CYCLIC CONJUGATED POLYENES

by

R. G. SHUTTLEWORTH

SUMMARY

Cyclic conjugated polyenes are discussed in relation to the benzene problem. It is suggested that much of the necessary information regarding $\Delta^{1,3,5,7}$-cyclooctatetraene may be more easily accessible through a study of the benz-substituted $\Delta^{1,3,5,7}$-cyclooctatetraenes, and attempts to synthesise such substances directly are described. The first of these visualised a cyclodehydration between a ketonic group and a methylene group conjugated with it, but the application of the method to simpler derivatives showed that there was little hope of success by such a route. (The investigation has, however, yielded a method whereby certain fluorene derivatives and certain polycyclic aromatic types can be prepared.) Three other attempts had as their goal the direct synthesis of 1,2:3,4-dibenz-$\Delta^{1,3,5,7}$-cyclooctatetraene. They included a study of the condensation of diphenyl-2:2'-dialdehyde with succinic acid, and with diethyl succinate, and of the action of copper on o:o'-di-iodo-1:4-diphenyl-$\Delta^{1,3}$-butadiene. 1,2:3,4-dibenz-$\Delta^{1,3,5,7}$-cyclooctatetraene did not result from these reactions.

Two attempts to obtain an intermediate for the synthesis of 1,2:3,4-dibenz-$\Delta^{1,3}$-cyclooctadiene-6:8-dione failed.

The Ullmann reaction between ethyl-ortho-iodophenylacetate and ethyl diphenyl -2-iodo-2'-carboxylate did not yield the required intermediate for the preparation of 1,2:3,4:5,6-tribenz-$\Delta^{1,3,5,7}$-cyclooctatetraene.

A number of attempts have been made to obtain diphenylene and tetraphenylene (1,2:3,4:5,6:7,8-tetrabenz-$\Delta^{1,3,5,6}$-cyclooctatetraene) In one experiment a small yield of a substance believed to be diphenylene was obtained. In particular, the action of sodium on 2:2'dibromodiphenyl has been re-investigated. The available evidence would seem to indicate the formation of free radicals in the Fittig reaction.

It has been established that the Ullmann reaction takes place by a mechanism involving the transitory existence of free radicals in solution.

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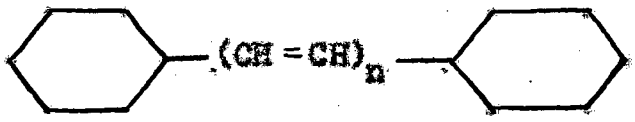
I N D E X

INTRODUCTION

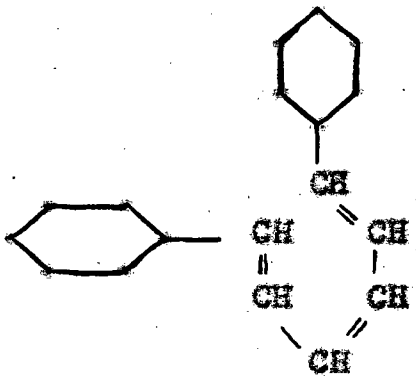
The problem of the structure and aromatic character of benzene has been considerably advanced towards the goal of its final solution during the last fifteen years. This has been made possible by simultaneous progress in both the theoretical and practical sides of organic chemistry. On the one hand, many new physical methods of structure determination have been evolved, while on the other, the elaboration of the theory of quantum mechanical resonance, besides giving great impetus to the practical investigations, has made predictions which so far have shown excellent agreement with the practical results. The modern conception of a benzene molecule is that of a regular coplanar hexagon (of side very nearly 1.39A), each carbon to carbon bond possessing half double-bond character. The molecule is stabilised and rendered less reactive by its considerable resonance energy, the amount of which has been both predicted and measured.

The extent to which conjugation alone can contribute to aromatic character is to be deduced from the properties of the diphenyl-substituted straight-chain conjugated polyenes of general formula (I), which have been prepared and investigated by Kuhn and Winterstein (Helv.Chim.Acta., 1928, 11, 87-151). These compounds show properties which are very reminiscent of those of benzene. They are surprisingly unreactive and

stable to alkaline permanganate, particularly 1:6-diphenyl-$\Delta^{1,3,5}$-hexatriene (II), while on reduction with aluminium amalgam, hydrogen is added to the ends of the conjugated



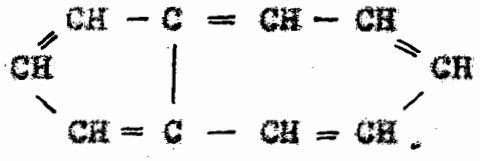
I.



II.

chain and the same abrupt change in reactivity is observable as when benzene is reduced to dihydrobenzene. 1:4-Diphenylbutadiene will not add hydrogen bromide under any conditions which have so far been devised (Blitz, Ann., 1897, 296, 231; Bauer, Ber., 1904, 37, 3321). This is another instance of the remarkable resemblance which these straight-chain compounds show to the cyclic conjugated structure, benzene.

An excellent example of the fact that all cyclic conjugated structures are not necessarily aromatic, however, is to be found in the properties of the azulenes (for a review and references see Haworth, Ann.Rep., 1937, 34, 393-397). The azulenes - e.g., azulene itself (III) (structure proved by Plattner and Pfau, Helv.Chim.Acta., 1937, 20, 224), and vetivazulene (IV) - are conjugated dicyclic structures consisting of fused five- and seven-membered rings, and they do not show any aromatic character. They are, for instance, easily oxidised by permanganate. Some of their properties, however, (e.g., their production from the corresponding hydroderivatives by dehydrogenation processes, formation of double-compounds with picric acid, etc.) are nevertheless reminiscent of those of aromatic hydrocarbons like naphthalene.



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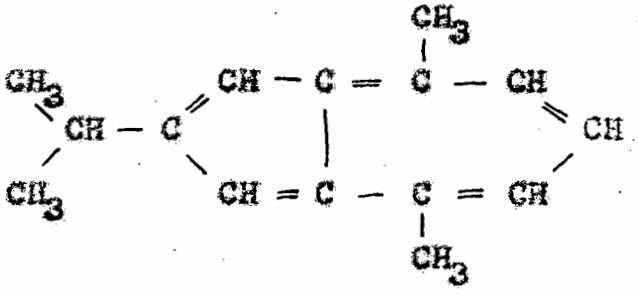
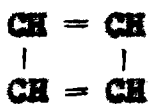
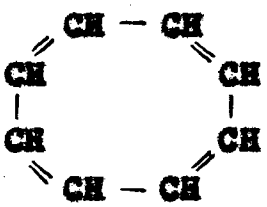
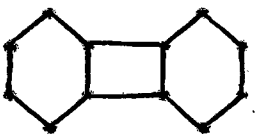


IV.

Ever since Thiele first called attention to the cyclic conjugated nature of benzene and its homologues, attention has naturally been directed towards the properties of other cyclic conjugated polyenes. Those which have been most discussed in reference to the benzene problem are those most nearly related to the latter substance, namely, $\Delta^{1,3}$-cyclobutadiene (V), and $\Delta^{1,3,5,7}$-cyclooctatetraene (VI).





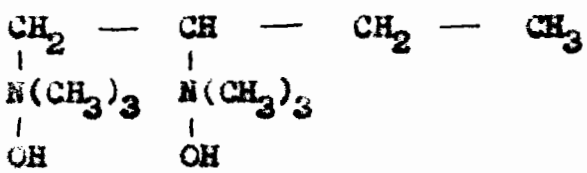


V. VI. VII.

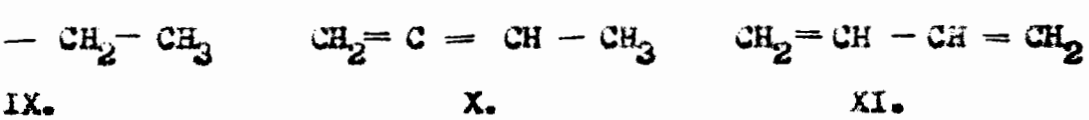
$\Delta^{1,3}$-cyclobutadiene (V) has never been prepared. It has been predicted that such a substance would not be symmetrical, would exhibit no resonance, and, in view of its energy content in relation to that of ethylene, would tend to dissociate (Lennard-Jones and Turkevich, Proc.Roy.Soc., 1937, 158A, 297). This supports the view long held that such a structure would be incapable of existence on the grounds of ring strain. The ring system appears to be more stable in diphenylene (VII). This substance was prepared in small quantities by Dobbie, Fox and Gauge (J., 1911, 99, 663; 1913, 103, 36), but it was not thoroughly investigated. Later attempts to prepare it have failed (see Mascarelli,

Gatti and Longo, Gazzetta., 1933, 63, 661). Its further examination by modern techniques would be of great interest, and for such purpose attempts to prepare it have been made in the present series of experiments.

Cyclooctatetraene was reported by Willstatter and his collaborators (Ber., 1911, 44, 3423; 1913, 46, 517) to possess properties typical of an unsaturated compound, and to show a tendency, particularly when slightly impure, to form a dicyclic structure by bridge-formation across the ring. The material was prepared by an exhaustive methylation procedure, and the structure of the intermediate dibromocyclooctadiene was not proved. Hurd and Drake (J.Amer.Chem.Soc., 1939, 61, 1943) doubt whether the cyclooctatetraene prepared in this way was the ^{1,3,5,7}-isomer (VI) since by pyrolysis of (VIII) they obtained only ethylacetylene (IX) and methylallene (X), and not the conjugated structure ^{1,3}-butadiene (XI). It might be



VIII.



IX. X. XI.

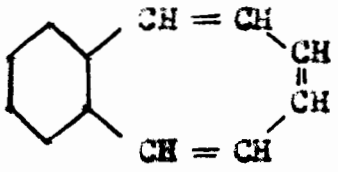
held that if the compound obtained by Willstatter was not the

$\Delta^{1,3,5,7}$-isomer, this would be an indication of the lesser stability of $\Delta^{1,3,5,7}$-cyclooctatetraene (VI) as compared with the isomeric products suggested by Hurd and Drake's results. This, however, is not necessarily so, since $\Delta^{1,3}$-butadiene (XI) is very much more stable than its isomers (IX) and (X), and has been calculated to have a resonance energy of 8 kg. cals. (Pauling and Sherman, J.Chem.Phys., 1933, 1, 606; 679).

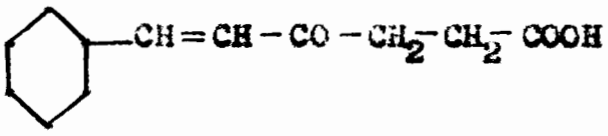
On the basis of the theory of quantum mechanics (Lennard-Jones and Turkevich, loc.cit.; Huckel, Z.Physik, 1931, 70, 204; Penney, Proc.Roy.Soc., 1934, 146A, 223), $\Delta^{1,3,5,7}$-cyclo-octatetraene (VI) will be next in stability to benzene, but since eight unsaturation electrons will be present in the molecule (six represents the most stable grouping possible) its resonance energy will be smaller than that of benzene, namely, 18.8 kg.cals. as against 30.2, calculated on the same basis. (Pauling and Sherman, loc.cit., calculating by another method, give 37.3 kg.cals. for benzene, and 25.1 for a straight-chain $\Delta^{1,3,5,7}$-tetraene. The most accurate observed value for benzene is 36.0 kg.cals. - Kistiakowsky, Ruhoff, Smith and Vaughan, J.Amer.Chem. Soc., 1936, 58, 146). The molecule will in all probability be not quite planar, alternate carbon atoms projecting slightly above and below the plane of the ring. The lengths of alternate carbon-carbon links have been calculated at 1.43A and 1.35A (cf. single-bond

1.54A, double-bond 1.33A), and as the energy barrier between the two equilibrium forms is only 8 kg.cals., the change from one to the other will take place rapidly at room temperature. The experimental confirmation of these results awaits the preparation of an authentic specimen of $\Delta^{1,3,5,7}$-cyclooctatetraene. There have lately been a number of indications (see Vincent, Thompson and Smith, J.Org.Chem., 1939, 3, 603; Kohler, Tishler, Potter and Thompson, J.Amer.Chem.Soc., 1939, 61, 1057; Steadman, ibid., 1940, 62, 1606) that experiments are in progress which have as one of their aims the synthesis of this substance. Since the announcement of the preparation of cyclooctatetraene by Willstatter, attempts have been made to account for the properties shown by this substance. The above predictions, and particularly the doubt which now exists as to the authenticity of Willstatter's material, make it unprofitable to discuss them.

It seemed possible at the outset of the investigations herein recorded, that the benz-substituted cyclooctatetraenes (e.g., XII), might present a simpler synthetic problem than that of cyclooctatetraene itself, and that these substances might well prove to be sufficiently stable for their chemical and physical examination to be possible without undue risk of complications arising owing to intra-molecular re-arrangements.



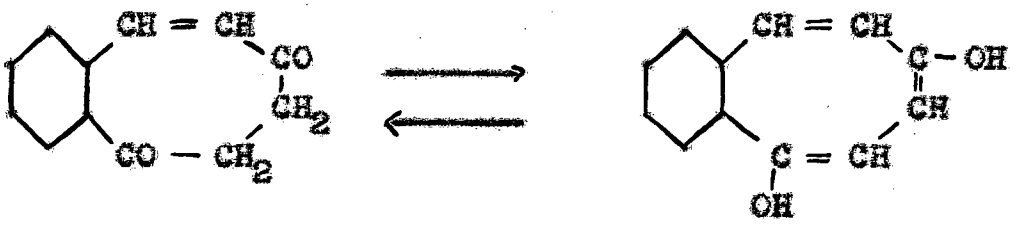
XII.



XIII.

The subjection of such substances to analysis by X-ray crystallographic, electron diffraction, or long-wave spectroscopic methods might yield much very valuable data concerning the $\Delta^{1,3,5,7}$-cyclooctatetraene ring-system, while direct measurement of heats of hydrogenation might allow an estimate of the resonance energy of these substances to be made. In this way, at least indirect evidence would be forthcoming regarding the aromatic character or otherwise of $\Delta^{1,3,5,7}$-cyclooctatetraene. A synthetic method which might well be made to yield 1,2-benz-$\Delta^{1,3,5,7}$-cyclooctatetraene (XII) is that of Sen and Roy (J.Ind.Chem.Soc., 1930, 7, 401). (This reference is extremely difficult to trace in connection with cyclooctatetraene or its derivatives, and was only encountered when the research embodied in this thesis was almost complete. It seems to have been likewise missed by other workers in the field. Its possibilities are now being investigated in this laboratory). These workers describe the cyclisation by acetic anhydride of δ-benzal-laevulinic acid (XII) to yield an enolic substance, the structure of which was not proved. It was formulated as (XIV) or (XV), and in view of the fact that the

material yielded a dibenzoyl derivative, there would seem to be little doubt that such a formulation is substantially

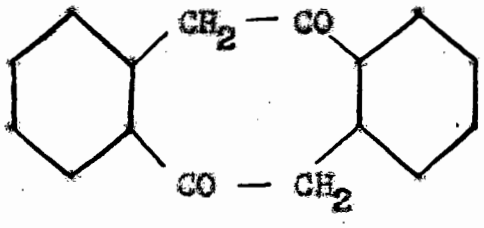


XIV. XV.

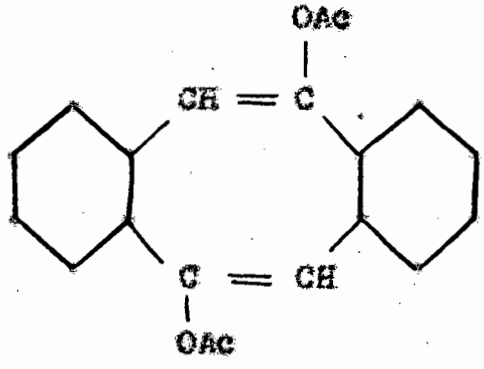
correct. If 1:2-benz-$\Delta^{1,3}$-cyclooctadiene-5,8-one (XIV) exists in the enolic form (XV), this could be accepted as evidence of a contribution by resonance to the stability of the 1,2-benz-$\Delta^{1,3,5,7}$-cyclooctatetraene structure (XII). Methylation of the hydroxy-groups of (XV) might make the examination by physical methods of such a structure possible, while by a route involving the application of elimination reactions (XII) itself may be accessible from (XIV, XV).

While the research herein to be described was in progress two publications appeared in which attempts have been made to prepare benz-substituted cyclooctatetraenes for the same reason (namely their probable greater stability) as prompted their investigation in the present series of experiments. Vawzonek (J.Amer.Chem.Soc., 1939, 61, 1943) by an ingenious route,

obtained the diketone (XVI). This substance behaved like an open-chain 1,5-diketone, and did not exist in an enolic form. That there was, however, some tendency on its part to yield the corresponding di-benz-cyclo-octatetraene ring system is clear from the fact that



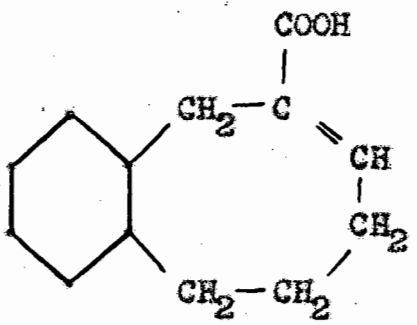
XVI.



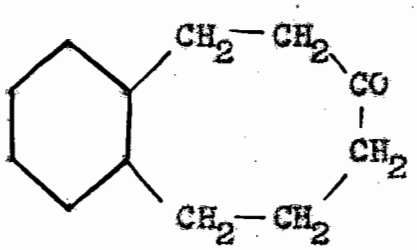
XVII.

it was possible to prepare the diacetate (XVII). The work so far completed by Fry and Fieser (J.Amer.Chem.Soc., 1940 62, 3469) includes the preparation of 1,2-benz-$\Delta^{1,4}$-cyclo-

octadiene-4-carboxylic acid (XVIII) and of 1,2-benz-Δ^1-



XVIII.

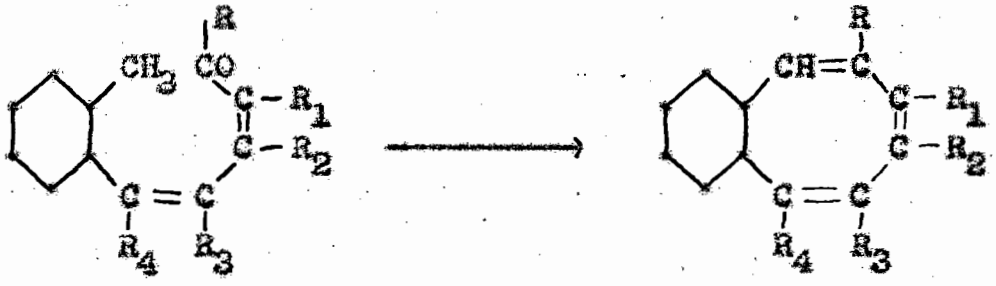


XIX.

cyclo8cta-5-one (XIX). Work along this route is still in progress, the objective being 1,2-benz-$\Delta^{1,3,5,7}$-cyclo8ctatetraene (XII).

ATTEMPTS TO EVOLVE METHODS OF BENZCYCLOOCTATETRAENE SYNTHESIS INVOLVING THE CYCLODEHYDRATION OF UNSATURATED KETONES

The investigations here recorded had as their ultimate object the elaboration of a synthesis of benzocyclooctatetraenes by a dehydration mechanism as follows:-

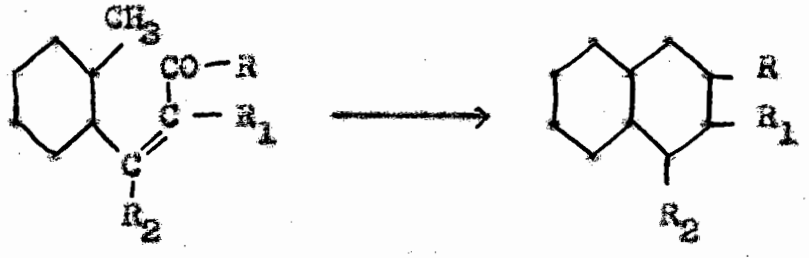


I.

A typical example of such syntheses would be the production of 1-phenyl-3:4-benz-$\Delta^{1,3,5,7}$-cyclooctatetraene by the cyclodehydration of a substance of structure (II):-

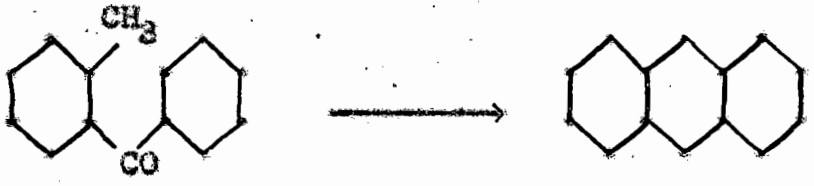
II.

So little is known concerning dehydrations of this type, however, that it was deemed desirable to begin the investigation with a study of simpler cases, where steric effects would not be so marked. Attention was first directed, therefore, to the dehydration of substances of the general type (III),



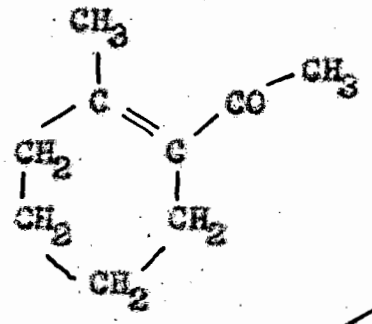
III. IV.

this course being decided on not only because of the valuable experience which it would give, but also because the elaboration of methods for effecting dehydrations of this type might provide a useful variation of the well-known Elbs synthesis for the production of polynuclear aromatic compounds. This synthesis, it will be remembered, is exemplified by the conversion of 2-methyl-benzophenone to anthracene by pyrolysis:-



Cyclodehydrations between carbonyl and reactive methylene groups have frequently been recorded. For example, Kipping and Perkin (J., 1889, 55, 335; 1890, 57, 16) by the action of concentrated sulphuric acid on α :ω -diacetylpentane, obtained 1-methyl-2-acetyl-Δ'-cyclohexene (V), while Bogert and Fourman (J.Amer.Chem. Soc., 1933, 55, 4670) prepared ionene (VII) by heating

the α- and β-ionones (VI) with iodine. Many other such examples are available.



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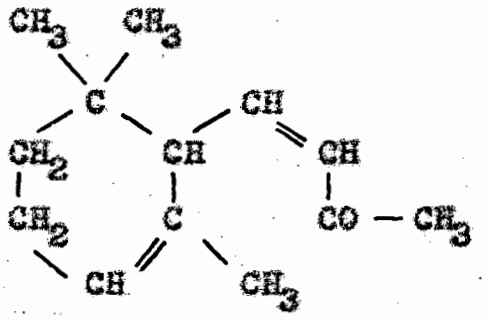

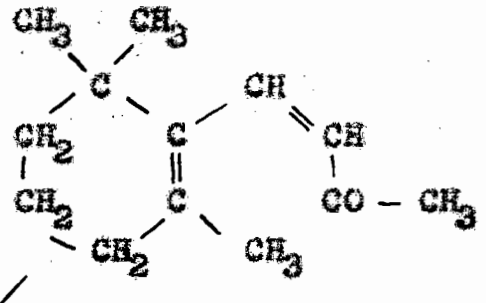

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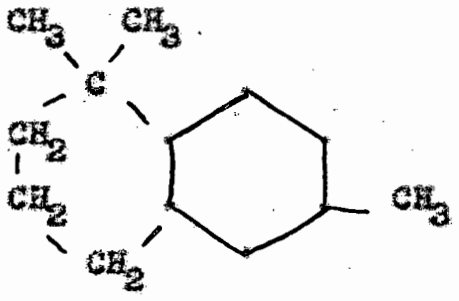
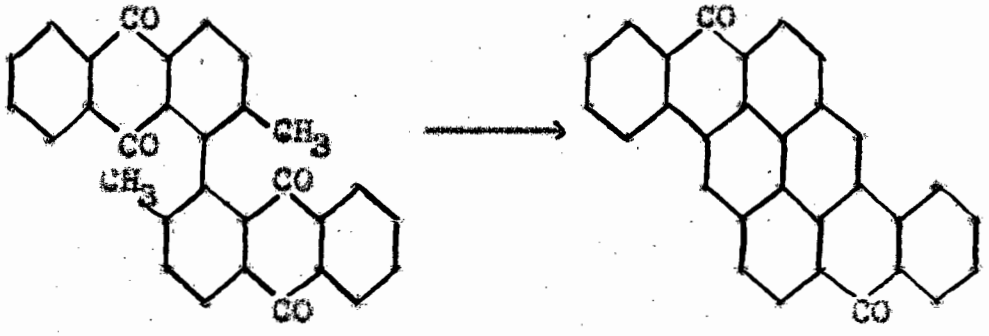


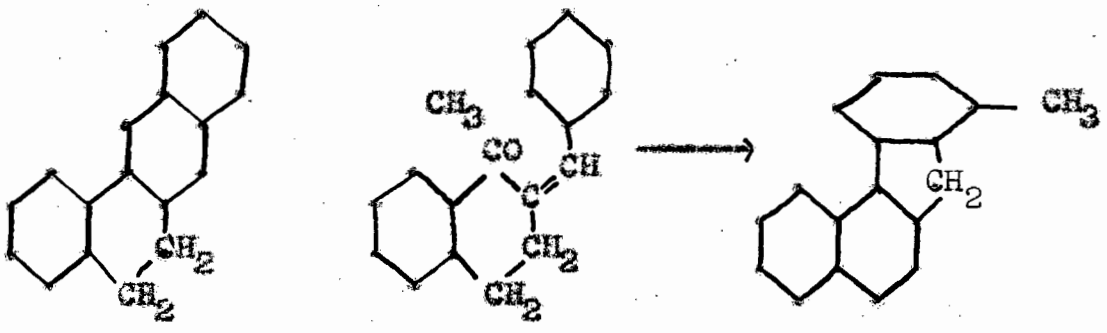
VII.

A careful examination of the literature has revealed but one example, however, in which the methylene group participating in such a dehydration, was part of a methyl group directly attached to a benzene ring, and depended for its reactivity

on the carbonyl group conjugated with it through the ortho-position. This is the case of the formation of pyranthrone from 2:2'-dimethyl-1:1'-dianthraquinonyl (VII) by the action of zinc chloride (Scholl, Ber., 1910, 43, 346):-

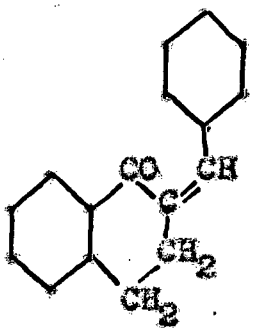


The first step in the investigation consisted then of an attempt to obtain dihydrobenzanthracene (VIII or isomer) from 2-ortho-tolylidene-α-tetralone (IX), and, of the various dehydrating agents employed in attempts to bring about this, and later, cyclisations, only sodamide and phosphoric oxide were found to be successful. Dehydration in this way of 2-ortho-tolylidene-α-tetralone gave a

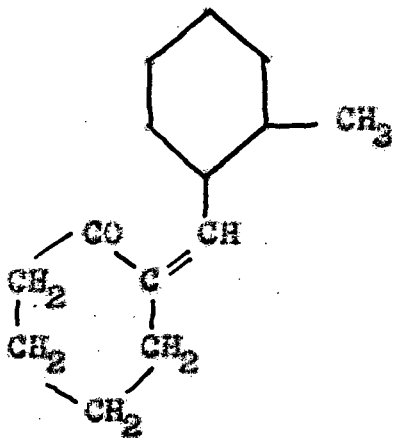


VIII. IX. X.

hydrocarbon $C_{18}H_{14}$, isomeric with dihydrobenzanthracene, but which could not be dehydrogenated. On oxidation it gave a ketone, $C_{18}H_{12}O$, presumably 8-methyl-3:4-benzfluorenone, indicating that hydrogen in the nucleus had been attacked in preference to that in the methyl group, with the production of 8-methyl-3:4-benzfluorene (X). This interpretation of the cyclisation was confirmed by subjecting 2-benzylidene-α-tetralone (XI) to the same conditions, when benzfluorene was obtained (Cook, et.al., J., 1935, 1323). Attempts to cyclise the simpler 2-ortho-tolylidene-cyclohexanone (XII) met with failure, an experience



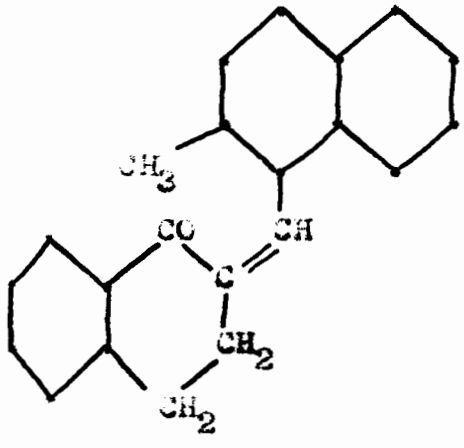
XI.



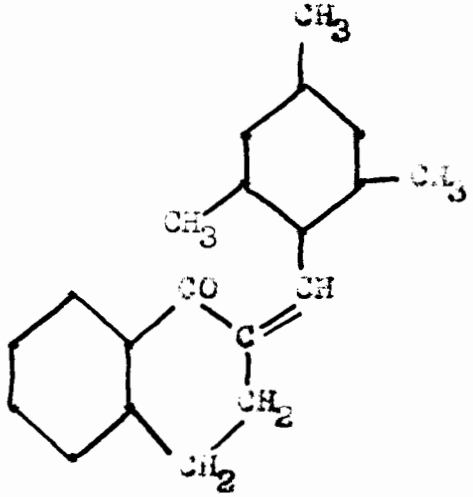
XII.

paralleled by that of Cook and co-workers (loc.cit.), who obtained fluorene derivatives by the action of sulphuric acid on 2-naphthylmethyl- and 3-phenanthrylmethyl-cyclohexenones, but were unable to cyclise simpler benzyl derivatives.

The fact that nuclear hydrogens in the ortho-position were preferentially attacked in the dehydrations studied, led to an investigation of the action of dehydrating agents on substances in which the free ortho-position was blocked, as would be the case in 2-(ortho-methylnaphthylidene)-α-tetralone(XIII). For the purpose of preparing such substances, an attempt was made to obtain 2-methyl-1-naphthaldehyde by the procedure described by Hinkel, Ayling and Beynon (J., 1936, 339), for the preparation of a number of aldehydes including that of 2:6-dimethyl-1-naphthaldehyde from 2:6-dimethylnapthalene. The product of the reaction, however, had the behaviour of a mixture, and the material could not be separated into its components by the usual methods. Recourse was, therefore, had to the use of 2:4:6-trimethyl benzaldehyde (mesitylaldehyde) (Hinkel, Ayling and Beynon, loc.cit) and the action of dehydrating agents on its condensation



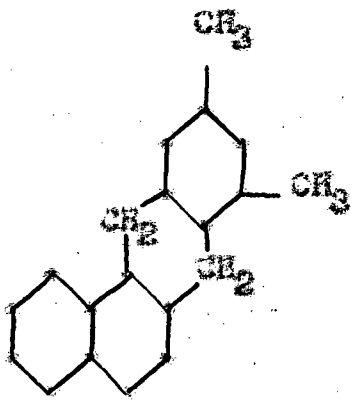
XIII.



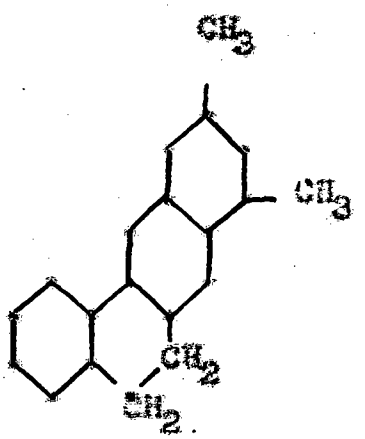
XIV.

products with ∝-tetralone and ∝-hydrindone studied.

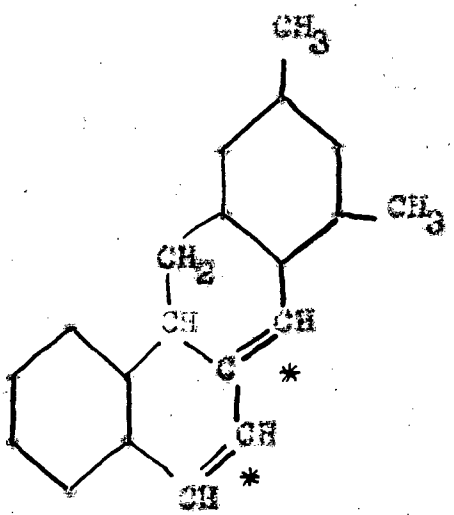
2-(2':4':6'-trimethylbenzylidene)-∝-tetralone (XIV) gave in this way a 34% yield of three isomeric hydrocarbons, formulated as 5:7-dimethyl-x:x'-dihydro-1:2-benzanthracenes. The action of selenium on one of these gave a hydrocarbon formulated as 5:7-dimethyl-1:2-benzanthracene. Five 5:7-dimethyl-x:x'-dihydro-1:2-benzanthracenes (XV, XVI, XVII, XVIII, XIX) might possibly result from the cyclo dehydration of 2-(2':4':6'-trimethylbenzylidene)-∝-tetralone (XIV). Of these, (XV) and (XVI) would be expected to form stable picrates, since they contain the naphthalene nucleus. Of the three hydrocarbons isolated, two did form stable picrates, and it is reasonable to assume, therefore, that they were (XV) and (XVI). That which formed an unstable picrate would be (XVII), (XVIII) or (XIX), since such structures would not be expected to give stable picrates. Of these, (XIX) on account of its "quinonoid" structure would almost certainly be coloured, and may probably be ruled out. Moreover, it, as well as (XVIII), would probably tend to revert to (XVII), in which both the asterisked double-bonds form a conjugated system between the terminal rings. Thus it is possible that the hydrocarbon which formed an unstable picrate was (XVII) rather than (XVIII) or (XIX).



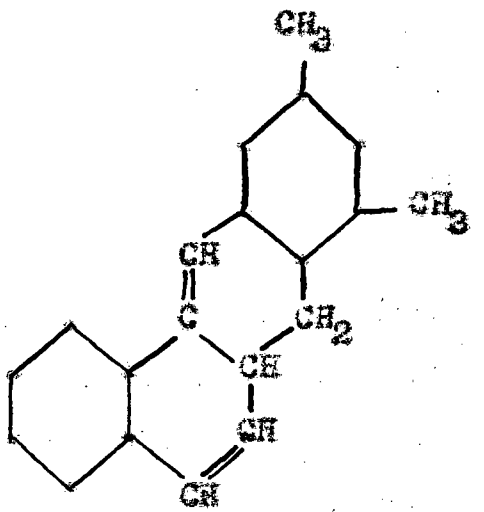
XV.



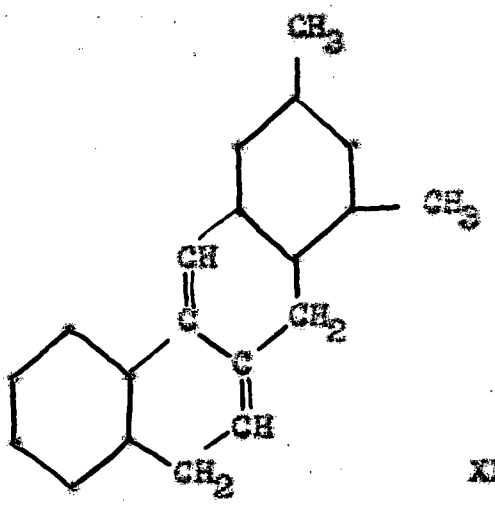
XVI.



XVII

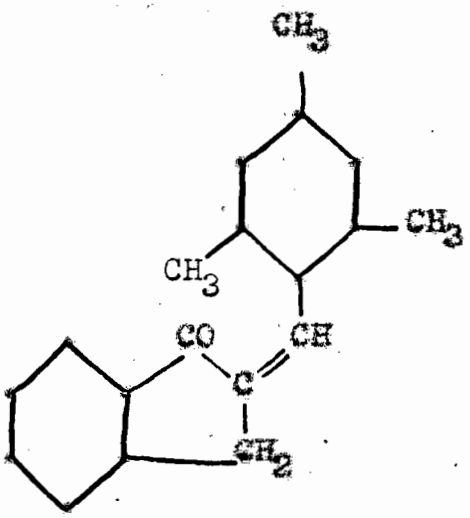


XVIII

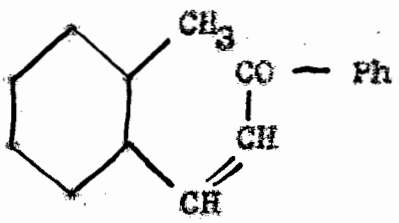


XIX.

It is clear from the foregoing that dehydration in the sense of (III) (IV) is possible only where an alternative mode of dehydration, resulting in the formation of fluorene derivatives, is rendered impossible by the introduction of blocking substituents into the aromatic ring. A further point with regard to these dehydrations is to be deduced from the failure of 2-(2'4'6'-trimethylbenzylidene)-α-hydrindone (XX) and ortho-tolylideneacetophenone (XXI)



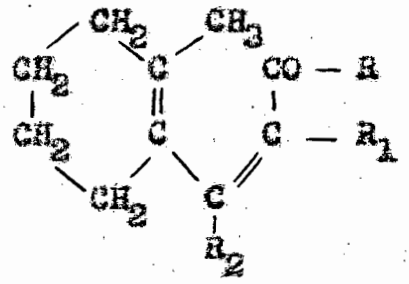
XX.



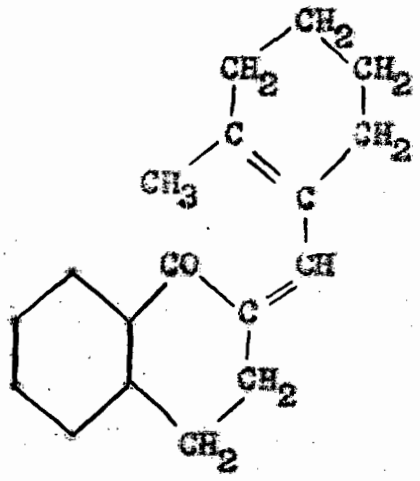
XXI.

to undergo dehydration, for both these substances are capable of enolisation only through the migration of a hydrogen atom from the methyl group attached to the aromatic ring system.

Assuming that dehydration does occur via an enolic phase, it seemed likely that dehydration in the sense desired would be facilitated by the use of compounds of

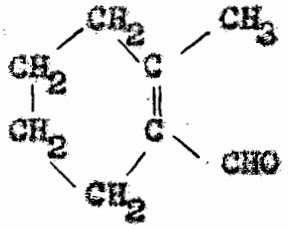


XXII.

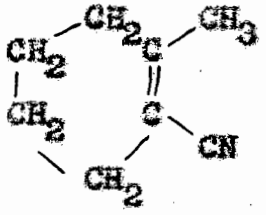


XXIII.

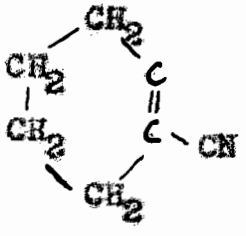
the type (XXII) in which the methyl groups would be expected to show enhanced reactivity; and at this stage, therefore, efforts were concentrated on the development of a convenient synthesis of the 6-methyl-Δ^{6}-cyclohexene-aldehyde (XXIV) which would be necessary for the production of substances of the desired type, e.g.,(XXIII).



XXIV.



XXV.



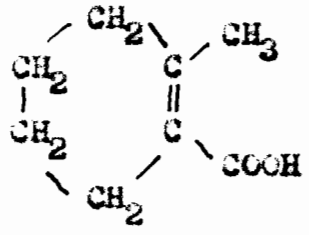
XXVI.

Since the tetra-hydro-ortho-toluonitrile of Linstead and Millidge (J., 1936, 482, 486) appeared from the small yield of its condensation product with ethyl malonate to be predominantly (XXV), attempts were made to reduce the material by the method of Stephen (J., 1925, 127, 1874). Only small yields of aldehyde were obtained, however, and besides unreacted nitrile, small quantities of a higher-boiling halogen-containing aldehydic material accompanied the product. This latter material was not investigated further. It seemed possible that it had been formed by the addition of hydrogen chloride across the double-bond.

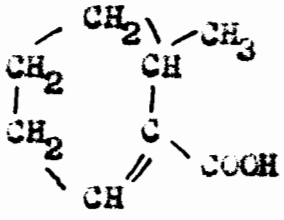
That the failure of the nitrile to reduce was not entirely due to the steric effect of the methyl group as in ortho-toluonitrile (Stephen*, loc.cit.), but is a property probably common to all cyclic α-β-unsaturated nitriles, was clear from the fact that Δ'-cyclohexene-nitrile (≡XXVI) was similarly unreactive in the Stephen's reduction. It also gave small quantities of a higher-boiling aldehydic material which contained halogen.

Numerous attempts to increase the yields of the required aldehydes by variations in the conditions operative during the reduction met with failure, and recourse was therefore had to the reduction method of Sonn and Muller (Ber., 1919, 52, 1927).

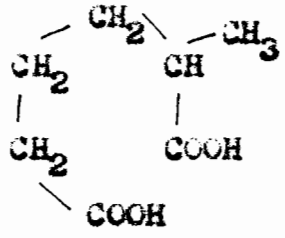
The first step in the application of this method was the hydrolysis of the tetra-hydro-ortho-toluonitrile to the corresponding carboxylic acid. The nitrile was very resistant to hydrolysis by alcoholic potassium hydroxide, and when strong sulphuric acid was used, much carbonisation with evolution of sulphur dioxide took place. It could, however, be hydrolysed smoothly by means of 95% phosphoric acid (cf. Berger and Olivier, Rec.Trav.Chim., 1927, 46, 600). All three methods gave the same homogeneous acid, which was identical neither with the 2-methyl-Δ^1-cyclohexenecarboxylic acid (XXVII) described by Kay and Perkin (J., 1905, 87, 1074), nor with the 6-methyl-Δ^1-cyclohexenecarboxylic acid as described by Mazza and Cremona (Gazzetta., 1927, 57, 318). That it was the latter acid (XXVIII), however, was clear from the fact that its degradation with ozone followed by dilute permanganate yielded 2-methyladipic acid (XXIX). (It was found impossible to obtain homogeneous degradation products by direct oxidation of the acid with permanganate, although Mazza and Cremona (loc.cit.) obtained 2-methyladipic acid in this way from the material prepared by them. Price (J.Amer.Chem.Soc., 1939, 61, 1847) has reported failure to obtain 2-methyladipic acid by the permanganate oxidation of 1-methyl-Δ^1-cyclohexene).



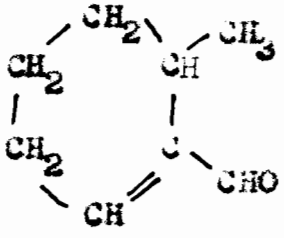
XXVII.



XXVIII.



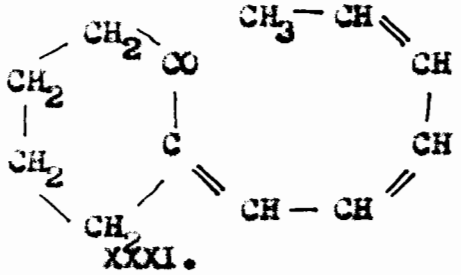
XXIX.



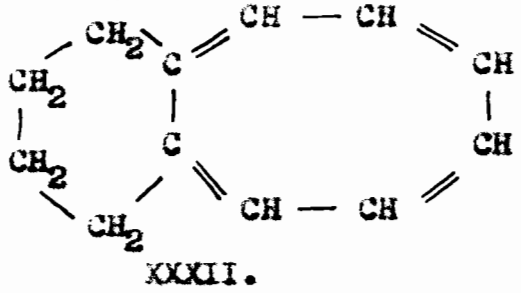
XXX.

Both reduction procedures gave the same aldehyde, namely, 6-methyl-Δ^{1}-cyclohexenealdehyde (XXX). Since alternative methods for the production of the Δ^{6}-isomer (XXIX) were all very long, it was not deemed possible to pursue this aspect of the investigation any further, and efforts were concentrated on another mode of approach.

It seemed possible that by interchanging the relative dispositions of the carbonyl and methyl groups as compared with (III), the cyclooctatetraene ring system might be produced by a reaction such as (XXXI) ⟶ (XXXII). As before

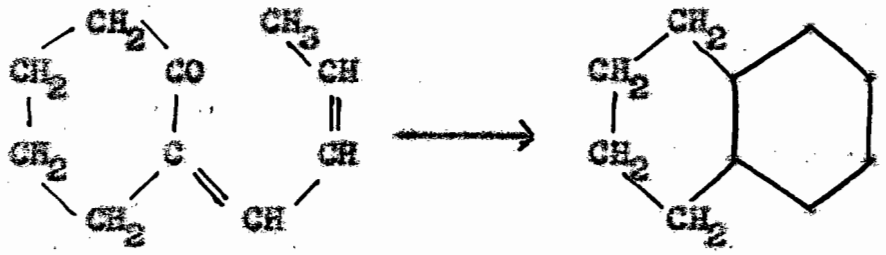


XXXI.



XXXII.

it was deemed advisable to confine first experiments to relatively simpler, but similar, dehydrations of the type (XXXIII) ⟶ (XXXIV). Such experiments would again have a

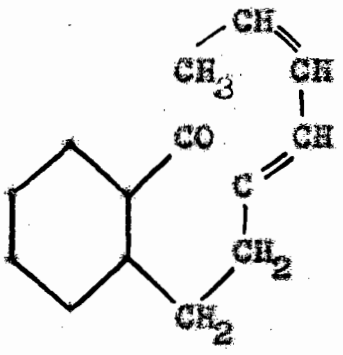


XXXIII. XXXIV.

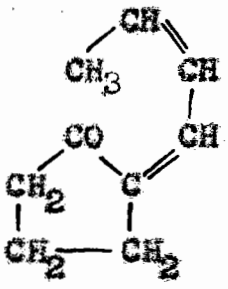
dual significance, since, if successful, they would not only form a model for the projected cyclooctatetraene studies, but would also provide a rapid and convenient synthetic method for the production of polynuclear aromatic types.

The condensation of crotonaldehyde with various ketones suggested itself as a very convenient method of obtaining structures of the general type of (XXXIII), but experiments along these lines have been somewhat disappointing. The structures aimed at for these preliminary experiments were the crotonylidene derivatives of α-tetralone, cyclohexanone, cyclopentanone and acetone (XXXV, XXXIII, XXXVI, XXXVII, respectively).

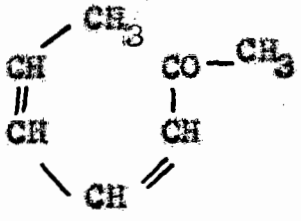
No condensation of crotonaldehyde with α-tetralone



XXXV.



XXXVI.



XXXVII.

could be achieved under conditions which were successful with the other ketones, and this method of preparing (XXXV) had to be abandoned. When cyclopentanone and crotonaldehyde were subjected to conditions successful for cyclohexanone, a resinous material, very similar in its physical characteristics to the product of the reaction between ethylene dichloride and sodiumpolysulphide, was produced. Its analytical figures showed it to be a polymerisation product of crotonaldehyde, although it was only formed in the presence of cyclopentanone. Milder conditions aided the condensation of the cyclopentanone with the crotonaldehyde, and prevented the formation of

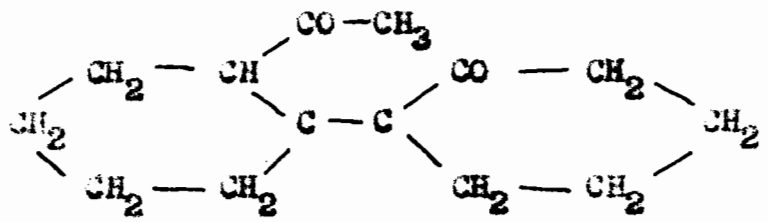
this resin.

Cyclohexanone, cyclopentanone and acetone, when condensed with crotonaldehyde, gave complex mixtures of products from which the crotonylidene derivatives could not be separated by distillation except in the case of the acetone condensation, the lower-boiling fractions from which were mainly crotonylidene acetone (XXXVII) (Meerwein Ann., 1909, 258, 85). An attempt to obtain toluene from this substance by the action of phosphoric oxide failed. Since the crotonylidene-cyclohexanone (XXXIII) and crotonylidene-cyclopentanone (XXXVI) could not be obtained in a pure state, they were not subjected to the action of dehydrating agents. That they were present in the mixtures of condensation products obtained was shown by the fact that their semicarbazones could be obtained from the lower-boiling fractions of these mixtures. Moreover, in an attempt to isolate and identify the other products of these condensations, the materials were subjected to hydrogenation, when 2-n-butylcyclohexanol, 2-n-butylcyclopentanone, and methyl-n-amyl-ketone were respectively isolated as one product in each of the three cases.

Repeated attempts to identify the other hydrogenation products failed. Their analytical figures in each case were inconclusive, and it has been impossible to come to

any definite conclusion as to their nature. It seems likely that the ketones react with the crotonaldehyde not only at the carbonyl group, but also at the double bond (cf. Stobbe, J.pr.Chem., 1912, 86, 209).

Further work in the same field consisted of an attempt to obtain 2'-acetyl-cyclohexylidene-cyclohexanone (XXXVIII)



XXXVIII.

by condensing cyclohexylidene-cyclohexanone with acetyl chloride in the presence of stannic chloride. Self-condensation of the cyclohexylidene-cyclohexanone took place, however, under these conditions. Further investigation showed that this did not occur in the absence of either the stannic chloride or the acetyl chloride, and that it was not a general reaction, since an analogous product was not obtained from cyclopentylidene-cyclopentanone under the same conditions.

The above investigation into methods of effecting cyclodehydrations of certain types of ketonic derivatives

has shown that cyclisation cannot be achieved in all cases, and that when it does occur more than one mode of dehydration may be possible. It would seem reasonable to suppose that where eight-membered ring-formation was projected (see II) such difficulties might be increased, by the operation of steric effects, and by the greater separation of the ketonic groups from the methyl groups - the latter having been found comparatively unreactive in compounds with shorter chains (type III). Moreover, cyclodehydrations when successful were found to require rather harsh conditions, and in view of the probable instability of the cyclooctatetraene ring-system, there would seem to be some risk of re-arrangement reactions occurring during the cyclodehydration of substances of types (II) and (XXXI), despite the possible greater stability of the benz-substituted cyclooctatetraenes as compared with cyclooctatetraene itself. For these reasons it was felt that some other mode of approach to the benz-cyclooctatetraene series should be sought, and the above investigation was therefore abandoned.

STABLE AND LABILE FORMS OF THE SEMICARBAZONE OF METHYL-n-AMYL KETONE

In an attempt to identify the methyl-n-amyl-ketone formed above as a result of the hydrogenation of crotonylidene acetone, the material was converted to the semicarbazone by treatment with an aqueous-alcoholic solution

of semicarbazide-hydrochloride and sodium acetate. The semicarbazone thus isolated had a melting-point of 96-97°, which remained constant on its recrystallisation from aqueous alcohol. After standing overnight the melting-point of this material changed to 121-123°, a value agreeing closely with that recorded in various places in the literature for the semicarbazone of methyl-n-amyl ketone. In further experiments it was established that the change occurred without loss of weight and that the final product was definitely a monomeric form of the expected semicarbazone. (Found: C, 56.0; H, 10.0; N, 24.2; M (ebullioscopic in ethyl alcohol), 155. $C_8H_{17}ON_3$ required: C, 56.1, H, 9.9; N, 24.6%; M, 171). The change took place with equal ease if the labile material were left in solution in ethyl alcohol in the cold, or if it were kept in the dark.

Successive preparations of the labile semicarbazone were more and more unstable, until this semicarbazone became unobtainable in the pure condition, crude materials melting between 103° and 110° being obtained, which altered rapidly to the pure stable form on recrystallisation. Many variations in the conditions of preparation were tried without effecting any change in the nature of the product, and after a period of two months it was found impossible -

using the same materials and conditions - to produce anything but the higher-melting modification.

This has prevented further study of the lower-melting material, a matter of importance in establishing whether or not the two forms are stereoisomers, and whether the higher-melting modification is not perhaps an equilibrium mixture of the lower-melting material and another stereoisomer.

The action of ultra-violet light has been known to convert stereoisomeric pairs of hydrazones into an equilibrium mixture (cf. Wilson and Macaulay, J., 1924, 125, 841). When the semicarbazone of melting-point 121-123°, or its solution in ethyl alcohol, was subjected to the action of ultra-violet light, no change in melting-point could be detected. On the other hand, it has been recorded in a large number of cases that by recrystallisation from acid- and alkali-containing solvents, the two stereoisomers may usually be obtained, but when the semicarbazone of melting-point 121-123° was recrystallised from aqueous alcohol containing traces of either sulphur dioxide or ammonia, no change in melting-point was observed. Recrystallisation from indifferent solvents such as benzene, chloroform, petroleum, etc., was equally ineffective.

Attempts were then made to isolate labile and stable forms of the semicarbazones of methyl-n-butyl and methyl-n-hexyl ketones without success. In the case of methyl-n-

butyl ketone the semicarbazone had melting-point 123.6° to 124.5°, whereas Michael (J.Amer.Chem.Soc., 1919, 41, 416) has recorded it as 118°.

E X P E R I M E N T A L

∝-Tetralone (cf. Hartmann and Seiberth, Helv.Chem.Acta., 1932, 15, 1390)

A slow current of air was passed for three days through tetralin heated to 60 to 80°, a little metallic tin being added as catalyst. The peroxide formed was decomposed by shaking with an excess of a concentrated solution of ferrous sulphate. After separation of the aqueous layer, the mixture was washed and dried and distilled through an efficient column. Yield of ∝-Tetralone about 12%, b.pt. $132^{\circ}/15mm.$, semicarbazone m.pt. 217°. In some experiments the yield of ∝-Tetralone was much lower, but a definite improvement appeared to result from the addition of a trace of benzoyl peroxide to the reaction mixture.

2-Benzylidene-∝-Tetralone

Benzaldehyde (21.2gms., 1 mol.) and ∝-Tetralone (29.2gms., 1 mol.) were treated with alcoholic potassium hydroxide solution (4%, 200ccs.). The solution became warm and crystals were deposited almost immediately. After standing for three hours the solution was neutralised with acetic acid, the crystals filtered off and the filtrate extracted with ether. Distillation gave 2-benzylidene-∝-tetralone b.pt. $210\text{-}212^{\circ}/2mm.$ which formed

light yellow rhombohedra from alcohol, m.pt. 105°. Yield 40gms., 85%. (Found: C, 87.0; H, 6.0. $C_{17}H_{14}O$ requires: C, 87.2; H, 6.0%). It did not give a semicarbazone.

3:4 Benzfluorene

2-Benzylidene-∝-tetralone (25gms), dissolved in xylene, was refluxed for 15 hours with successive portions of phosphoric oxide. The xylene was decanted, evaporated, and the residue distilled at 2mms. pressure. The distillate (7gms) was treated with an alcoholic solution of picric acid and the picrate filtered off (.8gm.). Recrystallised from alcohol it had m.pt. 130-131° and gave on decomposition 3:4 benzfluorene, m.pt. 124-125° (.35gm.) (Cook, et.al., J., 1935 1323). 3:4 benzfluorene was not obtained when the above material was distilled through hot zinc dust, but cyclisation was effected in slightly lower yield when sodamide was used in place of phosphiric oxide.

Ortho-tolualdehyde

Ortho-toluonitrile, prepared from ortho-toluidine, was hydrolysed to ortho-toluic acid by means of 95% sulphuric acid. The acid chloride, obtained by the action of thionyl chloride, was converted to the anilide in the usual way, and the action of phosphorus pentachloride on the latter gave the imid-chloride. Reduction of this by

the method of Sonn and Muller (Ber., 1919, 52, 1927) as described by King, L'Ecuyer and Openshaw (J., 1936, 352) gave ortho-tolualdehyde b.pt. 197°, $94^{\circ}/_{20mm.}$, $83^{\circ}/_{14mm.}$

2-Ortho-tolylidene-α-tetralone.

Ortho-tolualdehyde (12gms., 1 mol.), α-tetralone (14gms) 1 mol) and alcoholic potassium hydroxide solution (4%, 100ccs.) warmed up on mixing. After standing for three hours, the mixture was neutralised with acetic acid, the alcohol evaporated, and the residue extracted with ether and distilled. 2-Ortho-tolylidene-α-tetralone, b.pt. $213^{\circ}/_{2mm.}$ crystallised from aqueous alcohol in light yellow needles, m.pt. 68°. (Found: C, 86.9; H, 6.6. $C_{18}H_{16}O$ requires: C, 87.1; H, 6.5%)

8-Methyl-3:4-benzfluorene

2-Ortho-tolylidene-α-tetralone (20gms) in xylene (100ccs) was refluxed for 20 hours with five successive portions of phosphoric oxide. The xylene was decanted, evaporated, and the residue distilled in a vacuum. The distillate (8-10gms) was treated with its own weight of picric acid in alcohol and the picrate filtered off. The material obtained from the mother-liquors, after removal of the excess of picric acid, was again treated with phosphoric oxide as described above and in this way a total of 10gms of picrate obtained. It crystallised in red needles from absolute alcohol, m.pt. 127-128°. (Found: C, 62.8; H, 3.7. $C_{24}H_{17}O_7N_3$ requires: C, 62.8; H, 3.7%). Attempts to dehydrogenate the hydrocarbon

by heating with selenium at 300-340° failed, and it has been identified as 8-methyl-3:4-benzfluorene. It crystallised in colourless plates from absolute alcohol, m.pt. 104-105°, b.pt. 203-204°/2mm. (Found: C, 93.7; H, 5.8. $C_{18}H_{14}$ requires: C, 93.9; H, 6.1%)

8-Methyl-3:4-benzfluorenone

The hydrocarbon (.5gm.) in glacial acetic acid (20ccs) was heated with sodium dichromate (1gm) for thirty minutes. Dilution with water gave a solid product which was taken up in ether and washed with alkali to remove acidic impurities. Evaporation of the ether gave 8-methyl-3:4-benzfluorenone, which formed orange needles from alcohol, m.pt. 139.5-140.5° (Found: C, 88.2; H, 5.2. $C_{18}H_{12}O$ requires: C, 88.5; H, 4.9%)

Ortho-tolylidene-acetophenone (2'-Methyl-chalkone)

Acetophenone (6gms) was added to an ice-cold solution of sodium hydroxide (3gms) in water (25ccs) and alcohol (25ccs), followed immediately by ortho-tolualdehyde (6gms). After shaking for two hours at 30-35°C. the mixture was neutralised with acetic acid and extracted with ether. Ortho-tolylidene-acetophenone was obtained on distillation, b.pt. 210-220°/10mm. (Weygand, Schachter, Ber., 1935, 68, 231).

Attempts at Cyclisation

The ketone was gently refluxed at atmospheric pressure for four hours. Water appeared to collect in the air-condenser, but the product obtained on distillation at 4mms. pressure could

not be induced to crystallise, and did not form a picrate.

The ketone (2gms) was dissolved in toluene and refluxed in contact with phosphoric oxide for three hours. The liquid product obtained on distillation did not form a picrate.

When the ketone (2gms), in solution in xylene, was subjected to the action of finely crushed sodamide (.6gm, 1.5mols), ammonia was given off, but the distillate obtained could not be induced to crystallise and did not form a picrate.

Condensation of Ortho-tolualdehyde with Cyclohexanone.

(a) 2:6-Di-orthotolylidenecyclohexanone.

Ortho-tolualdehyde (3.4gms, 1 mol) and cyclohexanone (9gms, 3mols) were dissolved in alcohol (15ccs) and a solution of sodium hydroxide (1gm) in water (5ccs) added. The mixture immediately became warm and was mechanically shaken for two hours. The crystals (2.8gms, 50%) of 2:6-di-orthotolylidene-cyclohexanone were filtered off and washed with a little alcohol. Recrystallisation from alcohol gave bright yellow rhombohedra, m.pt. 138-139°, very soluble in benzene, soluble in ether, hot light petroleum and hot ethyl alcohol, and insoluble in methyl alcohol and water. (Found: C, 87.2; H, 7.3. $C_{22}H_{22}O$ requires: C, 87.4; H, 7.3%)

(b) 2-Orthotolylidenecyclohexanone.

Ortho-tolualdehyde (9.5gms) and cyclohexanone (8.5gms) were suspended in 4% aqueous potassium hydroxide solution (100ccs) and refluxed for two hours. Distillation of the residue obtained by evaporating the washed and dried ethereal extracts gave 2-ortho-tolylidenecyclohexanone, b.pt. 151-154°/4mm. (11.3gms, 72%), which rapidly crystallised in light yellow elongated prisms and had melting point 66-67° from light petroleum. (Found: C, 83.8; H, 8.0. $C_{14}H_{16}O$ requires: C, 84.0; H, 8.0%). It was extremely soluble in all the usual organic solvents with the exception of light petroleum, in which it was moderately soluble. The residue in the distillation flask (2-3gms.) consisted mainly of the di-derivative. Neutralisation of the reaction mixture filtrate, from the preparation of the di-derivative in (a) above, followed by extraction with ether and distillation, gave 1gm. of this mono-derivative.

Attempts to cyclise 2-orthotolylidenecyclohexanone.

Refluxing in xylene solution with either sodamide or phosphoric oxide caused extensive polymerisation, but only starting material was recovered on distillation. Distillation through hot zinc dust effected no change in the material.

Reaction between HCN/HCl and 2-Methyl-Naphthalene (cf. Rinkel, Ayling and Beynon, J., 1936, 339).

Powdered anhydrous aluminium chloride (40gms, 3mols) was suspended in dry chlorobenzene (80ccs) and treated at -10°C. with a current of dry hydrogen cyanide (4-5mols) prepared from sodium cyanide (34gms). The mixture was shaken at room temperature for fifteen minutes, and a solution of 2-methyl-naphthalene (14.2gms, 1mol) in chlorobenzene (20ccs) added. A slow current of dry hydrogen chloride was passed for fifteen minutes at room temperature, and then for four to five hours at 70°C., the mixture being vigorously shaken every ten minutes. The cooled mixture was poured on ice and concentrated hydrochloric acid, and then heated for fifteen minutes at the boiling point. The product was not very volatile in steam. The chlorobenzene and ethereal extracts were washed with alkali and water, the ether removed, and the residue distilled through an efficient column. The aldehydic material (13.8gms, 80%) of constant b.pt. 144°/4mm. set to a semi-solid mass of crystals. It was extremely soluble in most organic solvents, and insoluble in water. Attempted purification from aqueous alcohol was unsuccessful, since the material separated consistently in liquid form. Washing with alcohol gave needles, m.pt. 52°. (Found: C, 84.7; H, 5.7. $C_{12}H_{10}O$ requires: C, 84.7; H, 5.9%). It gave a semicarbazone which crystallised in colourless needles from

aqueous alcohol, m.pt. 185-186°. (Found: C, 68.9; H, 5.8. $C_{13}H_{13}ON_3$ requires: C, 68.7; H, 5.7%). The 2:4-dinitrophenylhydrazone was difficult to obtain in a crystalline form, but it separated in red needles, m.pt. 205-206° on slow cooling of its solution in acetic acid after the addition of a trace of water. (Found: C, 60.8, 60.7; H, 4.3, 4.3. $(C_{18}H_{14}O_4N_4)_3H_2O$ requires: C, 60.7; H, 4.5%). This roused the first suspicion that the aldehyde might be non-homogeneous in character, and this was confirmed in oxidation experiments.

The aldehydic material was extremely stable to aerial oxidation and to ammoniatal silver nitrate. Treated with this reagent in the cold as recommend by Delepine and Bonnet (Compt. rend., 1909, 149, 39), no reduction occurred, and after boiling for eight hours only a small yield of a very impure acid was obtained.

To the aldehyde (3gms) dissolved in cold acetone, was added very gradually (ca. 5 hours) a cold concentrated solution of potassium permanganate in acetone until the colour remained (ca.1,000ccs). After working up in the usual way a very impure acid (2gms) was obtained. After repeated recrystallisation from aqueous acetic acid, aqueous alcohol or light petroleum (120-130) the small amount of acid remaining gave a constant m.pt. 124-125°. The crude acid was converted through the acid chloride, b.pt. 169-172°/20mm., to the anilide. This gave a first m.pt. of 100-105° and after

repeated recrystallisation from aqueous alcohol the m.pt. had risen to 153-157° but there was too little left for further purification. 2-Methyl-1-naphthoic acid has been reported by Mayer and Sieglitz (Ber., 1922, 55, 1851) to have m.pt. 126-127° and to give an anilide m.pt. 167-168°. The 2-methyl-3-,4-, and 7-naphthoic acids have not been reported in the literature.

As no methods seemed available for the efficient separation of the isomeric products, the study of this reaction was abandoned.

Mesityl-aldehyde. (Hinkel, Ayling and Beynon, J., 1936, 342).

Dry hydrogen cyanide from sodium cyanide (203gms) was passed into a suspension of aluminium chloride (214gms) in tetrachlorethane (400ccs), cooled in a freezing mixture (-10°C). After fifteen minutes at room temperature, mesitylene (56ccs) was added, a slow current of dry hydrogen chloride passed for fifteen minutes at room temperature, and then for four hours at 80°C, the mixture being shaken every ten minutes. The mixture was cooled, poured on ice and concentrated hydrochloric acid, steam-distilled and the distillate extracted with ether. Distillation gave mesitylaldehyde, b.pt. $130^{\circ}/20mm.$ (40gms).

2-(2':4':6'-Trimethylbenzylidene)-α-tetralone.

Mesitylaldehyde (18gms) and α-tetralone (18gms) were treated with alcoholic potassium hydroxide solution (4%, 100ccs). After standing for three hours the solution

was neutralised with acetic acid and extracted with ether. The residue obtained on evaporation of the ether was distilled up to $160^{\circ}/1$mm. to remove starting materials. Recrystallisation of the residue from aqueous alcohol gave 2-(2':4':6'-trimethylbenzylidene)-α-tetralone as colourless rhombohedra m.pt. 92-92.5° (28gms, 85%). (Found: C, 86.9; H, 7.2. $C_{20}H_{20}O$ requires: C, 86.9; H, 7.2%).

Cyclisation

The material was not cyclised by distillation through hot zinc dust.

2-(2':4':6'-trimethylbenzylidene)-α-tetralone (10gms) was refluxed in xylene solution with successive portions of phosphoric oxide for a total of twenty-four hours. The residue obtained on evaporation of the decanted xylene solution was distilled at 2mms. pressure. The distillate (4.5gms) was dissolved in a concentrated solution of picric acid (4gms) in alcohol, and the picrate (5gms) filtered off. It formed red needles from benzene, m.pt. 190-191°. (Found: C, 64.3; H, 4.5. $C_{26}H_{21}O_7N_3$ requires: C, 64.1; H, 4.3%) Decomposition of this picrate gave an x:x'-dihydro-5:7-dimethyl-1:2-benzanthracene (2.5gms, 26%) which crystallised in colourless rhombohedra from glacial acetic acid, m.pt. 146-147°. (Found: C, 92.9; H, 7.0. $C_{20}H_{18}$ requires: C, 93.0; H, 7.0%).

Concentration of the mother-liquors from which the above picrate had been obtained gave two further picrates. The first to crystallise was very unstable and on attempted recrystallisation from absolute alcohol gave another x:x'-dihydro-5:7-dimethyl-1:2-benzanthracene, which crystallised in the form of colourless rhombohedra from absolute alcohol, m.pt. 114°. (.6gm, 6.5%) (Found: C, 93.4; H, 7.2%). The other picrate was stable, having m.pt. ca. 165°, but the small amount obtained did not allow of its further purification. Its decomposition yielded a third x:x'-dihydro-5:7-dimethyl-1:2-benzanthracene (.1gm, 1.1%), m.pt. 115.5-116.5°, colourless rhombohedra from alcohol, which gave a 20° depression in m.pt. with the isomer of m.pt. 114°. (Found, C, 92.7; H, 7.2%). Total yield of hydrocarbons, 3.2gms, 34%.

The solutions of these hydrocarbons in alcohol, acetic acid, benzene, etc., showed a faint blue fluorescence.

Dehydrogenation of x:x'-dihydro-5:7-dimethyl-1:2-benzanthracene.

The hydrocarbon m.pt. 146-147° was subjected to the action of selenium. No reaction took place at temperatures below 290° and above this temperature reaction was difficult to control since the hydrocarbon sublimed away from the selenium. A small yield of hydrocarbon, m.pt. 120-121°

from acetic acid was obtained, however. (Found: H, 6.4. $C_{20}H_{16}$ requires: H, 6.3%) (An accident to the carbon dioxide absorbing vessel vitiated the carbon value.) This substance is formulated as 5:7-dimethyl-1:2-benzanthracene.

α-Hydrindone (cf. Kipping, J., 1895, 65, 480)

Ethyl cinnamate (95gms) was dissolved in methanol, shaken with a little strontium carbonate, filtered, and a palladium-strontium carbonate catalyst added. Hydrogenation took place with extreme ease at atmospheric pressure. After working up in the usual way the product was distilled, b.pt. 240° (91gms). Hydrolysis for a few minutes at the boiling-point with aqueous sodium hydroxide gave 2-phenylpropionic acid, which was converted to the acid chloride by means of thionyl chloride. The acid chloride (40gms) dissolved in pure light petroleum (60-80, 100ccs) was treated slowly with finely crushed aluminium chloride (40gms). When effervescence had ceased the mixture was warmed to the boiling point, cooled, water added cautiously and the mixture steam distilled. Extraction with ether gave α-hydrindone (16gms).

2-(2':4':6'-trimethylbenzylidene)-α-hydrindone.

α-Hydrindone (16gms, 1mol) and mesitylaldehyde (18gms, 1mol) were treated with alcoholic potassium hydroxide solution (4%, 100ccs). After three hours standing, the solution was neutralised with acetic acid and diluted with

water. The crystals of 2-(2':4':6'-trimethylbenzylidene)-∝-hydrindone were filtered off and purified from aqueous alcohol, from which they separated as faintly yellow prisms of rectangular outline, m.pt. 93.5-94.5°, which turned bright yellow on exposure to light. Yield 26gms., 81%. Found: C, 86.9; H, 7.0. $C_{19}H_{18}O$ requires: C, 87.0; H, 6.9%).

Attempts at Cyclisation.

The material was not affected by distillation through hot zinc dust.

2-(2':4':6'-trimethylbenzylidene)-∝-hydrindone (25gms) was dissolved in xylene and refluxed for twenty-four hours with successive portions of phosphoric oxide. The distillate (12gms) was found to be almost pure starting material and gave no indications of picrate formation. The treatment was repeated on the distillate for a further twenty-four hours with the same result.

No hydrocarbon was obtained by a similar experiment with sodamide.

Tetra-hydro-ortho-toluonitrile (cf. Linstead and Millidge, J., 1936, 482, 485)

Potassium cyanide (.25gm in the minimum of water) was added to 2-methyl-cyclohexanone (50gms), and this then added dropwise to dry hydrogen cyanide (prepared from 50gms of potassium cyanide) cooled in a freezing mixture. The freezing mixture was then thoroughly insulated and the whole

left overnight. The excess of hydrogen cyanide was removed at the pump after the addition of a few drops of concentrated sulphuric acid.

It was found that under the conditions given by Linstead and Millidge (loc.cit.) dehydration was not complete, and since the cyanhydrin showed some tendency to decompose on distillation it was dehydrated as follows without further purification. To the ice-cold cyanhydrin was added pyridine (100gms) and immediately, dropwise with strong ice-cooling, thionyl chloride (76gms) (ca. .5 hour). The mixture was heated for two hours on the water-bath, cooled, ice and concentrated hydrochloric acid added, and the mixture shaken with ether and filtered through pulp. The ethereal extracts were washed with acid, alkali and water, dried, and the ether removed. In the best preparations in which neither cyanhydrin nor ortho-methylcyclohexanone was recovered, the nitrile was obtained in 80% yield, b.pt. $73^{\circ}/7mm.$, $92^{\circ}/16mm.$

Reduction of α-β-Unsaturated Nitriles by Stannous Chloride (cf. Stephens, J., 1925, 127, 1874).

Tetra-hydro-ortho-toluonitrile (5gms) was added to a solution of anhydrous stannous chloride (12gms) in dry ethereal hydrogen chloride, the mixture shaken for two hours and left overnight. A small amount of crystalline material

had separated and this was not increased by refluxing the solution for two hours. Dilute hydrochloric acid was added and the mixture steam-distilled. The products were worked up by ether extraction, followed by distillation, which always gave two fractions under varying conditions (e.g., standing for considerable periods) during the reduction:-

(a) 5.5gms, b.pt. 76-81°/9mm. which was mainly recovered nitrile, but contained aldehydic material. It gave a 2:4-dinitrophenylhydrazone, which separated as red needles from aqueous alcohol, m.pt. 179°, identical by mixed m.pt. with that obtained (see later) from 6-methyl- Δ^1-cyclohexenealdehyde. (Found: N, 18.3. $C_{14}H_{16}O_4N_4$ requires: N, 18.4%).

(b) 1.0gm., b.pt. 120°/9mm. This material was not further investigated. It was aldehydic, and contained halogen.

Δ^1-Cyclohexenenitrile was prepared for the purpose of this investigation from cyclohexanone in the manner above described for tetra-hydro-ortho-toluonitrile. The cyanhydrin of cyclohexanone was not dehydrated by thionyl chloride alone under the conditions described by Cook and Linstead (J., 1934, 959) for the cyanhydrin of cyclopentanone. Using thionyl chloride (1.5mols) and dimethylaniline (2.5mols) without a diluent and heating on the oil-bath at 120-130° for three hours, the yields were in the neighbourhood of

50% with considerable loss of material. Using pyridine (3mols) and thionyl chloride (1.4mols) as above described, the nitrile, b.pt. $74^{\circ}/9mm.$, $87^{\circ}/15mm.$ was obtained in 90% yield.

Δ^{1}-Cyclohexenenitrile (20gms) was added with vigorous shaking to a solution of anhydrous stannous chloride (54gms) in dry ethereal hydrogen chloride (200ccs). After standing for some hours, no crystalline material had separated and the lower layer was steam-distilled. After working up in the usual way, distillation gave 3.8gms, b.pt. $95\text{-}100^{\circ}/25mm.$, which contained Δ^{1}-cyclohexenealdehyde, since it formed a semicarbazone, m.pt. 212-213° (v. Braun, Danziger, Ber., 1913, 46, 107). Its 2:4-dinitrophenylhydrazone formed fine red needles from aqueous alcohol, m.pt. 216-217°. (Found: N, 19.1. $C_{13}H_{14}O_4N_4$ requires: N, 19.3%). A fraction, b.pt. $135\text{-}140^{\circ}/25mm.$, which was aldehydic but contained halogen, was also collected. The majority of the unreacted nitrile was recovered in a pure condition from the upper ethereal layer. After refluxing a reaction mixture containing 7gms of nitrile for six hours, a small amount of crystalline material had separated which yielded the required aldehyde (.5gm) on working up in the usual way. Reduction of the quantity of ether used in the reaction mixture so that only one layer was present did not increase the yield of aldehyde.

6-Methyl-Δ'-cyclohexenecarboxylic acid.

Tetra-hydro-ortho-toluonitrile (25gms) was heated for six to eight hours in an oil-bath at 120° with 95% phosphoric acid (100ccs) (cf. Berger and Olivier, Rec.Trav.Chim., 1927, 46, 600). After careful dilution with water, the mixture was extracted with ether, and the ethereal extracts shaken with sodium carbonate solution. Acidification gave 6-methyl-Δ'-cyclohexenecarboxylic acid in colourless needles, m.pt. 105.5° from water or aqueous alcohol. (Yield 60-70%). (Found: C, 68.4; H, 8.3. $C_8H_{12}O_2$ requires: C, 68.6; H, 8.6%) Evaporation of the ethereal solutions from these hydrolyses gave isomeric amides which formed colourless plates from alcohol-light petroleum and had sharp melting points ranging between 140° and 146°, while mixed melting points were sharp and immediate. (Found: C, 69.1; H, 9.2. $C_8H_{13}ON$ requires: C, 69.1; H, 9.3%). Hydrolysis of the nitrile by means of sulphuric acid of various strengths between 60% and 90% was tried, but carbonisation occurred with evolution of sulphur dioxide, and the yields of the acid (m.pt. 105.5°) were much lower than by the above method. Hydrolysis with alcoholic potassium hydroxide proceeded very slowly. The nitrile (5gms) was added to a solution of potassium hydroxide (7gms) in the minimum of water, and alcohol added until the mixture was homogeneous. After refluxing for nine days, two products were isolated:

The acid was not soluble in hydrobromic acid, but after long standing in the cold a dibromo-acid was produced, which crystallised in colourless rhombohedra, m.pt. 151° to 152°, from aqueous alcohol. (Found: Br, 52.2. $C_8H_{13}O_2Br$ HBr requires: Br, 52.9%).

Conversion of 6-Methyl-Δ'-cyclohexenecarboxylic acid to α-Methyl-adipic Acid.

Repeated attempts to obtain homogeneous degradation products from the acid with potassium permanganate failed. The acid (3gms) was, therefore, dissolved in water, the solution made very faintly alkaline and a current of ozonised oxygen passed through it until the ozone escaped freely. To the ice-cooled solution was then added N/10 potassium permanganate solution until the colour remained, a stream of carbon dioxide being passed during the addition. The colour was destroyed by the addition of a trace of sodium bisulphite, the manganese dioxide filtered off, and the solution almost neutralised and concentrated first on the water-bath and finally in vacuo over sulphuric acid. Acidification, followed by ether extraction, yielded -methyl adipic acid, its identity being proved by mixed melting point determination with an authentic specimen prepared from ethyl-cyclopentanone-2-carboxylate and methyl iodide. (Rysselberge, Bull.Acad.roy.Belgique, 1926, 12, 171-192)

6-Methyl-Δ'-cyclohexenealdehyde.

The acid chloride (8gms), b.pt. $92^{\circ}/12mm.$ of 6-methyl-cyclohexenecarboxylic acid, obtained by the action of thionyl chloride, was dissolved in benzene (25ccs), and with ice-cooling a solution of aniline (15gms) in chloroform (100ccs) added slowly. Aniline hydrochloride was removed by washing with dilute acid, and evaporation of the dried benzene-chloroform solution gave the anilide (12gms). It crystallised in colourless needles, m.pt. 106.5-107.5° from light petroleum (80-90°). (Found: C, 78.3; H, 7.6. $C_{14}H_{17}ON$ requires: C, 78.1; H, 7.9%.) The reaction between this anilide (10gms) and phosphorus pentachloride (10gms) in dry toluene (50ccs) was completed on the water-bath, and to the red syrup obtained by evaporating the toluene and phosphorus oxychloride under reduced pressure, was added with strong ice-cooling, a solution of stannous chloride (25gms) in dry ethereal hydrogen chloride (100ccs). Crystals separated, and after two hours the reaction mixture was distilled with steam. From the ethereal extracts of the distillate 6-Methyl-Δ'-cyclohexenealdehyde (3.5gms, 60%) was obtained, b.pt. $66-68^{\circ}/10mm.$ $n_D^{17^{\circ}}$ 1.4898. Its semicarbazone had melting point 207-209° from aqueous alcohol. (Found: C, 60.1; H, 8.5. $C_9H_{15}ON_3$ requires: C, 59.7; H, 8.3%). Its 2:4-dinitrophenylhydrazone, m.pt. 179°, was identical by mixed melting point with the material

prepared from the aldehyde obtained above by the reduction of tetra-hydro-ortho-toluonitrile. Shaken with an ammoniacal solution of silver nitrate, the above aldehyde gave 6-methyl-Δ'-cyclohexenecarboxylic acid.

Δ'-cyclohexenealdehyde.

Δ'-cyclohexenyl nitrile (70gms) was added to a solution of potassium hydroxide (80gms) in water, and the whole made homogeneous in the hot with alcohol. The solution was refluxed for twelve to eighteen hours until ammonia was no longer evolved, the alcohol distilled off, and the remaining solution acidified and extracted with ether. Distillation gave the acid, b.pt. $140^{\circ}/15mm.$ Yield 78gms.

The acid chloride (31.5gms), b.pt. $86^{\circ}/12mm.$ obtained by the action of thionyl chloride, was dissolved in dry benzene (70ccs), and a solution of aniline (42gms) in chloroform (250ccs) added slowly with ice-cooling. Aniline hydrochloride was removed by thorough washing with dilute hydrochloric acid, and evaporation of the benzene-chloroform solution gave the anilide (35gms) which crystallised in colourless needles from light petroleum (80-100), m.pt. $111-112^{\circ}$ (Found: C, 77.4; H, 7.6. $C_{13}H_{15}ON$ requires: C, 77.6; H, 7.4%).

The action of phosphorus pentachloride (10gms) on the anilide (10gms) suspended in toluene (40ccs) was completed at $100^{\circ}C.$ on the water-bath. To the syrup obtained by evaporating off the toluene and phosphorus oxychloride

under reduced pressure, was added with strong ice-cooling a solution of anhydrous stannous chloride (25gms) in ethereal hydrogen chloride. After two hours, the clear ether was poured off and the mass of yellow crystals treated with dilute hydrochloric acid and distilled in steam. Ether extraction of the distillate yielded the aldehyde, b.pt. $58^{\circ}/10mm.$ $n_D^{18^{\circ}}$ 1.4963 (3.3gms, 60%). Its semicarbazone, m.pt. 212-213° and its 2:4-dinitrophenylhydrazone, m.pt. 216-217° were identical with those obtained above by the reduction of Δ^1-cyclohexenenitrile.

Attempt to Cyclise the Anilide of Δ^1-cyclohexenecarboxylic acid.

To the anilide (4gms) in carbon disulphide (50ccs) was added finely powdered anhydrous aluminium chloride (4gms). The mixture warmed up, and a precipitate was suddenly formed. After standing overnight, ice and hydrochloric acid were added and the precipitate filtered off. It was found to be unchanged anilide, and evaporation of the carbon disulphide solution yielded the same material. Neutralisation of the acidic aqueous solution and extraction with ether yielded traces of an unidentifiable residue.

Condensation of Crotonaldehyde with Cyclohexanone.

After trial experiments, the procedure described below was adopted. With more vigorous condensing agents, self-condensation of the crotonaldehyde tended to take place to the exclusion of its condensation with the ketone.

Redistilled technical crotonaldehyde (100ccs), cyclohexenone (300ccs) and alcohol (300ccs) were mixed, potassium hydroxide solution (1%, 400ccs) added, and the corked flask occasionally shaken over three to four hours. The temperature was kept below 30°C. throughout. After neutralisation with acetic acid, the mixture was extracted with ether, and the products isolated by vacuum distillation. The main fraction had b.pt. 140-155°/14mm., leaving a residue of resinous material which appeared to undergo considerable decomposition at higher temperatures. Separation of this main fraction into its components was not possible, both on account of the small boiling range, and of the tendency of part of the material to polymerise on prolonged distillation. The lower-boiling fractions from it, however, were markedly more refractive than the later fractions, and yielded a semicarbazone which rapidly turned yellow on exposure to air. It scintered at 187° and gave a meniscus at 191°, and was in all probability the semicarbazone of crotonylidene-cyclohexanone, though the analytical figures would appear to indicate that autoxidation had occurred before the material was analysed. (Found on material exposed to air: C, 51.7; H, 7.3; N, 15.8. $C_{11}H_{17}ON_3 + H_2O + O_2$ requires: C, 51.3; H, 7.4; N, 16.3%) The highest boiling fractions gave none of this semicarbazone.

The crude product was dissolved in methyl alcohol, a palladium-strontium carbonate catalyst added, and the whole shaken with hydrogen at 1.5 to 2 atmospheres pressure. The

product of the reaction was fractionally distilled and the following fractions isolated:-

(a) 26gms., b.pt. $45^{\circ}/9mm.$ identified as cyclohexanol by its oxidation to adipic acid and its lack of ketonic properties.

(b) 38gms., b.pt. $90-100^{\circ}/9mm.$ This on redistillation gave 2-n-butyl-cyclohexenol, b.pt. $95^{\circ}/9mm.$ $n_D^{17^{\circ}}$ 1.4711, identified by its oxidation with chromic acid to 2-n-butylcyclohexenone, which gave a semicarbazone, m.pt. 144-145°, and a 2:4-dinitrophenylhydrazone, m.pt. 113-114°. (Weizmann, Bergmann and Haskelberg, Chem.and Ind., 1937, 56, 587).

(c) A fraction of b.pt. $146-153^{\circ}/17mm.$, $108-114^{\circ}/3mm.$, which constituted the bulk of the material. This was a mixture, since on further fractionation it yielded fractions of different refractive indices (Found: C, 70.1; H, 10.1; reactive hydrogen - Zerewitinow, .49. $C_{10}H_{16}O_2$ requires: C, 71.4; H, 9.5. $C_{10}H_{17}O(OH)$ requires: C, 70.6; H, 10.6; reactive hydrogen, .59. $C_{10}H_{20}O_2$ requires: C, 69.8; H, 11.6%). Oxidation by nitric acid did not yield adipic acid, and attempts to prepare a para-nitrobenzoate or an acetate failed. The material (16gms) was treated with a little alcohol and 2N sodium hydroxide (6ccs) and refluxed gently for three hours. Extraction with ether, followed by distillation gave 4.6gms of b.pt. $108-112^{\circ}/3mm.$ the rest of the material remaining as a resinous

residue in the distillation flask. (Found: C, 73.2; H, 10.3. $(C_6H_{10}O)_n$ requires: C, 73.5; H, 10.2%) These analytical figures are those of cyclohexanone.

Condensation of Crotonaldehyde with Cyclopentanone.

Crotonaldehyde (10ccs), cyclopentanone (30ccs), alcohol (30ccs) and potassium hydroxide solution (1%, 20ccs) yielded a partially solid product under the conditions described in the case of cyclohexanone. The oily material was washed away by organic solvents on the filter, and a residue of light yellow to brown resin (5.5gms) was left, very similar in physical characteristics to the product of the reaction between ethylene dichloride and sodium polysulphide. A portion of this was purified by repeated boiling with organic solvents in which it was insoluble. The light yellow product would appear from its analysis to be derived from the crotonaldehyde by polymerisation. (Found: C, 69.1; 68.8; H, 8.3, 8.1. $(C_4H_6O)_n$ requires: C, 68.6; H, 8.6%). With decreasing amounts of alkali the yield of this resin fell rapidly, and when one-quarter of the amount specified above was used, none could be isolated. The product of the reaction under these conditions was distilled, and yielded first cyclopentanone (7.5gms) and then a fraction (6gms), b.pt. 115-135°/10mm. residue of high-boiling material remained in the flask. The

product, b.pt. 115-135°/10mm. could not be separated into its components, and in trial fractionations a semicarbazone, m.pt. 215-216° (decomp.) could be isolated from all fractions of the distillate. It crystallised in needles from aqueous alcohol which turned yellow on exposure to air and light. The analytical figures correspond with those of the semicarbazone of crotonylidenecyclopentanone. (Found: C, 62.6; H, 7.5. $C_{10}H_{15}ON_3$ requires: C, 62.2; H, 7.8%).

In an attempt to characterise the other products of the reaction, the material (45gms) was hydrogenated as described above. From the hydrogenation mixture two fractions were obtained on distillation. A fraction (16gms), b.pt. 89°/10mm. $n_D^{20°}$ 1.4568, was identified as 2-n-butylcyclopentanone by comparison of its semicarbazone with a synthetic specimen:- α-n-butyladipic acid was prepared by hydrolysis in the usual way of ethyl 3-n-butylcyclopentane-2-one-1-carboxylate. It crystallised from benzene-light petroleum on ice-cooling in colourless prisms, m.pt. 59.5°. (Found: C, 59.4; H, 9.0. $C_{10}H_{18}O_4$ requires: C, 59.4; H, 8.9%). On distillation from a flask containing a little barium oxide, this acid yielded 2-n-butylcyclopentanone (yield 71%). Its semicarbazone crystallised from aqueous alcohol in colourless needles, m.pt. 185-186°, identical with the semicarbazone mentioned above. (Found: C, 61.1; H, 9.6. $C_{10}H_{19}ON_3$ requires: C, 60.9; H, 9.6%). A second fraction (12gms), b.pt. 127-135°/10mm. was obviously a mixture, and presented the same difficulties

with regard to its separation into its constituents as the corresponding product from cyclohexanone. It yielded a very impure semicarbazone, which gave needles from aqueous alcohol m.pt. 211-213° (decomp.), but the analytical figures from two separate samples were inconclusive although agreement is closest for the semicarbazone of a self-condensation product of cyclopentanone. (Found: C, 63.4, 63.6; H, 8.3, 8.1; N, 19.2, 19.6. $C_{10}H_{17}O_2N_3$ requires: C, 56.9; H, 8.0; N, 19.9. $C_{10}H_{19}O_2N_3$ requires: C, 56.3; H, 8.9; N, 19.7. $C_{11}H_{17}ON_3$ requires: C, 63.8; H, 8.3; N, 20.3%).

Condensation of Crotonaldehyde with Acetone.

Acetone (600ccs) and crotonaldehyde (100ccs) were neutralised to phenolphthalein, and 1% potassium hydroxide solution (170ccs) added with cooling. After standing for 1.5 to 2 hours, the mixture was neutralised with acetic acid, the acetone distilled off, and the residue extracted with ether. Distillation yielded a fraction, b.pt. 66-77°/15mm. (50gms) and a residue of resin (ca. 60gms). Fractionation of the distillate effected only its partial separation, though a fraction, b.pt. 73-77°/15mm. $n_D^{16°}$ 1.5210, so obtained, was chiefly crotonylideneacetone (Meerwein, Ann., 1909, 258, 85). It gave a semicarbazone which separated in white plates from aqueous alcohol, m.pt. 164-166°. (Found: C, 57.4; H, 7.7. $C_8H_{13}ON_3$ requires: C, 57.5; H, 7.8%). The crystals

gradually turned yellow on standing. An attempt to obtain toluene from the crude crotonylidene-acetone by the direct action of phosphoric oxide failed, the whole mass polymerising after a short period of refluxing.

In an attempt to elucidate the nature of the other products formed in the reaction, the crude material (50gms) was hydrogenated as described above and the product fractionally distilled. Methyl-n-amyl ketone (20gms), b.pt. $50^{\circ}/15mm.$ was identified as one product of the reduction; the other product was a liquid, b.pt. $61-63^{\circ}/15mm.$ $n_D^{18^{\circ}}$ 1.4253, which gave no reaction with ketonic reagents, and contained two reactive hydrogen atoms. (Found: C, 62.8, 63.4; H, 10.7, 10.9 (different samples); Reactive H (Zerewitinow), 1.47. $C_7H_{14}O_2$ (2 reactive H's) requires: C, 64.6; H, 10.8; reactive H, 1.54. $C_7H_{16}O_2$ requires: C, 63.6; H, 12.1; reactive H, 1.51. $(C_3H_6O)_n$ requires: C, 62.1; H, 10.3%).

Condensation of Crotonaldehyde with ∝-Tetralone.

∝-Tetralone (60gms), crotonaldehyde (40ccs) and 1% alcoholic potassium hydroxide solution (50ccs) were mixed and allowed to stand for two hours. Most of the ∝-tetralone was recovered on working up, and a product, b.pt. $140-185^{\circ}/6mm.$ did not appear to contain the ∝-tetralone nucleus, since a fraction, b.pt. $160-170^{\circ}/2mm.$ (3gms) did not give phthalic acid on oxidation with potassium permanganate.

When the amount of catalyst was either increased or

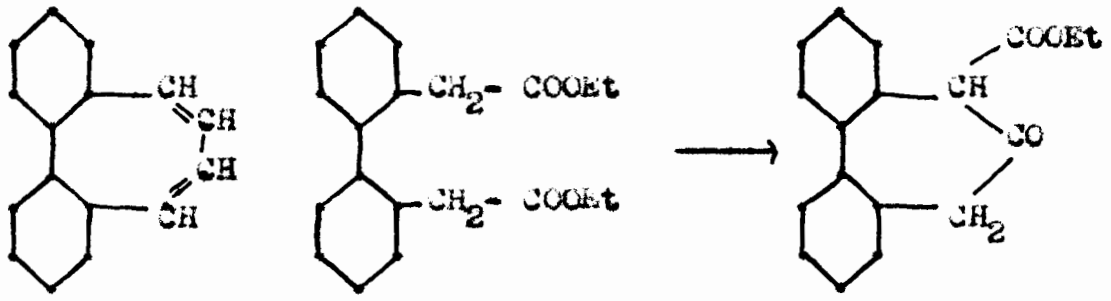
diminished, all the α-tetralone was recovered, lower concentrations causing slight, and higher, extensive polymerisation of the crotonaldehyde.

Reaction Between Cyclohexylidene-cyclohexanone, Acetyl-Chloride and Stannic Chloride.

The hydrochloride of cyclohexylidene-cyclohexanone was prepared from cyclohexanone as described by Wollach (Ber., 1907, 40, 70). Treated with pyridine (1mol) and heated on the water-bath for 1.5 hours, an almost quantitative yield of cyclohexylidene-cyclohexanone was obtained. To a solution at -15° to -20°C. of cyclohexylidene-cyclohexanone (178gms) and acetyl chloride (79gms) in carbon disulphide (50ccs), was added dropwise with shaking a solution of stannic chloride (261gms) in carbon disulphide (20ccs). Crystals separated and after three hours in the freezing mixture water was added. The crystalline material gradually changed to a liquid heavier than water, and insoluble in carbon disulphide and ether. Benzene extracts on evaporation gave a crystalline material very soluble in benzene and light petroleum, and insoluble in alcohol or acetic acid. Recrystallisation from pyridine gave a compound, m.pt. 132-134°, the analytical figures for which would appear to show that it is a self-condensation product of cyclo-hexylidene-cyclohexanone. (Found: C, 85.2; H, 9.8. $C_{24}H_{34}O$ requires: C, 85.2; H, 10.1%).

ATTEMPTS TO PREPARE 1,2:3,4-DIBENZ-$\Delta^{1,3,5,7}$-CYCLOOCTATETRAENE.

Methods which might lead to the direct production of cyclooctatetraene structure by cyclodehydration processes having been so unpromising, attention was directed to the synthesis of 1,2:3,4-dibenz-$\Delta^{1,3,5,7}$-cyclooctatetraene (I) by other routes.

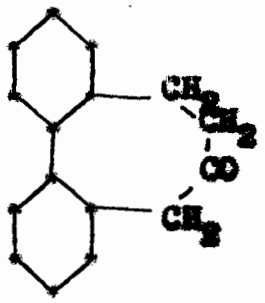


I. II. III.

This particular dibenzcyclooctatetraene was chosen chiefly because of the recorded ease of formation of ring systems across the 2:2'-positions of diphenyl - substituents in these positions having been stressed by Kenner (J., 1913, 103, 613) as behaving in many respects like ortho-substituents in the benzene ring. In particular, there was the observation by this author of the ease of formation (80% yield) of (III) from diphenyl-2:2'diacetic ester (II) by the Dieckmann reaction.

The ketone (III) might well itself have constituted a starting-point in the investigation, since by a ring-widening

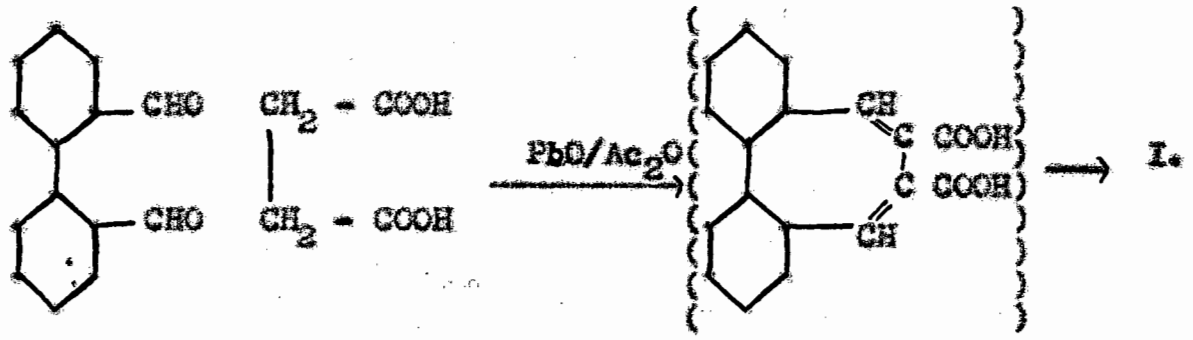
procedure the corresponding compound containing the cyclo-octane ring-system might be accessible. It was deemed more profitable, however, to explore first those synthetic methods which might yield the 1,2:3,4-dibenzo-$\Delta^{1,3,5,7}$-cyclooctatetraene structure directly, rather than to attempt the introduction of the requisite double-bonds into a substance such as (IV),



IV.

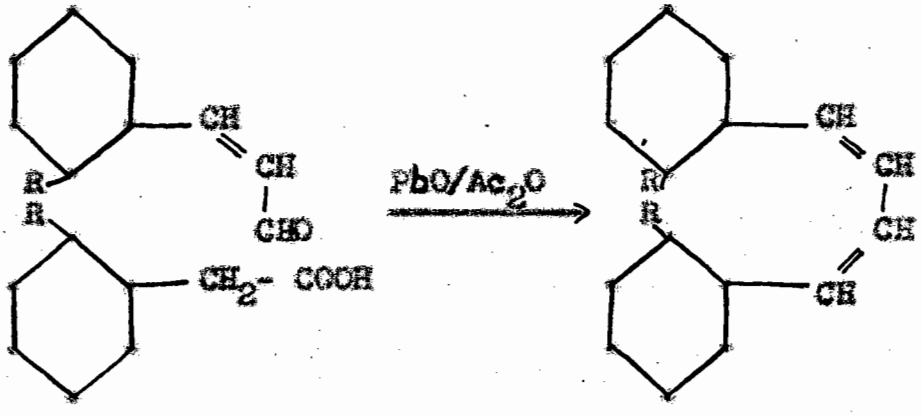
since in any experiments along the latter lines there would be considerable risk of molecular re-arrangements accompanying the elimination reactions which would have to be applied, and, moreover, very many stages would be involved.

Three distinct sets of experiments have, therefore, had as their goal the direct production of a structure such as (I). In the first, the condensation of diphenyl-2:2'dialdehyde (V) with succinic acid has been studied, a reaction which might be expected from the experience of Kuhn and Winterstein (Helv. Chim.Acta., 1928, 11, 87) in the production of diphenyl-butadiene and similar compounds, to yield (I) itself, as follows:-



V. VI.

However, the behaviour of aromatic aldehydes in this reaction has not previously been investigated - the analogous 1,4-diphenylbutadiene having been prepared by Kuhn and Winterstein from cinnamaldehyde and phenylacetic acid (VI(a)—— VII; R = H) - and experiments with both diphenyl-2:2'dialdehyde and benzaldehyde would appear to indicate that aromatic aldehydes cannot in fact be employed in the reaction. Thus 1:4-diphenylbutadiene could not be obtained by condensing benzaldehyde with succinic acid under these conditions. The product, as in the



VI. VII.

analogous condensation using diphenyl-2:2'dialdehyde, was a

mixture of acids which could not be separated by the usual procedures. This route, therefore, appeared closed.

The diphenyl-2:2'-dialdehyde used in the above investigation was prepared from ortho-iodobenzaldehyde by a method essentially that of Mayer (Ber., 1911, 44, 2304). It was found, however, that by conducting the reaction in an inert atmosphere and purifying the product by distillation his yields could be improved upon. The "wie benzaldehyd reichende" by-product of the reaction noticed by him has been identified as benzaldehyde itself. In early experiments the diethylacetal of ortho-iodobenzaldehyde was employed in the reaction, but a homogeneous product was not obtained.

Ortho-iodobenzaldehyde is now made available in excellent yield by the reduction of the phenylimidochloride of ortho-iodobenzoic acid. Patterson (J., 1896, 69, 1006), Bamberger and Demuth (Ber., 1901, 34, 1329), and Stuart (J., 1888, 53, 141) have described its preparation by other procedures, but these methods did not appear to lend themselves to the production of the aldehyde in quantity.

Attention was next directed to the preparation of o:o'-di-iodo-1:4-diphenylbutadiene (VII; R = I) since such a compound might possibly yield the dibenzcyclooctatetraene (I) by the Ullmann reaction. It seemed possible that (VII; R = I)

might result from the condensation of ortho-iodo-cinnamaldehyde with ortho-iodophenylacetic acid, by the procedure of Kuhn and Winterstein. Methods of preparing the above components were, therefore, investigated.

Ortho-iodocinnamaldehyde was easily obtained by condensing ortho-iodobenzaldehyde with acetaldehyde in the presence of diethylamine. The preparation of ortho-iodophenylacetic acid from ortho-iodotoluene has been described by Reum (Ber., 1894, 27, 3233; cf. Frederick, Dippy and Lewis, J., 1936, 646). The method, however, is rather time-absorbing, and involves much loss of material at one stage. The possibility of obtaining it from ortho-nitrophenylacetic ester was, therefore, investigated, but the methods tried for the reduction of this compound to the corresponding amine did not give good yields, and the ease of formation of oxindole from ortho-aminophenylacetic ester (Weber, Ber., 1922, 55, 834) made the isolation and subsequent diazotisation of the latter compound a matter attended by difficulty. The yields of ortho-iodophenylacetic ester obtainable by this method did not warrant its employment, and recourse was, therefore, had to the original method of Reum. In view of the statement by the latter that ortho-iodobenzylbromide is an extremely unpleasant substance to handle, attempts were made - with a view also to a possible improvement in yield - to chlorinate ortho-iodotoluene with

sulphuryl chloride, by a procedure analogous to that of Kharash and Brown (J.Amer.Chem.Soc., 1939, 61, 2142). Free iodine was produced during the reaction, however, and although vigorous decomposition of the sulphuryl chloride occurred, no ortho-iodobenzylchloride could be obtained. (Kharash and Brown were unable to chlorinate ortho- or para-nitrotoluene in this way, and state that iodine acts as an anticatalyst in the reaction). It was found, however, that the bromide can be handled with quite reasonable facility provided it is purified by distillation and kept in closed flasks away from water-vapour.

When ortho-iodocinnamaldehyde and ortho-iodophenylacetic acid were condensed by the procedure of Kuhn and Winterstein, two forms of o:o'-di-iodo-1:4-diphenylbutadiene (VII; R = I) were obtained. These differed considerably in their physical characteristics, notably solubility relationships, and no interconversion was observable. It seemed possible that they were geometrical isomers, since in the case of analogous 1:4-diphenylbutadiene (VII; R = H), the three such possible isomers are known (Straus, Ann., 1905, 342, 238-260). It is probably significant in this connection that in one reaction involving the higher-melting isomer, iodine was eliminated with the production of trans-1:4-diphenylbutadiene.

Attempts to obtain (I) by the Ullmann reaction on these isomeric o:o'di-iodo-1:4-diphenylbutadienes have failed. When such reactions were conducted with the substances alone or in high concentration in quinoline solution, inter-molecular condensation occurred with the production of substances of high molecular weight which contained iodine. In dilute solution in quinoline the higher-melting isomer reacted slowly with copper (the lower-melting isomer not at all), but the only low-molecular-weight product formed was trans-1:4-diphenyl-butadiene - a result which probably reflects the free-radical mechanism of the reaction. In view of the results obtained with 2:2'-dibromodiphenyl (see later) the actions of sodium and of magnesium with cupric chloride on (VII; X = I) were not investigated. Such reactions would in any case have presented difficulties in view of the general insolubility of the isomers, particularly the higher-melting, more reactive and more accessible of the two.

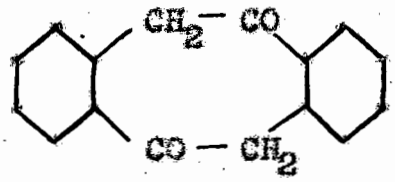
The third direct approach to a structure such as (I) consisted of an attempt to condense diphenyl-2:2'-dialdehyde (V) with diethyl succinate - a reaction which might be expected to produce 1,2:3,4-dibenz-$\Delta^{1,3,5,7}$-cyclocta-tetraene-6,7-dicarboxylic acid (VI). The analogous condensation involving benzaldehyde has been brought about in a number of ways, and the procedure of Cordier (Ann.Chim., 1931, 16, 228) was chosen, since it had apparently given

fewer undesirable by-products than the method of Stobbe and Naoum (Ber., 1904, 37, 2241). When, however, diphenyl-2:2'-dialdehyde and diethyl succinate were subjected to the action of sodium, an acid was produced which, from its equivalent weight, bore no relationship to the product desired.

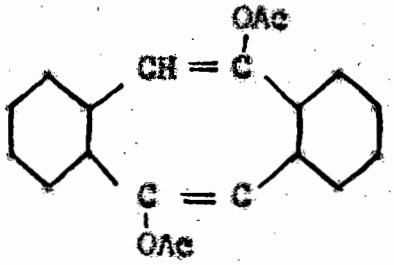
These more direct methods of approach to the structure (I) having failed, attention was directed to the possibility of utilising in the manner described above the reaction (II ⟶ III), and attempts were accordingly made to find a more convenient synthesis of (II) than that used by Kenner (loc.cit.). The action of diazomethane on the dichloride of diphenic acid by the method of Arndt and Eistert (Ber., 1935, 68, 200; 1936, 69, 1074) gave only small yields of diphenyl-2:2'-diacetic acid, and the method, moreover, did not seem to lend itself to operations on a reasonable scale. Ethyl diphenyl-2:2'-diacetate could not be obtained by the action of copper on either ethyl ortho-iodophenylacetate or the corresponding bromo-compound. The halogen groups in these substances were unreactive towards copper, and the reactions accordingly did not proceed in the desired manner. Thus the product from the iodo-compound was found to contain both phenylacetic acid and ortho-iodophenylacetic acid, besides ethyl phenylacetate, unreacted material, and a high-melting

unidentified substance. (Weitzenbock, Monatsh., 1912, 34, 193, records that methyl ortho-iodocinnamate when subjected to the Ullmann reaction gave phenanthrene and a small amount of diphenyl-2:2'-diacrylic acid, while the ethyl ester - which could not be distilled owing to its decomposition with the formation of ortho-iodocinnamic acid - gave oily products, but no phenanthrene.)

In view of these results and of the publication about this time by Wawzonek (J.Amer.Chem.Soc., 1940, 62, 745) of the synthesis of (VIII) and (IX) the projected preparation

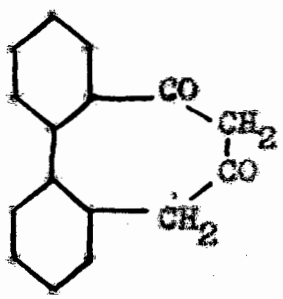


VIII.

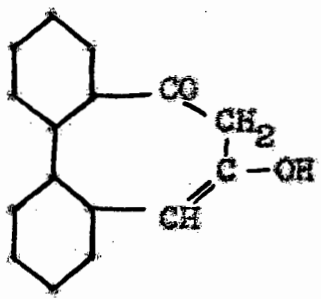


IX.

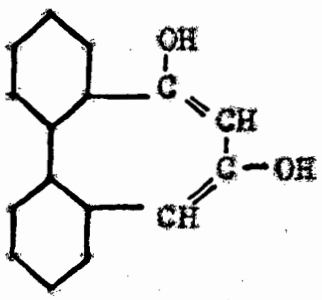
of (IV) was abandoned, and efforts were concentrated instead on the development of a synthesis of the diketonic derivative (X). This substance, being a β-diketone, would be expected to



X.



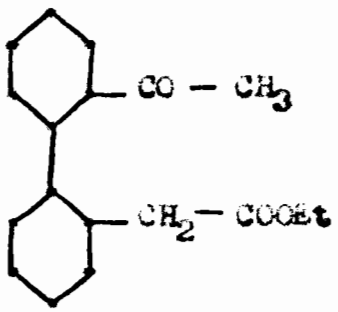
XI.



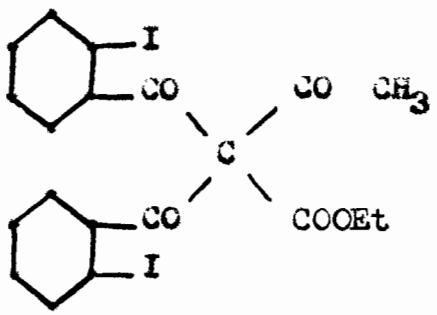
XII.

exist in a mono-enolic form (cf. ω-phenylacetylacetophenone (XI). Bulow and Grotowsky, Ber., 1901, 34, 1483; Lovett and Roberts, J., 1928, 1975), and any tendency on its part for both the carbonyl groups to enolise (as at XII) would be an indication of a contribution by resonance to the stability of a structure such as (I). Methylation of the hydroxy-groups of a substance such as (XII) would perhaps make an unambiguous analysis by X-rays of such a structure possible, while by a process involving the application of elimination reactions for the introduction of the requisite double-bonds (I) itself might be accessible from (X).

1,2:3,4-Dibenz-$\Delta^{1,3}$-cyclooctane-6:8-dione (X) might be expected to result from the Dieckmann reaction on ethyl diphenyl-2-aceto-2'-acetate (XIII), and two possible methods of obtaining the latter substance were, therefore, investigated.



XIII.



XIV.

It was hoped that ortho-iodoacetophenone, being more reactive towards copper and lower boiling, would couple in the Ullmann reaction with ethyl ortho-iodophenylacetate at a lower

temperature and thereby prevent the intervention of the undesirable side-reactions which had been found to supervene when the latter substance was treated alone with copper. The desired product (XIII) did not result from such a reaction, however, and although the large excess of ortho-iodoacetophenone employed in the reaction was used up, the expected by-product, 2:2'-diacetodiphenyl, could also not be isolated from the products.

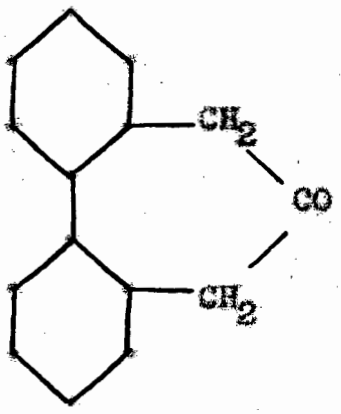
Ortho-iodoacetophenone was prepared for the purpose of the above reaction by hydrolysing the condensation product obtained by condensing equivalent quantities of ortho-iodobenzoylchloride and the mono-sodium compound of ethylacetoacetate. Such conditions were used by Gevekoht (Ann., 1883, 221, 323) in the analogous preparation of ortho-nitroacetophenone, but it has since been shown by Claisen (Ann., 1896, 291, 67) that with benzoylchloride the product under these conditions is dibenzoylethylacetoacetate and not the monoderivative. Hydrolysis in acidic media of the condensation product obtained in the manner stated, gave an approximately equimolecular mixture of ortho-iodoacetophenone and ethyl ortho-iodobenzoate. This occurred whether or not the acidic hydrolysing medium contained ethyl alcohol, and it was established that the material hydrolysed did not before hydrolysis contain ethyl ortho-iodobenzoate. It is concluded

therefore, that the condensation product obtained was in fact the di-derivative (XIV) and that hydrolysis of one of the benzoyl radicals in the molecule took place by a mechanism which involved the ester group in the ethyl acetoacetate residue.

The arylation of ethyl phenylacetate by diazotised ortho-aminoacetophenone (Gomberg reaction) seemed to offer an alternative means of preparing (XIII). Previous experience (see Gomberg and Pernert, J.Amer.Chem.Soc., 1926 48, 1374; Hey and collaborators, J., 1938, 106; 116; 699, etc.) has gone to show that either the ortho- or para-arylation product usually predominates in the mixture of the two which is obtained from these reactions. Thus, toluene is arylated almost exclusively in the ortho-position (Gomberg and Pernert, loc.cit.). It seemed necessary before proceeding further, therefore, to investigate the orientating influence in this reaction of the acetate group in ethyl phenylacetate. For this purpose aniline was substituted for ortho-aminoacetophenone in the reaction. The product obtained on distillation reacted positively for nitrogen. This, coupled with the fact that only a very small yield of diphenyl-2-acetic acid was obtained, would seem to indicate that the reactive methylene group in the ester molecule was taking a predominant part in the reaction. In view of the results obtained with aniline, the attempt to condense ortho-aminoacetophenone with ethyl

phenylacetate was not made, and, as no other simple method seemed available for the preparation of (XIII), the projected synthesis of (X) had to be abandoned.

Further efforts are now being concentrated on the synthesis in quantity of (XV) in order that its ring-widening



XV.

to the dibenz<u>cyclo</u>octanone (IV) may be studied. It is hoped that from the latter substance 1,2:3,4-dibenz-$\Delta^{1,3,5,7}$-<u>cyclo</u>octatetraene (I) may ultimately be obtained.

EXPERIMENTAL

Ortho-iodobenzoic acid.

Anthranilic acid (110gms) dissolved in a solution of concentrated hydrochloric acid (176ccs) and water (1,200ccs) was treated at 5°C with a solution of sodium nitrite (60gms) in water (150ccs). To the diazo-solution thus obtained was gradually added potassium iodide (168gms) in water (200ccs), and the reaction completed on the water-bath. Crude ortho-iodobenzoic acid (174gms, 87%) was precipitated on cooling.

Ortho-iodobenzoylchloride.

The crude acid (100gms) was refluxed for 1.5 hours with a large excess of thionyl chloride (4-5mols). After removal of the excess thionyl chloride, ortho-iodobenzoylchloride (97gms, 90%) was obtained by distillation, b.pt. $162^{\circ}/25mm.$, m.pt. 32° (cf. Cohen, Raper, J., 1904, 85, 1272).

(Ortho-iodobenzoyl)-aniline.

The acid chloride (158gms) dissolved in dry benzene (600ccs) was cooled in ice and treated slowly with shaking with a solution of aniline (120gms) in carbon tetrachloride (250ccs). The precipitated anilide was filtered off and freed from aniline hydrochloride by thorough washing with dilute hydrochloric acid and water. A further small quantity was obtained by evaporating the washed and dried benzene-carbon tetrachloride solution. Yield 135 gms., 97%. It was only slightly soluble in ether, and formed colourless needles m.pt. 142.5° from aqueous alcohol or toluene.

(Found: C, 48.6; H, 3.0. $C_{13}H_{10}ONI$ requires: C, 48.3; H, 3.1%)

Ortho-iodobenzaldehyde.

The anilide (100gms) suspended in dry toluene (100ccs) was treated with phosphorus pentachloride (65gms) and heated on the water-bath until hydrogen chloride was no longer evolved. The residue obtained by removal of the toluene and phosphorus oxychloride under reduced pressure on the water-bath was dissolved in the minimum of ether and treated under reflux, with very strong ice-cooling, with a solution of anhydrous stannous chloride (120gms) in dry ethereal hydrogen chloride (200ccs). Much heat was developed. After two hours standing and shaking, the clear ether was decanted and the orange-yellow crystals added slowly with vigorous stirring to water and ether. (More vigorous conditions caused extensive polymerisation.) The mixture was steam-distilled, the aldehyde taken up in ether, washed with sodium carbonate and water, and the solution dried, evaporated and the residue distilled. The aldehyde (55gms, 77%) had b.pt. $129^{\circ}/15mm$, m.pt. 37°, semicarbazone, m.pt. 206° (Stuart, J., 1888, 53, 141; Wilgeradt and Rieke, Ber., 1905, 38, 1479). Some resinous material, and 15gms of the anilide remained in the steam-distillation flask.

Ortho-iodobenzaldehydediethylacetal.

Ortho-iodobenzaldehyde (12gms), orthoformic ester (8gms) and absolute alcohol (8gms) were treated with dry powdered

ammonium chloride (.1gm) and refluxed for 1.5 hours. After removal of the alcohol by distillation, the mixture was extracted with ether and washed with water containing a trace of ammonium hydroxide. After drying over potassium carbonate, the ether was removed and the diethylacetal (12gms) obtained by distillation as a light yellow oil, b.pt. $159^{\circ}/_{23mm}$. $n_D^{18^{\circ}}$ 1.5428. Boiling with dilute hydrochloric acid regenerated the aldehyde.

Diphenyl-2:2'-dialdehyde. (cf. Mayer, Ber., 1911, 44, 2304)

Equal weights of ortho-iodobenzaldehyde and copper-bronze were heated, in an atmosphere of hydrogen, in an oil-bath gradually warmed to 200-220°C. The violent reaction which suddenly set in had to be carefully controlled in order to obtain good yields. Extraction with ether, followed by distillation, gave benzaldehyde, b.pt. $75^{\circ}/_{20mm.}$ (Yield 12%, identified by its oxidation by alkaline permanganate to benzoic acid, and the preparation of its semicarbazone, m.pt. 214°), and diphenyl-2:2'-dialdehyde (yield 70%) b.pt. $179^{\circ}/_{2mm}$, m.pt. 63°, dioxime m.pt. 186-7° (Hannon and Kenner, J., 1934, 138). The action of copper-bronze on ortho-iodobenzaldehyde-diethylacetal gave a product which did not have a constant boiling-point, and it seemed probable that reaction was far from complete.

Reaction between Diphenyl-2:2'-dialdehyde and Succinic Acid. (cf. Kuhn and Winterstein, Helv.Chim.Acta., 1928, 11, 87).

Succinic acid (5.5gms), diphenyl-2:2'-dialdehyde (10gms) lead oxide (10.5gms) and acetic anhydride (14.5gms) were heated

gently until the solution was clear. The flask was then heated in an oil-bath at 150°C for five hours and cooled slowly. No precipitation occurred. The material was treated in the cold with very dilute nitric acid and extracted with ether. Washing with alkali removed much acidic material, and evaporation of the ether gave diphenyl-2:2'-dialdehyde (2.7gms).

Reaction between Benzaldehyde and Succinic Acid.

A similar experiment using benzaldehyde (2mols), in place of the dialdehyde, gave analogous results. Some benzaldehyde was recovered on steam-distillation, and treatment of the dark brown liquid residue in the steam-distillation flask with very dilute nitric acid, as above, left a mixture of acids which could not be separated into its components. When this was attempted by distillation at 1mm. pressure, decomposition occurred with much effervescence. The distillate (b.pt. $150^{\circ}/1mm.$ to $250^{\circ}/10mm.$) was completely soluble in alkali, giving a deep red solution. (Diphenylbutadiene was obtained by Rebuffet - Gazzetta, 1885, 15, 107; 1890, 20, 154 - by distilling phenylcinnamylacrylic acid).

Ortho-nitrophenylacetic ester. (cf. Wislicenus, Thoma, Ann., 1924, 436, 45; Reissert, Ber., 1897, 30, 1036; 1908, 41, 3925)

Potassium (13gms) was covered with ether (50ccs) and treated dropwise with absolute alcohol (ca.60ccs). When solution was complete, oxalic ester (49gms) was added, the

solution set aside for fifteen minutes, and ortho-nitrotoluene (46gms) added. After standing overnight, the calculated quantity of concentrated sulphuric acid (10ccs) in ether was carefully added. The ethereal solution was washed with water, and the ortho-nitrophenylpyruvic ester removed with alkali. Acidification of these extracts gave the corresponding acid, which was not collected, but after again making the solution alkaline, hydrogen peroxide was run in until a test-portion no longer gave a deep red colour with strong alkali. Acidification gave ortho-nitrophenylacetic acid (40gms, 67%) m.pt. 141° from water. (An attempt to convert ortho-nitrophenylpyruvic ester by distillation at 4mm. directly to ortho-nitrophenylacetic ester failed. An extremely violent decomposition set in with gaseous effervescence and a tarry residue remained.) The acid (80gms) in absolute alcohol (350ccs) was treated with dry hydrogen chloride (10gms) and refluxed overnight. After working up in the usual way, the ethereal extracts on evaporation gave the ester (82gms, 90%) m.pt. 69°. (Reissert, Scherk, Ber., 1898, 31, 395).

Reduction of Ortho-nitrophenylacetic ester.

(a) By Aluminium Amalgam. Reduction was carried out in alcoholic or aqueous alcoholic solution with a large excess of amalgamated aluminium foil. The amine was obtained as a reddish-brown oil in 15-20% yield. (cf. Neber, Ber., 1922, 55, 826). Loss of material occurred on dissolving the amine

in dilute acid and precipitating with dilute alkali.

(b) By Stannous Chloride. The nitro-ester (50gms) in alcohol (300ccs) was added slowly with tap-cooling to stannous chloride (150gms) in concentrated hydrochloric acid (150ccs) and alcohol (100ccs). No stannichloride was deposited on standing overnight. An excess of ether was added, and 2N alkali slowly run in with cooling until the tin salts were just dissolved. Extraction of the ethereal solution with dilute hydrochloric acid and precipitation with dilute alkali gave the amine (13gms, 28%). The ethereal solution contained 12gms. of starting material.

Ethyl Ortho-iodophenylacetate.

Ortho-amino-phenylacetic ester (19gms) in ice-cold water (100ccs) and concentrated hydrochloric acid (23ccs) was treated slowly at 5°C with a solution of sodium nitrite (8gms) in water (20ccs). To the cold solution was added potassium iodide (20gms) in water (20ccs), and the reaction completed on the water-bath. Extraction with ether gave ethyl ortho-iodophenylacetate (5.8gms, 20%) b.pt. $128^{\circ}/3mm.$ It formed colourless needles, m.pt. 42-43°, from cold acetic acid by addition of water, identical with the material prepared as described below from ortho-iodotoluene.

Ortho-iodotoluene.

Ortho-toluidine (107gms) dissolved in concentrated hydrochloric acid (250ccs) and water (250ccs) was treated

at 5-7°C with sodium nitrite (76gms) in water (200ccs). To the cold diazonium solution thus obtained was added slowly potassium iodide (200gms) in water (200ccs). A reaction set in gradually on standing, the temperature rising spontaneously to 40°C. After heating on the water-bath to complete the reaction, the crude iodo-toluene was separated and steam-distilled from alkali. Distillation gave 160-170gms., b.pt. $85^{\circ}/13mm.$ $n_D^{18^{\circ}}$ 1.6050.

Ortho-iodobenzylbromide. (cf. Baum, Ber., 1894, 27, 3233).

Bromination was carried out in direct sunlight at an oil-bath temperature of 220-230°. Ortho-iodotoluene (153gms) was placed in a round-bottomed two-necked flask of about 100cc. capacity so that it was almost filled. An efficient condenser was used, and bromine (56gms, half the theoretical quantity) was added through a dropping-funnel on to the surface of the liquid at a constant rate over about thirty minutes. Heating was continued for a few minutes after the addition was complete, the liquid being then transferred to a flask and distilled. Ortho-iodotoluene, contaminated with iodine, was recovered (40gms, after purification and re-distillation), and ortho-iodobenzylbromide, m.pt. 52-3° (67.5gms, 65%) collected at $125^{\circ}/4mm.$ An attempt to prepare ortho-iodobenzylchloride by the action of sulphuryl chloride on ortho-toluene failed. (cf. Kharash and Brown, J.Amer.Chem.Soc., 1939, 61, 2142, who were unable to chlorinate either ortho- or para-nitrotoluene in this way).

Ortho-iodobenzylcyanide.

Ortho-iodobenzylbromide (112gms) was treated with potassium cyanide (75gms, 3mols) in alcohol, and heated under reflux on the water-bath for three hours. After distilling off the alcohol, the product was taken up in ether and the nitrile (73.5gms, 80%) distilled. It had b.pt. $155^{\circ}/_{4mm.}$ from a bare flame, but $140^{\circ}/_{4mm.}$ from an oil-bath or when a column was used.

Ortho-iodophenylacetic Acid.

The nitrile (72gms) was heated in an oil-bath at 170°C for two hours with concentrated sulphuric acid (150ccs) and water (150ccs.) After cooling and careful dilution with water the acid (60gms, 77%) was extracted with ether and removed with dilute alkali in the usual way. Recrystallised from light petroleum (80-100) it had m.pt. 114° (Frederick, Dippy and Lewis, J., 1936, 646).

Refluxed for twelve hours with alcohol containing a little sulphuric acid the ethyl ester was obtained in 90% yield. It had m.pt. 42-43° and was identical by mixed melting point with the material obtained, as described above, from ortho-nitrotoluene.

Ortho-iodocinnamaldehyde.

Ortho-iodobenzaldehyde (90gms) in dry alcohol (100ccs) was added to a solution of acetaldehyde (33gms, 2mols) in alcohol (150ccs). To the ice-cold solution was added dry diethyl-amine (1.5ccs) in alcohol 50ccs) and the whole left

at room temperature (ca.18°C) for three days. After just acidifying with 2N sulphuric acid, the solution was evaporated to about 125ccs., extracted with ether and the solution washed thoroughly with water. The product was separated by distillation into two fractions boiling above and below $140^{\circ}/_{3mm.}$ respectively. Redistillation of these fractions gave recovered ortho-iodobenzaldehyde, b.pt. $102^{\circ}/_{3mm.}$ (50gms), and ortho-iodocinnamaldehyde, b.pt. $155^{\circ}/_{3mm.}$ (30gms, 30%) which crystallised in prisms from light petroleum (80-90), m.pt. 78-79°. Oxidised by ammoniacal silver oxide, it gave ortho-iodocinnamic acid, m.pt. 216-217°. (Weitzenbock, Monatsh., 1913, 34, 193).

o:o'-Di-iodo-1:4-diphenylbutadiene.

Ortho-iodophenylacetic acid (18.3gms), ortho-iodocinnamaldehyde (18gms), lead oxide (7.8gms) and acetic anhydride (10ccs) were heated under reflux in an oil-bath at 150-160° for five hours with exclusion of moisture (cf. Kuhn and Winterstein, Helv.Chim.Acta., 1928, 11, 87). The hot liquid was transferred to a small beaker and left overnight. The almost solid mass was diluted with a little cold acetic acid, filtered, and washed with acetic acid (5ccs). The product (14gms) was extracted with boiling acetic acid (50ccs), the material which crystallised out on cooling being filtered off and the mother-liquor used again until four or five lots of crystals had been collected. The material which remained undissolved (10gms) had a very low solubility in

most organic solvents except pyridine and dioxane, in both of which it was extremely soluble. It separated as an oil from aqueous pyridine. Recrystallisation from a large volume of xylene gave o:o'-di-iodo-1:4-diphenylbutadiene in small colourless rhombohedra, m.pt. 249-250°. (Found: C, 42.0; H, 2.6. $C_{16}H_{12}I_2$ requires: C, 42.0; H, 2.6%). As obtained after the acetic acid extraction, the material was almost pure, and for ordinary purposes was best recrystallised from aqueous dioxane. The material which had crystallised from the acetic acid extractions was taken up in hot benzene (10-15ccs), filtered, and another form of o:o'-di-iodo-1:4-diphenylbutadiene (2.5gms) obtained by adding about 20ccs. of absolute alcohol to the filtrate. It crystallised in yellow needles, m.pt. 180-181°, which if left in contact with the mother-liquor formed rhombohedra of the same melting-point. It had a much higher and more general solubility in organic solvents than the isomer of m.pt. 249-250°. (Found: C, 42.2; H, 2.6. $C_{16}H_{12}I_2$ requires: C, 42.0; H, 2.6%). Total yield 40%.

Action of Copper Bronze on o:o'-di-iodo-1:4-diphenylbutadiene. (1) The isomer of m.pt. 249-250° (3gms) dissolved in quinoline (6ccs) was heated in a metal-bath until the quinoline was just refluxing. Copper bronze (3gms) was added in small portions and the heating continued for fifteen minutes after the addition was complete. Reaction was vigorous. After thorough extraction with benzene, the quinoline was removed by washing

with dilute hydrochloric acid, and the benzene evaporated. The product was mainly resinous in character, but after repeated recrystallisation from small volumes of benzene most of the resinous material was removed and the small amount of crystalline substance remaining had m.pt. 200-202°, but was probably not quite pure. It gave a positive reaction for iodine. (Found: C, 56.3; H, 2.9. $C_{32}H_{24}I_2$ requires: C, 58.0; H, 3.6%).

(2) When the reaction was carried out in the absence of quinoline, and the metal-bath maintained at 280° for a few minutes after the violent reaction had subsided, the product was identical with that described above but was present in smaller amount, there being more resinous material present.

Attempts to separate reaction products from these experiments by distillation at 2mm. pressure failed. Decomposition and resinification occurred, and no distillate was obtained.

(3) The material (m.pt. 249-250°) (4gms) in quinoline (40ccs) was gradually warmed with copper bronze (4gms) and then refluxed overnight. After cooling, the quinoline was removed by the addition of an excess of hydrochloric acid and the mixture filtered. Extraction of the precipitate with ether and evaporation of the latter gave a viscous reddish mass containing some crystalline material. Removal of this with light petroleum gave trans-1:4-diphenylbutadiene (.3gm, 16.8%)

m.pt. and mixed m.pt. 152.5-153.5°. The remaining material could not be obtained in a crystalline form.

Experiments similar to those described above were conducted with the isomer of m.pt. 160-161°. When a small quantity of quinoline was used as solvent, most of the starting material was recovered unchanged, even after refluxing for a considerable time in contact with the copper bronze. In dilute solution in quinoline no reaction occurred. When the heated material (2gms) was treated slowly, in an atmosphere of carbon dioxide, with copper bronze, and the temperature then maintained at 300° for fifteen minutes, the benzene extracts yielded on evaporation a very viscous substance which could not be distilled at 2mm. pressure, and did not form a picrate. In contact with absolute alcohol it solidified to a non-crystalline solid, soluble in ether, benzene, ethyl acetate and carbon tetrachloride, and insoluble in alcohol and acetic acid. Attempts to obtain the material in a crystalline form failed, but partial purification was achieved by repeated precipitation from ethyl acetate by addition of absolute alcohol. The material contained iodine and had m.pt. about 200°, although it liquefied when heated with some solvents of b.pt. below 80°. (Found, C, 69.0; H, 4.1. $C_{48}H_{36}I_2$ requires: C, 66.5; H, 4.2%).

Reaction between Diphenyl-2:2'-dialdehyde and Diethylsuccinate. (cf. Cordier, Ann.Chim., 1931, 15, 228)

The dialdehyde (8.4gms, 1mol) and diethylsuccinate (7.0gms 1mol) were treated with thin slices of sodium (2.5gms) and a

loc.cit., and Graebe and Aubin, Ann, 1888, 247, 263, give m.pt. 217°.)

Diphenic Dichloride. (Graebe and Aubin, loc.cit.)

Diphenic anhydride (34gms) was heated in an oil-bath at 180° with phosphorus pentachloride (34gms) until the reaction set in. After removal of the phosphorus oxychloride at the pump, the acid chloride (40gms, 97%, m.pt. 96-97°) was recrystallised from benzene.

Fluorenone-4-carboxylic Acid.

When an attempt was made to purify the crude acid chloride of diphenic acid as obtained above, by distillation at 4mm. pressure, decomposition occurred with gaseous effervescence. (It has been stated by Graebe and Aubin, Ann., 1888, 247, 261, that the acid chloride can be distilled unchanged, but when heated with phosphorus oxychloride, the chloride of fluorenone-4-carboxylic acid is obtained.) The residue in the distillation flask was washed with ether, boiled with alkali, and the acid precipitated with hydrochloric acid. Recrystallisation gave fluorenone-4-carboxylic acid, separating in yellow needles from aqueous alcohol, m.pt. 227°. It gave a red colour with concentrated sulphuric acid, depressed the melting-point of diphenic acid, and gave no depression when mixed with an authentic specimen prepared from diphenic acid by the action of sulphuric acid (Graebe and Aubin, loc.cit.).

Ethyl Diphenyl-2:2'-diacetate.

Diphenic dichloride (7gms) in dry ether (80ccs) was added slowly to diazomethane (ca.7gms) in ether (100ccs) cooled in a freezing mixture. After two hours at room temperature the ether was removed at the pump and the product (7gms) recrystallised from benzene. It formed minute plates which darkened at 115° and melted with decomposition at 121°. It was dissolved in absolute alcohol (150ccs) and heated on the water-bath for one hour with silver oxide prepared from 10% silver nitrate solution (40ccs). Charcoal was added, and the solution boiled and filtered. The residue obtained on evaporation of the alcohol was distilled giving diphenyl-2:2'-diacetic ester, b.pt. 180-200°/4mm. (2.5gms). Hydrolysed in the usual way with alcoholic potassium hydroxide solution, diphenyl-2:2'-diacetic acid was obtained, m.pt. 153-154° from water. (Kenner and Turner, J., 1911, 99, 2104).

The Action of Copper Bronze on Ethyl Ortho-iodophenylacetate.

Ortho-iodophenylacetic ester (20gms) was heated in a metal-bath at 270°. Copper bronze (10gms) was added in small portions, and the bath then maintained at 290° for thirty minutes. After cooling, the mixture was extracted with ether. Distillation gave phenylacetic ester, b.pt. 85-90°/4mm. (3gms, 26.7%), and recovered ortho-iodophenylacetic ester contaminated with phenylacetic acid, b.pt. 128°/4mm. (7gms). The material (1.5gms) boiling between 140°/4mm. and 220°/4mm. was hydrolysed with aqueous alcoholic alkali in the usual way. The small amount

of acid obtained was identified as ortho-iodophenylacetic acid. The neutral material remaining, which was not further examined, formed orange-coloured needles, which were still unmolten in a bath at 280°.

The same results were obtained when copper bronze which had been activated by the method of Kliedener and Adams (J. Amer. Chem. Soc., 1933, 55, 4225) was used.

Ortho-bromophenylacetic acid. (cf. Frederick, Dippy and Williams, J., 1934, 1891).

Phenylacetic acid (50gms) mercuric oxide (45gms) and water (400ccs) were cooled in ice and treated dropwise over one hour with bromine (13.5ccs). After stirring for a further hour, excess sodium hydroxide was added, the mixture filtered, acidified and extracted with ether. Distillation through an efficient column gave phenylacetic acid (15.6gms) b.pt. 127-128°/4mm, and a mixture of bromination products b.pt. 148-150°/4mm. (50gms). This material could not be separated into its components by repeated recrystallisation from light petroleum (80-90), but by removal of the first material to crystallise on each occasion, ortho-bromophenylacetic acid (10gms) m.pt. 104-105.5° was obtained. Oxidised by alkaline potassium permanganate it gave ortho-bromobenzoic acid, m.pt. 150°. The rest of the material could not be further separated into its components, and showed a remarkably constant melting-point of about 76-78°, not altered by numerous attempts at

purification. That it was almost pure para-bromophenylacetic acid, however, was shown by the fact that on oxidation with alkaline permanganate it gave pure para-bromobenzoic acid, m.pt. 251-253°, after one recrystallisation from aqueous alcohol. (Frederick, Dippy and Williams, loc.cit., obtained 4.5gms of the ortho-acid by the bromination of 10gms of phenylacetic acid.)

Ethyl Ortho-bromophenylacetate.

Ortho-bromophenylacetic acid (6.5gms) in alcohol (25ccs) was treated with concentrated sulphuric acid (.5cc) and refluxed overnight. The alcohol was removed, the product taken up in ether and washed with sodium carbonate solution. On distillation the ethyl ester was obtained as a colourless oil b.pt. $114^{\circ}/_{4mm.}$ which crystallised in colourless needles on standing, and had m.pt. 35-36° from cold aqueous acetic acid. Yield 6.6gms, 90%.

Action of Copper Bronze on Ethyl Ortho-bromophenylacetate.

The ester (6gms) and copper bronze (6gms) were heated for three hours in a sealed tube at 300°C. On warming the sealed end of the tube it opened with explosive violence, great pressure having been developed. The copper, after thorough extraction with ether was contaminated by a black insoluble powdery substance. Distillation of the material obtained from the ether extracts gave low-boiling materials (.2gm), phenylacetic acid (.2gm) (identified by melting point and mixed melting point), and a residue of resinous material (ca.1gm)

which decomposed on further distillation.

Condensation of Ortho-iodobenzoylchloride and Ethyl acetoacetate.

In the following preparation a key reference - (Needham and Perkin, J., 1904, 85, 151) - was missed, and difficulties were encountered as a result. Sodium (12.5gms, 1mol) in thin shavings was added slowly to a cooled solution of ethyl acetoacetate (76gms, 1.1mols) in dry ether (300ccs) and the reaction completed by standing overnight. A solution of ortho-iodobenzoylchloride (140gms) in ether (150ccs) was added, and the mixture refluxed for a short time to complete the reaction. (cf. Gevekoht, Ann., 1883, 221, 323). Removal of the precipitate and evaporation of the ether left a dark brown oily condensation product, probably di-(iodo-benzoyl)-acetoacetate. (cf. Claisen, Ann., 1896, 291, 67). That the material did not contain ethyl ortho-iodobenzoate was shown by warming a portion under reduced pressure, when all low-boiling impurities were removed below $100^{\circ}/4mm$. The material itself could not be distilled.

Hydrolysis of the above Condensation Product.

The condensation product (36gms) was refluxed with water (100ccs) and concentrated sulphuric acid (50ccs) for seven hours (cf. Gevekoht, loc.cit.). The product was taken up in ether, and alkali soluble material removed with 2N sodium hydroxide. Evaporation of the ether gave a product (6.3gms) b.pt. $110-125^{\circ}/4mm$. (Found: C, 39.0; H, 3.0. C_8H_7OI requires:

C, 39.0; H, 2.8. $C_9H_9O_2I$ requires: C, 39.1; H, 3.4%), which on saponification with dilute aqueous-alcoholic alkali gave both ortho-iodobenzoic acid (3gms) (m.pt. and mixed m.pt. 162°), and ortho-iodoacetophenone (2.5gms) b.pt. 112-113°/4mm. 140°/13mm. $n_D^{20°}$ 1.6180, oxime m.pt. 130-132°. (Auwers, Lechner and Bundesmann, Ber., 1925, 58, 50). It gave a semicarbazone, which separated in colourless needles from aqueous alcohol, m.pt. 178.5-179.5°. (Found: C, 35.9; H, 3.3. $C_9H_{10}ON_3$ requires: C, 35.7; H, 3.3%). Ethyl ortho-iodobenzoate (b.pt. 122°/4mm. $n_D^{21°}$ 1.5850) could be obtained in a pure state from the mixture by allowing sufficient time for complete formation of the oxime or semicarbazone to take place. The alkali-soluble material, precipitated with hydrochloric acid and refluxed for eight hours with alcohol (100ccs) and concentrated sulphuric acid (5ccs), gave 4.9gms b.pt. 110-125°/4mm. which on treatment as above gave ortho-iodobenzoic acid (2.3gms) and ortho-iodoacetophenone (2gms). The alkaline extracts from this experiment (alkali ca.N) on refluxing for two hours gave ortho-iodoacetophenone (4.5gms), isolated by extraction with ether, and the remaining alkaline solution on acidification gave ortho-iodobenzoic acid (1gm.)

The condensation product when hydrolysed with either alcohol or aqueous alcohol (1:1) containing 10% of sulphuric acid (cf. Kermack, Smith, J., 1929, 815) gave ethylacetate, which was removed by distillation with the alcohol, and ortho-iodoacetophenone and ethyl ortho-iodobenzoate in the approximate

ratio of 3:4 respectively.

Reaction between Copper, Ortho-iodoacetophenone, and Ethyl Ortho-iodophenylacetate.

Ortho-iodoacetophenone (28.5gms, 2mols) and ortho-iodophenylacetic ester (17gms, 1mol) were heated in a metal-bath at 275°C. Copper-bronze (30gms) was added in small portions. Reaction was vigorous, the internal temperature rising to that of the bath so that the mixture was just refluxing. When the addition was complete and the reaction had subsided, the metal-bath was kept at 290° for ten minutes. Extraction with ether and distillation gave acetophenone (5.5gms, 39%, b.pt. 90-100°/13mm $n_D^{19°}$ 1.5342, semicarbazone, m.pt. and mixed m.pt. 201°), recovered ortho-iodophenylacetic ester (9gms) (impure), a reaction product b.pt. 200°/4mm. (5gms), and a highly resinous residue which decomposed on further distillation. The material b.pt. 200°/4mm. was soluble in organic solvents with the exception of light petroleum, but could not be induced to crystallise. It formed a very impure semicarbazone, which could not be recrystallised to purity. Treated with solutions of picric acid in benzene, alcohol, etc., no colouration was produced and no picrate was obtained. The material was not hydrolysed by dilute alcoholic potassium hydroxide in the cold or after refluxing for thirty minutes, but when refluxed with its own weight (5gms) of potassium hydroxide in alcoholic solution for six hours, a potassium salt, insoluble in alkali, separated. Acidification

of the aqueous solution of this material gave an acid (1.0gms) soluble in organic solvents with the exception of light petroleum, and insoluble in water. It was not amenable to purification processes, however, and attempts to purify it were ultimately abandoned. The remaining neutral material was not investigated, further than to establish that it was not 2:2'-diacetodiphenyl (m.pt. 94-95°, Cook and Turner, J., 1937, 118), since it had a melting point very considerably higher than this.

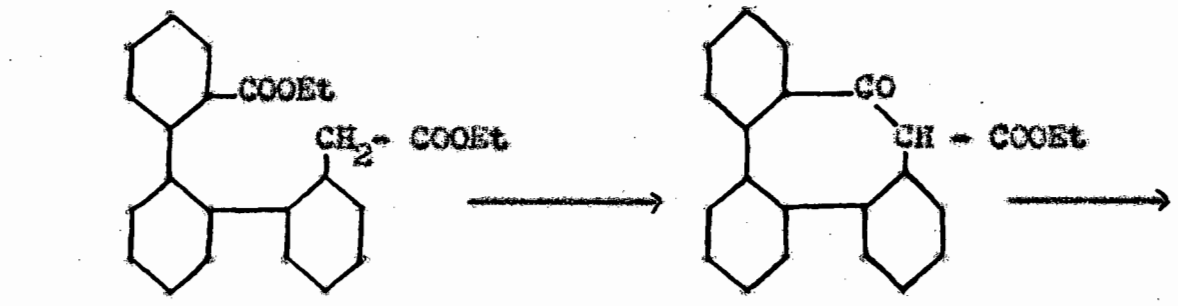
Reaction between Diazotised Aniline and Ethyl Phenylacetate. (cf. Grieve and Hey, J., 1938, 111). Aniline (31gms) in water (35ccs) and concentrated hydrochloric acid (83ccs) was diazotised in the usual way with sodium nitrite (25gms). The diazo-solution was treated with ethyl phenylacetate (350ccs) and at 3°C a solution of sodium hydroxide (27gms) in water (100ccs) added, with vigorous stirring, over three hours. Stirring was continued for 20 hours, the temperature being gradually raised to 25°C. After separation, the ester layer was distilled through an efficient column. The product, b.pt. 150-175°/4mm., was a red liquid which could not be further fractionated and which gave a positive test for nitrogen. Saponification in the usual way with aqueous alcoholic alkali gave a dark-coloured oily acid which reacted positively for nitrogen. Repeated decolourisation of the alkaline solution

of this acid followed by reprecipitation in the hot with strong acid and further repeated recrystallisation from aqueous acetic acid, gave a small quantity of an acid, which did not contain nitrogen, of m.pt. 116-117° (Found: Eq.wt. 210. $C_{14}H_{12}O_2$ requires: Eq.wt. 212). Diphenyl-2-acetic acid has been reported by Schonberg and Warren (J., 1939, 1840) as having m.pt. 116°.

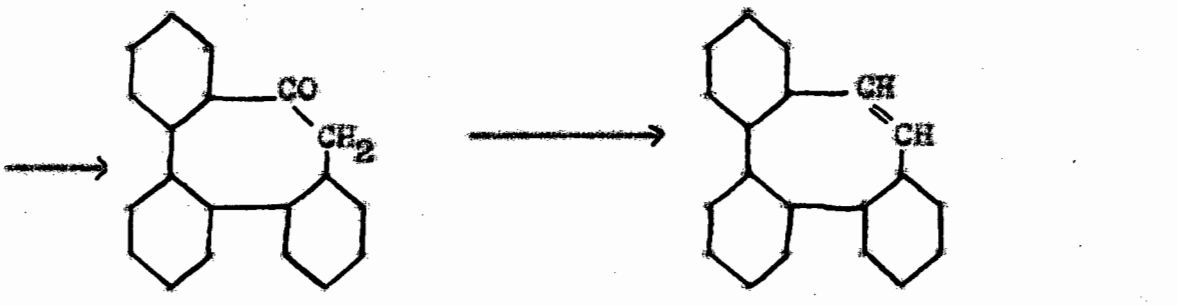
ATTEMPTS TO OBTAIN

1,2:3,4:5,6-TRIBENZ-$\Delta^{1,3,5,7}$-CYCLOOCTATETRAENE

It seemed possible that if diethyl diphenyl-2-carboxylate-2'-(ortho-phenylacetate) (I) could be prepared it might by the Dieckmann reaction yield the keto-ester (II). A study of the keto-enolic tautomerism of the ketone (III) which might be obtained from this compound by a process involving decarboxylation would be of interest, and (III) might possibly be convertible into 1,2:3,4:5,6-tribenz-$\Delta^{1,3,5,7}$-cyclooctatetraene (IV) by reduction and the elimination of the elements of water.



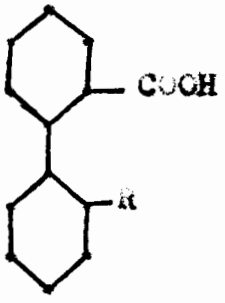
I. II.



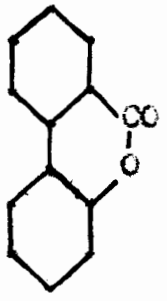
III. IV.

A possible method of obtaining (I) was by the Ullmann reaction on ethyl ortho-iodophenylacetate and ethyl diphenyl-2-iodo-2'-carboxylate (ester of V; R=I), and three possible routes to the latter substance were, therefore, investigated.

The first of these had as its starting-point 2-nitro-2'-carboxydiphenyl (V; $R=NO_2$). The production of this compound



V.



VI.

in low yield by the Ullmann reaction has been described by Bell (J., 1934, 835), Sadler and Powell (J.Amer.Chem.Soc., 1934, 56, 2650) and Finzi, Bellavita (Gazzetta., 1936, 66, 421). By increasing the proportion of ortho-iodonitrobenzene used in the reaction to 1½ mols., the yield of (V) was increased to 68%. Moreover, the product of the reaction under these conditions consisted of only two substances, instead of three, and since one of them was unaffected by alkali, separation was efficient. Attempts were made to prepare 2-amino-2'-carboxydiphenyl (V; $R=NH_2$) from the above nitro-compound without success. Since it was expected that the amino-acid would show a tendency to cyclise to phenanthridone (which is stable to boiling alkali - Graebe, Mauer, Ann., 1895,

276, 248), only those reduction methods were tried which employed salts of the nitro-acid. Successful reductions of somewhat similar compounds by these procedures have been described by Pschorr (Ber., 1906, 39, 3109) and Meber (Ber., 1922, 55, 834). These methods, however, did not succeed in this case. The fact that the ferrous hydroxide gave the characteristic colour change on addition of a solution of the ammonium or barium salt of the nitro-acid, seemed to indicate that reduction was occurring. No material was recoverable from the filtrate, however, and it is concluded therefore that an insoluble substance, doubtless phenanthridone, was formed as a result of the reduction.

This route to 2-iodo-2'-carboxydiphenyl being closed, the oxidation of 2-methyl-2'-iododiphenyl was investigated. It was found that this substance was oxidised completely by alkaline permanganate, and although it was somewhat more stable to chromic acid, the yield of 2-iodo-2'-carboxy-diphenyl was so low as to make the method of little value for the preparation of the latter compound in quantity. It would seem that 2-methyl-2'-iododiphenyl is much less stable to oxidation than either 4-bromo-4'-methyldiphenyl (since the methyl group here was almost quantitatively oxidised by chromic acid) or 2-bromo-4'-methyldiphenyl, which could be oxidised to the corresponding acid by either permanganate or chromic acid (Gomberg and Pernert, J.Amer. Chem.Soc., 1926, 48, 1378).

The method ultimately employed for the production of 2-iodo-2'-carboxydiphenyl was by the action of a restricted amount of copper upon ortho-iodobenzoic ester and a 2-molar proportion of ortho-di-iodobenzene. The reaction was difficult to control, and the respective yields of the three possible condensation products varied somewhat. By repeating the reaction with the easily recoverable ortho-di-iodobenzene quite reasonable yields of 2-iodo-2'-carboxydiphenyl were possible.

It was at this stage in the investigation that it was found that ethyl ortho-iodophenylacetate did not behave normally in the Ullmann reaction, but it was hoped that by using a three molar proportion of this compound in admixture with ethyl-2-iodo-2'-carboxylate, and conducting the reaction in a sealed tube, the required condensation product (I) might be obtained. The products obtained by this procedure, however, were phenylacetic acid and 3:4-benzcoumarin (VI). The free radical mechanism which is advanced (see later) for the Ullmann reaction could explain the formation of such a substance from ethyl 2-iodo-2'-carboxylate.

EXPERIMENTAL

Ortho-iodonitrobenzene. (cf. Ullmann, Ber., 1896, 29, 1880).

Ortho-nitraniline (30gms) was dissolved in concentrated sulphuric acid (45gms) and poured on ice (250gms). A solution of sodium nitrite (16.5gms) in water (50ccs) was then added slowly, with stirring, below the surface of the liquid. The cold diazo-solution was poured in a thin stream into a vigorously stirred solution of potassium iodide (60gms) in water (100ccs) originally at 40°C. After warming for a short time on the water-bath, the mixture was cooled, the ortho-iodonitrobenzene (50gms, 90%) separated, its ethereal solution washed with alkali and thiosulphate, and the material distilled, b.pt. $154^{\circ}/_{14mm.}$ m.pt. 54° from aqueous alcohol.

Ethyl Ortho-iodobenzoate.

Ortho-iodobenzoic acid (57gms) in absolute alcohol (300ccs) was treated with dry hydrogen chloride (10gms) and refluxed overnight. After working up in the usual way the ester (57gms, 90%) was distilled, b.pt. $122^{\circ}/_{4mm}$, $147^{\circ}/_{13mm.}$ $n_D^{21^{\circ}}$ 1.5850. Yields of 75% were obtained when sulphuric acid was used as catalyst. The methyl ester was obtained in 7% yield by the action of dimethyl sulphate on the solution of the acid in sodium carbonate.

2-Nitro-2'-carboxydiphenyl.

Ethyl ortho-iodobenzoate (34gms, 1mol) and ortho-iodonitrobenzene (50gms, 1½mols) were mixed in a large hard-glass

test tube and heated in a metal-bath at 250°. Copper bronze (45gms) was added slowly over twenty minutes with stirring. The internal temperature rose to between 290° and 340°, depending on the rate of addition, but the yield was reduced at temperatures above 300°. The bath was then kept at 300° for a few minutes, the tube cooled and the mixture extracted with organic solvents. Distillation gave 36gms, b.pt. 185-195°/2mm, which was hydrolysed by refluxing for two hours with potassium hydroxide (12gms) in alcohol. After distilling off the alcohol, water was added and the precipitated 2:2'-dinitrodiphenyl (10gms), m.pt. 124°, (Gull, Turner, J., 1929, 496) thoroughly extracted with ether. Acidification of the alkaline solution with acetic acid gave 2-nitro-2'-carboxydiphenyl (21gms, 68%) which formed yellow plates from aqueous acetic acid, m.pt. 166-168° (cf. Sadler, Powell, J.Amer.Chem. Soc., 1934, 56, 2650). No diphenic acid could be isolated on further acidification with mineral acid.

Action of Reducing Agents on 2-nitro-2'-carboxydiphenyl.

The nitro-acid (8gms) was dissolved in hot 2N ammonia (75ccs) and added slowly to a mixture, heated on the water-bath, of ferrous sulphate (65gms, 7mols) in water (175ccs) and concentrated ammonia (150ccs). (cf. Pschorr, Ber., 1906, 39, 3109). The mixture was kept hot for thirty minutes, filtered, and the precipitate thoroughly washed with boiling water. The filtrate gave a slight milkiness at the neutral point, and on evaporation to dryness yielded only traces of

organic material. In a number of experiments using less severe conditions (e.g. carrying out the reduction entirely in the cold) the results were the same.

Using barium hydroxide in place of ammonia (cf. Neber, Ber., 1922, 55, 834), a barium salt could not be isolated from the filtrate. Extraction of the precipitate with alcohol also did not result in the isolation of a product.

2-Methyl-2'-nitrodiphenyl.

Ortho-iodotoluene (32gms, 1mol) and ortho-iodonitrobenzene (64gms, 1½mols) were heated in a metal-bath at 230°. Copper bronze (45gms) was added in spoonfuls over fifteen minutes. The internal temperature rose to 245°, and the metal-bath was maintained at 260° for thirty minutes after the addition of the copper. Extraction with hot benzene, followed by distillation through a short efficient column, gave recovered ortho-iodotoluene (13gms), 2-methyl-2'-nitrodiphenyl (11.5gms, 37%) b.pt. $143^{\circ}/_{4mm}$, m.pt. 57-58° (Sadler and Powell, J.Amer.Chem.Soc., 1934, 56, 2650, give $150\text{-}155^{\circ}/_{2mm}$), and 2:2'-dinitrodiphenyl, b.pt. $194^{\circ}/_{4mm}$ (22.3gms).

2-Methyl-2'-aminodiphenyl. The nitro-compound (14gms) and a little alcohol was treated with tin (17gms) and concentrated hydrochloric acid (35ccs), added in four portions. When the reaction was complete, the flask was heated on a boiling water-bath for one hour, cooled, and sodium hydroxide (25gms) in water (35ccs) added. Extraction with carbon tetrachloride

followed by distillation gave 2-methyl-2'-aminodiphenyl (10gms., 83%) b.pt. 127-128°/4mm, m.pt. 37° (cf. Mascarelli and Gatti, Atti.Acad.Lincei., 1932, 15, 89).

2-Methyl-2'-iododiphenyl. (Mascarelli andGatti, loc.cit.)

The amine (10gms) was treated with concentrated hydrochloric acid (15ccs) and water (50ccs) and cooled to 5°C. Diazotisation was carried out with sodium nitrite (4.2gms) in water (10ccs) and then potassium iodide (11gms) in water (20ccs) added. Reaction started at 10°C and the flask was finally heated to 60°C on the water-bath. The 2-methyl-2'-iododiphenyl was extracted with ether, and purified by washing with alkali and thiosulphate. Distillation gave 10gms. (63%) b.pt. 135-138°/4mm, which solidified on standing.

Oxidation of 2-Methyl-2'-iododiphenyl.

The material was oxidised completely by alkaline potassium permanganate. 2-Methyl-2'-iododiphenyl (2gms) was dissolved in glacial acetic acid (40ccs) and to the ice-cold solution was added chromic anhydride (2gms). After standing overnight the flask was gradually warmed on the water-bath, which was then kept boiling for seven hours, a further 2gms of chromic anhydride being added slowly during the first two hours in small portions. The solution was diluted with water, the product taken up in ether and the acidic material removed with sodium carbonate. Acidification gave 2-iodo-2'-carboxydiphenyl (.5gm, 23%) m.pt. 149-150° from light petroleum (120-130) identical by mixed melting point with the material

prepared as described below. (Found: Eq.wt, 322. $C_{13}H_9O_2I$ requires: Eq.wt, 324).

Ortho-iodoaniline. (cf. Baeyer, Ber., 1905, 38, 2760).

Ortho-iodonitrobenzene (180gms) was slowly added either in the solid state or in solution in alcohol to a cold solution of stannous chloride (760gms) in alcohol (1,000ccs) and concentrated hydrochloric acid (900gms), the temperature being kept below 35°C throughout. After standing overnight the stannichloride was collected, treated with an excess of sodium hydroxide and the precipitate steam-distilled. The yield was never more than 100gms, although Baeyer (loc.cit.) gives 130gms. Evaporation of the alcohol from the mother-liquors under reduced pressure did not yield much steam-volatile material after treatment with alkali as above. McCombie, Ward (J., 1913, 103, 1999) and Montagne (Ber., 1918, 51, 1490) found it necessary to modify the above procedure in the case of the meta- and para-compounds respectively in order to obtain the yields given by Baeyer.

Ortho-di-iodobenzene.

Ortho-iodoaniline (125gms) was warmed with a solution of concentrated hydrochloric acid (150ccs) and water (200ccs), and cooled rapidly to obtain the crystals in a finely divided form. Diazotisation was carried out below 5°C by the gradual addition of sodium nitrite (ca.46gms) in water (100ccs) with stirring. To the diazo-solution thus obtained was added a layer of ether, and then cautiously at 0°C a solution of

potassium iodide (120gms) in water (200ccs). Had insufficient sodium nitrite been added, dangerous explosions occurred in the copious froth produced. The reaction set in at about 10°C, and after warming on the water-bath for some time, the product was separated, taken up in ether, and washed with alkali and thiosulphate. Distillation gave di-iodobenzene (134gms, 71%), b.pt. $109^{\circ}/_{3mm}$, $143^{\circ}/_{13mm}$.

2-Iodo-2'-carboxydiphenyl

Ortho-di-iodobenzene (50gms, 2 mols) and ethyl ortho-iodobenzoate (20gms, 1mol) were heated in a metal-bath maintained at 290-300°. Copper bronze (15gms, i.e., only 1.5 times the theoretical quantity) was added in spoonfuls so that the internal temperature remained at 280-285° and the vigour of the reaction did not subside. When the addition was complete (10-15minutes) heating and stirring were continued for a further ten minutes or more. The mixture was cooled, extracted with ether and the residue obtained on evaporation of the latter distilled from an oil-bath using a short efficient column. The condensation products, b.pt. $160\text{-}175^{\circ}/_{3mm}$, were refluxed with potassium hydroxide (16gms) in alcohol. The mixture, after evaporation of the alcohol, was extracted with ether, and the crude 2-iodo-2'-carboxy-diphenyl (7-10gms) precipitated from the alkaline solution by careful addition of acetic acid. Decolourisation with charcoal and recrystallisation from light petroleum (120-130)

or aqueous acetic acid, gave small colourless prisms, m.pt. 149-150°, identical by mixed melting point with the material obtained from 2-iodo-2'-methyldiphenyl as described above. Further acidification of the mother liquors gave diphenic acid (5-10gms), and evaporation of the above ethereal extract yielded 2:2'-di-iodo-diphenyl (2-4gms) which formed flat colourless prisms of hexagonal outline from alcohol, m.pt. 109°. (Mascarelli, Benati, Atti.Acad.Lincei., 1908, 16, 565, give needles m.pt. 108°, plates on sublimation, m.pt. 109°.)

Ethyl Diphenyl-2-iodo-2'-carboxylate.

The acid (18gms) in alcohol (150ccs) was refluxed for four hours after the addition of dry hydrogen chloride (8gms). The alcohol was distilled off and the ethereal extract washed with sodium carbonate. Distillation gave ethyl diphenyl-2-iodo-2'-carboxylate, b.pt. 168-169°/3mm, as a viscous oil which did not crystallise in the ice chest (17.6gms, 90%).

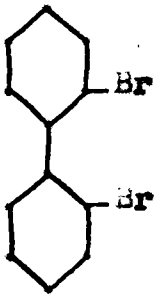
The Reaction between Copper Bronze, Ethyl Ortho-iodophenyl-acetate and Ethyl Diphenyl-2-iodo-2'-carboxylate.

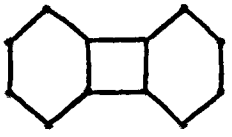
Ethyl diphenyl-2-iodo-2'-carboxylate (10gms, 1mol), ethyl ortho-iodophenylacetate (24gms, 3mols) and copper bronze (20gms) were heated in a sealed tube for three hours at 290-295°. Great pressure was developed in the tube. The copper bronze still retained much of its original lustre, and after extraction with ether and hot benzene, was contaminated

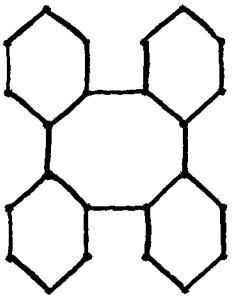
with a dark, powdery, insoluble material. Distillation of the product gave low-boiling materials (3gms), phenylacetic acid, b.pt. $128^{\circ}/_{3mm.}$ (3.4gms), identified by melting point and mixed melting point, and a product b.pt. $180\text{-}200^{\circ}/_{3mm}$ (2.9gms). The resinous material remaining in the flask decomposed on further distillation. The material b.pt. $180\text{-}200^{\circ}/_{3mm.}$ was refluxed for two hours with potassium hydroxide (3gms) in alcohol. After removal of the alcohol, neutral materials were extracted with ether. Acidification of the alkaline solution gave 3:4-benzcoumarin (1.8gms) m.pt. 92.5° from aqueous alcohol. (Graebe, Schestakow, Ann., 1894, 284, 317). (Found: C, 79.7; 79.5; H, 4.1, 4.0. $C_{13}H_8O_2$ requires: C, 79.6; H, 4.1%). The material was insoluble in dilute alkali in the cold, but dissolved slowly on warming. The equivalent weight was estimated by solution in an excess of $\frac{N}{50}$ alkali, followed by back titration. Due to the difficulty of preventing ingress of carbon dioxide during the necessary prolonged warming of the material with the alkali (ca.1-2 hours) before complete solutionwas obtained, the figures only approximated to the theoretical. (Found: Eq.wt. 202. $C_{13}H_8O_2$ requires: Eq.wt. 196).

ATTEMPTS TO OBTAIN DIPHENYLENE AND TETRAPHENYLENE

The action of sodium on 2:2'-dibromodiphenyl (I) was employed by Dobbie, Fox and Gauge (J., 1911, 99, 683; 1913, 103, 36) to produce diphenylene (II). It seemed possible that 1,2:3,4:5,6:7,8-tetrabenz-$\Delta^{1,3,5,7}$-cyclooctatetraene (tetraphenylene) (III) might also result from this or a somewhat similar reaction.





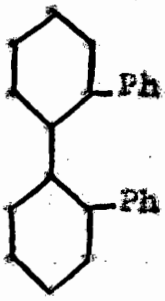


I. II. III.

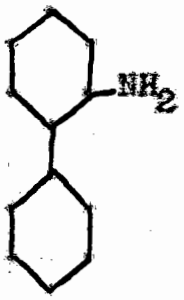
Dobbie, Fox and Gauge were obliged to limit their investigation of diphenylene because of the inaccessibility of 2:2'-dibromodiphenyl in anything but comparatively small quantities. The successful preparation of this substance by Schwechten (Ber., 1932, 65, 1605) made the further study of this hydrocarbon possible. Mascarelli, Gatti and Longo (Gazzetta, 1933, 63, 661), however, were unable to repeat the preparation of diphenylene. Whereas Dobbie, Fox and Gauge obtained diphenylene in almost theoretical yield by the action of sodium on an ethereal or light petroleum solution of 2:2'-dibromodiphenyl, Mascarelli, Gatti and

Longo recovered their 2-2'-dibromodiphenyl even after 200 hours with a large excess of sodium.

In an attempt to elucidate the position, the action of sodium on 2:2'-dibromodiphenyl has been subjected to further examination. When molten sodium was used in the absence of a solvent, only compounds of high molecular weight, of the same general nature as those described by Dobbie, Fox and Gauge, were produced. In the presence of ether the reaction, which was complete after about 200 hours, produced diphenyl and not diphenylene. In a series of experiments in which conditions were rigidly adhered to, it has been established that the formation of this substance is very gradual and cannot be due to ingress of water into the reaction mixture. Its formation is interpreted as reflecting the free-radical mechanism of the reaction, and as being due to steric hindrance preventing the immediate intra-molecular union of the aryl radicals in the manner desired, so that side-reactions occur in which the hydrogen of the solvent plays a part. It was hoped that this interpretation of the reaction might be confirmed by conducting the reaction in the presence of benzene as solvent, and establishing the presence of 2:2'-diphenyldiphenyl (IV) in the reaction products (cf. the Gomberg reaction). No reaction took place, however, when benzene was substituted for ether in this way.



IV.



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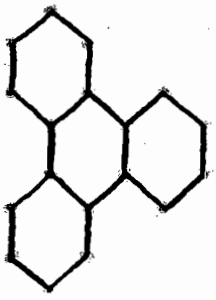

VI.

In view of these results, other possible routes to diphenylene and tetraphenylene were explored. The first of these had as its starting point 2-amino-diphenyl (V). The decomposition of the diazonium salt of this substance in aqueous solution by copper powder (cf. the formation of phenanthrene derivatives, Pschorr, Ber., 1896, 29, 496; 1906, 39, 3106) or by alkali in the presence of a non-ionising solvent (cf. Grieve and Hey, J., 1938, 110) produced diphenyl, a result which is in accord with the free-radical mechanism advanced for such reactions (Grieve and Hey, loc.cit., Hey and Waters, Chem.Reviews, 1937, 21, 169; see also Gomberg and Pernert J.Amer.Chem.Soc., 1926, 48, 1374).

Krizewsky and Turner (J., 1919, 115, 560) showed that by treating a Grignard compound with anhydrous cupric chloride the reaction 2 Ar Mg X ——→ Ar.Ar was facilitated. This reaction seemed to offer some hope of successful application to the production of tetraphenylene and diphenylene, and accordingly both 2:2'-dibromodiphenyl and ortho-di-iodo-

benzene were subjected to these conditions. In both cases by far the greater bulk of the product consisted of materials of high molecular weight. In the case of the 2:2'-dibromodiphenyl condensation, no tetraphenylene could be isolated from the non-steam-volatile part of the product. The steam-volatile material consisted of small amounts of diphenyl and a substance of m.pt. 107°, which formed a picrate and did not contain halogen. The quantity obtained was too small for further examination to be possible. From the ortho-di-iodobenzene condensation the high-molecular-weight material contained triphenylene (VI), while the steam-volatile portion of the product yielded diphenyl and a substance which was almost certainly diphenylene. In the absence of authentic material for mixed melting-point determination, however, and there being too little available for analysis, this could not be confirmed. The contamination of the products in both these condensations by diphenyl, would seem to indicate that in this reaction also a free-radical mechanism is involved.

EXPERIMENTAL

2:2'-Dinitrodiphenyl.

Copper bronze (55gms) was added slowly to ortho-iodonitrobenzene (100gms) heated in a bath at 230°C, so that the internal temperature did not rise above 280°C. Extraction with hot benzene gave 2:2'dinitrodiphenyl in 90% yield, b.pt. $194^{\circ}/_{4mm.}$, m.pt. 124° from alcohol (Gull, Turner, J., 1929, 496).

2:2'-Diaminodiphenyl.

The dinitro-compound was reduced either by the method of Sako (Chem.Abs., 1932, 26, 3246) or as follows:- 2:2'-dinitrodiphenyl (87gms), granulated tin (175gms), and alcohol (50ccs), were treated with concentrated hydrochloric acid (350ccs) in portions of 50ccs. After standing overnight the solution was decanted and treated carefully with sodium hydroxide (275gms) in water. Extraction with carbon tetrachloride gave the amine in 82% yield, b.pt. $168^{\circ}/_{4mm.}$, m.pt. 81° from alcohol.

2:2'-Dibromodiphenyl. (Schwechten, Ber., 1932, 65, 1605)

The amine (45.7gms) was dissolved in water (1,000ccs) and 2N sulphuric acid (600ccs). Diazotisation was carried out at 5°C with sodium nitrite (37gms) in water (100ccs). The cold diazo-solution thus obtained was treated slowly with vigorous stirring, with an ice-cold solution of mercuric

bromide (250gms) and potassium bromide (175gms) in water (2,000ccs). The precipitate was allowed to settle, and after filtration was washed with water, acetone, and finally with ether. The dry yellow powder (242gms) was mixed immediately with dry powdered potassium bromide (450gms) and heated in a hard-glass tube in the manner described by Schwechten (loc. cit.). The residue was extracted with water and ether, the ethereal extracts washed with alkali, water, dried, evaporated and the residue distilled. 2:2'-Dibromodiphenyl (61gms, 79%) had b.pt. 155-157°/4mm., m.pt. 81° from methyl alcohol.

Action of Sodium on 2:2'-Dibromodiphenyl.

(1) Clean sodium (1.5gms) and 2:2'-dibromodiphenyl (3gms) were heated in an oil bath at 115-120°C for five hours, using an air-condenser carrying a calcium chloride tube. Sublimed material was periodically shaken back into the flask. The dark coloured mass was extracted with ether, and evaporation of the latter left a brownish viscous mass which gave no evidence of picrate formation. Traces of 2:2'-dibromodiphenyl were obtained on steam-distillation, and no other steam-volatile material was present. Attempts to isolate a homogeneous product from the material remaining in the steam distillation flask failed.

(2) (cf. Dobbie, Fox and Gauge, J., 1911, 99, 683; 1913, 103, 36). Clean sodium (15gms) was cut under xylene into thin slices and transferred to dry ether contained in the reaction flask. After washing the sodium two or three

times by decantation in order to remove traces of xylene, dry ether (250ccs), which had previously been distilled from either phosphoric oxide or sodium, was added, and the mixture refluxed for 24 hours. Thoroughly dry 2:2'-dibromodiphenyl (10gms) was then added and the mixture refluxed for 250 hours. The apparatus was glass-sealed and adequate precautions were taken against the entrance of moisture. (At the end of 50 hours a reddish-brown precipitate had formed, but after 100 hours reaction was not complete, 2:2'-dibromodiphenyl accompanied by a little diphenyl being obtained on working up.) The ether and suspended matter were decanted and filtered. The material remaining on the filter (.5gm) after washing with water, was purified from benzene-alcohol. It contained halogen and had m.pt. 306°, in agreement with the compound $C_{84}H_{56}Br_2$ isolated in the same way by Dobbie, Fox and Gauge (loc.cit.). The fluorescent ethereal solution was evaporated, and the residue (4.5gms) steam-distilled. The product (2gms) was identified as diphenyl by melting point and mixed m.pt. (Found: C, 93.3; H, 6.4. $C_{12}H_{10}$ requires: C, 93.5; H, 6.5. $C_{12}H_8$ requires: C, 94.7; H, 5.3%). (More concentrated ethereal solutions aided in the formation of compounds of high molecular weight and reduced the yield of diphenyl). The material remaining in the steam-distillation flask had the character of the waxy material, soluble in ether, described by Dobbie, Fox and Gauge (loc.cit.).

(3) 2:2'-Dibromodiphenyl (6gms) in dry benzene (30ccs) was refluxed with molecular sodium for 100 hours. Sodium bromide was not formed, and the starting material was recovered unchanged on working up. An attempt to isolate 2:2'-diphenyldiphenyl from the reaction mixture was not successful.

Attempts to Obtain Diphenylene from Diazotised 2-Aminodiphenyl.

(1) (cf. Pschorr, Ber., 1896, 29, 496). 2-Aminodiphenyl (8.5gms) was warmed with water (450ccs) and 2N sulphuric acid (60ccs), and cooled rapidly with stirring. The solution was diazotised at 5°C by the gradual addition of sodium nitrite (4gms) in water (20ccs), and all insoluble matter filtered off. Copper bronze was added with vigorous stirring at 5-10°C but, although a slight evolution of gas occurred, the bulk of the diazo-compound was still undecomposed at the end of one hour. On slowly warming to 35°C, however, a reaction took place. The sludge was collected and steam-distilled. The product (1gm) was identified as diphenyl, m.pt. and mixed m.pt. 69-70°.

(2) (cf. Grieve and Hey, J., 1938, 110). 2-Aminodiphenyl (8.5gms) was melted with water (200ccs), and concentrated hydrochloric acid (12.5ccs) stirred in. Diazotisation was carried out at 2-4°C with sodium nitrite (3.8gms) in water (20ccs). The solution was filtered, and chloroform (50ccs) added. With temperature 0-2°C, a solution of sodium hydroxide (4.8gms) in water (25ccs) was added dropwise over 1.5 hours

with vigorous mechanical stirring. The mixture was gradually warmed over 10 hours to 50°C with stirring. The chloroform was separated, evaporated under reduced pressure, and the residue steam-distilled. The product (4.5gms) was diphenyl by m.pt. and mixed m.pt.

(3) When the solvent was omitted the yield of diphenyl was very much reduced. The non-steam-volatile material in all these reactions was tarry in character.

The Action of Magnesium and Cupric Chloride on 2:2'-Dibromo-Diphenyl (cf. Krizewsky and Turner, *J.*, 1919, 115, 560)

Magnesium (1.65gms) anhydrous cupric chloride (9gms) and ether (60ccs) were mixed and 2:2'dibromodiphenyl (10.4gms) added. After the initial reaction was over the brownish-red solution was refluxed for eight hours with frequent agitation to prevent caking. The mixture was poured on to ice, and concentrated hydrochloric acid added to dissolve the precipitated cuprous salts. After thorough extraction of the aqueous layer, the combined ethereal solutions were washed with water, dried and the ether removed. The light coloured residual mass was subjected to steam-distillation, the volatile material collected, and the residual glassy non-volatile mass, which could not be induced to crystallise and gave no evidence of picrate formation, subjected to distillation. Fractionation was not possible, the material having b.pt. 150-250°/2mm. and setting into a glassy non-crystalline mass which did not form

a picrate. The steam-volatile material was separated, dried, and treated with picric acid in alcohol. The picrate (.15gm) was filtered off, decomposed with aqueous ammonia, and the material, which did not contain halogen, recrystallised from aqueous alcohol. After five recrystallisations this substance had m.pt. 107°, and formed light yellow needle-like prisms. There was too little left at this stage for further examination. The picrate-formation mother-liquors contained diphenyl, m.pt. and mixed m.pt. 69-70°.

Action of Magnesium and Cupric Chloride on Ortho-di-iodobenzene. (cf. Krizewsky and Turner, loc.cit., and Bowden, J., 1931, 1113).

Magnesium (5.9gms) and ortho-di-iodobenzene (40gms) in ether (100ccs) were allowed to react with external cooling when necessary. After standing overnight, anhydrous cupric chloride (33gms) was added, and the violent reaction moderated by means of ice-cooling. After refluxing for five hours, the mixture was poured on to ice, and concentrated hydrochloric acid added. The precipitated copper salt did not dissolve, and was accordingly filtered off. It was greyish-white in colour, but gradually turned brown due to liberation of iodine. It was in all probability cupric iodide (cf. Krizewsky and Turner, loc.cit.). After thorough extraction of the aqueous solution and precipitate with ether, the combined ethereal extracts were washed with water and the ether removed. On steam-distillation volatile

materials were removed, contaminated with iodine. The very viscous residue distilled with much decomposition at 4mm. pressure, resinous materials remaining in the distillation flask. The lower-boiling fractions of the distillate contained triphenylene, m.pt. and mixed m.pt. 198°. The dried steam-volatile material (.5gm) was treated with picric acid in alcohol, when a picrate (.2gm), pale red needles from alcohol, m.pt. 96°, separated. This was decomposed with aqueous ammonia. The residue formed prisms from light petroleum, light yellow plates from aqueous alcohol, m.pt. 74.5-75.5°, with a diphenyl-like smell. (cf. Dobbie, Fox and Gauge, loc.cit., who give 74.5-75° as the melting point of diphenylene). The quantity obtained was very small. The picrate-formation mother-liquors contained diphenyl, m.pt. and mixed m.pt. 69-70°.

THE ULLMANN AND FITTIG REACTIONS:

FREE RADICALS IN SOLUTION

In carrying out a number of Ullmann condensations it was noticed that small amounts of a low-boiling product were always formed. Where these were further examined, they proved to be the aryl hydrogen compound (ArH) corresponding to the aryl halide (ArX) employed in the reaction. Thus, ortho-iodobenzaldehyde yielded 12% of benzaldehyde; ethyl ortho-iodobenzoate gave 5% of ethyl benzoate; o:o'-di-iodo-1:4-diphenylbutadiene (quinoline solution) gave 14% of 1:4-diphenylbutadiene, and so on. These results suggested a free radical mechanism for the Ullmann reaction.

It has been shown by Hey and Waters (Chem. Rev., 1937, 21, 169) that a property diagnostic of aryl free radicals is their ability to substitute invariably in the ortho- and para-positions of a benzene ring, regardless of any directing influence of a substituent already present in that ring. Accordingly, iodo-benzene, mixed with a large excess of ethyl benzoate, was heated with copper in a sealed tube. By treating the product with alkali, a mixture of diphenyl-2- and 4-carboxylic acids was obtained. The presence of the former was established by its easy conversion to fluorenone, while the latter was obtained by direct re-crystallisation. The formation of these substances

establishes the fact that the Ullmann reaction proceeds by a mechanism involving the transitory existence of free radicals in solution.

Free methyl radicals in the gas phase initiate the decomposition of butane (Frey, Ind.Eng.Chem., 1934, 26, 198) while the electrolytic oxidation of alkyl magnesium halides in ethereal solution causes the decomposition of the solvent (Evans and collaborators, J.Amer.Chem.Soc., 1934, 56, 654; 1935, 57, 489; 1936, 58, 720). The affinity of aryl free radicals for aliphatic hydrogen is pronounced (Hay and Waters, loc.cit.). When compounds containing reactive methylene groups were subjected to the action of copper, the proportion of aryl hydrogen compound formed was increased considerably, while the expected diaryls could not be identified in the products. Thus, ortho-iodoacetophenone yielded acetophenone in 36% yield, and the high-boiling product was not 2:2'-diacetodiphenyl. A violent reaction with apparent gaseous effervescence resulted from the action of copper on ethyl ortho-iodophenylacetate. No diphenyl-2:2'-diacetate could be isolated, the products consisting of ethyl phenylacetate (20%), small amounts of phenylacetic acid and ortho-iodophenylacetic acid, and a high-boiling product or products which could not be identified. It would seem reasonable to suppose that the reactive methylene groups in these substances were attacked by the free radicals formed by the action of the copper, thereby initiating the

decomposition of the aliphatic parts of the molecules. Thus when a mixture of ethyl ortho-iodophenylacetate and ethyl diphenyl-2-iodo-2'-carboxylate was treated with copper, free radicals apparently caused the elimination of the ethyl group in the latter substance, and 3:4-benzcoumarin appeared in the products of the reaction.

In attempts to prepare diphenylene, use was made of the Fittig reaction, and of the Grignard reagent. A detailed study of the action of sodium on chlorobenzene was made by Bachmann and Clarke (J.Amer.Chem.Soc., 1927, 49, 2089; cf. Weiler, Ber., 1896, 29, 111; 115), who cautiously suggested a free radical mechanism for this reaction. It was shown that when sodium reacted directly on chlorobenzene the products were benzene (24%), diphenyl (20%), and a considerable quantity of a complex mixture of hydrocarbons. Although this work was carried out before the property peculiar to free radicals, of substituting invariably in the ortho- and para-positions of a benzene ring, had been recognised, it is significant that the high-molecular-weight products identified in this mixture (2-phenyldiphenyl, 2:2'-diphenyldiphenyl, triphenylene, and 4-phenyldiphenyl) are ortho and para substitution products of diphenyl. When the reaction was carried out in the presence of toluene, 4-methyldiphenyl appeared among the products.

In view of the fact that the Fittig reaction is thus proved to take place by a free radical mechanism, the claim of Dobbie, Fox and Gauge to have isolated diphenylene "in

almost theoretical yield" from the action of sodium on an ethereal solution of 2:2'-dibromodiphenyl is open to serious doubt, since it would be expected that any free radicals formed might show a tendency to abstract the aliphatic hydrogen of the solvent, forming diphenyl. When attempts were made in the present series of experiments to repeat the preparation of diphenylene, the only low-molecular-weight product obtained was diphenyl. Attempts to confirm the free radical interpretation by conducting the reaction in benzene solution failed, since no reaction occurred in this aromatic solvent. It was hoped that some 2:2'-diphenyl-diphenyl would be formed under these conditions.

Further attempts to obtain diphenylene made use of the action of anhydrous cupric chloride on the Grignard reagents from 2:2'-dibromodiphenyl, and ortho-di-iodobenzene, both in ethereal solution. The products from these reactions had the same general nature as that obtained from the action of sodium on 2:2'-dibromodiphenyl in ethereal solution, and diphenyl was also present in them. A free radical mechanism has been suggested for certain reactions of the Grignard reagent by Bachmann and Clarke (loc.cit.)

EXPERIMENTAL

Action of Copper on Iodobenzene in the presence of Ethyl Benzoate.

Copper (20gms), iodobenzene (30gms) and ethyl benzoate (80ccs) were heated for five hours at 230°C in a sealed tube. Reaction was not complete, some iodobenzene being recovered on fractionation. The highest-boiling fraction of the distillate was hydrolysed in the usual way with aqueous alcoholic alkali. After extraction of the diphenyl with ether, acidification of the aqueous solution gave a mixture of acids. Repeated recrystallisation from aqueous acetic acid gave diphenyl-4-carboxylic acid in colourless needles (.03gm.) m.pt. 228° (Meyer, Hoffmann, Monatsh., 1917, 38, 335) (Found: Eq.wt. 198.7. $C_{13}H_{10}O_2$ requires: Eq.wt. 198.0) The combined mother-liquors on dilution gave an oil which did not solidify on attempted recrystallisation. The dried material was therefore warmed with a little concentrated sulphuric acid, the red solution diluted with water, and then rendered alkaline to remove all acidic impurities. The yellow crystalline material (.08gm) was identified as fluorenone by melting-point and mixed melting-point determination with an authentic specimen.