of the oxide (4% yield) was found in the liquid part of the product. Also obtained from the liquid part were some unreacted dialdehyde, a macromolecular compound with empirical formula $C_{31}H_{30}O_4$, the infrared spectrum of which showed that it contained a carbonyl group and the biphenyl skeleton, and a hydrocarbon containing the biphenyl skeleton; the analysis of the latter was not satisfactory and the rest of its infrared spectrum was not informative.

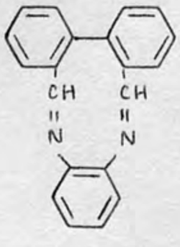
Successful reactions of the diphosphorane had been obtained [Wittig, *et.al.*, *loc.cit.*] with benzaldehyde and *o*-phthaldehyde in 65 and 22% yield, respectively. In this case it seems that steric factors were involved in the failure of the reaction. To form a four-membered cyclic transition stage at each of the 2,2'-positions would be very difficult. The yields of the reactions with benzaldehyde and *o*-phthaldehyde would seem to support this suggestion.

$$Ph_3P + \underset{(58)}{BrCH_2CH_2CH_2Br} \longrightarrow \underset{(59)}{Br\left\{ Ph_3PCH_2CH_2CH_2PPh_3 \right\} Br}$$

VI. Condensation Series

Condensation between biphenyl-2,2'-dialdehyde and o-phenylenediamine

In an attempt to obtain a 2,2'-bridged biphenyl with ten-membered bridging ring, biphenyl-2,2'-dialdehyde was condensed with o-phenylenediamine. A 1:1 mixture of the dialdehyde and the diamine was heated in ethylene glycol, at 160°. The solid obtained from the ethereal extract contained a carbonyl group in its infrared spectrum, and with a crude m.p. of 50° most of it could be the dialdehyde. When the acid washing of the ethereal extract was made alkaline, two products were obtained. One was water-soluble and had m.p. 227-230° (there was not enough substance for analysis). The other was water-insoluble and had m.p. 158-159°, the analysis of which gave a formula corresponding to 5,10-dihydro-2,3:6,7:8,9-tribenzo-1,4-diazecine (60), the required product. It also gave a picrate, m.p. 279-280° decomp.



(60)

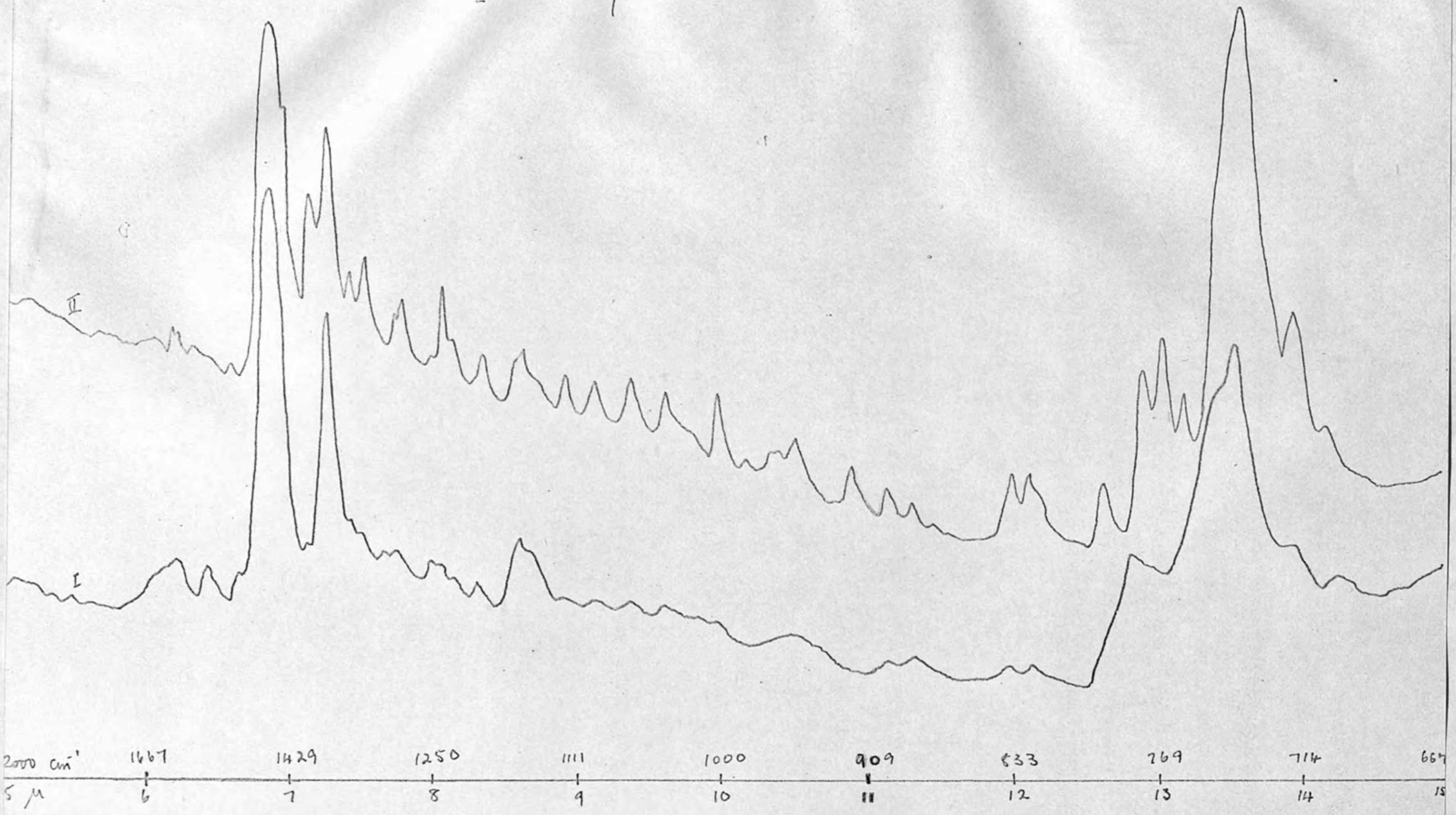
[For the infrared spectra of the two products, see Fig. 13.]

This condensation between the dialdehyde and the diamine was also reported by F. Sparatore [Ann. Chim. (Italy), 1959, 49, 2102] who condensed the same quantities of reactants in methanol at room temperature. The product was precipitated by water and its benzene solution was chromatographed repeatedly on neutral alumina

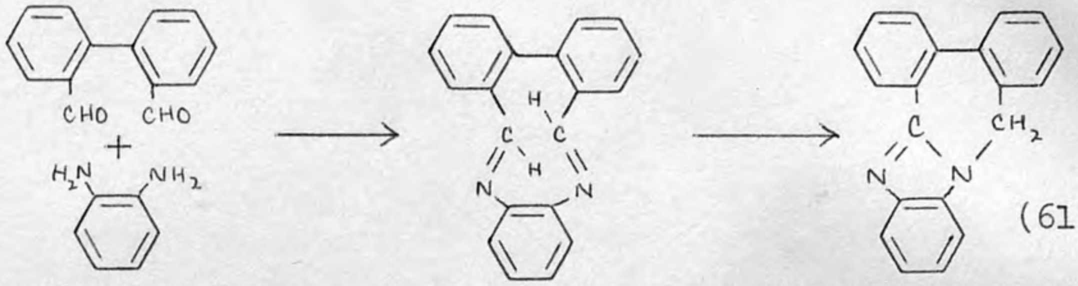
FIG. 13. INFRARED SPECTRA IN NUJOL OF CONDENSATION PRODUCTS (REACTION AT 160°).

I solid m.p. 224-230°

II solid m.p. 158-159°

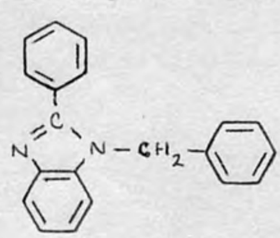


columns. His product had m.p. 52-57°, was obtained in 85% yield and the analysis also gave the empirical formula $C_{20}H_{14}N_2$. There are two possible compounds corresponding to this formula, (60) and (61), the latter having been formed because of the interference between hydrogen atoms and the electron pair on nitrogen, and the consequent ring contraction into one with the stable imidazole nucleus, forming the azepin [Sparatore, loc. cit.]. Sparatore thought that his compound was (61) because it was basic and the ultraviolet spectra obtained, in methanol and in hydrochloric acid, were fundamentally similar to that of 1-benzyl-2-phenylbenzimidazole (62), the only difference being a broad hump with a maximum at 259 mμ which could be attributed to biphenyl system. He did not give the infrared spectrum or any other evidence.



(61)

(62)



The ultraviolet spectra of Sparatore's compound and of the solid m.p. 158-159° obtained in the present work were almost identical [see Fig. 14]. Their picrates also had similar melting

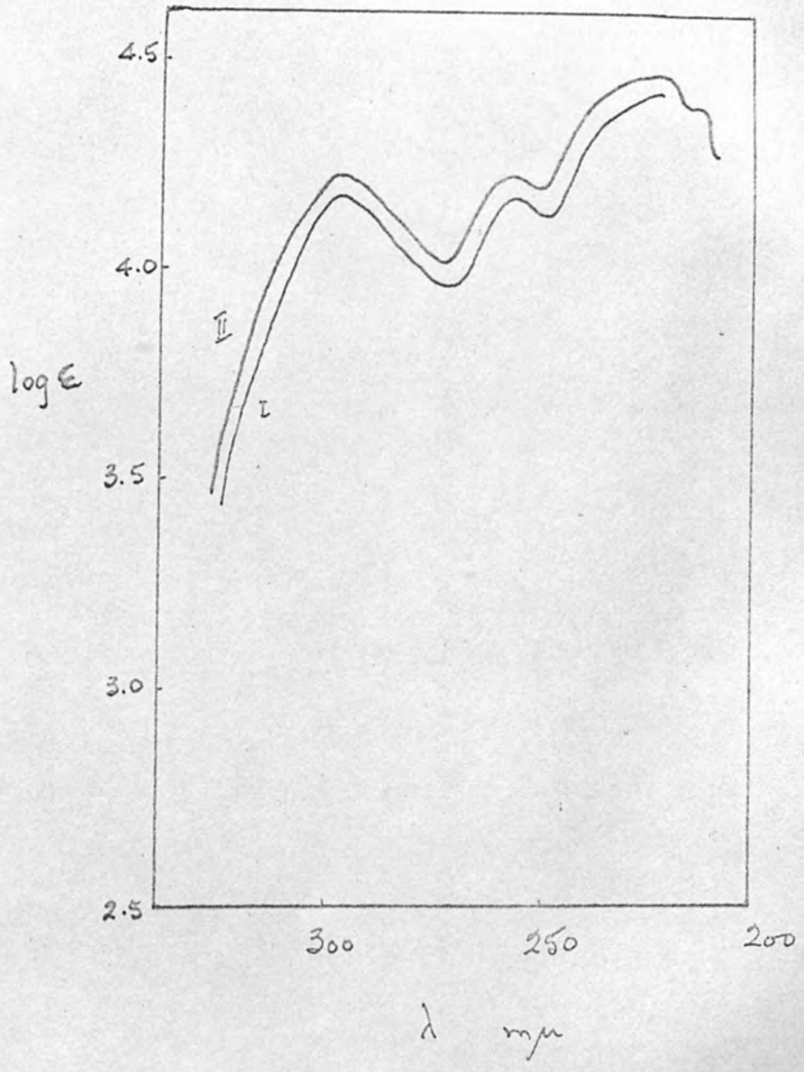


FIG. 14. ULTRAVIOLET ABSORPTION SPECTRA IN METHANOL OF CONDENSATION PRODUCT [REACTION AT 160°].

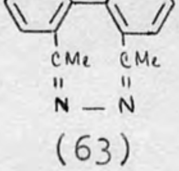
I SOLID, m.p. 158-159° : λ_{max} 298 258 mμ.
ε_{max} 14,600 14,300

II SOLID OBTAINED BY SPARATORE, m.p. 52-54°.

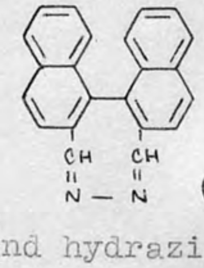
points. [Sparatore's was a monopicrate and had m.p. 278-280° decomp.]. Thus, apart from the m.p., the two compounds could be said to be the same, i.e. compound (61). However, when Sparatore's experiment was repeated, two solids, crude m.p. 189-191° and 216-217°, were obtained. The infrared spectrum of the latter was identical with that of the quinoxaline (65), m.p. 222-223° (mixed m.p. 219-221°) [see Fig. 15].

It thus seems that the condensation is not reproducible, and that at least four compounds, (61) and (65) among them, are obtained from it.

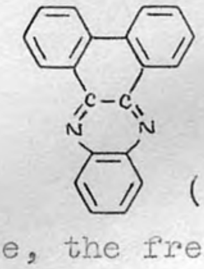
One piece of evidence in support of the formula (60) for the compound with m.p. 158-159° is the presence of a C=N peak in the infrared spectrum. Recent reports of this absorption frequency had been given by Bacon and his co-workers. In 3,8-dimethyl-4,5:6,7-dibenzo-1,2-diazocine (63), obtained from condensation between 2,2'-diacetylbiphenyl and hydrazine hydrate, the frequency of C=N was 1610cm^{-1} [Bacon and Lindsay, <u>J.</u>, 1958, 1382]; and in dinaphtho-[2,1-d:1',2'-f][1,2]diazocine (64), obtained from condensation between 1,1'-binaphthyl-2,2'-dialdehyde and hydrazine hydrate, the C=N frequency was 1625cm^{-1}. For comparative purposes, the quinoxaline (65) was prepared and the C=N frequency



(63)

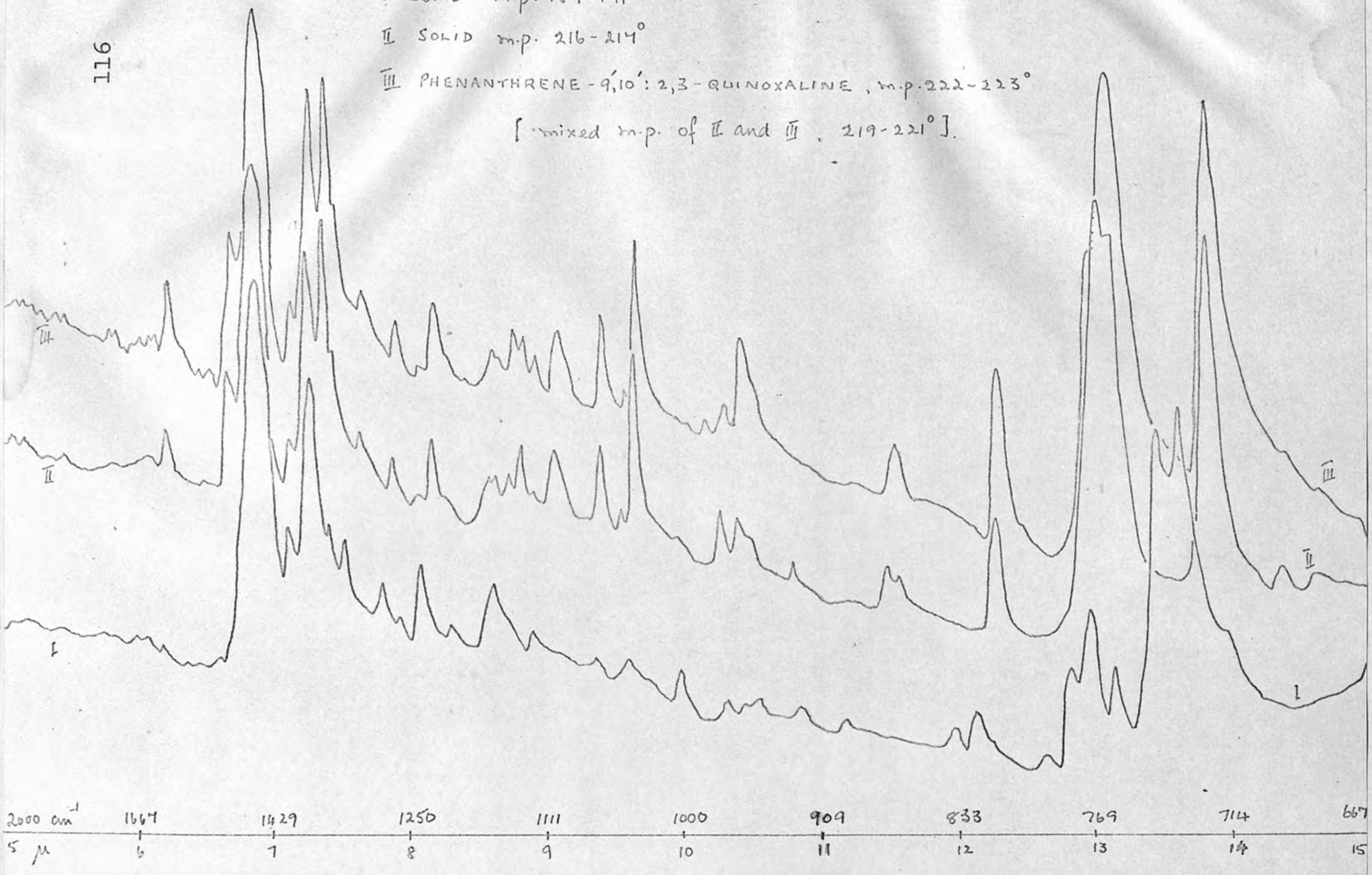


(64)



(65)

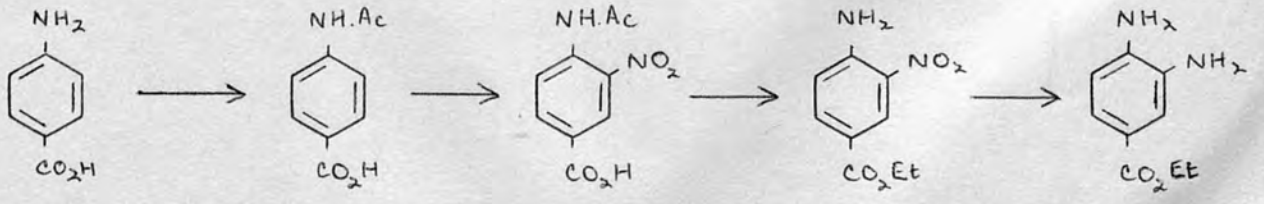
FIG. 15. INFRARED SPECTRA IN NUJOL OF CONDENSATION PRODUCTS (REACTION AT ROOM TEMP.)



in its infrared spectrum was $1608 cm^{-1}$. Fig. 16 showed the presence and comparative intensities of this peak in known and unknown compounds. Thus all four condensation products obtained in the present work could be said to contain C=N. The various intensities can perhaps be used to give some idea of the number of C=N groups present, e.g. the benzimidazole formula (61) requires one C=N bond, and the diazecine formula (60) and quinoxaline (65) require two C=N bonds. Hence it follows that, in Fig. 16, I and III contain one C=N group, while II and IV contain two C=N groups. This would make I and III benzimidazole derivatives, and would fit with the identification of IV as the quinoxaline (65). Consequently it would seem that II is the required diazecine. However, no very definite conclusion about the formation of a 2,2'-bridged biphenyl with a ten-membered bridging ring can be reached at the present [see, however, the following section].

Condensation between biphenyl-2,2'-dialdehyde and ethyl 3,4-diaminobenzoate

Ethyl 3,4-diaminobenzoate was obtained according to the following syntheses:



(66) (67) (68) (69) (70)

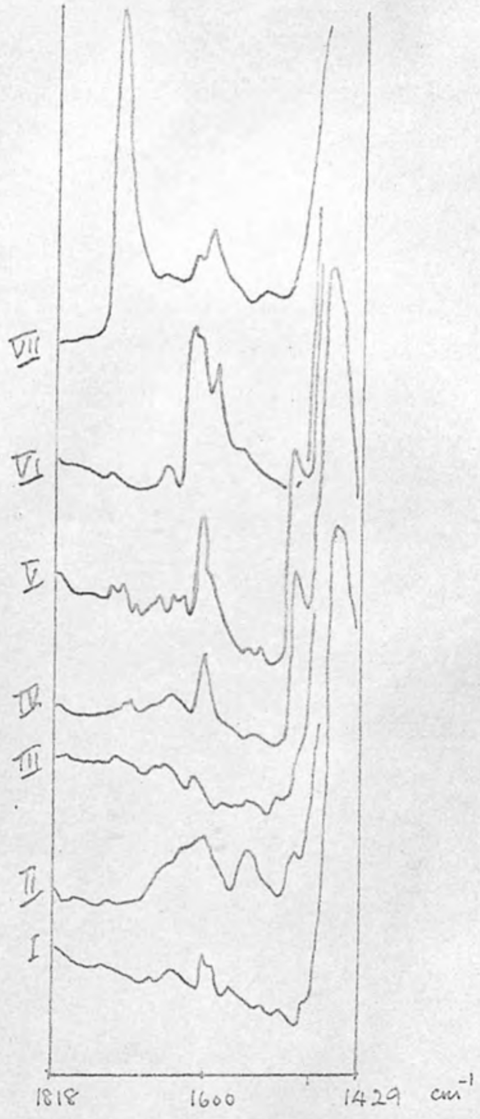


FIG. 16. INFRARED SPECTRA IN NUJOL SHOWING C=N FREQUENCY [1600 - 1630 cm⁻¹].

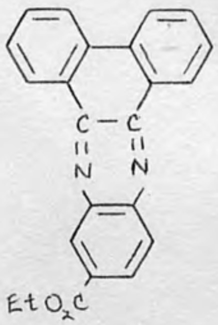
I CONDENSATION PRODUCT, m.p. 158-159°.
II CONDENSATION PRODUCT, m.p. 227-230°.
} REACTION IN ETHYLENE GLYCOL AT 160°. FIG. 13.

III CONDENSATION PRODUCT, m.p. 189-191°
IV CONDENSATION PRODUCT, m.p. 216-217°
} REACTION IN METHANOL AT ROOM TEMP. FIG. 15.

V PHENANTHRENE-9',10': 2,3-QUINOXALINE, m.p. 222-223°.
VI 3,8-DIMETHYL-4,5:6,7-DIBENZO-1,2-DIAZOCINE, m.p. 168-169°.
VII 3''-CARBETHOXY-PHENANTHRENE-9',10': 2,3-QUINOXALINE, (crude m.p. 197°) m.p. 216-217°.

p-Acetamidobenzoic acid (67) was prepared from p-aminobenzoic acid (66) in 55% yield [Ritstert and Epstein, Chem.Zentr. 1904, 1, 1587; Kl.12q. Nr. 151725 vom 7/4 1905,17/5 1904], and was then nitrated to give m-nitro-p-acetamidobenzoic acid (68) in 76% yield [Kaiser, Ber., 1885, 18, 2942]. The hydrolysis of acid (68) in ethanolic hydrochloric acid gave a mixture of ethyl m-nitro-p-aminobenzoate (69) and the corresponding acid. The ester (69) was obtained pure by fractional crystallisation from ethanol and had m.p. 131-133° (61% yield). This nitro-ester was then reduced with stannous chloride in hydrochloric acid [Ritstert and Epstein, loc.cit.] and ethyl 3,4-diaminobenzoate (70) was obtained in 30% yield.

The condensation between biphenyl-2,2'-dialdehyde and ethyl 3,4-diaminobenzoate (70) was carried out in ethanol at room temperature. The first lot of yellow crystals were filtered off. These had crude m.p. 178°, and when crystallised from alcohol, had m.p. 214-215°. This yellow solid had an infrared spectrum [see Fig. 17] identical with that of the quinoxaline (71), m.p. 216-217° (crude m.p. 197°) (mixed m.p. 214-216°) which had been prepared for comparison.



(71)

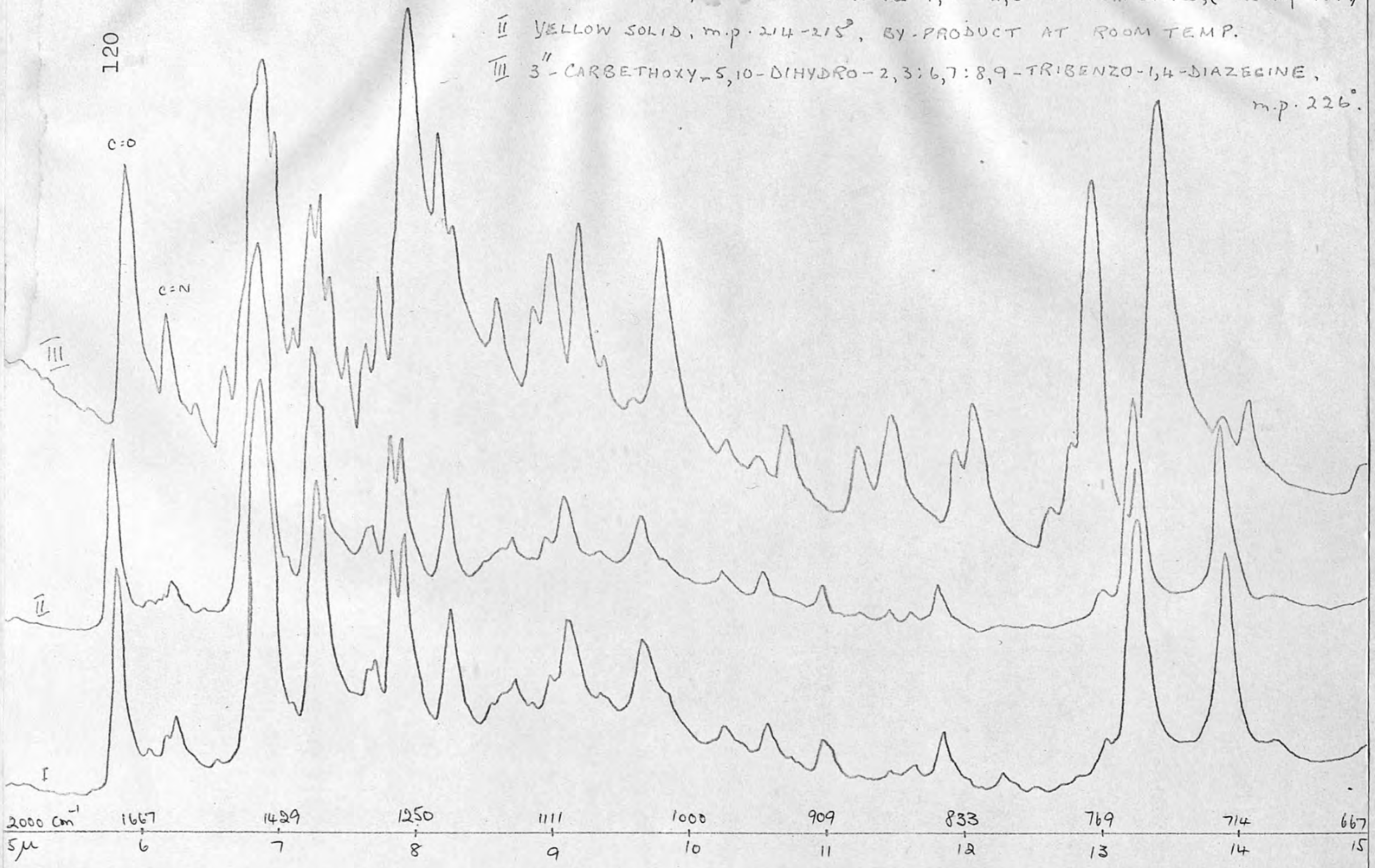


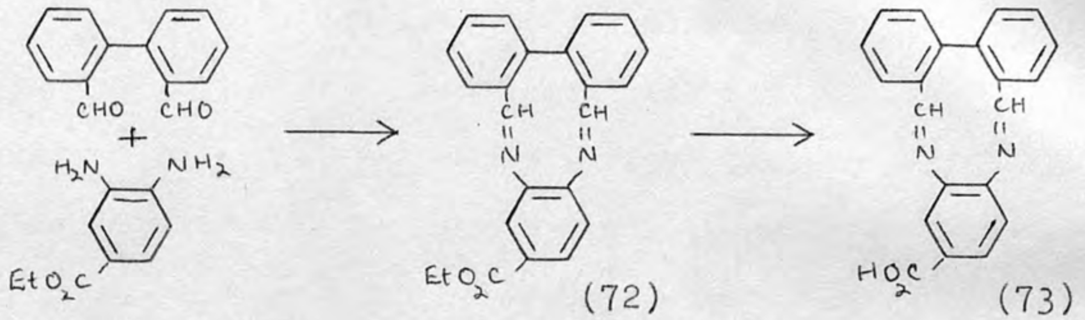
FIG. 17. INFRARED SPECTRA IN NUJOL OF

I 3"-CARBETHOXY-PHENANTHRENE-9',10':2,3-QUINOXALINE, (crude m.p. 197°) m.p. 216-217°.

II YELLOW SOLID, m.p. 214-215°, BY-PRODUCT AT ROOM TEMP.

III 3"-CARBETHOXY-5,10-DIHYDRO-2,3:6,7:8,9-TRIBENZO-1,4-DIAZEGINE, m.p. 226°.

When the mother liquor was left to stand, fine needles m.p. 226°, were obtained in 47% yield. The analysis showed that it was the desired product, 3''-carbethoxy-5,10-dihydro-2,3:6,7:8,9-tribenzo-1,4-diazecine (72), which, on subsequent hydrolysis,



gave the corresponding acid (73). Thus if the condensation was done at room temperature, the corresponding quinoxaline was obtained as well as the desired product. However, condensation at 150°, in ethylene glycol, gave only one product, the diazecine (72) in 39% yield. It was felt that, this yield could be improved and it seemed that the condensation reaction was best carried out at high temperature to avoid other by products. The infrared spectrum of the product, m.p. 226°, thought to be compound (72) contained a strong C=N peak at 1613cm^{-1}, so there was no question of its being a benzimidazole derivative.

EXPERIMENTAL

2,2'-Di-(1-hydroxy-1-methylethyl)-biphenyl

Preparation and attempted resolution

2,2'-Dinitrobiphenyl
(Shaw and Turner, *J.*, 1933, 135)

o-Chloronitrobenzene (120g., 1 mol.) in a wide hard-glass tube was boiled in a metal-bath (260-265°). Copper bronze (80g., 1.65 atoms) was added in four lots during 20 min., the mixture being stirred with a stout thermometer after each addition, and keeping the temperature inside the tube at 250°. After another 10 min. the reaction mixture was extracted with an equal volume of boiling *o*-dichlorobenzene, filtered hot using a preheated Buchner funnel and thick pad of filter papers, and the residue carefully washed with more *o*-dichlorobenzene. The total filtrate was treated with light petroleum (b.p.40-60°) until it was faintly cloudy. The resulting fine precipitate of 2,2'-dinitrobiphenyl was filtered off from the cooled solution and washed well with light petroleum. Yield 43-52.5g., m.p.122° (54-67%). This dark-coloured product was used as such. When crystallized from glacial acetic acid [Macrae & Tucker, *J*, 1933, 1520] it gave pale yellow crystals, m.p. 124°. This preparation was repeated 7 times and 302g. of the product were obtained. [Littlejohn and Smith, *J.*, 1954, 2552, gave m.p. 125.5° from light petroleum (b.p. 100-120°)].

2,2'-Diaminobiphenyl

a. Reduction with stannous chloride
[J. Insole. Ph.D. Thesis, London, 1961]

2,2'-Dinitrobiphenyl (12.2g., 1 mol.) was gradually added, with stirring, to the boiling mixture of stannous chloride (74.5g., 6.6 mols.) and concentrated hydrochloric acid (32.8g., 18 mols.) over ¼ hour. The heating was continued for another ½ hour and the mixture allowed to cool. A 30% solution of caustic soda was added in excess, with stirring, and 2,2'-diaminobiphenyl separated out as an oil. This was extracted with ether and washed well. After the ether had been distilled off, the remainder was distilled under reduced pressure and the diamino compound was obtained as a pale yellow solid. Yield 7.6g. b.p. 172^{o}/4.5mm.-182^{o}/3.5mm. (81%). It was crystallized from light petroleum (b.p. 60-80^{o}) and had m.p. 80^{o}. Altogether 124g. of the diamine were prepared by this method.

b. Catalytic hydrogenation
[Ross, Kahan and Leach, J., Amer.Chem.Soc., 1952, 74, 4122]

The dinitro compound (12.2g., 1 mol.) was dissolved in a mixture of 150c.c. ethylacetate and 50 c.c. absolute ethyl alcohol and the solution shaken with hydrogen in the presence of 0.29g. of platinum oxide (Adam's catalyst). The temperature of the mixture was kept at about 75^{o} and pressure at 50lb./in.^{2}. After 15 hours the colour of the solution changed from pale green to pale yellow. The solvent was removed on a water bath and the residue crystallized from light petroleum (b.p.60-80^{o}). Yield

7.5g. (82%), m.p. 80°.

2,2'-Dibromobiphenyl

[Schwechten, Ber., 1932, 65 B, 1605]

2,2'-Diaminobiphenyl was tetrazotised using concentrated sulphuric acid (7c.c., 2.5 mols.) and sodium nitrite (6.9 g., 2 mols.) at 5-10°. Mercuric nitrate (33.4 g., 2 mols.) was placed in 100 c.c. of water in a beaker and hydrobromic acid (56.7c.c., 4 mols) was added; a suspension of mercuric bromide was obtained. The tetrazotised solution was diluted and added to the mercuric bromide to give the yellow complex salt $[C_{12}H_8N_4][HgBr_3]_2$ which was washed with water by decantation and dried by washing with acetone. Yield of complex salt 53.5g. (98%).

The complex salt was ground well with twice its weight of potassium bromide and the mixture was decomposed gradually in a two-necked flask maintained at 185° in a metal-bath; the mixture was added by means of a spatula through one neck which was provided with a stopper; an air condenser was attached to the other neck. After the decomposition was complete the mixture was steam-distilled. Crude yield of the solid filtered from the ~~filtrate~~ distillate was 11 g. This was crystallized from aqueous methyl alcohol, giving 10g. of 2,2'-dibromobiphenyl (64%), m.p. 79.5°. This experiment was repeated 6 times and 42g. of this compound were obtained.

2,2'-Di-iodobiphenyl
[Lothrop, J. Amer. Chem. Soc., 1941, 63, 1187; Heaney, Heinekey, Mann and Millar, J., 1958, 3838.]

A solution of sodium nitrite (37g., 2.2 mols.) in water (125c.c.) was added slowly, with mechanical stirring, to a solution of 2,2'-diaminobiphenyl (47.5 g., 1 mol.) in hydrochloric acid (260c.c. of concentrated acid in 260 c.c. of water). After another 15 mins. a solution of potassium iodide (130g., 2 mols.) in water (250 c.c.) was added slowly. A thick black paste separated at once. The mixture was left to stand at room temperature for 3 hrs., then left overnight with an excess of sodium bisulphite. The yellow-green solid of diphenylene iodonium iodide was filtered off, washed well with bisulphite solution, water, and then with cold methanol. Yield 76g. (72.5%), m.p. 182°decomp. [Lothrop gave m.p. 205-210° as that of pure salt.]

Diphenylene iodonium iodide was then heated in a round-bottomed flask in an oil-bath at 215-220° for 30 mins. The residue was extracted with ether using a Soxhlet apparatus and the extract percolated through a short column of chromatographic alumina to remove coloured impurities not readily removed by charcoal. The solvent was removed and the residue crystallized from methylated spirit, giving pale yellow crystals of 2,2'-di-iodobiphenyl. Yield 35g. (60%), m.p. 109°.

2,2'-Di(1-hydroxyethyl)biphenyl

[Heinekey & Millar, J., 1959, 3101]

The preparation of the lithium compound and its subsequent reaction with acetaldehyde were performed under nitrogen, and the ether used was sodium-dried.

2,2'-Dibromobiphenyl (11g., 1 mol.) in ether (200 c.c.) was added slowly to the lithium (2 g., 4 mols., wire form) covered with 300 c.c. ether, and stirred mechanically. The addition took 3 hrs. and the mixture was stirred for a further 2 hrs. Freshly distilled acetaldehyde (12c.c., 2 mols.) was added gradually to the reaction mixture. Pale yellow solid appeared at once. The reaction flask was immersed in a water-bath at 18° during the addition of the aldehyde. The stirring was continued for another ½ hour after the addition, and the reaction mixture was allowed to warm up to room temperature. It was then poured onto crushed ice. Water, then dilute hydrochloric acid were added until two clear layers were obtained. The aqueous layer was extracted with ether. The combined ethereal layer and extracts was washed with brine then a little water, and dried (sodium sulphate). Ether was removed and the residue was crystallized from benzene. Yield 0.76g. (10%) m. p.144-146.5° [Hall, Ladbury, Lesslie and Turner, J., 1956, 3475 gave two forms. Diol A m.p. 147.5-149°; diol B m.p.153-155°. Mixed m.p. of diol obtained and diol A was 145-148°, while mixed m.p. of diol obtained and diol B was 127-132°.]

2,2'-Di(1-hydroxy-1-methylethyl)biphenyl

The preparation of the lithium compound (Heinekey and Millar, loc. cit.) and its subsequent reaction with acetone were carried out under nitrogen.

2,2'-Dibromobiphenyl (5.5g., 1 mol.) in sodium-dried ether (100 c.c.) was added slowly to the lithium (1 g., 4 mols., wire form) covered with 15 c.c. sodium-dried ether and stirred mechanically. The addition was made during 1 hr. at such a rate that the mixture boiled gently. After another $2\frac{1}{2}$ hrs. the solution of 2,2'-dilithiobiphenyl was decanted into a similar 3-necked flask. A solution of acetone (2.9 c.c., 2 mols.) in sodium-dried ether was then added gradually. The mixture was heated for $\frac{1}{2}$ hr. after the end of the addition, cooled, and then poured onto crushed ice. Water and dilute hydrochloric acid were added. The aqueous layer was extracted with ether. The combined ethereal layer and extracts were washed with brine and then a little water, and dried (sodium sulphate). Ether was removed and the solid residue was separated from the liquid. Crystallization of the solid from light petroleum (b.p. 60-80°) gave 1.1 g. (23%) of 2,2'-di(1-hydroxy-1-methylethyl)biphenyl, m.p. 138-139° (Hall, Ladbury, Lesslie and Turner, J., 1956, 3475, recorded m.p. 139-140°). The liquid residue was distilled under reduced pressure and gave some biphenyl (mixed m.p.).

Dimethyl-2,2'-diphenate
[Hall, Lesslie and Turner, J., 1950, 711]

Diphenic acid (100 g.) was dissolved in methyl alcohol (1,000 g.) and concentrated sulphuric acid (54 c.c.) was added gradually with shaking. The mixture was heated under reflux for 6 hrs., then poured into a large volume of water, and stirred. The solid obtained was filtered off from the cooled solution, washed with sodium bicarbonate solution and then with water. It was crystallized from methyl alcohol and gave 100 g. (90%) of dimethyl diphenate, m.p. 70-71°.

2,2'-Di-(1-hydroxy-1-methylethyl)-biphenyl
(Cook and Turner, J., 1957, 117)

A solution of methyl bromide (142.5 g., 6 mols.) in cold ether (50 c.c., sodium-dried) was added gradually to the magnesium turnings (36.5g., 6 mols.) which were covered with ether (sodium-dried). After a few drops of methyl bromide had been added the reaction flask was warmed by hand, but the reaction would not start. Some magnesium turnings were then activated by pouring neat methyl bromide onto them, and these were introduced into the reaction flask. The reaction soon started and became quite vigorous. The addition took 2½ hrs. A solution of dimethyl diphenate (68 g., 1 mol.) in ether (600 c.c., sodium-dried) was then added to the Grignard reagent, with stirring. The reaction was fairly vigorous and the addition took 3½ hrs. The reaction mixture was then boiled for further 3 hrs., poured onto crushed ice and any solid formed was dissolved by dilute hydrochloric acid. The aqueous layer was extracted with ether, the combined ethereal layer and extracts was washed with brine, and then a little water, and dried (sodium sulphate). Ether was removed and white crystals were obtained in the residue. These were recrystallized from light petroleum (b.p. 60-80°) giving white crystals, m.p. 139-141°; yield 34 g. (50%). A further yield of 7 g. (10%), m.p. 138-139°, was obtained from the mother liquor.

2,7-Dihydro-2,2:7,7-tetramethyl-3,4:5,6-dibenzoxepin
(Hall, Ladbury, Lesslie and Turner, *J.*, 1956, 3475)

2,2'-Di-(1-hydroxy-1-methylethyl)-biphenyl (2 g., 1 mol.) was suspended in 60 c.c. 4N-sulphuric acid and boiled under reflux for 1 hr. Some product collected in the condenser. This and the contents of the flask were extracted with ether, the ethereal solution was dried over potassium carbonate, and the ether removed. The residue was crystallized from ethanol, giving rhombic crystals m.p. 90-92°. After two more crystallizations from the same solvent it had m.p. 92-94°.

2,7,7-Trimethyl-3,4:5,6-dibenzocyclohepta-1,3,5-triene
[Hall, Ladbury, Lesslie and Turner, *J.*, 1956, 3475]

A suspension of 2,2'-di-(1-hydroxy-1-methylethyl)-biphenyl in hydrobromic acid (*d* 1.49; 60 c.c.) was boiled under reflux for 1 hr. The reaction was complete when all the solid had melted and oil then separated. The mixture was treated with hot water. On cooling the oil solidified. It was crystallized from ethanol and had m.p. 97.5-98.5°. A second crystallization from the same solvent gave m.p. 99-100°. [Hall, et.al. gave m.p. 100-101°].

Attempted optical activation of 2,2'-di-(1-hydroxy-1-methylethyl-biphenyl

1.0018 G. of the diol was dissolved in 20 c.c. of diethyl-(+)-tartrate. It would not dissolve at room temperature. At 60° it gradually dissolved and a clear solution was obtained in ½ hr. It was then left to stand in a water bath at 25° for 1 hr. Ice-water was added with stirring and scratching, and white precipitate was obtained. More ice-water was added until the solution was clear. The solid was filtered and washed repeatedly with ice-water and dried in vacuo. 0.8665 G. of solid was obtained, m.p. 91-92°. Mixed m.p. with the oxepin (m.p. 92-94°) was 89-92°, and the infra-red absorption spectrum was identical with that of the oxepin.

When another 1 g. of the diol was dissolved in diethyl-(+)-tartrate at 100° and kept at 50° for 1 hr., similar results were obtained. Both samples were found to be optically inactive when examined polarimetrically at 6° in chloroform (c,2.0015).

Attempted optical resolution of 2,2'-di-(1-hydroxy-1-methylethyl)-biphenyl by absorption on cellulose

4 G. of the diol were dissolved in 100 c.c. of chloroform and put through a column of cellulose. Fractions of 10 c.c. were collected and examined polarimetrically. All were found to be optically inactive. Diol was recovered from them.

Attempt to acetylate 2,2'-di-(1-hydroxy-1-methylethyl)-biphenyl

2.7 G. (1 mol.) of the diol were dissolved in 10 c.c. pyridine (dried over KOH) and 2 g. (2 mols.) of acetyl chloride were added. White solid appeared at first, then the reaction became vigorous giving yellow solid in a dark solution. When the solid was filtered it went soft on standing, so it was combined with the filtrate and treated with dilute hydrochloric acid. Ethyl alcohol was added and a white solid was obtained on scratching. It had m.p. 90-92°. Mixed m.p. with the oxepin was also 90-92°.

Attempted preparation of the hydrogen phthalate of the diol

The diol (1.35g., 1 mol.) was dissolved in 10 c.c. of dried pyridine. The phthalic anhydride (0.74 g., 1 mol.) was dissolved in 5 c.c. of dried pyridine and added to the diol solution. No immediate reaction was observed. It was left to stand at room temperature for ½ hr., then heated on a water-bath for 1 hr. and poured into 200 c.c. of dilute hydrochloric acid and stirred. A white precipitate was obtained. This was filtered off and washed with water. It was insoluble in cold sodium carbonate solution. When dried it had m.p. 85-124°; mixed m.p. with the oxepin 85-122°. When crystallized from aqueous acetone it had m.p. 87-130°. Further crystallization from aqueous alcohol and then aqueous acetone did not change its m.p.

In a similar experiment using 2 mols. of phthalic anhydride (1.48 g. in 10 c.c. pyridine) a white solid m.p. 85-88° was obtained. Crystallization from aqueous alcohol gave solid m.p. 91-93°, mixed m.p. with oxepin 81-87°. A second crystallization from aqueous alcohol gave solid m.p. 91-93° alone or when mixed with the oxepin.

Attempted preparation of the hydrogen phthalate via potassium salt of the diol

The potassium (0.3 g., 1 mol.) was cut and weighed under sodium-dried xylene and covered with 100 c.c. of sodium-dried benzene in a 500 c.c. round-bottomed three-necked flask. The diol (2 g., 1 mol.) was added, under an atmosphere of nitrogen, to the vigorously stirred solution. When the initial reaction subsided, the flask was warmed and the potassium shavings became small pellets. The warming and stirring was continued for 14 hrs. and no potassium pellets could be seen. However, *t*-butyl alcohol was used to get rid of the last traces of potassium. The mixture was then transferred, under nitrogen, to a solution of phthalic anhydride (1.1 g., 1 mol.) in 100 c.c. dry benzene. The resulting solution was clear. It was poured into ice and the two layers were separated. The benzene layer was washed with sodium carbonate solution (10%), the washings were acidified with dilute hydrochloric acid and then extracted with ether. The extracts were dried over anhydrous sodium sulphate. When ether was distilled off the white solid obtained had m.p. 201-212°

(soft 180°). When crystallized from methanol it had m.p. 197-201° with softening at 88°. A second crystallization from methanol gave flat prisms, m.p. 88-91°, as the first crop. What remained in the mother liquor was found to be phthalic acid by m.p. and mixed m.p.

Attempt to prepare the acetyl derivative of the diol via its potassium salt

The potassium salt was prepared as above, and the mixture was transferred into a solution of freshly distilled acetyl chloride (2.5g., 2 mols.) in 50 c.c. benzene. This also resulted in a clear solution which was poured into ice and the two clear layers were separated. The aqueous layer was found to be acidic (probably due to acetic acid). The benzene layer was washed with water until the washings were free from acid, and dried (magnesium sulphate). The solid obtained after benzene had been removed had m.p. 82-88°. Crystallization from alcohol gave a white solid, m.p. 87-90°. Mixed m.p. with the oxepin was 82-90°. A second crystallization from the same solvent gave solid m.p. 89-92° and mixed m.p. with the oxepin was 87-92°. It was confirmed as the oxepin by its infrared absorption spectrum.

2,2'-Bis(triphenylphosphoniomethyl)biphenyl Dibromide
Preparation and use in the Wittig Reaction

2,2'-Bishydroxymethylbiphenyl
[Hall, Lesslie and Turner, J., 1950, 711]

A solution of dimethyl diphenate (38 g., 1 mol.) in sodium-dried ether (350 c.c.) was added to lithium aluminium hydride (8.5g., 1.6 mols.) in sodium-dried ether (300 c.c.), with stirring, at such a rate that the ether boiled gently under reflux. Water, then dilute sulphuric acid ($<$ 2N) were added until two clear layers were obtained. Ether was then removed on a water bath and the white solid obtained in the aqueous layer was filtered off and dried. Crude yield 33 g. It was crystallised from benzene. Yield 29 g. (95%), m.p. 112-113°. Altogether 73 g. of the diol were prepared by this method.

2,2'-Bisbromomethylbiphenyl
[Hall, Lesslie, and Turner, J., 1950,711]

2,2'-Bishydroxymethylbiphenyl (15 g., 1 mol.) was added to hydrobromic acid (48-50%, 750 c.c.) at 90°, and the mixture was boiled for 20 min. When cooled, the solid was filtered off, washed with water, and dried. Crude yield 22g. When crystallised from light petroleum (b.p. 60-80°), with addition of charcoal, it had m.p. 89-90.5°. Yield 21 g. (88%). Altogether 145g. of 2,2'-bisbromomethylbiphenyl were prepared.

2,2'-Bis(triphenylphosphoniomethyl)biphenyl Dibromide

(1) In cold benzene.

2,2'-Bisbromomethylbiphenyl (3.4 g., 1 mol.) in 30 c.c. dry benzene, and triphenylphosphine (5.24 g. 2 mols.) in 15 c.c. dry benzene were mixed at room temperature, and stirred together in a flask provided with a drying tube (calcium chloride). After one day, 1.79 g. of solid, m.p. 238°, was filtered off. The filtrate, when stirred for two more days, gave 3.02 g. of solid m.p. 238°. These two lots, when purified by dissolving in chloroform and precipitating with ether, again had m.p. 238°. The infrared spectrum showed a weak, broad band at 604cm^{-1} [C-Br absorption frequency: 600-500 cm^{-1}, Bellamy, The Infrared Spectra of Complex Molecules, London, Methuen & Co., Ltd., 1958], and its empirical formula is $C_{32}H_{28}PBr_3$. The empirical formula for the monophosphonium salt is $C_{32}H_{27}PBr_2$. However, from the evidence of the infrared spectrum (C-Br absorption frequency in 2,2'-bisbromomethylbiphenyl is 600 cm^{-1}) and the product of the subsequent reaction on it, it was concluded that this solid, m.p. 238°, was 2-bromomethyl-2'-triphenylphosphoniomethylbiphenyl bromide.

(2) In boiling benzene.

2,2'-Bisbromomethylbiphenyl (3.4g., 1 mol.) and triphenylphosphine (7 g., 2.67 mols.) were heated under reflux in dry benzene (175 c.c.) for 10 days. The solid was filtered off, washed well with benzene and light petroleum (b.p. 40-60°), and dried. Crude yield 8.75g., m.p. 277-280°. When crystallised from a mixture of alcohol and ether, it had m.p. 277-280°. A second crystallisation from a mixture of alcohol and ethyl acetate gave solid m.p. 295-298°. It was later crystallised repeatedly from this mixture of solvent until the m.p. was constant at 323-326°.

(3) In boiling xylene.

2,2'-Bisbromomethylbiphenyl (34 g., 1 mol.) and triphenylphosphine (70 g., 2.67 mols.) were dissolved separately in sodium-dried xylene, and the two clear solutions were mixed and heated, with stirring, so that the xylene boiled gently under reflux. The total volume of xylene was 1200 c.c. After 140 hrs. of continuous heating and stirring, white solid was filtered off, washed well with benzene and light petroleum (b.p. 40-60°) and dried. Crude yield 90 g., m.p. 274-280°. Crystallisation from a mixture of ethyl alcohol and ethyl acetate gave the dibromide (70g., 81%), m.p. 323-326°. [Found: C,66.1; H,5.1; Br, 17.4; P,6.8. $C_{50}H_{42}Br_2P_2$, $2H_2O$ requires C, 66.7; H, 5.15; Br, 17.7; P,6.9%. In a separate gravimetric analysis: Br, 17.7%] Altogether 124 g. of the phosphonium dibromide were prepared by this method. Heating for a shorter period, e.g. 24 hrs., gave impure product, m.p. 238°, which required several crystallisations and therefore was obtained in smaller yield.

2,2'-Bis(triphenylphosphoniomethyl)biphenyl Dipicrate

The corresponding dibromide was dissolved in hot water and mixed with 2 equivalents of hot aqueous sodium picrate solution.

Yellow precipitate was at once obtained, m.p. 206-207°. After two crystallisations from squeous alcohol it had m.p. 209-210°. [Found: C,64.3; H, 4.3; N, 7.6; P, 5.4. $C_{62}H_{46}P_2N_6O_{14}$ requires C, 64.1; H, 4.0; N, 7.2; P,5.3%].

2,2'-Bis(triphenylphosphoniomethyl)biphenyl Dicamphorsulphonate

The corresponding dibromide was dissolved in warm ethanol and silver-d-camphorsulphonate was dissolved in warm water, and the two solutions were mixed with stirring. Silver bromide came down at once and the mixture was boiled gently until the supernatant liquid was clear. The precipitate was filtered off and the filtrate was evaporated to dryness on a water-bath. The residue was soluble in alcohol, ethyl acetate, and water, but when washed with ether a white solid was obtained, m.p. 70° (decomp.). [Found: C, 69.2; H, 6.1; P, 4.9; S, 5.1. $C_{70}H_{72}O_8P_2S_2$, $3H_2O$ required C, 68.8; H, 6.4; P, 5.1; S, 5.25%]. The dicamphorsulphonate showed no mutarotation in 95% ethanol at room temperature, the first reading being taken 1½ min. after wetting with solvent, $[\alpha]^{22^\circ}_{5461}$ + 21.5° (c, 0.500).

Use of 2,2'-bis(triphenylphosphoniomethyl)biphenyl dibromide in the Wittig reaction

Reaction with acetone

1. Using solid m.p. 238° (subsequently found to be mainly the monophosphonium bromide) in alcoholic sodium ethoxide in the cold.

The phosphonium salt (0.867 g.) was dissolved in alcohol (6 c.c.) and the solution was added to the sodium ethoxide (0.08g.)

sodium in 6 c.c. alcohol). After 10 min. sodium bromide started to come down. Acetone (1 c.c.) was then added, the reaction flask was stoppered and left to stand for 3 days. Alcohol was allowed to evaporate and water was added to the residue to dissolve sodium bromide. The organic material was extracted with ether, and the extract was washed and dried. When ether was removed the residue was digested with light petroleum (b.p. 40-60°) and filtered. Light petroleum was removed from the filtrate and the residue (0.208 g.) was crystallised from aqueous alcohol and then had m.p. 95°. Three successive crystallisations from the same solvent raised the m.p. to 97.5 - 98°. This solid was found to be phenanthrene by its infrared and ultraviolet absorption spectra; mixed m.p. with pure specimen (m.p. 99°) was 98-99°. [Found: C,93.8; H, 6.2. Calculated for $C_{14}H_{10}$: C, 94.35; H, 5.65%].

2. Using solid m.p. 238° in boiling alcoholic sodium ethoxide.

The quantities of the phosphonium salt, sodium ethoxide and acetone were the same as in the above experiment. The mixture was left to stand for 2 days, and was then heated under reflux, with more acetone, for 17 hrs. and then left overnight. Alcohol was removed, water was added and the mixture was extracted with ether. On distilling the dried ethereal extract a yellow liquid (b.p. 66-76°/4m.m.) and a solid (b.p. 156-166°/3.5m.m.)

were obtained. The solid was crystallised twice from aqueous alcohol and had m.p. 97-98°; its infrared absorption spectrum was identical with that of phenanthrene. The infrared absorption spectrum of the liquid showed a conjugated carbonyl peak at 1695 cm^{-1}. The liquid decolourised bromine water.

3. Using solid m.p. 278° (subsequently found to be a mixture of the monophosphonium and diphosphonium bromide) in boiling alcoholic sodium ethoxide.

The phosphonium salt (2.88g.) in alcohol (30 c.c.) was added to the sodium ethoxide (0.15 g. sodium in 50 c.c. alcohol) and dried acetone (5 c.c.), and the mixture was heated under reflux for 4 days. The alcohol was distilled off, water was added, and the organic material was extracted with ether. The dried ethereal extract was distilled, and a pale yellow liquid, b.p. 114°/6 m.m., was obtained. A darker liquid in the distilling flask would not distil at 200°/6m.m. The distillate obtained, 0.881g., was unsaturated (bromine water). Its infrared absorption spectrum showed a conjugated $C = O$ peak at 1698 cm^{-1}, a very strong peak at 1667 cm^{-1}, $C = C$ conjugated with aromatic ring at 1634 cm^{-1}, aromatic $C = C$ at 1575, 1477, and 1451 cm^{-1}, a two strong peaks at 1435 and 1379 cm^{-1}, medium peaks at 1299 and 1247 cm^{-1}, weak peaks at 1176 and 1140 cm^{-1}, a biphenyl peak at 1008 cm^{-1}, weak peaks at 900.9 and 887.6 cm^{-1}, and aromatic substitution peaks at 755 and 730 cm^{-1} (disubstituted).

Its empirical formula was $C_{29}H_{34}O_2$.

This yellow liquid was hydrogenated at room temperature with platinum oxide as catalyst, for 3 hrs. The carbonyl frequency of the product shifted to a higher value (1704 cm^{-1}) showing that the C = O group was no longer in conjugation and the double bond must be saturated. The biphenyl and the substitution peaks were still present. The infrared spectrum of the product did not change when it was hydrogenated for a further 5 hrs.

Reaction with benzaldehyde

1. In boiling alcoholic sodium ethoxide.

The phosphonium dibromide (m.p. 323°) in alcohol (4.5 g., 1 mol. in 50 c.c.) was added to the sodium ethoxide (0.46 g. sodium, 4 mols., in 50 c.c. alcohol) and freshly distilled benzaldehyde (21g., 4 mols.). The mixture was heated under reflux for 19 hrs. A tarry substance clung to the side of the reaction flask below the liquid surface. Alcohol was distilled off, water was added and the whole extracted with ether. The tarry substance did not go up in either the aqueous or ethereal layer. Ether was removed from the dried extract and the dark red residue (8.296 g.) was dissolved in 250 c.c. benzene and put through a column of silica-gel. It was eluted with a mixture of benzene and 10%, 20, 40, 60 and 80% methyl alcohol respectively, and finally 100% methyl alcohol. Only brown viscous substances were obtained in all fractions.

2. In ethereal phenyl-lithium.

The freshly distilled bromobenzene (3.1 c.c., 4 mols.) was added gradually to the finely cut lithium (0.9 g., 8 mols.) in sodium-dried ether (50 c.c.) contained in a 3-necked flask in an atmosphere of nitrogen. The mixture was stirred mechanically. At the end all lithium was dissolved. The finely powdered phosphonium dibromide (12.97 g., 1 mol.) was added to the phenyl lithium in solid form. The mixture turned orange-red and the stirring was continued for 10 min. after the end of the addition of the dibromide. The freshly distilled benzaldehyde (5 c.c., in excess of 4 mols.) was added gradually and the mixture was kept stirring for 4½ hrs. during which time the mixture gradually went paler and was colourless in the end. Some ice was then added but there was no vigorous reaction so water was used. A white solid between the aqueous and ethereal layers was filtered off, dried and had m.p. 296-299°. Its infrared absorption spectrum was identical with that of the starting material, and the weight recovered was 10 g. (78%). The ethereal extract of the filtrate contained benzaldehyde.

3. In ethereal _n_-butyl-lithium.

_n_-Butyl chloride was prepared [_Org_. _Syn_. Coll. Vol. 1, 142] in the fume cupboard. The sticks of zinc chloride (41 g., 2mols.) were crushed and placed in a 250 c.c. flask and concentrated hydrochloric acid (30 c.c., 2 mols.) was added quickly. The flask was lightly stoppered and cooled under the tap to prevent loss of hydrogen chloride. It was gently shaken until all the zinc chloride had dissolved. n-Butyl alcohol (15 c.c., 1 mol.) was added to this solution; the flask was attached to a vertical double-surfaced condenser at the top of which there were a thermometer and an outlet to a downward condenser. To this latter end was attached a 2-necked 250 c.c. flask connected to a 100 c.c. flask via an adaptor carrying a calcium chloride tube. The first receiving flask was cooled in an ice-bath. The reaction flask was heated in an oil-bath at 150°; the solution started to boil at 120° and n-butyl chloride began to distil. The temperature in the first condenser was controlled at 75-80°, by slow stream of water (only half-condenser full of water was needed). The reaction took 1½ hr. and n-butyl chloride was collected in the first receiver only. The reaction was finished when no more oily drops could be seen in the reaction flask. The distillate was washed with cold water, cold concentrated sulphuric acid, water, and finally 10% sodium carbonate solution, and was dried over calcium chloride. It was then distilled and the fraction boiling at 75.5-77.5° was collected. Yield 11 g. (79%).

The lithium (0.84g., 8 mols.) was pressed into a wire form and cut straight into the 3-necked reaction flask previously flushed out with oxygen-free nigrogen and containing sodium-dried ether (100 c.c.). n-Butyl chloride (5.55 g., 4 mols.) was then added gradually through the dropping funnel and the reaction was stirred mechanically. When once the reaction had started, the chloride was added as fast as refluxing permitted. The addition took ½ hr. and the mixture was heated for another ½ hr. There was some lithium left in the flask so the n-butyl-lithium was decanted through a bent tube carrying some glass wool into a similar reaction flask, under the atmosphere of nitrogen.

The phosphonium dibromide (13.5 g., 1 mol.) was ground and added to the butyl-lithium in small portions, occasionally being washed down with ether. The reaction proceeded smoothly and an orange-red solid resulted soon afterwards. The stirring was continued after the end of the addition until heat of reaction subsided. The freshly distilled benzaldehyde (3.2g., 2 mols.) was then added gradually and heat of reaction was observed. When this subsided the mixture was stirred and heated for 2½ hrs. and the colour changed to very pale yellow. The solid part (triphenylphosphine oxide formed an ether-insoluble complex with lithium bromide. See Wittig and Schöllkopf, Chem. Ber., 1954, **87**, 1318) was filtered off and washed well with ether. Ether was removed from the filtrate and the solid obtained was digested with a minimum amount of ethanol. Pale yellow solid (1.54 g.) was obtained. This was crystallised from n-hexane with addition of charcoal giving 2,2'-distyrylbiphenyl. First crop 0.75 g., m.p. 123°. [Found: C, 93.9; H, 6.4; $C_{28}H_{22}$ requires C, 93.8; H, 6.2%]. Second crop 0.234 g., m.p. 119°; when recrystallised from light petroleum (b.p. $60-80^{\circ}$) it had m.p. 147°. [Found: C,93.4; H, 6.3. $C_{28}H_{22}$ requires C, 93.8; H, 6.2%]. Mixed m.p. with the first crop was $145-146^{\circ}$. Total yield of these crops was 22%.

When the experiment was repeated on the same scale, the first two crops obtained from n-hexane had m.p. $144-146^{\circ}$ (0.315g. and 0.181g. giving a combined yield of 15%), and there was no low melting product. Both crops were unsaturated to tetranitromethane.

To investigate these melting points the following experiments were carried out:

(a) The low melting product (123°) was dissolved in n-hexane and seeded with the high melting one (147°). The resulting crystals had m.p. $146-147^{\circ}$.

(b) The high melting product was dissolved in n-hexane and seeded with the low melting one. The resulting crystals had m.p. $147-148^{\circ}$.

(c) The low melting product was recrystallised from n-hexane and had m.p. $146-147^{\circ}$.

(d) The melting point of the low melting one, taken one month later, was found to be $146-147.5^{\circ}$.

The infrared absorption spectra of the low melting product obtained immediately after m.p. determination, of the high melting product, and that of the low melting product on standing, are all identical.

4. Catalytic hydrogenation of 2,2'-distyrylbiphenyl.

0.7133 G. of the unsaturated hydrocarbon was dissolved in 150 c.c. ethyl acetate, and 0.1324 g. of platinum oxide catalyst was added. The mixture was hydrogenated at room temperature, 65 lbs./in.^{2} pressure, for $5\frac{1}{2}$ hrs. After being left to stand overnight, the mixture still gave a slight yellow coloration with tetranitromethane solution. So the mixture was filtered, the catalyst was washed with ethyl acetate, and the filtrate was put back into the reaction flask together with a fresh lot of catalyst (0.1836 g.). This mixture was hydrogenated for 7 hrs. under the same temperature and pressure. The solution was filtered and the filtrate gave a negative test with tetranitromethane. Ethyl acetate was then removed and pale yellow liquid of 2,2'-diphenethylbiphenyl (0.6002 g., 92.5%) was obtained. [Found: C, 92.4; H, 7.7, $C_{28}H_{26}$ requires C, 92.8; H, 7.2%]. The infrared absorption spectrum showed the CH_2 peaks at 2915, 2849 and 1449 cm^{-1}, no unsaturation peaks, the biphenyl peak at 1008 cm^{-1} and the aromatic substitution peaks at 754.3 and 695.5cm^{-1}. The ultra-violet absorption spectrum in cyclohexane showed λ_{max} 300, ε_{max} 3400.

As this product had not been distilled the experiment was repeated using 0.6058 g. of the unsaturated hydrocarbon, 150 c.c. ethyl acetate, 0.314 g. of the catalyst, 60 lbs./in.^{2} pressure, room temperature, and 21½ hrs. time. Ethyl acetate was distilled from the filtrate at ordinary pressure, the remainder was distilled under reduced pressure, b.p. $45^\circ/38$m.m. - $55^\circ/34$m.m. The analysis and the infrared spectrum showed that the benzene rings in the 2,2'-chains had also been hydrogenated to give 2,2'-bis(β-cyclohexylethyl)-biphenyl. [Found: C,88.85; H, 10.1. $C_{28}H_{38}$ requires C, 89.7; H, 10.2%]. The infrared spectrum showed the CH_2 peaks at 2907, 2841 and 1445cm^{-1}, the biphenyl peak at 1006cm^{-1} and the aromatic substitution peak at 749.7cm^{-1} only. The 2000-1660cm^{-1} region gave a different pattern from that of the previous product (2,2'-diphenethylbiphenyl) and the aromatic C = C peaks at 1597 and 3018cm^{-1} were also weaker in intensity. It was then concluded that during the extra 9 hrs. the benzene rings at the end of the chain had been hydrogenated.

Reaction with acetaldehyde

The *n*-butyl-lithium was prepared on the same scale as described above. The phosphonium dibromide (13.5 g.) was then added and a bright red solution resulted as before. After about 1 hr. freshly distilled acetaldehyde (5 c.c., in excess of 2 mols.) were added and a yellow solution was obtained. Heat was then applied but the colour did not go paler as in previous experiments. This yellow solid was filtered off and the filtrate was treated with a saturated solution of sodium bisulphite to remove any excess of aldehyde. The residue from ethereal extract was unsaturated to tetranitromethane. This was dissolved in 35 c.c. of benzene and put through a column of silica-gel, and eluted with light petroleum (b.p. 40-60°), followed by 1:1 mixture of methanol and light petroleum, and finally methanol. Three fractions of yellow liquid were collected, the last one being very viscous.

The first fraction (0.242 g.) was unsaturated to tetranitromethane and its infrared absorption spectrum showed the phenyl conjugated C = C peak at 1592 cm^{-1}, CH = CH at 1357, 693 and 962 cm^{-1}, all of which disappeared on hydrogenation. The biphenyl (1005 cm^{-1}) and aromatic substitution (750cm^{-1}) peaks were present both before and after the hydrogenation. The hydrogenation was carried out in presence of platinum oxide catalyst for 8 hrs. at room temperature and 70 lbs./in^2. pressure. The infrared absorption spectrum of the hydrogenated product [Found: C, 85.3; H, 10.2. $C_{18}H_{22}$ requires C, 90.7; H, 9.3%], was compared with that of 2-propylbiphenyl [API Research Project 44, Serial number 2094].

The yellow solid filtered off at the beginning was insoluble in water and dilute acid. With benzene, a yellow solution could be decanted off, and when benzene was removed, yellow needles (1.3g., m.p. 120-130°) remained. Attempts were made to crystallise it from various solvents, and from aqueous alcohol long white needles (0.5g., m.p. 155-155.5°) of triphenylphosphine oxide were obtained (mixed m.p. with genuine specimen 153°). The rest remained yellow gum.

Yellow solid, remained after decanting benzene solution off, had m.p. 200-250°.

Reaction with cyclohexanone

The n-butyl-lithium was prepared from n-butyl-chloride (7.4 g., 4 mols.) and lithium (1.12g., 8 mols.) as previously described. The phosphonium dibromide (18 g., 1 mol.) was added ½ hr. after the end of addition of n-butyl-chloride. Orange-red mixture resulted immediately. After ¾ hr. cyclohexanone (4 g., 2 mols.) were added all at once and the mixture warmed up slightly but the red colour was still present. So heat was applied and after ½ hr. the mixture turned yellow. Stirring and heating were continued for 13 hrs. and the mixture was then filtered. The solid obtained was decomposed with water and the solution extracted with ether. White solid (10.6 g., 60%), m.p. 270°, insoluble in both solvents, gave an infrared spectrum identical with that of the starting dibromide. The ethereal extract gave 3 g. (26%) of solid m.p. 135-140°, mixed m.p. with triphenylphosphine oxide 145-150°, and its infrared absorption spectrum was identical with that of Ph_3PO.

The filtrate, after removal of ether, gave pale yellow liquid which, on distillation, gave cyclohexanone (identified by its infrared spectrum) and a colourless liquid (b.p. of fraction 90-100°/4m.m.) the infrared spectrum of which showed that it contained a carbonyl group (1698 cm^{-1}), CH_2 groups (1443, 2921 and 2855 cm^{-1}). There was nothing in the regions 1660 and 800-650 cm^{-1} to indicate an aromatic substance. The residue of these two fractions could not be distilled and was then chromatographed on a silica-gel column in benzene, and eluted with 3:2 mixture benzene:methanol, methanol and finally light petroleum (b.p. 40-60°). Three fractions were collected. The first one, 0.121g., was a pale yellow, viscous liquid, unsaturated to tetranitromethane. Its infrared absorption spectrum showed two very strong bands at 1597 (phenyl conjugated $C = C$) and 1357 cm^{-1} (probably $CH = CH$, as in reaction with acetaldehyde), and a doublet at 2907 and 2841 cm^{-1} (CH_2 stretching). There were two medium bands at 1400 and 770 cm^{-1}, and two weak ones at 746 and 718 cm^{-1}. Hydrogenation of this fraction gave a product with rather poor infrared spectrum in 2000-650 cm^{-1} region, containing weak bands at 1706, 1447, 1376, 1120 and 747 cm^{-1}; the two medium peaks at 2912 and 2849 cm^{-1} were similar to those of the unsaturated material.

Preparation of 2,2'-Bis(triphenylphosphoniomethyl)-6-nitrobiphenyl Dibromide

4-Nitrophenanthraquinone

[Schmidt and Spoun, Ber., 1922, 55, 1194].

Phenanthraquinone (60g., 1 mol.) was nitrated in two batches by boiling with concentrated nitric acid (d. 1.42 g./c.c., 1800 c.c.) for twenty minutes. The cooled reaction mixture was poured into about 5 litres of ice-water. The product was filtered off, washed with water, dried in air, and boiled with 1 litre alcohol. The insoluble 2-nitrophenanthraquinone was filtered off (crude yield 33g., 47%). The filtrate was concentrated to about 400 c.c. and allowed to cool. The 4-nitrophenanthraquinone crystallised out; yield 20.8g. (29%) m.p. 170-173°. It was recrystallised from glacial acetic acid; yield 16.4 g. (24.5%) m.p. 173-174°. (1 lit. m.p. 176-177°). Altogether 51g. of pure 4-nitrophenanthraquinone were prepared by this method.

6-Nitrodiphenic acid

[Schmidt and Kämpf, Ber., 1903, 36, 3734].

[Modified according to Moore and Huntress, J. Amer. Chem. Soc., 1927, 49, 1328].

4-Nitrophenanthraquinone (12g., 1 mol.) was boiled under reflux for 1 hour with an aqueous solution of potassium dichromate (33g., 2.36 mols. in 456 c.c. water) and concentrated sulphuric acid (30.c.c.). The reaction mixture was cooled, the product was filtered off and washed well with water. It was purified by dissolving in dilute ammonium hydroxide, filtering and acidifying with dilute sulphuric acid. The 6-nitrodiphenic acid crystallised from the hot acid solution. It was recrystallised from aqueous alcohol as white plates, m.p. 252-255°, (lit. m.p. 248-250°) yield 9.5g., 71%. Altogether 45g. of 6-nitrodiphenic acid were prepared.

6-Nitrodiphenoyl dichloride

[Bell and Robinson, *J.*, 1927, 1695].

6-Nitrodiphenic acid (16g., 1 mol.) was covered with thionyl chloride (40 c.c., 65.6g., 10 mols.) and the mixture was heated under reflux for 72 hours. Excess of thionyl chloride was removed by distillation under reduced pressure under dry nitrogen. When most of the liquid had been removed, the residue was transferred to an evaporating dish and placed in a vacuum desiccator over potassium hydroxide until it went solid. Yield 20g., m.p. 75-78°. This crude product was used as such. Altogether 41g. of the acid chloride were prepared.

2,2'-Bishydroxymethyl-6-nitrobiphenyl

[T.M.Poole, Ph.D. Thesis, London, 1963].

Lithium borohydride (5g., 3.65 mols.) was dissolved at -10° in 300 c.c. sodium-dried ether, with stirring, under an atmosphere of nitrogen and then allowed to warm up to room temperature. The corresponding acid chloride (13g., 1 mol.) was added in solid form such that the temperature did not go above 27°. The reaction mixture was stirred for 1 hour, and hydrolysed with 50 c.c. water and 25 c.c. dilute hydrochloric acid. The ethereal layer was separated, and washed with 10% sodium hydroxide solution to remove any unreacted acid chloride, then with water, and was filtered through decolorising charcoal contained in a sintered glass crucible. Most of the ether was then distilled off and the residue dried on the water-bath. The yellow liquid obtained was covered with benzene and allowed to stand overnight. A solid m.p. 80° was obtained. Crude yield 8.8g. It was crystallised from benzene. Yield 7g., m.p. 85-87°. Altogether 20g. of the diol were obtained by this method.

2,2'-Bisbromomethyl-6-nitrobiphenyl

[T. M. Poole, Ph.D. Thesis, London, 1963].

The corresponding diol (10.6g., 1 mol.) was added to hydrobromic acid (48-50%, 500 c.c.) at 90°, and the mixture was boiled for 20 minutes. On cooling a solid was obtained. This was filtered off, washed with water and dried. Crude yield 15g. It was crystallised from light petroleum (b.p. 60-80°) with charcoal. First crop 8.51g., m.p. 102-103°. Second crop 1.85g., m.p. 95-97°.

Third crop 0.8g., m.p. 95°. Total yield 11.2g. (70%).

2,2'-Bis(triphenylphosphoniomethyl)-6-nitrobiphenyl dibromide

a. With solvent, using a heating mantle.

2,2'-Bisbromomethyl-6-nitrobiphenyl (1g., 1 mol.) and triphenylphosphine (2g., 2.67 mols) were dissolved separately in 50c.c. sodium-dried xylene, and the solutions were stirred mechanically in a 250 c.c., 3-necked, round-bottomed flask. Heat was then applied such that the solvent refluxed gently. In the first half hour the clear, pale yellow mixture began to go cloudy. It then changed to light, reddish brown in the second half hour. After another hour of heating and stirring the brown colour had collected as a mass at the bottom of the flask and the rest of the solution was quite clear. After 24 hours the brown mass consisting of fine solid and also sticky substance was filtered off. It was crystallised to a constant m.p. from a mixture of ethyl alcohol and ethyl acetate. Yield 0.23g. (10%), m.p. 212°. [Found: C, 62.2; H, 5.0; Br, 16.5; P, 6.2. $C_{50}H_{41}Br_2NO_2P_2$, $3H_2O$ requires C, 62.3; H, 4.9; Br, 16.6; P, 6.4%]

b. With solvent, using an oil-bath (controlled temperature).

2,2'-Bisbromomethyl-6-nitrobiphenyl(2g., 1 mol.) and triphenylphosphine (4g., 2.67 mols.) were dissolved separately in 50 c.c. sodium-dried xylene and then mixed in a 250 c.c. round-bottomed flask provided with a condenser and a calcium chloride tube. The reaction flask was then heated up slowly in an oil-bath and then the temperature was kept constantly at 140°, with occasional shaking. After 2 hours the brown mass lining the bottom of the flask appeared solid, so the clear solution was decanted off and the solid washed well with dry xylene. Crude yield 3.4 g. The filtrate on heating for another 8 hours gave 0.53 g. of the brown solid.

The first crude solid was crystallised from a mixture of ethyl alcohol and ether. First crop 0.8 g., m.p. 195°. Second crop 0.94 g., m.p. 165° (Soft 155°). The remainder was brown gum and could not be crystallised. The first crop was then recrystallised from acetone giving 0.54 g. of cream-coloured phosphonium dibromide, m.p. 256.5-257° (11%) [Found: C, 63.3; H, 5.0; Br, 16.4; P, 6.0. $C_{50}H_{41}Br_2NO_2P_2,2H_2O, (CH_3)_2CO$ requires C, 63.4; H, 5.1; Br, 15.9; P, 6.2 %] When the second crop was recrystallised from acetone it gave 0.7 g. of 2-bromomethyl-2'-triphenylphosphonio-methyl-6-nitrobiphenyl bromide, m.p. 157-160° [Found: C, 58.5; H, 4.3; Br, 23.4; P, 4.0. $C_{32}H_{26}Br_2NO_2P,\frac{1}{2}H_2O$ requires C, 58.5; H, 4.2; Br, 24.3; P, 4.7 %], i.e. the monophosphonium salt.

c. *Without solvent*, from the bisbromomethyl compound. [adapted from method by ~~Hauser, Brooks, Miles, Raymond &~~ Horner and Lingnau, *Annalen*, 1955, *591*, 135]

~~Butler, J. Org. Chem. , 1963, 28, 372~~].

2,2'-Bisbromomethyl-6-nitrobiphenyl (2.5 g., 1 mol.) and triphenylphosphine (6 g., 2.67 mols) were ground together in a mortar and then placed in a 100 c.c. bolt-head flask which was then heated in a previously heated oil-bath, the temperature of which was 190°. When the powdered mixture began to melt it was stirred with a glass rod until a hard mass was formed. After 5 minutes it was cooled, washed well (in a mortar) with xylene and filtered. Crude yield 6.5 g., m.p. 190°. It was then crystallised from acetone. Yield 4.4 g. (68%), m.p. 260°.

d. Without solvent, from the monophosphonium salt. [adapted from method by Mondon, Annalen, 1957, 603, 115].

2-Bromomethyl-2'-triphenylphosphoniomethyl-6-nitrobiphenyl bromide (0.9 g., 1 mol.) and triphenylphosphine (0.4 g., 1 mol.) were mixed and powdered together and then heated in a bolt-head flask in a previously heated oil-bath (200°) for 1 hour. The dark brown mass was cooled, dissolved in warm chloroform and passed through an alumina column. Ether was added to the collected fraction until the solution was cloudy. It was then cooled in ice and 0.22 g. of solid was obtained (17%), m.p. 250°.

Silver-(+)-camphorsulphonate

Freshly prepared silver oxide (1.2 mols.) was added to an aqueous solution of (+)-camphorsulphonic acid (1 mol.)

and kept warm for half an hour. The excess of silver oxide was filtered off, and the filtrate evaporated to dryness in a water-bath. The residue was dissolved in a minimum amount of hot distilled water and filtered to remove any precipitate of silver. The filtrate was evaporated to dryness again and used as such.

2,2'-Bis(triphenylphosphoniomethyl)-6-nitrobiphenyl Dicamphorsulphonate

The corresponding dibromide (4.37 g., 1 mol.) and silver-(+)-camphorsulphonate (2,95 g., 2 mols.) were dissolved separately in aqueous alcohol, warmed, and filtered into the same beaker with stirring. The mixture was then boiled gently for half an hour, cooled, and the silver bromide precipitate filtered off. The filtrate was evaporated to dryness on a water-bath. Crude yield 5.75 g. It was crystallised from a mixture of 100 c.c. acetone and 120 c.c. ether. Each crop was then dried in a vacuum desiccator. First crop 3.88 g., m.p. 172°, $[\alpha]_{5461}^{22^\circ}+21^\circ$(c,1.0). Second crop 0.35 g., m.p. 168°, $[\alpha]_{5461}^{22.6^\circ} + 21^\circ$ (c, 1.0), both in 95% ethanol.

The first crop was recrystallised from a mixture of 65 c.c. acetone and 90 c.c. ether, giving 2.46 g. of solid m.p. 170-172°. [Found: C, 67.2; H, 6.2; P, 4.8; S, 5.1; $C_{70}H_{71}NO_{10}P_2S_2$, $2H_2O$ requires C, 67.3; H, 6.1; P, 5.0; S, 5.1 %] $[\alpha]_{5461}^{22^\circ}+ 21^\circ$ (c, 1.0), $[\alpha]_{5461}^{50^\circ}+ 21^\circ$ in

95% ethanol; $[\alpha]^{94.5^{\circ}}_{5461} + 21^{\circ}$ (c, 1.0) in dimethyl-formamide. 2 G. of this solid was recrystallised from ~ 5 c.c. of acetone and the solid obtained (1.686 g.) had a rotation: $[\alpha]^{21.9^{\circ}}_{5461} + 20.5^{\circ}$, $[\alpha]^{50^{\circ}}_{5461} + 20.5^{\circ}$ (c, 1.0), which were unchanged after 40 hours.

2,2'-Bis(triphenylphosphoniomethyl)-6-nitrobiphenyl Di-iodide

The corresponding dicamphorsulphonate was dissolved in aqueous alcohol and a saturated solution of potassium iodide was added. After a while yellow precipitate came down. When precipitation was complete the solid was filtered off and dried in a vacuum desiccator. It was then crystallised from alcohol and had m.p. 280-282°. [Found: C, 58.3; H, 4.25; I, 25.6; P, 6.0, $C_{50}H_{41}I_2NO_2P_2,H_2O$ requires C, 58.8; H, 4.2; I, 24.8; P, 6.1 %]

2,2'-Bis(triphenylphosphoniomethyl)-6-nitrobiphenyl Dipicrate.

The corresponding dibromide was dissolved in alcohol, and an aqueous solution of sodium picrate was added, and stirred. After a few seconds, dark red gum resulted. The supernatant liquid was decanted and the gum was dissolved in alcohol. After some time it would not crystallise, so it was evaporated slowly to dryness. Intense yellow needles, m.p. 140° (decomp.) remained. These were crystallised from alcohol, giving the dipicrate m.p. 135-136° (decomp). [Found: C, 61.7; H, 4.2; N, 8.2; P, 4.8. $C_{62}H_{45}N_7O_{16}P_2$ requires C, 61.7; H, 3.8; N, 8.1; P, 5.1 %]

Silver-(+)-α-bromocamphor-π-sulphonate

(+)-Ammonium-α-bromocamphor-π-sulphonate (22 g., 1 mol.) was dissolved in warm water (60-70°) which was added gradually, with stirring, to obtain a saturated solution (about 90 c.c. used). A warm concentrated solution of silver nitrate (11.5 g., 1 mol., dissolved in 5 c.c. water) was then added with stirring. The suspension was cooled in ice, filtered in the dark room and dried over calcium chloride in a desiccator, also in a dark room. It was then crystallised from hot water. Yield 7 g., m.p. 259-262°.

2,2'-Bis(triphenylphosphoniomethyl)-6-nitrobiphenyl Dibromocamphorsulphonate

The corresponding iodide (1.79 g., 1 mol.), previously obtained from the camphorsulphonate, was dissolved in warm ethanol, and silver-(+)-α-bromocamphor-π-sulphonate (1.55 g., 2 mols) was dissolved in warm water, and the two solutions were mixed, with stirring, and then boiled gently for 1 hour. The silver iodide was filtered off, and the filtrate was evaporated to dryness on a water-bath. Crude yield 2.532 g. The gum was then crystallised from a minimum amount of ethyl acetate. First crop 1.526 g., m.p. 168° (decomp.) after drying in a vacuum desiccator overnight. [Found: C, 58.6; H, 5.4; Br, 11.3; P, 4.55; S, 4.55. $C_{70}H_{69}Br_2NO_{10}P_2S_2$, $3H_2O$ requires C, 59.0; H, 5.3; Br, 11.2; P, 4.35; S, 4.6 %]

Preparation of carbomethoxymethylenetriphenylphosphorane and its subsequent reactions with acetone, benzaldehyde, acctophenone, 2,2'-diacetylbiphenyl and biphenyl-2,2'-dialdehyde

Carbomethoxymethyltriphenylphosphonium bromide

[Isler, Gutmann, Montavon, Rüegg, Ryser, and Zeller, Helv. Chim. Acta , 1957, 40, 1242]

Triphenylphosphine (39.3 g., 1 mol.) was dissolved in benzene (200 c.c.) and methyl bromoacetate (23 g., 1 mol.) was added, with stirring, during 5 minutes. The phosphonium bromide began to crystallise out during the addition. The reaction mixture was stirred mechanically for 2 hours, the solid was filtered off, washed well with benzene and light petroleum (b.p. 40-60°) and dried. Yield 40.5 g., m.p. 164-164.5°. The filtrate was put back in the reaction flask and stirred for 2 hours, another 9 g. of the solid m.p. 163-164° were obtained. The filtrate was found to give more white solid on stirring for another hour (12 g., m.p. 163-164°). Total yield 60 g. (96%).

The experiment was repeated with 6 hours stirring and the same yield of the phosphonium bromide was obtained. [Isler *et al*. gave m.p. 163°]

Carbomethoxymethylenetriphenylphosphorane

[Isler, Gutmann, Montavon, Rüegg, Ryser, and Zeller, *Helv. Chim. Acta*, 1957, *40*, 1242]

The corresponding phosphonium bromide (41.5 g., 1 mol) was dissolved in cold water (1 litre) and sodium hydroxide solution (10%) was added dropwise, with stirring, until the solution was alkaline to phenolphthalein (about 50 c.c. of the alkali required). White precipitate came down during the addition. It was filtered off, washed with water, and dried. Yield 30 g. (90%), m.p. 163°. It was crystallised from hot ethyl acetate by addition of light petroleum (b.p. 40-60°) and then had m.p. 170-172°. [Isler *et al.* gave m.p. 162-163°]. Altogether 60 g. of the phosphorane were prepared by this method.

Attempted reaction between the phosphorane and acetone

Carbomethoxymethylenetriphenylphosphorane (3.5 g., 1 mol.) in alcohol (50 c.c.) and acetone (2 c.c., in excess of 1 mol.) were heated under reflux for 10 hours. Alcohol was removed until white solid started to appear. This solid was filtered off. Yield 1.4 g., m.p. 155°. The remaining alcohol was distilled off from the filtrate and left a residue of a white solid, m.p. 156-157°. Both were identified as triphenylphosphine oxide by its infrared spectrum (P = O band, 1189 cm^{-1}). No volatile product was isolated.

Reaction between the phosphorane and benzaldehyde

The phosphorane (4 g., 1 mol) in alcohol (50 c.c.) and freshly distilled benzaldehyde (1.27 g., 1 mol.) were heated under reflux for 6 hours. Alcohol was then removed and the residue was digested with light petroleum (b. p. 40-60°). White solid was obtained, yield 3.12 g., m.p. 155-156° corresponding to that of triphenylphosphine oxide (94% yield) as confirmed by mixed m.p. and infrared absorption spectrum. After removal of the solvent, the filtrate was distilled and a colourless liquid was collected between 124°/ 2 mm. and 130°/ 9 m.m. Yield 1.33 g. (69%). After standing overnight part of the liquid solidified. The solid was filtered off, m.p. 32-35° corresponding to that of methyl <u>trans</u>-cinnamate; this was also confirmed by the infrared absorption spectrum (CH = CH band, 1312 cm^{-1} and 979.5 cm^{-1} with absence of 694.4 cm^{-1} band). The liquid separated was found, by the infrared absorption spectrum, to be the <u>cis</u> ester (CH = CH <u>cis</u> band, 694.4 cm^{-1}; see Bellamy, Infrared spectra of complex molecules, Methuen, London, 1958). Both <u>cis</u>- and <u>trans</u>- esters, on hydrolysis with alcoholic potash, gave acid, m.p. 132° alone or when mixed with cinnamic acid, their infrared absorption spectra were identical.

Attempted reaction between the phosphorane and acetophenone

a. In benzene

Carbomethoxymethylenetriphenylphosphorane (10 g., 1 mol.) in sodium-dried benzene (150 c.c.) and acetophenone (3.6 g., 1 mol.) were heated under reflux for 4 hours under an atmosphere of nitrogen. When the solution was cooled, unchanged phosphorane, m.p. 169-170°, separated. It was then dissolved in 100 c.c. sodium-dried benzene and heated under reflux with the same quantity of acetophenone for 9 hours. After cooling, the phosphorane was again obtained.

b. In alcohol

The phosphorane (4 g., 1 mol.) in alcohol (50 c.c.) and acetophenone (1.4 g., 1 mol.) were heated under reflux for 50 hours. Alcohol was removed and light petroleum (b.p. 40-60°) was added to the residue. Triphenylphosphine oxide, m.p. 153-155° (2.5 g.), was obtained. The filtrate was dried and distilled; after removal of the solvent, acetophenone was collected at 70°/ 6 m.m. (Confirmed by its infrared spectrum). The solid remaining in the flask was shown to be triphenylphosphine oxide by m.p. and infrared spectrum. No other product could be isolated.

c. In alcohol with the phosphorane generated in solution.

0.3 G. sodium was dissolved in 50 c.c. alcohol. A solution of 5.2 g. of the corresponding phosphonium bromide in 40 c.c. alcohol was added. Slowly the yellow colour of the latter faded and white precipitate of sodium bromide appeared. 1.5G. of acetophenone in 5 c.c. alcohol were added meanwhile. The mixture was left to stand for 2 days by which time it appeared orange with some white solid at the bottom. Removal of the alcohol left a residue (including the sodium bromide) which could not be distilled.

Preparation of biphenyl-2,2'-dialdehyde

I. From o-Iodobenzaldehyde

a. *o*-Iodobenzaldehyde from *o*-iodoaniline.

[Adapted from method by Beech, *J.*, 1954, , 1297, for preparation of *o*-nitrobenzaldehyde from *o*-nitroaniline].

A 10% solution of formaldoxime for use in conjunction with 0.25 mole of *o*-iodobenzenediazonium chloride was prepared by heating paraformaldehyde (11.5 g.) with hydroxylamine hydrochloride (26.3 g.) in water (170 c.c.) until a clear solution was obtained. Hydrated sodium acetate (51 g.) was then added and the mixture boiled gently under reflux for 15 minutes. It was cooled ($10-15^{\circ}$), and copper sulphate (12.5 g.), anhydrous sodium sulphite (2 g.), and sodium acetate (165 g.) in water (180 c.c.) were added. The solution was now ready for the diazonium salt.

A solution of o-iodobenzenediazonium chloride was prepared from o-iodoaniline (54.75 g.), concentrated hydrochloric acid (23 g. in 70 c.c. of water) and sodium nitrite (17.5 g. in 25 c.c. of water) at 0-2°. It was made neutral towards Congo red paper by addition of hydrated sodium acetate, and was then introduced below the surface of the formaldoxime solution, with stirring. The mixture was stirred for another hour. Dilute hydrochloric acid was added until the mixture was acid towards Congo red. It was then left to stand overnight. The clear liquid was decanted off and the tarry oxime that remained was boiled gently under reflux together with an aqueous solution of iron alum (250 g.) for 1 hour. The mixture was steam-distilled and the distillate extracted with ether. After ether had been removed the residue was shaken with a saturated solution of sodium metabisulphite, and water at 50° was added. The cooled solution was extracted with ether for non-aldehydic product. The aqueous bisulphite solution was made alkaline towards Titan yellow by addition of 10% sodium hydroxide solution. The aldehyde which separated as an oil was taken up in ether; the ethereal solution was washed and dried, and the ether was removed. Yield 9 g. (15%).

A similar preparation gave a yield of 8.6 g. Both were distilled together under reduced pressure, b.p.

110°/7 m.m. - 120°/ 6 m.m. *o*-Iodobenzaldehyde solidified on cooling, m.p. 57-59°. Yield 15 g.

b. *o*-Iodobenzaldehyde from *o*-Iodobenzoic acid [Rapson and Shuttleworth, *J.*, 1941, , 487]

o-Iodobenzoic acid (62 g., 1 mol.) and thionyl chloride (31 c.c., 1.7 mols.) were heated together under reflux for 8 hours. The excess of thionyl chloride was distilled off under reduced pressure, and the residue solidified on cooling, giving *o*-iodobenzoyl chloride, yield 65. 5 g. This was dissolved in dry benzene (50 c.c. dried over calcium chloride) and cooled in ice. A solution of aniline (58 g., 2.5 mols.) in dry benzene (25 c.c.) was added gradually with shaking. A yellow precipitate appeared immediately. The solid was filtered off, washed with benzene until the washings were colourless, and finally with light petroleum (b.p. 40-60°), giving a white precipitate of *o*-iodobenzanilide. Crude yield 88 g. It was crystallised from aqueous alcohol. Yield 60 g. (75%), m.p. 140-142°. Some aniline hydrochloride was obtained in the mother liquor.

The anilide was suspended in dry toluene (60 c.c.) and heated under reflux with phosphorus pentachloride (37.5 g.) on a water-bath until no more hydrogen chloride was evolved (about 3 hours). Toluene and phosphorus oxychloride were removed by distillation under reduced pressure. A solution of anhydrous stannous chloride (50 g., prepared by stirring freshly distilled acetic anhydride with half its weight of hydrated stannous chloride) in ether (100 c.c.), saturated with dry hydrogen chloride, was poured onto the residue to which a small amount of dry ether had already been added. Yellow solid was produced in clear ethereal solution and heat evolved kept the reaction going for a while. It was heated under reflux on a water-bath for 2 hours, using an efficient condenser; orange-red solid resulted. After standing overnight, ether was decanted off, the solid was poured into water and the mixture was steam-distilled. Pale yellow oily drops in the distillate solidified on cooling, giving 11.2 g. (19%) of *o*-iodobenzaldehyde, m.p. 57-59°. Altogether 44 g. of the aldehyde were prepared by this method.

c. Biphenyl-2,2'-dialdehyde

[Rapson and Shuttleworth, *J.*, 1941, , 487]

o-Iodobenzaldehyde (32 g.) was placed in a large boiling tube provided with a cork carrying a nitrogen inlet, a stirring thermometer and an outlet; the tube had been previously flushed out with nitrogen. A small amount of copper bronze was added and the tube was placed in a metal-bath at 145°. The reaction mixture was continually stirred under the atmosphere of nitrogen while the temperatures inside and outside the tube went up gradually. After about 20 minutes, when the temperature of the metal-bath was 190°, the temperature inside the tube was observed to go up suddenly to 210°, and remained there for 3 - 4 minutes. More copper bronze was added when the temperature of the mixture started to come down. The reaction finished when addition of copper bronze did not increase the temperature; 12 g. of copper were used and total time taken was 50 minutes.

The reaction mixture was then extracted with boiling toluene and filtered through a preheated Buchner funnel. Care was taken so as not to let much air come into contact with the product. Toluene was distilled off from the filtrate under reduced pressure, a little o-iodobenzaldehyde followed, and then the product was obtained in the form of yellow liquid, yield 9.4 g. (69%), b.p. 161-168°/ 3 m.m. It was then left to stand in a partly evacuated desiccator for 3 days and solid was obtained, m.p. 56-59°.

It was dissolved in a minimum amount of dry ether (50 c.c.), and light petroleum (b.p. 40-60°, 150 c.c.) was gradually added with stirring and scratching; pale yellow crystals started to appear. The flask was cooled in ice-water and yellow crystals were obtained. These were collected on a sintered glass funnel and dried. Yield 6.65 g. (49%), m.p. 61-62°. The filtrate was cooled in ice, and a second crop (0.2 g., m.p. 58-60°) was obtained.

The first crop was recrystallised from aqueous ethanol (20 c.c. warm absolute alcohol, 10 c.c. warm water). The colour did not change. Yield 5.8 g., m.p. 61-62° (43%) [Rapson and Shuttleworth gave m.p. 63°].

II. <u>From o-bromobenzaldehyde</u>

a. In dimethylformamide

[Kornblum and Kendall, J. Amer. Chem. Soc., 1952, 74, 5782].

o-Bromobenzaldehyde (20 g.) and dimethylformamide (100 c.c.) were heated, under an atmosphere of nitrogen, in a metal-bath at 160°. Half of the copper bronze (10 g.) was added; the mixture was stirred mechanically (Herschberg-type stirrer) and the temperature was maintained at 165° such that the solvent boiled gently under reflux. After 4 hours, the other half of the copper bronze was added. At the end of the 8-hour period the bath was removed and the reaction mixture was cooled to room temperature overnight, still under nitrogen. The next day it was poured into 1½ L. of water; a milky solution was obtained and most of the copper sank to the bottom. The solid was filtered quickly and dried in a desiccator. Both solid and filtrate were extracted with benzene and the extracts were combined, dried and distilled. The fractions collected were benzene, bromobenzaldehyde at 80-100°/4 m.m. (8.62 g.) and the dialdehyde at 120°/ 4 m.m. (0.4 g.).

As only half of the bromobenzaldehyde had reacted the experiment was re-peated with 30 hours heating and with only 50 c.c. of dimethylformamide. Similar procedure was followed in the working up. Only a little of the bromobenzaldehyde was obtained in the distillate. The next fraction (7.45 g.) had b.p. 160°/ 3 m.m. to 180°/ 3 m.m. It was redistilled and collected between 160°/ 3 m.m. and 170°/3 m.m. The solid obtained (6.33 g.) was crystallised from a mixture of dry ether and light petroleum (b.p. 40-60°). First crop (0.45 g.), m.p. 129-130.5°, later confirmed to be the ε-lactone of the corresponding hydroxy acid [2-Hydroxymethyl-2'-carboxybiphenyl, see Kenner and Turner, *J.*, 1911, 2101; m.p. of lactone given there was 132°; the infrared absorption spectrum of this compound showed C = O band at 1724 c.m.$^{-1}$, = C-O-band at 1274 c.m.$^{-1}$, and -C-O-band at 1110 c.m.$^{-1}$]. Second crop (0.5 g.), m.p. 54-55°, was the dialdehyde, together with an unidentified intense yellow oil.

b. Without solvent

o-Bromobenzaldehyde (20 g.) was placed in a large test-tube previously filled with nitrogen. A little copper bronze (out of total 20 g.) was added and the tube was placed in the metal-bath at 140°. The reaction mixture was stirred continuously under nitrogen and the reaction started when the temperature in the bath was 200°, while that inside the tube went up to 212°. After about 6 minutes, more copper was added and the temperature inside the tube went up to 225° while that outside was 216°. This time the higher temperature remained for 10 minutes. After that addition of copper did not elevate the temperature inside. Heating and stirring was continued at this temperature for ½ hour. The reaction mixture was then cooled to 120°, extracted with boiling toluene, and filtered. Toluene was removed from the filtrate, and the remainder was distilled under reduced pressure. Some bromobenzaldehyde was recovered (0.5 g.) and the dialdehyde was collected between 160°/ 3 m.m. and 170° / 2 m.m. The residue was again intense yellow oil which was not distilled. The crude dialdehyde was crystallised from a mixture of dry ether and light petroleum (b.p. 40-60°), yield 1.97 g. (17%), m.p. 53-55°.

III. From phenanthraquinone

a. trans-9,10-Dihydroxy-9,10-dihydrophenanthrene.

(i) In tetrahydrofuran

Tetrahydrofuran was purified by allowing it to stand over potassium hydroxide (pellets) overnight, then distilling it from lithium aluminium hydride and keeping it in a dark container.

Phenanthraquinone was first dried over phosphorus pentoxide. It was then dissolved in tetrahydrofuran (4 g., 1 mol., in 200 c.c.) and added to the lithium aluminium hydride in tetrahydrofuran (1 g., 3 mols., in 100 c.c.) in a 3-necked round-bottomed flask. The mixture became warm but the reaction was not vigorous. Where the two solutions were in contact a green substance was formed which then decomposed to give a darker yellow substance than the quinone itself. The mixture appeared green. The addition took half an hour. The mixture was then heated under reflux for 3 hours, cooled, and water was added. Part of the mixture became dark red and this layer stayed on top. When dilute sulphuric acid (2 N) was added this layer disappeared, and a clear, orange-red solution was obtained. Excess of water was now added in an attempt to precipitate the product and any unreacted quinone. The total volume was $2\frac{2}{3}$ l. After standing overnight, crystalline solid was filtered off. Yield 2.54 g. This was recrystallised from benzene; 1st crop 0.56 g., m.p. 187-188°; 2nd crop gave yellow crystals. These together with more yellow solids collected from the filtrate was made into a bisulphite compound of the quinone, and the quinone recovered was 0.84 g. The ethereal extract from the bisulphite solution gave 0.72 g. more of the required product. The total yield was 15%. More yellow solid collected from the original filtrate had m.p. 206° and was the unreacted quinone.

When the experiment was repeated with less solvent (half as much) and much more lithium aluminium hydride (7 mols., 2.5 g.), the reaction did not improve and phenanthraquinone was recovered almost quantitatively.

(ii) In ether

[Booth, Boyland, and Turner, *J.*, 1950, 1188]

The experiment was first performed using a Soxhlet apparatus. The lithium aluminium hydride (1 g., 3 mols.) was placed in sodium-dried ether and the quinone (4 g., 1 mol.) was extracted for 5 hours. Water (45 c.c.) and dilute sulphuric acid (150 c.c.) were added, the aqueous layer was extracted with ether, and the combined ethereal layer and extracts was washed with brine and three times with 2N-sodium hydroxide solution, and then dried (sodium hydroxide pellets). Green substance collected at the bottom of the flask. When it was filtered and ether was removed from the filtrate 0.8 g. of solid, m.p. 169-170°, was obtained. First crystallisation from benzene gave 0.25 g., m.p. 175°. Second crystallisation from toluene gave 0.19 g., m.p. 189° (5%). 3.1 G. of the quinone were left in the Soxhlet thimble.

The experiment was then repeated without the Soxhlet. The lithium aluminium hydride in sodium-dried ether was stirred mechanically while the quinone was added in solid form, occasionally being washed down with ether. After the addition the mixture was heated under reflux for 4½ hours, with stirring, and cooled. Water (50 c.c.) and dilute sulphuric acid (50 c.c.) were added. When all the excess of lithium aluminium hydride had been decomposed the aqueous layer was grey and the ethereal layer yellow. But when more ether was added, with shaking, green solid was formed, and more so when the mixture was transferred to a bigger container. This green solid was decomposed by the acid and more ether was added to dissolve the yellow substance formed. When the ethereal layer was clear it was separated, the aqueous layer was extracted with ether, and the combined ethereal layer and extract was dried over sodium hydroxide. Green substance was seen to collect at the bottom of the flask again. When ether was removed, 3.58 g. of solid was obtained. Crystallisation from benzene gave 1.97 g., m.p. 193°; 2nd crop 0.42 g., m.p. 189°. Total yield 2.39 g. (59%). It was found that the best yield was obtained when the volumes of the aqueous layer and ethereal layer were about the same. Altogether 80 g. of the diol were prepared by this method, some on a larger scale.

b. Biphenyl-2,2'-dialdehyde

[Criegee, Marchand, and Wannowius, Annalen, 1942, 550, 99]

trans-9,10-Dihydroxy-9,10-dihydrophenanthrene (2.12 g., 1 mol.) was suspended in 50 c.c. dry benzene and stirred mechanically in a 250 c.c., 3-necked flask. Lead tetraacetate (4.43 g., 1 mol.) was then added in the solid form, and the mixture stirred for 2 hours. When the reaction had finished, white solid of lead diacetate collected at the bottom of clear yellow solution. This was filtered off and the filtrate was distilled under reduced pressure. The dialdehyde was collected at 164-174°/ 3.m.m. as a yellow oil which solidified on cooling, giving 1 g. of solid m.p. 58° (50%). Altogether 37 g. of the dialdehyde were prepared by this method, some on a larger scale.

Reaction between the phosphorane and biphenyl-2,2'-dialdehyde

Carbomethoxymethylenetriphenylphosphorane (15.9 g., 2 mols.) and biphenyl-2,2'-dialdehyde (5 g., 1 mol.) were heated under reflux in dry toluene ($CaCl_2$) for 16 hours. Toluene was removed and the residue then quickly solidified. To separate the mixture it was dissolved in toluene and put through a column of silica-gel, and eluted with 50% solution of methanol in toluene, and then with 100% methanol.

1. From the methanol/toluene eluate, 15.64 g. of solid m.p. 140-145° were obtained. The solid was dissolved in benzene and put through a column of silica-gel; but this did not effect the separation, so it was put through a column of alumina and two fractions were collected:

Fraction 1: 9.05 g. of solid, m.p. 108-128°, were obtained. It was crystallised from light petroleum (b.p. 80-100°): 1st crop, needles, m.p. 148-149°, 3.93 g.; 2nd crop, prisms, m.p. 118-119°, 1.84 g.; 3rd crop, prisms, m.p. 106°, 0.72 g.

Fraction 2: 3.68 g. of solid m.p. 145-148° were obtained. It was crystallised from light petroleum (b.p. 80-100°): 1 st crop, needles, m.p. 148-149°, 2.9 g.; 2nd crop, prisms, m.p. 106-107°, 0.38 g.

2. From the methanol eluate, 6.29 g. of solid, m.p. 80-90°, were obtained. It was crystallised from light petroleum (b.p. 80-100°): 1st crop, needles, 0.8 g., m.p. 152-153°; 2nd crop, prisms, 2.2 g., m.p. 106-107°.

The solid m.p. 148-149° or 152-153° was found to be triphenylphosphine oxide by mixed m.p. and infrared absorption spectra. The solid m.p. 106-107° [Found: C, 75.0; H, 5.6; $C_{20}H_{18}O_4$ requires: C, 74.5; H, 5.6 %] was shown by its infrared absorption spectrum to be the <u>cis</u>-form of 2,2'-di(β-carbomethoxyvinylene)biphenyl with unsaturation peaks at 1314, 973, and 693 c.m.$^{-1}$ The solid m.p. 118-119° [Found: C, 74.0; H, 5.7. $C_{20}H_{18}O_4$ requires C, 74.5: H, 5.6 %] was shown by its infrared absorption spectrum to be the <u>trans</u>-form of 2,2'-di(β-carbomethoxyvinylene) biphenyl with unsaturation peaks at 1316 and 974 c.m.$^{-1}$

Total yield of <u>cis</u>-ester 3.3 g. (43%)

Total yield of <u>trans</u>-ester 1.84 g. (24%)

Total yield of 2,2'-di(β-carbomethoxyvinylene)-biphenyl

5.14 g. (67%)

Total yield of triphenylphosphine oxide 8.63 g. (65%)

Hydrolysis of 2,2'-di(β-carbomethoxyvinylene)biphenyl

cis-Series

The ester, m.p. 106-107°, was hydrolysed with alcoholic potash in the usual manner. The acid obtained had m.p. 291-293° [Found: C, 73.6; H, 5.1. Calculated for $C_{18}H_{14}O_4$: C, 73.5; H, 4.8%]. Its infrared absorption spectrum showed that it was a trans-acid with unsaturation peaks at 1318, and 977 c.m.$^{-1}$

trans-Series

The ester, m.p. 118-119°, was similarly hydrolysed. The acid obtained had m.p. 289-290°, and when crystallised from glacial acetic acid it had m.p. 296° [Mayer, Ber., 1911, 44, 2298 gave m.p. as 286°][Found: C, 72.8; H, 5.0. Calculated for $C_{18}H_{14}O_4$: C, 73.5; H, 4.8 %]. Mixed m.p. with above acid was also 289-290°. Its infrared absorption spectrum again showed that it was a trans-form with unsaturation peaks at 1323, and 979 c.m.$^{-1}$. This spectrum was identical with the one obtained from hydrolysis product of cis-ester.

Esterification of the acids in cold methanol and HCl.

cis-Series

The acid from cis-ester was suspended in cold methanol and dry hydrogen chloride was passed through until all the solid went into solution. The methanol was removed and white solid obtained had m.p. 115-116°. When crystallised from light petroleum (b.p. 80-100°) it had m.p. 117-118°, corresponding to that of _trans_-ester.

trans-Series

The acid from _trans_-ester was similarly treated with hydrogen chloride in cold methanol. The solid obtained had m.p. 119-120°. When crystallised from light petroleum (b.p. 80-100°) it had m.p. 119-120°. Mixed m.p. with the ester obtained in the _cis_-series was 117-118°. Mixed m.p. with the original _trans_-ester was 118-119°. The infrared spectra of this ester, of the ester obtained in the _cis_-series, and of the original _trans_-ester were all identical.

Preparation of 2,2'-diacetylbiphenyl

9,10-Dihydro-9,10-dimethylphenanthrene

[Hall, Ladbury, Lesslie, and Turner, *J.*, 1956, 3475]

All the apparatus was dried and rinsed out with sodium-dried ether just before use. Magnesium turnings (20 g., 4 mols.) were covered with 300 c.c. of sodium-dried ether in a 1-litre three-necked flask provided with a dropping funnel and two condensers. A little of the magnesium was activated in a test-tube and then added to the main bulk. Methyl iodide (53 c.c., 4 mols.) was added gradually, with shaking. After the addition, heat was applied until all the magnesium had reacted. Phenanthraquinone (42 g., 1 mol.) was added in small quantities, vigorous reaction occured each time. The addition took three quarters of an hour with solid changing from yellow to green. 250 c.c. of benzene were added and the mixture was heated under reflux for 2 hours, ether being allowed to distil off slowly through the Dufton columns. The cooled mixture was added carefully to an ice and water mixture and was kept well stirred; a dark green solution was obtained. Dilute sulphuric acid was added, with stirring, until no further colour change occurred (about 500 c.c. were used). The clear yellow aqueous layer was separated from the dark green benzene layer. Any solid between the two layers was dissolved in ether and the solution was combined with the benzene layer. The aqueous layer was extracted three times with ether. The extracts were washed twice with brine and several times with concentrated aqueous sodium hydrogen sulphite solution (50 g. in 300 c.c. of water) until the washings gave no phenanthraquinone when treated with alkali. The benzene layer was also washed with concentrated sodium hydrogen sulphite solution. The benzene and ethereal layers were combined and washed with brine (5% solution) and then distilled without being dried until the volume was about 300 c.c. On cooling, the diol separated and more was obtained from the mother liquor. It was crystallised from benzene. Yield 25 g. (54%), m.p. 165-167°. The combined bisulphite washings were treated with alkali, giving 2 g. of phenanthraquinone.

2,2'-Diacetylbiphenyl

[Hall, Ladbury, Lesslie and Turner, J., 1956, 34, 3475]

The above diol (19 g., 1 mol.) was dissolved in glacial acetic acid (190 c.c.) on a water-bath at 70°. A solution of chromic anhydride (12.5 g., 1.5 mols., in 80 c.c. of water) was added during 5 minutes. After a further 10 minutes water was gradually added until the total volume was 1 litre. The diacetylbiphenyl which was precipitated was filtered off and washed with water. Yield 18 g., m.p. 80-82°. It was crystallised from alcohol; yield 12 g. (60%), m.p. 82-84°. Three successive crystallisations from cyclohexane finally gave 9 g. of the product, m.p. 93-94°.

Attempted reaction between the phosphorane and 2,2'-diacetylbiphenyl

a. In absolute alcohol

Carbomethoxymethylenetriphenylphosphorane (3.34 g., 1 mol.) and 2,2'-diacetylbiphenyl (1.19 g., 1 mol.) were heated under reflux in 50 c.c. absolute alcohol for 190 hours. The mixture was then distilled. After alcohol had distilled, a liquid was collected, yield 0.96 g., b.p. 218°/9 m.m. to 228°/ 7 m.m. It would not solidify completely. A combination of cyclohexane and ether gave white solid which was filtered and crystallised from cyclohexane. But only gum could be obtained.

b. In toluene

The same quantities of the phosphorane and the diacetylbiphenyl were heated under reflux in toluene for

21 hours. Toluene was distilled off and the residue was cooled. White needles (triphenylphosphine oxide by m.p.) was filtered off, and the filtrate was distilled. A liquid was collected at 180°/4 m.m. - 190°/4m.m., and it solidified on cooling, m.p. partly 75°, and partly 125°. When it was crystallised from light petroleum (b.p. 80-100°) the solid obtained had m.p. 154-155°, indicating triphenylphosphine oxide. Its infrared spectrum was also identical with that of the oxide.

Polyalkylene dibromide series

Ethylenebis(triphenylphosphonium)dibromide

[Wittig, Eggers, and Duffner, Annalen, 1958, 619, 10]

Triphenylphosphine (60 g., 2 mols.) and ethylene dibromide (180g., 1 mol.) were boiled together for 45 min. (b.p. of the dibromide 134°). The solution was cooled, the solid was filtered off and washed with benzene and light petroleum (b.p. 40-60°). Crude yield 75 g., m.p. 309-312°. It was dissolved in 1l. chloroform and cyclohexane were added until the mixture started to go cloudy (100 c.c.). Crystals soon appeared in the form of colourless plates. First crop 41 g., m.p. 318-321°; second crop 33g., m.p. 315-318°. Total yield 91%.

Attempted reaction between the dibromide and biphenyl-2,2'-dialdehyde

n-Butyl-lithium was prepared in sodium-dried ether, from lithium (3g., 4 mols. and n-butyl chloride (9 c.c., 2 mols.), under an atmosphere of oxygen-free nitrogen. Ethylenebis-(triphenylphosphonium)dibromide (14.2g., 1 mol.) was added in small portions. The mixture turned reddish brown and became darker on heating. After ½ hr. heating, the colour test (according to Gilman and Schulze, J.Amer.Chem.Soc., 1925, 47, 2002) was negative indicating that there was no butyl-lithium left. The mixture was cooled, biphenyl-2,2'-dialdehyde (4.2g., 1 mol.) in ether was added. At the point of contact the mixture was green, and when stirred the whole mixture became buff colour.

This was heated and stirred for 10 hrs. and then cooled. The solid was filtered off, ether was removed from the filtrate, and the residue was distilled under reduced pressure. Pale yellow solid obtained had a characteristic smell and was found to be triphenylphosphine by m.p. and mixed m.p. 80°.

Trimethylene-1,3-bis(triphenylphosphonium) dibromide
[Wittig, Eggers and Duffner, Annalen, 1958, 619, 10]

Triphenylphosphine (63 g., 2 mols.) and 1,3-dibromopropane (20g., 1 mol.) were warmed slowly to 200°, with stirring. First, the triphenylphosphine melted, then the reaction set in and the whole mixture turned solid. All this took 3/4 hrs. It was then left to cool for ½ hr. The solid mass was dissolved out of the flask with warm chloroform, boiled up with decolorising charcoal, the solution was filtered, and acetone was added to start crystallisation. After standing overnight, crystals were obtained and dried in vacuo at 120°. The dibromide (54 g., 75%) had m.p. 344-345°.

Attempted reaction between the dibromide and biphenyl-2,2'-dialdehyde

n-Butyl-lithium was prepared on the same scale as described previously. Trimethylene-1,3-bis(triphenylphosphonium) dibromide (14.52 g., 1 mol.) was added gradually. The mixture turned very bright red. No heat of reaction was observed. It was stirred at room temperature for 2 hrs. Biphenyl-2,2'-dialdehyde (4.2g., 1 mol.) was then added. The ether did not seem to boil until a considerable amount of the dialdehyde had been added. It was then heated under reflux for 2 hrs. After being left to stand overnight, still under a nitrogen atmosphere, the ethereal layer seemed to change from yellow to pale green.

The mixture was filtered. The filtrate went cloudy so it was washed with water and the washing was discarded. Ether was removed and the viscous mixture remaining was shown by its infrared spectrum to contain mainly the unreacted dialdehyde and triphenylphosphine oxide. When it was digested with light petroleum (b.p. 40-60°), triphenylphosphine oxide (0.39 g., 4%, m.p. 147°) was obtained. The residue was stirred on a water-bath to expel the dialdehyde. The remainder was dissolved in ether and chromatographed on an alumina column.

The first fraction was pale yellow gum which when digested with light petroleum (b.p. 40-60°) gave white solid m.p. 210-213°; when twice crystallised from light petroleum (b.p. 60-80°) it had m.p. 234-235°. The analysis was not satisfactory [Found: C,91.9; H, 6.7. $C_{17}H_{14}$ requires C, 93.5; H, 6.5%]. The infrared spectrum showed that it was a biphenyl derivative with the absence of C = O and C - P peaks.

The second fraction of the chromatogram was a mixture of a solid (m.p. 135-140°, infrared spectrum of which was similar to that of the original mixture, i.e. containing C = O, P - Ph and phosphonium salt peaks) and a liquid which when digested with light petroleum (b.p. 40-60°) gave a solid m.p. 122°, the infrared spectrum of which showed a C = O peak, biphenyl peak and phosphonium salt peaks; the empirical formula was $C_{31}H_{30}O_4$. This must therefore be a polymer of some kind containing carbonyl groups.

The solid that was filtered off from the beginning, when decomposed with water, gave no triphenylphosphine oxide as expected. Instead, it gave some of the starting phosphonium dibromide (shown by infrared spectrum).

Condensation between biphenyl-2,2'-dialdehyde and o-phenylenediamine

1. At 160°, in ethylene glycol.

The dialdehyde (1.05g., 1 mol.) and the diamine (0.55g., 1 mol.) were heated in ethylene glycol (25 c.c.) in a large test tube in a metal-bath kept at 160° for 5 hrs. The dark solution was cooled and poured into 125 c.c. of water and left overnight. The cloudy mixture could not be filtered satisfactorily. It was therefore extracted with ether and the extracts were washed with dilute hydrochloric acid, and water and dried. From the ethereal layer 0.26g. of solid (crude m.p. ~ 50°) was recovered.

The acid washing was made alkaline and the solid obtained (1.14g., m.p. 125-130° decomp., soft 75°) was filtered off. It was digested with water. The aqueous part gave 0.12g. of solid m.p. 227-230°. The water-insoluble residue (0.27g.) had m.p. 154°, and when crystallised from aqueous alcohol it had m.p. 158-159° [Found: C, 85.0; H, 5.2; N, 10.0. $C_{20}H_{14}N_2$ requires C, 85.1; H, 5.0; N, 9.9%]. This solid gave a picrate which when crystallised from benzene had m.p. 279-280° decomp.

2. At room temperature in methanol (under Sparatore's condition)

The dialdehyde (1.05g., 1 mol.) and the diamine (0.55g., 1 mol.) were dissolved separately in methanol at room temperature, and the two solutions were mixed. The mixture remained clear after 20 days. It was then poured into 80 c.c. of water and cooled in the refrigerator. After 4 days, the mixture was filtered and the solid obtained had m.p. 93-95° (soft 80°). This was then dissolved in benzene and put through an alumina column.

The first batch of eluate gave a pale yellow solid, m.p. 216-217°, and was later thought to be phenanthrene-9',10':2,3-quinoxaline. The second batch gave solid m.p. 189-191°.

Phenanthrene-9',10':2,3-quinoxaline

o-Phenylenediamine (1.08g., 1 mol.) was dissolved in 15 c.c. ethanol and phenanthraquinone (2.08g., 1 mol.) was dissolved in 200 c.c. warm ethanol. The diamine was then added to the quinone. The mixture first went dark red, and after a few more seconds solid started to come down. When cool pale yellow needles of the quinoxaline were filtered and had m.p. 222-223° (lit. m.p. 217°). Yield 2.58g. (92%).

p-Acetamidobenzoic acid

[Ritstert and Epstein, *Chem. Zentr.*, 1904, *1*, 1587. Kl.12q. 151725]

p-Aminobenzoic acid (100g., 1mol.) was added in small quantities to the mixture of acetic acid (400c.c.) and acetic anhydride (400c.c.). The mixture was heated under reflux for 6 hrs., cooled slightly and poured into 2 l. of water. The solution started to go cloudy and when cool the solid was filtered off. Yield 60g., m.p. 258°. The filtrate on standing gave 21g. more solid. When crystallised from alcohol it had m.p. 260-262° (lit. m.p. 250-251°). Total yield, 55%.

m-Nitro-p-acetamidobenzoic acid
[Kaiser, Ber., 1885, 18, 2942]

Fuming nitric acid (d. 1.51, 90 c.c.) was cooled to 0° in a freezing mixture. p-Acetamidobenzoic acid (47g.) was added gradually to the nitric acid, with stirring, at such a rate that the temperature did not rise above 7°. After the addition of the solid the solution was left in the freezing mixture for another hour. It was then poured onto crushed ice and stirred. When the precipitation was complete the pale yellow solid (53g., m.p. 215°) was filtered off. When crystallised from alcohol (45g., 76%) it had m.p. 226-228° (lit. m.p. 220-221°) [Found: C, 47.9; H, 3.7; N, 12.3. Calc. for $C_9H_8N_2O_5$: C,48.2; H, 3.6; N, 12.5%].

Ethyl m-nitro-p-aminobenzoate

m-Nitro-p-acetamidobenzoic acid (25g.) was boiled under reflux for 5 hrs. with concentrated hydrochloric acid (150 c.c.) and ethanol (500 c.c.). It was poured into a beaker and water was added slowly until the first sign of turbidity appeared (500 c.c. were used). It was left to cool slowly to room temperature. The solid filtered off (17 g.) had m.p. 130-295°. When crystallised from ethanol, the first crop (14 g.) had m.p. 131-133° [Found: C, 51.6; H, 4.8; N, 13.5. Calc. for $C_9H_{10}N_2O_4$: C, 51.4; H, 4.8; N, 13.3%]. Second crop (3 g.) had m.p. 230-260° (soft 130°) and was thought to be the mixture of the ester and m-nitro-p-aminobenzoic acid (m.p. 284°, given by Ullmann and Mauthner, Ber., 1903, 36, 4026).

Ethyl 3,4-diaminobenzoate

[Ritstert and Epstein, *loc.cit.*]

The above nitro ester (12 g., 1 mol.) was dissolved in 10 c.c. of warm ethanol and the solution was added to a boiling solution of stannous chloride (45 g., 3.3 mols.) in concentrated hydrochloric acid (56 c.c., 9 mols). The yellow colour of the nitro compound faded and the solution was pale green at the end of the addition. Sodium hydroxide solution (30%) was added until the mixture was alkaline. The white solid resulted (4.68 g., m.p. 110°) was filtered off, washed with water and dried. Crystallised from water, it had m.p. 110-111° (3 g., 30%).

Condensation between biphenyl-2,2'-dialdehyde and ethyl-3,4-diaminobenzoate

1. In alcohol at room temperature.

Biphenyl-2,2'-dialdehyde (2.12g., 1 mol.) and ethyl-3,4-diaminobenzoate (1.78g., 1 mol.) were dissolved separately in a minimum amount of ethanol and mixed well (~ 30 c.c. ethanol). The solution was left to stand, and after 1 hour crystals started to form at the centre of the liquid surface and fell to the bottom. These were filtered off and crystallised from ethanol: first crop 1.6 g., m.p. 224-225°; second crop 0.07g., m.p. 223°. The first crop was recrystallised from ethanol, giving needles of the diazecine m.p. 226° [Found: C, 77.4; H, 5.3; N, 8.2. $C_{23}H_{18}N_2O_2$ requires C, 77.95; H, 5.1; N, 7.9%].

The mother liquor, after standing overnight, produced fine, pale yellow crystals (0.019g., m.p. 178°). It was crystallised from ethanol (~ 20 c.c.) and had m.p. 214-215°. This was subsequently found to be the corresponding quinoxaline.

2. In ethylene glycol at 150°.

The dialdehyde (0.623 g.) and the diamino ester (0.522 g.) were ground together and placed in a large test tube and ethylene glycol (15 c.c.) was added. The mixture was shaken well and the tube was placed in a metal-bath maintained at 150° for 2 hrs. It was then poured into water (25 c.c.) and left overnight. As no solid separated, the cloudy mixture was extracted with ether and the extract was washed with dilute hydrochloric acid. Sodium hydroxide solution (10%) was then added to the acid washing, until alkaline, and the cloudy solution was extracted with ether. After removal of ether, the residue was crystallised from ethanol giving 0.41 g. of solid m.p. 222°. This had an infrared spectrum identical with that of the solid m.p. 226° from 1., i.e. it was the required diazecine. There was no other product.

Hydrolysis of the product m.p. 222° or 226°

The ester was heated under reflux with aqueous alcoholic potash for 1 hour. Alcohol was removed and the residue was dissolved in water, and acidified with dilute hydrochloric acid. The solid obtained was filtered off and dried, m.p. > 360°

∠Found: C, 77.0; H, 4.3; N, 8.7. $C_{21}H_{14}N_2O_2$ requires

C, 77.3; H, 4.3; N, 8.6%/.

3"-Carbethoxy-phenanthrene-9',10':2,3-quinoxaline

Ethyl 3,4-diaminobenzoate (0.22g., 1 mol.) was dissolved in 7 c.c. ethanol and phenanthraquinone (0.25 g., 1 mol.) was dissolved in 70 c.c. warm ethanol. The diamino-ester was then added to the quinone and the mixture was left to cool. The quinoxaline, obtained as fine, pale lemon solid, was filtered, and had m.p. 214-215°. When crystallised from ethanol (it is not very soluble in ethanol), it had m.p. 216-217°. /Found: C, 78.4; H, 4.6; N, 7.9; O, 8.9. $C_{23}H_{16}O_2$ requires C, 78.4; H, 4.6; N, 7.95; O, 9.1%/.