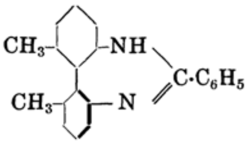
THE FORMATION OF CYCLIC COMPOUNDS FROM DERIVATIVES OF DIPHENYL. PART II.⁽¹⁾ THE FORMATION OF 4, 5, 9, 10-DIBENZOPYRENE AND 4, 5-DIPHENYL-DIPHENYLENE OXIDE FROM 6, 6′-DIPHENYL-DIPHENYL-2, 2′-TERAZONIUM SULPHATE.

By Shin-ichi SAKO.

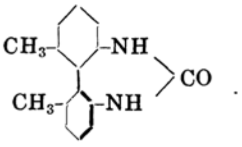
Received November 20th, 1933. Published February 28th, 1934.

It has been found that 7- or 8-membered rings formed through the 2, 2′-positions of diphenyl compounds assume nonplanar unstrained configurations. This was demonstrated by the fact that when 7- or 8-membered rings were formed through the 2, 2′-positions of certain optically active 2, 2′, 6, 6′-substituted diphenyls the products still retained optical activity. Thus, the compounds (I), (II) and (III) produced respectively from *l*-2, 2′-dimethyl-6, 6′-diaminodiphenyl⁽¹⁾ and *d*-2, 2′-diamino-1, 1′-dinaphthyl⁽²⁾ were optically active.



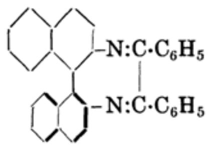
(active)

(I)



(active)

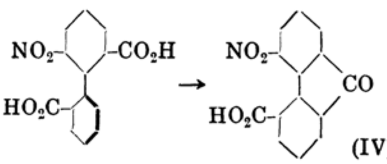
(II)



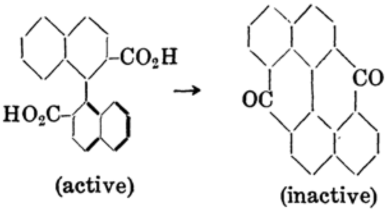
(active)

(III)

On the other hand, it has been shown by a number of examples that the products obtained by the closure of 5- and 6-membered rings through the 2, 2′-positions of optically active diphenyl compounds are optically inactive. *d*-2-Nitro-6,6′-dicarboxydiphenyl and *d*-2,2′-dicarboxy-1,1′-dinaphthyl, on heating with sulphuric acid, gave respectively the inactive compounds (IV) and (V).⁽³⁾



(active) (inactive) (IV)



(active) (inactive) (V)

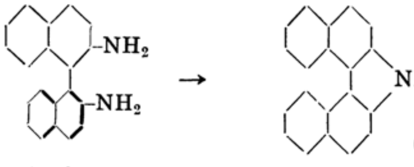
---

(1) For previous paper see Sako, *Mem. Coll. Eng. Kyushu Imp., Univ.*, **6** (1932), 263.

(2) Kuhn and Goldfinger, *Ann.*, **470** (1929), 183.

(3) Bell and Robinson, *J. Chem. Soc.*, **1927**, 2238; Kuhn and Albrecht, *Ann.*, **465** (1928), 282.

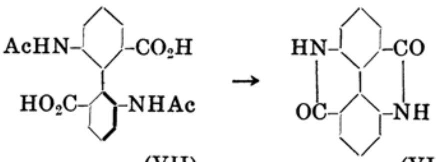
Similarly, inactive naphthocarbazol (VI) was obtained by heating either the *d*- or *l*-form of 2, 2′-diamino-1, 1′-dinaphthyl with hydrochloric acid.[2]

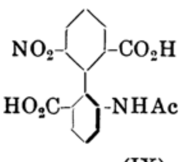


(VI)

(active) (inactive)

when *l*-6, 6′-diacetamidodiphenic acid (VII) was hydrolysed by cold sulphuric acid an inactive dilactam (VIII) was produced.[4]





(VII) (VIII) (IX)

(active) (inactive)

Since most of these active substances are stable toward heat or toward chemical reagent, the disappearance of optical activity is supposed to be due, not to racemization, but to the change from a spatial arrangement to a coplanar structure. But in view of the fact that the formation of all but one of the 5- or 6-membered rings in the above examples was effected by heating and also that such a compound as (VII), the only substance from which ring formation was accomplished in the cold, does not appear to be a suitable substance, for it has been found that the active forms of the compound (IX) which is a somewhat similar substance to (VII) in constitution easily racemizes in hydrochloric acid solution even at ice-cold temperatures (the unpublished result of the author.), it may be stated that the evidence furnished by these examples is not as conclusive as is desirable for demonstrating the correctness of this supposition.

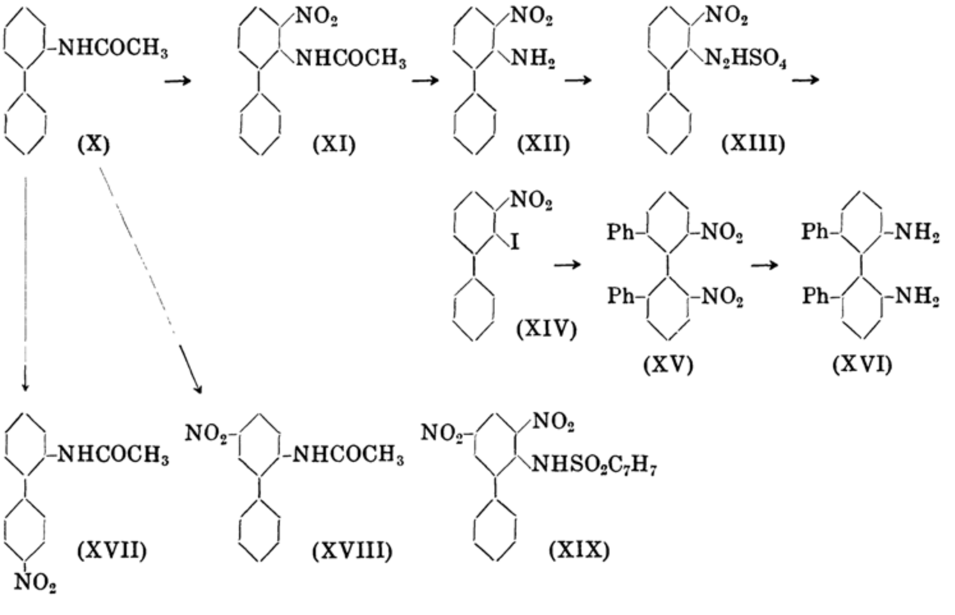
Meisenheimer and Höring[4] stated that the sodium salt of the active substance (VII) is stable toward heat but this can not be taken as indicating the stability of the free acid, for the author found that the active form of (IX), though not stable as free acid, was stable in the form of its sodium or ammonium salt in similar circumstances. In order to place this supposition on a firmer ground it is desirable to use an active substance which is not

---

(4) Meisenheimer and Höring, *Ber.*, **60** (1927), 1433.

only quite resistant to racemization but also produces 5- or 6-membered rings through the 2, 2′-positions with ease at as low a temperature as possible. The substance which adequately fulfils these conditions seemed to be 2, 2′-diamino-6, 6′-diphenyl diphenyl (XVI) in which the presence of the phenyl groups would perhaps stabilize the optical isomers. It is to be expected also that the tetrazonium salt prepared from (XVI), judging from its constitution, might decompose in three ways resulting in the formation of either two 6-membered rings or one 5-membered ring through the 2, 2′-positions or of two hydroxyl groups in the 2, 2′-positions. Although the intended object was not attained on account of the fact that attempts to separate 2, 2′-diamino-6, 6′-diphenyl diphenyl into optical antipodes have not so far been unsuccessful, a description of the preparation of this compound (XVI) and the decomposition products of the tetrazonium salt derived therefrom may be of use.

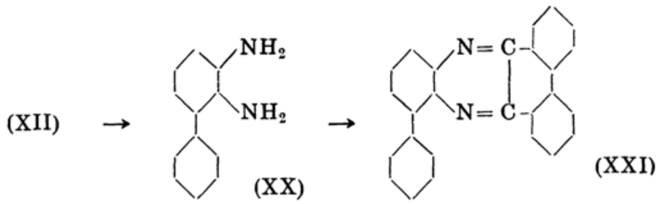
The starting substance for the preparation of 2, 2′-diamino-6, 6′-diphenyl diphenyl was 2-acetamidodiphenyl (X) which on nitration with a specially devised method yielded 3-nitro-2-acetamidodiphenyl (XI). This could be successively converted into 2-amino-3-nitrodiphenyl (XII), its diazonium sulphate (XIII) and 3-nitro-2-iododiphenyl (XIV), and the latter treated according to the Ullmann method with copper powder. 2, 2′-Dinitro-6, 6′-diphenyl diphenyl (XV) produced in this way on reduction gave 2, 2′-diamino-6, 6′-diphenyl diphenyl (XVI):



Two mononitro derivatives of 2-acetamidodiphenyl have been recorded in the literature: one of these, 4′-nitro-2-acetamidodiphenyl (XVII) was obtained as the primary product by acting nitric acid on 2-acetamidodiphenyl in a mixture of sulphuric acid and acetic acid,(5) while the other, 5-nitro-2-acetamidodiphenyl (XVIII) was obtained in the presence of acetic acid alone.(6) The only substance recorded, having a nitro-group in the ortho-position to the amino-group, was a dinitro-compound, 3, 5-dinitro-2*p*-toluene sulphonamidodiphenyl (XIX).(6)

Applying the method of Witt and Utermann(7) for the preparation of *o*-nitroaniline which consisted in nitrating the acetanilide in a mixture of acetic anhydride and acetic acid it was found that 3-nitro-2-acetamidodiphenyl could be obtained as one of the two products, the other product being 5-nitro-2-acetamidodiphenyl (XVIII). The Witt and Utermann method thus seems capable of general application for the preparation of similar derivatives of *o*-nitroaniline, for 3-nitro-*o*-toluidine proved also to be obtainable in a good yield from *o*-acetotoluidide by the same method.(8)

The constitution of the 3- and 5-nitro-2-aminodiphenyl thus obtained were confirmed by the examination of their reduction products, the diamino-compounds. 2, 3-Diaminodiphenyl (XX) obtained from (XII) on treatment with hydrochloric acid and ferric chloride gave the deep red diaminophenazine derivative and with phenanthrene quinone the 2, 3-(*oo*′-diphenylene)-5-phenyl quinoxaline (XXI):



Similarly, 2-amino-5-nitrodiphenyl was converted into 2, 5-diaminodiphenyl which showed characteristic reactions of *p*-phenylene diamine.

Although the yield of 3-nitro-2-acetamidodiphenyl (XI) from 2-acetamidodiphenyl was but 22.6% of the theoretical, thanks to the fact that, in the subsequent stages of preparations, 3-nitro-2-iododiphenyl (XIV), 2, 2′-dinitro-6, 6′-diphenyl diphenyl (XV), and 2, 2′-diamino-6, 6′-diphenyl diphenyl (XVI) were under favourable conditions all produced in the almost quantitative

---

(5) Scarborough and Waters, *J. Chem. Soc.*, **1927**, 89.

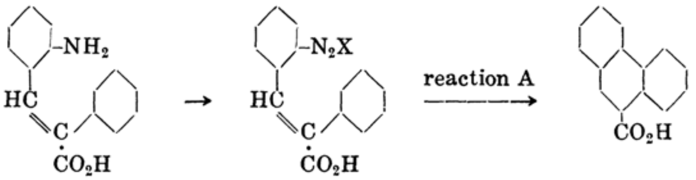
(6) Bell, *J. Chem. Soc.*, **1928**, 2773.

(7) *Ber.*, **39** (1906), 3061; **41** (1908), 3090 Anm.

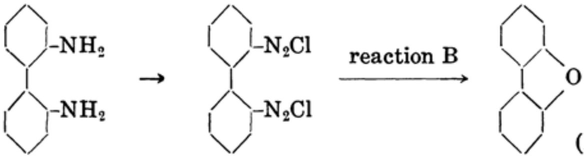
(8) Gabriel and Thieme, *Ber.*, **52** (1919), 1080.

yield, this work was made possible to proceed to further stages. At first, the problem of diazotizing 2-amino-3-nitrodiphenyl (XII) which had difficultly salt-forming property seemed a difficult one, but this could be surmounted by the use of conc. sulphuric acid in which the compound was diazotized smoothly.

It has already been stated that the tetrazonium salt derived from 2, 2′-diamino-6, 6′-diphenyl diphenyl (XVI) might decompose in three different ways. In the first place it will be remembered that there exists among compounds containing two benzene rings between which two carbon atoms are present and having in the ortho-position of one of the benzene rings a diazonium salt group a marked tendency with the loss of nitrogen to form a 6-membered ring resulting in the direct linking of the benzene rings. As an example for this may be cited the well-known synthesis of phenanthrene carboxylic acid by Pschorr's method⁽⁹⁾ from α-phenyl *o*-aminocinnamic acid (reaction A):



These conditions are as a matter of fact present on either side of the molecule of the tetrazonium salt obtainable from 2, 2′-diamino-6, 6′-diphenyl diphenyl (XVI). On the other hand, it will be recalled that when tetrazonium chloride solution prepared from 2, 2′-diaminodiphenyl, of which (XVI) is a derivative, was heated⁽¹⁰⁾ diphenylene oxide (XXII) was produced in a 70 per cent. yield (reaction B):



(XXII)

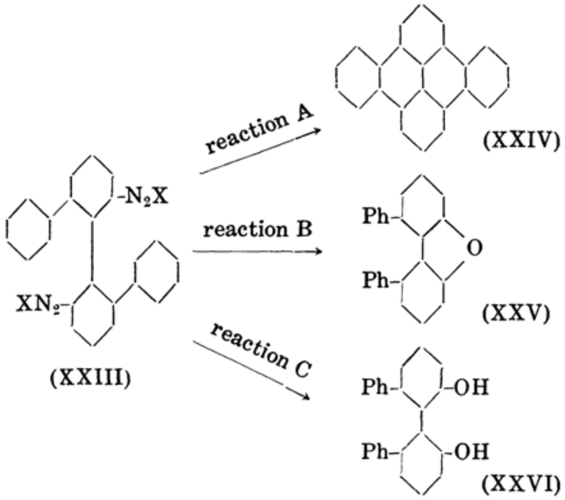
Finally, another possible decomposition of the tetrazonium salt is the production of the dihydroxyl compound without ring formation (reaction C). Thus in the decomposition of the tetrazonium salt (XXIII) obtained from 2, 2′-diamino-6, 6′-diphenyl diphenyl, according to whether reaction A,

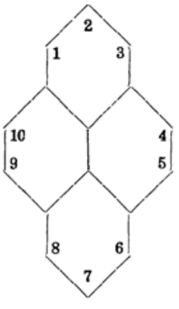
---

(9) *Ber.*, **29** (1896), 496.

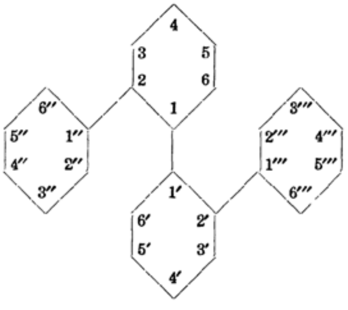
(10) Täuber and Halberstadt, *Ber.*, **25** (1892), 2745.

reaction B or reaction C occurs 4, 5, 9, 10-dibenzopyrene (XXIV),⁽¹¹⁾ 4, 5-diphenyl diphenylene oxide (XXV), or 2, 2′-dihydroxy-6, 6′-diphenyl diphenyl (XXVI) would result:





(XXVII)



(XXVIII)

It would be reasonably supposed that the general principles stated in those views on the ease of formation of carbon rings⁽¹²⁾ can be applied equally to the formation of rings other than saturated. And if so, it may be stated at once that in the decomposition of the tetrazonium salt (XXIII) reaction A should take place more easily than reaction B, since, if the accepted formula for diphenyl is correct, the condition under which 4, 5, 9, 10-dibenzopyrene (XXIV) is to be formed is perhaps one of the most favourable one

---

(11) The numbering for pyrene (XXVII) is one that was described in C., *Gen. Reg.*, VI (1922–1924), T. II, 816, for naming the then only known dibenzopyrene, 1, 2, 7, 8,-dibenzopyrene, obtained by Scholl and Neumann (*Ber.*, **55** (1922), 123), who originally adopted another mode of numbering for pyrene.

(12) Sako, this Bulletin, **9** (1934), 41.

which can be imagined in ring formation ; in (XXVIII)(13) the carbon atoms 6 and 2‴ (or 6‴) and 6′ and 2″ (or 6″) can not but come close together when the four benzene nuclei are rotated around each common axis (Normally in the central diphenyl system which has two diazonium salt groups in the 6, 6′-positions only the semi-circular rotation is possible), and moreover no strain would be produced by the ring formation, a fact which imply that 4, 5, 9, 10-dibenzopyrene should be a stable substance as it is the case with pyrene, having the carbon atoms in one plane. In reaction B however there are at least two conditions which would be unfavourable to the production of the 5-membered ring in (XXV) : one, the more important of the two, is the presence of the two phenyl groups in the 2, 2′-positions which should hinder the two diazonium salt groups in the 6, 6′-positions to approach each other and the other is the production of strain which has to be overcome in forming the 5-membered ring. As a matter of fact, this inference was fully borne out by the experiment.

It has been found that, although 4, 5, 9, 10-dibenzopyrene (XXIV) is produced by the decomposition of the tetrazonium salt (XXIII) even at ice-cold temperatures, 4, 5-diphenyl diphenylene oxide (XXV) can be obtained only when the decomposition is carried out at high temperatures. And whereas the yield of the dibenzopyrene (XXIV) is almost unchanged (36–40% of the theor.) whether the tetrazonium salt (XXIII) is decomposed in the cold or by heating, the yield of 4, 5-diphenyl diphenylene oxide (XXV) shows an increase with the rise of temperature at which the decomposition is effected (null below 45°C., 12 per cent. of the theor. at 60–70°C. and 30 per cent. at 100°C.).

It is remarkable that neither the decomposition of the tetrazonium salt (XXIII) is at all promoted nor the yield of the dibenzopyrene (XXIV) is increased by the addition of copper powder to (XXIII), a phenomenon which is quite distinct from the production of phenanthrene carboxylic acid by Pschorr's method. As expected, 4, 5, 9, 10-dibenzopyrene is a very stable substance which melts without decomposition at 353–355°C. and can be distilled under reduced pressure.

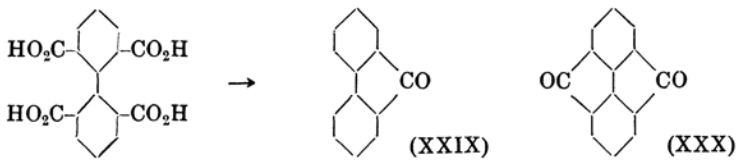
The remarkable facility with which two six-membered rings in the dibenzopyrene (XXIV) are produced is in contrast with the repeated failure in attempting to produce two 5-membered rings, one on either side of the diphenyl molecule. Thus, fluorenone (XXIX) is produced in place of the substance (XXX) when diphenyl-2, 2′, 6, 6′-tetracarboxylic acid is distilled,(14)

---

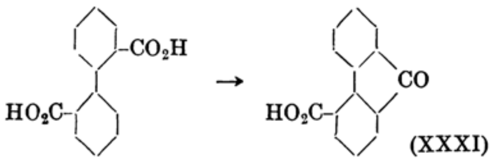
(13) For the ring system of 2, 2′-diphenyl diphenyl, the numbering shown by (XXVIII) is proposed.

(14) Meyer, Meyer and Taeyer, *Ber.*, **53** (1920), 2034.

and the action of dehydrating agents on diphenic acid does not proceed beyond the stage of fluorenone carboxylic acid (XXXI):



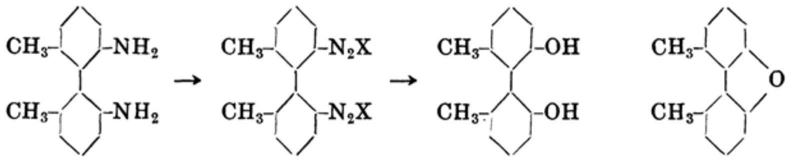
(XXIX) (XXX)



(XXXI)

This is probably due to the fact that by the formation of the 5-membered ring which may approximately be represented by a regular pentagon the distance between the carbon atoms in the 4, 5-positions is increased so that the production of the other 5-membered ring is impossible. At the same time it suggests that the fluorenone molecule has probably a coplanar structure, since if it is possible to incline the plane of the benzene rings toward each other as in the manner of the Kaufler formula for diphenyl two five-membered rings should be formed without difficulty.

The view stated above that the non-production of the diphenyl diphenylene oxide (XXV) at low temperatures is due to the blocking effect of the two phenyl groups is supported by the fact that (1) diphenylene oxide (XXII) is produced by the decomposition of the tetrazonium salt obtained from 2, 2′-diaminodiphenyl in which no such blocking group is present in nearly as good a yield at ordinary temperature (60% of the theor.) as at a high temperature (70%) and (2) the tetrazonium salt (XXXIII) derived from 2, 2′-dimethyl-6, 6′-diaminodiphenyl (XXXII) in which the methyl groups are the blocking groups on decomposition even with heating yields solely 2, 2′-dimethyl-6, 6′-dihydroxydiphenyl (XXXIV):

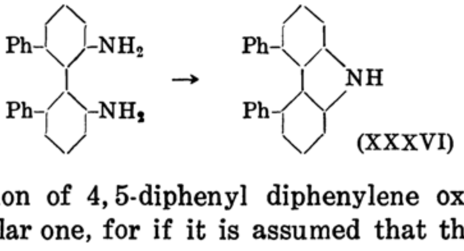


(XXXII) (XXXIII) (XXXIV) (XXXV)

In the decomposition of the tetrazonium salt (XXXIII) reaction C apparently predominates over reaction B, no trace of the diphenylene oxide derivative (XXXV) being produced even when the decomposition is effected by heating at 100°C. This is remarkable in view of the fact that, as already stated, 4, 5-diphenyl diphenylene oxide (XXV) can be obtained in a 30 per cent. yield by heating the tetrazonium salt (XXIII) at the same temperature. This difference in behaviour between the two tetrazonium salts may be attributable to the fact that the tetrazonium salt (XXXIII) is very much less stable than (XXIII),(15) since it is possible that when heating the cold solution of (XXXIII) its decomposition is completed before ever the temperature is reached which is necessary to enforce the production of the 5-membered ring against the blocking effect of the methyl groups. As a support for this view may be adduced the fact that, as already stated, whilst the yield of diphenylene oxide (XXII) from the tetrazotized solution of 2, 2′-diaminodiphenyl in which no blocking group is present is not much influenced by the temperature at which the decomposition is effected, 4, 5-diphenyl diphenylene oxide (XXV) is produced from the tetrazonium salt (XXIII) only at high temperatures, its yield being increased with the rise of temperature.

It has been found that reaction C occurs to a very slight extent when the tetrazonium salt (XXIII) is decomposed at 100°C., the 2, 2′-dihydroxy-6, 6′-diphenyl diphenyl (XXVI) being obtained in about 5% of the theoretical. No trace of the latter (XXVI) could be detected in the product obtained by decomposing (XXIII) at lower temperatures. In the decomposition of the tetrazotized solution of 2, 2′-diaminodiphenyl either in the cold or by heating reaction C does not occur at all, the product being solely diphenylene oxide (XXII) resulting from reaction B. The difference between the two cases may again be regarded as evidence demonstrating that the closure of the diphenylene oxide ring through the 2, 2′-positions is hindered by the blocking effect of the large groups in the 6, 6′-positions.

4, 5-Diphenyl carbazol (XXXVI), the constitution of which is analogous to 4, 5-diphenyl diphenylene oxide, has been obtained by heating 2, 2′-diamino-6, 6′-diphenyl diphenyl with hydrochloric acid:



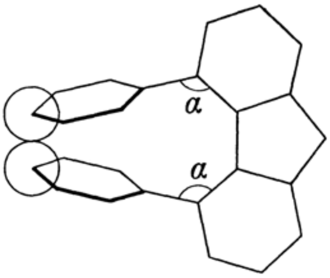
(XXXVI)

The constitution of 4, 5-diphenyl diphenylene oxide or 4, 5-diphenyl carbazol is a singular one, for if it is assumed that the diphenylene oxide

---

(15) The decomposition of (XXXIII) is complete in two to three days at ordinary temperature, while (XXIII) requires about a month to complete the decomposition under similar conditions.

and carbazol molecule each has a uniplanar configuration which can be roughly represented by a regular pentagon bearing regular hexagons on two of its sides, then as is clear from the diagram (XXXVII), the phenyl groups can not occupy their normal positions. In this diagram (XXXVII), the atoms constituting the carbazol or the diphenylene oxide molecule proper are supposed to be lying in the plane of the paper. The most probable form which the molecules of the substances may assume, that is to say, the least strained spatial arrangement for the valencies carrying the phenyl groups would be one in which the phenyl residues lie in planes perpendicular to the plane in which the carbazol or diphenylene oxide molecule proper lies. This is illustrated in the diagram (XXXVII) in which the heavily printed lines indicate the sides of hexagons which are nearer to the reader. If it is assumed, as shown in (XXXVII), that the relative position of the phenyl groups are to be altered only by the deflection of the angle α and that the p- and p'-carbon atoms of the phenyl groups are in contact with each other with the distance of 1.45 Å between the centres of the atoms, the angle α will be 125.1°, but as the p- and p'-carbon atoms are not in actual combination, actually the distance from the centre to centre of the carbon atoms will be somewhat longer and consequently the angle α will be somewhat larger than this. At any rate, whatever arrangement the molecule may assume, it is certain that the phenyl groups can not rotate about the bonds in these circumstances.



(XXXVII)

Experimental.

(A) *Preparation and Nitration of 2-Acetamidodiphenyl.*

2-Aminodiphenyl. The preparation of 2-aminodiphenyl from 2-nitrodiphenyl has been described by Scarborough and Waters.⁽⁵⁾ In the following is described a method improved by the author by which this substance can be easily obtained in the theoretical yield.

To a solution prepared by passing dry hydrogen chloride into a mixture of $SnCl_2 \cdot 2H_2O$ (880 gr.) and EtOH (1000 c.c.) was added drop by drop 2-nitrodiphenyl (200 gr.) obtained by the method of Bell, Kenyon and Robinson⁽¹⁶⁾

---

(16) *J. Chem. Soc.*, **1926**, 1242.

in the course of one hour, HCl being led in all the time (The nitro-compound must not be added too rapidly, otherwise a violent reaction would ensue, which may be beyond control). Shortly after the addition of the nitrodiphenyl the double chloride commenced to separate as needles which was collected on the following day. The crystals thus obtained contained about 60 per cent. of the theoretical amount of 2-aminodiphenyl, the rest, 40%, being obtained from the filtrate. The crystals was then dissolved in water, treated with alkali and the base thus set free extracted with ether. The ethereal residue, on distillation under diminished pressure gave pure 2-aminodiphenyl which had b.p. 135°C./5.5 mm. The filtrate from the double salt was concentrated in a basin on the water bath into half the original bulk, made alkaline, and the base thus separated purified as before.

2-Acetamidodiphenyl (X). For the acetylation of 2-aminodiphenyl Scarborough and Waters(15) preferred acetyl chloride to acetic anhydride, the reason for this being, according to their statement, that the oily product obtained by heating the base with acetic acid or a mixture of acetic acid and acetic anhydride crystallized only with difficulty and with considerable loss. The author found however that the apparently poor yield of 2-acetamidodiphenyl when acetic anhydride was used was due to its extremely soluble property in acetic acid. The theoretical yield of the acetamidodiphenyl could therefore be obtained when the acid was removed. This was not the only instance observed by the author that such was the case. On more than one occasion it was found that the difficulty of crystallizing the products obtained by acetylating certain amines with acetic anhydride was due to the same cause.

Acetic anhydride (110 gr.) was added to a solution of 2-aminodiphenyl (176 gr.) in benzene (200 c.c.) at ordinary temperature. The reaction occurred at once, but it was allowed to stand until the next day to complete the separation of the crystals. 2-Acetamidodiphenyl thus obtained, 92 gr., formed needles melting at 120°C. The mother liquor containing the major part of the product was greatly diluted with benzene, shaken with a sodium carbonate solution and the benzene layer greatly concentrated. In this way 2-acetamidodiphenyl was obtained in the theoretical yield.

3-Nitro-2-acetamidodiphenyl (XI). As stated in the introduction 3- and 5-nitro-2-acetamidodiphenyl were produced by the mononitration of 2-acetamidodiphenyl in presence of acetic anhydride and acetic acid. As however the yield of the 3-nitro-compound was not good, the nitration was carried out under a great variety of conditions, but even under the best conditions thus arrived at the combined yield of the two nitration products amounted to only 50 per cent. of the theoretical, the rest being an uncrystallizable syrup and tarry matter. It will be noticed in the experiment described below that the quantities of both nitric acid and acetic anhydride employed are about one and a half time the theoretical amount required for the mononitration, the reason for this being that when the theoretical quantities of these substances were used, 25 per cent. of the original compound remained unattacked. The use of more than the amount given in the direction led however to a lower yield of the desired substance.

2-Acetamidodiphenyl (42.2 gr.) was dissolved with heating in a mixture of acetic anhydride (30 c.c.) and glacial acetic acid (35 c.c.). The solution was agitated mechanically and cooled with water which was kept at about 22°C.

When the temperature of the liquid reached 23–24°C., the solution from which some crystals reappeared was treated with a solution of fuming nitric acid (20 gr.; $D = 1.5$) in glacial acetic acid (15 c.c.) in the manner described below. Two-fifths of the nitrating mixture was added during 20 minutes, when the reaction set in with a rise of temperature, the crystals gradually disappearing. After this stage was reached, the nitration mixture must be added more slowly so that the reaction mixture, which as stated above was cooled with water at 22°C., was maintained below 26.5°C. It should be added here that the nitration does not proceed at all should the temperature of the liquid fall below 20°C. Under the conditions described above, about 100 minutes were required for the addition of the nitrating mixture. After three additional hours' agitation, it was allowed to stand over night in an ice box. It was then poured on 600 gr. of ice water, shaken with 300 c.c. of benzene and the upper layer left in an ice box for some hours to complete the separation of 3-nitro-2-acetamidodiphenyl. The light-yellow needles were then collected and washed once with benzene. 3-Nitro-2-acetamidodiphenyl thus obtained, 9 gr., was practically pure. From the mother liquor which was shaken with a sodium carbonate solution and then concentrated into a small bulk, was obtained a further crop of the same crystals which, on crystallization once from benzene, gave 2.6 gr. of 3-nitro-2-acetamidodiphenyl which had the same purity as the main portion. The total yield of the 3-nitro-compound was therefore 11.6 gr. or 22.6% of the theoretical. It may be recrystallized easily from benzene, from which it separated as light-yellow needles melting at 188–188.5°C. (Found.: $N = 11.2$. $C_{14}H_{12}O_3N_2$ requires $N = 10.9\%$). Twenty c.c. of boiling benzene dissolve about 1 gr. of 3-nitro-2-acetamidodipheyl.

The combined mother liquors separated from 3-nitro-2-acetamidodiphenyl, containing 5-nitro-2-acetamidodiphenyl produced simultaneously by the nitration, were used for the isolation of the latter substance as described below.

2-Amino-5-nitrodiphenyl. As stated in the introduction, this compound has been obtained by Bell.(6) It was found that 5-nitro-2-acetamidodiphenyl contained in the filtrate separated from 3-nitro-2-acetamidodiphenyl did not crystallize even when the filtrate was greatly concentrated. The solvent was therefore removed and the dark residual gum was purified by distillation under reduced pressure. At first some decomposition was noticeable but it ceased after a time.

The first fraction, 2.0 gr., distilled below 200°C./6 mm., the main fraction, 29.3 gr., boiling at about 245°C./6 mm. The main fraction, being also an uncrystallizable syrup, was hydrolyzed by boiling under reflux with 20 per cent. hydrochloric acid solution (90 c.c.) in an oil bath for 3 hours. The oily product was extracted with benzene and the solution, after being washed with an alkaline solution, evaporated off. The residual syrup thus obtained, on distillation under diminished pressure, yielded a distillate, 21.3 gr., which for the most part had b.p. 220–225°C./6 mm. On crystallization of the distillate from ethyl alcohol (25 c.c.), 2-amino-5-nitrodiphenyl, 10.2 gr., separated in an almost pure condition. The mother liquor was once more evaporated into dryness and the residue divided by vacuum distillation into two fractions boiling below and above 200°C./6 mm. From the higher fraction was obtained by crystallization from ethyl alcohol 1 gr. of 2-amino-5-nitrodiphenyl, making the total yield to 25.7 per cent. of the theoretical. The pure 2-amino-5-nitrodiphenyl had m.p. 125°C. (Found: $C = 67.0$; $H = 5.2$; $N = 13.1$. $C_{12}H_{10}O_2N_2$ requires $C = 67.3$; $H = 4.7$; $N = 13.1\%$).

On reduction this compound yielded the diamino-derivative which showed the characteristic reactions of *p*-phenylene diamine, a fact which prove the constitution of the parent substance.

2, 5-Diaminodiphenyl Dihydrochloride. A well-ground mixture of 2-amino-5-nitrodiphenyl (3.2 gr.) and $SnCl_2 \cdot 2H_2O$ (13.2 gr.) was treated with conc. HCl (25 c.c.). No change was observed at ordinary temperature, but on gentle heating the reaction started, which then proceeded to completion without further heating, the double chloride separating while still hot. After cooling, the crystals, 7.2 gr. were collected and the tin removed in the usual way. The filtrate from the tin sulphide was greatly concentrated and left to crystallize. 2, 5-Diaminodiphenyl dihydrochloride, 2.8 gr., was thus obtained as almost colourless plates. It was found that, during the concentration of the solution mentioned above, the solution was kept almost colourless and that, even if it became coloured, it could be restored colourless by passing hydrogen sulphide. For purification, the hydrochloride was dissolved in a small quantity of water and the solution thus obtained treated with conc. HCl. The colourless plates thus precipitated were dried over soda lime (Found: HCl = 28.5. $C_{12}H_{12}N_2 \cdot 2HCl$ requires HCl = 28.4%). That the amino-groups in this substance are in the 2, 5-positions was proved by the fact that a solution of the hydrochloride, on treatment with H_2S and then with $FeCl_3$ solution, gave a deep violet precipitate.

2-Amino-3-nitrodiphenyl (XII). A hot solution of 3-nitro-2-acetamidodiphenyl (13 gr.) in ethyl alcohol (240 c.c.) was treated with conc. HCl (60 c.c.) and heated under reflux on the water bath for 5 hours. The greater part of alcohol was then removed by heating without reflux and water added. The oil thus separated was extracted with ether and the ethereal residue distilled under reduced pressure. The reddish oil thus obtained, 9.5 gr., boiling at 194–196°C./6 mm., became crystalline after a time. It melted at 44–45°C. The real m.p. might have been somewhat higher than this, but as no suitable solvent was found from which it could be crystallized, the matter was not further pursued. The analysis of the distillate gave the following result: Found, C = 67.7; H = 5.3. $C_{12}H_{10}O_2N_2$ requires C = 67.3; H = 4.4%.

2, 3-Diaminodiphenyl Dihydrochloride. A well-ground mixture of 2-amino-3-nitrodiphenyl (2 gr.) and $SnCl_2 \cdot 2H_2O$ (8 gr.) was heated with conc. HCl (25 c.c.) on the water bath for some hours until the disappearance of the original substance. After allowing to stand for the night, the double salt was filtered off and dried over soda lime in a vacuum. It was then dissolved in water, treated with H_2S and the clear filtrate concentrated until its bulk was 7–8 c.c. On addition of conc. HCl (15 c.c.), the hydrochloride of the diamino-compound separated quickly in somewhat brown needles. For purification, its solution was treated with animal charcoal and the substance reprecipitated by conc. HCl.

Like most of the orthodiamines the substance was not stable, the chlorine determination of the hydrochloride giving a figure much lower than that required by theory. But the properties and the behaviour of the substance left no doubt whatever as to its being an ortho-diamine. Thus, an aqueous solution of the hydrochloride, on treatment with ferric chloride, yielded the red precipitate of the diaminophenazine derivative, a reaction which is characteristic of orthodiamines. Further, the most convincing evidence was afforded by the formation of the quinoxaline compound by the action of phenanthrene quinone on the hydrochloride as described below.

2, 3-(*oo'*-Diphenylene)-5-phenyl Quinoxaline (XXI). Crystalline potassium acetate (0.6 gr.) was added to a warm solution of 2, 3-diaminodiphenyl hydrochloride (0.77 gr.) in ethyl alcohol (10 c.c.). After cooling, the precipitated potassium chloride was filtered off and the filtrate added to a boiling solution of phenanthrene quinone (0.55 gr.) in glacial acetic acid (100 c.c.), when the quinoxaline derivative separated in yellow needles. Heating was continued for an hour and the crystal was collected after cooling. It melted sharply at 221°C. (Found: $N = 8.1$. $C_{26}H_{16}N_2$ requires $N = 7.9\%$). The yield was 0.9 gr. or 95.6 per cent. of the theoretical, calculated on the phenanthrene quinone employed.

(B) *Preparation of 2, 2′-Diamino-6, 6′-diphenyl Diphenyl and its Converison into 4, 5-Diphenyl Carbazol.*

3-Nitro-2-iododiphenyl (XIV). A suspension of 2-amino-3-nitrodiphenyl (21.4 gr.) in conc. H_2SO_4 (100 c.c.) was agitated at ordinary temperature for about one hour, that is, until a clear solution was obtained. It was then cooled with ice water and treated with ice (50 gr.) and solid sodium nitrite (7.5 gr.) with vigorous stirring which was continued for one hour. Twenty grams of ice were then added and agitation continued for 40 minutes. The addition of a further quantity (20 gr.) of ice was followed after a short time by the production of a thick foam. When this foam disappeared, a large quantity of ice was added and the solution filtered to remove a trace of insoluble matter and then treated with a solution of potassium iodide (20 gr.). A vigorous decomposition occurred, the iodo-compound separating as an oil which at once crystallized. The crude compound, 32.5 gr., was dissolved in ether, shaken with a potassium hydroxide solution, and the ether removed. The ethereal residue on distillation in a vacuum gave the 3-nitro-2-iododiphenyl (30 gr.) in a state of purity. It had b.p. 178°C/4 mm. Recrystallized from ethyl alcohol it formed yellow needles which melted at 90–91°C. (Found: $I = 38.73$. $C_{12}H_8O_2NI$ requires $I = 39.05\%$).

2, 2′-Dinitro-6, 6′-diphenyl Diphenyl (XV). The copper powder (20 gr.) prepared by the method of Piccard and Larsen(17) was added within 7 minutes with vigorous agitation to 3-nitro-2-iododiphenyl (26 gr.) which was heated in an oil bath at 210–215°C, the heating being continued for 5 additional minutes. The mixture was extracted with benzene and the solution treated with animal charcoal. The crystalline residue from the benzene solution, 15.7 gr., was dissolved in boiling alcohol (800 c.c.) and the solution concentrated until half the original bulk. 2, 2′-Dinitro-6, 6′-diphenyl diphenyl separated on cooling as light-yellow crystals, 15 gr., melting at 201–

---

(17) *J. Am. Chem. Soc.*, **39** (1917), 2007.

202°C. The m.p. did not change with further crystallization (Found: N = 7.42. $C_{24}H_{16}O_4N_2$ requires N = 7.10%).

2, 2′-Diamino-6, 6′-diphenyl Diphenyl (XVI). A suspension of powdered 2, 2′-dinitro-6, 6′-diphenyl diphenyl (10 gr.) in a solution prepared by passing dry HCl to a mixture of stannous chloride (50 gr.) and glacial acetic acid (190 c.c.) was heated in a water bath at 50–60°C. with frequent shaking. The original substance disappeared in one hour but the heating was continued for 2.5 hours longer, hydrogen chloride being led in all the time. The solvent was then removed by distillation in a vacuum(18) and the residue thus obtained, made alkaline and extracted with ether. The ethereal residue, 8.5 gr., quickly set to a mass of crystals, which on two crystallizations from alcohol gave almost colourless prims, 6.5 gr., melting at 163–164°C. (Found: C = 85.5; H = 6.3. $C_{24}H_{20}N_2$ requires C = 85.7; H = 5.9%). The separation of the crystals from alcohol proceeded very slowly. The substance should be colourless when pure, but perfectly colourless crystals are difficult to obtain owing to oxidation. The hydrochloride as well as the sulphate of 2, 2′-diamino-6, 6′-diphenyl diphenyl are very difficultly soluble in water. Attempts to resolve the diamino-compound into optical isomers with *d*-tartaric, *d*-camphorsulphonic and *d*-bromocamphorsulphonic acids have been unsuccessful.

4, 5-Diphenyl Carbazol (XXXVI). 2, 2′-Diamino-6, 6′-diphenyl diphenyl (2 gr.) and 2n HCl (36 c.c.) were heated in a sealed tube in the atmosphere of carbon dioxide at about 200°C. for 7 hours. The brown mass thus obtained, on three crystallizations from ethyl alcohol, yielded colourless needles, 0.8 gr., which melted at 145–146°C. (Found: C = 90.0; H = 6.0; N = 4.4. $C_{24}H_{17}N$ requires C = 90.3; H = 5.3; N = 4.4%).

(C) *Decomposition of the Tetrazonium Sulphate* (XXIII) *obtained from 2, 2′-Diamino-6, 6′-diphenyl Diphenyl* (XVI).

The solution obtained by tetrazotizing 2, 2′-diamino-6, 6′-diphenyl diphenyl was decomposed under varied conditions: the decomposition was performed (i) at 100°C. in absence of copper powder, (ii) at 60–70°C. without the use of copper powder, (iii) at 40–45°C. in presence of copper powder and (iv) at ordinary temperature (5–15°C.) in absence of copper powder. It was found that 4, 5, 9, 10-dibenzopyrene (XXIV) was produced in each experiment with the yields varying from 36 to 40 per cent. of the theoretical, the other possible product, 4, 5-diphenyl diphenylene oxide (XXV) being

---

(18) The removal of the solvent must not be carried out under ordinary pressure, as in that case the product is darkened considerably by oxidation.

isolated only from the products obtained in (i) and (ii). 2, 2′-Dihydroxy-6, 6′-diphenyl diphenyl (XXVI) was found to be present only in the products obtained in (i). Possibly the latter (XXVI) might have been produced in the other experiments but its yield must have been very poor. The yields of the three substances obtained in the four experiments are tabulated below, the figures representing the percentages of the theoretical yields calculated on the 2, 2′-diamino-6, 6′-diphenyl diphenyl employed.

	(i)	(ii)	(iii)	(iv)
4, 5, 9, 10-dibenzopyrene	38%	40%	40%	36%
4, 5,-diphenyl diphenylene oxide	30	12	0	0
2, 2′-dihydroxy-6, 6′-diphenyl diphenyl	5	0	0	0

The decomposition of the tetrazonium salt solution occurred even at ice-cold temperatures yielding the dibenzopyrene but the reaction velocity was very small. A feature in the decomposition of the tetrazonium salt was that the addition of copper powder to it had no effect to promote the decomposition as used to be the case in many diazonium salts. The only way to accelerate the reaction was to apply heating. The experiments were carried out as follows.

Experiment (i).—A suspension of powdered 2, 2′-diamino-6, 6′-diphenyl diphenyl (2.0 gr.) in a 15 per cent. sulphuric acid solution (25 gr.) was well agitated at 40–50°C. until completion of the salt formation. It was then cooled with ice water and treated with sodium nitrite (0.9 gr.). The very difficultly soluble sulphate of the base gradually disappeared forming after half an hour's agitation an almost clear solution. After filtration, the clear solution was poured into hot water in a beaker heated with boiling water bath. A short time later a vigorous decomposition took place yielding a dark gray precipitate which was collected and washed with water. The precipitate thus obtained, 1.9 gr. was found to contain the three substances, 4, 5, 9, 10-dibenzopyrene (0.66 gr.), 4, 5-diphenyl diphenylene oxide (0.55 gr.) and 2, 2′-dihydroxy-6, 6′-diphenyl diphenyl (0.05 gr.), which were separated as described on p. 72–73.

Experiment (ii).—The tetrazonium sulphate solution prepared from 2, 2′diamino-6, 6′-diphenyl diphenyl in the same way as in the experiment (i) was heated without adding copper powder at 60–70°C. In this way 1.0 gr. of the diamino-compound gave 0.79 gr. of the precipitate from which 0.36 gr. of the dibenzopyrene (XXIV) and 0.12 gr. of 4, 5-diphenyl diphenylene oxide were obtained.

Experiment (iii).—The tetrazotized solution of 2, 2′-diamino-6, 6′-diphenyl diphenyl (1.0 gr.) was heated in presence of copper powder at 40–45°C. for two hours, at the end of which the reaction was complete.

The yield of the dibenzopyrene was 0.36 gr. Neither 4, 5-diphenyl diphenylene oxide nor 2, 2′-dihydroxy-6, 6′-diphenyl diphenyl was produced.

Experiment (iv.)—The tetrazonium sulphate solution obtained in the same way as before was allowed to decompose at room temperature (5–15°C.). The decomposition proceeded very slowly with separation of bluish green precipitate. From time to time a test portion was acted on an alkaline β-naphtol solution. It was thus found that no less than a month was required to complete the reaction. That the decomposition is very considerably hastened by heating will be seen from the fact that, as stated in the experiment (ii), it was completed at 40–45°C. in two hours. From 1 gr. of 2, 2′-diamino-6, 6′-diphenyl diphenyl, 0.32 gr. of 4, 5, 9, 10-dibenzopyrene was obtained. As in the experiment (iii), 4, 5-diphenyl diphenylene oxide and 2, 2′-dihydroxy-6, 6′-diphenyl diphenyl were not found among the products.

4, 5, 9, 10-Dibenzopyrene (XXIV). As described above, this compound was formed in the almost equal yields in the experiments (i), (ii), (iii) and (iv). In the following are described the method which was used for the separation of the three substances produced in the experiment (i).

An attempt was first made to extract the decomposition product (1.9 g., p. 71) obtained in the experiment (i) which contains the three substances (XXIV), (XXV) and (XXVI) with ethyl alcohol in which 4, 5, 9, 10-dibenzopyrene (XXIV) alone is insoluble. But as the dibenzopyrene was in such a fine state that it passed freely through the filter the solvent was removed and the residue dissolved in boiling benzene (600 c.c.) and concentated into a small bulk (60 c.c.). 4, 5, 9, 10-Dibenzopyrene thus obtained, 0.66 gr., was, though somewhat brown, almost pure as was evidenced by the fact that it showed no change in appearance at 350°C. It was purified by distillation under reduced pressure (4 mm.) and then by crystallization from benzene. It formed lustrous minute crystals with faintly yellowish shade, which melted without decomposition sharply at 353–355°C. (Found: $C = 95.3$; $H = 4.7$. $C_{24}H_{14}$ requires $C = 95.4$; $H = 4.6\%$). 4, 5, 9, 10-Dibenzopyrene is insoluble or very difficultly soluble in usual organic solvents except boiling benzene in which it is slightly soluble. Thus in order to dissolve 1.0 gr. of the hydrocarbon, it must be boiled for a long time with 900–1000 c.c. of benzene.

The benzene filtrate separated from 4, 5, 9, 10-dibenzopyrene which contained 4, 5-diphenyl diphenylene oxide and 2, 2′-dihydroxy-6, 6′-diphenyl diphenyl was used for the isolation of these substances as described below.

4, 5-Diphenyl Diphenylene Oxide (XXV). The benzene solution separated from 4, 5, 9, 10-dibenzopyrene as described above was evaporated off and the residue thus obtained extracted with ether. Some insoluble substance (0.06 gr.) was removed and the clear solution shaken with a dilute potassium hydroxide solution. The alkaline layer was used for the isolation of 2, 2′-dihydroxy-6, 6′-diphenyl diphenyl as will be described later. The ethereal layer was then evaporated into dryness and the dark residue, 0.77 gr. crystallized from ethyl alcohol (50 c.c.). The crystals (0.45 gr.) thus obtained, though coloured dark, formed uniform needles melting at 150–153°C. and found to be fairly pure 4, 5-diphenyl diphenylene oxide. It was purified first by vacuum distillation and then by crystallization from ethyl alcohol. The colourless needles thus obtained melted at 154–155°C. (Found: $C = 89.8$; $H = 5.5$. $C_{24}H_{16}O$ requires $C = 90.0$; $H = 5.0\%$). From the alcoholic mother liquors a further crop (0.10 gr.) of the 4, 5-diphenyl diphenylene oxide was obtained, making its total yield to about 0.55 gr. It is easily soluble in ether and fairly soluble in boiling ethyl alcohol but difficultly so in cold alcohol.

2, 2′-Dihydroxy-6, 6′-diphenyl Diphenyl (XXVI). This substance was contained in the alkaline layer separated from the ethereal layer containing 4, 5-diphenyl diphenylene oxide (see above). The alkaline solution on acidification precipitated this compound which was extracted with ether. As the ethereal residue was found to contain a trace of something which was insoluble in alkaline solution, it was treated with a warm aqueous potassium hydroxide solution and the insoluble matter filtered off. The filtrate was acidified, extracted with ether, and the ethereal residue recrystallized from petroleum ether (b.p. 60–70°C.). It formed colourless, slender needles melting at 145–147°C. The yield was 0.05 gr. The substance thus obtained was not quite pure (Found: $C = 82.92$; $H = 5.85$. $C_{24}H_{18}O_2$ requires $C = 85.2$; $H = 5.3\%$), but there is no other alternative formula possible.

2, 2′-Dihydroxy-6, 6′-diphenyl diphenyl is easily soluble in ether, fairly soluble in ethyl alcohol and slightly soluble in boiling petroleum ether (b.p. 60–70°), but practically insoluble in cold petroleum ether.

(D) *Decomposition of the Tetrazonium Sulphates obtained from 2, 2′-Dimethyl-6, 6′-diaminodiphenyl and 2, 2′-Diaminodiphenyl.*

2, 2′-Dimethyl-6, 6′-dihydroxydiphenyl (XXXIV). This compound was obtained as the only isolable product when the tetrazotized solution of 2, 2′-dimethyl-6, 6′-diaminodiphenyl was decomposed. It was produced by effecting the decomposition either on heating or at ordinary temperature, but in the latter case its yield was only a trace.

A solution of 2, 2′-dimethyl-6, 6′-diaminodiphenyl, (4.24 gr.) in conc. sulphuric acid (12.0 gr.) and water (60 c.c.) was treased with sodium nitrite (2.9 gr.).

The tetrazonium sulphate solution was then poured into a beaker which was immersed in a boiling water bath. The decomposition was soon complete, a bluish dark precipitate being separated. The precipitate, 4.5 gr., was then submitted to steam distillation, a time-consuming work owing to the high b.p. of the product. The distillate was shaken with ether and the ethereal residue, about 1.5 gr., on crystallization from benzene (10 c.c.) gave 0.9 gr. of large colourless plates melting at 161–162.5°C. The m.p. was not altered by further crystallization (Found: $C = 78.6$; $H = 7.0$. $C_{14}H_{14}O_2$ requires $C = 78.5$; $H = 6.5\%$).

2, 2′-Dimethyl-6, 6′-dihydroxydiphenyl is easily soluble in aqueous alkaline solution. It was found that, compared with the tetrazonium sulphates obtained from 2, 2′-diaminodiphenyl (see below) and 2, 2′-diamino-6, 6′-diphenyl diphenyl (see p. 72), the tetrazonium sulphate prepared from 2, 2′-dimethyl-6, 6′-diaminodiphenyl was very much less stable, its decomposition being completed at about 25°C. in two days or so.

Diphenylene Oxide (XXII). As stated in the introduction Täuber obtained this substance in a 70 per cent. yield by heating the tetrazonium salt solution made from 2, 2′-diaminodiphenyl. It was found that as described below the same compound was produced in a 60 per cent. yield by allowing the tetrazonium salt to decompose at ordinary temperature.

2, 2′-Diaminodiphenyl (3.68 gr.) dissolved in conc. H_2SO_4 (12.0 gr.) and water (60 c.c.) was treated with a solution of sodium nitrite (2.9 gr.) in water and the resulting tetrazonium salt solution left to decompose at ordinary temperature (about 25°C.), until a test portion of the liquid reacted no more with an alkaline β-naphthol solution. The reaction was complete in 24 days. The darkish precipitate was filtered off and the dried product, 3.1 gr., distilled under diminished pressure. The distillate (2.1 gr.) boiling at 120–125°C./5 mm. quickly set to a mass of crystals which, after being powdered, was extracted with an aqueous alkaline solution, by which treatment however no appreciable loss was observed in the weight of the distillate, a fact which indicates the absence in the distillate of the other possible product, 2, 2′-dihydroxydiphenyl. In order to be sure on this point, the alkaline solution was acidified, but no precipitation occurred. Furthermore, the acidified solution was shaken with ether and the ethereal layer evaporated off, but there was no residue. As a matter of fact, the distillate obtained above was almost pure diphenylene oxide. The crystals on crystallization from alcohol-water gave colourless crystals melting at 85–86°C.

Chemical Department, Faculty of Engineering,
Kyushu Imperial University, Fukuoka.