gave 0.84 g. (22%) of VId, m.p. 193–194°, and 1.1 g. (30%) of IIId. In a separate experiment, the oil when treated with excess triethylamine gave tribenzoylethylene (II) in 62% yield.

(b).—Excess chlorine reacted with I to give only oil which was converted by morpholine to VId in 55% yield, m.p. 190–193°. No solid derivative was obtained when the oil was treated with triethylamine (room temperature, 10 hr.).

(c).—When 1 g. of 2-chloro-1,1,2-tribenzoylethane (IIIa) was treated with chlorine (3 hr.) 0.62 g. of unchanged material was recovered. The residual oil reacted with morpholine to give 0.12 g. (10%) of VId, m.p. 190–194°.

(d).—Chlorination of 1.5 g. of II (6 hr.) gave 0.36 g. (22%) of VIa, m.p. 88–90°, 0.05 g. (3%) of IIIa, m.p. 134–136°, and an oil which upon treatment with morpholine gave 0.92 g. (49%) of VId, m.p. 190–193°.

(e).—Bromination of 1 g. of I proceeded smoothly at room temperature with rapid discharge of bromine color and evolution of hydrogen bromide to give 0.84 g. (68%) of IIIb, m.p. 129–130°. This product IIIb resisted further reaction with excess bromine (14 hr.).

(f).—Bromination of 1 g. of II (12 hr.) gave 0.42 g. (35%) of 4-bromo-3-benzoyl-2,5-diphenylfuran (Vb[8b]), m.p. 116–118°; purified, m.p. 119–120°; λ_{max} 227.5, 253, 305, ϵ 21,200, 20,200, 24,100; λ_{min} 242.5, 274, ϵ 18,900, 14,050. An oil obtained as by-product reacted with morpholine to give 0.22 g. (18%) of VId, m.p. 188–192°.

CHARLOTTESVILLE, VA.

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

The Benzidine Rearrangement. VII. The Rearrangements of 3,3'-Dibromo-5,5'-dimethylhydrazobenzene in 2:1 Sulfuric Acid[1]

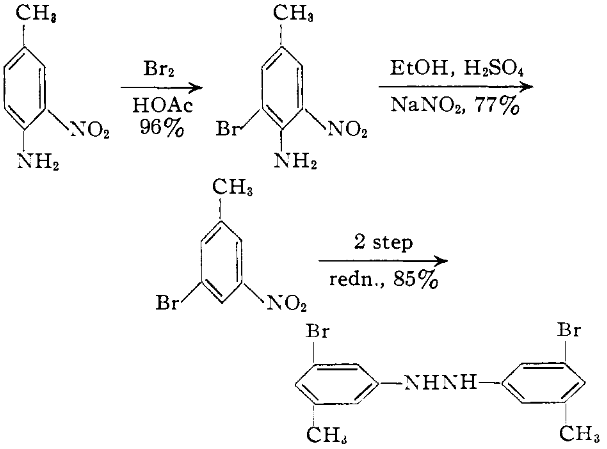
BY ROBERT B. CARLIN AND GEORGE E. FOLTZ[2]

RECEIVED SEPTEMBER 30, 1955

Treatment of 3,3'-dibromo-5,5'-dimethylhydrazobenzene (I) with 2:1 sulfuric acid at 85–90° yielded a benzidine (II), dimorphic diphenylines (IIIa and IIIb), a 2,2'-diaminobiphenyl (IV), 5-bromo-3-toluidine (V), the azobenzene (VI) corresponding to I and a trace of a rearrangement product which may have been a semidine. The structures of the rearrangement products II–IV were established by catalytic reductive debromination to diaminodimethylbiphenyls which were synthesized by other means. Relatively more benzidine product and less diphenyline, 2,2'-diaminobiphenyl and disproportionation products are formed from I than from the related symmetrical compounds, 3,3',5,5'-tetrabromo- and -tetramethylhydrazobenzenes under similar conditions. Also, only one of two possible diphenyline structures and one of three possible 2,2'-diaminobiphenyls could be identified among the products. These observations make it clear that the relationship, deduced from previous investigations, between steric size of the four *meta* substituents and product ratios is valid only for those cases in which all four substituents are alike. The factor of polar symmetry affects the product ratios, and it also appears to have a decisive effect on the choice among the transition states leading to the several possible products. No mechanism thus far proposed for the benzidine rearrangement seems capable of yielding a satisfactory explanation of the behavior of I.

Previous investigations of the rearrangements of 3,3',5,5'-tetrasubstituted hydrazobenzenes in 2:1 sulfuric acid at 85–90° have led to results suggesting that benzidine : diphenyline : 2,2'-diaminobiphenyl product ratios are governed largely, though not entirely, by the steric size of the four substituents under the imposed conditions.[3] In all of the 3,3',5,5'-tetrasubstituted hydrazobenzenes thus far subjected to these conditions, the four substituents have been alike, and the question of the effects on the product ratios of introducing new elements of dissymmetry into the molecule arose. The choice of 3,3'-dibromo-5,5'-dimethylhydrazobenzene (I) as the first unsymmetrically tetrasubstituted hydrazobenzene to be investigated was based upon the fact that the two related symmetrical compounds, 3,3',5,5'-tetrabromo- and -tetramethylhydrazobenzenes already had been studied[4] and had been shown to give quite similar product ratios. Inasmuch as bromine and methyl have effectively identical van der Waals radii,[5] the steric character of I should not differ appreciably from those of its two related symmetrically substituted analogs; it follows that if steric size of the four substituents is the chief operative factor in determining product ratios, then compound I should behave like the tetrabromo and tetramethyl analogs in this respect. This article reports the products of the action of 2:1 sulfuric acid on I at 85–90°, their relative amounts, and the proof of their structures.

The dibromodimethylhydrazobenzene I was prepared by means of the synthetic scheme



The action of 2:1 sulfuric acid on I at 85–90° for a half-hour gave a mixture from which two disproportionation products and four rearrangement products were separated in 82% total yield. Of the remaining 18% of material, some survived the complex separation procedures as tarry residues and some was lost. The separation procedures, described in the Experimental part, involved countercurrent liquid–liquid extraction, steam distillation,

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[1] Submitted in partial fulfillment of the requirements for the degree of Doctor of Philosophy at the Carnegie Institute of Technology.

[2] Institute Graduate Fellow in Organic Chemistry, 1951–1952.

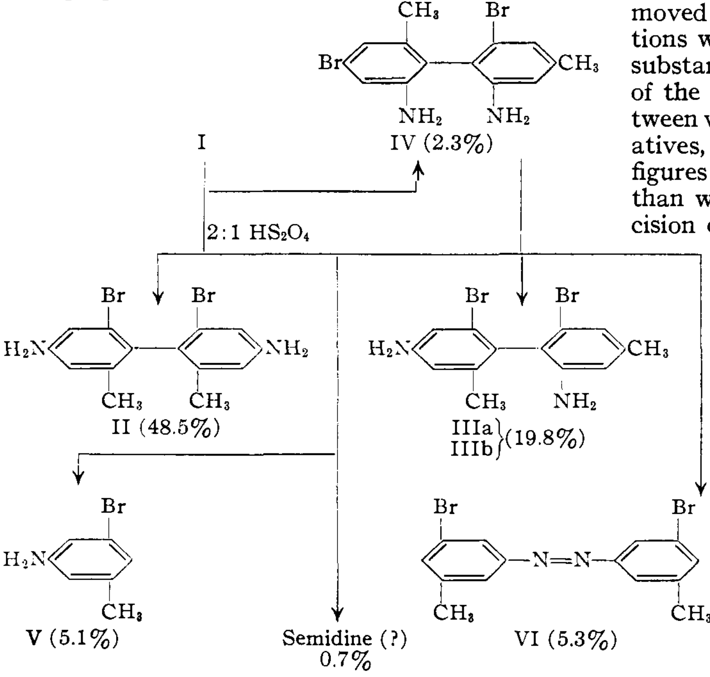
[3] *Cf.* R. B. Carlin and S. A. Heininger, THIS JOURNAL, **77**, 2273 (1955).

[4] R. B. Carlin and W. O. Forshey, Jr., *ibid.*, **72**, 793 (1950).

[5] W. A. Waters, "Physical Aspects of Organic Chemistry," 4th Ed., Van Nostrand, New York, N. Y., 1950, p. 58.

high vacuum sublimation and fractional crystallization.

The structures of the three rearrangement products II–IV were established by catalytic reductive debromination to the respective diaminodimethylbiphenyls, which were synthesized independently by reducing the corresponding dimethyldinitrobiphenyls. The latter were prepared by Ullmann reactions reported in the accompanying paper.[6] Each of the diaminodimethylbiphenyls derived from II–IV by catalytic reductive debromination was converted into its diacetyl and its bis-salicylal derivative; all of these derivatives proved to be identical with specimens prepared from the appropriate diaminodimethylbiphenyls obtained through the Ullmann synthesis.[6] All three of the rearrangement products II–IV were themselves characterized by formation of their diacetyl derivatives, and bis-salicylal derivatives of all but IV also were prepared.



Two crystalline substances, both of which were assigned structure III, were separated from the mixture of rearrangement and disproportionation products of I. Differing decisively in melting point, IIIa (m.p. 140°) and IIIb (m.p. 167°) nevertheless formed identical diacetyl derivatives, m.p. 258°, and bis-salicylal derivatives, m.p. 270°. Furthermore, IIIa and IIIb gave identical diaminodimethylbiphenyls on complete reductive debromination. On the other hand, the fact that each diacetyl derivative was hydrolyzed to the base from which it had been formed cast doubt, at the time, that the two crystalline bases were dimorphs. However, solutions of the two forms in carbon disulfide showed essentially identical infrared spectra, and these differed decisively from the spectra of the isomeric substances II and IV determined in the same solvent.[7] The dimorphic character of IIIa and IIIb was confirmed when IIIa was converted to IIIb by repeated recrystallizations, with seeding by IIIb, from petroleum ether and from benzene–petroleum ether.[7]

In the course of reductive debromination, some samples of III were converted to a monobromodiaminodimethylbiphenyl. The position occupied by the remaining bromine atom was not determined. Continued hydrogenation of the monobromo derivative afforded the same diaminodimethylbiphenyl that was produced when III was completely debrominated in a one-stage operation. No intermediate monobromo derivative was ever isolated from the reductive debromination of either II or IV.

A fourth rearrangement product, isolated from the reaction mixture in the form of its acetyl derivative in 0.7% yield, was not completely characterized. This compound was markedly less basic in nature than its three isomers; the latter were removed from benzene solution by repeated extractions with 0.5 N hydrochloric acid, but the fourth substance was not extracted. Elementary analysis of the acetyl derivative gave results which lay between values calculated for mono- and diacetyl derivatives, and though agreement with the computed figures for the monoacetyl derivative was better than with those for the diacetyl derivative, no decision could be based on these data. An attempt to prepare a salicylal derivative by hydrolyzing the acetyl derivative and treating the crude, oily hydrolysate with salicylaldehyde led to a crystalline product of varying and uncertain composition which evidently was not a pure substance.

The structures of 5-bromo-3-toluidine (V) and 3,3'-dibromo-5,5'-dimethylazobenzene (VI) were established by comparison of samples with known specimens. The isolation of these two compounds in nearly equal amount must be interpreted to mean that they were formed by disproportionation of I.

Table I shows the yields of products from six aromatic hydrazo compounds, including I, whose rearrangements in 2:1 sulfuric acid at 85–90° have been examined by essentially identical techniques.

TABLE I

YIELDS OF PRODUCTS FROM 3,3'-DI-R-5,5'-DI-R'-HYDRAZOBENZENES IN 2:1 SULFURIC ACID AT 85–90°

	Yield, %					
Product type	R = R' = CH_3[4]	R = R' = Br[4]	R = R' = Cl[4]	R = R' = F[3]	R = R' = H[3]	R = CH_3 R' = Br
Benzidine	26.8	18.9	36.4	68.7	78.6	48.5
Diphenyline	30.3	25.8	21.3	9.8	10.5	19.8[a]
2,2'-Diaminobiphenyl	10.9	8.2	16.0	2.1	0.0	2.3
Azobenzene	7.7	9.3	8.0	3.7	2.7	5.5
Aniline	..	8.7	7.5	3.8	2.7	5.1
Total	75.7	70.9	89.2	88.1	94.5	81.2
Ratio of benzidine: diphenyline: 2,2'-diaminobiphenyl	2.5 2.8 1.0	2.3 3.1 1.0	2.3 1.3 1.0	34.2 4.9 1.0	7.5 1.0 0.0	21.1 8.6 1.0

[a] Sum of yields of both diphenylines IIIa and IIIb.

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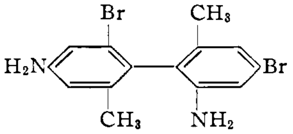
(6) R. B. Carlin and G. K. Foltz, THIS JOURNAL, 78, 1997 (1956).

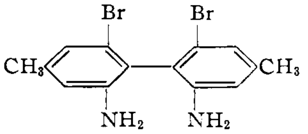
(7) The authors acknowledge with thanks the help of Dr. Luis M. Amoros, who carried out these experiments.

Examination of the data of Table I reveals that the systematic qualitative relationship between steric size of the four substituents and rearrangement product ratios (benzidine:diphenyline:2,2′-diaminobiphenyl) observed in the series of compounds in which all four substituents are alike is no longer applicable when the substituents are not alike. Whereas generalizations based on the behavior of the four symmetrically tetrasubstituted hydrazobenzenes and of hydrazobenzene itself had led to the prediction that compound I would give rearrangement products in relative amounts very similar to the rearrangement product ratios from the tetrabromo- and the tetramethylhydrazobenzenes, actually the rearrangement product ratios from I more closely resemble those from the tetrafluorohydrazobenzene and from hydrazobenzene. The amount of disproportionation accompanying rearrangement from I is roughly a mean between that shown by the three symmetrical "hindered" compounds (Table I, $R = R' = CH_3$, Br and Cl) on the one hand and the two symmetrical "unhindered" compounds (Table I, $R = R' =$ F and H) on the other.

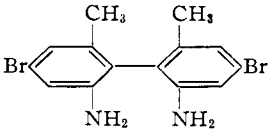
A second striking observation derived from this investigation is that only one (III) of two possible diphenylines (III and VII) and one (IV) of three possible 2,2′-diaminobiphenyls (IV, VIII and IX) were found among the products of rearrangement of I. The diaminodimethylbiphenyls related to VII, VIII and IX by debromination were synthesized by Ullmann reactions and subsequent reduction of the resulting dimethyldinitrobiphenyls,[6] but no compounds having the properties of any of these three substances could be obtained by catalytic reductive debromination of any of the rearrangement products of I. It is particularly noteworthy that IV, the only one of three possible 2,2′-diaminobiphenyls actually isolated, corresponds to the only unsymmetrical structure of the three.



VII



VIII



IX

Discussion

That the polar effects of substituents in the four *meta* positions of hydrazobenzene exert a strong influence on rearrangement product ratios is evident from the results of this work. Compared to 3,3′,5,5′-tetrabromo- and -tetramethylhydrazobenzenes, compound I contains a greater element of polar dissymmetry, but compound I cannot be significantly different in steric character. The conclusion then seems inescapable that the very different rearrangement product ratios and the smaller amount of disproportionation from I compared with those from the two related symmetrically substituted compounds must be ascribed to polar and not to steric factors. The generalization previously advanced[8] which related product ratios from 3,3′,5,5′-tetrasubstituted hydrazobenzenes chiefly to steric size of the substituents therefore is apparently restricted in its validity to those compounds in which all four substituents are alike and in which polar symmetry of substituents can thus be said to exist.

Both the effect of polar symmetry of 3,3′,5,5′-tetrasubstituted hydrazobenzenes on their product ratios and the exclusive formation of one of two possible diphenylines and one of three possible 2,2′-diaminobiphenyls from I constitute evidence that the transition states of the rearrangements are tightly and selectively oriented. None of the mechanisms proposed for the benzidine and related rearrangements during the past 15 years[8] seem capable of yielding a satisfactory interpretation of the observations recorded above. It would appear wise to investigate the rearrangements of other unsymmetrical 3,3′,5,5′-tetrasubstituted hydrazobenzenes before proposing generalizations of their behavior. Such investigations are now in progress.

Experimental[9]

3-Bromo-4-amino-5-nitrotoluene.—A solution of 105 g. of 3-nitro-4-aminotoluene (Eastman Kodak Co.) in 1 l. of hot glacial acetic acid was cooled until crystallization began; then it was stirred as it was treated dropwise with 42 ml. of bromine. The mixture was poured into excess water, and the solid was collected by filtration after the aqueous sludge was cooled. The product (153 g., 96%) formed bright orange prisms, m.p. 63–64°; reported m.p. 64.5°.[10]

3-Bromo-5-nitrotoluene.—A boiling solution of 86.7 g. of 3-bromo-4-amino-5-nitrotoluene in 435 ml. of ethanol and 58 ml. of concentrated sulfuric acid was treated with 58 g. of sodium nitrite as quickly as possible without causing excessive foaming, and the mixture was boiled for a half-hour following the addition of the last of the sodium nitrite. The cooled reaction mixture was poured into excess water, and the precipitated product was collected by filtration and washed with water. The crude product was steam distilled, the distillate was extracted into ether, the ether was removed from the extract, and the residue was recrystallized from ethanol. The product (62.5 g., 77%) formed yellow needles, m.p. 81–83°. The m.p. 83° has been reported.[11]

3,3′-Dibromo-5,5′-dimethylazobenzene (VI) and **3,3′-dibromo-5,5′-dimethylhydrazobenzene** (I) were prepared in 95 and 90% yields, respectively, by means of procedures employed in the preparations of the analogous tetrabromo-azo- and hydrazobenzenes.[4] The azo compound VI formed fluffy orange needles, m.p. 162–163°, from ethanol.

Anal. Calcd. for $C_{14}H_{12}N_2Br_2$: C, 45.65; H, 3.26. Found: C, 45.83; H, 3.10.

The hydrazo compound I formed white cubes, m.p. 132.5–134.5°, from petroleum ether (b.p. 65–110°).

Anal. Calcd. for $C_{14}H_{14}N_2Br_4$: C, 45.40; H, 3.78. Found: C, 45.94; H, 4.01.

The Rearrangement of 3,3′-Dibromo-5,5′-dimethylhydrazobenzene (I) and the Separation of the Rearrangement and Disproportionation Products.—A stirred mixture of 125 g. of hydrazo compound I and 1 l. of 2:1 (by volume) sulfuric acid was stirred and maintained at 85–90° for a half-hour.

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[8] R. Robinson, *J. Chem. Soc.*, 220 (1941); E. D. Hughes and C. K. Ingold, *ibid.*, 608 (1941); 1638 (1950); C. K. Ingold, "Structure and Mechanism in Organic Chemistry," Cornell Univ. Press, Ithaca, N. Y., 1953, pp. 631–642; M. J. S. Dewar, *J. Chem. Soc.*, 406 (1946); *Disc. Faraday Soc.*, **2**, 50 (1947); "Electronic Theory of Organic Chemistry," Oxford Univ. Press, 1949, pp. 235–240; D. Ll. Hammick and S. F. Mason, *J. Chem. Soc.*, 638 (1946); 1938 (1949); D. Ll. Hammick and D. C. Munro, *ibid.*, 2049 (1950).

[9] All melting points are corrected.

[10] E. Wroblewsky, *Ann.*, **192**, 203 (1878).

[11] C. S. Gibson and J. D. A. Johnson, *J. Chem. Soc.*, 1245 (1929).

The mixture was cooled to 40° and filtered free of **3,3'-dibromo-5,5'-dimethylazobenzene (VI)**, which weighed 6.63 g. (5.3%) after washing with water and drying. It had the m.p. 162–163° after recrystallization from ethanol, and the mixed m.p. with an authentic sample was undepressed.

The acid filtrate from VI was cooled to 0°, and the sparingly soluble sulfate salts of two of the rearrangement bases were collected by filtration through a sintered glass funnel. These salts were washed with 75 ml. each of ethanol and ether and were then converted to the mixture of the respective bases by treatment with 30% aqueous sodium hydroxide. The mixture of bases was extracted into ether, the ether was removed from the solution, and the residue was sublimed (<1 μ). The 9.32 g. of white crystalline sublimate was partitioned through five separatory funnels (no. 11–15) each of which was charged with 100 ml. of benzene and 100 ml. of 0.25 *N* hydrochloric acid. The product was recovered from each funnel by making the aqueous layer alkaline with sodium hydroxide and extracting the organic material formerly in the aqueous layer into the benzene solution. The separated benzene layer was then reduced in volume by distillation and finally evaporated to dryness. Each product was recrystallized once from aqueous ethanol before the melting point was observed. This recovery and purification scheme also was followed in all of the liquid-liquid extraction procedures to be described subsequently. Funnels 13–15 yielded 6.31 g. (5.1%) of **2,2'-dibromo-6,6'-dimethylbenzidine (II)**. The properties of this and of the isomeric rearrangement products III and IV, together with those of their derivatives, are collected in Table III. Funnel no. 11 gave 2.85 g. (2.3%) of **2,2'-diamino-4,6'-dibromo-4',6-dimethylbiphenyl (IV)**. Although II and IV had identical melting points, a mixture showed a 40° melting point depression. Funnel no. 12 contained but 0.17 g. of solid material, m.p. 134–153°, which was discarded.

The acid filtrate from the sulfate salts was cooled to −20°, and the dark solid which separated was collected by filtration. When treated with aqueous sodium hydroxide, this dark solid gave 3.3 g. of an intractable tar from which nothing could be isolated or identified.

The cold filtrate from the dark solid was neutralized cautiously with 30% aqueous sodium hydroxide, the neutralized solution was cooled, and the precipitated bases were collected by filtration. The filtrate was diluted with water, and the diluted solution was extracted with ether. The ether extracts were combined with the solid bases obtained by filtration, the ether was removed, and the residue was subjected to distillation by steam heated to 190°. The distillate was extracted with ether, and the ether solution (of 5-bromo-3-toluidine) was treated with acetic anhydride. The ether was removed, the residue was poured into water, and the white solid which formed after excess anhydride had been destroyed was recrystallized from aqueous ethanol. **This 5-bromo-3-acetotoluidide** (7.72 g.) accounted for 5.1% of original I; it had the m.p. 166–168°, which was not depressed by admixture with an authentic sample whose preparation is described below. The reported m.p. is 167–168°.[12]

The dark-colored solid residue from the steam distillation was sublimed (<1 μ); the sublimate (93.9 g.) consisted of light yellow crystalline material mixed with a somewhat darker yellow glass, and the residue (1.7 g.), a very dark tar, was discarded. The sublimate was dissolved in sufficient benzene to give a solute concentration of 0.033 g./ml., and the benzene solution was extracted four times with equal volumes of 0.5 *N* hydrochloric acid. Each aqueous acid extract was shaken with an equal volume of benzene. All of the benzene solutions were combined, the benzene was removed by distillation, and the residue (5.0 g. of dark tar) was sublimed (<1 μ). The yellow glassy sublimate (4.8 g.) was dissolved in ether, and the ether solution was treated with excess ketene and then allowed to stand at 5° for a week. The crystalline solid, presumably an **N-acetylsemidine**, gave 1.0 g. (0.7%) of small white needles, m.p. 167–169°, after a high vacuum sublimation and recrystallization from aqueous ethanol.

Anal. Calcd. for monoacetyl deriv. $C_{16}H_{16}N_2OBr_2$: C, 46.63; H, 3.91. Calcd. for diacetyl deriv. $C_{18}H_{18}N_2O_2Br_2$: C, 47.60; H, 3.99. Found: C, 46.97; H, 3.87.

An attempt to prepare a salicylal derivative of this "semidine" by hydrolyzing a sample of the acetyl derivative and treating the oily hydrolyzate with salicylaldehyde led to a yellow crystalline material which after high vacuum sublimation and recrystallization from aqueous methanol, had the m.p. 138–140°. Samples of this solid gave no consistent analytical results, however, and this fact, together with the failure of the analytical figures to accord with any postulated structure, made it appear certain that the solid was not a pure substance.

That (major) portion of the sublimed basic rearrangement products which had been extracted into 0.5 *N* hydrochloric acid was precipitated by neutralizing the solution with 40% aqueous sodium hydroxide. The tan crystalline solid (90 g.) was dissolved in benzene to a solute concentration of 0.05 g./ml. and partitioned through nine separatory funnels (no. 21–29). The mutually immiscible solvents, used in equal volumes in each separatory funnel, were benzene and 0.25 *N* hydrochloric acid. Of the 89.67 g. of material recovered after the counter-current distribution, 53.77 g. was present in funnels no. 27–29. This material, having the total melting range 174–178°, was the benzidine II; together with the 6.31 g. of II isolated earlier in the separation procedure, this made 60.08 g. of II (48.5%) recovered from the rearrangement of I.

Funnels no. 21–24 yielded 29.03 g. of solids having a total melting range 128–143°. On sublimation at 145° (<1 μ), this fraction afforded 24.5 g. of pale yellow crystalline material which was dissolved in benzene to a concentration of 0.05 g./ml. and again partitioned through nine separatory funnels (no. 31–39) with the same pair of immiscible solvents as those used in the preceding distribution. The product from each funnel was recrystallized once from benzene–petroleum ether (b.p. 65–110°) before the melting point was observed. Funnels no. 38 and 39 contained but 0.09 g. of material, which was discarded. The contents of funnels no. 25 and 26 were combined with those of funnels no. 31–34, to give a fraction weighing 26.8 g., no component fraction of which melted above 152°. This fraction was dissolved in 500 ml. of benzene and partitioned through nine separatory funnels (no. 41–49) each of which was charged with 500 ml. of benzene and an equal volume of 0.4 *N* hydrochloric acid. The contents of funnels no. 47–49, all of which had melting points greater than 158°, were combined with the contents of funnels no. 35–37, which melted similarly, to give 11.57 g. of material which yielded 5.4 g. (4.4%) of **2,4'-diamino-6,6'-dibromo-2',4-diamethylbiphenyl (IIIb)**, m.p. 165–167°, after recrystallization from aqueous ethanol. When concentrated, the mother liquors from the crystallization of IIIb yielded 2.3 g. of crystalline material, m.p. 135–138°.

The contents of funnels no. 41–46, which weighed 20.37 g. and melted over the total range 130–149°, were combined and recrystallized from aqueous ethanol. The product, which weighed 16.3 g. and melted at 131–132°, was combined with the crystalline material from the mother liquors of the recrystallization of IIIb, and the new fraction was dissolved in 500 ml. of benzene. This solution was extracted with 100 ml. of 0.4 *N* hydrochloric acid. The acid extract yielded 6.20 g. (5.0%) of **2,4'-diamino-6,6'-dibromo-2',4-dimethylbiphenyl (IIIa)**, m.p. 139–140°, which gave long white prisms of the same melting point when recrystallized from aqueous ethanol. The benzene was removed from the solution remaining after the extraction of IIIa, the residue was dissolved in ether, and ketene was introduced into the solution. The sparingly soluble product, m.p. 255–257°, was subjected to hydrolysis by boiling for three hours with a solution of 20 ml. of concentrated hydrochloric acid, 20 ml. of water and 90 ml. of ethanol. The cooled reaction mixture was diluted with water, neutralized with aqueous sodium hydroxide, and the product was collected by filtration. Recrystallization of this material from aqueous ethanol afforded 12.9 g. of tan prisms, m.p. 128–130°. When 3.7 g. of this solid was subjected to catalytic hydrogenolysis by the procedure to be described presently, it gave a mixture of 1.5 g. (71%) of 2,4'-diamino-2',4-dimethylbiphenyl and 0.5 g. (17%) of the monobromo derivative of the latter. The two compounds were separated readily by a recrystallization from aqueous ethanol. The monobromo derivative was identified with an independently prepared specimen by its m.p. and mixed m.p. The completely debrominated product was a liquid which was characterized through its bis-salicylal derivative, identical in m.p. and mixed m.p. with a specimen prepared by hydrogenation of the corresponding nitro compound.[6] The hydrogenation

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[12] R. H. C. Nevile and A. Winther, *Ber.*, **13**, 964 (1880).

experiment therefore showed that the 12.9 g. of tan prisms, m.p. 128–130°, was a mixture of the dimorphic forms of III.

Table II summarizes the products and their yields from the interaction of I with 2:1 sulfuric acid at 85–90°.

TABLE II

YIELDS OF PRODUCTS FROM THE REACTION OF 125 G. OF 3,3'-DIBROMO-5,5'-DIMETHLHYDRAZOBENZENE IN 2:1 SULFURIC ACID AT 85–90°

Product	Yield, g.	%
3,3'-Dibromo-5,5-dimethylazobenzene (VI)	6.63	5.3
5-Bromo-3-toluidine (V)	6.33	5.1
2,2'-Dibromo-6,6 -dimethylbenzidine (II)	60.08	48.5
2,4'-Diamino-6,6'-dibromo-2',4-dimethylbiphenyl (IIIa and IIIb)	24.50	19.8
2,2'-Diamino-4,6'-dibromo-4',6-dimethylbiphenyl (IV)	2.85	2.3
"Semidine"	0.90	0.7
Total	101.29	81.7

N,N'-Diacetyl Derivatives of Rearrangement Products. General Procedure A.—A solution of the diamine in acetic anhydride was boiled for 15 minutes and then poured into water. The solid remaining after destruction of excess acetic anhydride was recrystallized from aqueous ethanol. The diacetyl derivative of II crystallized from acetic anhydride solution soon after the mixture was warmed to 100°.

General Procedure B.—An ether solution of the diamine was treated with ketene until precipitation of the ether-insoluble derivative was complete. The derivative was recrystallized from aqueous ethanol. The properties of diacetyl derivatives from both procedures are listed in Table III.

TABLE III

PROPERTIES OF THE THREE REARRANGEMENT PRODUCTS OF I AND OF THEIR DERIVATIVES

Compound	M.p., °C.	Carbon, % Calcd.	Carbon, % Found	Hydrogen, % Calcd.	Hydrogen, % Found
Benzidine II	179–181[b,c]	45.43[i]	45.62	3.81[i]	3.99
Diphenyline IIIa	139–140[g,c]	45.43[i]	45.07	3.81[i]	3.80
Diphenyline IIIb	165–167[g,c]	45.43[i]	45.64	3.81[i]	3.95
2,2'-Diaminobiphenyl IV	179–181[b,c,f]	45.43[i]	45.74	3.81[i]	3.89
Diacetyl deriv.[l]					
of II	295[b,c]	47.60[j]	47.24	3.99[j]	4.05
of III[a]	256–258[h,c]	47.60[j]	48.06	3.99[j]	4.09
of IV	208.5–209[g,c]	47.60[j]	47.75	3.99[j]	4.07
Bis-salicylal deriv. of II	254–255[d,e]	58.15[k]	58.25	3.84[k]	4.07
of III[a]	268–270[d,e]	58.15[k]	58.12	3.84[k]	3.89

[a] IIIa and IIIb gave identical derivatives, showing no mixed m.p. depression. [b] White needles. [c] From aqueous ethanol. [d] Yellow prisms. [e] From benzene–petroleum ether (b.p. 65–110°). [f] A 40° depression on mixture with II. [g] White prisms. [h] White leaflets. [i] For $C_{14}H_{14}N_2Br_2$. [j] For $C_{18}H_{18}N_2O_2Br_2$. [k] For $C_{28}H_{22}N_2O_2Br_2$. [l] All prepared by Procedure A.

N,N'-Bis-salicylal Derivatives of Rearrangement Products. General Procedure.—The diamine was heated in excess salicylaldehyde at 190° for 15 minutes. If the derivative failed to crystallize when the mixture was cooled, it was diluted with petroleum ether (b.p. 65-110°) until the solid derivative separated. The yellow product was purified by recrystallization from benzene-petroleum ether. Properties of these derivatives are reported in Table III.

Catalytic Reductive Debromination of II, III and IV to Diaminodimethylbiphenyls.—A sample of the rearrangement product was dissolved in sufficient absolute ethanol to form a stable solution at room temperature (usually about 4 g./100 ml.). Sodium hydroxide was dissolved in the solution in sufficient quantity to neutralize evolved hydrogen bromide, Raney nickel was added, and the mixture was exposed to the action of hydrogen at 50–60 p.s.i. for four hours at room temperature. The catalyst was separated by filtration and extracted with boiling ethanol. The filtrate and washings were combined, and the product was separated by evaporation of the ethanol solution to dryness, by concentration and dilution with water, or simply by pouring the original ethanol solution into water. The debromination products of II and of IV were crystalline solids; that of III was obtained as an unstable crystalline solid (probably a hydrate) which changed rapidly to an oil on standing. The two solid products had the same m.p.'s as samples prepared as described in the accompanying paper, and no mixed m.p. depression was observed in either case. All three debromination products were characterized as diacetyl and as bis-salicylal derivatives, which did not depress the m.p.'s of corresponding derivatives of synthetic specimens.[6]

Catalytic Reductive Debromination of III to a Monobromo Derivative.—A sample of IIIb, when subjected to the general procedure just described, afforded white prisms, m.p. 128–130°, after recrystallization from aqueous ethanol. A sodium fusion test for bromine was positive.

Anal. Calcd. for $C_{14}H_{15}N_2Br$: C, 57.80; H, 5.18; N, 9.61. Found: C, 58.58; H, 5.33; N, 9.80.

N,N'-Diacetyl derivative, prepared by procedure B, formed small, white needles, m.p. 194–196°, from ethanol.

Anal. Calcd. for $C_{18}H_{19}N_2O_2Br$: C, 57.63; H, 5.10; N, 7.49. Found: C, 57.31; H, 5.32; N, 8.00.

N,N'-Bis-salicylal derivative was prepared by heating a solution of the diamine in salicylaldehyde for a half-hour on the steam-bath. Excess salicylaldehyde was removed by distillation. The residual derivative, after two recrystallizations from ethanol, formed short, yellow needles, m.p. 164–165°.

Anal. Calcd. for $C_{28}H_{23}N_2O_2Br$: C, 67.34; H, 4.64. Found: C, 67.62; H, 4.81.

Catalytic Reductive Debromination of Monobromo Derivative from III.—The general procedure was changed only to the extent of permitting the reduction to proceed for 24 hours. The product was the unstable hydrate previously mentioned, which turned to an oil on standing. The oil was characterized as the crystalline diacetyl and bis-salicylal derivatives, which were identical in m.p. and mixed m.p. with the appropriate synthetic specimens.[6]

Hydrolysis of N,N'-Diacetyl Derivatives of IIIa and IIIb.—A sample of the diacetyl derivative of IIIa, m.p. 255–256°, prepared from a specimen of IIIa, m.p. 138–140° by procedure A above, was boiled for 3 hours in a solution made from 25 ml. of ethanol and 10 ml. of concentrated hydrochloric acid. After the base was precipitated from the solution by treatment with aqueous sodium hydroxide, it was recrystallized twice from aqueous ethanol; m.p. 144–146°. This m.p. corresponded to a mixture containing principally IIIa, contaminated with some IIIb. The same procedure was applied to a sample of the diacetyl derivative of IIIb, m.p. 258–259°, prepared by acetylating a sample of IIIb, m.p. 167–168°, by means of procedure A above. The regenerated base had the m.p. 169–171°, after recrystallization from aqueous ethanol. The m.p. corresponded to pure IIIb.

5-Bromo-3-acetotoluidide.—A sample of 5-bromo-3-nitrotoluene was reduced in aqueous ethanol by the action of powdered iron and 10% aqueous hydrochloric acid. The reaction mixture was made basic by treatment with aqueous sodium hydroxide and steam distilled. The distillate was extracted with ether, the ether was removed from the extract, and the residual oil was treated with acetic anhydride in accordance with procedure A above. The product formed white needles, m.p. 166–168°, from aqueous ethanol.

Infrared absorption spectra were determined in a Perkin-Elmer model 21 infrared spectrophotometer equipped with sodium chloride cell windows and prism. The spectra were measured in carbon disulfide solutions of about 20 mg./ml. concentration contained in a 0.5-mm. cell. Both dimorphic modifications of the diphenyline III showed the same bands; therefore there is no occasion to report the spectra of the two samples separately. The following legend will be employed to indicate intensity of bands: intense (i). 0–25% transmission; moderate (m). 25–60%; weak (w), 60–80%; very weak (v.w.), 80–100%; shoulder (s); wave lengths are reported in microns.

The following bands are shown by all three isomers I, II and III: 2.85(m); 2.94(m); 3.13(v.w.); 3.30–3.32(v.w.); 3.38(w, s); 3.43(m-w); 3.50(v.w.); 7.27(w-m); 7.79–7.82(m-i); 7.97(m-w); 8.22–8.24(m); 9.70–9.72(w-m); 12.04–12.20(i).

The benzidine II and the 2,2'-diaminobiphenyl IV yield bands at 5.83(v.w.) and at 8.77(m-i) that are not shown by the diphenyline III. Both II and III give bands at 7.42 (v.w.), 9.92(w-m), 11.78(m) and 11.95(m-i) where none exist in the spectrum of IV. Both III and IV show bands at 8.84(m) and at 10.19–10.22(w-m) that II does not possess.

The benzidine II possesses unique bands at 7.64(w) and 7.74(i); the diphenyline III shows unique bands at 7.66(m), 13.28(m) and 13.52(m); and the 2,2'-diaminobiphenyl IV has unique bands at 7.68(i), 11.86(i, s) and 13.44(m).

PITTSBURGH, PENNSYLVANIA

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

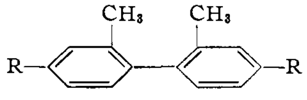
Ullmann Synthesis of Six Dimethyldinitrobiphenyls and their Reduction to the Corresponding Diaminodimethylbiphenyls[1]

BY ROBERT B. CARLIN AND GEORGE E. FOLTZ[2]

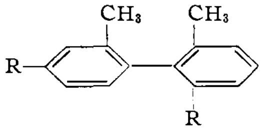
RECEIVED SEPTEMBER 30, 1955

Six dimethyldinitrobiphenyls (I–VI) were prepared by simple and mixed Ullmann reactions. Catalytic reduction of these afforded six corresponding diaminodimethylbiphenyls (VII–XII), all of which were converted to diacetyl and bis-salicylal derivatives. Comparison of the diamines and of their derivatives with three diaminodimethylbiphenyls and their derivatives obtained by catalytic reductive debromination of the rearrangement products of 3,3'-dibromo-5,5'-dimethylhydrazobenzene showed VII, IX and XII to be the structures of the compounds derived from the rearrangement and thereby proved the structures of the rearrangement products themselves. Some aspects of the behavior of halonitrotoluenes in mixed Ullmann reactions is reminiscent of the behavior of monomer mixtures in copolymerization. This analogy may prove useful in the development of a satisfactory mechanism for the Ullmann reaction.

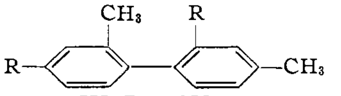
The rearrangement of 3,3'-dibromo-5,5'-dimethylhydrazobenzene[3] conceivably could lead to six different diaminodibromodimethylbiphenyls. Catalytic reductive debromination of these rearrangement products could in turn yield six diaminodimethylbiphenyls (VII–XII). In order that all of the rearrangement products could be identified by comparison of their debrominated derivatives with synthetic specimens, the preparations of VII–XII were carried out. This report is concerned with these preparations, all of which were achieved by Ullmann coupling of appropriate halonitrotoluenes and subsequent reduction of the resulting dimethyldinitrobiphenyls.



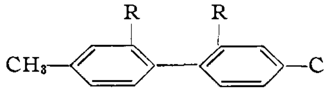
I, R = NO_2
VII, R = NH_2
VIIa, R = NHAc
VIIb, R = NC_7H_7O



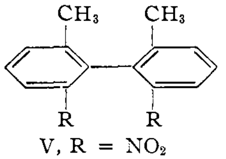
II, R = NO_2
VIII, R = NH_2
VIIIa, R = NHAc
VIIIb, R = NC_7H_7O



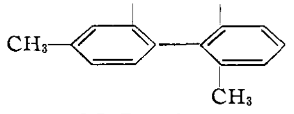
III, R = NO_2
IX, R = NH_2
IXa, R = NHAc
IXb, R = NC_7H_7O



IV, R = NO_2
X, R = NH_2
Xa, R = NHAc
Xb, R = NC_7H_7O

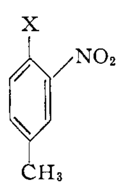


V, R = NO_2
XI, R = NH_2
XIa, R = NHAc
XIb, R = NC_7H_7O

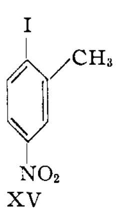


VI, R = NO_2
XII, R = NH_2
XIIa, R = NHAc
XIIb, R = NC_7H_7O

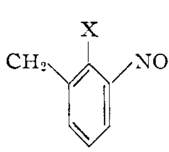
The known compounds I, IV and V were obtained in 25, 46 and 79% yields, respectively, by the symmetrical Ullmann coupling of 2-iodo-5-nitrotoluene, 4-iodo-3-nitrotoluene and 2-iodo-3-nitrotoluene respectively. Each of the three unsymmetrical dimethyldinitrobiphenyls II, III and VI was prepared by a mixed Ullmann reaction. Only one of these (II) was obtained in crystalline form; III and VI were isolated as oils which probably were not entirely free of isomers. The synthesis of III affords a typical example of the behavior encountered in all three mixed Ullmann couplings. A 35% yield of III was realized by treating equal weights of 4-bromo-3-nitrotoluene (XIII) and 2-iodo-5-nitrotoluene (XV) with copper at elevated temperatures. A 4% yield of IV, from the symmetrical coupling product I (from XV) was detected. When 4-iodo-3-nitrotoluene (XIV) was used in place of its bromine analog XIII in an attempted synthesis of III, only IV and unchanged XV were obtained from the mixture. The unsymmetrical dimethyldinitrobiphenyl II was prepared in a similar way in 16% yield from XV and 2-bromo-3-nitrotoluene (XVI); II was accompanied in the mixture by a 12% yield of V, from the self-coupling of XVI, but again no self-coupling product of XV was detected. Finally, a 32% yield of VI was obtained by coupling



XIII, X = Br
XIV, X = I



XV



XVI, X = Br
XVII, X = I

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(1) Submitted in partial fulfillment of the requirements for the degree of Doctor of Philosophy at the Carnegie Institute of Technology.

(2) Institute Graduate Fellow in Organic Chemistry, 1951–1952.

(3) R. B. Carlin and G. E. Foltz, THIS JOURNAL, **78**, 1992 (1956).