STUDIES IN DIPHENYLS AND DINAPHTHYLS.

Thesis presented by
FATIMA MINHAJ
in requirement for the degree of
Doctor of Philosophy
in the University of London.
1956.

ProQuest Number: 10098014

All rights reserved

INFORMATION TO ALL USERS
The quality of this reproduction is dependent upon the quality of the copy submitted.

In the unlikely event that the author did not send a complete manuscript
and there are missing pages, these will be noted. Also, if material had to be removed,
a note will indicate the deletion.

ProQuest 10098014

Published by ProQuest LLC(2016). Copyright of the Dissertation is held by the Author.

All rights reserved.
This work is protected against unauthorized copying under Title 17, United States Code.
Microform Edition © ProQuest LLC.

ProQuest LLC
789 East Eisenhower Parkway
P.O. Box 1346
Ann Arbor, MI 48106-1346

ABSTRACT.

The first section of this thesis deals with the synthesis of some derivatives of a substituted diphenic acid with seven membered bridges across the 2:2'- positions. It was hoped to obtain these compounds in optically active forms also. This was, however, not found possible as the 4:4':6:6'-tetrachlorodiphenic acid from which the above compounds were derived could not be resolved into optically pure isomers. The ultra-violet absorption spectra of these compounds were studied in order to investigate the relation between conjugation and configuration in the diphenyls and the results lend further support to the conclusions drawn by other workers in this field.

A new series of compounds were prepared from 2:2'-dinaphthyl-3:3'-dicarboxylic acid with the view to resolving the azepinium salt obtained from it. This salt and the dinaphthyl oxepin both have a seven membered ring. The study of the ultra-violet absorption spectra of these compounds provide basically important spectral data for the dinaphthyls.

In the next section are described the attempts to prepare dialdehyde-2:2'-diphenyl which would have provided a starting material for many interesting syntheses but the yield of the dialdehyde was low and its preparation presented considerable practical difficulties.

2:2'-Diacyldiphenyls are known to give anomalous results on reduction and 2:2'-dipropionyldiphenyl was prepared to study the effect of different reducing agents on it. 9:10-Diethylphenanthrene and 2:2'-bis-B-methylethenyldiphenyl were obtained from it in good yields. The ultra-violet absorption spectrum of this unsaturated hydrocarbon was also studied.

ACKNOWLEDGEMENTS.

The author wishes to acknowledge the continued help and advice of Dr. D.M.Hall, to thank Professor E.E.Turner, F.R.S. for all the facilities provided, Bedford College for a grant towards the end of the research period, Aligarh University (India) for granting leave and finally her family for their encouragement.

CONTENTS.

SECTION I.

PART A. Stereochemistry of compounds derived from 4:4':6:6'-tetrachlorodiphenic acid. Page.

PART B. Stereochemistry of 3:3'-bridged 2:2'-dinaphthyls.

SECTION II.

PART A. Study of dialdehyde-2:2'-diphenyl.

PART B. Study of 2:2'-diacyldiphenyls.

CONTENTS (contd.)

SECTION III.

SECTION I.

PART A.

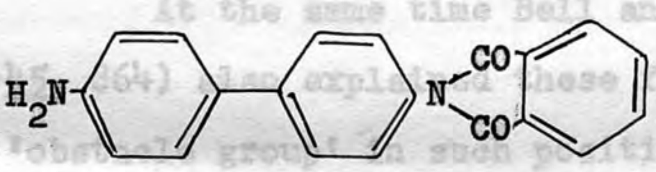
STEREOCHEMISTRY OF COMPOUNDS DERIVED FROM 4:4':6:6'-TETRACHLORODIPHENIC ACID.

INTRODUCTION.

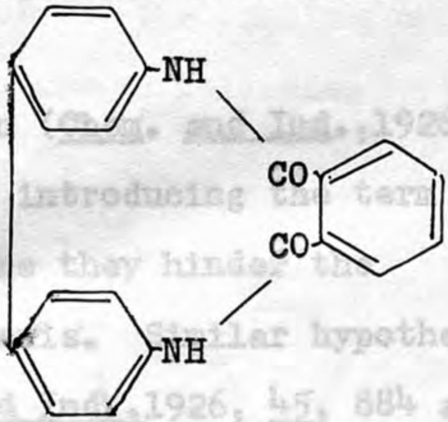
The explanation, put forward by vant' Hoff and Le Bel, that optical activity exhibited by organic molecules was due to molecular dissymmetry rather than to an asymmetric carbon atom had been widely accepted but experimental evidence followed much later. The first case of optical resolution reported, of a compound with dissymmetric structure, was that of 1-methyl*cyclo*hexylidene-4-acetic acid by Perkin, Pope and Wallach (*J.*,1909, *95*, 1789). Later, amongst many workers' contribution to this field may be mentioned the name of Mills (*J.*,1920, 1407) who resolved the (*spiro*)dilactone of benzophenone-2:4:2':4'-tetracarboxylic acid and also Backer and Schurink (*Proc. Acad. Sci. Amsterdam*,1928, *31*, 370) who obtained the two active forms of *cyclo*-butane *spiro*-1:1'-dicarboxylic acid. Kohler, Walker and Tishler (*J.Amer.Chem.Soc.*,1935, *57*, 1743) obtained the active forms of carboxymethyl ester of $\alpha\gamma$-diphenyl-γ-1-naphthylallene-α-carboxylic acid.

Investigations into the structure of diphenyl and its derivatives started afresh after some doubts were cast upon the configuration propounded by Kaufler (*Annalen*, 1907, *351*, 151) for the condensation products of benzidine with various reagents when Ferriss and Turner (*J.*,1920, 1140) could not repeat Kaufler's work. Meanwhile Brady and

McHugh ($\underline{J}$.,1923, 2047) also reinvestigated the isomeric dinitrobenzidines, which were earlier studied by Cain and his coworkers ($\underline{J}$.,1912, 2298; 1913, 586; 1914, 1437). Brady pointed out that the isomerism in the above compounds was structural. This received further support from the work of Le Fevre and Turner ($\underline{J}$.,1926, 1759), who also proved that several of the condensation product obtained by Kaufler had free amino groups. To quote an example monophthalylbenzidine was shown to have the structure (I) and not (II) as suggested by Kaufler.



(I)



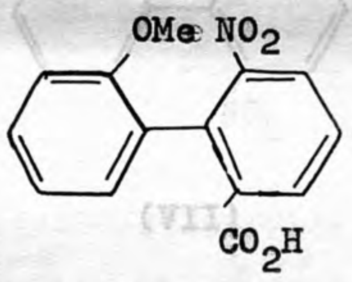
(II)

Several workers obtained substituted diphenyls in optically active forms e.g. 6:6'-dinitrodiphenic acid (Kenner and Stubbings, $\underline{J}$.,1921, 593) and 4:4':6:6'-tetranitrodiphenic acid. There were also known many ortho substituted diphenyls which were not resolvable. To explain these observations a coaxial, coplanar (preferred) structure was proposed by Le Fevre and Turner, (Chem. and Ind., 1926, $\underline{45}$, 831 and 833) for the diphenyl skeleton. They also postulated that there exists some affinity between the 2:2' positions, because of Thiele's residual affinity effect. The substituents in the 2, 2', 6 or 6' positions owing to the volume effect or electrical repulsion tend to force the two benzene nuclei to twist at the co-axis, and thus overcome the 2:2' affinity effect and destabilise the coplanar form.

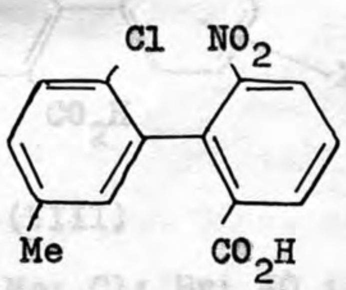
At the same time Bell and Kenyon (*Chem. and Ind.*,1926, *45*, 864) also explained these facts by introducing the term 'obstacle group' in such positions where they hinder the free rotation of the nuclei at the co-axis. Similar hypothesis was also postulated by Mills (*Chem. and Ind.*,1926, *45*, 884 and 905).

These theories and the obvious fact that both rings should be unsymmetrically substituted for the mirror images to be non-superimposable were supported by the experimental evidence that the substituted diphenyls resolved had more than one group in the collision positions whilst those which were not optically stable contained not more than two groups in the *ortho* positions.

Turner and coworkers carried out researches on finding the minimum substitution in the 2, 2', 6, or 6' positions which would result in detectable optical activity. They successfully demonstrated optical activity in phenyl benzidine-2:2'-disulphonate and diphenyl-2:2'-disulphonic acid (Lesslie and Turner, J.,1932, 2021 and 2394) and o-(2-dimethylaminophenyl)phenyltrimethylammonium iodide, (Shaw and Turner, J.,1933,135). Adams and his coworkers also carried out a series of experiments on compounds of the type (III) and (IV) to determine the extent of hinderance caused by the substituent groups and came to the conclusion that the calculated interference is not always reliable.



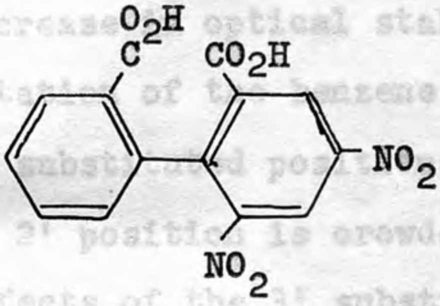
(III)



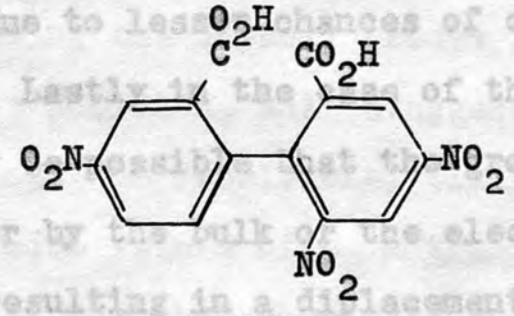
(IV)

(J.Amer.Chem.Soc., 1932, 54, 4426; and 2966.)

Another interresting phenomenon which may be mentioned here is that in the optically active diphenyls the substituents at positions other than the blocking ones namely 3, 3', 4, 4', 5 or 5' also have some effect on the optical stability. The work on (V), (VI), (VII) and (VIII) shows that the effect of the substituent group on the stability of the optical activity varies with the position and the nature of the substituent. In (VIII) the optical stability decreased in

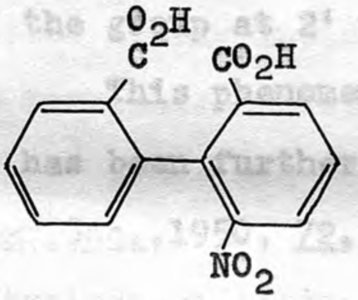


(V)

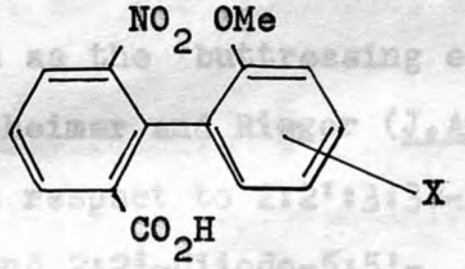


(VI)

(Kuhn and Albrecht, <u>Annalen,</u> 1927, <u>455</u>, 272; <u>458</u>, 221.)



(VII)



(VIII)

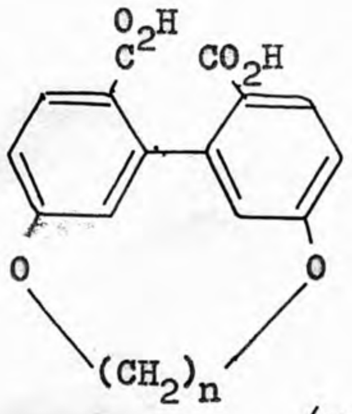
(X- OMe; Me; Cl; Br; NO_2; H at positions 3', 4' or 5').

(Adams and Hale, <u>J.Amer.Chem.Soc.,</u>1936, <u>61</u>, 2825).

the order 3' > 4' > 5' for which the following explanations (Adams and Yuan, <u>loc.cit.</u>) have been put forward. The substituent groups may produce firstly a change in the bond length of 2' carbon atom to substituent link and also a change in length of the internuclear bond, secondly the bending in the pivot bend so that the rings are not co-axial any more, thirdly a decrease in the rate of the semi circular oscillations of the benzene rings resulting in the comparative increase in optical stability due to lesser chances of complete rotation of the benzene rings. Lastly in the case of the 3' substituted positions it may be possible that the group in 2' position is crowded either by the bulk or the electrical effects of the 3' substituent resulting in a diplacement of the 2' carbon atom to the substituent bond and consequently to the substituent at that position thus enhancing the blocking power of the group at 2' position.

This phenomenon is now known as the 'buttressing effect'. It has been further studied by Westheimer and Rieger (J.Amer. Chem.Soc.,1950, 72, 19 and 28) with respect to 2:2':3:3'-tetraiodo-5:5'-dicarboxyldiphenyl and 2:2'-diiodo-5:5'-dicarboxydiphenyl. The ~~latter~~ former racemises 30,000 times ~~as~~ more slowly ~~fast~~ than ~~as~~ the ~~former~~ latter owing to the buttressing effect of the two iodine atoms in the 3,3' positions.

In every instance the asymmetry required for optical activity amongst the substituted diphenyls has resulted from restricted rotation about the single bond produced by ortho substituents. A novel way of achieving restricted rotation was suggested by Adams and Kornblum (J.Amer.Chem.Soc., 1941, 63, 188,) by means of many membered rings at 5,5' positions of diphenic acids,(IX). Four possibilities can be recognised: (i) for very small values of n, the molecule may be so strained

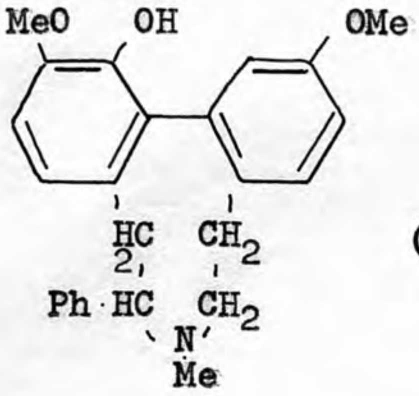


(IX)

that the carboxy groups do not interfere; (ii) for slightly bigger values of n, the molecule having the carboxy groups in the cis position, but 'staggered', should be resolvable; (iii) for medium values of n, a trans configuration should be possible, and this should be interconvertible with the cis form, but otherwise the rotation is restricted; (iv) for very large values of n, the diphenyl system should rotate freely inside the large ring, and such compounds should be incapable of resolution.

Adams and Kornblum successfully resolved two such compounds with value of n as 8 and 10, both representative of class (iii). The active compound with n = 8 was more optically stable than that with n = 10.

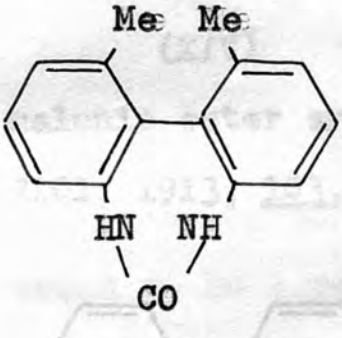
Another interesting example of diphenyl stereoisomerism has been described by Robinson (Proc. Roy. Soc. A.,1948, 192, 14) in the case of phenyldihydrothebaine (X). This molecule possesses two sources of asymmetry, one of these is a non-coplanar diphenyl configuration and the other is the asymmetric carbon atom



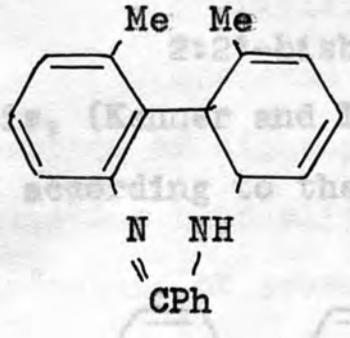
(X)

carrying the phenyl group. The ultraviolet absorption spectrum does not show the characteristics of diphenyl.

The following compounds have been obtained in an optically active condition by starting with resolved diphenyls;



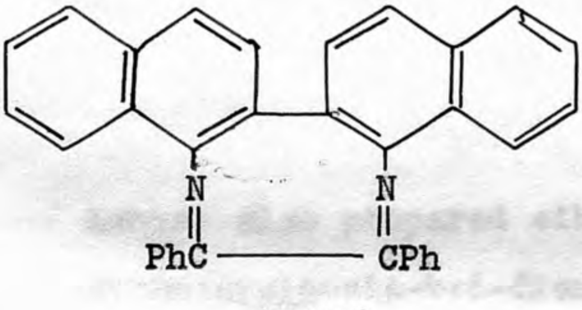
(XI)



(XII)

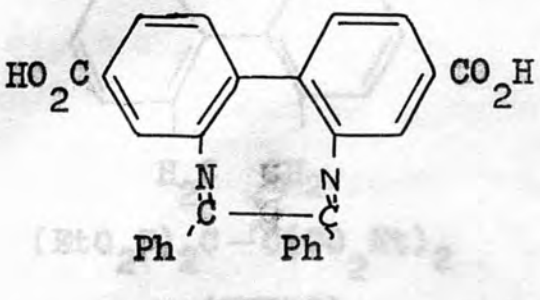
(Sako, Mem.Coll.Eng. Kyushu,1932, 6, 283)

(−) 2:2'-diamino-6:6'-dimethyldiphenyl for (XI) and (XII) and with (+) 2:2'-diamino-1:1'-dinaphthyl for (XIII). For the obvious conclusion that a ring system based on the 2:2' positions of the diphenyl exists in a non-planar form, the presence of ortho substituents was considered necessary in order to preserve non-planarity.



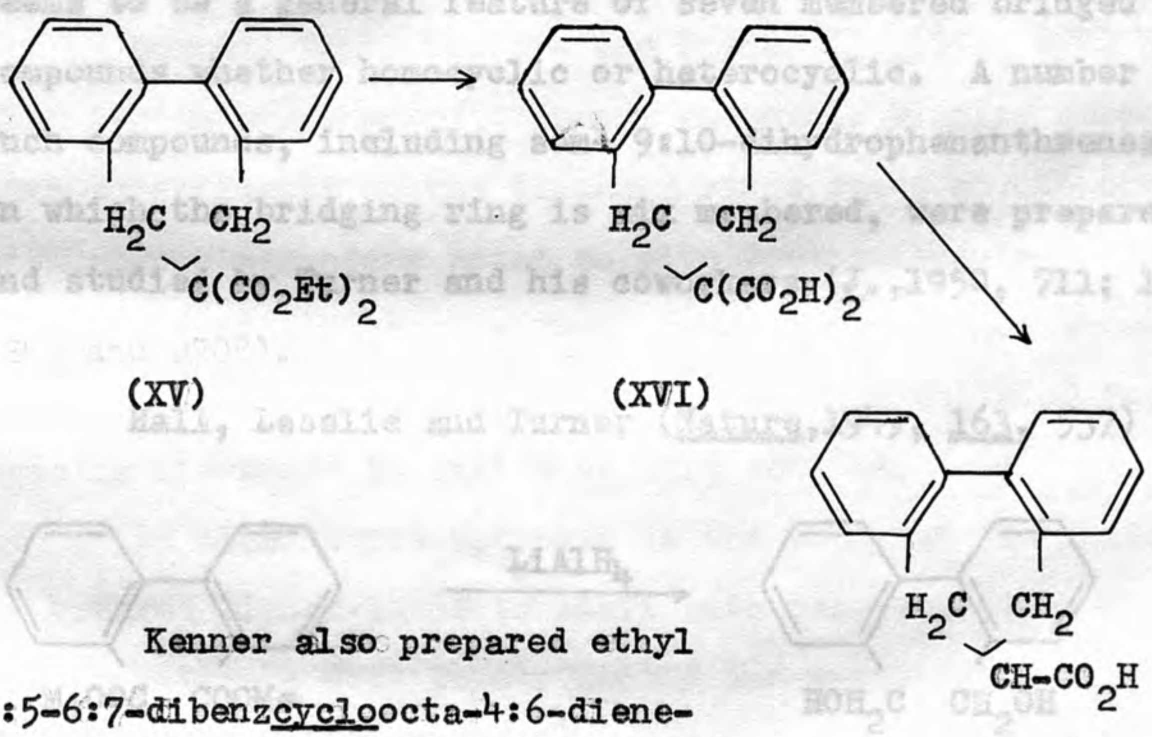
(XIII)

The latter point has now been disproved by the work of Bell (J.,1952, 1527) who resolved 6:7-diphenyl-5:8-diaza-1:2-3:4-dibenz*cyclo*octatetraene-2':2"-dicarboxylic acid (XIV) through its brucine salt.



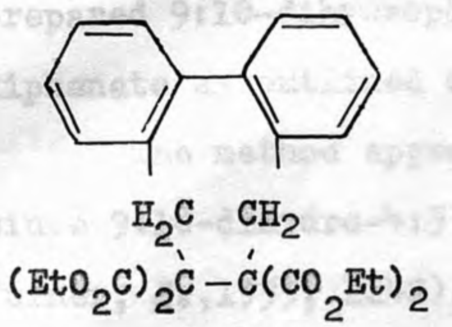
(XIV)

Neither Bell (*loc.cit.*) nor Beavan, Bird, Hall, Johnson, Ladbury, Lesslie and Turner (*J.*,1955,2708) were able to resolve (XVII), obtained from 2:2'-bisbromomethyldiphenyl by malonic ester synthesis, (Kenner and Turner, *J.*,1911, *96*, 2101; 1913, *103*, 633) according to the following scheme:



(XV) (XVI) (XVII)

Kenner also prepared ethyl 4:5-6:7-dibenz*cyclo*octa-4:6-diene-1:1:2:2-tetracarboxylate (XVIII) but its identity was establised only recently by the work of Turner *et. al.* (*ibid*) who studied compounds in which the 2:2' bridge of diphenyl forms a part of seven or more membered rings to determine the relation between comfiguration

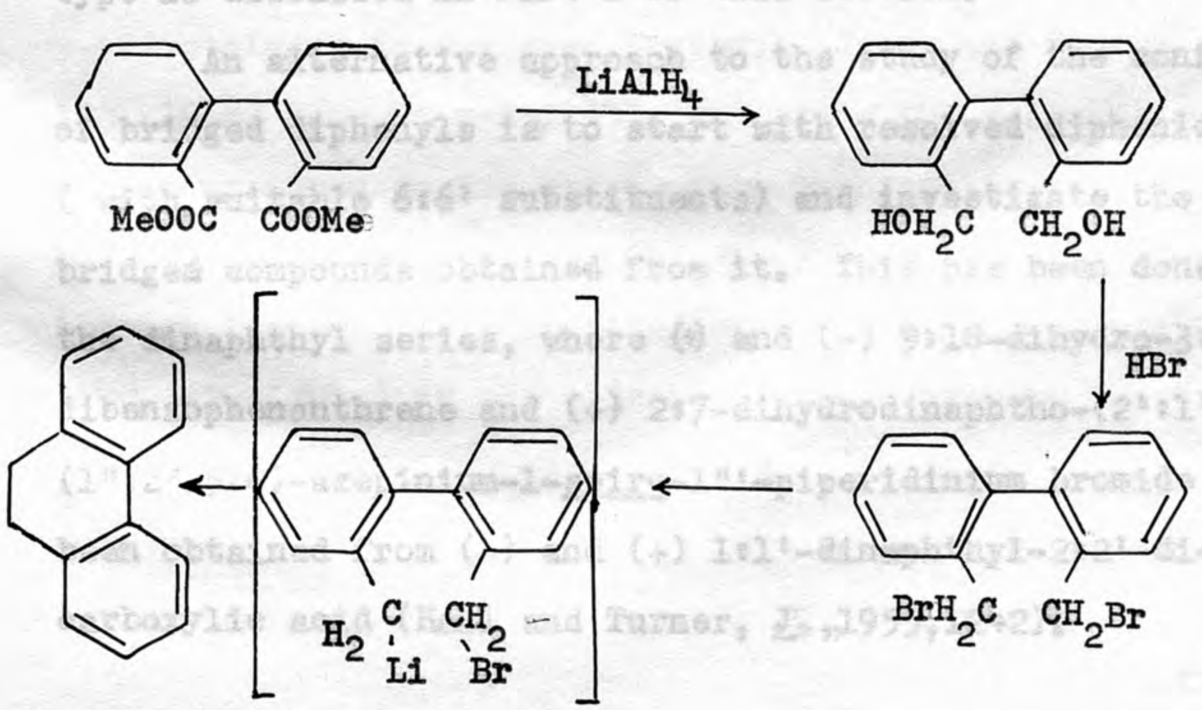


(XVIII)

and conjugation in diphenyl derivatives with the help of absorption spectra.

The absorption spectram of (XVII) in 96% ethanol as observed by Turner et. al. were very much like the spectrum of diphenyl itself with only the intensity of the conjugation band slightly reduced which seems to be a general feature of seven membered bridged compounds whether homocyclic or heterocyclic. A number of such compounds, including some 9:10-dihydrophenanthrenes, in which the bridging ring is six membered, were prepared and studied by Turner and his coworkers (J.,1950, 711; 1955, 1242 and 2708).

Hall, Lesslie and Turner (Nature,1949, 163, 537)



prepared 9:10-dihydrophenanthrene in 70% yield from dimethyldiphenate as outlined on the previous page.

The method appears to be of general applicabilities since 9:10-dihydro-4:5-dimethoxyphenanthrene (Hall and Turner, *J.*, 1955, 1242), 9:10-dihydro-3:6-dimethoxyphenanthrene (Beavan, Hall, Lesslie and Turner, *J.*, 1952, 854) and 9:10-dihydro-4:5-dimethylphenanthrene (Wittig and Zimmermann, *Ber.*, 1953, *86*, 629; Bergman and Pelchowicz, *J.Amer.Chem.Soc.*, 1953, *75*, 2663) have also been obtained in this way.

Beavan, Hall, Lesslie and Turner (*J.*, 1952, 854) found that 2:2'-bisbromomethyldiphenyl and other similar compounds with substituents in the diphenyl rings react spontaneously with strong secondary bases to give dibenzazepinium compounds. Their attempts to resolve these compounds were not successful in all cases. The resolution of quaternary salts of this type is discussed in Part B of this section.

An alternative approach to the study of the configuration of bridged diphenyls is to start with resolved diphenic acids (with suitable 6:6' substituents) and investigate the bridged compounds obtained from it. This has been done in the dinaphthyl series, where (+) and (-) 9:10-dihydro-3:4-5:6-dibenzophenanthrene and (+) 2:7-dihydrodinaphtho-(2':1'-3:4)-(1":2"-5:6)-azepinium-1-*spiro*-1"'-piperidinium bromide have been obtained from (-) and (+) 1:1'-dinaphthyl-2:2'-dicarboxylic acid (Hall and Turner, *J.*, 1955, 1242).

In the present work, it was hoped to extend such an investigation to the diphenyl series and also to study the effect of ortho substituents (which would, of necessity, be bulkier than the methoxyl groups studied by Beavan, Hall, Lesslie and Turner, J.,1952, 854) on the absorption spectra of such bridged compounds.

As starting material a 6:6' disubstituted diphenic acid was needed which would fulfil the following requirements:

(I) It should be readily resolvable,

(ii) It should be optically stable and

(iii) The 6:6' substituents should be unaffected by the reactions necessary to produce six and seven membered rings.

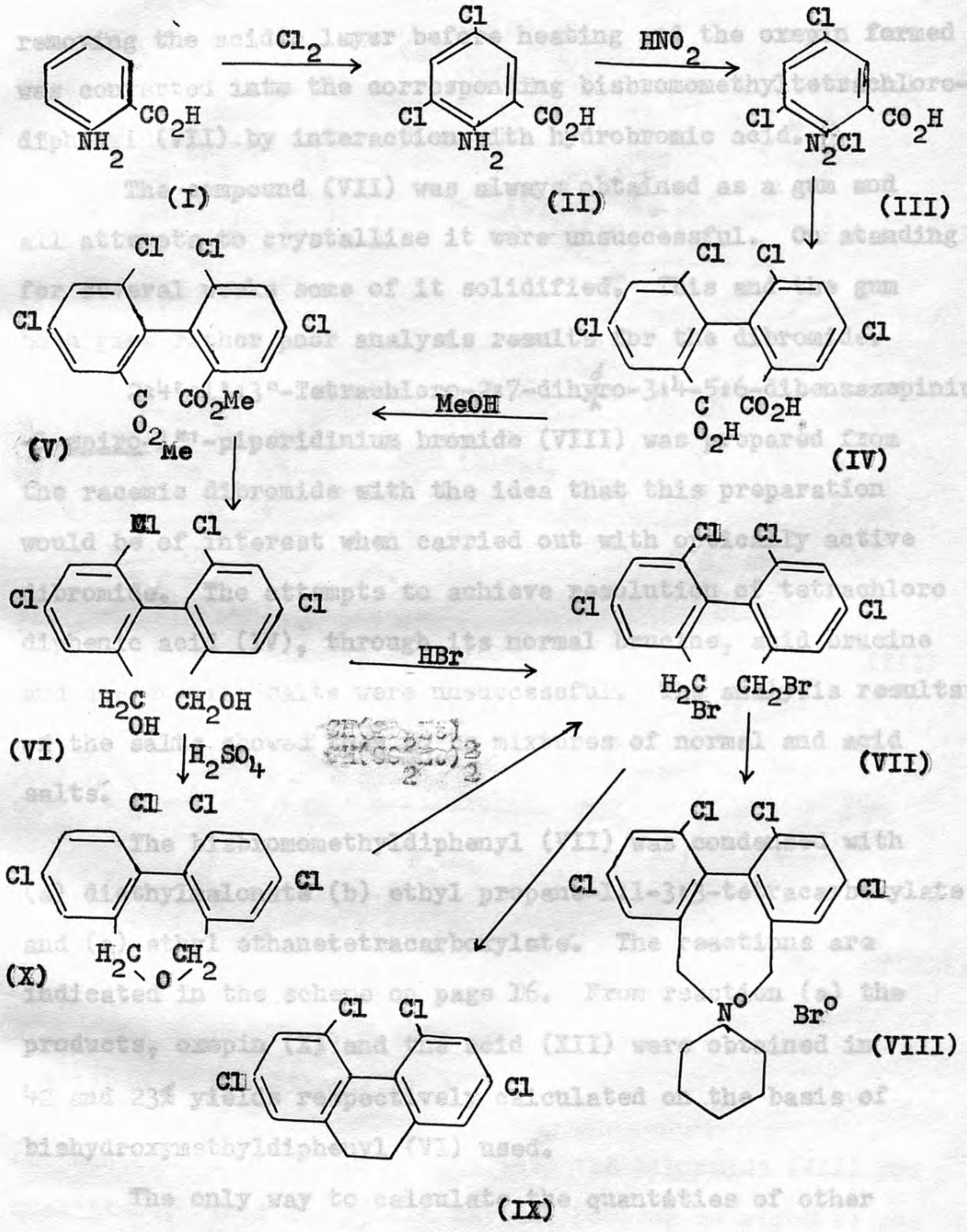
6:6'-Dichlorodiphenic acid and 4:4':6:6'-tetrachlorodiphenic acids appeared to fulfill these requirements. However, the long synthesis of the former acid (from 2-amino-3-nitrotoluene in 8stages; Christie, James and Kenner, J.,1923, 123, 1948) made it unsuitable and since the tetrachloro acid can be prepared in two stages from anthranilic acid (Atkinson, Murphy and Lufkin, Org. Synth.,31, 94) and has been resolved through the brucine salt (Atkinson and Lawler, J.Amer.Chem.Soc., 1940, 62, 1704) it was selected for the present investigation.

DISCUSSION.

The preparation of 4:4':6:6'-tetrachlorodiphenic acid, according to the method of Atkinson et. al. (loc.cit.), requires no special comment except that the acid obtained had a higher melting point viz. 264-265° as compared with the m.p. given in Org. Synth. (258-259°).

Attempts to obtain the above acid by an alternative route i.e. by adding diazotised 2-amino-3:5-dichlorobenzoic acid to the reducing agent cuprammonium hydroxide, sodium metabisulphite, anhydrous ferrous sulphate, however, failed.

The yield of dimethyl 4:4':6:6'-tetrachlorodiphenate was improved from 72% to almost theoretical quantity. The lower yield was due to the formation of mono methyl ester which was avoided by prolonging the time of reaction from 6 to 18 hrs. The reduction of the dimethyl ester to the corresponding bishydroxymethyldiphenyl by using lithium aluminium hydride gave excellent results. The yield of the diol (VI) was 98%. The diol was dehydrated to form 2':4':1":3"-tetrachloro-2:7-dihydro-3:4-5:6-dibenzoxepin (X) for the interest in its absorption spectrum which is discussed in section (III). The oxepin was also obtained as a by-product during the preparation of the diol when the latter was separated from the reaction mixture by distilling off the ether from the acidic layer. This was avoided by


Cl_2
HNO_2
MeOH
HBr
H_2SO_4
(I)
(II)
(III)
(IV)
(V)
(VI)
(VII)
(VIII)
(IX)
(X)
CO_2H
NH_2
Cl
N_2Cl
CO_2Me
H_2C
CH_2OH
CH_2Br
Br^o
N^o

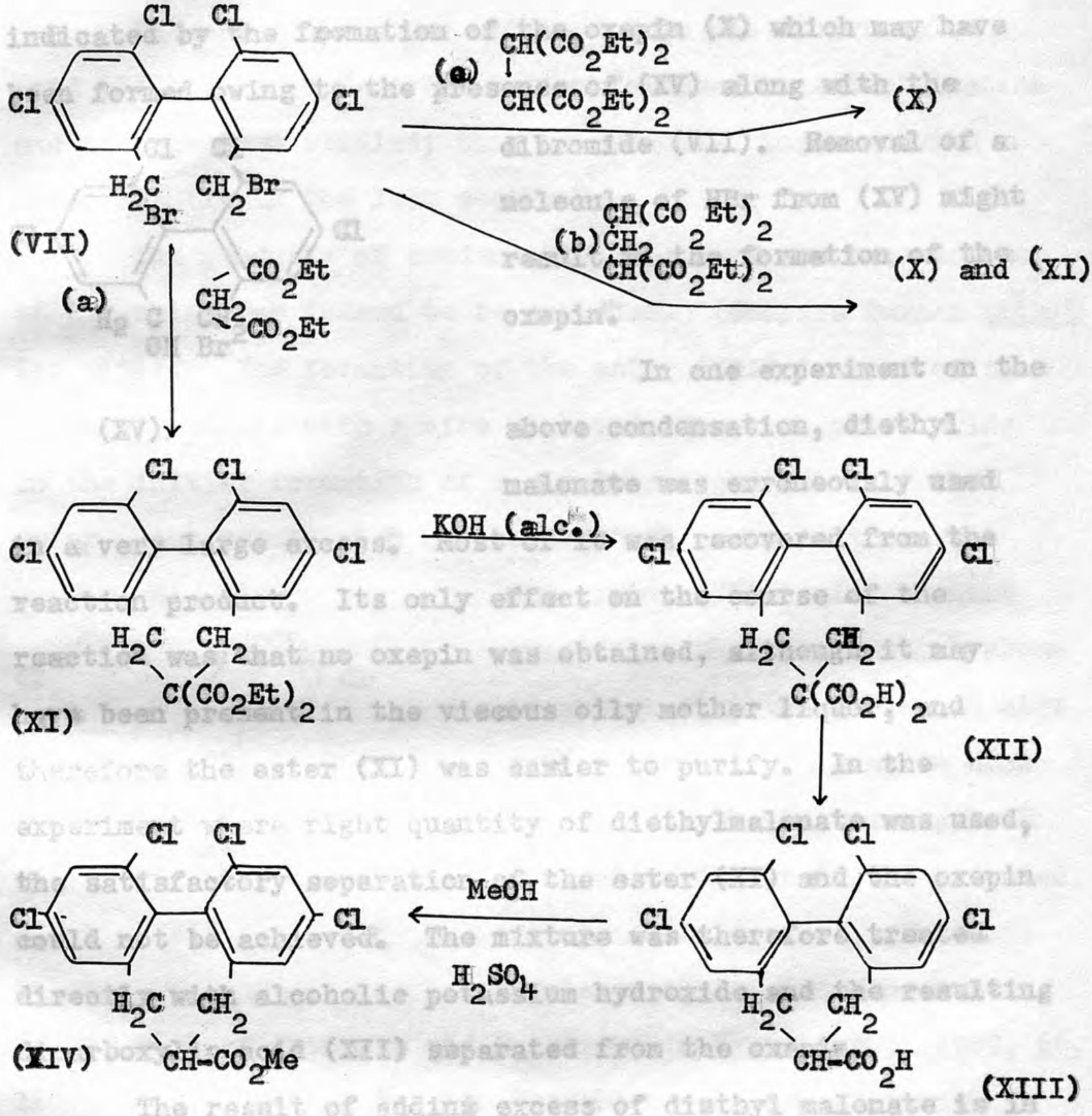
removing the acidic layer before heating and the oxepin formed was converted into the corresponding bisbromomethyltetrachlorodiphenyl (VII) by interaction with hydrobromic acid.

The compound (VII) was always obtained as a gum and all attempts to crystallise it were unsuccessful. On standing for several weeks some of it solidified. This and the gum both gave rather poor analysis results for the dibromide.

2:4':1':3"-Tetrachloro-2:7-dihydro-3:4-5:6-dibenzazepinium-1-*spiro*-1'''-piperidinium bromide (VIII) was prepared from the racemic dibromide with the idea that this preparation would be of interest when carried out with optically active dibromide. The attempts to achieve resolution of tetrachloro diphenic acid (IV), through its normal brucine, acid brucine and amphetamine salts were unsuccessful. The analysis results of the salts showed them to be mixtures of normal and acid salts.

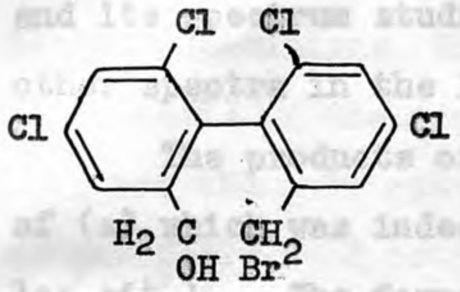
The bisbromomethyldiphenyl (VII) was condensed with (a) diethylmalonate (b) ethyl propane-1:1-3:3-tetracarboxylate and (c) ethyl ethanetetracarboxylate. The reactions are indicated in the scheme on page 16. From reaction (a) the products, oxepin (X) and the acid (XII) were obtained in 42 and 23% yields respectively calculated on the basis of bishydroxymethyldiphenyl (VI) used.

The only way to calculate the quantities of other reagents to be used in these condensations was to assume that



(N.B. The compounds from (VI) onwards have not so far been described in the literature.)

the conversion of the diol (VI) into the dibromide (VII) was quantitative. This assumption may not however be right as was indicated by the formation of the oxepin (X) which may have been formed owing to the presence of (XV) along with the dibromide (VII). Removal of a molecule of HBr from (XV) might result in the formation of the oxepin.



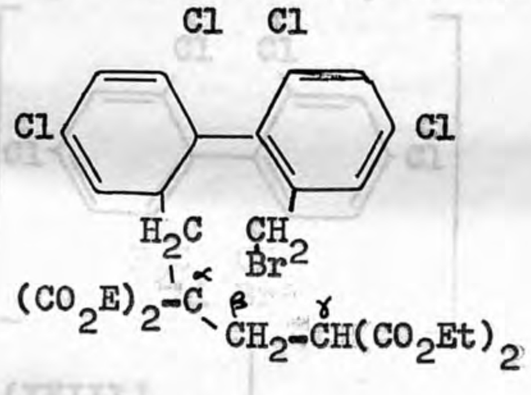
(XV)

In one experiment on the above condensation, diethyl malonate was erroneously used in a very large excess. Most of it was recovered from the reaction product. Its only effect on the course of the reaction was that no oxepin was obtained, although it may have been present in the viscous oily mother liquor, and therefore the ester (XI) was easier to purify. In the experiment where right quantity of diethylmalonate was used, the satisfactory separation of the ester (XI) and the oxepin could not be achieved. The mixture was therefore treated directly with alcoholic potassium hydroxide and the resulting dicarboxylic acid (XII) separated from the oxepin.

The result of adding excess of diethyl malonate is in agreement with the results of Kenner (J.,1913, 103, 613) who found that even when two molecular proportions of diethyl malonate are used, only the seven membered ring ester is obtained from 2:2'-bisbromomethyldiphenyl.

The ester (XIV) was obtained from the dicarboxylic acid (XII) through decarboxylation followed by esterification and its spectrum studied; this is discussed together with other spectra in the last section.

The products of condensation (b) were the same as that of (a) which was indeed to be expected. (Compare Turner et.al. loc.cit.). The formation of the ester (XII) instead of the hypothetical one with a nine membered ring took place owing to the initial formation of a singly charged anion of the ester which reacts with one bromomethyl group in the usual way giving (XVI). In the next stage the other bromomethyl group is attacked by the α-carbon atom rather than the γ-carbon atom even though the latter may have a negative charge in the presence of the ethoxide ions. This explanation is also supported by the work of Guthzeit and Engelmann (J.Prakt.chem., 1902, 66, 104) on the reaction between the above ~~malonic~~ ester with ethyl bromoacetate when both α and γ carbon atoms take part in the attack.

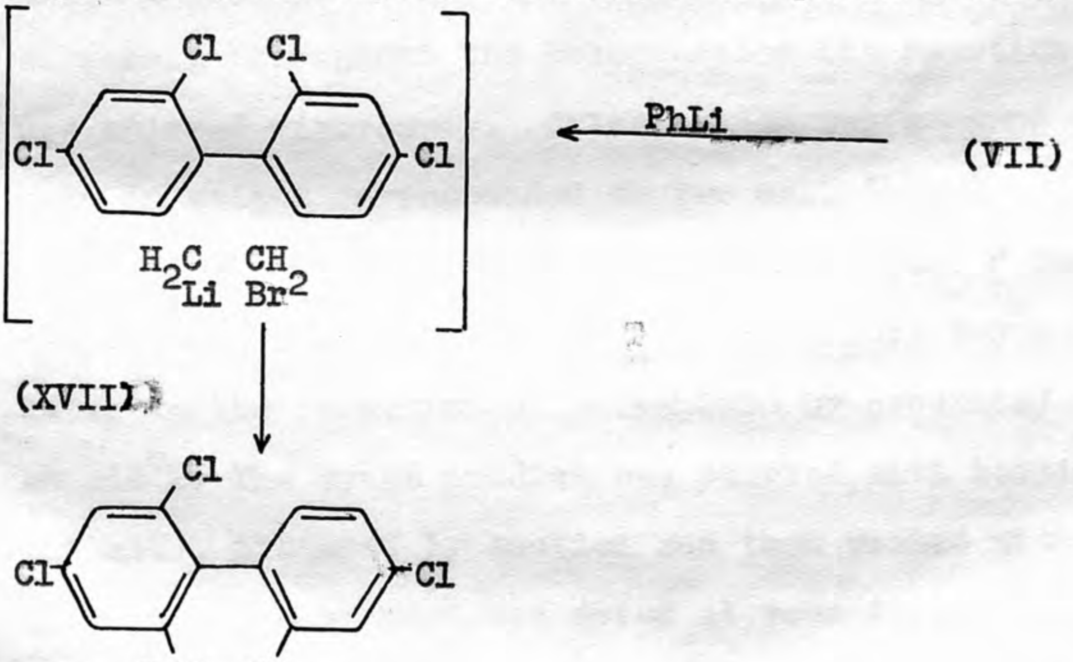


(XVI)

The reason for the formation of oxepin in this condensation (b) is presumably the same as in the previous reaction.

In the next condensation (c), the only pure reaction product was oxepin and 74% of ethyl ethanetetracarboxylate was recovered unchanged. Probably with the two chlorine atoms in the 6:6' blocking positions, the formation of seven membered ring ester (XII) or the oxepin which also has a seven membered ring are the only possibilities. In this reaction, since the ester (XII) could not be formed, the only possibility was the formation of the oxepin.

Attempts to prepare compound (IX) from bisbromomethyl tetrachlorodiphenyl (VII) and phenyl lithium failed but the m.p. and the analysis results of the product (XVIII) suggest



(XVIII)

that it was a pure compound. The percentage composition from the two analyses is in fair agreement and indicates that one chlorine atom was knocked out. The chlorine atom most likely to be removed would be one of the two at 6:6' positions since these two together prevent the sufficiently close approach of the methyl lithium and the bromomethyl groups in the intermediate compound (XVIII). Unfortunately, there was not enough of this substance left for conformation of this idea of further identification.

EXPERIMENTAL.

Preparation of 4:4':6:6'-tetrachlorodiphenic acid.

(Atkinson, Murphy and Lufkin, *Org.Synth.31*,96).

2-Amino-3:5-dichlorobenzoic acid: Anthranilic acid (45g., 1mol.) was dissolved in dilute hydrochloric acid (150ml.,conc acid in 850ml. water) in a 2 litres three-necked flask. The flask was placed in an iced water bath so as to maintain the temperature at 20°-30° during the reaction. Chlorine was passed through the reaction mixture at such a rate as to keep the solution saturated with the gas with some escaping from the surface. Throughout the chlorination the reaction mixture was stirred vigorously. Chlorination was stopped when the gain in weight corresponded to two mol. (45g.).

The solid product was filtered off,and dried at room temperature (drying at elevated temperature lowers the yield owing to the formation of polychloro by-products) and melted at 210°. The crude product was stirred with boiling benzene (275ml.), filtered by suction and then washed with some cold benzene. The product was dried at room temperature. Yield 47.6g. (70%), m.p.218°-220°.

This preparation was repeated several times. It was observed that the use of a moderate excess of chlorine did not affect the yield. The m.p. of the product varied from 217° to 224°. Yields varied from 65% to 76%.

Diazotisation of 2-amino-3:5-dichlorobenzoic acid: Crude dichloroaminobenzoic acid (55g.,1mol.) was dissolved in a solution of sodium hydroxide (14.5g.,1.1mol., in 750ml. water). Sodium nitrite (22g.,1.05mol.) was added and the solution cooled to 10°. At lower temperatures precipitation of the sodium salt occurred. Hydrochloric acid (120ml.,d.1.18;1.12mol) and water (230ml.) were placed in a 2 litre three-necked flask in an ice-bath and the temperature therein maintained at 10° throughout the following procedure.

The cold solution of sodium 2-amino-3:5-dichlorobenzoate and sodium nitrite was added through a dropping funnel, with stirring , at such a rate that no appreciable accumulation of undiazotised amine took place. The diazotisation was completed in about 2hrs., after which stirring was continued for another 15min. with 2g. of diatomaceous earth. The diazo solution was then filtered clear of any insoluble gelatinous material immediately before adding it to the reducing agent, using an ice-cold buchner funnel and flask.

Preparation of the reducing agent: A solution of copper sulphate pentahydrate (138g.,2mol.) in water (550ml.) was placed in a 4 litre beaker fitted with an efficient mechanical stirrer and ammonium hydroxide (d.0.88.,240ml.) added to it with stirring. The solution was cooled to 10°. Hydroxylamine hydrochloride (40g.,2mol.) was dissolved in water (140ml.)

and filtered after cooling to 10°. To the clear solution was added 6N sodium hydroxide solution (100ml.). This solution was then immediately added to the ammoniacal solution of cupric sulphate with stirring. With reduction the solution became pale blue. The temperature of the reaction mixture was maintained at 10°-15°.

<u>4:4':6:6'-Tetrachlorodiphenic acid</u>: The cold diazo solution was added to the reducing solution from a dropping funnel, to the stem of which was attached a capillary bent upwards. This arrangement ensured that the diazo solution reacted only after entering the reducing solution as no ammonia could go up in the dropping funnel stem through the bent feed tube with ascending bubbles of nitrogen. The reaction was accompanied by excessive foaming which was controlled by the addition of a little ether every few minutes. After the addition of all the diazo solution, the reaction mixture was stirred for another half hour. Half of it was then transferred to another 4 litre beaker; both parts were heated to 90° and rapidly acidified to litmus with concentrated hydrochloric acid. More hydrochloric acid was added until the reaction mixture was acid to congo red. Another 110ml. of the acid was then added. The basic copper salts which were precipitated while the solution was being made acidic to litmus redissolved before it was acidic to congo red. The acidification was carried out

with very vigorous stirring. The solution was allowed to stand overnight and a dirty yellow precipitate settled down. This was filtered and washed on the Buchner funnel several times with water. The crude yellow product was dried in an air oven at50°. Yield 35.5g. (70%), m.p.195°- 197°.

This was dissolved in concentrated sulphuric acid (4ml. per gram.), heated with stirring at 150° for 5min. and allowed to stand overnight. The resulting product was filtered through a sintered glass funnel and washed on the funnel with three 20ml. portions of concentrated sulphuric acid, and then several times with water. The product was transferred to a beaker and boiled with water (_ca_. 60ml.) to remove traces of sulphuric acid that may be present. It was filtered hot, washed with hot water and dried.

It was recrystallised twice in the manner described above, whence pure 4:4':6;6'-tetrachlorodiphenic acid (11.5g.) was obtained in beautiful colourless needles; m.p.264°-265° (_Org.Synth_.gave m.p. 258°-259°). Yield calculated on the basis of 3:5-dichloro-2-aminobenzoic acid was 23%. Recovery of the pure acid from the crude product was 32%.

The preparation of 4:4':6:6'tetrachlorodiphenic acid from aminodichlorobenzoic acid was repeated several times. It was found that the use of purified dichloroaminobenzoic acid (m.p. 228°-229° from alcohol) had no particular advantage over the use of the crude material as the overall yield of tetrachlorodiphenic acid did not improve appreciably.

The sulphuric acid mother liquor obtained after filtering off the first crop of the tetrachloroacid, when diluted with water, gave a yellowish green precipitate which was mostly inorganic but also contained some low melting (*ca.* 170°) organic by-product. This was discarded.

The yield of crude tetrachlorodiphenic acid varied from 68% to 85% and that of the pure acid (m.p. 263°-264°) between 20% to 25%.

Attempted preparation of 4:4':6:6'-tetrachlorodiphenic acid employing sodium metabisulphite and cuprammonium hydroxide as reducing agent.

Copper sulphate pentahydrate (45g.) was dissolved in water and ammonium hydroxide (*d.*0.88, 50ml.) added with stirring. This solution was cooled to 10° and 102g. of powdered sodium metabisulphite and ammonia (*d.*0.88, 105ml.) were added. The solution became brownish with the appearance of a precipitate. It was cooled to 10° and the diazo solution added to it in the same way as in the previous preparation. The addition took about 45min. and the temperature of the reaction mixture was maintained at 10°-15°. It was vigorously stirred throughout.

Anhydrous ferric chloride (66g.) was dissolved in water and 330ml. of concentrated hydrochloric acid (*d.*1.18) added to the filtered solution. This was added to the above reaction mixture and a yellow orange coloured precipitate was formed. It was allowed to settle overnight, then filtered and washed several times with water. Yield 5.8g., m.p. 200°-202°. It was crystallised from concentrated sulphuric acid by heating it to 150° and then letting it cool overnight. About 1 gram of a dirty white substance with the same m.p. was recovered. It depressed the m.p. of the authentic tetrachloro-acid.

The above experiment was repeated using pure 2-amino-3:5-dichlorobenzoic acid (m.p.229°-230°) when a product with m.p. 159°-162° was obtained. This on crystallisation from concentrated sulphuric acid did not give 4:4':6:6'-tetrachlorodiphenic acid.

Preparation of dimethyl 4:4':6:6'-tetrachlorodiphenate.

Tetrachlorodiphenic acid (20g.) was dissolved in ten times its weight of methanol (267ml.) and concentrated sulphuric acid (*d*. 1.84, 20g.) added. The solution was heated on a water bath under reflux for 6hrs. It was cooled to room temperature and poured into three times its volume of water. The crude ester was filtered and washed successively with water, five percent sodium hydrogen carbonate, and water, and dried. It had m.p. 154°-155°.

The combined filtrates were acidified with dilute hydrochloric acid. The precipitate formed was filtered off and washed well with water. On drying on a water bath it melted. At room temperature it solidified to a cream coloured solid. After recrystallisation from methanol it had m.p.102°-104°, weight 2.0g.

Incomplete esterification was found to be the cause of the formation of this low melting product which was mainly the mono acidic ester. Another 4.5g. of it (m.p.85°-90°) were obtained, when the mother liquor from the crystallisation of the dimethyl ester was evaporated to dryness.

The two solids (2g. and 4.5g.) were combined, dissolved in methanol and heated with concentrated sulphuric acid for another 6hrs. On leaving overnight colourless well defined plate-like crystals separated. These were filtered off and the filtrate poured into water. Very little of a sticky precipitate was formed and was extracted with ether.

All the solids obtained were combined and recrystallised twice from methanol. Yield 15.4g.,(72%), m.p.160°-161°. (Found: C,47.0; H,3.0; Cl,35.2. $C_{16}H_{10}O_4Cl_4$ requires C,47.0; H,2.5; Cl,34.5 %).

The above preparation was repeated several times; it was found that by increasing the time of continuous heating from 6 to 18 hrs. the yield of the crude ester, m.p. 156°-157°, was theoretical and the ester was pure enough to use for all subsequent reactions. The percentage yield of the pure ester was 98.5%.

Preparation of 4:4':6:6'-tetrachloro-2:2'-bishydroxymethyldiphenyl.

The method used by Hall, Lesslie and Turner (Nature, 1949, 163, 537) for the preparation of bishydroxymethyldiphenyl was adopted.

Dimethyl tetrachlorodiphenate (26g.,1mol.) dissolved in sodium dried ether (400ml.) was added from a dropping funnel to a suspension of lithium aluminium hydride (4.4g.,1.8mol.) in dry ether (300ml.) placed in a 2 litre two necked flask fitted with a reflux condenser. The reduction was slow at room temperature. After the addition of all the ester solution the reaction mixture was heated under reflux on a water bath for 40min. to complete the reaction. The flask was then cooled to room temperature and water added very cautiously from a dropping funnel. This was followed by 2N sulphuric acid (160ml.). Two clear layers were formed overnight. These were separated, the water layer washed twice with ether and the ether extracts combined.

On distilling off all the ether a yellow oily residue was left which on cooling solidified to a white solid, m.p. $136^{\circ}-138^{\circ}$, 4:4':6:6'-tetrachloro-2:2'-bishydroxymethyldiphenyl crystallised from carbon tetrachloride in small needles, m.p. $137^{\circ}-138^{\circ}$. Yield 22.2g. (98%).

(Found: C,47.8; H,2.9; Cl,40.6. $C_{14}H_{10}O_2Cl_4$ requires C,47.8; H,2.9; Cl,40.3 %).

When this preparation was repeated it was found more comvenient to add the ester as a finely powdered solid in small quantities through a dropping funnel followed each time by a few ml. of dry ether as the ester was not very soluble in ether and this procedure dispensed with the use of large volumes of ether.

Preparation of 2':4':1":3"-tetrachloro-2:7-dihydro-3:4-5:6-dibenzoxepin.

The method of Hall and Turner (J.,1951, 3072) for the preparation of dihydro-dimethoxy-dibenzoxepin was used.

The tetrachlorobishydroxymethyldiphenyl (1g.,m.p.136°-137°) was heated with 50% sulphuric acid (20ml.) in a beaker on a hot plate with stirring until the solid melted. The solution was boiled for about 10min. On cooling a glassy substance along with a little white precipitate separated. It was filtered and washed with water. Yield 0.7g. (74%), m.p.146°-148°.

It was crystallised from methyl alcohol three times and then had m.p. 148°-149°.

(Found: C,50.3; H,2.5; Cl,42.2. $C_{14}H_8OCl_4$ requires C,50.4; H,2.4; Cl,42.5 %).

Preparation of 2:2'-bisbromomethyl-4:4':6:6'-tetrachloro-diphenyl.

The method used by Hall, Lesllie and Turner (Nature, 1949, 163, 537) for the preparation of 2:2'-bisbromomethyl-diphenyl was adopted.

4:4':6:6'-Tetrachloro-2:2'-bishydroxymethyldiphenyl (1g.) was dissolved in boiling glacial acetic acid (12ml.) and hot hydrobromic acid (15ml., 48% w/w) added to it. The solution first turned cloudy, then cleared on shaking but became cloudy again with heating. It was heated under reflux for 10min. and then another 10ml. of hydrobromic acid added to the solution. Heating under reflux was continued for another 15min. when some oily drops appeared. The mixture was poured into a beaker and the clear supernatant liquid decanted after cooling.

A sticky substance was obtained which could not be crystallised from any of the following solvents: carbon tetrachloride, benzene, light petroleum (b.p. 60°-80°, 80°-100°) methyl ethyl ketone, or glacial acetic acid.

In an effort to obtain crystalline dibromide the preparation was carried out by the following different methods.

(A). The diol (3.0g., 1mol.) was added to phosphorus tribromide (14g., 3mol.) placed in a flask fitted with a calcium chloride tube and cooled externally in an ice bath. After the addition of the diol, the flask was allowed to warm up to room temperature and then kept at 30° for 15 to 20min. It was cooled to room temperature and the contents of the flask poured onto crushed ice in a beaker. A little of a white precipitate was obtained but all the rest settled down as a sticky mass. The water was decanted off and the residue washed several times with water.

The residue was dried in vacuum for several days but it did not solidify. The small amount of precipitate mentioned above had m.p.72°-75° but could not be purified any further. The sticky product on leaving on a watch glass for several weeks became slightly brittle but still would not crystallise.

(B). The diol (1g.) was boiled under reflux with excess of hydrobromic acid (48% w/w) for 1hr.,which resulted in the separation of some oily drops. Overnight it settled to sticky mass of the same type as described in the very first preparation

(C). From tetrachloro-dihydro-dibenzoxepin; The oxepin (1g.,m.p.148°-149°) was heated under reflux with excess of hydrobromic acid (48% w/w) with which it did not react. The supernatant acid was poured off and the residual solid dissolved in hot glacial acetic acid. The above acid was added back and this turned the solution cloudy. It cleared again after about 15min. boiling under reflux. Heating was continued for another half hour. The supernatant liquid was removed by decantation and the sticky product left was dried over potassium hydroxide in vacuum overnight but it was not found possible to crystallise it either.

In some more experiments for obtaining the 2:2'-bisbromomethyl-4:4':6:6'-tetrachlorodiphenyl, the proportions of reagents and the time of reaction was varied but with no success.

For all successive work, the required amount of dibromide was prepared afresh preceding its use in each experiment, dried over caustic potash in vacuum overnight and the gummy product used as such by dissolving it in suitable solvents.

In a dibromide solution in glacial acetic acid after several months few crystals were formed, m.p. 96°-104°. Recrystallisation from glacial acetic acid raised the m.p. to 102°-104°.

(Found: C,34.6; 34.4; H,1.5, 1.8; Hal,62.3. $C_{14}H_8Cl_4Br_2$ requires C,35.2; H,1.7; Hal,63.1 %).

In some of the dibromide solution in acetic acid, when inoculated by crystals from the above sample, were formed some crystals, but attempts to crystallise larger quantities proved futile.

Preparation of 2':4':1":3"-tetrachloro-2:7-dihydro-3:4-5:6-dibenzazepinium-1-spiro-1"'-piperidinium bromide.

Beavan, Hall, Lesslie and Turner (*J.*,1952, 854) have prepared a similar compound by this method.

From the diol (1.0g.) the 2:2'-bisbromomethyl-4:4':6:6'-tetrachlorodiphenyl was prepared in the usual manner, the supernatant liquid poured off, the crude dibromide washed well with cold water, dissolved in benzene (10ml.), washed with 2% sodium hydrogen carbonate solution, the two layers separated and then the benzene solution was washed well with water. To it, piperidine (0.40g.,1.1mol.) dissolved in benzene (5ml.) was added. The solution remained clear. It was warmed for about 5min. (*ca.*70°), with cooling; a white flocculant precipitate was formed. It was filtered and dried, m.p.151°-153°. It weighed 0.7g. The yield calculated on the basis of the diol used was 48%.

Some was crystallised from acetophenone, small needle-shaped crystals were obtained m.p. 234°-235° (decomp.). Some more was crystallised from water; first crop, m.p. 120° to 121° (decomp.), second crop, m.p.190°-195° (decomp.).

A mixture of the acetophenone purified product and the one from water (first crop) had m.p. 150°-152° (decomp.).

The preparation of dihydro-dibenzazepinium-*spiro*-piperidinium bromide was repeated with 5.0g. of diol when

5.5g. of the [illegible]bromide, m.p. 141°-143° (decomp.), (75.3% yield calculated on the basis of the weight of diol used) was obtained. It crystallised from water in two crops, first, m.p. 210°-212° (decomp.), 4g.; second crop with m.p. 195°-200° (decomp.). The m.p. of the first crop on further crystallisation rose to 212°-213° (decomp.).

Attempts to isolate the compound with m.p. 120°-121° failed. This difference in m.ps. was attributed to the different amount of water of crystallisation.

The product with m.p. 212°-213° was dried in vacuum for several days and analysed.

(Found: C,42.7; H,4.1. $C_{19}H_{18}Cl_4BrN, 2H_2O$ requires C,44.0; H,4.2 %. Bromine ionic, estimated as AgBr, 15.5, 15.4% $C_{19}H_{18}Cl_4BrN, 2H_2O$ requires 15.6%).

Attempted optical resolution of 4:4':6:6'-tetrachlorodiphenic acid.

(In all polarimetric observations $l = 2$dcm.)

Drying of Brucine: The method was essentially that of Turner (J.,1951, 842).

Commercial brucine (May and Baker), 10.0g., was dissolved in least possible amount of dry chloroform and left for half hour over anhydrous sodium sulphate (preheated in an air oven at 80° for ca. 2hrs.). It was filtered first by suction and then through an ordinary funnel directly into a three litre beaker containing 2000ml. of dry light petroleum (b.p. 40°-60°). Precipitated brucine was allowed to settle down and then filtered off.

It was kept overnight in vacuum over anhydrous calcium chloride and then dried in an air oven at 60° for 24hrs. The product had m.p. 177°-179° (decomp.) and $[\alpha]^{18}_{5461}$ -149.9° in chloroform (c=1).

It was earlier noted that if the chloroform solution of brucine was not very concentrated or if higher boiling light petroleum (60°-80°) was used for its precipitation it resulted in the loss of brucine. The product also had a lower m.p. and the specific rotation was $[\alpha]^{18}_{5461}$ -140°.

Formation of normal brucine salt of 4:4':6:6'-tetrachlorodiphenic acid:

The acid (4.5g.,1mol.) dissolved in boiling ethyl acetate (55ml.) was quickly added to a boiling solution of anhydrous brucine (9.3g.,2mol.) in ethyl acetate (210ml.). Most of the salt crystallised out in the first crop; three more crops were collected by successive concentration of the mother liquors. After obtaining the fourth crop, the mother liquor on evaporation to dryness, left a dirty yellow pasty mass which was discarded. Total weight of salt collected was 13.2g. (95%).

The polarimetric reading were taken in chloroform (B.P.) solution.

CROP.	Wt.	M.p.		$[\alpha]_{5461}$	$[\alpha]_{5791}$
A	10.0g.	250°-252°	(decomp.)	-22.7°	-18.9°
B	1.8g.	270°-272°	"	-21.5°	-20.3°
C	0.6g.	273°-274°	"	-60.2°	-49.7°
D	0.8g.	232°-234°	"	-35.1°	--

Crops A and B having similar specific rotations were mixed and crystallised from ethanol. 5.3G. of this solid did not dissolve on boiling with a fairly large volume of ethanol. This was collected (crop E) and the alcoholic solution deposited crop F (3.75g.), m.p. 237°-239°, it had

$[\alpha]_{5461}$ -22.2°.

(Found: C,57.7; H,4.6; Cl,14.6. $C_{14}H_6O_4Cl_4.(C_{23}H_{26}O_4N_2)_2$ requires C,61.6; H,5.5; Cl,12.1 %.

$C_{14}H_6O_4Cl_4.(C_{23}H_{26}O_4N_2)$ requires C,57.3; H,4.5; Cl,18.3%).

A little of crop E was decomposed by dilute sodium hydroxide solution, washed well with chloroform to remove liberated brucine and its absence tested for by a drop of nitric acid. Tetrachlorodiphenic acid was precipitated by acidifying the sodium hydroxide solution with 2N sulphuric acid. The acid had $[\alpha]_{5461}$ -11.3°. The rest of crop E was crystallised from chloroform-ligroin and from 2-ethoxyethanol but the specific rotation was unchanged.

In view of the very slight separation achieved and the analysis of the salt (above) no further experiments were carried out on the normal brucine salt.

<u>Attempted optical resolution through the acid brucine salt.</u>

The method of Atkinson and Lawler (J.Amer.Chem.Soc., 1940, 62, 1704) was used with some modification.

In this experiment, 4:4':6:6'-tetrachlorodiphenic acid (4.0g.,1mol.) was added to one half equivalent of brucine (4.4g.,1mol.) using alcohol as a solvent.

Only one crop of salt was obtained (6.0g.,71%.). The mother liquor on further concentration left a yellow oily residue which did not solidify and was rejected. The solubility of the acid salt in ethanol was low and the above mentioned crop was split up to give three solutions namely A, B, and C on the basis of solubility.

From solution B, the first crop obtained (no. B_1) had the lowest rotation as compared to all other crops obtained. Crop B_1, m.p. 253°-255° (decomp.), $[\alpha]_{5461}$ -16.8° was analysed which shows that it probably was a mixture of mono acid brucine salt and the normal salt.
(Found: C, 59.0; H, 5.0; Cl, 14.3. $C_{14}H_6O_4Cl_4 \cdot C_{23}H_{26}O_4N_2$ requires C, 57.3; H, 4.5; Cl, 18.3 %; $C_{14}H_6O_4Cl_4 \cdot (C_{23}H_{26}O_4N_2)_2$ requires C, 61.6; H, 5.5; Cl, 12.1 %).

Crop B_1 (2.8g.) was dissolved in ethanol (1500ml.) from which, after obtaining two crops nos. B_4 and B_5, a last crop B_6, m.p. 252°-255°, $[\alpha]_{5461}$, and $[\alpha]_{5791}$ -39.9° and -31.9° respectively was obtained.
From 0.4g. of crop B_6 decomposed in the same manner as described in the previous experiment, 0.14g. of (+) acid was obtained, $[\alpha]_{5461}$ +8.9°, $[\alpha]_{5791}$ +8.1°. From solution B, after filtering off crop B_1, the filtrate on further concentration gave crop B_2 which had the highest specific rotation, $[\alpha]_{5461}$ -61.4°, $[\alpha]_{5791}$ -50.1°. This was also decomposed and the acid obtained from it was also <u>dextro</u> rotatory, $[\alpha]_{5461}$ +8.2°, $[\alpha]_{5791}$ + 7.4°. The specific rotation as well was not very different from the active acid obtained from a salt B_6 of medium

specific rotation.

Extensive fractional crystallisation of all crops was carried out from ethanol. In some cases 2-ethoxyethanol was also tried as a solvent. In view of the negligible difference in the specific rotation of the two <u>dextro</u> rotatory acids obtained from the brucine salts with very different rotations and the analysis results of the salt , further experiments were not carried out.

<u>Attempted resolution of 4:4':6:6'-tetrachlorodiphenic acid through its amphetamine salt.</u>

To a concentrated solution of amphetamine sulphate (Light and Co.'s), m.p.322°-324° (darkening at 300°)(2.9g., 1mol.) in water, was added a solution of an equivalent amount of sodium carbonate in water. Finely ground tetrachlorodiphenic acid (3.0g.,1mol.) was added to the above solution. A crystalline solid appeared. It was allowed to stand overnight, filtered and dried, 3.5g.(86% yield of acid amphetamine salt), m.p.180°-182° was obtained. It was optically inactive. According to the analysis result it had not formed the normal salt but had formed the acid salt. (Found: C,53.9; H,3.8; Cl,26.7. $C_{14}H_6O_4Cl_4 . C_{18}H_{26}N_2$ requires C,59.3; H,4.7; Cl,21.9; $C_{14}H_6O_4Cl_4 . C_9H_{13}N$ requires C,53.6; H,3.7; Cl,27.5 %).

The above solid was dissolved in water (300ml.) and left overnight at about 4°. Very little solid appeared, the solution was concentrated to 150ml. whereby it became turbid before cooling. After standing overnight at 4°, 0.5g. of an optically inactive solid was collected from it, m.p.180°-183°. All crops obtained by further concentration of the mother liquor had the same m.p. and were optically inactive. The mother liquor on evaporation to dryness left a sticky noncrystallisable residue.

As there was no evidence of separation into diastereoisomeric salts, the attempted resolution with amphetamine was given up.

Preparation of 1":4':2':3"-tetrachloro-3:4-5:6-dibenzcyclohepta-3:5-diene-1:1-dicarboxylic acid.

In the following condensations and for the subsequent stages, the method of Kenner (J.,1913, 103, 621) with some modifications, and Beavan, Bird, Hall, Johnson, Ladbury, Lesslie and Turner (J.,1955, 2708) were adopted.

2:2'-Bisbromomethyl-4:4':6:6'-tetrachlorodiphenyl was prepared from tetrachloro-bishydroxymethyldiphenyl (35.2g., 1mol.) by heating its solution in glacial acetic acid (110ml.) with hydrobromic acid (500ml.48%w/w) under reflux for 2½hrs. The sticky product was dried in vacuum over potassium hydroxide for 48hrs. and then dissolved in sodium dried ether (300ml.).

The quantities of other reactants were calculated on the basis of the diol used with the assumption that its conversion into the dibromide was theoretical, (47.8g.,1mol.).

Commercial absolute ethanol was dried by heating it (200ml.) with sodium (2.0g.) and diethyl phthalate (200g.) for 1½hrs under reflux. The apparatus was then rearranged for distillation. The middle fraction of the dry alcohol (100ml.) was collected directly in the dropping funnel which was to be used in the reaction apparatus.

In an electrically heated mantle, a 1 litre three necked flask was fitted with a mechanical stirrer, reflux condenser and the dropping funnel containing the dry alcohol.

The condenser and the funnel were equipped with calcium chloride tubes.

The apparatus was dried immediately before use. Alcohol was run into the flask, freshly cut sodium (4.6g., 2atoms) was added to it. Most of this dissolved at room temperature in about 15min. with intermittent stirring. The flask was then warmed to dissolve the last traces of the metal.

Heat was turned off and diethyl malonate (15.0g., 1mol.), previously redistilled under reduced pressure, was run in. After half hour's stirring, the ethereal solution of bisbromomethyl-tetrachlorodiphenyl was added gradually through the dropping funnel. The solution gradually became cloudy. Stirring was continued and the reaction mixture heated for 40min.

The condenser was fitted for distillation and ether was removed. Most of it distilled at 36° and the rest between 38° to 41°. In all, about 250ml. of ether was recovered. The apparatus was refitted for reflux. Heating with stirring was continued for 2½hrs.

Gradually, the reaction mixture became thicker; the colour changed to yellow and then pink. When tested in water, the reaction medium was found to be neutral to litmus. Tested with universal indicator paper the pH. was 8. The flask was cooled, 200ml. of water added to it, and allowed to stand overnight.

A waxy solid separated. This was removed, weighed 43.0g., m.p. 105° to 125°. The water layer was extracted twice with ether, the combined ether extracts were washed with water, dried over anhydrous potassium carbonate and then ether was removed by distillation. From this very little waxy solid was obtained.

The reaction product was crystallised twice from ethanol, 23.8g. recovered, m.p. 120°-128°. From the oily mother liquor no more solid could be obtained.

The above product was dissolved in ethanol. Caustic potash solution (48g. in a few ml. water) was added to the hot alcoholic aolution and boiled under reflux for 4hrs. It was then cooled, poured into a large volume of water and the precipitate allowed to settle overnight. The solid (x) was removed by filtration and the filtrate which was still milky was acidified with dilute hydrochloric acid. A very sticky white precipitate which could not be collected by filtration, was formed. The suspension was extracted three times with ether the ether removed by distillation, the yellow oily residue on cooling formed a waxy solid, 9.5g., m.p. 172°-175°, with evolution of carbondioxide.

The yield of 1":4'-2':3"-tetrachloro-3:4-5:6-dibenz-*cyclo*hepta-3:5-diene-1:1-dicarboxylic acid calculated on the basis of tetrachlorobishydroxymethyldiphenyl used in

this three step synthesis was 23%.
(Found: C,48.8; H,2.4; Cl,34.0. $C_{17}H_{10}O_4Cl_4$ requires C,48.6; H,2.4; Cl,33.8%).

The solid (x) was washed well with water and dried, m.p.145°-150°, 13.9g. It was crystallised from methanol, m.p.147°-149°. Mixed m.p. of this with an authentic sample of the oxepin and of the pure oxepin were the same. This was also verified by a comparative study of the ultra-violet absorption spectra of the authentic oxepin and a sample from this experiment.

The yield of oxepin calculated on the basis of the tetrachloro-bishydroxymethyldiphenyl used was 42%.

In the above experiment,pure diethyl 1":4'-2':3"-tetrachloro-3:4-5:6-dibenz*cyclo*hepta-3:5-diene-1:1-dicarboxylate was not obtained. The m.p. of the reaction product was (120°-128°) as it was a mixture of the above ester and the oxepin. In a former experiment on the same condensation an excess of diethylmalonate was erroneously added, 81% of which was recovered by distillation from the oily reaction product. The yield of the above diethylester was 23%, m.p.140°-141°.
(Found: C,52.9; H,3.0; Cl,29.8. $C_{21}H_{18}O_4Cl_4$ requires C,52.9; H,3.8; Cl,29.8%).

The oily mother liquor, after removal of the above ester probably contained some oxepin dissolved in diethyl malonate. No proof of this was, however, obtained.

The attempt to obtain any solid by hydrolysing the oil was also unsuccessful. It was discarded after standing for several weeks.

Preparation of 1":4'-2':3"-tetrachloro-3:4-5:6-dibenzcyclohepta-3:5-diene-1-carboxylic acid.

The dicarboxylic acid (5.0g.) was heated in a dry test tube with stirring by a thermometer in a metal bath at 160°. The temperature of the bath was gradually raised to 200°. Carbon dioxide was given off and when the temperature inside the tube was about 190°, the liquid solidified with slight darkening in colour. The total time of heating was about 8min.

Alcohol was added to the test tube whilst still at about 180°. The acid was completely dissolved in an excess of boiling ethanol. On concentration and cooling to about 4°, the mono carboxylic acid was obtained in clusters of fine needle shaped crystals. It was crystallised twice from ethanol, m.p. 219°-221°, and weighed 2.0g., 50% yield. As it was slightly coloured it was crystallised after boiling with charcoal when long rectangular plates, with the same m.p., were obtained.

(Found: C, 51.5; H, 2.8; Cl, 37.3. $C_{16}H_{10}O\,Cl_4$ requires C, 51.5; H, 2.4; Cl, 37.3 %).

Preparation of Methyl 1":4'-2':3"-tetrachloro-3:4-5:6-dibezncyclohepta-3:5-diene-1-carboxylate.

A solution of tetrachloro-dibenz*cyclo*heptadiene-1-carboxylic acid (1.0g.) was prepared in methanol (14ml.) and concentrated sulphuric acid (*d*.,1.84; 1.0g.) was added to it. The solution was heated under reflux for 7hrs. On cooling some solid separated out. It was all added to an excess of water, the precipitate formed was filtered. It was washed successively with water, 10% sodium hydrogen carbonate solution and water. It was dried in an air oven at about 50°. It melted at 158°-160°, 0.95g., 98% yield. It crystallised from methanol in clusters of fine needles, m.p.159°-160°.

(Found: C,52.7; H,3.2; Cl,36.1. $C_{17}H_{12}Cl_4O_2$ requires C,52.3; H,3.1; Cl,36.3 %).

Attempted condensation of 2:2'-bisbromomethyl-4:4':6:6'-tetrachlorodiphenyl with ethyl propane-1:1-3:3-tetracarboxylate.

(Compare Beaven, Bird, Hall, Johnson, Ladbury, Lesslie and Turner, *J.*,1955, 2708).

From 4:4'-6:6'-tetrachloro-2:2'-bishydroxymethyl-diphenyl (23.9g.,1mol.), the bisbromomethyl tetrachloro diphenyl was prepared in the usual manner, stirred with boiling light petroleum (40°-60°) and the light petroleum removed in vacuum overnight.

To a solution of sodium ethoxide prepared from sodium (3.1g.,2atoms) and ethanol (52ml.), ethyl propane tetracarboxylate (22.1g.,1mol.) was added at room temperature with stirring. After some time the solution of the above mentioned bisbromomethyl-tetrachlorodiphenyl in dry ether (250ml.) was gradually added whereby the reaction mixture became turbid. The reaction mixture was heated under reflux on a heating mantle for 45min. after the addition of all reactants.

Ether was then distilled off at 36°-42° and the apparatus was rearranged for heating under reflux. Heating, with gentle stirring, was continued for 1¼hrs.

The flask was allowed to cool down to room temperature and water (_ca._ 200ml.) was added to it. On shaking for some time an oil separated which solidified on cooling the flask in an ice-salt mixture. It was left overnight at _ca._ 4°. The supernatant liquid was filtered, the waxy solid was washed several times with water on the Buchner funnel and dried as much as possible on the funnel.

It was crystallised from ethanol; 18.0g. of a cream coloured solid, m.p.121°-125° was obtained. On admixture with diethyl 1":4'-2':3"-tetrachloro-3:4-5:6-dibenz_cyclo_-hepta-3:5-diene-1:1-dicarboxylate (m.p.140°-141°) it melted at 121°-138°. The crystallisation of the ester from ethanol was however not very satisfactory and it was hydrolysed in the crude form. No trace of ethyl 2':4':1":3"-tetrachloro-5:6-7:8-dibenz*cyclo*nona-5:7-diene-1:1-3:3-tetracarboxylate was detected.

Hydrolysis of the above condensation product.- An alcoholic solution of the above ester was heated under reflux with a large excess of a saturated aqueous solution of potassium hydroxide for 12hrs. It was cooled and poured into three times its volume of water, some solid appeared. The solution was acidified when more white solid separated. It was filtered, washed with water and dried, m.p.175°-179°, 16.5g. This solid (1g.) was crystallised from dilute ethanol, the first crop obtained, 0.4g., melted at 147°-149° with no evolution of gas. The second crop separated as an oil solidified on cooling to a waxy solid , 0.4g., m.p.180°-183° (with evolution of CO_2).

The rest of the white solid, m.p.175°-179°, was heated with 5% sodium carbonate solution for a few min. on a water bath. It was filtered after cooling to room temperature, 7.2g. of the substance had not dissolved. On acidifying the clear filtrate with dilute hydrochloric acid a sticky precipitate was formed. It was filtered, washed twice with water and crystallised from aqueous ethanol. The first crop, 1.1g., melted at 216°-217°; the second crop, 4.6g., which separated as an oil but solidified on cooling, also melted at the same temperature; both depressed the m.p. of an authentic sample of 1:4":2':3"-tetrachloro-3:4-5:6-dibenz*cyclo*hepta-3:5-diene-1:1-dicarboxylic acid but not that of the mono carboxylic acid. Decarboxylation had obviously taken place and to complete it the two crops were together heated in a dry test tube in a metal bath at 200° gradually raising the temperature to 215° and there kept constant for 35min. The solid softened slightly and some carbon dioxide was evolved. A few drops of benzene were added whilst the tube was still very hot and then more to get a clear solution which was very dark brown in colour. It was cooled and allowed to crystallise overnight. First crop obtained, 4.4g., m.p. 218°-219° and the second, 0.4g., melted at 216°-217°.

An alcoholic solution of 7.2g. of the solid insoluble in sodium carbonate was heated again under reflux with an excess of caustic potash for 48hrs. when a little more of the mixture of mono and di carboxylic acids was obtained. The solid after being washed with water, dried and crystallised from dilute ethanol melted at 149°-150°. Its mixed m.p. with an authentic sample of 2:7-dihydro-4':1"-2':3'-tetrachloro-3:4-5:6-dibenzoxepin and its ultra-violet absorption spectrum proved it to be the oxepin.

(Found: C,51.2; H,2.4; Cl,42.8. Calc. for $C_{14}H_8OCl_4$: C,50.4; H,2.4; Cl,42.5 %).

The oxepin was obtained in 20% yield and the mono carboxylic acid in the same yield also. Both calculated on the basis of the diol used.

Condensation of 2:2'-bisbromomethyl-4:4':6:6'-tetrachlorodiphenyl with ethyl ethane tetracarboxylate.

The apparatus used in this experiment was the same as described in the preceding condensations of bisbromomethyltetrachlorodiphenyl. The latter compound and pure ethanol were also obtained in the manner already described. Bisbromomethyltetrachlorodiphenyl after being kept over caustic potash in vacuum was stirred with a few ml. of petroleum ether (b.p. 40°-60°) and that also removed in vacuum overnight.

Sodium ethoxide was prepared from sodium (3.1g., 2atoms), and absolute ethanol (45ml.). Powdered ethyl ethane tetracarboxylate (21.2g., 1mol.) was added to it and the reaction mixture stirred for half an hour. The solution of bisbromomethyltetrachlorodiphenyl (32.2g., 1mol.) obtained from the diol (23.5g., 1mol.) in dry ether (150ml.) was added through the dropping funnel, after which the reaction mixture was heated under reflux for half hour. The apparatus was then rearranged for distillation and ether (130ml.) collected in about an hour, most of which distilled between 36°-38° in 45min. In the next 15min., the temperature rose to 65° when distillation was stopped and the reaction was allowed to proceed with gentle refluxing and continuous stirring for another 1½hr.

The reaction medium was alkaline to litmus throughout the reaction but the pH (universal indicator paper) was found to fall from 10 to 9 soon after the removal of ether.

Water was then added to the reaction product and it was allowed to stand overnight. A waxy solid settled down. It was filtered and dried as much as possible on the funnel, m.p.<u>ca</u>.90°, 28g.

The water layer was extracted with ether three times but no residue was left on removal of the solvent.

The above waxy solid was crystallised twice from <u>n</u>-hexane, m.p.130°-143°, 23.4g. Mixed m.p. with ethyl ethanetetracarboxylate was inconclusive. Further crystallisation from <u>n</u>-hexane did not change the melting range but crystals formed had two different well defined shapes. It was recrystallised from ethanol, crop A m.p.145°-151°, 8.0g.; crop B m.p.85°-92°, 16.0g. were obtained.

Some of the crop B was recrystallised from ethanol, most of it was very soluble and a little was not which was filtered off. From the clear solution, a white solid melting at 73°-75°, 15.0g, was obtained. On admixture with pure ethyl ethane tetracarboxylate no depression was produced. in the melting point. The less soluble part, m.p.147°-149°

was added to crop A.

Crop A (8.0g.) was recrystallised twice from ethanol, a white solid m.p.151°-152°, 7.0g., was obtained.

Attempts were made to hydrolyse this solid in order to detect the presence of any ester (8membered ring) expected to be formed in the above condensation, by heating its alcoholic solution with excess of (a) saturated caustic potash solution; (b) with sodium ethoxide but the above solid was recovered in both cases. Its mixed m.p. with authentic 2:7-dihydro-4':1":2':3"-tetrachloro-3:4-5:6-dibenzoxepin was the same as that of the pure oxepin. The oxepin was obtained in 40% yield calculated on the basis of the diol used. Of the total weight of ethyl ethane tetracarboxylate used, 74% was recovered unchanged.

Attempted preparation of 2:4:5:7-tetrachloro-9:10-dihydrophenanthrene.

Hall, Lesslie and Turner, (J.,1950,711) have used this method for the preparation of 9:10-dihydrophenanthrene.

A little more than the required amount of lithium (0.5g.,2.1atoms) was put into a lithium press and the issuing wire was cut into small pieces as it entered a 3½litre three necked flask previously washed with nitrogen and containing about 25ml. of dry ether. After all the lithium had been added, a double surface reflux condenser with a calcium chloride tube and a dropping funnel were attached to the reaction flask. A solution of bromobenzene (5g., 1mol., in ca. 20ml. dry ether) was added slowly with gentle warming of the flask to start the reaction. When all the bromobenzene solution had been added in about 2hrs., the mixture was boiled on a water bath until all the lithium had dissolved which took about 40min.

The flask was removed from the water bath and the solution of tetrachloro-bisbromomethyldiphenyl (prepared from the diol 9.5g.,1mol. and dried in the usual manner) in 200ml. dryether was added through the dropping funnel at a fairly fast rate. When all this solution had been run in, the reaction mixture was boiled under reflux for 35min.

The flask was then cooled to room temperature and hydrochloric acid was added. Two clear layers were formed. These were separated and the aqueous layer was extracted twice with ether. Ethereal extracts were combined and the ether was removed by distillation. Bromobenzene was then distilled off under reduced pressure.

The residue set to a hard mass on cooling to room temperature. This was extracted first with light petroleum (b.p. 40°-60°) and then with light petroleum (b.p. 60°-80°). On distilling off the light petroleum (b.p. 60°-80°), hardly any solid was obtained. After removal of the solvent from the first extract (b.p. 40°-60°), the residual mass was left in the flask for 3 days, when very small needle-like crystals appeared in it. These were filtered off and washed twice with n-hexane, and then crystallised from the same solvent. Pale yellow needles, m.p.205°-210° (considerable softening at170°) were obtained. After recrystallisation from n-hexane it softened at the same temperature as above with m.p.205°-208°.

(Found: C,61.5; 61.0; H,2.8, 2.8; Cl,36.2. $C_{14}H_8Cl_4$ requires C,52.8; H,2.5; Cl,44.6 %. $C_{14}H_9Cl_3$ requires C,59.3; H,3.2; Cl,37.5 %).

Attempted preparations of 4:4':6:6'-tetrachlorodiphenic anhydride.

(A) 4:4':6:6'-Tetrachlorodiphenic acid (1.0g., m.p. 264°-265°) was dissolved in a few ml. of glacial acetic acid and an equal volume of acetic anhydride was then added. The solution was heated at 145°-150° for about 40min.

A solid separated on cooling and was filtered off. A second crop was obtained by pouring the filtrate into water. Both crops had m.p.262°-264° and were soluble in sodium bicarbonate solution. The mixed m.p. with authentic tetrachlorodiphenic acid produced no depression in the m.p. of the acid.

(B) Pure tetrachlorodiphenic acid (1.0g.) was heated with excess of acetic anhydride for 6hrs. The reaction product was diluted with water, filtered, washed and dried.

It was soluble in dilute sodium hydroxide solution. The starting material was recovered on acidifying this alkaline solution, m.p.260°-262° (softened at 258°).

SECTION I.

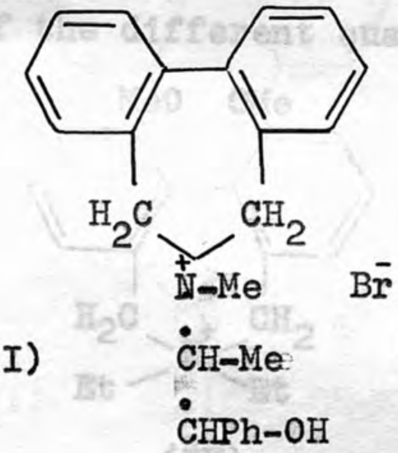
PART B.

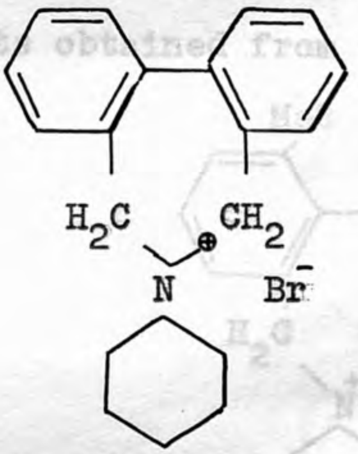
STEREOCHEMISTRY OF 3:3'-BRIDGED 2:2'-DINAPHTHYLS.

INTRODUCTION.

Beaven, Hall, Lesslie and Turner (J., 1952, 854) prepared 2':7-dihydro-1-(2-hydroxy-1-methyl-2-phenylmethyl)-1-methyl-3:4-5:6-dibenzazepinium bromide (I), by interaction of 2:2'-bisbromomethyldiphenyl and (+) ephedrine, also 2:7-dihydro-3:4-5:6-dibenzazepinium-1-spiro-1'''-piperidinium bromide (II), and 2:7-dihydro-4'''-phenyl-3:4-5:6-dibenzazepinium-1-spiro-1'''-piperidinium bromide (III) by treating the bisbromomethyldiphenyl with piperidine and phenylpiperidine respectively.

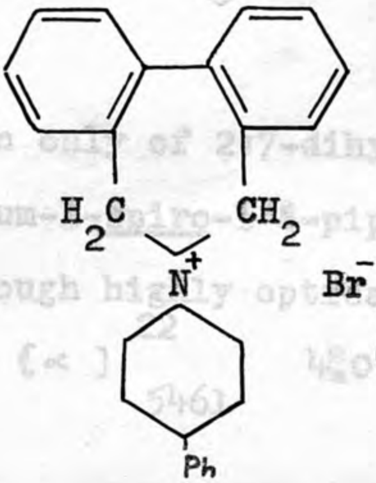
(I)





(II)

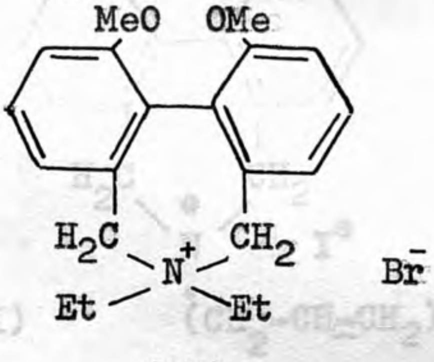
In compound (I), if the cyclic system is dissymmetric, it should be a mixture of diastereoisomerides but Turner et. al. were unable to separate the



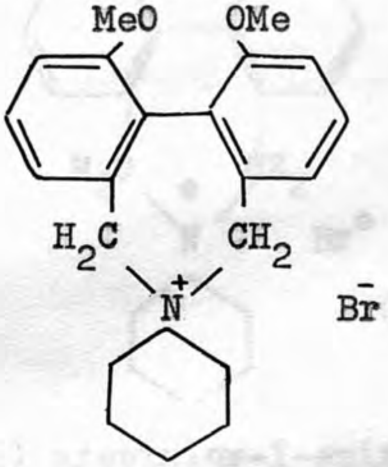
(III)

compound into two substances as mentioned (p.11). They also could not resolve compound (II) through the (+) camphorsulphonate or the (+)-α-bromocamphor-π-sulphonate. In the hope of augmenting the rotatory power they prepared (III) where -CHPh can only take part in the general dissymmetry of the twisted diphenyl skeleton but resolution could not be achieved.

In order to achieve resolution ; they introduced methoxyl groups in the 6:6' positions which might enhance the rotation without determinative effect upon the order of stability of the configuration of the quaternary salts. as compared to that of compounds (I), (II) and (III). Out of the different quaternary salts obtained from compounds (IV)



(IV)



(V)

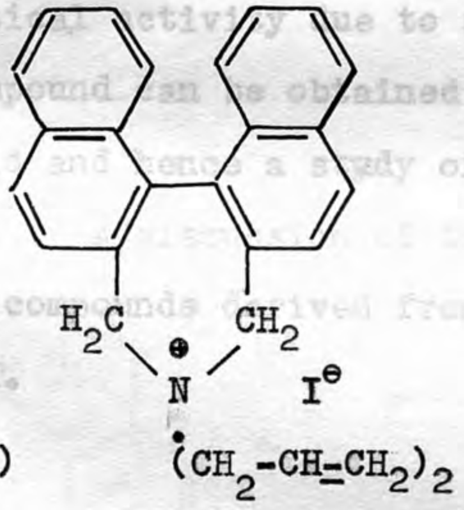
and (V) successful complete resolution only of 2:7-dihydro-4':1"-dimethoxy-3:4-5:6-dibenzazepinium-1-spiro-1"8-piperidinium iodide was affected. The compound though highly optically stable, had a small specific rotation $[\alpha]_{5461}^{22}$ 4.0 and

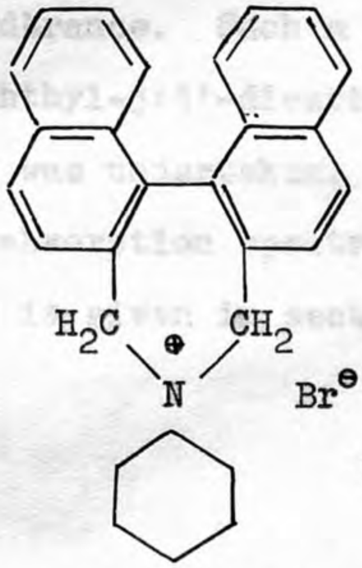
3.8°). These facts provided evidence for their view that methoxyl groups in the above compounds were of only secondary importance in affecting configurational stability.

Their inability to resolve compounds (I), (II) and (III) may, however, be due to the small specific rotation of such a compact rigid structure. Diastereoisomeric salts formed from these compounds would show only a little change in the specific rotation of different crops which may be even within experimental error or nearly so andhence the difficulty in effecting practical optical resolution.

Hall and Turner (J., 1955, 1242) have also prepared

(VI)





(VII)

2:7-dihydrodinaphtho(2':1-3:4)(1":2"-5:6) azepinium-1-<u>spiro-</u>1"'-piperidinium bromide (VII) with $[\alpha]^{20}_{5461}$ 306.5° starting with resolved dinaphthyl acid. This compound (VII) is optically very stable. They racemised it in hot ethylene glycol solution and it had a half life period of the order of 26hrs. at 172°. The other dinaphthyl compounds that they obtained in optically active forms were also very stable and had high specific rotation e.g. (VI) had $[\alpha]^{20}_{5461}$ 205.3°.

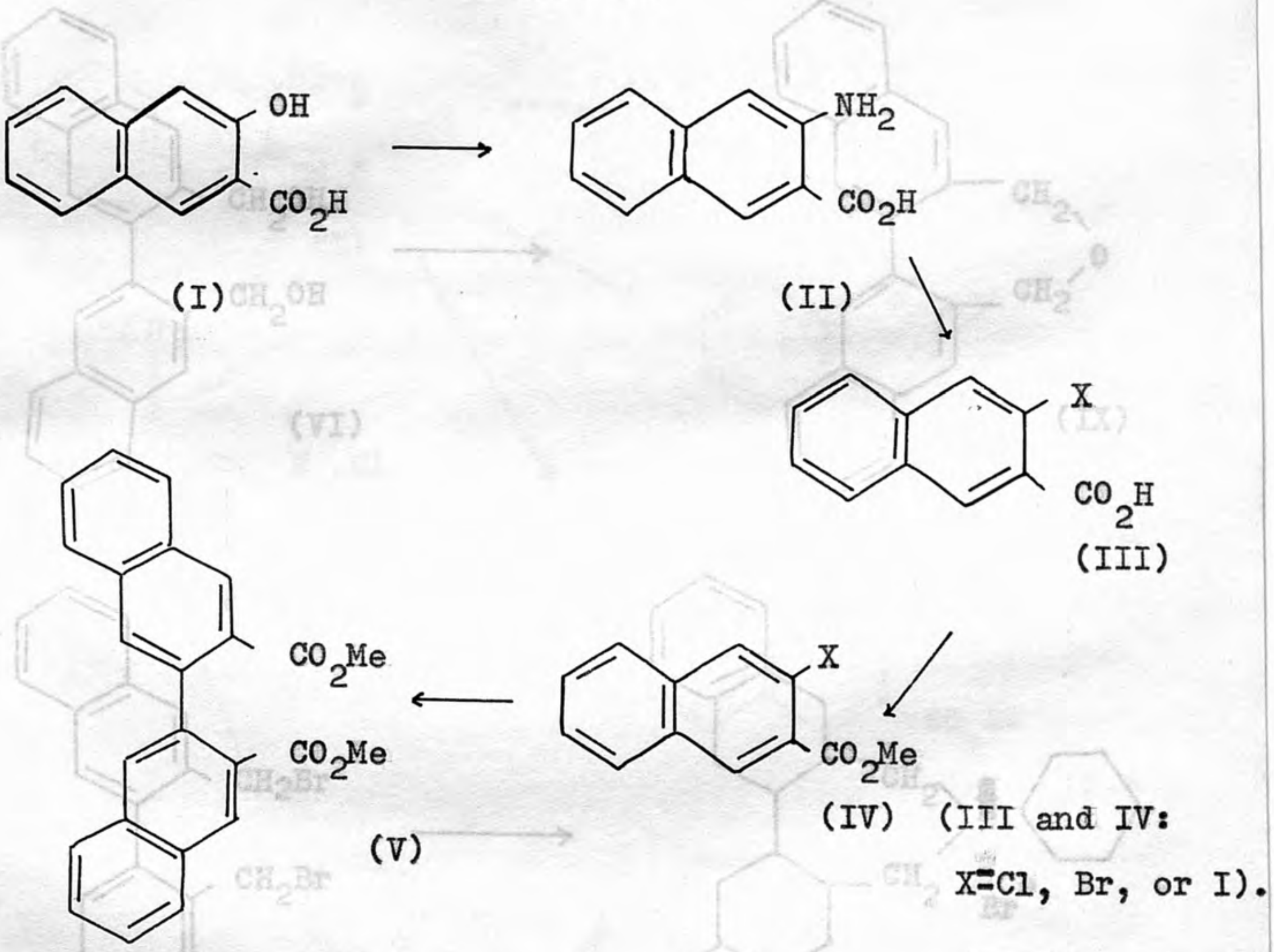
Coupling the observations that the compounds of the above types are resolvable and that the specific rotation is high amongst the dinaphthyl series, it was considered likely that a similar 2:2'-dinaphthylquaternary salts would not be so difficult to resolve as it ~~would~~ might have a higher specific rotation than the similar diphenyl compounds (I, II and III). Also in such a compound the two substituents benzene rings would be in positions other than the blocking ones. Thus there would be no chance of increasing the optical activity due to added steric hindrance. Such a compound can be obtained from 2:2'-dinaphthyl-3:3'-dicarboxylic acid and hence a study of this synthesis was undertaken.

A discussion of the ultra-violet absorption spectra of compounds derived from the above acid is given in section III.

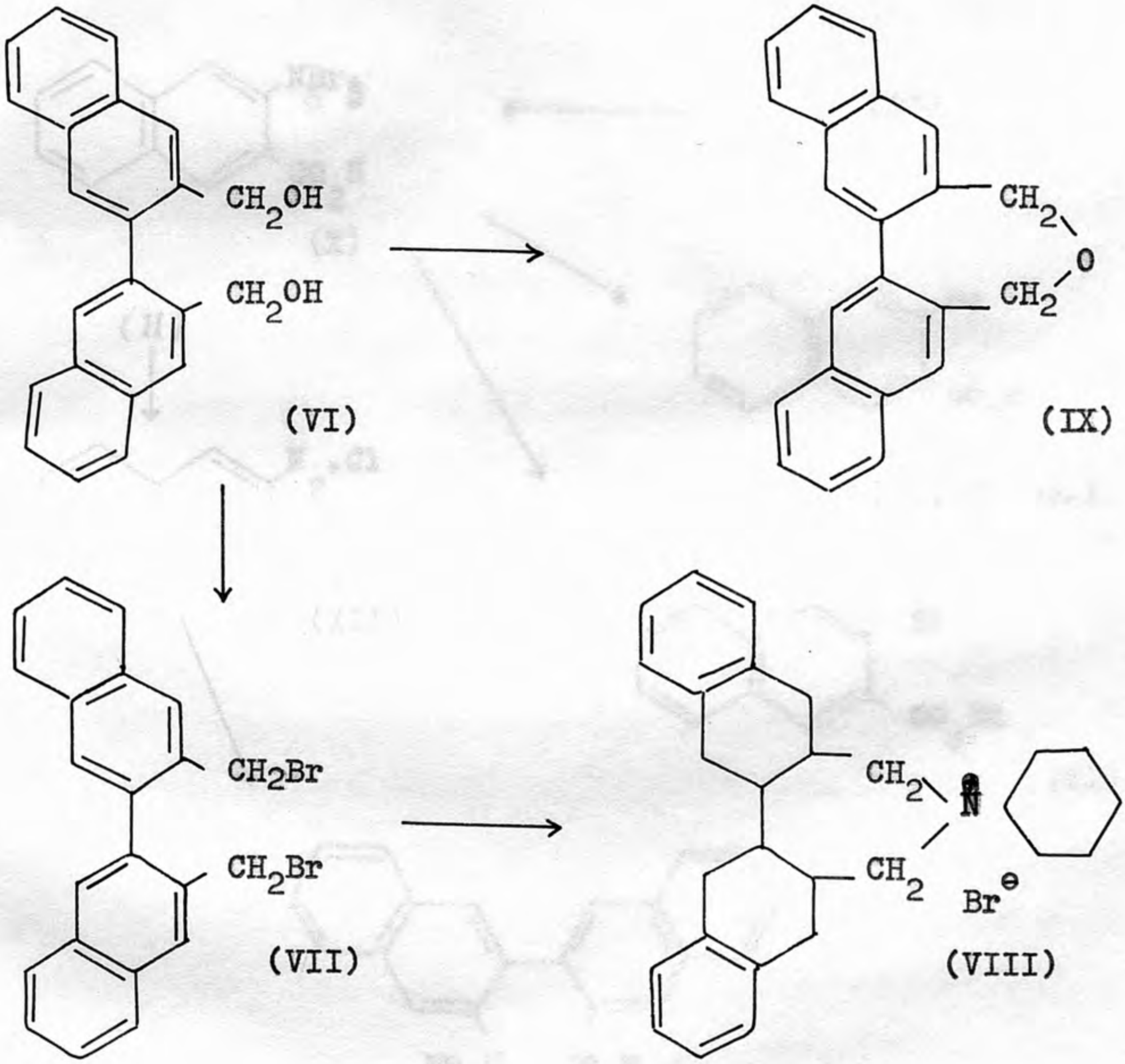
DISCUSSION.

The most obvious route to methyl 2:2'-dinaphthyl-3:3'-dicarboxylate (V) and hence to (VIII) and (IX) was from 3-hydroxy-2-naphthoic acid (I) according to the following scheme:

SCHEME A.



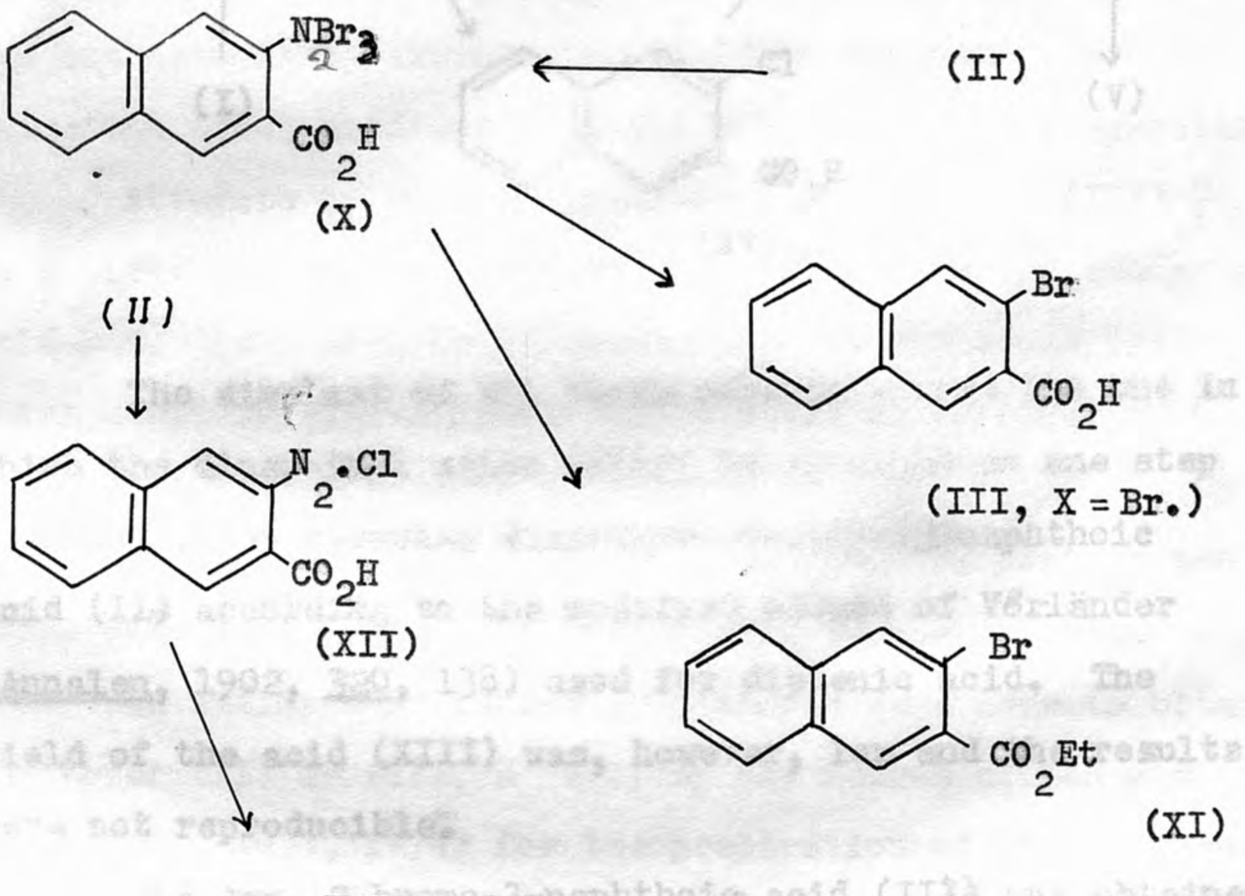
The preparation of 2-amino-2-naphthoic acid (II) from the hydroxy naphthoic acid (I) involves the use of a stirring autoclave (Allen and Bell, Org.Synth.,22,19). It could not be carried out in these laboratories and hence the supply of the amino acid (II) was limited. Accordingly alternative routes to 2:2'-dinaphthyl-3:3'-dicarboxylic acid (XII) or its ester (V) were considered. Several methods were tried



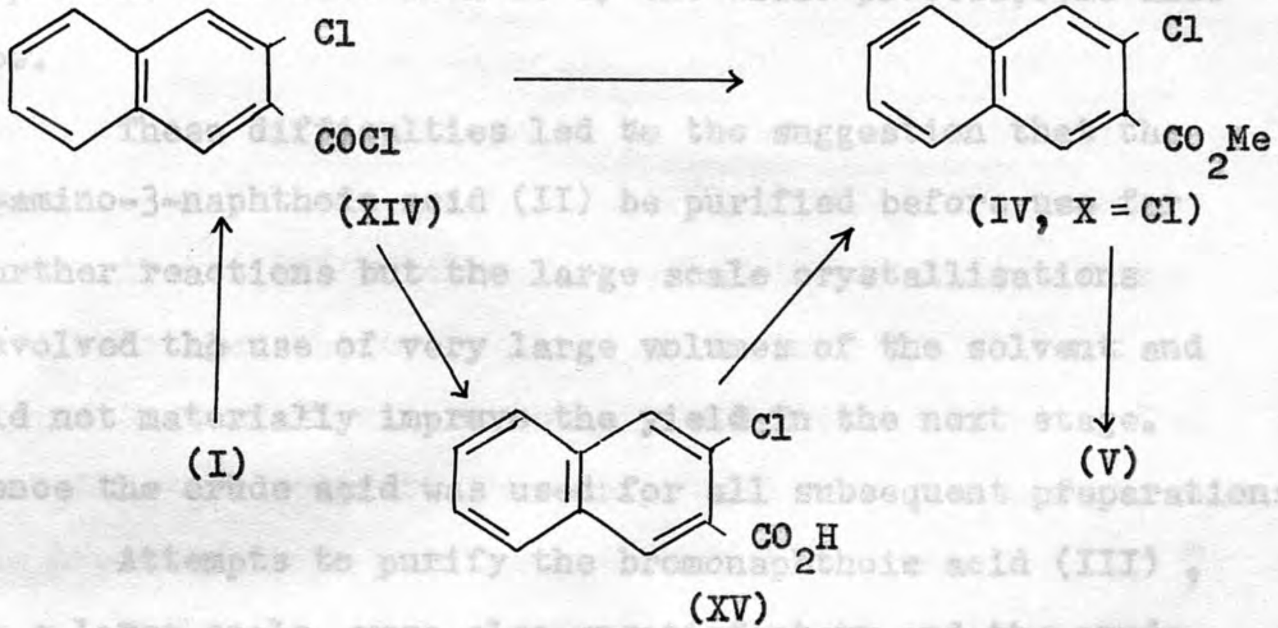
(N.B. The four compounds derived from the ester V have not

been described in the literature previously).
including those which were considered likely to give a higher yield of the dinaphthyl compound from the amino naphthoic acid (II) as compared to the process outlined on page 60. All the attempted reactions are illustrated below.

SCHEME B.



SCHEME C.



The simplest of all these schemes seemed the one in which the dinaphthyl ester (XIII) is obtained in one step (scheme B) by reducing diazotised 2-amino-3-naphthoic acid (II) according to the modified method of Vörländer (<u>Annalen</u>, 1902, <u>320</u>, 138) used for diphenic acid. The yield of the acid (XIII) was, however, low and the results were not reproducible.

The 2-bromo-3-naphthoic acid (III) was obtained from the amino naphthoic acid (II) in a low yield by the method of Kenner, Ritchie and Wain (<u>J.</u>, 1937, 1526) who obtained it in almost quantitative yield. The low yield may have been due to impurities present in 2-amino-3-naphthoic acid since it proved impossible to diazotise the acid completely; the yield of 2-chloro-3-naphthoic acid and 2-iodo-3-naphthoic acid made from it by the diazo process, were also low.

These difficulties led to the suggestion that the 2-amino-3-naphthoic acid (II) be purified before use for further reactions but the large scale crystallisations involved the use of very large volumes of the solvent and did not materially impruve the yield in the next stage. Hence the crude acid was used for all subsequent preparations.

Attempts to purify the bromonaphthoic acid (III), on a large scale, were also unsatisfactory and the crude acid had, therefore, to be converted into its ester (IV), which could be crystallised easily after distilling it in vacuum. The preparations of all the esters (IV, X Cl, Br or I) were carried out in fairly good yield by heating the acids with methanol in the presence of sulphuric acid.

As outlined in scheme B, attempts were made to obtain the ester (XI) or (III, X Br.) by the method of Loh and Turner (J., 1955, 1274) for the preparation of bromo compounds via diazonium perbromides. From (XI), the diol (VI) could have been prepared in the same way as from (III), scheme A. The attempts, however, were unsuccessful.

Finally, scheme C was tried and methyl 2-chloro-3-naphthoate was obtained from the hydroxy acid (I) by the action of phosphorus pentachloride on it and the acid chloride

(XIV) decomposed either with methyl alcohol or by first hydrolysing with water and then esterifying the acid (XV). The yield of the acid chloride was only 26%. Also the yield of the dinaphthyl ester (V) was 27% when it was prepared by Ullmann reaction on (IV, X = Cl.) whereas when X = Br it was 62% which was an added disadvantage of the acid chloride scheme C.

In view of all these difficulties, it was concluded That the best route to the dinaphthyl ester (V) was through the bromonaphthoic acid as outlined in scheme A.

In the preparation of the diol (VI), the only difficulty encountered was its crystallisation which was affected through ethoxy-ethanol. The yield, however, was 95%. The dibromide (VII) was obtained in almost quantitative yield. The reaction between the dibromide and piperidine to form the azepinium compound (VIII) requires no comment. The yield in this case , of the crude product, was also almost theoretical. It could be crystallised from organic solvents as well as water but in the latter it dissolved only after prolonged boiling. Its purity was, however, difficult to determine from the m.p. since it did not melt up to 340°. Its crystals in different crystallisation experiments varied in appearance.

The oxepin (IX) was obtained from (VI) by no means as easily as was expected. If stronger sulphuric acid was used or if heating was prolonged, charring took place. The oxepin was formed in very small amout but could be purified without much difficulty since the diol (VI) is nearly insoluble in methanol whereas the oxepin crystallises out only on dilution with water.

The difficulty encountered in obtaining the oxepin indicates that the diphenyls with benzene as substituents do not favour the formation of oxepins which is supported by the inability, so far, of Hall and Turner (unpublished) to obtain the oxepin from 1:1'-dinaphthyl-2:2'-bishydroxymethyl.

EXPERIMENTAL.

Preparation of 2-amino-3-naphthoic acid.

This was prepared from 2-hydroxy-3-naphthoic acid by the method of Allen and Bell (Org. Synth., 22, 19). For the initial reaction a stirring autoclave was required and Dr. E. A. Coulson very kindly carried out this reaction at the Chemical Research Laboratories, Teddington.

Preparation of 2:2'-dinaphthyl-3:3'-dicarboxylic acid.

This was a modification of the method of Vorländer (Annalen, 1902, 320, 138) used for the preparation of diphenic acid.

2-Amino-3-naphthoic acid, m.p. 212°-213° (62.3g., 1mol.) was finely ground and boiled with hydrochloric acid (d.1.16; 174ml.,6mol.) diluted with an equal volume of water. Some of it dissolved. It was cooled rapidly to 0° and diazotised with solid sodium nitrite (23g.,1mol.) with stirring, maintaining the temperature of the reaction mixture at 0° to 4°. Solid diazonium salt was obtained.

To a solution of copper sulphate (161g. in 770ml. water of pentahydrate), ammonium hydroxide (d.0.88, 175ml.) was added with stirring, followed by sodium metabisulphite (366g.) and then another 360ml. of ammonium hydroxide (d.0.88). The mixture was cooled to 10°.

The diazo solution was added to the above mixture gradually at 10° to 14° with stirring. Nitrogen was given off. After the addition stirring was continued for another half hour.

Anhydrous ferric chloride (238g.) was dissolved in water (350ml.), any insoluble material removed by filtration and hydrochloric acid (<u>d</u>.1.18,1170ml.) was added to the clear filtrate. This was then added to the product from the above process. The mixture first turned green and then dirty yellow. The precipitate formed was allowed to settle overnight. It was filtered, washed twice on the funnel with water and dried at 50°.

2:2'-Dinaphthyl-3:3'-dicarboxylic acid, m.p.262°-270°, was obtained; 19.0g., 37% yield. It was crystallised from ethanol (charcoal) and then recrystallised twice from ethanol. The acid then melted at 298°-300°, 10.5g., 21% yield. (Found: C,76.8; H,4.1. Calc. for $C_{22}H_{14}O_2$ C,72.2; H,4.1 %).

This preparation was repeated twice with some modifications but the acid obtained was very impure and further attempts were, therefore, not made to obtain the dinaphthyl-dicarboxylic acid by this method.

<u>Preparation of methyl 2:2'-dinaphthyl-3:3'-dicarboxylate.</u>

The above acid (6.0g.,m.p.298°-300°) was heated under reflux with methanol (900ml.) for half an hour but the acid did not dissolve completely. Concentrated sulphuric acid (d.1.84, 30g.) was added to this suspension. The mixture was heated under reflux for 1hr. on a heating mantle whereby the dinaphthyldicarboxylic acid dissolved completely. The heating was continued for another 5½hrs.

It was cooled to room temperature and then poured into water (2.5 litres.). A dirty yellow substance with some oily drops separated. It was left overnight, filtered, washed successively with water, 5% sodium hydrogen carbonate solution and water again. The product was dried at 50° in an air oven, m.p. 163°-170°, 7.0g., theoretical yield. Its crystallisation from methanol, however, proved to be difficult. The pale yellow pure ester melted at 173°-174°. (Found: C,77.3; H,5.0. Calc. for $C_{24}H_{18}O_4$ C,77.8; H,4.9 %).

Preparation of 2-bromo-3-naphthoic acid.

Several different methods were used in an attempt to obtain this compound in good yield, but the yields in general were low. It was attributed to the impurity of amino naphthoic acid. This compound was purified by crystallisation from ethanol using 15ml. alcohol per gram of the acid. The volume of alcohol used was very large and the acid, m.p. 215°-216° could be recovered in about 65% yield only. The overall yield of 2-bromo-3-naphthoic acid, taking into consideration the amino naphthoic acid lost during crystallisation, was not improved. In view of this fact the amino naphthoic acid was used in its crude form for all preparations.

(A) This method has been used by Kenner, Ritchie and Wain, (J., 1937, 1526).

Aminonaphthoic acid (6.2g.,1mol.) was heated with hydrobromic acid (d.1.48 12ml.) and water (20ml.) and then cooled in a freezing mixture to -3°. It was diazotised with a saturated solution of sodium nitrite (2.3g.,1mol.) in water, at -2° to -3° in about ½hr. The product was kept at the above temperature for 2hrs with occasional stirring. The dirty yellow diazonium compound was then collected by filtration on a Buchner funnel, cooled previously in ice-salt mixture to 0°.

Cuprous bromide was freshly prepared from copper sulphate pentahydrate (16.2g.), potassium bromide (9.0g.) and sodium sulphite (6.0g.). It was filtered and washed twice on the funnel with a very dilute solution of sulphur dioxide in water. It was dissolved in hydrobromic acid (d.1.48 ;10ml.) and cooled to 0°.

The cold diazonium salt was added to the solution of cuprous bromide with stirring. The colour changed to dark brown after 10min. The temperature was maintained at

0° for ½hr. and the product was diluted with water(15ml.). It was left at room temperature for ½hr. and the reaction completed by heating on the water bath for 1hr.

The solid was filtered off, and after air drying, had m.p.198°-201° (clear at 210°). It was extracted with formic acid and the solid obtained from this solution melted at 204°-207°, weight 3.4g., 42% yield. The second crop obtained was dissolved in 10% sodium hydroxide solution with heating, filtered and precipitated with dilute hydrochloric acid, a dark brown solid melting at 198°-202° was obtained. No more attempts were made to purify the acid and it was esterified directly.

(B) This method was used by Loh and Turner (J.,1955, 1274) for the preparation of bromocompounds via diazonium perbromides.

2-Amino-3-naphthoic acid (2.5g.,1mol.) was dissolved in acetic acid (40ml.) with heating and cooled to room temperature. Sodium nitrite (1.0g.,1mol.) dissolved in concentrated sulphuric acid (d.1.84, 15ml.) was added to the above solution dropwise with controlled shaking, maintaining the temperature at 12° to 15°. It was allowed to stand for ½hr. at 15° and then diluted by adding ice. This was then treated with bromine (d.3.18, 0.8ml.) dissolved in hydrobromic acid (5.0ml.), stirred for 15min. and the solid perbromide filtered. It was washed on the funnel with water (20ml.) and dried over concentrated sulphuric in vacuum.

The perbromide was decomposed by dissolving it in glacial acetic acid (30ml.) at 95°. The mixture was boiled to expel excess of bromine. It was allowed to stand overnight, and filtered. A yellow solid, 0.7g. m.p.210°-213° was obtained. It was recrystallised from glacial acetic acid twice, m.p.234°-236°. It depressed the m.p. of authentic 2-bromo-3-naphthoic acid.

This experiment was repeated twice with some modification but without success. In an experiment, the perbromide was decomposed in ethanol in an attempt to obtain ethyl-2-bromo-3-naphthoate directly. The product obtained after crystallising twice from dilute ethanol (charcoal) and once from glacial acetic acid melted at 167°-169° but was discarded as it was found to be soluble in 5% sodium hydrogen carbonate solution.

(C) Aminonaphthoic acid (4.7g.,1mol.) was heated with glacial acetic acid(50ml.) and cooled rapidly in iced water. Diazotisation was carried out by adding the ice-cold solution of sodium nitrite (1.9g.,1.1mol.) in concentrated sulphuric acid (d.1.84; 6ml.) in about 45min. The temperature of the reaction mixture was maintained at 15° to 20°. The colour changes first to orange then to violet , the intensity increasing as the reaction proceeded. It was allowed to stand for 20min. with occasional stirring. Commercial cuprous bromide (7.0g.,2mol.) was dissolved in hydrobromic acid (d.1.48, 10ml.) and the diazo solution, diluted with crushed ice, added to it. The colour of the mixture be⊃came dark grey. It was warmed to 60° on a water bath. A violet coloured precipitate settled down after some time.

It was cooled to room temperature, filtered and dried at 50°. The product obtained, 6.5g., contained a considerable proportion of inroganic matter. From the filtrate on standing a bright yellow solid, m.p.185°-190°, was obtained. The first crop (6.5g.) was crystallised from various solvents. A very small quantity of the 2-bromo-3-naphthoic acid, m.p.215°-217° was obtained after dissolving it in 10% sodium carbonate solution, precipitation with dilute hydrochloric acid and crystallising from dilute acetone and glacial acetic acid.

Preparation of 2-chloro-3-naphthoic acid.

(This preparation had been carried out with almost quantitative yield by diazo process described by Bogmann and Hirshberg, J.,1936, 33).

2-Amino-3-naphthoic acid hydrochloride (31.5g.,1mol.) was suspended in concentrated hydrochloric acid (d.1.18, 100ml., 7mol.) and sodium nitrite (10.0g.,1mol.) in aqueous solution added to the stirred, cooled suspension during 1½hr. Stirring was continued for ½hr. and urea was then added to remove some of the unreacted nitrous acid.

During the reaction much of the solid hydrochloride disappeared but a brown solid was present at the end. This suspension was added to a solution of cuprous chloride (prepared freshly from 36.0g. of copper sulphate pentahydrate) in hydrochloric acid. After a time the mixture was warmed and finally heated over a flame until no more nitrogen was evolved. The solid was filtered off and stirred with an aqueous solution of sodium hydrogen carbonate (12.0g.). A small amount of dark solid was removed by filtration and the filtrate was acidified. The precipitated 2-chloro-3-naphthoic acid was crystallised from ethanol and had m.p.220°-221°. Yield 17.2g. (59%). The m.p. was not depressed on admixture with 2-bromo-3-naphthoic acid (m.p. 219°-221°). Lassaigne tests showed that the acids contained chlorine and bromine respectively.

<u>Preparation of methyl 2-chloro-3-naphthoate.</u>

2-Chloro-3-naphthoic acid (17.0g.), concentrated sulphuric acid (d.1.84, 17.0g.) and methanol (170ml.) were heated together under reflux for seven hours. The solution was poured into water and the solid ester collected, washed with sodium hydrogen carbonate and water, and crystallised from light petroleum (b.p. 40°-60°) (charcoal). After recrystallisation from methanol, methyl 2-chloro-3-naphthoate had m.p. 62.5°-64°. Yield 14g. (77%). Ullmann and Dootson, (Ber., 1918, 51, 9) gave m.p. 58°.

Preparation of methyl 2-iodo-3-naphthoate.

It was prepared on a very small scale by the method of Goldstein and Cornamusaz (Helv.Chim.Acta., 1931, 14, 200) by esterifying 2-iodo-3-naphthoic acid with methyl alcohol in the presence of sulphuric acid which they obtained by the diazo process from 2-amino-3-naphthoic acid.

This preparation was not repeated on a larger scale as more of the aminonaphthoic acid was not available and also that the yield was not very different from the corresponding chloro and bromo esters.

Preparation of 2-chloro-3-naphthoyl chloride.
(Compare Strohbach, Ber., 1901, 34, 4159; Ullmann and Dootson, Ber., 1918, 1, 9).

2-Hydroxy-3-naphthoic acid (63g., 1mol.) was mixed with phosphorus pentachloride (208.0g., 3mol.) in a flask fitted with a condenser carrying a calcium chloride tube. The reaction started a few minutes after the two finely groung solids had been well mixed. When the initial reaction was over, the flask was heated at 200°-210° for ½hr.

Excess of phophorus pentachloride and phosphorus oxychloride were removed by distillation under reduced pressure. The acid chloride distilled at 232°-238°/8mm. The second fraction distilled at 250°-260°/8mm. as a yellow oil which did not solidify on cooling and was discarded. The pure 2-chloro-3-naphthoyl chloride weighed 19.3g., (26% yield).

This preparation was repeated several times but the yield could not be improved.

Preparation of 2-chlbro-3-naphthoic acid from the acid chloride.

The acid chloride (6.6g.) was treated with water at room temperature and then heated to 80° on a water bath. The solid melted and then reacted vigorously solidifying to a white substance and then gradually changed to yellow.

It was cooled, filtered, washed with water and dried, m.p. 198°-205°. On recrystallisation from dilute methanol it melted at 213°-215°, 2.0g.,(33% yield).

Preparation of methyl 2-chloro-3-naphthoate.

(A) From 2-chloro-3-naphthoic acid: The ester was prepared in the usual manner from 2.0g., of acid by heating it under reflux for 4hrs. with methanol (20ml.) and concentrated sulphuric acid (d.,1.84, 2.0g.). The ester obtained had m.p. 57°-59°, 1.9g., (86% yield).

(B) From 2-chloro-3-naphthoyl chloride: Methanol was cautiously added to 2-chloro-3-naphthoyl chloride at room temperature and the mixture was then heated under reflux on a water bath for 45min. to complete the reaction. Excess of methanol was removed by distillation and the product then poured into water (500ml.). The solution became milky and ~~the~~ a yellow oil separated. On keeping overnight at about 4° it solidified. The waxy solid melted at 57°-59°, 10.5g., (51% yield). It was recrystallised from methanol, m.p. 58°-59°.

The diazotisation of 2-amino-3-naphthoic acid was carried out in several batches of 54g. each. Reaction on a larger scale was too voluminous to carry out safely. The method was essentially that of Kenner, Ritchie and Wain (*J.*, 1937, 1526) as described earlier. Several minor modifications were tried in these preparations but without appreciable improvement on the yield.

Preparation of methyl 2:2'-dinaphthyl-3:3'-dicarboxylate by the Ullmann reaction.

(A) Copper bronze (50.0g.) was added in small batches to methyl 2-bromo-3-naphthoate (51.0g.) in a tube at 250° placed in a metal bath. The temperature of the reaction mixture gradually rose to 310°. The temperature of the bath was controlled at 290°-300° towards the end of the reaction for 15min. The whole reaction took about 35min.

The dinaphthyl ester was extracted with toluene (400ml.) and filtered twice. Half of the volume of toluene was removed by distillation. The solution was left overnight at about 4°. The first crop of the ester obtained had m.p. 169°-172°, 7.2g; second crop had m.p.166°-168°, 4.1g. The yield was 62%.

(B) To methyl 2-chloro-3-naphthoate (17.5g.), was added an equal weight of copper bronze at 175° in a tube placed in a metal bath at 185°-190°. The temperature of the reaction mixture rose to 200°. The reaction was completed in about ½hr. The reaction product was extracted with hot toluene. It was filtered, excess of toluene was removed by distillation and the solution was left overnight for crystallisation. The methyl 2:2'-dinaphthyl-3:3'-dicarboxylate was obtained in 27% yield. First crop had m.p. 169°-170°, 2.5g.; second crop had m.p. 164°-169°, 1.5g.

Preparation of 3:3'-bishydroxymethyl-2:2'-dinaphthyl.

A suspension of finely ground lithium aluminium hydride (10.0g.,2.6mol.) was prepared in dry ether (ca.800ml.) in a 2 litre three necked flask equipped with a reflux condenser, a dropping funnel and a mechanical stirrer. The above ester (37.6g.1mol.) was ground to a fine powder and added to this suspension in small batches followed by a few ml. of dry ether (<u>ca</u>.300ml. used in all). The reaction was fairly vigorous. To complete the reaction the flask was heated on a water bath for 3¼hrs. It was cooled to room temperature and the hydrolysis was carried out by water, followed by 2N sulphuric acid (1000ml.) with stirring. The excess of sulphuric acid was added in order to dissolve the aluminium salts which may have been present in the white flocculant precipitate of the diol. It was allowed to stand overnight. The diol was collected by filtration. From the ethereal part, when ether was distilled off, no residue was left. The above flocculant precipitate was dissolved by heating under reflux with excess of ethoxy ethanol (2000ml.) and then crystallised from it.

The first crop of the diol obtained as fine flat needles, m.p.236°-237°, weighed 26.0g. The mother liquor was concentrated to half its volume and left overnight at 4° but no solid appeared. It was diluted and allowed to stand overnight. The second crop, m.p.233°-234°, weighed 3.8g. Some more diol was collected by diluting the mother liquor further. It had m.p. 229°-231°, 0.7g. The total weight of the diol obtained was 30.5g., 95% yield.

The diol presented considerable difficulties during crystallisation. Earlier benzene was used as a solvent but with little success.

(Found: C,82.9; H,5.8. $C_{22}H_{18}O_2$ requires C,84.1; H,5.7 %).

Preparation of 3:3'-bisbromomethyl-2:2'-dinaphthyl.

The above diol (20.0g.) was dissolved in boiling glacial acetic acid (15ml. acid per g. of diol) and hydrobromic acid (10ml.acid per g. of diol; 48% w/w) was added to it. It was heated under reflux for 3hrs. The flask was then cooled and the reaction product poured into water (1000ml.). The precipitate was filtered and dried, m.p.161°-164°, 27.8g., 99% yield.

The cream coloured crude dibromide was crystallised from glacial acetic acid (charcoal), m.p.161°-163°. On recrystallisation it melted at 164°-166°.

(Found: C,60.3; H,3.8; Br,35.4. $C_{22}H_{16}Br_2$ requires C,60.0; H,3.7; Br,36.3%).

The above reaction, on a small sscale, was also carried out by adding solid diol directly to boiling hydrobromic acid. The bisbromomethyl-dinaphthyl from this experiment melted at 149°-151° and the yield was also lower.

Preparation of 2:7-dihydrodinaphtho(2':3'-3:4)(2":3"-5:6) azepinium-1-spiro-1"'-piperidinium bromide.

Bisbromomethyl-dinaphthyl (8.8g.,1mol.; m.p.161°-163°)

was dissolved in warm benzene (ca.80ml.) and piperidine (3.8g.,2.2mol.) mixed with 20ml. benzene was added to it. Cloudiness appeared almost at once. The mixture was warmed on a water bath (100°) for about 5min. The salt settled down as an oil. On cooling, it solidified in a few hours to a hard cream coloured solid. It was filtered off, m.p. ca.200° (decomp),12.2g.

It was recrystallised from water, in which it was sparingly soluble; the first time in large silvery plates and the second time in small rectangular plates. It did not melt up to 340°.
(Found: C,69.8; H,5.7; N, 3.1 Br, 17.6 $C_{27}H_{26}NBr, H_2O$ requires C,70.1; H,6.1; N, 3.0 Br, 17.3 %).

From another experiment on crystallisation, it formed two types of crystals. One type was white and the other slightly cream in colour. When dried in air at 50°, the white form changed in appearance and then melted at 332°. Some of the cream coloured form also changed to the same appearance on drying, with the same m.p. This was probably due to different amount of water of crystallisation, or perhaps due to some piperidine present as an impurity.

The spectrum of the azepinium compound is discussed in section III.

Preparation of 2:7-dihydrodinaphtho(2':3'-3:4)(2":3"-5:6)oxepin.

3:3'-Bishydroxymethyl-2:2'-dinaphthyl (1.0g.,m.p. 236°-237°) was heated with sulphuric acid (50% w/W; 50ml.) in a beaker on a hot plate for about 30min. The temperature gradually rose to 150°. It was cooled, diluted with water and filtered, m.p.220°-223°, 1.8g. The mixed m.p. with the diol was ca.220° (softens at 208°) which was inconclusive.

Attempts to crystallise the above product from (i) glacial acetic acid, (ii) ethoxy ethanol, (iii) methanol, and (iv) n-propyl alcohol failed. In the first three solutions on dilution with water, some fine needle shaped crystals appeared. All the solid was recovered by diluting the solutions and boiled with methanol (ca.200ml.). The white insoluble residue (x), 0.63g., had m.p.220°-225° (not clear) and did not depress the m.p. of the pure diol.

The above alcoholic solution was allowed to cool down to room temperature and then filtered again in order to remove the slight turbidity which was probably caused by the precipitation of ~~a~~ the diol that may have dissolved. The filtrate was diluted with water. The oxepin was obtained in fine long needle shaped crystals, m.p.223°-224°, 0.12g. On admixture with the diol, it melted at 205°-210°. It was recrystallised from dilute methanol, m.p.223.5°-224.5°. On further crystallisation the m.p. remained unchanged.

(Found: C,87.1; H,5.6. $C_{22}H_{16}O$ requires C,87.1; H,5.6%).

In other experiments in an effort to improve the yield of the diol, charring took place, on increasing the concentration of sulphuric acid or the time of heating the diol with the acid.

The spectrum of the above oxepin is described in section III.

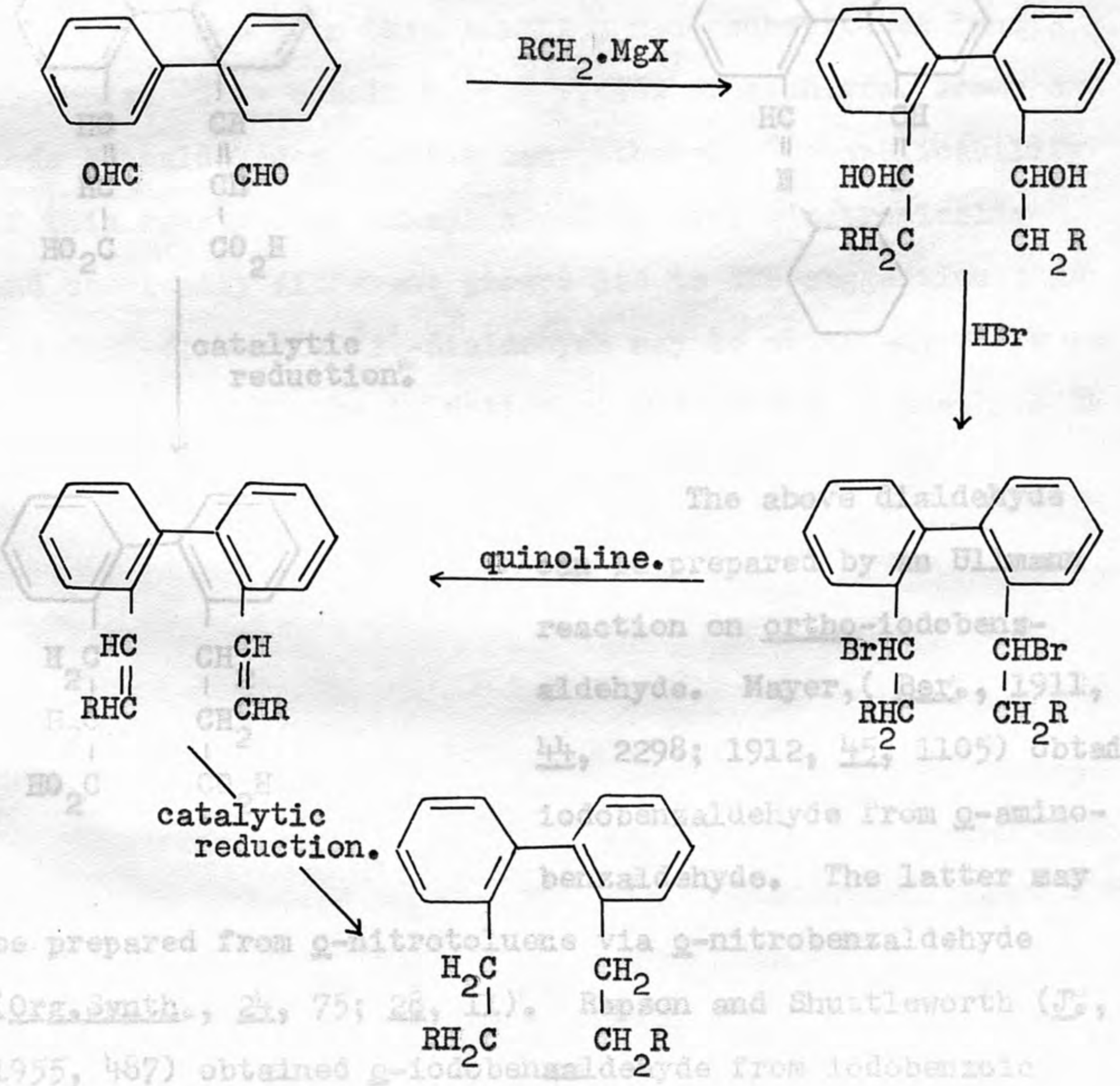
SECTION II.

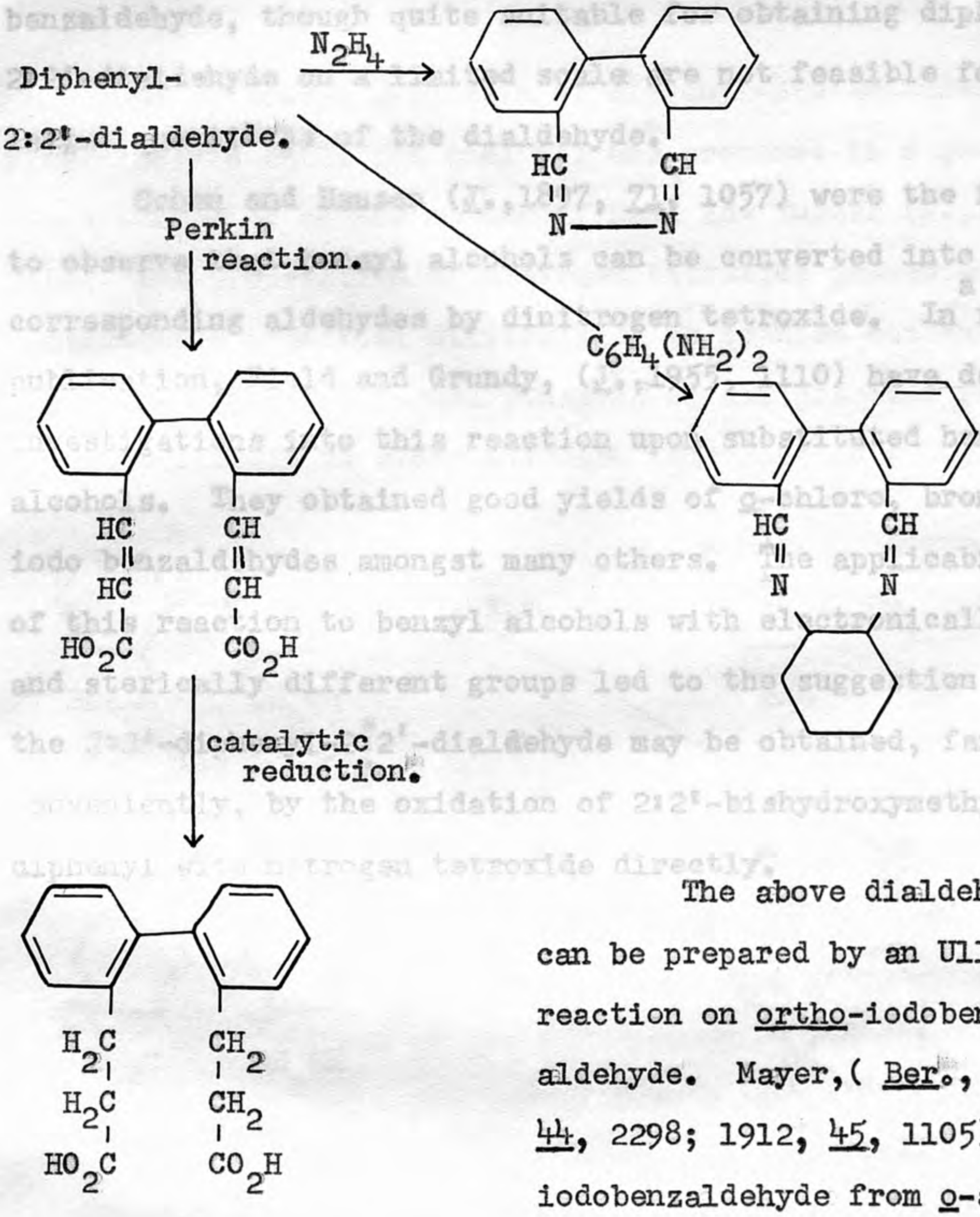
PART A.

STUDY OF DIALDEHYDE-2:2'-DIPHENYL.

INTRODUCTION.

Substituted diphenyls with two ortho carbonyl groups can lead to the formation of a large number of compounds which may not otherwise be easily obtainable. The preparation of diphenyl-2:2'-dialdehyde was started with the idea of carrying out the interesting synthesis outlined below.



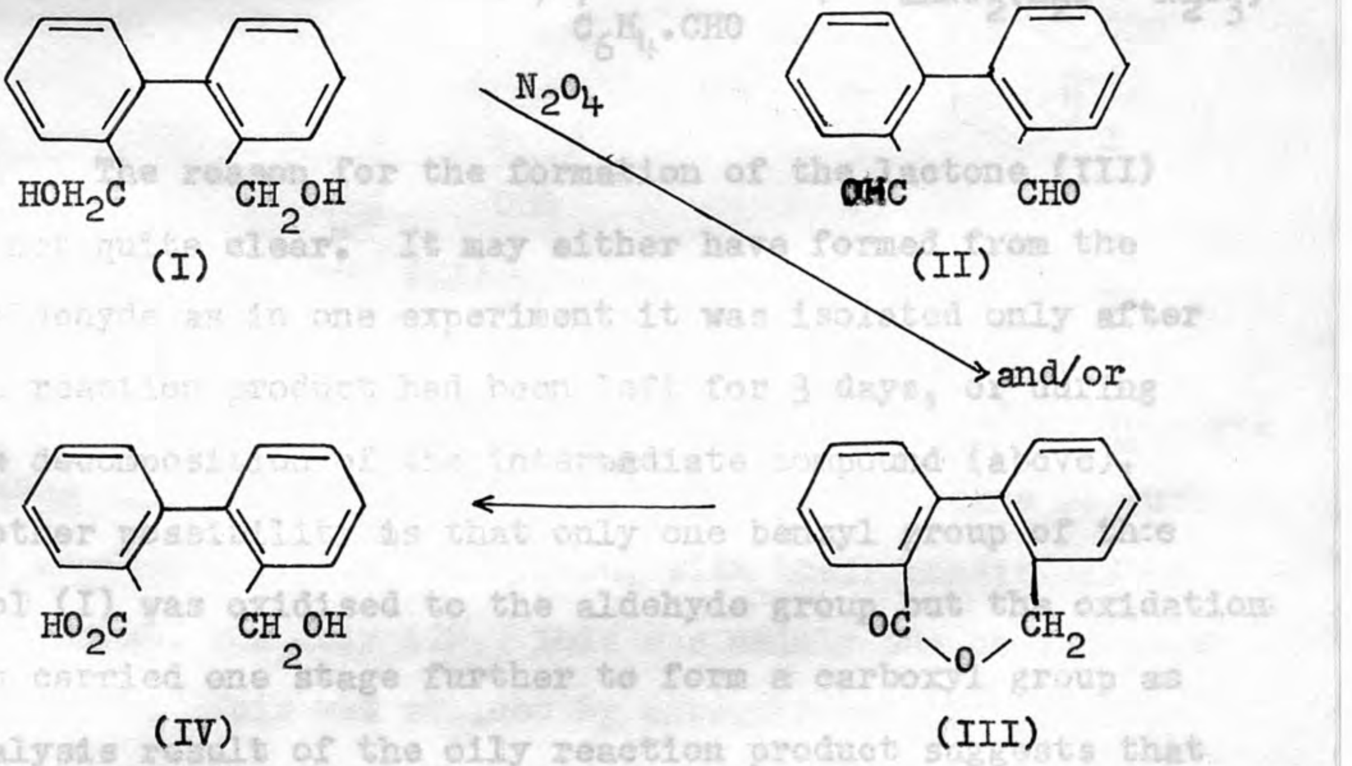


The above dialdehyde can be prepared by an Ullmann reaction on ortho-iodobenzaldehyde. Mayer, (Ber., 1911, 44, 2298; 1912, 45, 1105) obtained iodobenzaldehyde from o-aminobenzaldehyde. The latter may be prepared from o-nitrotoluene via o-nitrobenzaldehyde (Org. Synth., 24, 75; 28, 11). Rapson and Shuttleworth (J., 1955, 487) obtained o-iodobenzaldehyde from iodobenzoic acid in three stages. These methods of preparing o-iodobenzaldehyde, though quite suitable for obtaining diphenyl-2:2'-dialdehyde on a limited scale are not feasible for larger quantities of the dialdehyde.

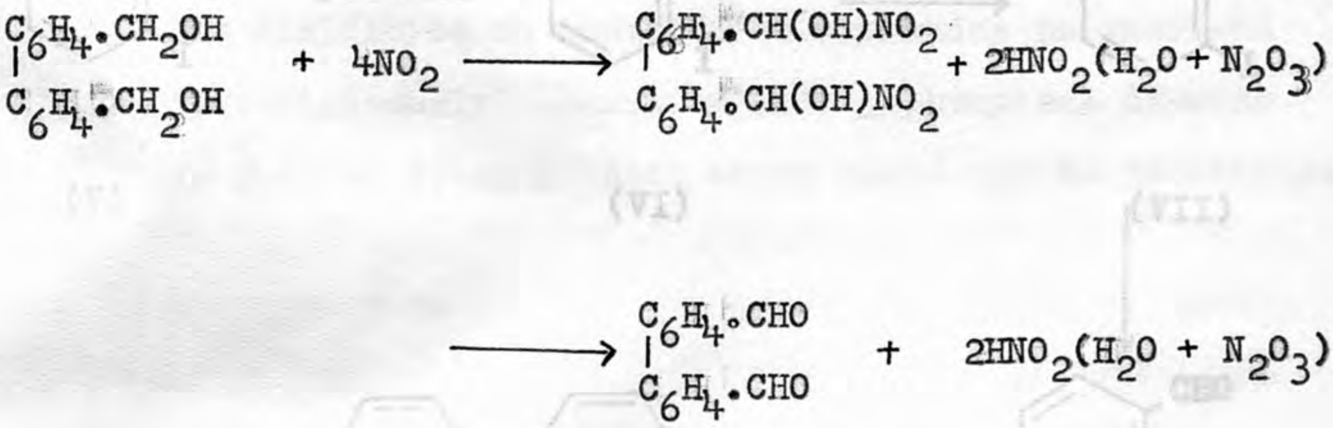
Cohen and Hausen (J.,1897, 71, 1057) were the first to observe that benzyl alcohols can be converted into the corresponding aldehydes by dinitrogen tetroxide. In a recent publication, Field and Grundy, (J.,1955, 1110) have described investigations into this reaction upon substituted benzyl alcohols. They obtained good yields of o-chloro, bromo and iodo benzaldehydes amongst many others. The applicability of this reaction to benzyl alcohols with electronically and sterically different groups led to the suggestion that the diphenyl-2:2'-dialdehyde may be obtained, far more conveniently, by the oxidation of 2:2'-bishydroxymethyl-diphenyl with nitrogen tetroxide directly.

DISCUSSION.

In attempted synthesis of diphenyl-2:2'-dialdehyde from diphenic acid, the diol (I) was prepared in a good yield according to the method of Hall and Turner (J.,1950, 711). The preparation of nitrogen tetroxide presented considerable practical difficulties as pointed out in the experimental that follows. Inspite of all possible precautions, it was difficult to store nitrogen tetroxide in a dry state.



The reaction of the diol (I) with nitrogen tetroxide gave an oil, from which the only pure compound isolated was (III) in 61% yield. According to the mechanism of reaction postulated by Field and Grundy (J.,1955, 1110) it should have proceded by homolytic attack of $\cdot NO_2$ radicals on the α -methylene groups and then decomposing to form the aldehyde as follows:

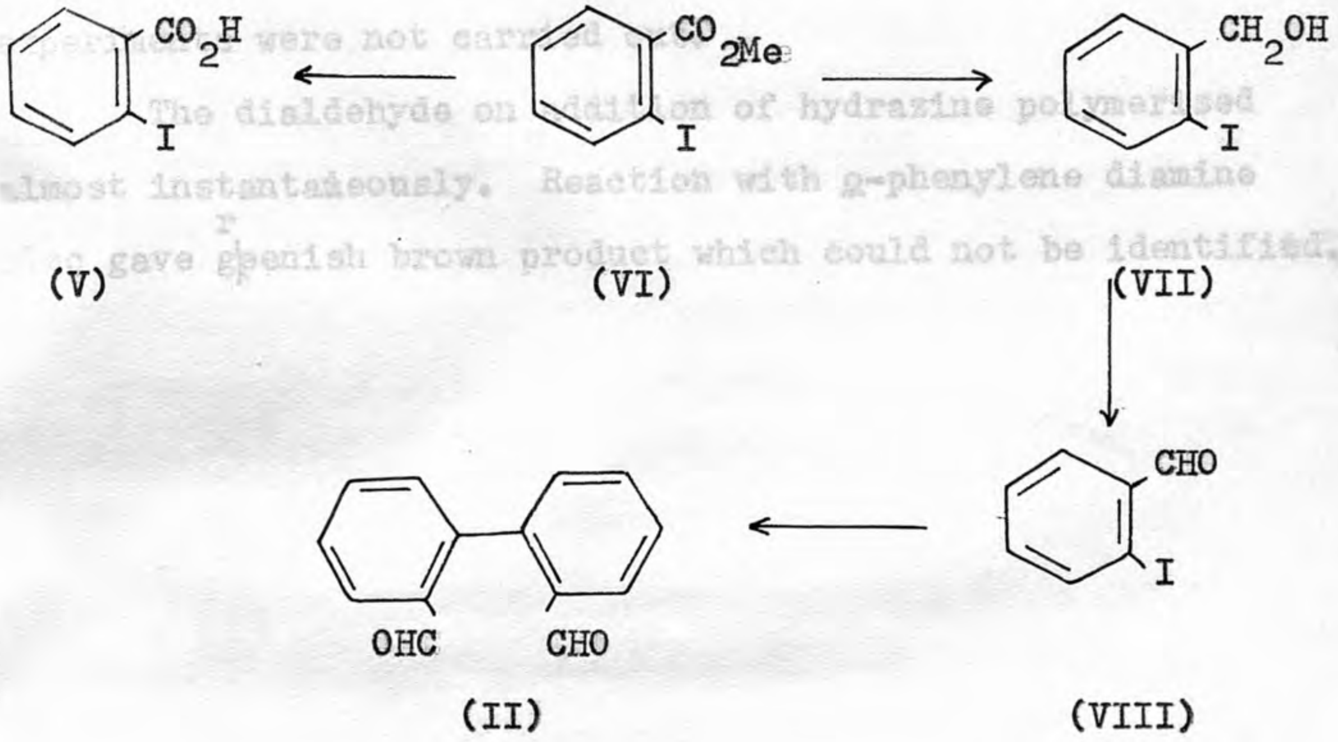


$$\begin{array}{l} C_6H_4\cdot CH_2OH \\ | \\ C_6H_4\cdot CH_2OH \end{array} + 4NO_2 \longrightarrow \begin{array}{l} C_6H_4\cdot CH(OH)NO_2 \\ | \\ C_6H_4\cdot CH(OH)NO_2 \end{array} + 2HNO_2(H_2O + N_2O_3)$$

$$\longrightarrow \begin{array}{l} C_6H_4\cdot CHO \\ | \\ C_6H_4\cdot CHO \end{array} + 2HNO_2(H_2O + N_2O_3)$$

The reason for the formation of the lactone (III) is not quite clear. It may either have formed from the dialdehyde as in one experiment it was isolated only after the reaction product had been left for 3 days, or during the decomposition of the intermediate compound (above). Another possibility is that only one benzyl group of the diol (I) was oxidised to the aldehyde group but the oxidation was carried one stage further to form a carboxyl group as analysis result of the oily reaction product suggests that it probably was a mixture of (IV) with either its lactone (III) or / and the dialdehyde. Attempts to detect the presence of the dialdehyde through its dioxime (Mayer, *Ber.*, 1911, **99**, 2101; m.p. 175° to 176°) or 2:4-dinitrophenylhydrazone (Weygand *et. al.*, *Angew.Chim.*,1953, **65**, 525) were, however, inconclusive.

Recourse was then taken to the following method.



_o_-Iodobenzylalcohol was obtained by Field and Grundy's method (_loc.cit._) but the reaction was by no means as successful as they claimed. The yield, with their conditions of experiment, was only 12%. This was mainly due to the loss of iodine. This was avoided by carrying out the reaction at -40° to -30° when the yield increased to 54%. The aldehyde (VIII) was, however, obtained in 97% yield from the iodobenzyl alcohol. The Ullmann reaction (Rapson and Shuttleworth, _loc.cit._) on the aldehyde (VIII) did not give such a good result as obtained by these authors.

In view of the difficulties encountered at various stages in preparing *o*-iodobenzyl alcohol and then also the low yield of the dialdehyde from the latter, further experiments were not carried out.

The dialdehyde on addition of hydrazine polymerised almost instantaneously. Reaction with *o*-phenylene diamine also gave greenish brown product which could not be identified.

EXPERIMENTAL.

Preparation of dimethyl 2:2'-diphenate.

Hall and Turner (*J.*,1950, 711).

Diphenic acid (63.0g.) was dissoved in methanol (850ml.) and concentrated sulphuric acid (*d*.1.84, 63.0g.) was added to it. It was heated under reflux for 8hrs. Excess of methanol was removed by distillation and the ester was precipitated by pouring the reaction product in a large volume of water.

The ester weighed 56.7g. m.p.73°-74°, 80% yield. It was recrystallised from methanol, m.p.74°-75°.

Preparation of 2:2'-bishydroxymethyldiphenyl.

Hall and Turner (*J.*,1950, 711).

A solution of methyl 2:2'-diphenate (38.0g.,1mol.) in dry ether (350ml.) was slowly run into a suspension of lithium aluminium hydride (8.5g.,1.6mol.) in dry ether (300ml.) contained in a flask equipped with a reflux condenser, a dropping funnel and a mechanical stirrer.

When the reaction was over, the hydrolysis was carried out with water followed by dilute sulphuric acid. Two clear layers were formed. The ether was removed by distillation and the diol set to a white solid on the water layer. It was filtered and dried, m.p.107°-109°, 23.4g., 78% yield. It crystallised from benzene in beautiful white needles with m.p. 112°-113°.

In one of the above experiments, some 2:7-dihydro-3:4-5:6-dibenzoxepin, m.p.71°-72°, was formed. This was caused by the dehydration of bishydroxymethyldiphenyl on heating with sulphuric acid. The formation of oxepin was later prevented by separating the aqueous and ethereal layers and then isolating the diol from the ethereal solution.

Attempted preparation of diphenyl-2:2'-dialdehyde.

(Compare Field and Grundy, J.,1955, 1110.).

Preparation of dinitrogen tetraxide: (Dodd and Robinson, Experimental Inorganic Chemistry, p.234). Lead nitrate (140g.), after being heated in an air oven for 3hrs. at 70°,was put into a round bottomed flask placed in a cone and heated very strongly. Through the flask a current of dry oxygen was passed. Nitrogen tetroxide was led first into a tube packed with red phosphorus and then into an other packed with phosphorus pentachloride. It was collected in two U-tubes placed in a alcohol-solid carbon dioxide mixture at ~~Cax~~ ca.-80°. To the end of the second U-tube a small wash bottle containing a few ml. of water was attached in order to ensure free outlet passage for excess of dinitrogen tetroxide and oxygen. This preparation presented considerable practical difficulties.

The flask had to be heated with a very strong flame and it cracked before the completion of the reaction. The rate of flow of nitrogen tetroxide could not be maintained at a steady rate which resulted in sudden disconnection of the different joints. The gas as it solidified blocked the U-tubes. Variation in temperature in the alcohol-solid CO_2 bath resulted in inefficient cooling and consequently in the loss of nitrogen tetroxide. It was difficult to store the liquid or solid dinitrogen tetroxide overnight and in view of the above difficulties its preparation could not be undertaken each time an oxidation was to be carried out. The preparation of nitrogen tetroxide, however, was carried out three times.

Oxidation of 2:2'-bishydroxymethyldiphenyl: Finely ground diol (10.0g.,1mol.) was suspended in chloroform (25ml.) which had been dried over anhydrous sodium sulphate, in a glass stoppered bottle and cooled to 0°. A solution of dinitrogen tetroxide (6.1g.,1.3mol.) in dry choroform (30ml.) was cooled to 0° and added to the above solution. The stopper of the bottle was secured in position tightly. The temperature of the reaction mixture was maintained at 0° for 15min. by external cooling. Then it was allowed to stand overnight at room temperature.

Chloroform and the oxides of nitrogen were removed by vacuum distillation. To the orange residue few ml. of ether were added. A pale yellow solid separated which was filtered and washed with ether on the funnel. It weighed 4.0g.m.p.

128°-133°.

Some of the orange liquid was distilled in vacuum at 183°-192°/7-10mm. but the distillate did not solidify.

On standing for a few days, more of the yellow solid was obtained (2.0g.m.p.130°-133°). It was soluble in cold ammonium hydroxide and when reprecipitated, a white solid with the same m.p. was obtained. The yellow solid was washed well with ether and analysed.

(Found: C,79.6; H,4.9. Calc. for $C_{14}H_{10}O_2$, C,80.0; H,4.8%)

Diphenyl-2:2'-dialdehyde has m.p.62° (Kenner and Turner,J.,1911, 89, 2101). However the lactone of 2'-hydroxymethyldiphenyl-2-carboxylic acid (obtained by Kenner and Turner, loc.cit. by a Cannizzaro reaction on the dialdehyde) has m.p.132° and is evidently the main product in the above oxidation, total yield of the lactone being 61%.

To establish the identity of the lactone further, its alcoholic solution was heated with aqueous potassium hydroxide for 2hrs. It was cooled and poured into water and filtered. The filtrate was acidified with dilute hydrochloric acid. The acid was filtered off and purified by dissolving it in ammonium hydroxide and reprecipitating with dilute hydrochloric acid; m.p.144°-145°. It was crystallised from ether and lightt petroleum (b.p. 40°-60°) for analysis; m.p.146°-147°.

(Found: C,72.9; H,5.4. Calc. for $C_{14}H_{12}O_3$. C,73.7; H,5.3%).

Another attempt was made at ~~reducing~~ the oxidation of bishydroxymethyldiphenyl (5.3g.,1.0mol.) with nitrogen tetroxide (3.1g.,1.3mol.). The process for the initial reaction was the same as described previously.

After removing chloroform and the oxides of nitrogen, the residual oil was taken up in ether, washed with 5% sodium hydrogen carbonate solution, and then twice with water. The ether was removed by distillation and the viscous oil left was kept overnight at about 4°. A trace of white solid appeared which could not be separated. Some of the oil was distilled in vacuum at 195°/6mm. and then the temperature rose suddenly to 215° with the residue in the distillation flask turning brown. Heating was stopped. The residual brown oil solidified at room temperature. It was dissolved in ether, filtered and precipitated with light petroleum (b.p.40°-60°). A dirty yellow precipitate was collected,m.p.*ca*.130°. It was ~~a~~ the lactone of hydroxymethyldiphenyl carboxylic acid. Some brown solid from the distillation flask melted at 53°-58° (clear at 70°) but was too little for further identification.

The yellow oily distillate (b.p.195°/6mm.) did not solidify. A few ml. of ether were added to it; some lactone separated after a short while.

The rest of the reaction product was warmed with 15ml. ether on a water bath. After some time the lactone separated. The total weight of lactone collected was 1.0g. With the orange oily mother liquor, attempts were made to form the crystalline derivatives characteristic of the aldehyde group. Although precipitates were obtained with 2:4-dinitrophenylhydrazones, hydroxylamine and o-phenylenediamine, these melted over a long range of temperature and could not be purified satisfactorily.

The analysis result of the oily product suggests that it was probably a mixture of the diphenyl-2:2'-dialdehyde ($C_{14}H_{10}O_2$), the lactone ($C_{14}H_{10}O_2$) and the 2-hydroxymethyldiphenyl-2'-carboxylic acid ($C_{14}H_{12}O_3$).
(Found: C,77.4: H,5.1. Calc. for $C_{14}H_{10}O_2$, C,80.0; H,4.8% ; $C_{14}H_{12}O_3$, C,73.7; H,5.3%).

Since the dialdehyde could not be obtained free of the lactone, further preparations by this method were not carried out.

Preparation of methyl o-iodobenzoate.

o-Iodobenzoic acid (British Drug Houses) m.p.158°-160°, 93.0g, was dissolved in methanol (1240ml.) and concentrated sulphuric acid (d.1.84;93.0g.) was added to it. It was heated under reflux for six hours. Most of the alcohol was then removed by distillation and the residual solution was poured into 5 times its volume of water. An oil separated

The mixture was neutralised with sodium carbonate and the process completed with sodium hydrogen carbonate solution. The mixture was extracted with ether three times and the combined ether extracts were washed with water and dried over anhydrous magnesium sulphate.

Ether was removed by distillation and the residual ester purified three times by vacuum distillation. The fraction distilling at 119°-122°/7mm. was collected. The average yield of several preparations on this scale was 75%.

Preparation of o-iodobenzyl alcohol.

Field and Grundy (J.,1955, 1110) obtained this compound in 94% yield but under their conditions of experiment the alcohol was obtained in 12% yield only. When the reaction was carried out at ca. -30°, the average yield was 45%.

A solution of methyl o-iodobenzoate (52.4g.,1mol.) was prepared in dry ether (100ml.) in a 2 litre three necked flask fitted with a reflux condenser carrying a calcium chloride tube, a dropping funnel and a mechanical stirrer. Lithium aluminium hydride, finely ground, suspended in ether (dry, 400ml.) was added to the above solution at -40° to -30°. The mixture was stirred for 1$\frac{1}{2}$hrs. Hydrolysis was carried out by adding first water and then 1N sulphuric acid. The ethereal layer was separated , and the water layer was extracted with ether (1.5 litres). Ether extracts were combined and washed successively once with water, twice with 5% sodium hydrogen carbonate solution, three times with water and then dried over anhydrous sodium sulphate. The ether was removed by distillation. Most of the yellow oily product solidified on cooling to about 4°.

It was filtered through a sintered glass funnel. Some more iodobenzyl alcohol was recovered from the mother liquor after a few days. The alcohol melted at 87.5°-89°, weight 26.0g., 55% yield. It was recrystallised from dilute methanol, m.p. 91°, 23.5g., 45% yield.

Preparation of o-iodobenzaldehyde.

Field and Grundy (loc.cit.).

The above alcohol (23.4g., 1mol.) was suspended in dry chloroform (60ml.) and cooled to 0°. Dinitrogen tetroxide (13.8g., 1.5mol.) was dissolved in dry chloroform (30ml.) and added to the alcohol in chloroform. The stopper of the bottle was tightly secured in position. The temperature of the reaction mixture was controlled at 0° for 15min. A clear solution resulted in a few seconds. It was allowed to stand overnight at room temperature.

The chloroform was removed by distillation under reduced pressure along with the oxides of nitrogen. The residue was taken up in ether, washed successively with water, 1% sodium hydrogen carbonate and then water. It was dried over anhydrous sodium sulphate for 1hr. and then filtered.

The ether was removed by distillation and the yellow oily product was kept at 4° for 24hrs. It solidified completely, m.p. 34.5°-36°, 22.5g., 97% yield.

This experiment was repeated three times, the yields varying considerably.

Preparation of diphenyl-2:2'-dialdehyde.

The method of Rapson and Shuttleworth (J., 1941, 487) was adopted.

Nitrogen was passed to displace air in a boiling tube placed in a metal bath at 200°. o-Iodobenzaldehyde (23.2g.) was placed in this tube and an equal weight of copper bronze was added gradually whilst a steady stream of nitrogen was being passed. The temperature in the reaction mixture rose from 185° to 265°. After the temperature had stopped increasing and was steady at 200°, the reaction mixture was stirred for 5min. and then heating was stopped.

The reaction product was extracted several times with hot chlorobenzene. The solution was filtered through a number of filter papers from a Buchner funnel and then through an ordinary funnel to remove the last traces of copper and its salt.

The solvent was removed by distillation under reduced pressure. The brown residue was distilled at 171°-182°/3mm. The orange coloured oily distillate, 6.0g., solidified partly on cooling overnight at about 4°. Some crystals, m.p.58°-61°, were separated but the whole was difficult to filter.

It was all dissolved in excess of boiling ether, cooled and filtered. The filtrate was concentrated and light petroleum (b.p.40°-60°) was added to it. It was allowed to stand overnight.

Diphenyl-2:2'-dialdehyde, m.p.60°-62°, 1.7g., was obtained. A second crop was obtained by adding more light petroleum to the mother liquor and leaving overnight at ca. 4°: m.p.52°-61°, 1.8g. The total yield (3.5g.) was 33%.

Reaction between diphenyl-2:2'-dialdehyde and hydrazine hydrate.

A solution of the dialdehyde (0.52g.,1mol.) was prepared in ethanol (12ml.) with heating. To this was added a solution of hydrazine hydrate (0.162g.,1.1mol.) in ethanol (6ml.). A white solid appeared almost immediately. The reaction mixture was heated under reflux on a water bath for 1hr.

The reaction product was cooled to room temperature and filtered. A pale yellow solid was obtained,0.23g. It melted at 235°-245° with silght previous softening.

It was insoluble in the common organic solvents at their boiling points. The test for nitrogen was negative.

The filtrate was concentrated and diluted with water. An emulsion was formed which was extracted with ether, the ethereal solution was dried over anhydrous sodium sulphate, filtered and concentrated. A sticky solid was obtained, m.p._ca_.85°. It was too little for further satisfactory purification.

The main reaction product (0.23g.) was a polymer of the dialdehyde as was confirmed by analysis.
(Found: C,80.3; H,5.7. $(C_{14}H_{10}O_2)_n$ requires C,80.0; H,4.8%).

Reaction with _o_-phenylene diamine also gave a greenish brown unidentified product.

SECTION II.

PART B.

STUDY OF 2:2'-DIACYLDIPHENYLS.

INTRODUCTION.

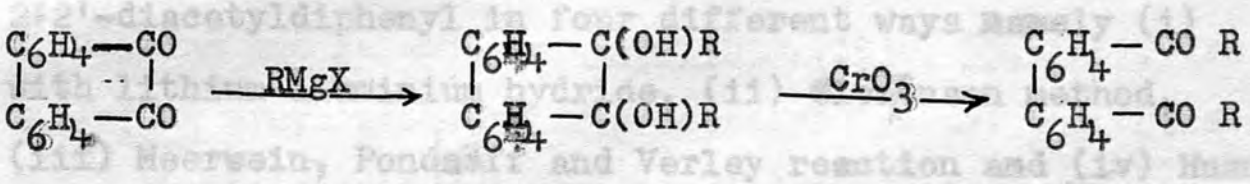
The reaction of dialkyl cadmium with aromatic acid chlorides to form ketones was first used by Gilman and Nelson, (Rec.trav.chim.,1936, 55, 518) who obtained acetophenone from benzoyl chloride and dimethyl cadmium in 84% yield.

De Benneville (J.Org.Chem.,1941, 6, 462), Cason (Chem. Rev., 1947, 40, 15), Johnson and Offenhauer(J.Amer.Chem.Soc., 1945, 67, 1045) and several other workers have prepared different types of aromatic ketones by this process. Cason has investigated the effect of various factors such as the solvent, temperature of reaction etc. on the course of this reaction. Cole and Julian (J.Amer.Chem.Soc., 1945, 47, 1369) used both dimethyl zinc and dimethyl cadmium in their experiments and obtained higher yields of ketones from the latter.

Suter and Weston (J.Amer.Chem.Soc.,1939, 61, 234) obtained propiophenone from benzoyl chloride, and diphenoyl chloride (Nightingale, Wagner and Wise, J.Amer.Chem.Soc., 1953, 75, 4701) gave 2:2'-dibenzoyl diphenyl in 83% yield on reaction with diphenyl cadmium.

The availability of 2:2'-dibenzoyl diphenyl in such a high yield and also that of acetophenone suggested that substituted diphenyls with ortho ketonic groups carrying acyl groups would, as pointed out earlier (p.84), form very convenient starting materials for 2:2'-diacyl diphenyls and a large number of other compounds. With this aim in view, the above and other methods for synthesising the diketones were considered.

Another route to approach these sterically hindered diketones was from phenanthraquinone. This was first introduced by Zincke and Tropp, (*Annalen*, 1908, *362*, 242; *363*, 302) who outlined the general method as follows:



$$\begin{array}{l} C_6H_4-CO \\ |\qquad\quad | \\ C_6H_4-CO \end{array} \xrightarrow{RMgX} \begin{array}{l} C_6H_4-C(OH)R \\ |\qquad\quad | \\ C_6H_4-C(OH)R \end{array} \xrightarrow{CrO_3} \begin{array}{l} C_6H_4-CO\ R \\ | \\ C_6H_4-CO\ R \end{array}$$

Ladbury, Hall, Lesslie and Turner (unpublished) have greatly improved upon this method. They have extended its use for the preparation of dialkyl diphenyls. These reactions thus form a comparatively easy way of preparing 2:2'-dialkyl diphenyls of which only two were known until recently *viz*. 2:2'-ditolyl (Fittig, *Annalen*, 1867, *138*, 178; Ullmann, *Annalen*, 1904, *332*, 42) and 2:2'-diethyldiphenyl (Mascarelli and Longo, *Gazzetta*, 1941, *71*, 289). Everatt, Hall and Turner, (in the press) have prepared 2:2'-diethyldiphenyl, 2:2'-di*iso*propyldiphenyl and 2:2'-di*tert*iarybutyldiphenyl by other routes.

The method of Hall, Ladbury, Lesslie and Turner (unpublished) has, in the following section, been utilised to prepare 2:2'-dipropionyldiphenyl with the view to study the effect of various reducing agents on this diketone and then to study the ultra-violet absorption spectra of the products obtained from them. Similar diketones had been known to give anomalous results on reduction (Braston, Patterson, Fidler, <u>J.Amer.Chem.Soc.</u>,1954, <u>76</u>, 6368). Hall, Ladbury, Lesslie, Hall and Turner (unpublished) have reduced 2:2'-diacetyldiphenyl in four different ways namely (i) with lithium aluminium hydride, (ii) Clemmensen method, (iii) Meerwein, Pondorff and Verley reaction and (iv) Huang Minlon method.

The first reduction proceeded normally and they obtained a mixture of two isomeric 2:2'-bis-α-hydroxyethyl-diphenyls. The Clemmensen reduction gave 9:10-dimethyl-phenanthrene. The results of the third reduction have been inconclusive. The Huang Minlon method gave unsaturated 7-membered cyclic hydrocarbon.

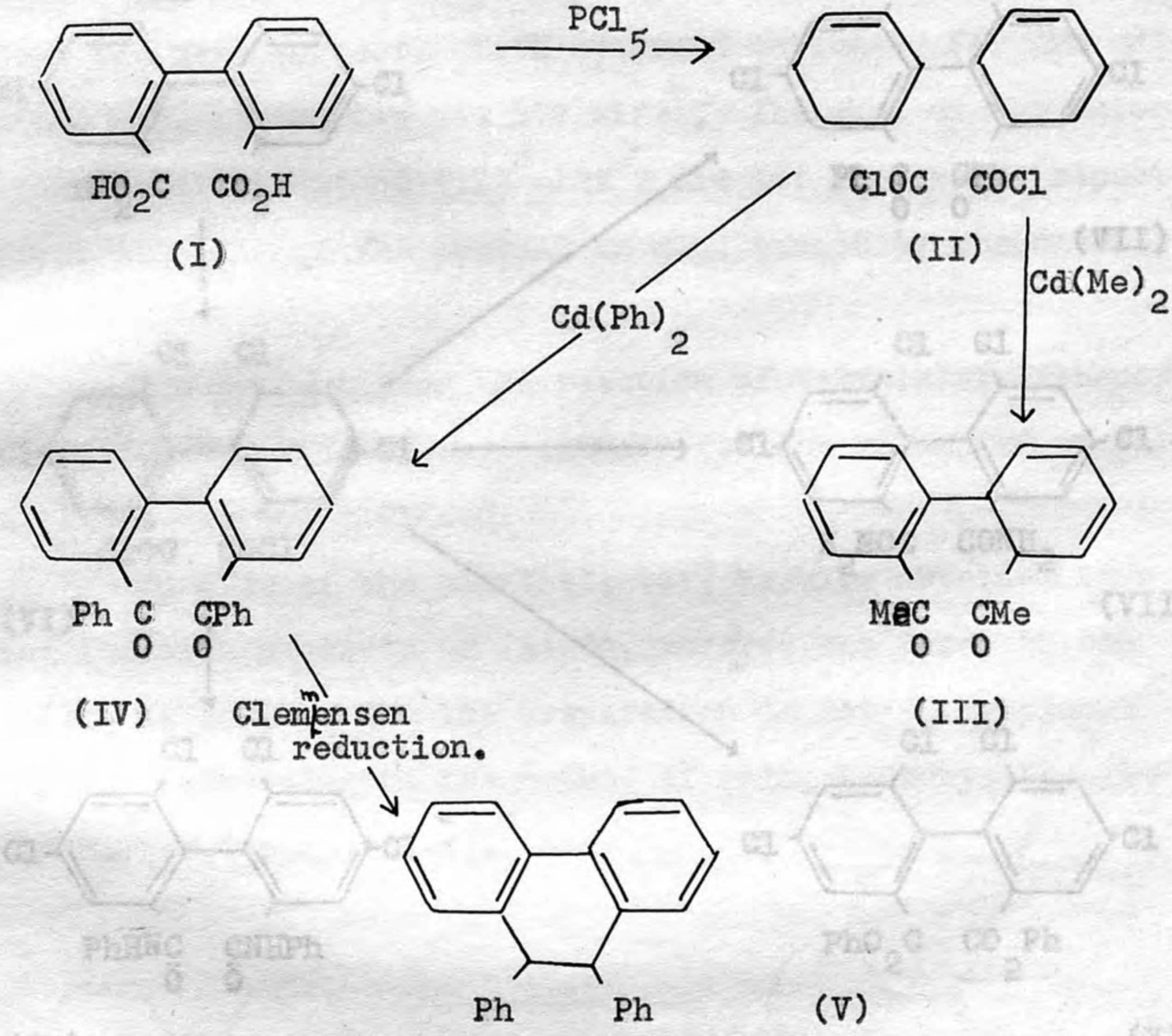
DISCUSSION.

The preparation of 2:2'-diphenoyl dichloride presented considerable difficulties when carried out according to the method of Underwood and Kochmann, (J.Amer.Chem.Soc.,1924, 46, 2072) and the yield was only 20%, but later it was improved to 97% by the introduction of some modifications as described in the experimental section that follows.

Although acetophenone has been obtained in 84% yield by Gilmann and Nelson (Rec.trav.chim.,1936, 55, 518), the analogous preparation of 2:2'-diacetyldiphenyl was unsuccessful. Diphenic acid and its anhydride were the only pure compounds isolated from the oily reaction products. The former was probably formed by hydrolysis, during the last stage, of the reaction product. Many workers have reported unidentifiable oily products from the reaction of dialkyl cadmium compounds with acid chlorides, (e.g. Nightingale et.al., J.Amer.Chem.Soc., 1953, 75, 4701). The conditions of experiment play a very important role in determining the nature of the reaction product, differ widely for different preparations and consequently are not easily determined. Several modifications in the procedure made no improvement in the results.

In the experiment with diphenyl cadmium and diphenoyl dichloride, the percentage yield of 2:2'-dibenzoyl diphenyl (IV) was only 16% whereas Nightangale et.al. (loc.cit.)

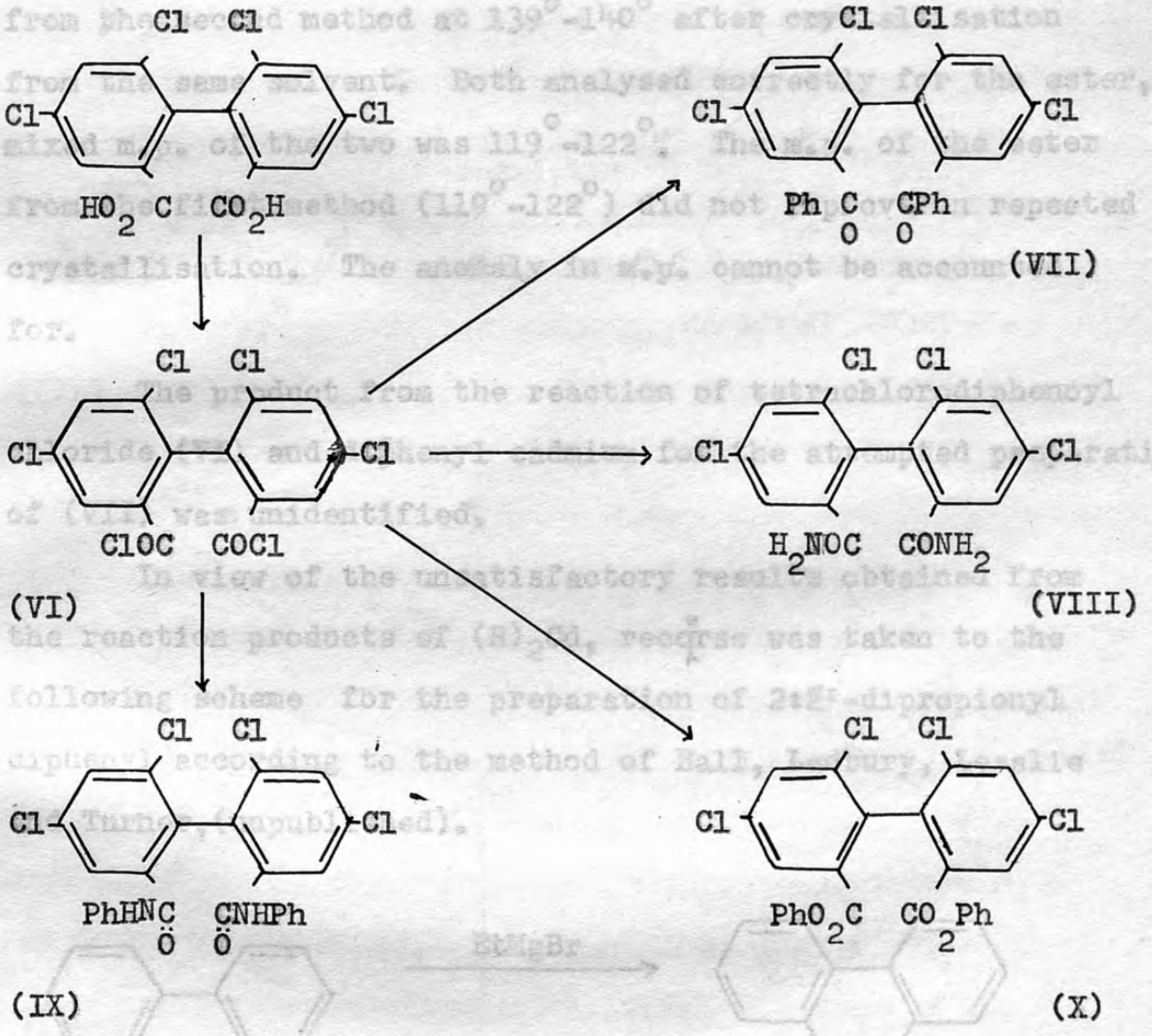
obtained it in 83% yield.



In view of the above results, it appears that the possibilities of side reactions are not so limited as mentioned by Cason (<u>Chem.Rev.</u>, 1947, <u>40</u>, 15).

The Clemmensen reduction of 2:2'-dibenzoyldiphenyl gave 9:10-diphenylphenanthrene as would be expected from a diketone of this type. (Compare Hall, Ladbury, Lesslie and

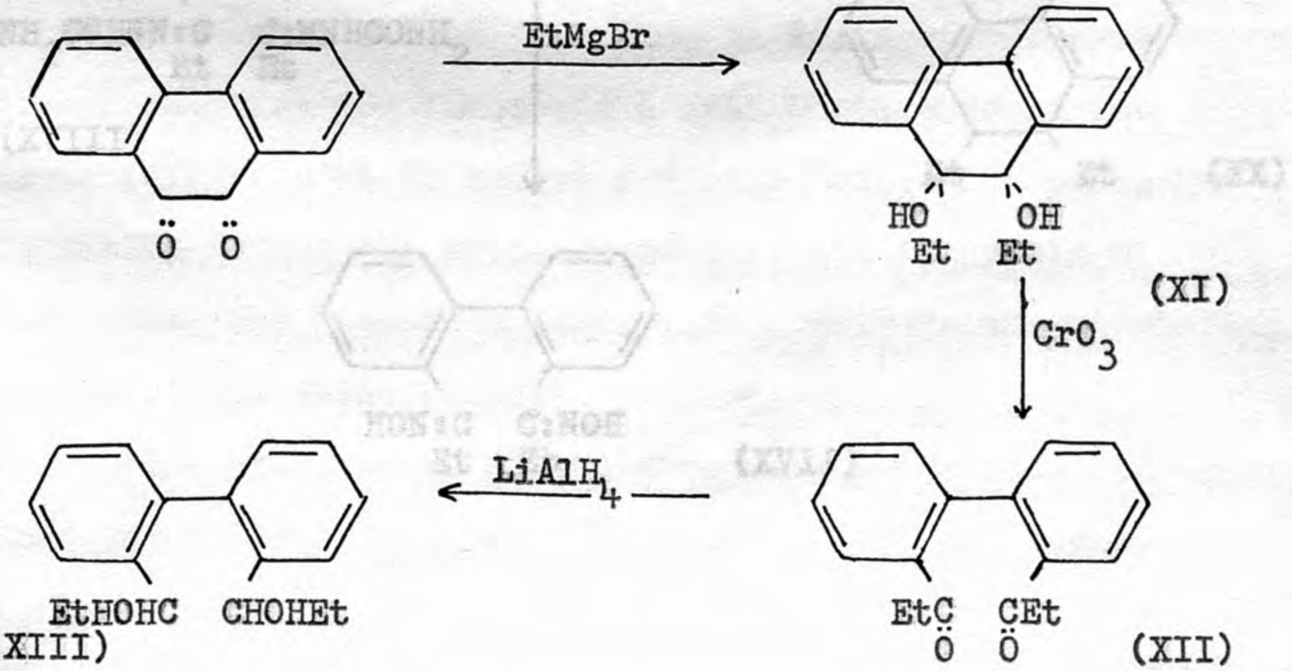
Turner's experiments with dicetyldiphenyl mentioned in the introduction, p.104).

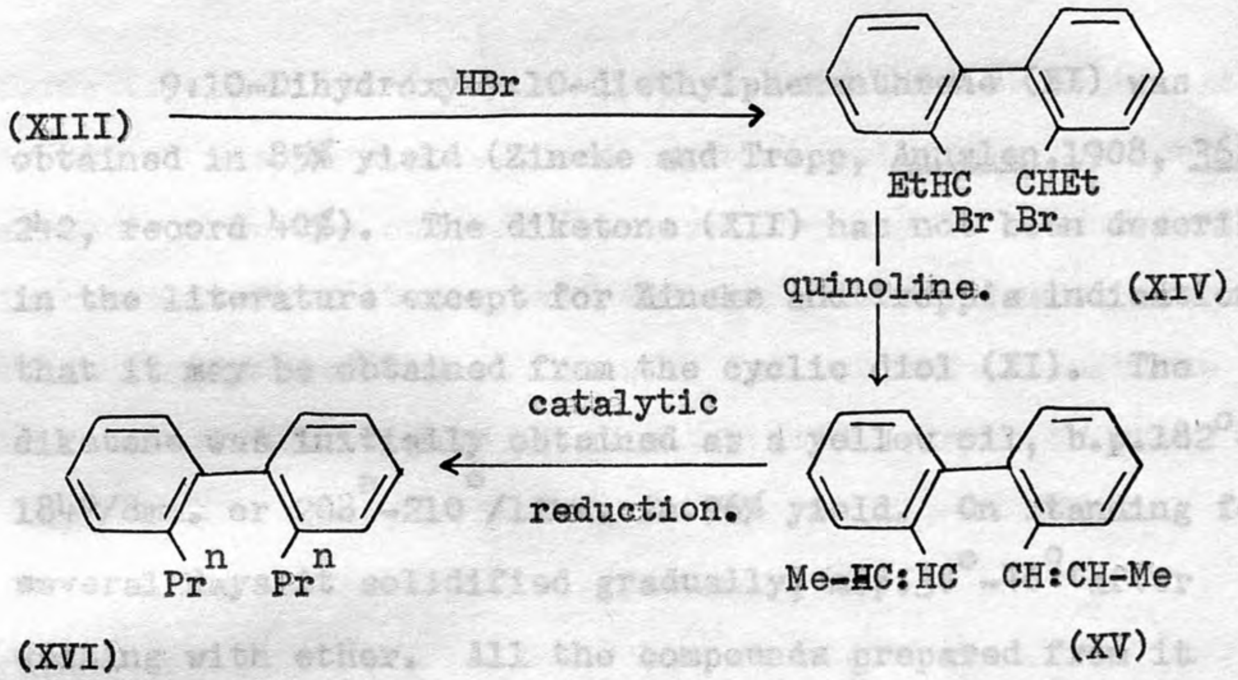


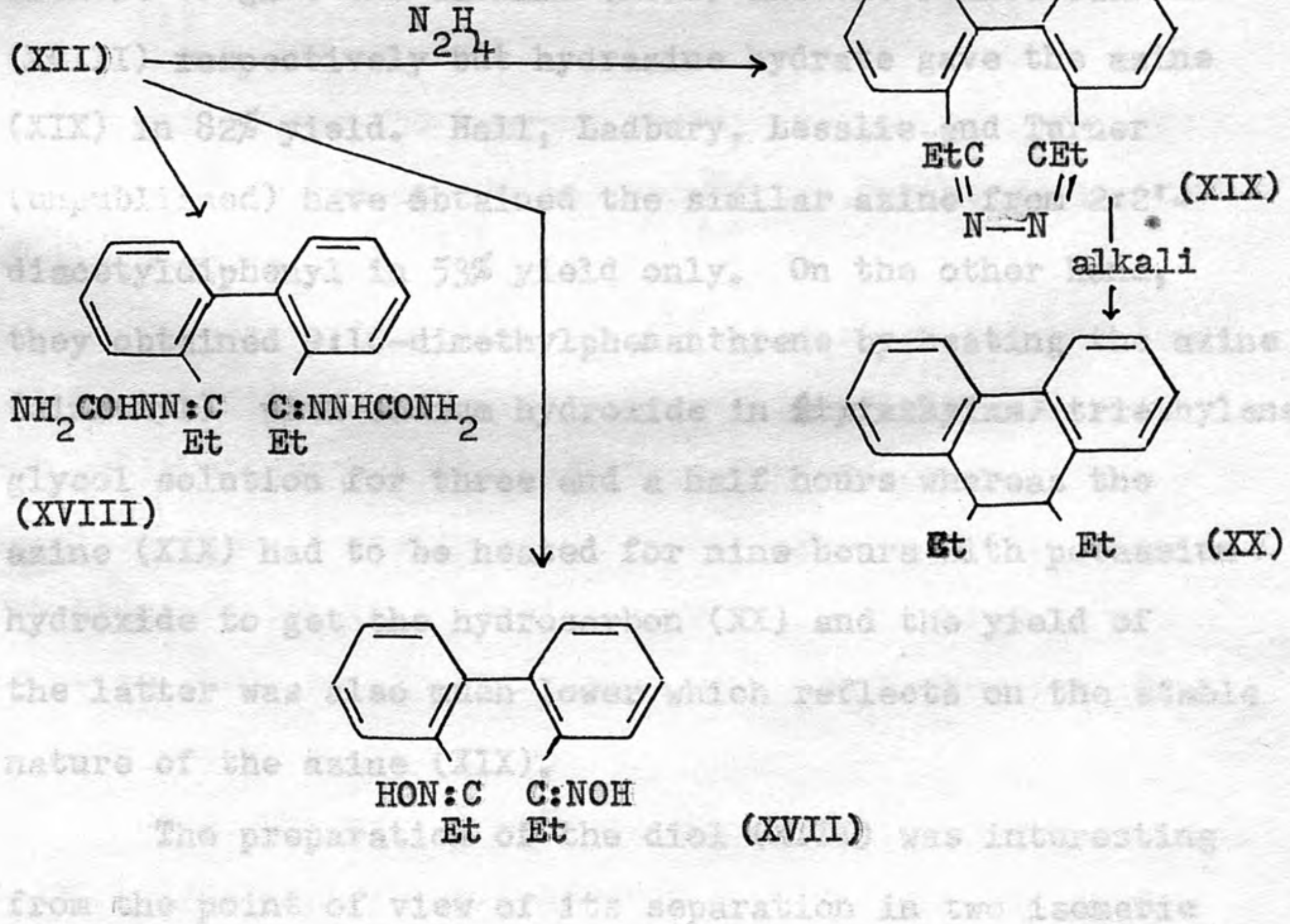
4:4'6:6'-Tetrachlorodiphenoyl chloride (VI), not previously described in the literature, was obtained in very good yield from tetrachlorodiphenic acid and three new compounds (VIII, IX and X) were prepared from the former. The ester (X) was prepared by two methods. The product from the first method after crystallisation from light petroleum (b.p. 40°-60°) melted at 119°-122° and the one from the second method at 139°-140° after crystallisation from the same solvent. Both analysed correctly for the ester, mixed m.p. of the two was 119°-122°. The m.p. of the ester from the first method (119°-122°) did not improve on repeated crystallisation. The anomaly in m.p. cannot be accounted for.

The product from the reaction of tetrachlorodiphenoyl chloride (VI) and diphenyl cadmium for the attempted preparation of (VII) was unidentified.

In view of the unsatisfactory results obtained from the reaction products of $(R)_2Cd$, recourse was taken to the following scheme for the preparation of 2:2'-dipropionyl diphenyl according to the method of Hall, Ladbury, Lesslie and Turner,(unpublished).

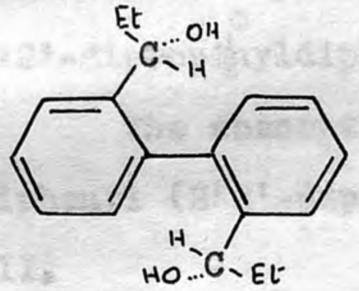



(XIII)
HBr
EtHC CHEt
Br Br
(XIV)
quinoline.
Me-HC:HC CH:CH-Me
(XV)
catalytic
reduction.
Pr^n Pr^n
(XVI)

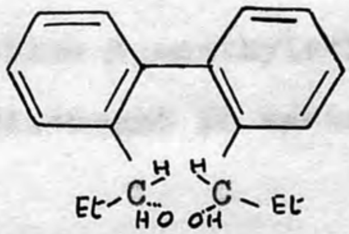

(XII)
N2H4
EtC CEt
N—N
(XIX)
alkali
Et Et
(XX)
NH2COHNN:C C:NNHCONH2
Et Et
(XVIII)
HON:C C:NOH
Et Et
(XVII)

9:10-Dihydroxy-9:10-diethylphenanthrene (XI) was obtained in 85% yield (Zincke and Tropp, <u>Annalen</u>,1908, <u>362</u>, 242, record 40%). The diketone (XII) has not been described in the literature except for Zincke and Tropp's indication that it may be obtained from the cyclic diol (XI). The diketone was initially obtained as a yellow oil, b.p.182°-184°/8mm. or 208°-210°/12mm. in 96% yield. On standing for several days it solidified gradually, m.p.38°-40° after washing with ether. All the compounds prepared from it except diethylphenanthrene (XX) are new. Hydroxylamine hydrochloride and semicarbazide hydrochloride reacted normally with it to give the dioxime (XVII) and the semicarbazone (XVIII) respectively but hydrazine hydrate gave the azine (XIX) in 82% yield. Hall, Ladbury, Lesslie and Turner (unpublished) have obtained the similar azine from 2:2'-diacetyldiphenyl in 53% yield only. On the other hand, they obtained 9:10-dimethylphenanthrene by heating the azine (dimethyl) with sodium hydroxide in triethylene glycol solution for three and a half hours whereas the azine (XIX) had to be heated for nine hours with potassium hydroxide to get the hydrocarbon (XX) and the yield of the latter was also much lower which reflects on the stable nature of the azine (XIX).

The preparation of the diol (XIII) was interesting from the point of view of its separation in two isomeric forms (A) and (B); (A) had m.p.118°-119° and (B) melted at 72°-75°. The racemic and meso forms result from the two asymmetric carbon atoms. The meso compound is of particular interest in that it can pass through a configuration in which it has a centre of symmetry (i) but not through one in which it has a plane of symmetry (ii) because in the latter whilst the two benzene nuclei are coplanar the two substituent groups cannot be accommodated on the same side of the diphenyl.



(i).



(ii)

The dibromide (XIV) was obtained as an oil and could not be solidified. The analysis results of the oil were not satisfactory but the unsaturated hydrocarbon (XV) was obtained from it easily by dehydrobrominating with quinoline. The hydrocarbon (XV) is also capable of existing in two isomeric forms but it seems that only one isomer was obtained in this work.

Unfortunately, there was not enough 2:2'-bis-β-methylethenyldiphenyl (XV) left to reduce to obtain 2:2'-di-n-propyldiphenyl (XVI). Hall, Ladbury, Lesslie and Turner (unpublished) have obtained 2:2'-diethyldiphenyl by catalytic reduction of 2:2'-divinyldiphenyl and the hydrogenation of 2:2'-bis- β -methylethenyldiphenyl (XV) would presumably proceed equally smoothly.

The effect of other reducing agents mentioned in the introduction (p.104), have not so far been studied on 2:2'-dipropionyldiphenyl.

The absorption spectrum of 2:2'-bis- β -methylethenyldiphenyl (2:2'-dipropenyldiphenyl) is discussed in section III.

EXPERIMENTAL.

Preparation of diphenic acid.

(Modification of the method of Vorländer, *Annalen*, 1902, **320**, 138).

Anthranilic acid (50g., 1mol.) was dissolved in 1:1 hydrochloric acid (300ml.) with heating. It was cooled to 0° and diazotised with sodium nitrite (24g., 1mol.) maintaining the temperature at 0°-2°. This solution was filtered to remove any suspended substance, the diazonium salt being soluble in the acid.

Cupric sulphate pentahydrate (176g.) was dissolved in water (1 litre) in a 3 litre beaker and the following added successively to it, with stirring: ammonia (200ml., *d.* 0.88), sodium metabisulphite (400g.) and ammonia (400ml., *d.* 0.88). The solution turned bluish. It was cooled to 10°.

The clear diazo solution was added to the above solution through a dropping funnel with its stem dipping in the solution in 1¼hrs., with vigorous stirring. The temperature was maintained between 10° to 14°. It was found difficult to run in a steady continuous stream of the diazo solution as its passage was blocked by the deposition of the solid reaction products in the stem of the funnel. Nitrogen was evolved during the above procedure.

Anhydrous ferric chloride (260g.) was dissolved in water (400ml.), filtered and then ~~added~~ concentrated hydrochlori acid (d.1.18, 1300ml.) was added to it. This solution was next poured into the product from the previous process. The solution turned brown and diphenic acid was precipitated. It was filtered and washed 2 to 3 times with water on the Buchner funnel.

The crude acid melted at 226°-227° and weighed 27.5g., yield 60%. On crystallising from dilute ethanol, it melted at 229°-230° and the yield was 59%.

The above preparation was repeated several times. The blocking of the funnel stem, when the diazo solution was added from it to the catalyst, was prevented by attaching a tube bent upwards with one end drawn into a capillary.

The yields in the different experiments varied from 59% to 75% and in one case was as high as 88%.

For some of the subsequent preparations, Light's commercial diphenic acid was used which was pink in colour and was crystallised from acetic acid. The pure colourless acid was obtained in 88% yield and melted at 229°-230°.

Preparation of 2:2'-diphenoyl dichloride.

(Underwood and Kockmann, J.Amer.Chem.Soc., 1924, 46, 2072).

Diphenic acid (15g., 1mol.) was mixed with phosphorus pentachloride (27.1g., 2mol.) in a flask fitted with an air condenser and calcium chloride tube. The reaction started after a few minutes and the solid mixture liquefied. After the initial reaction was over, the flask was heated in an oil bath at 190°-195° for 20min. Its temperature was then allowed to fall down to 140°-145° and dry air was passed in for half hour. The reaction mixture solidified. It was allowed to cool down to room temperature and was extracted with dry boiling benzene. The extract was filtered hot and then allowed to stand for crystallisation. The solid obtained was filtered, m.p.218°-220°. It was washed with a little ether, and then it had m.p.221°-222°. Mixed m.p. with diphenic acid and that of the pure acid were the same.

All the recovered solid was dried and heated again with one molecular proportion of phosphorus pentachloride in the same way as above. The first crop from the benzene extract melted at 215°-216° and the second at 92°-95°. It was recrystallised from benzene, m.p.93°-95°, 3.5g., yield 20%.

The above preparation was repeated with diphenic acid (7.5g.,1mol) and phosphorus pentachloride (13.5g.,2mol.) but air was not passed into the hot reaction mixture. To decompose the chlorides of phosphorus, the reaction mixture after being allowed to cool a little was poured into ice-cold water and filtered immediately. The sticky precipitate formed was extracted with ether. It was filtered and then the ether was removed by distillation. It was dried in vacuum. It melted at 110°-112° with considerable softening at 85°-95°.

Several more attempts were made with slight modifications in the experimental procedure but the yields obtained were low and the results inconsistant.

Diphenoyl chloride was successfully prepared by heating diphenic acid and phosphorus pentachloride at 180°-190° and then removing the oxychloride by distillation under reduced pressure. The residue was put in a vacuum before it solidified. The crude acid chloride thus obtained melted at 93°-96° and the yield was 97%. Further purification was not found necessary.

Attempted preparation of 2:2'-diacetyldiphenyl.

(Compare Gilman and Nelson, Rec.trav.chim.,1936, 55, 518 and Nightangale et.al.,J.Amer.Chem.Soc.,1950, 72, 875; 1952, 74, 2557; 1953, 75, 4701).

In a 1 litre three necked flask fitted with a dropping funnel, reflux condenser with calcium chloride tube, and a mechanical stirrer was placed magnesium (2.4g.,1mol.) with a crystal of iodine. The reaction was started by adding a few ml. of the solution of freshly distilled methyl bromide (14.2g.,1.5mol.) in dry ether (ca.45ml.). The flask was cooled externally by an ice-bath. After the reaction had started, the solution of the halide was run in at such a rate as to maintain a gentle refulxing of the ether. This solution was added in ½hr. Stirring was continued for another 20min. after this.

Finely ground anhydrous cadmium chloride (9.1g.,0.5mol.), heated previously in an air oven at 140°-160° for three hours, was added gradually and then the flask was allowed to warm to room temperature. Negative Gilman test (Mischler's ketone test) was obtained after ½hr.

The flask was again cooled in the ice-bath and the acid chloride (14.0g.,1mol.) was added in 10min. The reaction was very gentle. The ice-bath was removed and the reaction mixture was heated under reflux on a water bath with stirring for ½hr. ~~The~~ Hydrolysis was then carried out by adding 10% sulphuric acid.

The ether layer was separated, the water layer extracted twice with ether and all the ethereal solutions were combined and washed respectively with water, 5% sodium hydrogen carbonate, and water again. It was then dried over anhydrous sodium sulphate. Ether was removed by distillation.

The residue was subjected to vacuum distillation. At 90°-100°/14mm. an orange coloured vapour was formed which did not condense. A yellow liquid distilled at 205°-220°/14mm. It was(~~This solidified on cooling and was found to be~~) washed with methanol and filtered. The white substance obtained had m.p.212°-220°.

The above experiment was repeated as follows: For the preparation of methyl magnesium bromide, and from it the dimethyl cadmium, magnesium (2.4g.,1atom), methyl bromide

(14.2g.,1.5mol.) and anhydrous cadmium chloride (9.1g.,0.5mol.) were used. Diphenoyl chloride (10.0g.,0.8mol.) was then added. The theoretical quantity of the acid chloride was 12.9g. but ~~only~~ lesser amount was used so as to ensure its complete utilisation.

In this experiment, on neutralisation of the ether extract with 5% sodium hydrogen carbonate, a white precipitate was obtained which was filtered and washed with water. It melted at 210°-218°(decomp.). It was insoluble in dilute alkalis and dilute sulphuric acid.

The ethereal solution was washed with water, dried over anhydrous sodium sulphate and the ether removed by distillation. In the residue obtained, after a couple of days, some crystals were formed which could not be separated completely and melted at 205°-220°.

The same experiment was again repeated with a few modifications. Methyl magnesium bromide was prepared at room temperature and after the addition of cadmium chloride, ether was removed by distillation and dry toluene was then added. The acid chloride was added to the latter in a toluene solution. The reaction product was treated as in the last two experimemts. From the ethereal extracts, a sticky solid m.p.200°-210° was obtained.

These substances were found to be diphenic acid and its anhydride.

In view of the above facts, no further experiments were carried out for the preparation of 2:2'-diacetyldiphenyl.

Preparation of 2:2'-dibenzoyldiphenyl.

(Compare Nightingale, Wagner and Wise, J.Amer.Chem.Soc., 1953, 75, 4701).

To magnesium (2.4g.1atom) in a three necked flask, with a condenser, dropping funnel and stirrer, was added a solution of bromobenzene (16.0g.,1mol.) in dry ether. The flask, after the completion of this reaction, was cooled in an ice-bath and anhydrous cadmium chloride (9.2g.,0.5mol.) was added to it. After some time the flask was allowed to warm up to room temperature and then heated on a water bath for ½hr. A negative Gilman test was obtained after that time.

Ether was replaced by dry toluene (50ml.). The acid chloride (14g.,0.5mol.) was added to it after cooling the flask in an ice bath. To complete the reaction, the reaction mixture was heated on a water bath for 1½hrs.

The reaction product was treated in the same manner as described under the attempted preparation of 2:2'-diacetyldiphenyl. From the oily residue a crystalline solid separated which was collected by filtration, m.p. 220°-224°. It was crystallised from trichloroethylene, m.p. 222°-224°. The total weight of this product was 2.0g. It was insoluble in boiling 10% sodium carbonate. It was later identified as diphenic anhydride, the acid being precipitated from the 10% sodium hydroxide solution that was used to hydrolyse the reaction product. It analysed for diphenic anhydride. (Found for the reaction product: C,75.0; H,3.6. Calc. for diphenic anhydride, $C_{14}H_8O_3$, C,75.1; H,3.7%).

In another experiment, phenyl magnesium bromide was prepared from magnesium (2.4g.,1atom.) and bromobenzene (16.0g.,1mol.). The flask was cooled in a freezing mixture and cadmium chloride (9.1g.,0.5mol.) was added to it. The formation of diphenyl cadmium was completed by heating on a water bath for 2hrs. Although negative Gilman test was obtained after 40min. Ether was replaced by dry toluene (100ml) and diphenoyl chloride (10.0g.,0.36mol.) suspended in dry toluene was added in about $\frac{1}{2}$hr. at 60°-80°. Heating under reflux was then continued for another 2hrs. with stirring.

The reaction flask was cooled in an ice-bath and the product hydrolysed by ice-cold 1:1 hydrochloric acid.

On cooling a white crystalline substance separated which was filtered, m.p.150°-154°. Some more diketone was obtained from the mother liquor on standing for a few days, m.p.147°-152°; 4.0g. On crystallisation from ethanol, it melted at 165°-167°; 2.5g., 16% yield.

Preparation of 9:10-diphenylphenanthrene.

A large excess of zinc amalgam was prepared by treating zinc wool (25g.) with mecuric chloride (2.0g.) in water (15ml.) with a few drops of concentrated hydrochloric acid. The liquid was decanted off and zinc amalgam washed once with water.

To the zinc amalgam in a 500ml. flask fitted with a reflux condenser was added water (15ml.), concentrated hydrochloric acid (25ml.) followed by a solution of 2:2'-dibenzoyldiphenyl (5.3g.) in toluene (50ml.). The reaction mixture was heated under reflux for 6hrs., adding at intervals another 10ml. of concentrated hydrochloric acid.

It was allowed to stand overnight. Two layers were formed which were separated and the water layer extracted with a few ml. of toluene. The combined toluene extracts were dried over anhydrous magnesium sulphate. Toluene was removed by distillation under reduced pressure. The yellow residue solidified gradually, 1.2g.,m.p.200°-205°(softening at 185°). It crystallised in long needles from ethanol, 1.0g.;m.p.232°-235°. The yield was 21%.

For analysis it was recrystallised from benzene, m.p.237°-238°.

(Found: C,94.1; H,5.7, Calc. for $C_{26}H_{18}$: C,94.5; H,5.5%).

Preparation of 4:4'.6:6'-tetrachlorodiphenoyl dichloride.

Tetrachlorodiphenic acid (5.0g.,1mol.) and phosphorus pentachloride (5.5g.,1.1mol.) were mixed in a flask fitted with an air condenser carrying a calcium chloride tube. The flask was warmed to start the reaction. After the initial reaction had subsided, the flask was heated in a metal bath at 160°-18$\overset{8}{0}$ for 3hrs. Phophorus oxychloride was then removed from it by distillation under reduced pressure. The residue was left overnight in a vacuum over potassium hydroxide. It solidified to a white hard mass, 5.25g., 98% yield. It had m.p.80°-83°., and after crystallisation from light petroleum (b.p.40°-60°) it melted at 81°-83°. (Found: C,40.7; H,1.2; Cl,52.7. $C_{14}H_4O_2Cl_6$ requires C,40.3; H,1.0; Cl51.0 %).

It was, however, found that the crude acid chloride was sufficiently pure to be used for all subsequent preparations. ~~The experi.~~ In order to establish the identity of the above acid chloride, methyl tetrachlorodiphenate was prepared from it and found to be identical with the ester prepared previously.

The following three new derivatives were also prepared from the acid chloride.

4:4'.6:6'-Tetrachlorodiphenanilide: The acid chloride (1.0g.) was heated with an excess of aniline on a water bath for ½hr. It was then cooled to room temperature and poured into dilute hydrochloric acid. The product was filtered, washed with water, 2% sodium hydrogen carbonate, water and then dried. It melted at 240°-244°, 1.2g., 91% yield.

It crystallised from acetone in rectangular plates m.p. 243°-244°.

(Found: C,59.0; H,3.0; Cl,24.1; N,6.0. $C_{26}H_{16}O_2N_2Cl_4$ requires C,58.9; H,3.0; Cl,26.7; N,5.3%).

4:4':6:6'-Tetrachlorodiphenamide: The acid chloride (1.0g.) was boiled gently with an excess of ammonium hydroxide (d.0.88) for 15min. It was cooled and filtered, and the precipitate washed with water. The dry product weighed 0.5g., 55% yield. It had m.p. 240°-242° and after crystallisation from chloroform melted at 246°-247°.

(Found: C,44.4; H,1.9; Cl,37.8; N,7.6. $C_{14}H_8O_2N_2Cl_4$ requires C,44.4; H,2.1; Cl,35.5; N,7.4 %).

Phenyl 4:4':6:6'-tetrachlorodiphenate: (a) A solution of phenol (0.8g., 4mol.) was prepared in pyridine (32ml.) and to this tetrachlorodiphenoyl chloride (1.66g., 1mol.) was added. The flask was heated on a water bath under reflux for 45min. After this time it was cooled to room temperature and poured into water with stirring. A brown oil separated which was left overnight at about 4°. The solid was filtered off , washed successively with water, 5% sodium hydrogen carbonate solution, water, dilute hydrochloric acid and lastly with water. After drying it melted at 112°-122° and weighed 2.1g.,60% yield. It was finely powdered and left exposed to air for several days in order to remove the odour of pyridine. It was then kept in a vacuum over concentrated sulphuric acid for the same purpose.

On recrystallising from light petroleum its m.p. was 119°-122° but still carried a faint smell of pyridine. (Found: C,58.6; H,2.7.; Cl27.9. $C_{26}H_{14}O_4Cl_4$ requires C,58.6; H,2.7; Cl,26.7%).

(b) The diphenyl ester was also prepared by warming a mixture of phenol (0.4g.,4mol.) and the acid chloride (0.83g., 1mol.) in about 15ml. water till the solid liquefied and then adding sodium carbonate (0.32g.,3.0mmol.) followed by heating on the water bath for 1½hrs. It was cooled to room temperature and poured into 4 times its volume of water. Dilute hydrochloric acid was added to the reaction mixture with cooling to 0° and stirring. The precipitate was collected on a Buchner funnel and dried after washing with water, 10% sodium hydrogen carbonate and finally with water. The product had m.p.131°-136°, 0.83g.,83% yield.

From light petroleum (b.p.60°-80°) it crystallised in small prisms with m.p.139°-140°. The m.p.of the above on admixture with the diphenyl ester prepared by method (a) and the m.p. of the latter were the same viz. 119° -122°.

(Found: C,58.6; H,2.7; Cl,27.0. Calc. for $C_{26}H_{14}O_4Cl_4$ C,58.6; H,2.7; Cl,26.7%).

Attempted preparation of 2:2'-dibenzoyl-4:4':6:6'-tetrachlorodiphenyl.

Phenyl magnesium bromide was prepared from magnesium (1.2g.,1atom.) and bromobenzene (8.0g.,1mol.). Anhydrous cadmium chloride (4.6g.,0.5mol.) was added to it after cooling the flask in iced water. The stirring was continued in cold for ½hr. and then to complete the reaction, the flask was heated on a boiling water bath for 1hr. The ether was then replaced by dry toluene (15ml.). In the next ½hr. the solution of 4:4':6:6'-tetrachlorodiphenoyl chloride (8.4g., 0.4mol.) in toluene (50ml.) was added and the heating with stirring was continued for another 2hrs.

The reaction mixture was cooled and treated in a similar way as in the preparation of 2:2'-dibenzoyldiphenyl. After the removal of toluene in vacuum, a yellow sticky substance was obtained. This was warmed with ethanol and the supernatant clear liquid was decanted off. In the residue, after standing for three days a solid appeared which was collected in a Hersch funnel and washed with ethanol. The white solid thus obtained melted at 104°-106°. From the filtrate on standing for several more days some more of the white substance was obtained. The two crops were combined and crystallised from ethanol, m.p.111°-113°.

(Found: C,49.3,49.5; H,3.4,3.4; Cl,32.5. $C_{26}H_{14}O_2Cl_4$ requires C,62.4; H,2.8; Cl,28.3 %).

These analyses results do not also agree with the percentage of carbon, hydrogen and chlorine in tetrachlorodiphenic acid or its anhydride. Unfortunately there was not enough material left for further investigation.

Preparation of 9:10-dihydroxy-9:10-diethylphenanthrene.

The method was that of Zincke and Tropp, (Annalen, 1908, 362, 242), modified by Hall, Ladbury, Lesslie and Turner, (unpublished) for dihydroxydimethylphenanthrene.

To ethyl magnesium bromide prepared from magnesium (19.4g., 4atoms) and ethyl iodide (150g., 5mol.) in dry ether (600ml.), was added slowly phenanthraquinone (41.6g., 1mol; m.p.205°-206°) in 15min. with vigorous stirring. Phenanthraquinone had previously been ground, sieved (60 mesh) and left in a vacuum over potassium hydroxide/concentrated sulphuric acid overnight as the commercial material contained acetic acid. It reacted vigorously with the Grignard reagent.

After the addition was complete, dry benzene (250ml.) was added. The reaction mixture was heated on a water bath allowing ether to distil off ~~readily~~ gradually in about 1hr. Heating was continued for another 1½hrs. with benzene boiling gently under reflux.

The greyish yellow reaction mixture was cooled to room temperature and poured into ice-cold water(1500ml.).

A green solid precipitated. To this was added dilute sulphuric acid (1800ml.) and the solid was mostly dissolved by extracting with ether (5000ml.) and benzene (1500ml.). The colour of the solution gradually changed from green to orange. The benzene and ether extracts were combined and washed twice with brine, then with concentrated sodium bisulphite solution until the latter on adding aqueous sodium hydroxide gave no phenanthraquinone. On washing with sodium bisulphite all the solid which had not dissolved so far, dissolved completely. The solution was washed again twice with brine.

All the ether was removed by distillation and the residual benzene solution allowed to stand for crystallisation. In all, four crops of dihydroxydiethylphenanthrene were obtained. Crop I had m.p.121°-123°, 10.0g.; Crop II, m.p.119°-121°, 15.1g.; Crop III, m.p.112°-116°, 7.0g. and Crop IV, m.p. 107°-115°, 4.7g.. The last crop, 1.0g.,m.p. below 100° and the dirty red mother liquor were discarded.

From the sodium bisulphite solution, phenanthraquinone (8.0g.) was collected by adding aqueous sodium hydroxide. Allowing for this recovery, the yield of 9:10-dihydroxy-9:10-diethylphenanthrene (36.8g.) was 85%. (Zincke and Tropp, <u>loc.cit.</u>, 40% yield.).

Some of the first crop was recrytsallised twice from benzene when it had m.p.122°-123°. (Zincke and Tropp give m.p. 120°-122°).

Preparation of 2:2'-dipropionyldiphenyl.

The general method of Zincke and Tropp (loc.cit.) as used for 2:2'-diacetyldiphenyl and other similar compounds was used.

The above diol (26.7g.) was dissolved in glacial acetic acid (250ml.) with warming up to 80° on a hot plate in a beaker. To this a 10% aqueous solution of chromium trioxide (10.0g.) with stirring was added in about 5min. The temperature of the reaction mixture was maintained at 70° for 20min. It was then cooled to room temperature, poured into water (800ml.) and allowed to stand overnight.

A yellow oil separated which could not be solidified. It was extracted with ether, and this was then washed successively twice with water, once with 20% sodium hydrogen carbonate solution, four times with water and finally dried over anhydrou sodium sulphate. Ether was removed by distillation and the residual orange coloured oil was distilled under reduced pressure.

The first fraction, b.p. 182°-184°/8mm., 12.3g. and the second fraction, b.p. 184°-190°/8mm. weighed 8.6g. The total yield was 96%. Both were inoculated by crystalline diketone from a previous preparation (some of the oily product which had solidified on standing for several weeks). The above two fractions solidified only partly after being allowed to stand overnight and longer.

For analysis the oily diketone after redistilling twice was used. The crystalline diketone from the previous preparation after being washed twice with ether on a Buchner funnel had m.p.38°-40°.

(Found: C,81.0; H,6.6. $C_{18}H_8O_2$ requires C,81.1; H,6.8%).

Derivatives of 2:2'-dipropionyldiphenyl.

(A) Oxime: It was prepared from hydroxylamine hydrochloride (1.5g.) in a few ml. of water, 10% sodium hydroxide solution (3ml.) and the diketone (0.3g.) dissolved in ethanol (3ml.). It was heated on a water bath for 15min., cooled and left overnight at ca.4°. The crystalline solid was filtered off, m.p.180°-183°; recrystallised twice from dilute ethanol, m.p.181°-183°.

(Found: C,72.3; H,6.7; N,10.0. $C_{18}H_{20}O_2N_2$ requires C,72.9: H,6.8; N,9.5%.)

(B) Semicarbazone: A solution of semicarbazide hydrochloride (0.5g.) and sodium acetate (0.75g.) in water (5ml.) was shaken well with an ethanolic solution of the diketone (0.5g.) in ethanol (4ml.) for some time. No precipitate appeared. It was allowed to stand for 2 weeks when the greenish oil that had separated earlier, solidified. It was filtered off and crystallised from ethanol. The semicarbazone was obtained in clusters of fine needles,

crop I, m.p.219°-220° and crop II, m.p.213°-215°.
(Found: C,63.1; H,6.3. $C_{20}H_{24}O_2N_6$ requires C,63.1; H,6.3 %).

Preparation of 1:2-diaza-3:8-diethyl-4:5-6:7-dibenzocyclo-octa-2:4:6:8-tetraene.

Dipropiophenone (2.0g.,b.p.180°-182°/8mm.) was dissolved in ethanol (20ml.) and hydrazine hydrate (1.2ml.; 1mol., 85%) was added to it. The reaction mixture was heated for 7 hrs. at 60°. A flake-like solid appeared. The flask was cooled and left for crystallisation overnight. The crystalline solid, long plates, was filtered off,m.p.124°-125°, 1.3g. Another crop was collected by concentrating the mother liquor, m.p. 125°-126°, 0.25g. By further concentration a sticky third crop was obtained which was discarded. The yield of the azine (1.55g.) was 82%.

For analysis it was crystallised twice from ethanol, m.p.125°-126°.
(Found: C,82.9; H,6.9; N,10.3. $C_{18}H_{18}N_2$ requires C,82.4; H,6.9; N.10.8 %).

Preparation of 9:10-diethylphenanthrene.

The above azine (0.6g.) and sodium hydroxide (0.6g.) were ground finely, added to triethylene glycol (15ml.) and heated in a metal bath at 200° - 205° for 3hrs.

The reaction mixture was cooled, diluted with water (50 ml.) and carefully acidified with dilute hydrochloric acid. The precipitate was filtered and dried, m.p.91°-119°, 0.45g. It was crystallised from dilute acetic acid. Two types of solids were obtained,;transparaent silvery plates, m.p. *ca*.105°, white hard solid, m.p.92°-95°. Some greyish substance that was insoluble in acetic acid melted at 110°-115°. The mother liquor from the above crytsallisation on further concentration and addition of water gave the azine, m.p. 121°-123°.

That the reaction had been incomplete was evident from the long-range of melting of the above products and was further confirmed by mixed m.ps. with pure azine.

All the solids described above were mixed and added to triethylene glycol (15ml.) with ground caustic potash (0.9g.). The mixture was heated under reflux for 6hrs. at 195°-200°. It was cooled, poured into water (60ml.), neutralised with dilute hydrochloric acid, the precipitate was filtered off and crystallised from dilute acetic acid, m.p.103°-105°; recrystallised, m.p.105°-107°. (The m.p. recorded for 9:10-diethylphenanthrene in literature : 106°-107°).

(Found: C,92.1; H,7.7. Calc. for $C_{18}H_{18}$ C,92.2; H,7.8 %).

Preparation of 2:2'-bis(α-hydroxy-n-propyl)diphenyl.

A reducing mixture was prepared from lithium aluminium hydride (1.9g.,1.5mol.) and anhydrous ether (100ml.) in the usual apparatus. 2:2'-Dipropionyldiphenyl (8.9g.,1mol.) dissolved in dry ether (<u>ca</u>.300ml.) was added to the above at a fairly fast rate. The reaction was gentle. When the addition of the diketone was complete, the reaction mixture was allowed to stand for 1hr. before decomposing the excess of the reducing agent, which was then carried out by the addition of ethyl acetate,(10ml.), followed by water (50ml.) and then N/10 sulphuric acid (30ml.).

A white sticky mass separated between the aqueous and the ethereal layer which was dissolved on adding another 50ml. of sulphuric acid (2N acid). The ethereal layer was separated and the aqueous layer was extracted thrice with ether. The combined ether extracts were dried over anhydrous sodium sulphate. The ether was distilled off, leaving a yellow oil from which the following six crops were obtained, each of which was collected by filtration through a sintered glass funnel and the solid diol washed on the funnel with a few ml. of ether. Attempts to solidify the oil completely using different solvents were, however, not successful.

The total weight of the diol obtained in the six crops, listed below, was 5.4g. (60% yield).

CROP.	M.p.	WEIGHT.
no. 1	118°-119°; crystallised from benzene: 118°-119°.	3.2g. (36% of the theoretical yield)
no. 2	109°-111°	0.55g.
no. 3	75°-80° (clear at 106°); crystallised from benzene:	0.4g.
	73° (clear at 90°)	0.22g.
no. 4	72°-76° (clear at 82°); crystallised from benzene:	0.28g.
	73° (clear at 90°).	0.18g.
no. 5	70°-75°.	0.34g.
no. 6	72°-75°.	0.65g.

A little more solid appeared in the oily mother liquor which was difficult to filter and was therefore discarded. Crop 1 recrystallised from benzene, m.p. 118°-119°, and crop no. 6, washed with a few drops of ether, were analysed. (Found: Crop no. 1: C, 80.1; H, 8.1. Crop no. 2: C, 79.8; H, 8.2. $C_{18}H_{22}O_2$ requires C, 80.0; H, 8.2 %).

In another experiment for the preparation of the above diol, the sticky white precipitate which separated after the reduction of the diketone was over was dissolved completely in sulphuric acid (1N.) by letting it stand for 2 days. The ethereal solution, before removing the ether, was washed with dilute sodium hydrogen carbonate solution, water and then dried. It solidified completely on cooling but had a strong smell of ethyl acetate which was removed by washing the diol with ether and then heating it at 30°-35° for 2 days. Its m.p. was 100°-107° (softening at 78°); 9.5g. From the ethereal washing, on removal of ether, a second crop m.p. 58°-74°, 2.2g. was obtained. The total yield of the diol (11.7g.) was 94%.

Preparation of 2:2'-bis(α-bromo-n-propyl)diphenyl.

It was prepared by heating under reflux the above diol (2.0g.) with hydrobromic acid (48% w/w; 40ml.) for 30min. It was then cooled, diluted with water and the dibromide was extracted with ether. The combined ethereal extracts were washed with water and dried over anhydrous sodium or magnesium sulphate. Ether was removed by distillation. The oily residue obtained could not be crystallised.

(Found: C, 61.9; H, 5.7; Br, 27.8. $C_{18}H_{20}Br_2$ requires C, 54.6; H, 5.1; Br, 40.3 %).

When the two isomeric diols (m.p. 118°-119° and 72°-75°) were heated separately with hydrobromic acid same result was obtained.

Preparation of 2:2'-bis-β-methylethenyldiphenyl. (2:2'-dipropenyldiphenyl.)

To the oil from the above experiment, excess of dried and freshly distilled hot quinoline was added and the mixture was heated under reflux for 10min. It was cooled and poured into dilute hydrochloric acid. The hydrocarbon was extracted with ether. The combined ethereal extracts were washed twice with water, dried over anhydrous magnesium sulphate and ether removed by distillation. From the oily residue, after standing overnight, a white solid separated in hexagonal plates. It was filtered and washed with a few drops of ether, m.p. 72°-76°, 0.65g.

The yield was 41% on basis of the calculation from the diol but this could be improved upon if the reaction was carried out on a larger scale.
(Found: C,92.3; H,7.8. $C_{18}H_{18}$ requires C,92.2; H,7.7%).

The ultra-violet absorption spectrum of this compound is discussed in the next section.

SECTION III.

STUDY OF THE

ULTRA-VIOLET ABSORPTION SPECTRA.

STUDY OF ULTRA-VIOLET ABSORPTION SPECTRA.

Unicam spectrophotometer (SP/500) was used for the measurement of the ultra-violet spectra discussed in the following pages.

The solvent used in each case was 95% ethanol but for some sparingly soluble compounds the 20ml. of stock solution contained 1ml. of "B.P." chloroform. In all cases the stock solution was subsequently diluted 50 to 100 times with the above alcohol to concentrations of approximately 5×10^{-5} g. moles/ litre.

The optical density measurements were first determined using 10mm. cells and subsequently checked by 5mm. and 2mm. cells and occasionally also by the use of a solution of different concentration.

The prominent features of the spectra have been tabulated along with those of the reference compounds. For the curves, molar extinction coefficients $\times 10^{-4}$ have been plotted against increasing wave numbers.

The use of ultra-violet light absorption of compounds with conjugated systems for the investigation of their configuration has developed very rapidly during the last two decades. The configuration of the diphenyl skeleton, as it is present in many important types of compounds, has been investigated by five different methods namely (a) X-ray crystal analyses, (b) electron diffraction in vapour phase, (c) dipole moment measurements, (d) optical resolution and (e) ultra-violet light absorption.

Dhar (*Indian. J. Physics*,1933, *1*, 606 and 679) concluded from his X-ray crystallographic studies of diphenyl that the molecule is coplanar in the crystal. The molecule in this particular physical state is subject to the influence of intermolecular cohesive forces which are not present in solution or vapour states. The study of the configuration of 3:3'-dichlorobenzidine (Toussaint, *Acta.Cryst.*, 1948,*1*,43) further illustrates this point. Toussaint found that in the crystal form the molecule was planar and the two chlorine atoms were in a "*trans*" position; whereas in 2:2'-dichlorobenzidine Smare (*Acta.Cryst.*, 1948,*1*,150) found that the two chlorine atoms were in a "*cis*" relationship and the two phenyl rings were at an angle of 72° with the 1:1' bond length as 1.53 Å. Similar results were obtained for 2:2'-dimethylbenzidine hydrochloride by Fowweather and Hargreaves (*Acta. Cryst.*, 1950, *3*,81).

Electron diffraction measurements of vapour give data about the isolated molecule. Karle and Brockway, (J.Amer. Chem.Soc., 1944, 66, 1974) have suggested a non-coplanar structure for diphenyl on the basis of this method of study and Bastiansen (Acta.Chem.Scand., 1949, 3, 408) has calculated the angle between the benzene rings for several substituted diphenyls, that for diphenyl itself being 45° in a collinear molecule. Littlejohn and Smith (J., 1953, 2456; 1954, 2552) by the measurements of dipole moments found that the configuration of diphenyl was non-coplanar.

Substituted diphenyls, which are sterically hindered owing to the presence of large ortho substituents can be resolved and these obviously cannot attain the coplanar form. **However, there are certain** ortho substituted diphenyls, in which the size of the substituent is such that the compound is not even optically activable, nevertheless these compounds have been found to have ultra-violet absorption spectra showing decreased conjugation between the two phenyl groups, which is associated with the non-coplanar form. The spectrum of 2:2'-dimethyldiphenyl (O'Shaughnessy and Rodebush, J.Amer. Chem.Soc., 1940, 62, 2906; Everitt, Hall and Turner, in the press; see also Williamson and Rodebush, J.Amer.Chem.Soc., 1941, 63, 3018) shows few of the characteristics of the 'diphenyl type' absorption which is due to the overlapping of the π orbitals of the 1:1' carbon atoms. An intermediate case is that of 2:2'-dihydroxydiphenyl (Williamson and Rodebush, loc.cit.) which has a spectrum showing bands characteristic of a conjugated system as well as of a phenol.

With the introduction of ortho substituents in a diphenyl system, two new factors have to be considered: firstly the space requirements of the new group relative to 2' and 6' positions and secondly the electronic interaction of the new substituent with the parent phenyl ring. The space requirement of the ~~two~~ 2- substituent opposes the fundamental diphenyl resonance but the second factor may or may not do so.

In 2:2'-dimethyldiphenyl, the two o- substituents decrease the conjugation between the two benzene nuclei and consequently the compound has very little 'diphenyl type' absorption whereas if two nitro groups are introduced at the 4:4'- positions (Sherwood and Calvin, J. Amer. Chem. Soc., 1942, 64, 1350; Pickett, Groth, Duckworth and Cuncliffe, ibid., 1950, 72, 44), the second factor mentioned above comes into play in such a manner that this compound has a spectrum like that of diphenyl.

Beaven, Hall, Lesslie and Turner (J., 1952, 854; 1954, 131; 1954, 2498; 1955, 2708) have studied the relationship between the configuration and conjugation of several substituted diphenyls and also of those bridged in the 2:2'- positions forming a six, seven or eight membered ring compound and have concluded that coplanarity of the two benzene rings is not essential for the compound to exhibit a conjugation band. Some similar compounds derived from methyl 4:4':6:6'-tetrachlorodiphenate studied in this work, provide an interesting comparison for further investigation of this relationship in this series of compounds.

Some similar compounds derived from 2:2'-dinaphthyl have also been studied as well as a 2:2' substituted unsaturated hydrocarbon.

An intense short wave band (λ_{max} 205-215 mμ), which just comes within the limit of study by quartz spectrophotometer, is present in all the compounds listed in tableI.

In methyl 4:4':6:6'-tetrachlorodiphenate (tableI,no.1; fig.no.i) the short wave absorption band is very intense and the conjugation band is absent indicating lack of conjugation between the phenyl groups. This would indeed be expected because of the blocking effects of the <u>ortho</u> substituents. A similarity may be drawn between this ester and 2:4:6-2':4':6'-hexachlorodiphenyl and dimesityl (Pickett, Walter and France, <u>J.Amer.Chem.Soc.</u>,1936,<u>58</u>,2296) which have longwave fine structure at 267.7, 275.1, 283.6 mμ and at 264.6, 274.1, 277.3 mμ respectively. The presence of longwave absorption bands in all the three compounds and the absence of a diphenyl conjugation band (at <u>ca.</u> 250mμ) is indicative of benzenoid characteristics. This is further supported by a comparative study of the absorption spectra of these compounds with

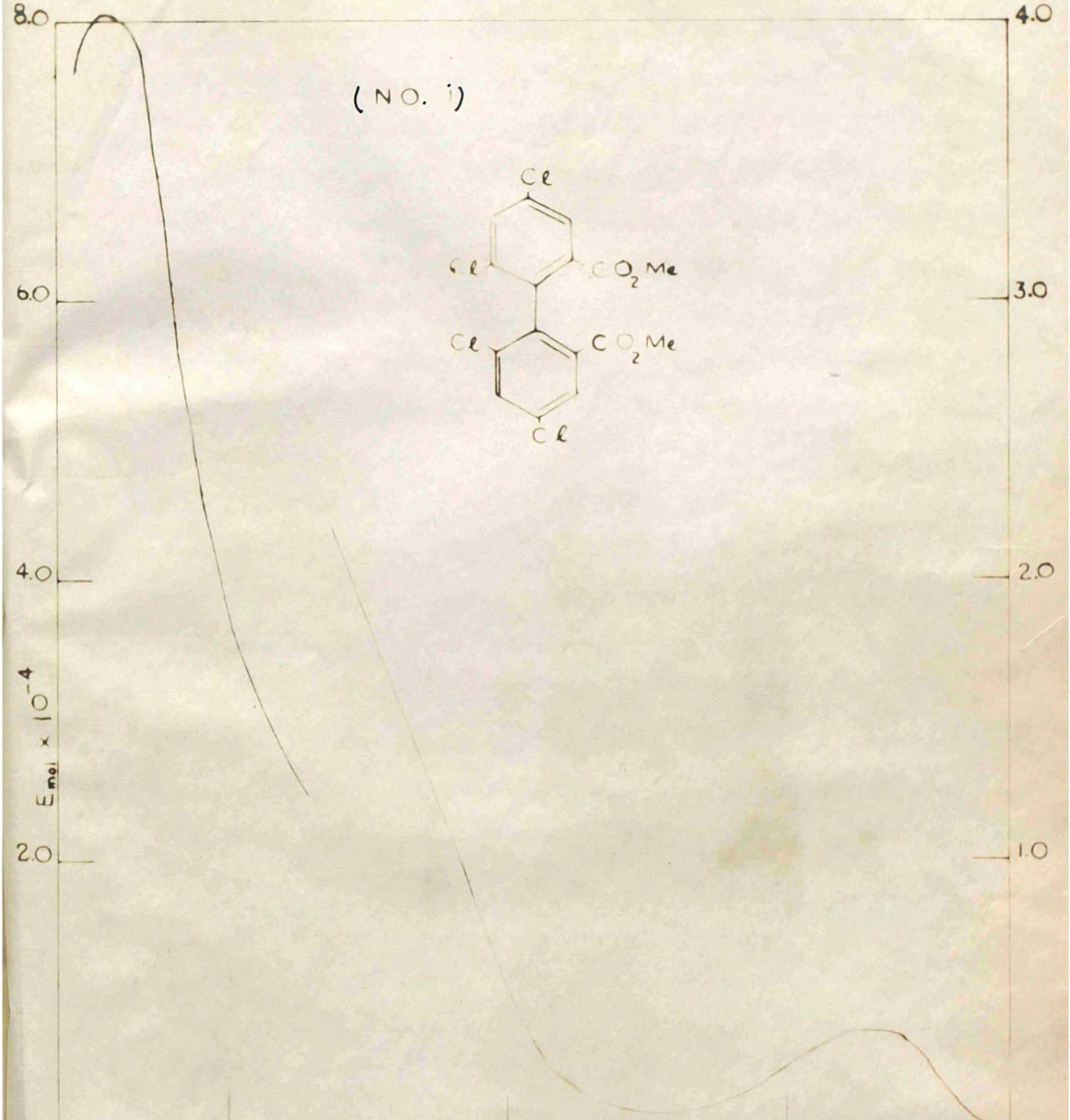
TABLE I

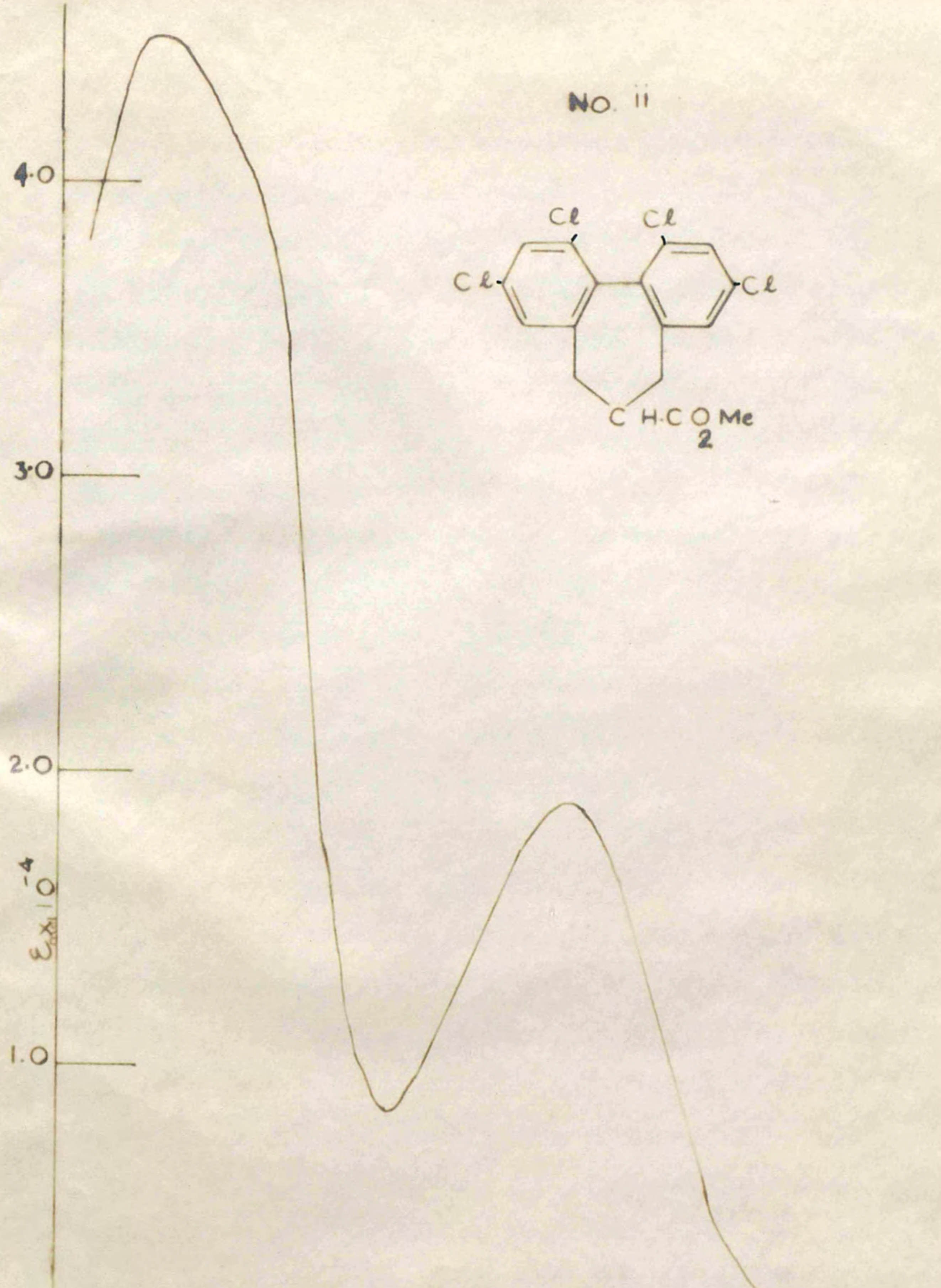
					Conjugation band		Long Wave Structure			
	λ_{max}	ε_{max}	λ_{min}	ε_{min}	λ_{max}	ε_{max}	λ_{min}	ε_{min}	λ_{max}	ε_{max}
1. Methyl 4:4'-6:6'-tetrachlorodiphenate (Fig.no.i)	212.2	80,600	-	~~1,060~~ -	-	-	268.8	1,000	297.2	3,900
2. Methyl 1":4'-2':3"-tetrachloro-3:4-5:6-dibenz*cyclo*hepta-3:5-diene-1-carboxylate (Fig.no.ii)	215.4	44,800	236.1	8,400	254.4	19,000				
3. Methyl 3:4-5:6'dibenz*cyclo*hepta-3:5-diene-1-carboxylate	207.5	42,500	227.5	5,700	278.5	15,500			*(*ca*.274)	*ca*.1,700
4. 3:4-5:6-Dibenzo*cyclo*hepta-3:5-diene-1-carboxylic acid	205	43,000	228	5,800	249	15,300			*(*ca*.274)	*ca*.1,750
5. 1-Hydroxymethyl-3:4-5:6-dibenzo-*cyclo*-hepta-3:5-diene.	205.5	43,000	227.5	5,400	248.5	15,400			*(*ca*.269) (*ca*.277)	3,200 1,500

Solvent 95% Ethanol.

*Wavelengths in brackets denote inflections and are the values obtained by direct examination of large scale plots

Nos. 3,4 and 5 Beaven, Bird, Hall, Johnson, Ladbury, Lesslie and Turner *J.*, 1955, 2708.


8.0
6.0
4.0
2.0
4.0
3.0
2.0
1.0
(NO. 1)
Cl
Cl
CO2Me
Cl
CO2Me
Cl
$E_{mol} \times 10^{-4}$
4.8
4.5
4.0
3.5
3.1
ν̄ (Cm × 10⁻⁴)


No. 11
Cl
Cl
Cl
Cl
CH·CO2Me
4.0
3.0
2.0
1.0
ε × 10⁻⁴
4.8
4.5
4.0
3.5
ν̄ (Cm⁻¹ × 10⁻⁴)

2:4:6-trichlorobenzene amd mesitylene (Pickett <u>et.al,loc.cit.</u>) which absorb in the same regions.

There is a general bathochromic shift in methyl 1":4'-2':3"-tetrachloro-3:4-5:6-dibenz<u>cyclo</u>hepta-3:5-diene-1-carboxylate (tableI,no.2;fig.ii) compared to compounds no. 3, 4 and 5 (tableI) which are not substituted in the diphenyl nucleus. This shift is probably, therefore, caused by the presence of four chlorine atoms.

The intensities of absorption in the shortwave region of the four compounds with seven membered rings are, however, not widely different but there is a general increase in the intensities throughout in the seven membered tetrachloro ester (no.2). The diphenyl absorption band is present in all the four 2:2'- bridged diphenyls but there is a bathochromic shift in the tetrachloro ester.

In view of the above observations, it may be concluded that the <u>ortho</u> chlorine atoms, can, therefore, be having only a negligible steric effect which is more than compensated for by the presence of <u>para</u> substituents. This strongly supports the view that in the parent compound (no.3), the rings are already twisted through a large angle with respect to one another, so that the <u>ortho</u>-chlorine atoms can be accomodated without much further twisting. The compound no.2 is thus in marked contrast to non-bridged diphenyls in which the steric effect of <u>o</u>-chlorine atoms is sufficient to cause almost complete disappearance of the conjugation band, (e.g. in 2:2'-dichlorodiphenyl, Williamson and Rodebush, J.Amer.Chem.Soc., 1941,63,3018; Beaven and Hall,unpublished).

2':4':1":3"-Tetrachloro-2:7-dihydro-3:4-5:6-dibenzoxepin (table II, no.4; fig.iii) has an intense shortwave absorption band (λ_{max} 217.0, ε_{max} 42000) like m,m'-dimethoxyoxepin (table II,no.3. λ_{max} 222.0, ε_{max} 51000). The conjugation band has undergone a gradual bathochromic shift starting from the parent oxepin (no.1) to the tetrachloro one (no.4) through nos. 2 and 3. The intensity of absorption, on the other hand, has decreased in the case of the two methoxy substituted oxepins but is slightly increased in the tetrachloro oxepin which is a feature common to the conjugation band of all the derivatives of 4:4':6:6'-tetrachlorodiphenic acid studied in this work, which in all cases may be accounted for as in the case of the 2:2'- bridged ester (page no.142).

The last compound in the series of 2:2'- bridged diphenyls, was 2':4':1":3"-tetrachloro-2:7-dihydro-3:4-5:6-dibenzazepinium-1-spiro-1"'-piperidinium (table III, no.1; fig.iv) examined as the bromide in 95% ethanol.

It has an intense shortwave absorption band (λ_{max} 223.0, ε_{max} 43800) like the oxepin (table II,no.4.) and the m,m'-dimethoxy compound (table III,no.2).

The conjugation band absorption is at a higher wavelength

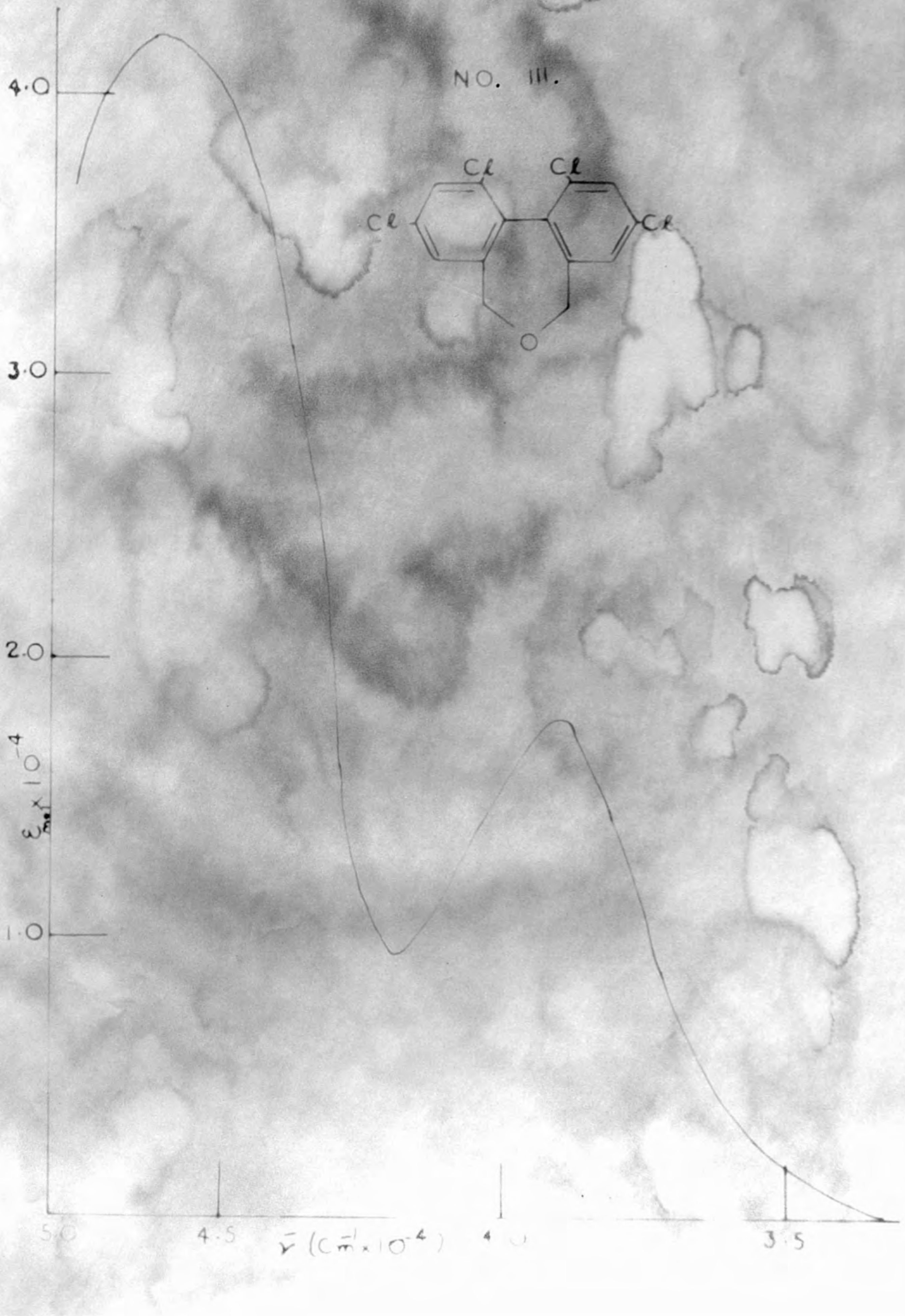
TABLE II

	λ_{max}	ε_{max}	λ_{min}	ε_{min}	λ_{max}	ε_{max}	λ_{min}	ε_{min}	λ_{max}	ε_{min}
1. 2:7-Dihydro-3:4-5:6-dibenzoxepin.	-	-	226.0	5700	250.0	16,500				
2. 2:7-dihydro-4':1"-dimethoxy-3:4-5:6-dibenzoxepin.	-	-			253.0 (246.0)	8650 9300	263.0	2,450	293.5 283.5	9,950 9,400
3. 2:7-Dihydro-3':2"-dimethyl-3:4-5:6-dibenzoxepin.	222.0	51,000	246.0	9450	255.0	11,000	2710	3,200	(2960) 2860	4,800 5.600
4. 2':4'-1":3"-tetrachloro-2:7-dihydro-3:4-5:6-dibenzoxepin. (Fig.no.iii)	217.0	42,000	238.9	9300	257.0	17,800				

Solvent 95% Ethanol.
Wavelength in brackets denote inflections.

Nos. 1 and 2, Beaven, Hall, Lesslie and Turner J., 1952, 854.

No. 3, Idem, J., 1954, 131.


NO. III.
Cl
Cl
Cl
Cl
O
4.0
3.0
2.0
1.0
$\varepsilon_{mol} \times 10^{-4}$
5.0
4.5
4.0
3.5
$\bar{\nu}$ (cm^{-1} × 10^{-4})

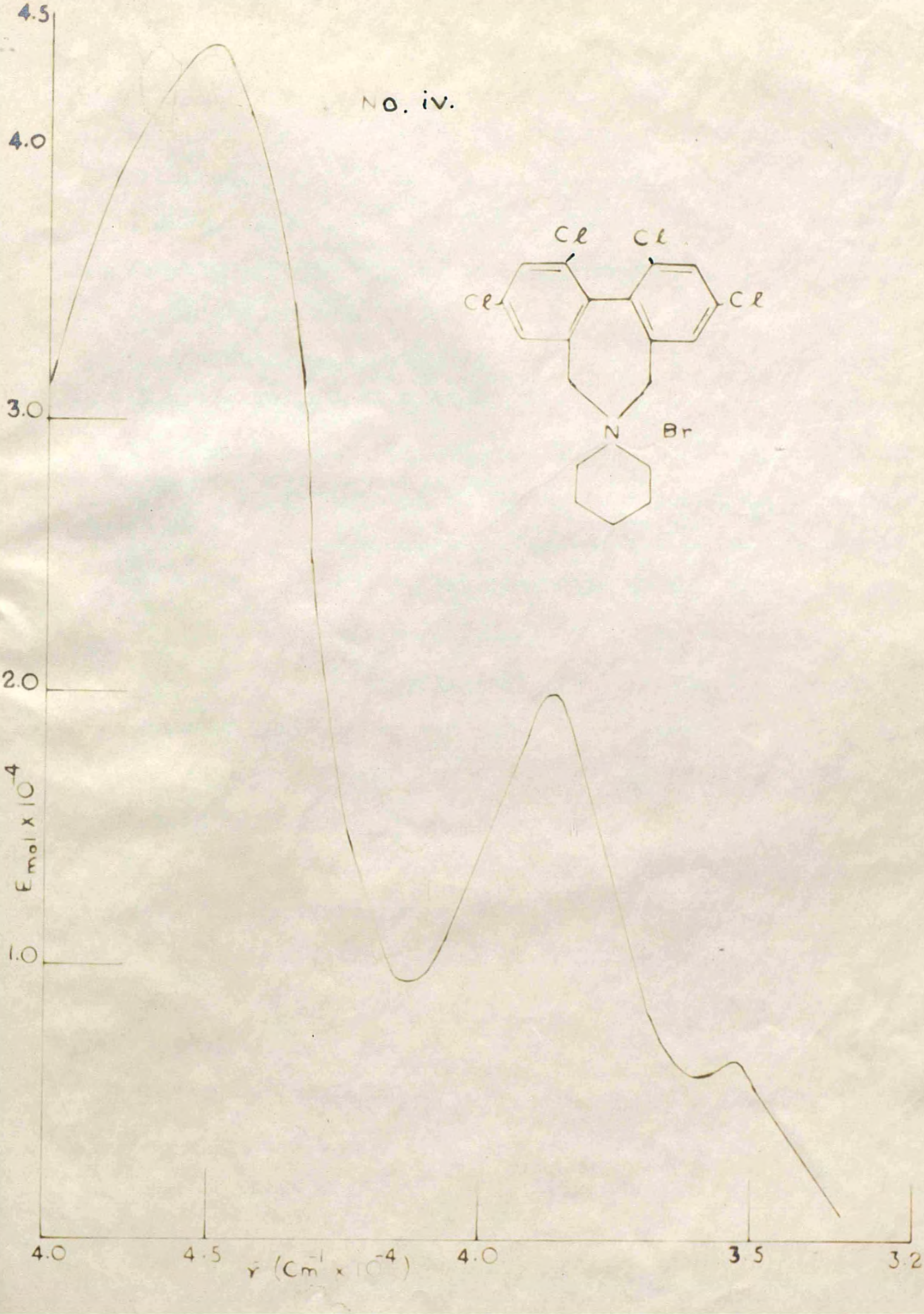
T A B L E III

	λ_{max}	ε_{max}	λ_{min}	ε_{min}	λ_{max}	ε_{max}	λ_{min}	ε_{min}	λ_{max}	ε_{max}
1. 2':4':1":3"-Tetrachloro-2:7-dihydro-3:4-5:6-dibenzazepinium-1-*spiro*-1"'-piperidinium bromide. (Fig.no.iv)	222.9	43,800	241.7	9,700	259.4	20,100	279.0	5,900	283.6	6,600
2. 2:7-Dihydro-3':2"-dimethoxy-3:4-5:6-dibenzazepinium-1-*spiro*-1"'-piperidinium bromide	226.0	54,500	250.0	9,900	257.0	10,500	277.0	3,650	(2970) 2845	3,000 4,200
3. 2:7-dihydro-4':1"-dimethoxy-3:4-5:6-benzazepinium-1-*spiro*-1"'-piperidinium bromide			233.5	11,000	237.5	11,500	261.0	1,450	297.5	10,500
4. 2:7-dihydro-3:4-5:6-dibenzazepinium-1-*spiro*-1"'-piperidinium bromide			224.0	4,500	248.0	15,000			(2815) 2720	2,250 4,750

Solvent 95% Ethanol.

No.2, Beaven, Hall, Lesslie, Turner and Bird, *J.*, 1954, 131.
Nos.3 & 4, Beaven, Hall, Lesslie and Turner, *J*, 1952, 854.

No. iv.



(λ_{max} 259.4, ε_{max} 20100) as compared to diphenyl wheras the other azepinium salts (table III, nos.2, 3 and 4) absorb at a lower wavelength. This difference with regard to the location of the conjugation band is similar to the compounds discussed earlier.

The above results of the study of the spectra of derivatives of 4:4':6:6'-tetrachlorodiphenic acid lend further support to the theory of Beaven, Hall, Lesslie and Turner (loc.cit.) that in the o,o'- substituted diphenyls, coplanarity of the benzene rings is not essential for the exhibition of the conjugation band by a compound and that large departure from coplanarity may be accommodated without complete loss of conjugation. The introduction of more substituents (in the 6:6'- positions) may without having any further steric effects decrease the intensity of conjugation band but it may be more than compensated for by substituents in the p,p'- positions as was observed in all the compounds studied.

A comparative study of the absorption spectra of the unsaturated hydrocarbon 2:2'-bis-β-methylethenyldiphenyl (2:2'-dipropenyldiphenyl) (table IV, no.1; fig.v), 2:2'-bis-α-methylethenyldiphenyl (Beaven, Hall and Johnson, unpublised. Table IV, no.2) and also 2:2'-divinyldiphenyl (idem.,ibid., table IV, no.3) reveals very close similarity in the location of the absorption bands, but the intensities in 2:2'-dipropenyl-

TABLE IV.

	λ_{max}	ε_{max}	λ_{min}	ε_{min}	λ_{max}	ε_{max}	
1. 2:2'-Bis-β-methylethenyldiphenyl.	215.5	18800	236.0	13600	251.2	14700	Fig.v.
2. 2:2'-Bis-γ-methylethenyldiphenyl.	209 (214)	31500 31200	–	–	(252)	11000	
3. 2:2'-Divinyldiphenyl.	213.5	34200	240.5	24400	247	24900	
4. β-Methylstyrene.	–	–	224	2820	245	12600	
5. Diphenyl.	–	–	222.0	4300	249	17300	

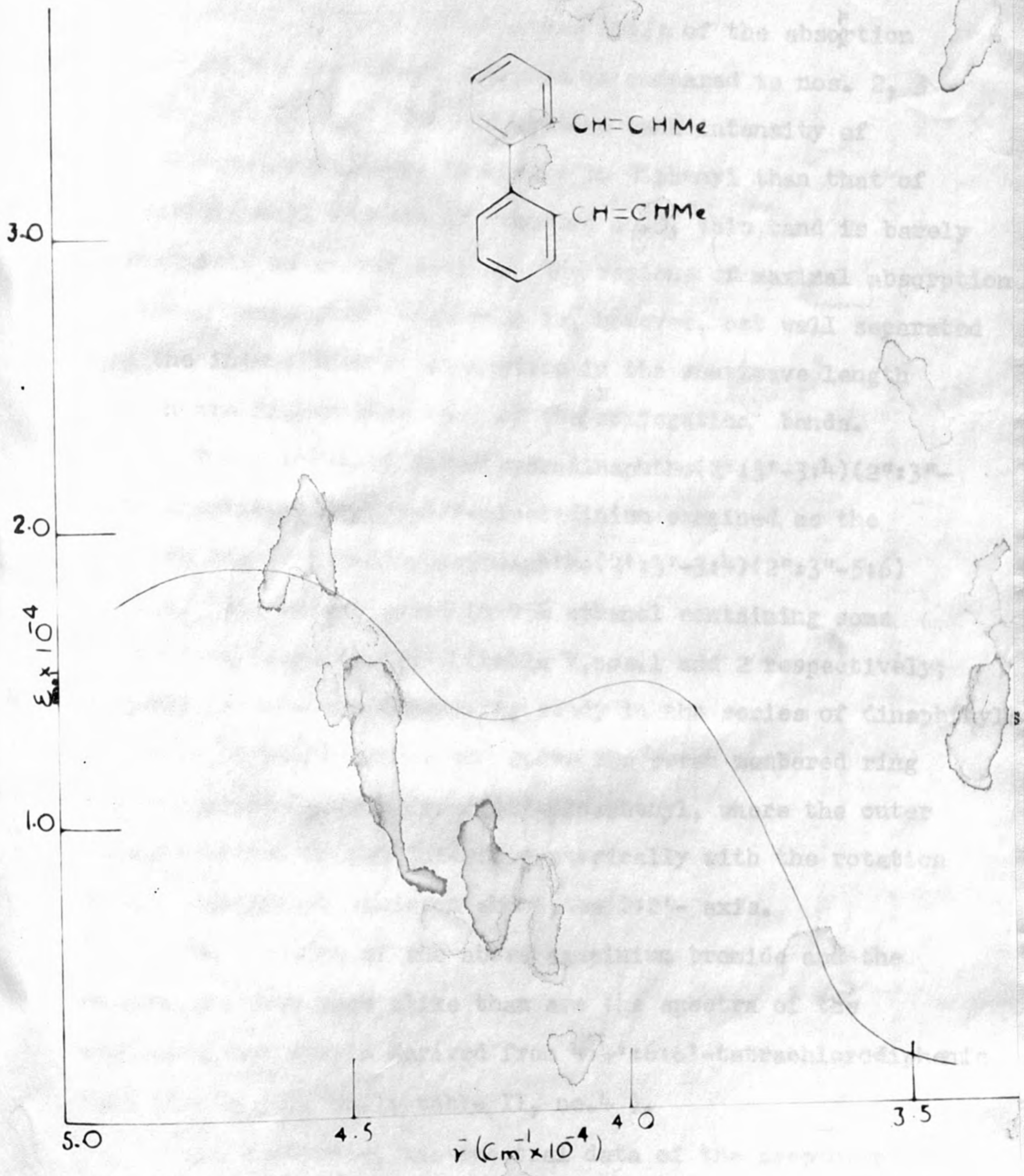
Solvent: 95% ethanol.

Nos. 2 and 3, Beaven, Hall and Johnson, unpublished.

No. 4, Friedel and Orchin, 'Ultra-violet spectra of Aromatic Compounds', John Wiley and Sons Inc. New York, 1951, no. 25.

No. 5, Everitt, Hall and Turner, in the press.

NO. V



CH=CHMe
CH=CHMe
3.0
2.0
1.0
$\varepsilon_{mol} \times 10^{-4}$
5.0
4.5
4.0
3.5
$\bar{\nu}$ (Cm^{-1} x 10^{-4})

diphenyl are much lower than those of the other two hydrocarbons. There is also a small bathochromic shift of the absorption maxima in the dipropenyl compound as compared to nos. 2, 3 or diphenyl (no.5). The conjugation band intensity of 2:2'-dipropenyldiphenyl is nearer to diphenyl than that of divinyldiphenyl whereas in compound no.2, this band is barely discernible as an inflection. The region of maximal absorption in these unsaturated compounds is, however, not well separated and the intensities of absorption in the shortwave length region are higher than that of their conjugation bands.

The spectra of 2:7-dihydrodinaphtho(2':3'-3:4)(2":3"-5:6) azepinium-1-<u>spiro</u>-1"'-piperidinium examined as the bromide and of 2:7-dihydrodinaphtho(2':3'-3:4)(2":3"-5:6) oxepin, both investigated in 95% ethanol containing some chloroform (page no.136) (table V,nos.1 and 2 respectively; fig.vi) provide an interesting study in the series of dinaphthyls and also diphenyls since the above two seven membered ring compounds are derived from 2:2'-dinaphthyl, where the outer benzene nuclei do not interfere sterically with the rotation of the dinaphthyl skeleton about the 2:2'- axis.

The spectra of the above azepinium bromide and the oxepin are even more alike than are the spectra of the azepinium and oxepin derived from 4:4':6:6'-tetrachlorodiphenic acid (table III, no.1; table II, no.4).

For reference, the spectral data of the azepinium

TABLE V

	λ_{max}	ε_{max}	λ_{min}	ε_{min}	λ_{max}	ε_{max}	λ_{min}	ε_{min}	λ_{max}	ε_{max}
1.2:7-Dihydrodinaphtho (2':3'-3:4)(2":3"-5:6) azepinium-1-spiro-1" piperidinium bromide (95% Ethanol with chloroform). Fig. no. VI.	215.2	58,700	226.4	26,100	255.2	89,200			(298)	13,900
2.2:7-Dihydroxydinaphtho-(2':3'-3:4)(2":3"-5:6) oxepin (solvent as above)	215.1	53,100	227.6	263,300	256.5	90.700			(300)	13,850
*3.2:2'-Dinaphthyl (In 95% ethanol)	213.0	40,000	223.0	20.000	254.0	95,500	286.0	14,500	308.0	19,000
*4.1:1'-Dinaphthyl (in 95% ethanol)	221.0	89,000	249.0	4.500					283.0 294.0	13,500 13,000

* nos. 3 and 4, Friedel, Orchin and Reggel, 1948, 70, 199. The figures are estimated from the published curves log ε against λ and the intensities are, therefore, subject to error.

(nos 3 and 4. See also Ultraviolet Spectral Data. American Petroleum Institute Research Project 44. Nos. 260 and 258.

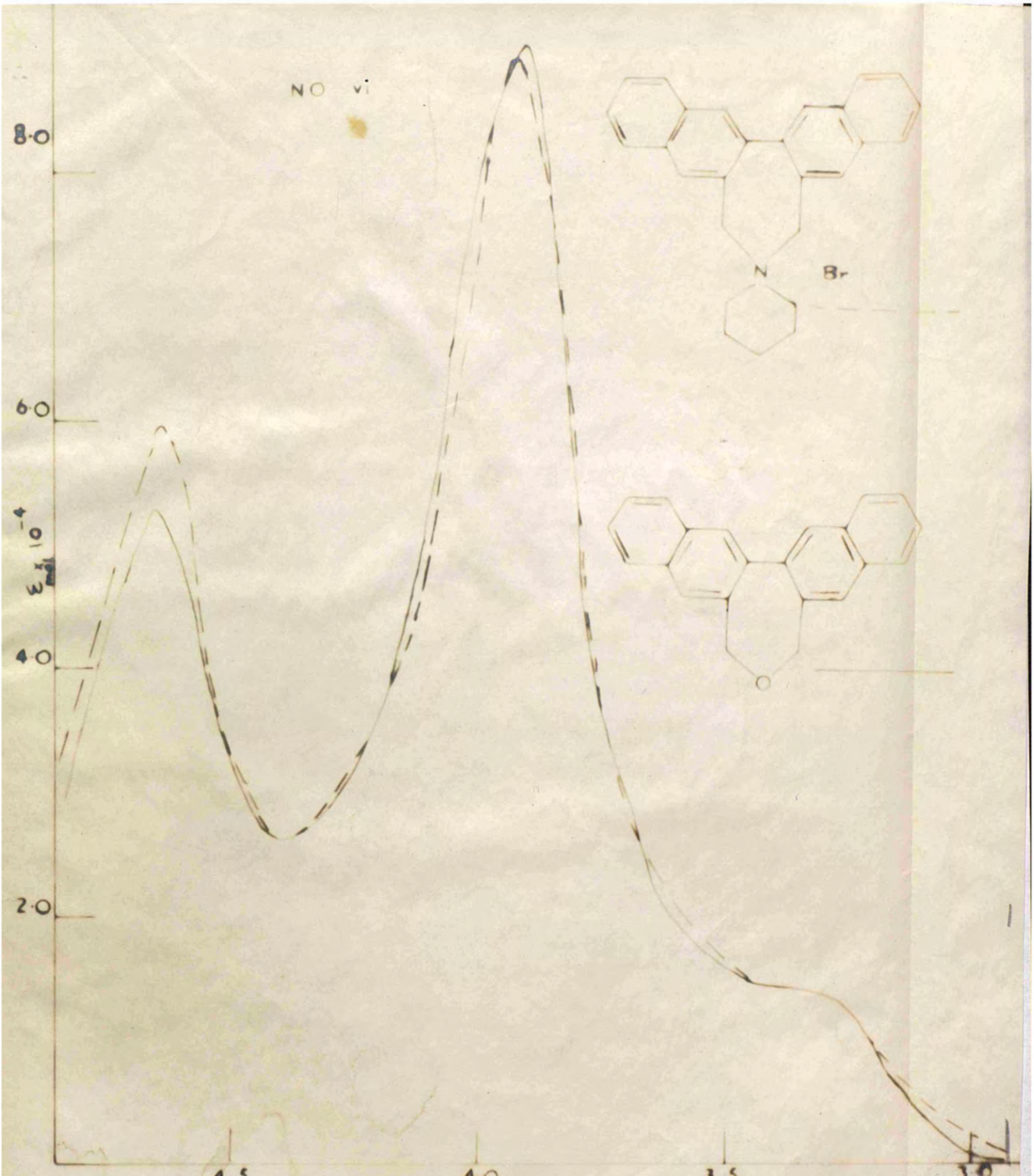

NO vi
8·0
6·0
4·0
2·0
ε mol x 10⁻⁴
4 5
4 0
3 5
3 0
ν̄ (cm⁻¹ x 10⁴)
N
Br
O

TABLE VI

	λ_{max}	ε_{max}	λ_{min}	ε_{min}	λ_{max}	ε_{max}	λ_{min}	ε_{min}	Fine structure (Long wave)	
2:7-Dihydrodinaphtho-(1':2'-3:4)(1":2"-5:6) azepinium-1-spiro-1"'-piperidinium bromide) (In 95% Ethanol).	218.2	117,400	225.8	75,400	229.3	80,600	260.5	5,960	266.5 275.5 304.3 313.8 324.0	6,240 6,840 12,600 11,400 7,960

derivative of 1:1'-dinaphthyl (Hall and Turner, unpublished) have also been given (table VI). This has more or less the same salient features as naphthalene (Friedel and Urchin, <u>loc.cit.</u>no.195) because of the steric hindrance to the rotation at the pivot bond between the naphthalene nuclei. In the case of compounds no.1 and 2 (table V), the spectra are more or less on the lines of diphenyl as is the case with their parent hydrocarbon 2:2'-dinaphthyl which absorbs in the region 205-390 $m\mu$ (American Petroleum Institute Research Project 44, no.260). Compounds no.1, 2 and 3 have strong conjugation bands which is absent in 1:1'-dinaphthyl (table V, no.4) and its azepinium salt (table VI). The intensities of maximal absorption in compounds 1, 2 and 3 are very high as was to be expected.

A notable difference from 1:1'-dinaphthyl and its azepinium salt is the absence of longwave fine structure which is just discernable as inflection at(298) and(300) $m\mu$ in compound no.1 and 2 respectively.

The spectra of the above compounds provides some basically important data for a comparative study of substituted dinaphthyls for the investigation of their configuration.