ATTEMPTED FORMATION OF RINGS ATTACHED TO THE *p*-POSITIONS OF THE PHENYL GROUPS IN 2,2′-DIPHENYLDIPHENYL.

By Shin-ichi SAKO.

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In a previous communication dealing with the relative ease of formation of carbon rings,⁽¹⁾ it was pointed out that the difficulty attending formation of large carbon rings should be attributed mainly to free rotation of atoms constituting open carbon chains, and consequently that this difficulty should be reduced by inhibiting free rotation. One of the examples cited in support of this view was that which was encountered in the facile formation of seven-membered rings attached to the 2,2′-positions of diphenyl. The present paper deals with the case of 2,2′-diphenyldiphenyl (I), in the *p*-positions of the phenyl groups of which are present suitable substituents through which cyclization may be effected.

Although the number of carbon atoms separating the *p*-substituting atoms in the phenyl groups in 2,2′-diphenyldiphenyl exceed that separating the 2,2′-substituting atoms in diphenyl by as many as eight, it is clear that, as a result of inhibition of free rotation, the relative position of the *p*-substituting atoms in the former compound is altered only by free rotation of the benzene nuclei around the common axis of the central diphenyl system, a condition which is precisely the same in the case of 2,2′-substituting atoms in diphenyl. Thus, in regard to one of the main factors which determine the ease of ring formation, there is a close similarity between the 2,2′-positions and the *p*-positions of the phenyl groups. We are however not as yet certain whether substituting atoms in the *p*-positions of the phenyl groups in 2,2′-diphenyldiphenyl can approach each other or not, for, in order to do so, the compound will have to assume a strained configuration. It should be noted that in this case the valency angle will have to be increased in order to bring the *p*-substituting atoms close together, just as Baeyer⁽²⁾ has erroneously supposed to be the case in alicyclic rings composed of six carbon atoms and more, but in the present case the condition is altogether different and there seems to be no means whereby strain can be relieved.

On the other hand, although the supposed condition of 2,2′-diphenyldiphenyl molecule involves strain, this is not large (here it is assumed that the

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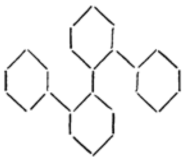
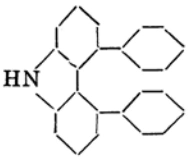
(1) This Bulletin, **9** (1934), 41.

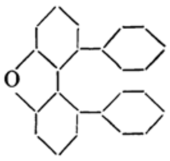
(2) *Ber.*, **18** (1885), 2277.

valency deflection is possible only in the planes in which the benzene nuclei lie(3)). Further, a fact from which we may assume that there is a possibility of the *p*-substituting atoms coming close together is to be found in the ready formation of 4,5-diphenyl carbazole (II)(4) and 4,5-diphenyldiphenylene oxide (III)(5) from 2,2′-diamino-6,6′-diphenyldiphenyl, since, as has been shown some time ago,(3) the closure of five-membered rings in these substances must necessarily be accompanied by the two atoms in question being in close proximity.


(I)

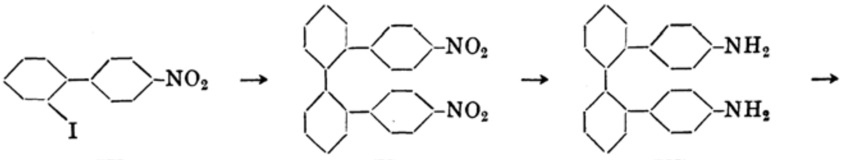


(II)

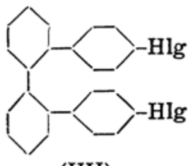


(III)

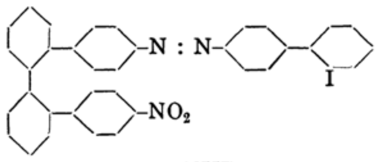
With these considerations in mind, the possibility of effecting cyclization in 2,2′-bis-(*p*-nitrophenyl)-diphenyl (V), 2,2′-bis-(*p*-aminophenyl)-diphenyl (VI), and 2,2′-bis-(*p*-halogenophenyl)-diphenyl (VII) has been investigated. 4′-Nitro-2-iododiphenyl can be obtained from 4′-nitro-2-aminodiphenyl, and the compound has been treated with copper powder to yield (V), which has been converted successively into (VI) and (VII).



(IV) (V) (VI)



(VII)



(VIII)

The yield of (V) has been found to be unexpectedly small. After a large number of comparative experiments, it has been found that the best yield (53% of the theoretical) is obtained when the quantity of copper powder is 1.4 times the theory, a larger amount giving a lower yield. The rather poor

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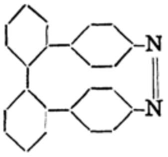
(3) This Bulletin, **9** (1934), 63-64.

(4) This Bulletin, **9** (1934), 70.

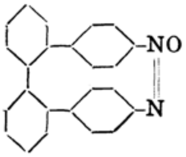
(5) This Bulletin, **9** (1934), 72.

yield seems due mainly to the reducing action of copper powder on the nitro-groups, for, in addition to (V), there is also produced a small quantity of a crystalline substance which appears to have the constitution (VIII). Search has naturally been made for the compound (IX) amongst the products, as it has been thought possible that, if the compound (VIII) is producible by the condensation of (IV) with (V) as would be supposed most probable, the compound (IX) may be produced from (V) alone, since, in general, combination of two atoms by an intramolecular reaction leading to a ring compound takes place more readily than that by an intermolecular one, provided of course that in the former case the atoms can approach each other easily. No crystalline substance other than (V) and (VIII) has however been isolated. It is possible that even though the compound (IX), the structure of which is not a stable one, is produced during the reaction, it cannot survive at such a high temperature as employed in this reaction.

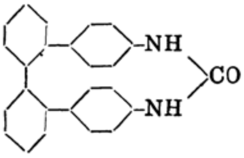
The comparison of the compounds (V), (VI), and (VII) respectively with 2,2′-dinitro-, 2,2′-diamino-, and 2,2′-dihalogeno-diphenyl shows at once that relative positions of the nitro-groups, the amino-groups, and the halogenoradicals in both series of compounds are altered in exactly the same way as already mentioned, and therefore if the methods such as those used for producing (i) phenazone(6) or phenazone oxide(7) from 2,2′-dinitrodiphenyl, (ii) 2-keto-2,3-dihydrodiphenimidine(8) from 2,2′-diaminodiphenyl and urea, (iii) carbazole(9) from 2,2′-diaminodiphenyl, (iv) diphenylene(10) from 2,2′-dibromodiphenyl can be applied to the compounds (V), (VI), and (VII), the result would be the formation of large ring compounds (IX), (X), (XI), (XII) and (XIII).



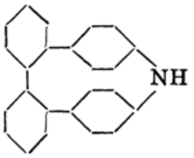
(IX)



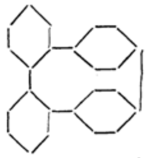
(X)



(XI)



(XII)



(XIII)

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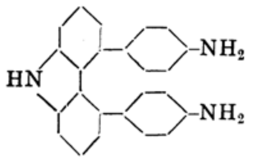
(6) Täuber, *Ber.*, **24** (1891), 3085.
(7) Ullmann and Dieterle, *Ber.*, **37** (1904), 23.
(8) Niementowski, *Ber.*, **34** (1901), 3330.
(9) Täuber, *Ber.*, **24** (1891), 200.
(10) Dobbie, Fox, and Gauge, *J. Chem. Soc.*, **99** (1911), 683.

The strain in substances such as the hypothetical (XII) and (XIII) would undoubtedly be very large, and indeed with a Kekulé nucleus such formulæ can not be constructed. As a matter of fact, 2,2′-bis-(*p*-bromophenyl)-diphenyl and 2,2′-bis-(*p*-iodophenyl)-diphenyl (VII), on treatment with metallic sodium in absolute ether, gives 2,2′-diphenyldiphenyl (I) as the only crystalline product, and no reaction occurs when 2,2′-bis-(*p*-aminophenyl)-diphenyl is heated with hydrochloric acid at high temperatures.

In the case of hypothetical substances (IX), (X) and (XI), however, there appears to be less reason for instability, and if the nitrogen atoms in the compounds (V) and (VI) can only come close together, they may pass into the respective compounds (IX), (X), and (XI). In practice, however, it has been found that such cyclization cannot be effected. Whether this failure is due to the impossibility of bringing the nitrogen atoms close together or to the instability of the hypothetical rings, it is impossible at present to say, but if due to the former cause, it is possible that, in a compound such as (XIV) in which the two amino-groups would be in close proximity, cyclization reactions similar to those which take place in 2,2′-diaminodiphenyl as well as in *o*-phenylenediamine can be applied. It is proposed to investigate the possibility of ring formation in this or similarly constituted compounds.



(XIV)

Experimental.

4′-Nitro-2-aminodiphenyl hydrochloride. Scarborough and Waters,(11) by the nitration of 2-acetamidodiphenyl, obtained 4′-nitro-2-acetamidodiphenyl in 44 per cent. yield. The following method, which is an improvement of theirs, gave 78 per cent. yield.

To a solution of 53 g. of 2-acetamidodiphenyl in 53 c.c. of acetic acid and 106 c.c. of conc. H_2SO_4 was added at 0–2°C. a mixture of 15 c.c. of fuming HNO_3 (d=1.51) and 53 c.c. of acetic acid with stirring. About one hour was required for the addition of the mixed acid. After one more hour's agitation, the mixture was poured on ice, when the product formed a faintly yellow syrup which solidified after a time. The dried crude product weighed 63 g. On crystallization from chloroform, it gave light-yellow thin needles melting at 193°. The yield of pure 4′-nitro-2-acetamidodiphenyl was 50 g.

The acetyl compound was hydrolysed with moderate ease by alcoholic HCl and with difficulty by alkali. As the action of the 10 per cent. alcoholic HCl employed by Scarborough and Waters(11) proved too weak, the hydrolysis was conducted as follows: a suspension of 70 g. of 4′-nitro-2-acetamidodiphenyl in a mixture of 140 c.c. each of EtOH and conc. HCl was refluxed on the water bath for 90 minutes. The original substance disappeared in 15 minutes to be followed after a time by the separation of the crystalline

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(11) *J. Chem. Soc.*, **1927**, 95.

4-′nitro-2-aminodiphenyl hydrochloride. After cooling the crystals were collected and washed with 20 per cent. HCl solution (Found: Cl, 13.94. Calc. for $C_{12}H_{11}O_2N_2Cl$: Cl, 14.16%). The dried crystals weighed 65 g. The mother liquor, on concentration, gave a second crop, 2.8 g. The hydrochloride readily loses HCl either on heating or on washing with water, showing that it is a weak base.

4′-Nitro-2-iododiphenyl (IV). A mixture of 68 g. of 4′-nitro-2-aminodiphenyl hydrochloride, 100 c.c. of conc. HCl, and 80 g. of cracked ice was, with external cooling by ice, treated with 20.7 g. of solid sodium nitrite with stirring. The diazotized solution was filtered if necessary, treated with a solution of 60 g. of potassium iodide, and allowed to stand for three days until completion of the reaction (the decomposition by heating on the water bath somewhat lowers the yield of the iodo-compound). The crude iodo-compound thus precipitated, 89.7 g., was dissolved in ether and shaken with a KOH solution. After the removal of the ether, the residue was distilled in vacuum. It had b p. 203°/5 mm. On crystallization from EtOH, beautiful yellow needles melting at 100–101.5° separated. The yield of the purified substance was 64.6 g. (Found: C, 44.2; H, 2.7. Calc. for $C_{12}H_8O_2NI$: C, 44.3; H, 2.5%). 4′-Nitro-2-iododiphenyl is very easily soluble in boiling EtOH and sparingly so in the cold.

4′-Amino-2-iododiphenyl, its hydrochloride and the acetyl derivative. A hot solution of 10.8 g. of 4′-nitro-2-iododiphenyl in 100 c.c. of EtOH was mixed with 27 g. of $SnCl_2 \cdot 2H_2O$ and 33 c.c. of conc. HCl, and heated on the water bath for 15 minutes, at the end of which the yellow colour of the original substance had disappeared. The solution was concentrated to one half the original bulk, and, while still hot, diluted with 100 c.c. of water, when 4′-amino-2-iododiphenyl hydrochloride separated at once as colourless needles which were collected and washed with EtOH-water. The hydrochloride thus obtained was pure and weighed 10.6 g. It can be crystallized from EtOH or EtOH-water (Found: Cl, 10.60. Calc. for $C_{12}H_{11}NClI$: Cl, 10.70%).

The free base was obtained as follows: the hydrochloride obtained above was shaken with a sodium hydroxide solution and ether, and the ethereal layer evaporated up. The residual syrup resisted all attempts at crystallization. It was therefore purified by vacuum distillation (Found: I, 43.20. Calc. for $C_{12}H_{10}NI$: I, 43.02%).

The gummy free base on acetylation gave the crystalline acetyl derivative: on treatment of a conc. ethereal solution of 4′-amino-2-iododiphenyl with the calculated quantity of acetic anhydride, 4′-acetamido-2-iododiphenyl separated in colourless needles after a short time. It had m.p. 162–163°C. (Found: I, 37.49. Calc. for $C_{14}H_{12}ONI$: I, 37.66%).

The action of copper powder on 4′-nitro-2-iododiphenyl. Formation of 2,2′-bis-(*p*-nitrophenyl)-diphenyl (V) and 4-(*o*-iodophenyl)-4′-[*o*-(*p*′-nitro-*o*-diphenylyl)-phenyl]-azobenzene (VIII). As stated in the introduction the preparation of 2,2′-bis-(*p*-nitrophenyl)-diphenyl from 4′-nitro-2-iododiphenyl present unexpected difficulties, and, in spite of the many experiments made under a great variety of conditions, no more than a 50 per cent. yield could be obtained. The best result was obtained as follows.

2,2′-Bis-(p-nitrophenyl)-diphenyl (V). Copper powder (1.8 g.) prepared by the method of Piccard and Larsen⁽¹²⁾ was added with stirring to 6.5 g. of 4′-nitro-2-iododiphenyl which was heated in an oil bath at 220-225°, and the heating and agitation continued for 80 minutes. After cooling, the solidified mass was extracted with 700 c.c. of C_6H_6. The

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

extract was treated with animal charcoal and concentrated until, while heating, the crystals began to separate (about 180 c.c.). The yellow thin needles thus obtained, 2.1 g., was almost pure 2,2′-bis-(*p*-nitrophenyl)-diphenyl. The pure substance obtained by crystallization from benzene melted at 290° (Found: N, 7.2. Calc. for $C_{24}H_{16}O_4N_2$: N, 7.1%). By a couple of analyses on carbon and hydrogen, it was shown that the dinitro-compound is one of those rare organic compounds which do not give the correct figure for carbon, although a good result was obtained for the hydrogen content. About 100 c.c. of boiling benzene is required to dissolve 0.5 g. of this compound.

4-(o-Iodophenyl)-4′-[o-(p′-nitro-o-diphenylyl)-phenyl]-azobenzene (VIII). This substance was contained in the mother liquor of the yellow needles of 2,2′-bis-(*p*-nitrophenyl)-diphenyl described above. On concentration of this solution to about 10 c.c., 2,2′-bis-(*p*-nitrophenyl)-diphenyl (V), 0.14 g., separated, which was filtered off. The filtrate was evaporated off and the residue, after the removal of the alcohol-soluble part by extraction with EtOH, crystallized from 4 c.c. of benzene, inoculation being desirable if possible. The orange crystals of (VIII) thus obtained weighed 0.10 g. It happened at times that the orange crystals were contaminated with the yellow needles of (V). The mechanical separation of the two substances could be effected fairly completely by means of decantation, if proper care was taken that the orange crystals of (VIII) are made to grow large enough. A fact which should be noted in this connection is that, although the orange compound (VIII) used to separate from C_6H_6 in a compact granular form, it crystallized at times in short prisms and rarely in thin needles, and that these forms were capable of coexistence in benzene. The purified substance (VIII) melted, irrespective of crystalline forms, at 312–313° (Found: C, 64.8; H, 3.9; N, 6.7; I, 18.8. Calc. for $C_{36}H_{24}O_2N_3I$: C, 65.8; H, 3.7; N, 6.4; I, 19.3%). Rast's method for molecular weight determination could not be applied because of its slight solubility in camphor. On heating the powdered orange compound with a mixture of stannous chloride, conc. HCl, and acetic acid it disappeared slowly forming a colourless solution. This was probably the indication that the molecule was cleaved at the double bond to give the two amines, a reaction characteristic of an azo-compound. The substance is insoluble or very slightly soluble in usual organic solvents. Ten c.c. of boiling benzene dissolves about 0.1 g. of the orange crystals.

2,2′-Bis-(*p*-aminophenyl)-diphenyl (VI). This substance can be obtained by the reduction of 2,2′-bis-(*p*-nitrophenyl)-diphenyl (V) either with stannous chloride or with sodium sulphide.

Dry HCl was passed into a mixture of 5.3 g. of powdered 2,2′-bis-(*p*-nitrophenyl)-diphenyl, 2.7 g. of stannous chloride, and 150 c.c. of acetic acid, and the mixture heated on the water bath at 60–70°C. The sparingly soluble dinitro-compound slowly disappeared to be replaced by the voluminous, powdery double salt. As the mixture became very thick, frequent shaking was necessary. Heating was continued for some hours till the complete disappearance of the dinitro-compound, HCl being passed in all the time. After cooling, the fine bluish precipitate was collected, dissolved in 150 c.c. of water, treated with an excess of KOH solution, and the liberated base dissolved in ether. On removal of ether, the residue completely crystallized, which was distilled under reduced pressure. It had b.p. 290°/5 mm. The distillate was dissolved in boiling EtOH (36 c.c.), concentrated to about 18 c.c., and allowed to stand for crystallization. Inoculation was found often necessary. The large colourless crystals, 3.9 g., melted at 163-164°C. (Found: N, 8.6. Calc. for $C_{24}H_{20}N_2$: N, 8.3%). By concentration of the mother liquor, some more crystals separated, and the yield was quantitative.

The reduction of the dinitro-compound (V) with sodium sulphide was carried out as follows: a mixture of 2 g. of (V), 7.5 g. of sodium sulphide, 90 c.c. of EtOH, and 30 c.c. of H_2O was refluxed for three hours. The original substance disappeared in 30 minutes. On concentration of the reaction mixture to a small bulk, followed by the addition of water, an oil separated, which solidified at once. It was crystallized from EtOH. The crystals thus formed melted, either alone or when mixed with the diamino-compound obtained by the stannous chloride method described above, at 163–164°C.

2,2'-Bis-(*p*-iodophenyl)-diphenyl (VII). A suspension of 1.7 g. of 2,2'-bis-(*p*-aminophenyl)-diphenyl (VI) in 33 g. of 8 per cent. HCl solution was gently heated with agitation, when the difficultly soluble hydrochloride was deposited in needles. It was then cooled in ice and treated with 0.76 g. of sodium nitrite with agitation. After an hour's agitation, a clear solution resulted, which was treated with a solution of 2.4 g. of KI. It was then allowed to stand at ordinary temperature for two hours and finally heated at 50°C. The brown precipitate thus obtained was dissolved in ether, shaken with a KOH solution, and the ether removed. The residue, 2.6 g., was purified first by vacuum distillation and then by two crystallizations from C_6H_6-EtOH. It was obtained in yellow needles melting at 205–206°C. (Found: I, 44.4. Calc. for $C_{24}H_{16}I_2$: I, 45.5%). It is readily soluble in C_6H_6, less so in ether, and very difficultly soluble in EtOH.

2,2'-Bis-(*p*-bromophenyl)-diphenyl (VII). 2,2'-Bis-(*p*-aminophenyl)-diphenyl (1.7 g.) was gently heated with a 5 per cent. HBr solution. The clear solution thus obtained, on cooling with ice water, separated the dihydrobromide in needles. The latter, on treatment with a solution of 0.76 g. of sodium nitrite, disappeared in a short time. To the bisdiazonium bromide solution was added cuprous bromide, which was prepared by boiling a mixture of 1.26 g. of $CuSO_4 \cdot 5H_2O$, 0.40 g. of copper powder, 2.28 g. of anhydrous NaBr, 0.60 g. of conc. H_2SO_4, and 10 c.c. of water for some hours. The reaction mixture was allowed to stand for decomposition at ordinary temperature. The decomposition proceeded very slowly. After one week, it was heated at 50°, and the precipitated substance collected and extracted with ether. The ether was removed and the residue, on distillation under reduced pressure, gave a crystalline distillate (0.55 g.), which was twice recrystallized from EtOH (10 c.c.). The almost colourless needles thus obtained had m.p. 170–171°C. (Found: Br, 34.0. Calc. for $C_{24}H_{16}Br_2$: Br, 34.5%).

Instead of leaving, as described above, the bis-diazonium bromide solution at ordinary temperature, when it was heated at 50–60°, the decomposition was complete in one hour, but the product was contaminated with a larger quantity of impurities which rendered the purification difficult. In any case, the yield of the desired substance was far from being satisfactory.

The action of sodium on 2,2'-bis-(*p*-iodophenyl)-diphenyl. A solution of one gram of 2,2'-bis-(*p*-iodophenyl)-diphenyl in 150 c.c. of absolute ether was heated under reflux in a water bath at 45° with a large excess of finely divided sodium metal, with constant stirring (mercury seal). The separation of sodium iodide was noticeable after 20 hours' heating. The yellow colour of the solution gradually disappeared. After 63 hours' heating, it was filtered and the filtrate evaporated off. The residue which consisted of beautiful colourless crystals was dissolved in EtOH, treated with animal charcoal to remove a trace of an amorphous matter and the filtrate concentrated to a few c.c. The colourless crystals thus separated melted at 117–118°C. and found by the mixed melting point method to be identical with 2,2'-diphenyldiphenyl made from 2-iododiphenyl.(13)

The action of metallic sodium on 2,2'-bis-(*p*-bromophenyl)-diphenyl. A solution of 0.4 g. of 2,2'-bis-(*p*-bromophenyl)-diphenyl in 100 c.c. of absolute ether was refluxed in a water bath at 45° for 100 hours with stirring. It was then filtered and the ether removed. The partly solidified residue was collected on a filter, washed first with EtOH and then with petroleum ether. The almost colourless needles thus obtained, 0.21 g., on crystallization from EtOH gave slender needles which proved to be the original dibromo-compound (mixed m.p.). The oily filtrate and the washings were united and the solvents removed. The residual gummy substance persistently resisted crystallization, but when seeded with a crystal of 2,2'-diphenyldiphenyl(13) prepared from 2-iododiphenyl, gradual increase of the crystals was observed, showing the presence of the same substance among the products. That some of the dibromo-compound was acted on by sodium was further shown by the fact that the aqueous solution of the solid separated from the original ethereal solution, on treatment with HNO_3 and $AgNO_3$, deposited AgBr.

Attempts to prepare the hypothetical large ring compounds (IX) and (X). As already described on p. 591, the action of sodium sulphide on 2,2'-bis-(*p*-nitrophenyl)-diphenyl (V) gave rise to the diamino-compound (VI), and not to the cyclic azoxy-compound (X). Another method of preparation of azoxy-compounds, namely, the use of alkaline arsenite(14) as the reducing agent was also attempted, but with indifferent success. Thus, although 2,2'-bis-(*p*-nitrophenyl)-diphenyl (0.5 g.), As_2O_3 (0.5 g.), NaOH (0.6 g.), H_2O (3 c.c.), and toluene (3.0 c.c.) were heated together in an oil bath at 145–160° for 40 hours with stirring, no change occurred, the original substance being recovered almost unchanged (in this reaction, in order to facilitate the reaction, toluene was used as solvent for the dinitro-compound which does not melt at the temperature). The use of alkaline stannite solution in an attempt to obtain the azo-compound (IX)(15) was also a failure.

The action of heat on 2,2'-bis-(*p*-aminophenyl)-diphenyl (VI) hydrochloride. 2,2'-Bis-(*p*-aminophenyl)-diphenyl (VI) and dil. HCl were heated in a sealed tube at high temperatures, but the only crystalline substance isolable was the unchanged diamino-compound.

The action of urea on 2,2'-bis-(*p*-aminophenyl)-diphenyl (VI). 2,2'-Bis-(*p*-aminophenyl)-diphenyl (VI) was heated either with urea alone or with a mixture of urea and *m*-cresol at varied temperatures. The liberation of ammonia gas was observed, but the reaction seemed to be a deep-seated one and no crystalline product could be isolated.

Chemistry Department, Imperial University
of Kyushu, Fukuoka.

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(13) Bowden, *J. Chem. Soc.*, **1931**, 1112.
(14) Loesner, *J. prakt. Chem.*, (2), **50** (1894), 564.
(15) Witt, *Ber.*, **18** (1885), 2912.