Derivatives of Phenols and Pyridines.—The compounds listed in Tables I and II were prepared by the usual methods. Melting points of all derivatives of phenols and of 4-picoline and 2,6-lutidine were not depressed when admixed with authentic samples.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, CARNEGIE INSTITUTE OF TECHNOLOGY]

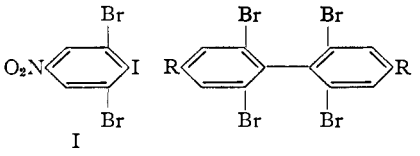
Anomalous Ullmann Reactions. The Unsymmetrical Coupling of 2,6-Dibromo-4-nitroiodobenzene[1]

BY ROBERT B. CARLIN AND EDWARD A. SWAKON[2]

RECEIVED AUGUST 11, 1954

When 2,6-dibromo-4-nitroiodobenzene (I) was treated with copper at 180–220°, four products were isolated and characterized: the "normal" product, 2,2′,6,6′-tetrabromo-4,4′-dinitrobiphenyl (II); plus the by-products 2,3′,6-tribromo-2′-iodo-4,5′-dinitrobiphenyl (IV), 2,6-bis-(2,6-dibromo-4-nitrophenyl)-4-nitroiodobenzene (V), and 3,5-dibromonitrobenzene (VI). The structures of II, IV and V were established by degradations to known compounds or to compounds which were synthesized by other methods. The formation of IV must be the result of an unsymmetrical Ullmann coupling of I, in which one of the two coupling I molecules undergoes displacement of a bromine atom rather than of the normally more active iodine atom, which in this case is further activated by a *p*-nitro group. The interaction of I and IV undoubtedly accounts for the formation of V. The hydrogenolysis of the carbon–iodine bond of I yields VI; reactions of this type have been observed by other investigators.

During an investigation of the benzidine rearrangement of 3,3′,5,5′-tetrabromohydrazobenzene,[3] an independent synthesis of 2,2′,6,6′-tetrabromobenzidine (III) appeared desirable. A synthetic route starting with 2,6-dibromo-4-nitroiodobenzene (I) offered some promise; the Ullmann transformation of I should yield the tetranitrobiphenyl II, which should be reducible to III.

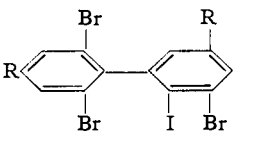


II, R = NO_2
III, R = NH_2
VII, R = NHAc

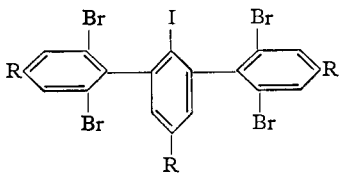
Known behavior of the halogenated benzenes in the Ullmann reaction suggested that the iodine atom of I should be far more readily displaced than the bromine atoms in the coupling by copper, for iodobenzenes are in general more active than bromobenzenes, and nitro groups *para* to halogen exert a pronounced activating effect whereas *meta* nitro groups have little influence.[4]

The synthesis I → II → III has now been accomplished, but an investigation of the action of copper on I disclosed that other products than II were formed. The by-products proved to be 2,3′,6-tribromo-2′-iodo-4,5′-dinitrobiphenyl (IV), 2,6-bis-(2,6-dibromo-4-nitrophenyl)-4-nitroiodobenzene (V) and 3,5-dibromoaniline (VI). This report is concerned with the isolation of the products from the Ullmann mixture, the characterization and proof of structure of each product and something of its mode of formation.

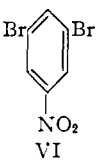
After I was mixed with sand and heated with copper–bronze powder at 180–220° for about a half hour, II, IV, V and VI were isolated in 30, 20, 4 and 5% yields, respectively; I was recovered unchanged in 10% yield, and a glassy resin accounted for an additional 15% of the weight of the starting material. No appreciable changes in the nature or ratio of products were effected by using nitrobenzene or mesitylene as solvents, by "activating" the copper powder,[5] by excluding atmospheric moisture from the mixture or by carrying out the reaction in a nitrogen atmosphere. The components of the reaction mixture were separated by solvent extraction and fractionation, steam distillation and high-vacuum sublimation. Such were the properties of IV and V that they were isolated from the mixture more easily than was II. Indeed, despite the fact that more II is formed than IV or V, the presence of II among the products was not discovered until long after both IV and V had been found. The operational details of the separation are described in the Experimental Section.



IV, R = NO_2
VIII, R = NH_2
IX, R = NHAc
X, R = H



V, R = NO_2
XV, R = NH_2
XVI, R = NHAc



VI

Proof of Structure of II.—The symmetrical tetrabromodinitrobiphenyl II could be obtained in either of two apparently dimorphic modifications; one, m.p. 174–175°, crystallized from methanol, but this form gave the second one, m.p. 184–185°, when subjected to high-vacuum sublimation. Analysis showed the two forms to be isomeric.

The structure of II was established on the basis of the following evidence. Treatment of a solution of II in ethanol with hydrogen in the presence of Raney nickel gave benzidine identified by com-

(1) From the D. Sc. Thesis by Edward A. Swakon.

(2) Institute Graduate Fellow in Organic Chemistry, 1950–1951.

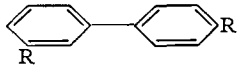
(3) R. B. Carlin and W. O. Forshey, Jr., THIS JOURNAL, **72**, 793 (1950).

(4) (a) *Cf.* P. E. Fanta, *Chem. Revs.*, **38**, 139 (1946); (b) W. Davey and R. W. Lattner, *J. Chem. Soc.*, 264 (1948).

(5) E. C. Kleiderer and R. Adams, THIS JOURNAL, **55**, 4219 (1933).

parison of it and of its N,N′-diacetyl derivative with authentic samples. Reduction of II by "activated" iron and water, a method reported by Hazlet and Dornfeld[6] to lead to no group migration, substitution or loss of halogen, gave 2,2′,6,6′-tetrabromobenzidine (III). The identity of this product and of its N,N′-diacetyl derivative (VII) with the corresponding substances derived from the rearrangement of 3,3′,5,5′-tetrabromohydrazobenzene[3] make it appear extremely unlikely that either the benzidine rearrangement of the tetrabromohydrazobenzene or the Ullmann reaction of I was accompanied by halogen migrations.

Proof of Structure of IV.—Despite the lower order of symmetry of the molecule IV compared to II, the compound IV had a higher melting point and was less soluble in the common solvents and less volatile under high vacuum. When analysis disclosed the presence of one iodine and three bromine atoms in the molecule, it was at once apparent that IV was the product of an unusual Ullmann reaction. That it was a biphenyl derivative was demonstrated by transforming IV to biphenyl (XIV) through the intermediates VIII and X. The reduction of IV to VIII was effected by the method of Hazlet and Dornfeld[6] and also by hydro-



XI, R = NO_2
XII, R = NH_2
XIII, R = NHAc
XIV, R = H

genation in the presence of Raney nickel of a benzene solution of IV which contained a small amount of pyridine. No reference could be found in the literature to this or any other procedure for the catalytic reduction of aromatic nitro compounds which does not simultaneously bring about the removal by hydrogenolysis of any iodine or bromine present. The deamination of VIII to X was accomplished by the usual ethanol reduction of the tetrazonium salt from VIII. Biphenyl (XIV) was the product when X in ethanol was hydrogenated over Raney nickel.

The structure of IV was effectively proved by its conversion to 3,4′-diaminobiphenyl (XII) through the intermediates VIII, IX and XIII. The location of the nitro groups of IV at the 3- and 4′-positions unambiguously fixes the positions of the halogens, barring halogen rearrangements for which no evidence could be found. The acetylation of VIII to IX was readily accomplished with ketene; in fact, the most effective way to purify VIII was to acetylate it and then reconvert the easily purified IX to VIII by boiling in ethanolic potassium hydroxide. Hydrogenolysis over Raney nickel in ethanol solution transformed IX to XIII, and XIII yielded XII after boiling with ethanolic hydrochloric acid.

Because 3,4′-diaminobiphenyl (XII) and its N,N′-diacetyl derivative (XIII) were not reported in the literature, their syntheses were required to complete the structure proof of IV. The hydrogenation of 3,4′-dinitrobiphenyl (XI) afforded XII easily enough, but a disparity between reports in the literature on the properties of 3,4′-dinitrobiphenyl made it necessary to establish the correct properties of XI before the structure of XII and thence of IV could be considered settled. Accordingly, XI was synthesized by each of three independent methods: (1) nitration of 3-nitrobiphenyl, which is obtained from the action of N-nitroso-*m*-nitroacetanilide on benzene; (2) the reaction of N-nitroso-*m*-nitroacetanilide with nitrobenzene; and (3) dinitration of 4-acetamidobiphenyl, followed by hydrolysis and deamination. These three methods were the ones employed by the two groups of investigators who reported products having different properties. In our hands all three methods gave a dinitrobiphenyl melting in the range 185–188°, which agrees with the melting point 189° for 3,4′-dinitrobiphenyl reported by Scarborough and Waters[7] but not with the 137° value recorded by Hodgson and Marsden.[8] Only the first of the three methods gave a product from which the isomeric 2,3′-dinitrobiphenyl could also be isolated. All three synthetic specimens of XI were reduced and acetylated to identical N,N′-diacetyl derivatives (XIII). The fact that these compounds were also identical with corresponding samples obtained by degrading IV constituted the final link in the structure proof of IV. The N,N′-dibenzoyl and the N,N′-bis-salicylal derivatives of XII were also prepared for characterization purposes.

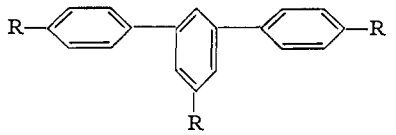
Proof of Structure of V.—The high melting point of V, its slight solubility in most of the common organic solvents and its failure to sublime at a noticeable rate at 235° (10^{-4} mm.) all suggested that its carbon skeleton was more complex than that of biphenyl. Reduction of the nitro groups, followed by acetylation of the resulting amino compound and then removal by hydrogenolysis of all the halogen produced a compound which was different from any known diacetamidobiphenyl. When a qualitative test showed the presence of iodine in V, it was evident that like IV, V was the product of an unusual Ullmann reaction.

The carbon structure of V was established by its degradation to *m*-terphenyl (XX). When a degradative scheme identical with the one by means of which IV was converted to biphenyl failed to yield a product from V which could be characterized, an alternative plan was followed with better results. Hydrogenation of V in benzene solution over Raney nickel gave a product which presumably had the structure XV. Neither this nor any of the succeeding intermediates in this degradation scheme was isolated or characterized but were submitted without purification to the next reaction in the series. Following the reduction of V, the solvent was removed and replaced by ethanol containing sodium hydroxide, and hydrogenation over Raney nickel was carried out again; this time the presumed product was XVII, the result of hydrogenolysis of halogen from XV. The crude solid product was treated with nitrosylsulfuric acid and then with potassium iodide, and the product, doubtless the triiodoterphenyl XIX, was again submitted to hydrogenolysis over Raney nickel. The final product, isolated by high vacuum sublimation in 22%

(6) S. E. Hazlet and G. A. Dornfeld, THIS JOURNAL, **66**, 1781 (1944).

(7) H. A. Scarborough and W. A. Waters, *J. Chem. Soc.*, 1133 (1927).

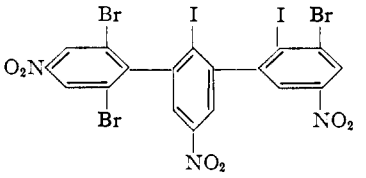
(8) H. H. Hodgson and E. Marsden, *ibid.*, 208 (1940); see also W. A. Waters, *ibid.*, 474 (1940).



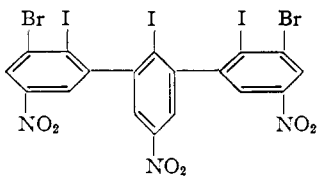
XVII, R = NH_2
XVIII, R = NHAc
XIX, R = I
XX, R = H
XXIII, R = NO_2

over-all yield from V, melted at 86.5–87° after further purification. Of the linear polyphenyls, only *m*-terphenyl (XX, m.p. 86°) and 3,3′-diphenylbiphenyl (m.p. 87°) are reported to have melting points corresponding to that of the degradation product. Accordingly, both XX and 3,3′-diphenylbiphenyl were synthesized. The synthesis of XXII was accomplished by treating benzene with N-nitroso-3-acetamidobiphenyl, and 3,3′-diphenylbiphenyl was prepared by the Ullmann coupling of 3-iodobiphenyl. The quaterphenyl depressed the melting point of the degradation product; XX did not.

If no halogen migrations accompanied the transformation of I to V, then only three *m*-terphenyl derivatives could have been formed from I. One of these has the structure V, and the other two are formulated as XXI and XXII. Although the ana-



XXI



XXII

lytical data clearly point to V as the correct structure, additional evidence was sought. To this end, V was converted through the intermediates XV and XVI to the triacetamidoterphenyl XVIII, which was synthesized by another method. Although completely satisfactory analytical results on XVIII were never obtained and although the mixed melting point method of identifying two samples of XVIII may not be valid because XVIII melts with decomposition, there can be little doubt that XVIII is the correct structure for the end product of both reaction series.

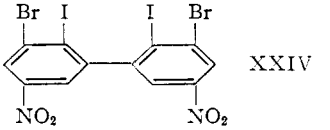
The reduction of V to XV was accomplished both by the method of Hazlet and Dornfeld[6] and by the catalytic method employing benzene containing a little pyridine as the solvent and Raney nickel as the catalyst. Acetylation of XV either by acetic anhydride or by ketene yielded XVI, from which XV could be regenerated by boiling with ethanolic hydrochloric acid. Hydrogenolysis of XVI in the presence of Raney nickel gave XVIII, and iodide ion was shown to be present in the aqueous washings from the reaction mixture.

The independent synthesis of XVIII started with 5-nitro-1,3-phenylenediamine, which was converted to N,N′-dinitroso-1,3-diacetamido-5-nitrobenzene. When this compound reacted with nitrobenzene in the presence of sodium carbonate, a mixture was formed in which at least two isomeric trinitro-*m*-terphenyls were present; the one considered most likely to have the symmetrical structure XXIII melted at 263–268° and was substantially less soluble in benzene than its isomer, m.p. 177–183°. Reduction of the higher melting isomer and acetylation of the product by ketene gave a compound apparently identical with the sample of XVIII derived from V. This synthesis of XVIII, though it does not lead to a product of certain structure, does supply additional evidence favoring the assignment of the structure V to the highest melting product of the Ullmann reaction of 2,6-dibromo-4-nitroiodobenzene; for it is unlikely that the interaction of N,N′-dinitroso-1,3-diacetamido-5-nitrobenzene with benzene would give as a major product a *m*-terphenyl derivative having the same orientation of nitro groups as either XXII or XXIV, the alternatives to V.[9]

Discussion.—Although the product II of the symmetrical Ullmann coupling of I was formed in a larger amount than any of the by-products, nevertheless, IV and V, both products of unsymmetrical Ullmann couplings, were formed in 24% combined yields. There appears to be no other recorded example of an unsymmetrical Ullmann coupling of a single aromatic di- or polyhalide, though the coupling of two different aryl halides to give an unsymmetrical product is well known.[4a] The unsymmetrical coupling of I to form IV is remarkable in a second sense; one of the two I molecules which leads to IV undergoes displacement of a bromine atom, rather than of the normally more active iodine atom which is further "activated" toward Ullmann displacement by a *p*-nitro group.

The *m*-terphenyl derivative V must have been formed by the Ullmann coupling of IV, at the 3-position occupied by the bromine atom, with I functioning through its iodine atom. Efforts to demonstrate that this reaction does occur proved inconclusive when mixtures of I and IV gave no more V than could be accounted for on the assumption that all of the V formed had come from I alone.

Any satisfactory mechanism for the Ullmann reaction must be capable of yielding an explanation for the formation of the unsymmetrical coupling products IV and V from I. An account must also be given for the observation that the "normal" symmetrical coupling product II, but no "abnormal" symmetrical coupling product XXIV, was isolated.



XXIV

A fundamental understanding of the Ullmann reaction probably cannot be derived from the information now on record, extensive though this information may be. Interpretation of the available data

(9) *Cf.* D. F. De Tar and H. J. Schiefele, THIS JOURNAL, **73**, 1442 (1951).

is rendered uncertain because (a) the widely varying conditions under which Ullmann reactions have been carried out make a valid comparison of the results impossible; and (b) the practice of measuring "reactivities" of aryl halides in terms of yields of products under varying and poorly specified and controlled conditions has little meaning with respect to the nature of the reaction, although data of this nature may prove most useful in a more practical way. A program aimed at providing systematic information about the Ullmann reaction is being developed in this Laboratory.

The isolation of 3,5-dibromonitrobenzene (VI) as a by-product from the Ullmann reaction of I presents no new features. The hydrogenolysis of halogen from aryl halides by copper and organic acids[10] and by copper and tetralin[11] have been demonstrated. But substitution of aromatic halogen by hydrogen has also been observed when no obvious hydrogen source was present. Hydrogenolysis has been reported as a side reaction to Ullmann coupling in several cases when no solvent was used[12-15]; indeed, in one instance some hydrogenolysis occurred in an "inert" atmosphere.[13] The fact that VI was isolated from I in the present investigation even when the mixture was carefully dried and protected from atmospheric moisture indicates that the hydrogen which replaced the iodine probably came from I or its products. It is significant, also, that the iodine atom of I was removed by hydrogenolysis, but no debromination product of I was detected.

Finally, the resinous glass isolated from the mixture resulting from the action of copper on I may consist of a mixture of polyphenyls derived from the coupling of II, IV, V and analogs of these with each other and with I.

Experimental

2,6-Dibromo-4-nitroiodobenzene (I).—The method used by Schoutissen[16] to convert 2,6-dibromo-4-nitroaniline[17] to I was improved by diazotizing the amine in accordance with the procedure described by Hodgson and Walker.[18] With vigorous stirring, 25 g. of finely powdered sodium nitrite was added slowly to 150 ml. of concentrated sulfuric acid while the temperature was maintained at 0°. The mixture was warmed at 70° until all solids dissolved, cooled to 15° and then added gradually to a well-stirred suspension of 75 g. of 2,6-dibromoaniline in 600 ml. of glacial acetic acid which was cooled at 15°. The temperature of the mixture was kept below 25° during the addition, and stirring was continued until no insoluble solids remained. The yellow solution was diluted with 2 l. of a water–ice slurry, and 25 g. of urea was added. The resulting solution was stirred vigorously and treated dropwise with a solution of 60 g. of sodium iodide in 300 ml. of water. The mixture was permitted to warm to room temperature overnight; then it was treated with a little sodium bisulfite (to remove traces of iodine), and the buff-colored product (I) was collected by filtration. After two recrystallizations from "Cellosolve," I formed light tan needles (185–195 g., 84–88%), m.p. 153–155°. The m.p. 153.5° has been reported.[16]

(10) W. T. Smith, Jr., THIS JOURNAL, **71**, 2855 (1949).

(11) R. W. Hardacre and A. C. Perkin, *J. Chem. Soc.*, 180 (1929); M. S. Lesslie and E. E. Turner, *ibid.*, 281 (1932).

(12) F. B. McAllister and J. Kenner, *ibid.*, 1913 (1928).

(13) W. S. Rapson and R. G. Shuttleworth, *ibid.*, 487 (1941).

(14) M. Rindl, *ibid.*, 1911 (1913).

(15) H. C. Yuan and M. Tsao, *J. Chinese Chem. Soc.*, **3**, 358 (1935); *C. A.*, **30**, 2187, 7095 (1936).

(16) H. A. J. Schoutissen, THIS JOURNAL, **55**, 4531 (1933).

(17) R. Meyer, W. Meyer and K. Taeger, *Ber.*, **53**, 2034 (1920).

(18) H. H. Hodgson and J. Walker, *J. Chem. Soc.*, 1620 (1933).

Reactions of 2,6-Dibromo-4-nitroiodobenzene (I) with Copper.—An intimate mixture of 100 g. of 2,6-dibromo-4-nitroiodobenzene (I), 65 g. of copper[19] and 150 g. of clean sand was stirred with a large paddle and heated to 180°. The spontaneous temperature rise which occurred at this point was not permitted to continue beyond 220°; then the mixture was maintained at about 210° for a half-hour. The dark grey sludge was boiled with four 500-ml. portions of benzene, and the combined extracts were allowed to trickle through a 1 × 12 in. column of activated alumina to remove carbonaceous material, tars and traces of inorganic solids. The solvent was removed from the light yellow solution, the residue was treated with 100 ml. of acetone and the mixture was cooled in the refrigerator for several hours before the insoluble solids were collected by filtration. This mixture of 2,2′,6,6′-tetrabromo-4,4′-dinitrobiphenyl (II), 2,3′,6-tribromo-2′-iodo-4,5′-dinitrobiphenyl (IV) and 2,6-bis-(2,6-dibromo-4-nitrophenyl)-4-nitroiodobenzene (V) was separated into its components by high vacuum sublimation. At 0.1 μ the fraction which sublimed at temperatures below 190° was II, the 190–235° fraction was IV, and the residue was V.

The acetone solution after removal of the insoluble solids contained some unchanged I, some II and IV, some 3,5-dibromonitrobenzene (VI), and resinous material. The acetone was distilled from the solution and the mixture was subjected to sublimation at 0.1 μ. A mixture of I and VI separated at temperatures below 140°, and VI was separated from I by steam distillation. The fraction subliming at 140–190° was II, and the fraction subliming at 190–235° was IV. The dark, viscous, acetone-soluble residue congealed to a glass on cooling.

A series of five Ullmann reactions of 100 g. of I each was carried out in accordance with the procedure just described. The benzene extracts of the crude products from the five runs were combined and the components of the mixture were separated by means of the procedure described in the preceding paragraph. The per cent. yield of each product, shown in Table I, then represents the average yield over five runs.

TABLE I

YIELDS OF PRODUCTS FROM 500 G. OF 2,6-DIBROMO-4-NITROIODOBENZENE (I)

Cpd. no.	In acetone-insoluble fraction, g.	In acetone-soluble fraction, g.	Total yield G.	Total yield %
I	..	42	42	10.3
II	44	60	104	30.2
IV	54	20	74	19.4
V	16	..	16	4.8
VI	..	18	18	5.2
Resin	..	55	55	

When nitrobenzene, mesitylene or xylene was used as a solvent for the reaction, it was removed by steam distillation, and then the procedure described above was followed for the isolation of the products.

2,2′,6,6′-Tetrabromo-4,4′-dinitrobiphenyl (II) formed light yellow, flat needles, m.p. 174–175°, from methanol.

Anal. Calcd. for $C_{12}H_4N_2O_4Br_4$: C, 25.71; H, 0.71; N, 5.00. Found: C, 25.74; H, 0.84; N, 5.12.

Sublimation of II (m.p. 174–175°) at 175° (10^{-5} mm.) gave a cream-colored solid, m.p. 184.5–185.5°.

Anal. Calcd. for $C_{12}H_4N_2O_4Br_4$: C, 25.71; H, 0.71; N, 5.00. Found: C, 25.65; H, 0.78; N, 5.19.

2,3′,6-Tribromo-2′-iodo-4,5′-dinitrobiphenyl (IV) formed pale yellow needles, m.p. 233–233.5°, from benzene. The compound gave a positive sodium fusion test for iodine.

Anal. Calcd. for $C_{12}H_4N_2O_4Br_3I$: C, 23.73; H, 0.66; N, 4.61. Found: C, 24.15; H, 0.66; N, 4.71.

2,6-Bis-(2,6-dibromo-4-nitrophenyl)-4-nitroiodobenzene (V) as it was obtained by high vacuum sublimation was recrystallized from boiling chlorobenzene, once with and twice without charcoal treatment. It formed pale yellow crystals, m.p. 388.5–390°, which gave a positive sodium fusion test for iodine.

(19) O. Hommel Co., No. 1 Extra Fine, No. 5743. Activation of this copper by the procedure reported by Kleiderer and Adams[5] had no noticeable effect on the results.

Anal. Calcd. for $C_{18}H_6N_3O_6Br_4I$: C, 26.77; H, 0.74; N, 5.20. Found: C, 27.12; H, 0.63; N, 5.04.

3,5-Dibromonitrobenzene (VI) after a rapid steam distillation and three recrystallizations from methanol, formed yellow crystals, m.p. 103–105.5°. No m.p. depression was observed when this sample of VI was mixed with an authentic specimen.[17]

Structure Proof of 2,2',6,6'-Tetrabromo-4,4'-dinitrobiphenyl (II). Hydrogenation of II to Benzidine.—A solution of 2 g. of II (m.p. 174–175°) and 0.7 g. of sodium hydroxide in 150 ml. of ethanol was treated with hydrogen under 500 p.s.i. pressure at room temperature in the presence of Raney nickel. The product solution was filtered free of catalyst, concentrated to 25 ml. and poured into water. The resulting solid gave a silver-gray, crystalline product (0.6 g., 91.5%), m.p. 124–126.5°, after one recrystallization from water. A mixture of this sample with authentic benzidine showed no m.p. depression.

N,N'-Diacetylbenzidine.—Benzidine prepared from II (preceding paragraph) was boiled in acetic anhydride for 15 minutes, and the solution was poured into water. The aqueous mixture was cooled overnight in a refrigerator, and the solid was collected by filtration. After two recrystallizations from aqueous acetic acid, the product formed white needles, m.p. 327–330°, alone or when mixed with authentic N,N'-diacetylbenzidine.

2,2',6,6'-Tetrabromobenzidine (III).—"Activated" iron was prepared by adding 20 ml. of concentrated hydrochloric acid to 100 g. of iron filings, slowly and with stirring. The product was dried over sodium hydroxide and potassium hydroxide in a vacuum desiccator and used at once.

Small amounts of water were added periodically over 24 hours to a stirred, boiling mixture of 200 ml. of thiophene-free benzene, 2.5 g. of II and 100 g. of "activated" iron. The mixture was filtered, and the iron sludge was extracted twice with boiling benzene. Half of the combined filtrate and extracts was concentrated to 20 ml. and diluted with 20 ml. of boiling cyclohexane. On cooling, the solution deposited 0.9 g. (81.8%) of III, m.p. 249–250°, and another 0.1 g. (9%) of III was recovered when the filtrate from the first fraction was concentrated. The m.p. 249–250° has been reported[3] for III obtained from 3,3',5,5'-tetrabromohydrazobenzene. This procedure just described is adapted from the one reported by Hazlet and Dornfeld.[6]

N,N'-Diacetyl-2,2',6,6'-tetrabromobenzidine (VII).—The second half of the benzene solution of crude III was treated with a stream of ketene. The product, which precipitated from solution as it was formed, gave white needles, m.p. 337–339° with slight decomposition, after two recrystallizations from aqueous acetic acid. A mixture of a sample of this substance and one, m.p. 336.5–338.5°, which had been obtained *via* the benzidine rearrangement showed no m.p. depression.

Structure Proof of 2,3',6-Tribromo-2'-iodo-4,5'-dinitrobiphenyl (IV). 2,3',6-Tribromo-2'-iodo-4,5'-diaminobiphenyl (VIII). A. Activated-Iron–Water Reduction.—The best results were obtained when the filtered benzene solution from an "activated" iron and water reduction like that previously described was subjected to the reduction procedure a second time. The filtered benzene solution from the second reduction procedure was dried by distilling benzene from the solution until the distillate was no longer cloudy. The dry solution was cooled, and dry hydrogen chloride was introduced until precipitation of the amine hydrochloride, which decomposes below 100°, was complete. The hydrochloride was collected by centrifugation and dissolved in dilute hydrochloric acid. The amine was precipitated from the acid solution by treatment with concentrated sodium hydroxide and purified by three recrystallizations from methanol–cyclohexane, methanol–benzene, or benzene–cyclohexane. The light orange crystals, m.p. 225–270° dec., obtained at this stage in 50% yield, gave colorless crystals, m.p. 250° dec., from ethanol.

B. Reduction by Raney Nickel in Benzene Containing Pyridine.—A spoonful of Raney nickel catalyst which had been stored under ethanol was treated with 100 ml. of thiophene-free benzene, and liquid was distilled from the mixture until the alcohol had been removed from the contents of the flask. The catalyst was added to a solution of 7 g. of IV in 175 ml. of thiophene-free benzene to which a few ml. of pyridine had been added, and the mixture was treated with hydrogen under 3 atmospheres pressure at room temperature for four hours. The solution was filtered free of catalyst and treated with dry hydrogen chloride until no more precipitation occurred. The mixture was centrifuged and the solvent was decanted from the viscous, colorless oil which constituted the mixed hydrochlorides of VIII and of pyridine. The oil was dissolved in dilute hydrochloric acid, and VIII (5 g., 80%) was precipitated from the solution by treatment with concentrated aqueous ammonia. Crystallization of this product as described in Part A afforded light orange crystals, m.p. about 250° dec., when the sample was heated gradually or 270° dec. when placed in a bath at that temperature. There was no m.p. depression when this sample was mixed with one obtained as described in Part A.

C. Hydrolysis of Diacetyl Derivative IX.—A boiling solution of 3.4 g. of 2,3',6-tribromo-2'-iodo-4,5'-diacetamidobiphenyl (IX) (*cf.* next paragraph) in 30 ml. of ethanol was treated portionwise with a solution of 3 g. of potassium hydroxide in 6 ml. of water, and the resulting solution was boiled for two hours, diluted with 30 ml. of water, concentrated to 30-ml. volume, and poured into 50 ml. of water. The mixture was cooled in the refrigerator for several hours, and the crude VIII (2.9 g., 98%), m.p. 250° dec., was then collected by filtration. Recrystallization of VIII from ethanol gave white crystals, m.p. about 250° dec. The m.p. depended upon the rate of heating.

Anal. Calcd. for $C_{12}H_6N_2Br_3I$: C, 26.34; H, 1.46; N, 5.12. Found: C, 26.44; H, 1.62; N, 5.12.

N,N'-Dibenzoyl Derivative of VIII.—This compound was prepared in about 30% yield by following a procedure to be described presently for the conversion of 3,4'-diaminobiphenyl into its N,N'-dibenzoyl derivative. It formed white needles, m.p. 185° dec., after two recrystallizations from methanol–benzene.

Anal. Calcd. for $C_{26}H_{16}N_2O_2Br_3I$: C, 41.40; H, 2.12; N, 3.71. Found: C, 41.96; H, 2.07; N, 3.30.

2,3',6-Tribromo-2'-iodo-4,4'-diacetamidobiphenyl (IX).—When ketene was introduced into a benzene solution of crude VIII, the diacetyl derivative IX precipitated from solution in 80–95% yield. Boiling crude VIII with a large excess of acetic anhydride containing a drop of sulfuric acid gave a solution from which IX was isolated in 92–96% yield by dilution with water. Recrystallization from methanol-benzene or sublimation at 250° (10^{-5} mm.) gave white samples of IX which first melted over the range 160–180°, then resolidified over the range of 180–205°, and finally melted again at 280–283°.

Anal. Calcd. for $C_{16}H_{12}N_2O_2Br_3I$: C, 30.44; H, 1.90; N, 4.44. Found: C, 31.04; H, 1.85; N, 4.48.

When IX was recrystallized from aqueous acetic acid, it formed cream-colored needles, m.p. 283–284°; the lower melting range was not observed.

Anal. Calcd. for $C_{16}H_{12}N_2O_2Br_3I$: C, 30.44; H, 1.90; N, 4.44. Found: C, 30.73; H, 1.98; N, 4.25.

Apparently IX exists in dimorphic modifications, the lower melting form of which readily passes to the more stable higher-melting form at the melting point of the former.

2,3',6-Tribromo-2'-iodobiphenyl (X).—The crude hydrochloride of VIII, obtained by the iron–water reduction of IV, was dissolved in 100 ml. of concentrated hydrochloric acid, and the solution was stirred, cooled to 0°, and then treated portionwise with 3 g. of finely powdered sodium nitrite. The clear tetrazonium solution was dropped into 500 ml. of boiling ethanol, and the solution was filtered free of precipitated sodium chloride and concentrated to 75 ml. Cooling the concentrated solution caused the precipitation of a yellow-brown product which yielded 2.4 g. (56.5% based on IV) of 2,3',6-tribromo-2'-iodobiphenyl (X), m.p. 130–147°, on sublimation at 140° (10 μ). Repeated recrystallization from ethanol afforded white needles, m.p. 156.5–158°.

Anal. Calcd. for $C_{12}H_6Br_3I$: C, 27.87; H, 1.16. Found: C, 27.36; H, 1.27.

Biphenyl from X.—A solution of 0.9 g. of the tribromoiodobiphenyl X in 100 ml. of ethanol was reduced over Raney nickel for four hours at room temperature under three atmospheres pressure of hydrogen. The solution was filtered free of catalyst, concentrated to 15 ml. and poured into 300 ml. of water. After four hours standing in the refrigerator, the diluted mixture yielded on filtration a white solid which afforded 0.2 g. (75%) of biphenyl, m.p. (and mixed m.p. with an authentic sample) 69–70.5°, after sub-

limation at 70–80° (2–3 mm.) onto a Dry Ice–acetone chilled cold finger.

3,4′-Diacetamidobiphenyl (XIII) by Hydrogenolysis of IX.—A solution of 5.75 g. of 2,3′,6-tribromo-2′-iodo-4,5′-diacetamidobiphenyl (IX) and 1.5 g. of sodium hydroxide in 125 ml. of ethanol was treated with 3 g. of Raney nickel and then shaken with hydrogen at three atmospheres pressure for 12 hours at room temperature. The catalyst was extracted several times with boiling ethanol, and the filtrate and extracts were combined, concentrated to 40 ml. and poured into water. The mixture was cooled in the refrigerator for several hours; then the solid (2.4 g., 98%) was collected by filtration and washed with water. After two recrystallizations from any of the solvent combinations benzene–absolute ethanol, benzene–methanol, chlorobenzene–absolute ethanol or aqueous acetic acid, 1.8 g. (74%) of white needles, m.p. 185–186.5°, was obtained.

Anal. Calcd. for $C_{16}H_{16}N_2O_2$: C, 71.64; H, 5.97; N, 10.45. Found: C, 71.88; H, 6.11; N, 10.46.

3,4′-Diaminobiphenyl (XII) by Hydrolysis of XIII.—A boiling solution of 2 g. of XIII in 20 ml. of ethanol was treated slowly with 4 ml. of concentrated hydrochloric acid. After a half-hour continued boiling, the hydrochloride of XII began to separate from the solution. The solution was cooled, and 1.9 g. (99%) of the hydrochloride, m.p. 280° dec., was collected by filtration and washed with absolute ethanol. The hydrochloride was dissolved in 20 ml. of water, and the solution was made basic with sodium hydroxide. The amine XII was extracted into ether, and the ether solution was dried over sodium hydroxide. When efforts to crystallize XII succeeded only after its preliminary separation from solutions as an oil, it was purified by several sublimations at 90° (0.1 μ), which gave 0.65 g. (48%) of a white crystalline solid, m.p. 85.5–86.5°.

Anal. Calcd. for $C_{12}H_{12}N_2$: C, 78.26; H, 6.52; N, 15.22. Found: C, 78.20; H, 6.68; N, 15.20.

N,N′-Dibenzoyl derivative of XII was prepared by dropping 2 ml. of benzoyl chloride into a solution of 0.55 g. of XII in 15 ml. of benzene and 6 ml. of pyridine and warming the resulting mixture for an hour on the steam-bath. The mixture was poured into 100 ml. of water, and the insoluble solid (1.1 g., 94%) was collected by filtration and washed with aqueous sodium bicarbonate, with water and finally with ethanol. The N,N′-dibenzoyl derivative of XII formed tiny white needles, m.p. 223–224°, from absolute ethanol.

Anal. Calcd. for $C_{26}H_{20}N_2O_2$: C, 79.59; H, 5.10; N, 7.14. Found: C, 79.29; H, 4.88; N, 7.26.

N,N′-Bis-salicylal Derivative of XII.—This compound was prepared by following a procedure previously described for use on analogous substances.[3] It formed yellow needles, m.p. 148–149°, from benzene–*n*-heptane.

Anal. Calcd. for $C_{26}H_{20}N_2O_2$: C, 79.59; H, 5.10; N, 7.14. Found: C, 79.31; H, 5.21; N, 7.00.

3,4′-Dinitro-4-acetamidobiphenyl. Procedure A.—With efficient stirring 35 g. of 4-acetamidobiphenyl was added to 400 ml. of fuming nitric acid at such a rate that the temperature of the mixture remained below 5°. Stirring was continued for an hour after addition had been completed; then the solution was poured onto ice. The yellow solid was collected by filtration and washed once with water, then with dilute aqueous ammonia and then again with water. One recrystallization from acetic acid and one from "Methyl cellosolve" afforded 36 g. (72%) of a yellow crystalline solid, m.p. 244–244.5°. The reported m.p. is 243–244°.[7]

Procedure B.—A solution of 50 g. of 4-acetamidobiphenyl in 50 ml. of glacial acetic acid and 90 ml. of concentrated sulfuric acid was cooled to 0° and treated slowly with a solution of 40 ml. of nitric acid in 90 ml. of glacial acetic acid. After two hours the mixture was allowed to warm to room temperature, permitted to stand for 24 hours and then poured into 2 l. of crushed ice. The yellow precipitate was collected by filtration and washed with 2% aqueous sodium hydroxide and then with water. Purification as in Procedure A yielded 13 g. (18.2%) of a yellow crystalline solid, m.p. 241°. A mixture of the products of Procedure A and of Procedure B showed no m.p. depression.

3,4′-Dinitro-4-aminobiphenyl.—A solution of 36 g. of 3,4′-dinitro-4-acetamidobiphenyl in 120 ml. of cold sulfuric acid was warmed on the steam-bath for two hours. The dark solution was poured onto 3 l. of crushed ice, and the acid was neutralized with aqueous ammonia. The orange product was collected by filtration and washed with water. After a single recrystallization from "Cellosolve," 16 g. (52%) of orange crystalline aminodinitrobiphenyl was obtained, m.p. 230.5–232.5°. The reported m.p. is 233–234°.[7]

3,4′-Dinitrobiphenyl (XI). A. By Deamination of 3,4′-Dinitro-4-aminobiphenyl.—The detailed procedure given for the deamination of 2,4,6-tribromoaniline[20] was adapted to the deamination of 3,4′-dinitro-4-aminobiphenyl. A 78% yield of a yellow product was obtained which, after two recrystallizations from benzene–ethanol, afforded long, yellow needles of 3,4′-dinitrobiphenyl (XI), m.p. 186–188.5° Blakey and Scarborough have reported the m.p. 189°.[21]

B. By Nitration of 3-Nitrobiphenyl.—The procedure reported by Blakey and Scarborough[21] was modified as follows. While the temperature of the mixture was kept below 0°, 5 g. of 3-nitrobiphenyl[22] was stirred into 100 ml. of fuming nitric acid. The crude product was precipitated by pouring the solution onto crushed ice, collected by filtration, washed with water and dried. The 2,3′-dinitrobiphenyl in the crude product was dissolved out of the product by digesting it at the boiling point in 170 ml. of methanol. The 3,4′-dinitrobiphenyl was filtered from the cooled mixture and purified by a sublimation at 155° (1 μ) and two recrystallizations from benzene–methanol. Cream colored needles (2.1 g., 34%), m.p. 185–188°, were obtained.

C. From *m*-Nitroaniline and Nitrobenzene.—The preparation of 3-nitrobiphenyl from *m*-nitroaniline and benzene[22] was adapted to the preparation of 3,4′-dinitrobiphenyl simply by substituting 1.25 l. of nitrobenzene for 3 l. of benzene. Excess nitrobenzene was removed from the reaction mixture by steam distillation, and the residue was dissolved in 1750 ml. of benzene. The benzene solution was allowed to trickle through a 1 × 10 in. column of activated alumina, the benzene was removed by distillation, the residue was treated with 40 ml. of acetone, and the resulting mixture was allowed to cool in the refrigerator overnight. The orange, amorphous solid was removed by filtration and subjected to sublimation at 190° (0.01 mm.). The sublimate yielded 11 g. (12.4%) of light tan needles, m.p. 187–188°, after two recrystallizations from benzene–methanol.

3,4′-Diacetamidobiphenyl XIII by Hydrogenation and Acetylation of XI.—Three different samples of 3,4′-dinitrobiphenyl (XI), one prepared by each of the three procedures described above, were hydrogenated in benzene solution at room temperature in the presence of Raney nickel under three atmospheres pressure. The benzene solutions were filtered free of catalyst and treated with ketene until precipitation of XIII was complete. In each case, the m.p. of the product was essentially identical with that of a sample of XIII obtained by hydrogenolysis of IX, and none of the three mixtures showed a m.p. depression.

Structure Proof of 2,6-Bis-(2,6-dibromo-4-nitrophenyl)-4-nitroiodobenzene (V). 2,6-Bis-(2,6-dibromo-4-aminophenyl)-4-aminoiodobenzene (XV). Procedure A. By Reduction of V.—Hydrogenation of V in benzene solution containing a little pyridine was carried out by the same method used to effect the reduction of the tetrahalogendinitrobiphenyl IV to the corresponding diamine VIII. The precipitated mixed hydrochlorides of pyridine and of the product amine were treated with dilute hydrochloric acid, in which the product hydrochloride was effectively insoluble. It was separated from the solution by centrifugation, washed with water, and treated with aqueous ammonia. The amine thus freed (0.9 g., 57%) formed light tan crystals, from a large volume of benzene–ethanol, m.p. about 315° dec.

Procedure B. By Hydrolysis of 2,6-Bis-(2,6-dibromo-4-acetamidophenyl)-4-acetamidoiodobenzene (XVI).—A solution of 0.5 g. of XVI (see next paragraph) in 15 ml. of 95% ethanol was treated with 5 ml. of concentrated hydrochloric acid, and the resulting solution was boiled for three hours. The slightly soluble hydrochloride of the amine XV (0.3 g., 61%) was collected by filtration, suspended in ethanol, and treated with aqueous sodium hydroxide. The crude free amine was collected by filtration and washed twice with water and once with ethanol. After two recrystallizations

(20) A. H. Blatt, "Organic Syntheses," Coll. Vol. II, John Wiley and Sons, Inc., New York, N. Y., 1943, p. 592.

(21) W. A. Blakey and H. A. Scarborough, *J. Chem. Soc.*, 3000 (1927).

(22) W. E. Bachmann and R. A. Hoffmann, *Org. Reactions*, **2**, 249 (1944).

from ethanol–benzene, the crude product yielded 0.1 g. (24%) of XV, m.p. about 315° dec.

Anal. Calcd. for $C_{18}H_{12}N_3Br_4I$: C, 30.13; H, 1.67; N, 5.86. Found: C, 30.32; H, 1.80; N, 5.77.

2,6-Bis-(2,6-dibromo-4-acetamidophenyl)-4-acetamidoiodobenzene (XVI).—The triamine XV was acetylated in 75% yield by acetic anhydride containing a drop of sulfuric acid, following the procedure used to acetylate benzidine. White needles, m.p. 341–344° dec., were obtained after two recrystallizations from aqueous acetic acid.

The same product was also prepared directly from the trinitroterphenyl derivative V by reducing the latter *via* the "activated" iron–water procedure employed in the preparation of 2,2′,6,6′-tetrabromobenzidine and treating the benzene solution of the triamine reduction product with ketene. During the reduction it was necessary to use 1 l. of benzene for 2 g. of V in order to prevent the product from precipitating from solution before the reaction was complete. The precipitated triacetamidoterphenyl (XVI) (1.2 g., 57%), m.p. 332–334° dec., gave a positive sodium fusion test for iodine. After three recrystallizations from aqueous acetic acid, XVIII formed white needles, m.p. 340–341° dec.

Anal. Calcd. for $C_{24}H_{18}N_3O_3Br_4I$: C, 34.16; H, 2.14; N, 4.98. Found: C, 34.67; H, 1.70; N, 4.88.

Conversion of V to *m*-Terphenyl (XX) by Hydrogenolysis, Hydrogenation and Deamination.—A solution of 3.5 g. of the trinitroterphenyl derivative V in 600 ml. of benzene was treated at room temperature with Raney nickel and hydrogen at three atmospheres pressure. The catalyst was separated by filtration, and the solution was concentrated to 50 ml. by distillation. Excess ethanol was added to the concentrate, and distillation was carried out until the benzene was removed as its azeotrope with ethanol. The residue in the distilling flask was diluted with a solution of 0.85 g. of sodium hydroxide in 100 ml. of ethanol, and the resulting solution was hydrogenated under three atmospheres pressure for 12 hours at room temperature in the presence of 1 g. of Raney nickel. Catalyst was removed by filtration and extracted once with 100 ml. of boiling ethanol and once with 100 ml. of boiling benzene. The product solution was combined with the extracts, concentrated to 20 ml. and poured into 200 ml. of cold water. The precipitated product was cooled to facilitate coagulation, and 1.2 g. of white solid, presumably 3,3′-bis-(4-aminophenyl)-aniline (XVII) was collected by filtration. The aqueous filtrate contained iodide ion.

The presumed triaminoterphenyl (XVII) was diazotized and converted to the presumed corresponding triiodoterphenyl (XIX) by the procedure used to prepare 2,6-dibromo-4-nitroiodobenzene. The brown, solid product (2.6 g., 98%) was only very slightly soluble in ethanol but was moderately soluble in benzene. Accordingly, its solution in ethanol–benzene was treated with about 1.5 g. each of sodium hydroxide and Raney nickel, and the mixture was shaken at 78° with hydrogen at 1000 p.s.i. pressure for three hours. The catalyst was removed by filtration and washed with boiling benzene. The washings were combined with the product solution, concentrated by distillation, diluted with alcohol, and distillation was continued until no benzene remained in the distilling flask. The ethanol solution was concentrated to 25 ml. and poured into 350 ml. of cold water. After 12 hours standing in the refrigerator, a brown product was separated by filtration; it became sticky at room temperature. From it 0.22 g. (22%) of crude *m*-terphenyl (XX), m.p. 71–76°, was isolated by sublimation at 125° (0.1 μ). After several sublimations at 85° (0.1 μ) and two recrystallizations, one from ethanol and one from methanol, white needles were obtained, m.p. 86.5–87°, alone or when mixed with a specimen prepared by the method described below. A mixture of this product with 3,3′-diphenylbiphenyl (preparation described below) melted at 70–78°.

3-Aminobiphenyl.—A solution of 11 g. of 3-nitrobiphenyl[22] in ethanol was treated at room temperature with hydrogen at three atmospheres pressure in the presence of Raney nickel. The catalyst-free solution, which quickly turned purple on standing in air, was concentrated to 20 ml. and poured into water. The water solution was extracted with three portions of ether, and the combined ether extracts were dried over sodium hydroxide overnight in the refrigerator. The solvent was removed from the ether solution on the steam-bath, and the residue was used as 3-aminobiphenyl without purification.

3-Iodobiphenyl was obtained in 71% yield from 3-nitrobiphenyl by subjecting crude 3-aminobiphenyl (from the procedure described in the preceding paragraph) to the same conditions used for the preparation of 2,6-dibromo-4-nitroiodobenzene. The reported yield is based on 3-iodobiphenyl which had been vacuum distilled twice; the final distillation was carried out at 164° (5 mm.). The reported b.p. is 188–189° (16 mm.).[23]

3-Acetamidobiphenyl.—A solution of crude 3-aminobiphenyl, prepared as previously described from 22 g. of 3-nitrobiphenyl, in 50 g. of pyridine was cooled to 0°, stirred and treated dropwise with 15 ml. of acetyl chloride. While the acetyl chloride was being added, the temperature was not permitted to rise above 8°. The mixture was allowed to stand for a half-hour and then poured into 1 l. of cold dilute hydrochloric acid. The white crystalline product (23.3 g., 100% yield from 3-nitrobiphenyl) was collected by filtration and washed with water. Without further purification it had the m.p. 141–143°; the m.p. 148° has been reported.[24]

***m*-Terphenyl (XX).**—A solution of 13 g. of nitrosyl chloride[25] in 25 ml. of ice-cold acetic anhydride was introduced dropwise into a stirred mixture of 12 g. of 3-acetamidobiphenyl, 100 ml. of glacial acetic acid, 30 ml. of acetic anhydride, 15 g. of potassium acetate and 0.75 g. of phosphorus pentoxide, all of which was cooled to 5°. After an additional half-hour stirring, the mixture was poured into ice-water. The oily nitroso derivative which appeared at first soon began to crystallize. The entire mixture was extracted with four portions of thiophene-free benzene, and the benzene extracts were washed with ice-water. The benzene solution (1 l.) was treated with 30 g. of anhydrous sodium sulfate and 25 g. of anhydrous sodium carbonate, and this mixture was stirred for 24 hours at room temperature. During this period the solution turned red, and carbon dioxide and nitrogen were evolved. Distillation of the filtered benzene solution was begun on the steam-bath and continued under diminished pressure until the benzene and acetic anhydride had been removed. A fraction (4.5 g., 35%) which distilled as a yellow oil, b.p. 185–190° (2–4 mm.) crystallized on cooling, and after one recrystallization from methanol it yielded long white needles of *m*-terphenyl (XX), m.p. 86.5–87.5°. The m.p. 87° has been reported.[26]

3,3′-Diphenylbiphenyl.—When a mixture of 11 g. of 3-iodobiphenyl, 15 g. of copper and 25 g. of sand was heated to 250°, heat was evolved from the mixture for a few minutes. After the temperature of the mixture had dropped following its spontaneous rise, the mixture was heated at 260° for 20 minutes. The sludge was extracted with several portions of boiling benzene, and the combined filtered benzene solutions (1 l.) were allowed to flow through a 1 × 3 in. column of activated alumina. Removal of the benzene from the solution left 5 g. (83%) of crude XXIII, which, after one recrystallization from ethanol and one from methanol, gave white crystals, m.p. 84.5–86°. The m.p. 86° has been reported.[26]

1,3-Diacetamido-5-nitrobenzene.—Treatment of 24 g. of 5-nitro-1,3-phenylenediamine[27] with 124 g. of acetic anhydride under a reflux condenser produced a vigorous reaction. The mixture was boiled for a half-hour after the spontaneous reaction ceased and then poured into 1 l. of cold water. The yellow crystalline product (25 g., 94%), m.p. 270° dec., appeared when the mixture was allowed to stand in the refrigerator.

3,5-Bis-(4-nitrophenyl)-nitrobenzene (XXIII).—A solution of 15 g. of nitrosyl chloride[25] in 40 ml. of cold acetic anhydride was added slowly to a stirred mixture of 17 g. of 1,3-diacetamido-5-nitrobenzene, 100 ml. of acetic anhydride, 200 ml. of acetic acid, 12 g. of potassium acetate and 1 g. of phosphorus pentoxide; the temperature was maintained at 5° throughout the addition. Stirring was maintained for an additional hour; then the mixture was poured into 1.5 l. of ice-water. The aqueous mixture was extracted with three portions of nitrobenzene, and the liter of nitrobenzene ex-

(23) S. T. Bowden, *J. Chem. Soc.*, 1111 (1931).

(24) F. Fichter and A. Sulzberger, *Ber.*, **37**, 878 (1904).

(25) H. S. Booth, "Inorganic Syntheses," Vol. 1, McGraw-Hill Book Co., New York, N. Y., 1939, p. 55; also see ref. 22, p. 251.

(26) G. Egloff, "Physical Constants of Hydrocarbons," Reinhold Publ. Corp., New York, N. Y., 1946, Vol. III, pp. 478, 529.

(27) R. B. Carlin and S. A. Heininger, to be published.

tracts was washed with 1% aqueous potassium hydroxide. The nitrobenzene solution was treated with 75 g. of anhydrous sodium carbonate, and the resulting mixture was stirred for 18 hours. The dark red, filtered reaction mixture was subjected to distillation until the vapor temperature reached 205°; then it was steam distilled until the nitrobenzene was removed. The dark tars were separated from the aqueous residue in the distilling flask and extracted with benzene for three days in a Soxhlet apparatus. Fresh benzene then replaced the extract solution, and extraction was continued for three additional days. The combined extracts were allowed to flow through a 1 × 18 in. column of activated alumina, and the light yellow solution which emerged from the column was concentrated to 50 ml. On cooling, this solution deposited 5 g. (19%) of a solid mixture which gave evidence of containing at least two compounds, one of which melted at about 175° and the other at about 270°.

One 0.75-g. sample of the solid mixture was chromatographed on a 1 × 20 in. column of activated alumina from 1 l. of carbon tetrachloride solution. The chromatogram was developed with benzene containing 0.2% ethanol. A yellow crystalline solid was obtained, which, after several recrystallizations from *n*-heptane–benzene, yielded white crystals, m.p. 177–183°. This compound corresponded in composition to a trinitroterphenyl.

Anal. Calcd. for $C_{18}H_{11}N_3O_6$: C, 59.18; H, 3.01; N, 11.51. Found: C, 59.38; H, 3.07; N, 11.5.

In the course of several efforts to recrystallize the crude mixed solid product from benzene and from acetic acid, a small fraction of the mixture remained insoluble in the boiling solvents and was collected by filtration. About 0.4 g. of this material was dissolved in 120 ml. of boiling benzene; when the filtered hot solution was allowed to cool, it deposited a gelatinous solid which, when collected by filtration and dried, became a white powder, m.p. 250–256°. Several recrystallizations from "Cellosolve" gave a yellow crystalline solid (about 0.1 g.), m.p. 263–268°. This substance also corresponded in composition to a trinitroterphenyl.

Anal. Calcd. for $C_{18}H_{13}N_3O_6$: C, 59.18; H, 3.01; N, 11.51. Found: C, 59.39; H, 3.30; N, 11.32.

The higher melting isomer appeared more likely to be the one having the structure XXIII; it appears likely that the lower-melting isomer may be 3,5-bis-(2-nitrophenyl)-nitrobenzene or 3-(2-nitrophenyl)-5-(4-nitrophenyl)-nitrobenzene, although no experimental work has been carried out on this isomer.

3,5-Bis-(4-acetamidophenyl)-acetanilide (XVIII). A. From the Trinitroterphenyl XXIII.—About 50 mg. of XXVI, m.p. 263–268°, was dissolved in 1:1 benzene–ethanol and hydrogenated under three atmospheres pressure at room temperature in the presence of Raney nickel for four hours. The solvent was removed on the steam-bath from the filtered solution, the residue was redissolved in benzene and the solution was treated with ketene until precipitation of the acetyl derivative was complete. After two recrystallizations from benzene–ethanol, the product formed light tan needles, m.p. 311.5–313° dec.

Anal. Calcd. for $C_{24}H_{23}N_3O_3$: C, 71.50; H, 5.70; N, 10.40. Found: C, 70.10; H, 5.72; N, 9.37; ash, 0.90.

Apparently a small amount of inorganic material contaminated the analytical samples; there was not enough additional sample for further purification and analysis.

B. By Hydrogenolysis of 2,6-Bis-(2,6-dibromo-4-acetamidophenyl)-4-acetamidoiodobenzene (XVI).—A solution of 1.3 g. of XVI and 1 g. of sodium hydroxide in 150 ml. of ethanol was treated with hydrogen under three atmospheres pressure at room temperature in the presence of Raney nickel for 12 hours. The filtered ethanol solution was concentrated to 25 ml. and poured into 50 ml. of water. The solid product was collected by filtration; the filtrate gave a positive test for iodide ion. The crude solid product (0.6 g., 96%) was dissolved in 200 ml. of benzene, and the solution was treated with ketene to ensure complete acetylation of amino groups present. After concentration of the benzene solution to 30 ml. and cooling, a white solid deposited which, after several recrystallizations from methanol–benzene and from aqueous acetic acid, gave tan needles, m.p. 315° dec., alone or when mixed with a sample prepared as described in the preceding paragraph.

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[CONTRIBUTION NO. 1230 FROM THE STERLING CHEMISTRY LABORATORY, YALE UNIVERSITY]

Pyrolysis of Aryl Glycolic Acids. III. The Structure of Langenbeck's Compound[1]

BY HARRY H. WASSERMAN, HERVEY W. ACKERMAN,[2] HERBERT H. WOTIZ[2] AND TIEN-CHUAN LIU

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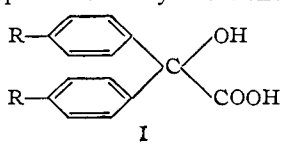
Langenbeck's compound, formed in the pyrolysis of benzilic acid, has been shown to have the quinodimethan structure VII. Chemical and spectroscopic evidence supporting this structure and the structures of a number of derivatives is presented. An independent synthesis is described which discloses the main structural features of Langenbeck's compound, and suggests a logical reaction sequence for its formation during the pyrolysis. The conclusive proof of structure is based on an unambiguous synthesis of one of the degradation products containing all of the essential features of Langenbeck's compound.

The formation of intensely colored materials during the pyrolysis of benzilic acid (I, R = H) was reported many years ago by Klinger,[3] Nef[4] and others, but Langenbeck[5] was the first to isolate a pure, crystalline, colored substance from among the pyrolytic products. By short energetic heating of benzilic acid in the presence of a small amount of sodium carbonate he obtained a red melt from which brilliant violet-black crystals, m.p. 169°, were isolated. The analysis and molecular weight of this substance appeared to be in accord with the composition $C_{28}H_{20}O_2$ and, based on this molecular formula, Langenbeck assumed that the brilliantly colored product was a dimer of diphenylketene.[6] Although this product was treated with a large variety of reagents, these reactions give little clue as to the structure of this material, since they led to no crystalline derivatives. For example, treatment with alcoholic potassium hydroxide, alcoholic potassium cyanide, zinc and acetic acid,



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(1) Presented at the 124th Meeting of the American Chemical Society, Chicago, Ill., September 6 to 11, 1953.

(2) Taken, in part, from the doctoral dissertation of Herbert H. Wotiz, Yale University, 1951, and Hervey W. Ackerman, Yale University, 1952.

(3) H. Klinger and O. Standke, *Ber.*, **22**, 1213 (1889).

(4) J. U. Nef, *Ann.*, **298**, 242 (1897).

(5) W. Langenbeck and H. Langenbeck, *Ber.*, **61B**, 938 (1928).

(6) This reasoning was supported by the fact that diphenylketene had earlier[7] been reported to occur among the products of decomposition of benzilic acid.

(7) H. Staudinger, *Ber.*, **44**, 543 (1911).