

Palmolive-Peet Co. for their interest throughout the work and Dr. Turner Alfrey of this Institute for his helpful suggestions regarding the reaction mechanism.

Summary

A mechanism based on the formation and reactions of allylic free radicals has been proposed to

explain the thermal transformations of simple unsaturated compounds.

Evidence which supports this allylic radical mechanism was obtained from a study of two terminally unsaturated compounds, methyl undecylenate and 1-octene.

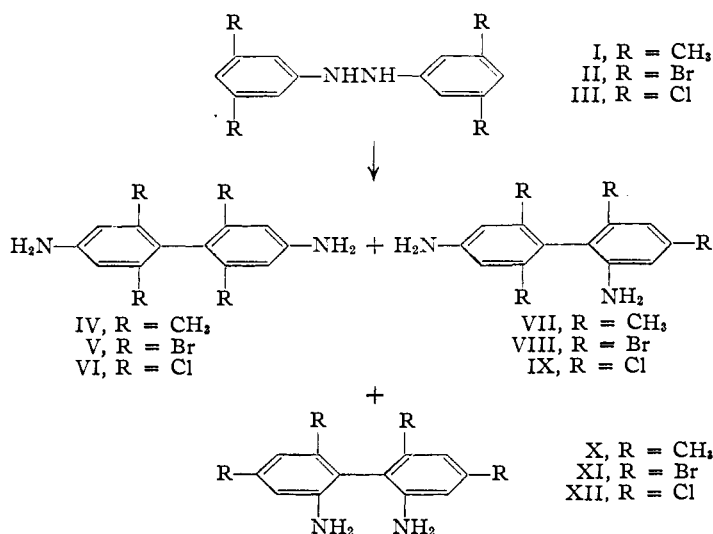
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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, CARNEGIE INSTITUTE OF TECHNOLOGY]

The Benzidine Rearrangement. II. The Rearrangements of Three 3,3',5,5'-Tetrasubstituted Hydrazobenzenes in 2:1 Sulfuric Acid^{1,2}

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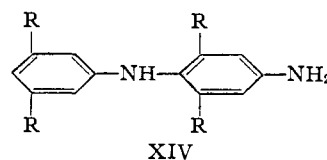
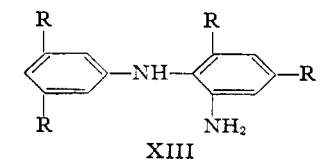
An investigation of the action of aqueous and alcoholic hydrochloric acid on 3,3',5,5'-tetramethylhydrazobenzene (I) disclosed that the only clearly qualitative effect of the methyl groups upon the transformations of I was an abnormally small benzidine (IV)-to-diphenylene (VII) product ratio.⁴



Other possible effects of the methyl groups, such as (1), increased disproportionation ($2\text{ArNHNHAr} \rightarrow \text{ArN}=\text{NAr} + 2\text{ArNH}_2$); (2), unusually severe conditions required to bring about reaction; and (3), the formation of one or both semidines (XIII and XIV, $\text{R} = \text{CH}_3$), were not observed. In an effort to discover the effects of other substituents upon the rearrangements of aromatic hy-

drazo compounds and, if possible, to distinguish the polar and steric contributions to these effects, a study of the rearrangements of a series of 3,3',5,5'-tetrasubstituted hydrazobenzenes has been undertaken; and an investigation of the rearrangements of 3,3',5,5'-tetrabromohydrazobenzene (II) and of its tetrachloro analog (III) has now been completed. Because 2:1 sulfuric acid is the best medium yet found for the rearrangement of II, and because it was desirable to be able to compare the rearrangements of I, II and III under identical reaction conditions, the rearrangements of I and III were also carried out in 2:1 sulfuric acid. In this paper, the rearrangements and related reactions of I, II and III in 2:1 sulfuric acid are reported and compared. In addition, the effects of changes in reaction medium upon the transformations of I are noted.

Some time ago, Meyer, Meyer and Taeger⁵ observed that the rearrangement of the tetrabromohydrazobenzene II occurs in 2:1 but not in 1:1 sulfuric acid and that concentrated sulfuric acid brings about disproportionation exclusively. Beyond establishing the presence of two primary amino groups in each of the two rearrangement products which they isolated, they attempted



(1) This paper has been abstracted from a thesis submitted by William O. Forshey, Jr., to the Committee on Graduate Degrees, Carnegie Institute of Technology, in partial fulfillment of the requirements for the D. Sc. degree.

(2) Presented in part before the Organic Division of the American Chemical Society, New York, N. Y., September, 1947, and Chicago, Ill., April, 1948.

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(4) Carlin, *THIS JOURNAL*, **67**, 928 (1945).

(5) Meyer, Meyer and Taeger, *Ber.*, **53**, 2034 (1920).

no structure proofs but assumed, on the basis of extensive previous work⁶ on *p,p'*-unsubstituted hydrazobenzenes, that the product formed in larger amount had the benzidine structure V and that the other product had the diphenylene structure VIII. In the course of the work reported here, four isomeric rearrangement products of II were isolated. Of these, two had properties which identified them with the two substances reported by Meyer, Meyer and Taeger. However, the product isolated in largest amount, which corresponded in properties to the German investigators' "major product" has now been shown to have the diphenylene structure VIII, and their "minor product" was actually the benzidine V. The third rearrangement product of II was 2,2'-diamino-4,4',6,6'-tetrabromobiphenyl (XI); and the fourth rearrangement product, isolated in amounts so small that complete characterization could not be accomplished, may have been a semidine (XIII or XIV, R = Br) since it reacted with but one equivalent of salicylaldehyde.

The tetrachlorohydrazobenzene (III) gave three isomeric rearrangement products when treated with 2:1 sulfuric acid. Each of the three compounds reacted with two equivalents of salicylaldehyde and with two equivalents of acetic anhydride; therefore, none could be a semidine (XIII or XIV, R = Cl). On the basis of evidence to be cited presently, the three products were assigned the structures VI, IX and XII, in order of decreasing yields from III. In a similar manner, the tetramethylhydrazobenzene (I), which underwent reaction in 2:1 sulfuric acid with noticeably greater speed than II or III in this medium, was shown to form VII, IV and X, in order of decreasing yields.

Disproportionation products of II and III were isolated in 18 and 16% yields, respectively. The fact that nearly equivalent amounts of 3,3',-5,5'-tetrahaloazobenzene and 3,5-dihaloaniline were isolated in each case indicated that nearly all of the azo compounds must have been formed by disproportionation, and not by direct oxidation, of the hydrazo compounds. Although a 7.7% yield of tetramethylazobenzene was obtained from the reaction mixture after I was subjected to the action of 2:1 sulfuric acid, no 3,5-xylidine was isolated. Whereas the 3,5-dihaloanilines are crystalline solids, 3,5-xylidine is an oil, and the failure to obtain it may mean only that the comparatively small amount of it present in the residual oils from the separation of the crystalline transformation products of I escaped notice. If it may be assumed that an amount of the xylidine equivalent to that of the corresponding azo compound was formed from I, an assumption which appears reasonable in view of the behavior of II and III under the same conditions, then the yield of disproportionation products from I was about 15%; and disproportionation of I, II and III in 2:1 sul-

furic acid may be judged to have occurred to substantially the same extent.

In these investigations, every effort was made to give the most nearly complete account possible of the fate of all the substituted hydrazobenzene charged into each reaction mixture. The method of countercurrent extraction,⁷ by means of which the rearrangement products were separated and purified, is particularly well suited to the accomplishment of a nearly quantitative stoichiometric accounting. The application of this procedure made possible the separation and identification of products from I, II and III in total yields of 80, 78 and 91%, respectively. In no case was any considerable portion of material for which no account could be given lost mechanically; in each case nearly all of this material was at hand in the form of a resinous oil which could not have contained appreciable amounts of any of the previously separated products. These resins resisted all efforts to separate crystalline solids from them. Because the three hydrazo compounds gave different amounts of these resinous by-products, their rearrangement reactions are better compared on the basis of the molar ratios (Table I) of the three rearrangement products formed from each hydrazo compound than on the basis of per cent. yields. If it may be assumed that the resins are not formed from the rearrangement products, then the molar ratios of the three rearrangement products formed from a hydrazo compound are also the ratios of their rates of formation.

TABLE I

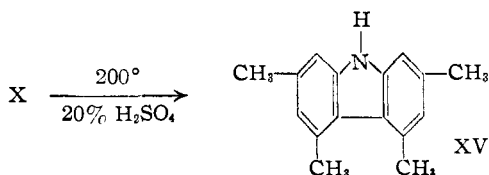
Type rearrangement product	Relative molar amounts formed from I, II and III			
	III ^a (R = Cl)	II ^a (R = Br)	I ^a (R = CH ₃)	I ^b (R = CH ₃)
Benzidine	2.3	2.3	2.4	3.0
Diphenylene	1.3	3.2	2.8	2.0
2,2'-Diaminobiphenyl	1.0	1.0	1.0	0.0

^a In 2:1 sulfuric acid. ^b In 10% aqueous hydrochloric acid.⁴

The structures of the rearrangement products V, VI, VIII, IX, XI and XII of the tetrahalohydrazobenzenes II and III were established by converting them, or their derivatives, through hydrolysis of the carbon-halogen bonds to the known simple diaminobiphenyls, or their derivatives. Thus, structures V and VI were assigned to the two compounds whose N,N'-diacetyl derivatives gave N,N'-diacetylbenzidine on hydrogenolysis. Similarly, the N,N'-diacetyl derivatives of VIII and IX were converted to N,N'-diacetyldiphenylene, and both XI and XII gave 2,2'-diaminobiphenyl. Of the three rearrangement products of I, only X had not been characterized previously.⁴ Its reaction with two equivalents of salicylaldehyde indicated the presence of two primary amino groups, and its conversion to 2,4,5,7-tetramethylcarbazole (XV) on heating with sul-

(6) Cf. Jacobson, *Ann.*, **428**, 76 (1922).(7) Cf. Craig, *J. Biol. Chem.*, **155**, 519 (1944).

furic acid established the existence of the 2,2'-diaminobiphenyl structure.



Support for the carbazole skeletal structure of XV was supplied by its ultraviolet absorption spectrum, which is compared in Fig. 1 with the reported⁸ spectrum of carbazole itself. A comparison of the extinction curve for XV with that for X (Curve III, Fig. 5) leaves no doubt that the conversion of the latter to the former involved a considerable structural alteration.

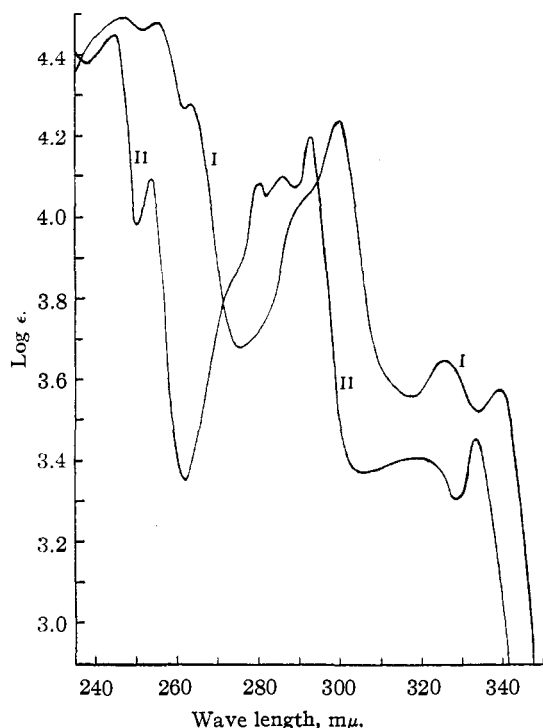


Fig. 1.—Ultraviolet absorption spectra of I, 2,4,5,7-tetramethylcarbazole (XV) (95% ethanol); II, carbazole (hexane).⁸

The ultraviolet extinction curves for the rearrangement products IV–XII are shown in Figs. 3–5. For purposes of comparison, the curves for benzidine and aniline are given in Fig. 2. It is at once evident that the curves for the rearrangement products are more nearly comparable with that for aniline than they are with that for benzidine. This absorption behavior of IV–XII was to be expected in view of the body of evidence which has accumulated on the effects of ortho substitution on the ultraviolet absorption spectra of biphenyl de-

(8) Ramart-Lucas and Biquard, *Bull. soc. chim.*, [5] 3, 430 (1936).

rivatives⁹ and in view of the fact that the benzidines (IV–VI), diphenylines (VII–IX), and 2,2'-diaminobiphenyls (X–XII) all are substituted in the 2,2',6 and 6' positions by amino or by atoms or groups which have been shown to be more effective than amino in preventing biphenyl ring coplanarity.¹⁰

In the absence of all interaction between adjoining rings or between substituents on adjoining rings, each of the compounds IV–XII should be characterized by a molecular extinction curve which should be virtually identical with twice the curve for the corresponding 3,5-disubstituted aniline and only slightly displaced toward longer wave lengths and larger extinction coefficients with respect to twice the curve for aniline itself.¹¹

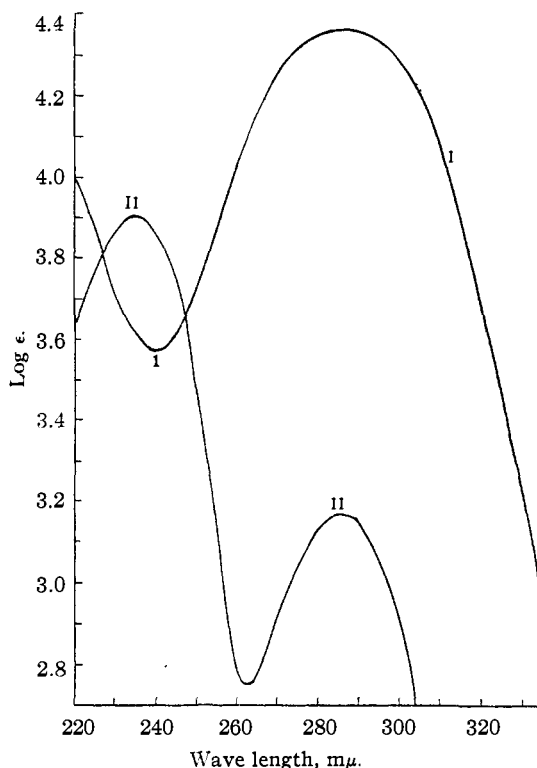


Fig. 2.—Ultraviolet absorption spectra of I, benzidine; II, aniline. We are indebted to Mr. Robert G. Nelb, University of Rochester, for his permission to reproduce these curves, which he has determined. They agree satisfactorily with the curves for aniline¹² and for benzidine¹³ which have been published previously.

(9) Pickett, Walter and France, *THIS JOURNAL*, **58**, 2296 (1936); Calvin, *J. Org. Chem.*, **4**, 256 (1939); O'Shaughnessy and Rodebush, *THIS JOURNAL*, **62**, 2906 (1940); Williamson and Rodebush, *ibid.*, **63**, 3018 (1941).

(10) Cf. Shriner and Adams in Gilman, "Organic Chemistry," Vol. I, second ed., John Wiley and Sons, Inc., New York, N. Y., 1943, pp. 361, 362.

(11) Conrad-Billroth, *Z. physik. Chem.*, **B20**, 227 (1933); Forster and Wagner, *ibid.*, **B35**, 343 (1937); Morton and Stubbs, *J. Chem. Soc.*, 1347 (1940).

(12) Wolf and Herold, *Z. physik. Chem.*, **B13**, 201 (1931).

(13) Williamson and Rodebush, *THIS JOURNAL*, **63**, 3018 (1941).

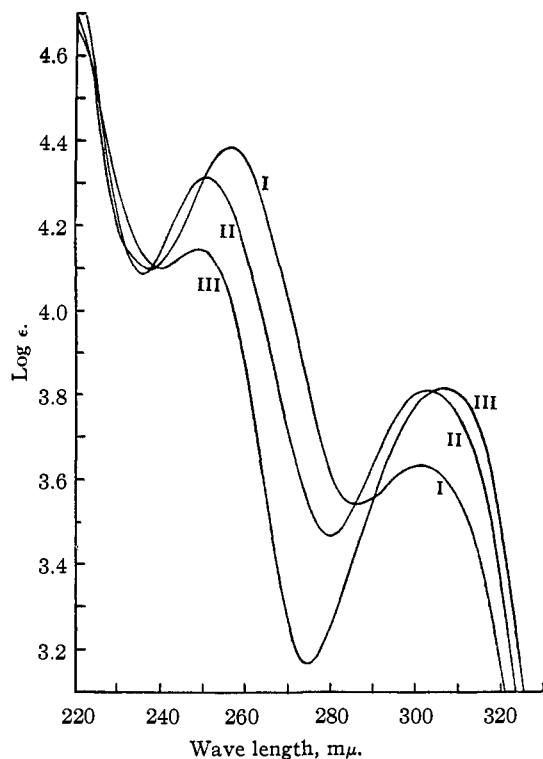


Fig. 3.—Ultraviolet absorption spectra of I, 2,2',6,6'-tetrachlorobenzidine (VI); II, 2,2',4,6'-tetrachlorodiphenylene (IX); 2,2'-diamino-4,4',6,6'-tetrachlorodiphenyl (XII) (95% ethanol).

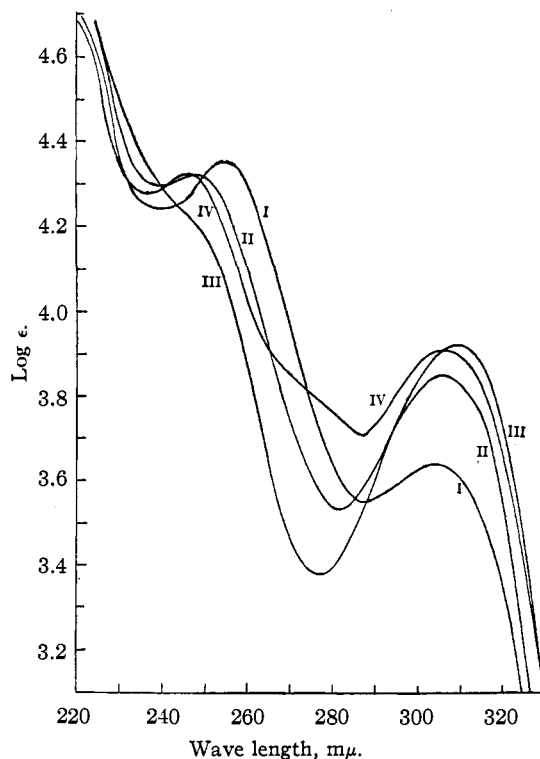


Fig. 4.—Ultraviolet absorption spectra of I, 2,2',6,6'-tetrabromobenzidine (V); II, 2,2',4,6'-tetrabromodiphenylene (VIII); III, 2,2',4,4'-tetrabromo-6,6'-diaminobiphenyl (XI); IV, possible semidine (95% ethanol).

Furthermore, in the absence of interaction, each curve should be identical with those for its two isomeric rearrangement products. Reference to Figs. 3-5 discloses that the curves for any group of isomers are not, in fact, superposable. Indeed, variations in extinction curves with structure within a group of isomers are consistent throughout all three groups. In all cases, the molecular extinction coefficients (ϵ) for the substituted benzidines (IV-VI) are larger than those for their isomers in the region of the shorter wave-length maxima, and these maxima occur at wave lengths as long or longer than do those of their isomers. On the other hand, in the region of the longer wave-length maxima, the substituted benzidines have smaller ϵ values, and their maxima occur at wave lengths as short as or shorter than those for their isomers. The curves for the substituted 2,2'-diaminobiphenyls (X-XII) show the opposite behavior. Compared with the curves for their isomers, their maxima (or inflection points) in the 240-260 $m\mu$ region occur at as short or shorter wave lengths and smaller ϵ values, while in the 290-310 $m\mu$ region, their maxima are found at longer wave lengths and larger ϵ values. These generalizations might provide a basis for the tentative assignment of structures to the rearrangement products of 3,3',5,5'-tetrasubstituted hydrazobenzenes which have not as yet been investi-

gated. However, the extinction curves for such a group of isomers are not likely to be sufficiently different from each other so that deductions concerning their structures could be made without comparing the curves for all three isomers.

Curve IV, Fig. 4 is the extinction curve for the rearrangement product of the tetrabromohydrazobenzene (II) which may be a semidine. The position of this curve relative to those for the other three isomers supports the belief that the compound is truly different from the others and that it is not a molecular compound or a eutectic formed from some combination of its isomers.

Discussion

The behavior of the hydrazo compounds I, II and III on rearrangement in 2:1 sulfuric acid differs in two significant respects from the behavior of previously investigated *p,p'*-unsubstituted hydrazobenzenes. First, in all three cases, rearrangements to derivatives of 2,2'-diaminobiphenyl (X, XI and XII) were observed. Although certain hydrazonaphthalenes rearrange to diaminobiphenyls analogous to 2,2'-diaminobiphenyl,¹⁴ there appears to be no previous report of a rearrangement of this type in the hydrazobenzene series. The formation of diphenyls VII and VIII

(14) Meisenheimer and Witte, *Ber.*, **36**, 1153 (1903); Hodgson, Habeshaw and Murli, *J. Chem. Soc.*, 1390 (1947).

in larger amounts than the benzidines IV and V, from I and II, respectively, is the second aspect of behavior for which no previous example has appeared. If the fourth rearrangement product of the tetrabromohydrazobenzene II is indeed a semidine, then this, too, is a product of a rearrangement of an unusual type from a *p,p'*-unsubstituted hydrazobenzene.

Effects of Substituents.—It is a temptation to ascribe the formation of 2,2'-diaminobiphenyls and the abnormally small benzidine-to-diphenylene ratios observed from the rearrangements of I, II and III to the steric size of the substituents. If the factors which govern steric interference with the formation of biphenyl derivatives from hydrazobenzenes are related to the van der Waals radii¹⁵ of the groups which appear in the *ortho* positions of the products and to the factors governing the relative ease of racemization of *ortho* substituted biphenyls,¹⁰ then bromine atoms and methyl groups should offer about an equal amount of steric interference with the benzidine and related rearrangements, and chlorine atoms and amino groups should interfere to a somewhat lesser degree, in that order. If this is true, then mechanical interference with the formation of the rearrangement products of any of the substituted hydrazobenzenes I, II and III should decrease in the order: benzidine > diphenylene > 2,2'-diaminobiphenyl—an order which is the reverse of that to be expected in the rearrangements of hydrazobenzene itself. If, however, the chlorine atom does not differ in size from the amino group as much as do the bromine atom and the methyl group, then the differences between the mechanical interference with benzidine formation, with diphenylene formation and with 2,2'-diaminobiphenyl formation should not be as great from III as from I or II. Thus, on purely steric grounds, the benzidine:diphenylene:2,2'-diaminobiphenyl ratios should be greater from the rearrangements of III than from I or II. Examination of the first three columns on the right side of Table I reveals that the benzidine:diphenylene ratios do follow this order, III giving the largest ratio; however, the diphenylene:2,2'-diaminobiphenyl ratios are in the opposite order to that predicted on steric grounds, and the benzidine:2,2'-diaminobiphenyl ratios remain essentially constant. Therefore, the steric size of substituents in 3,3',5,5'-tetrasubstituted hydrazobenzenes is by no means the sole factor in determining product ratios.

The fact that the tetramethylhydrazobenzene (I) rearranges much more rapidly than either tetrahalohydrazobenzene (II or III) under similar conditions lends support to the concept that a substituent whose polar nature is such that it would be expected to operate to increase the base strength of the parent hydrazobenzene will also operate to increase its rate of rearrangement—a

(15) Cf. Pauling, "The Nature of the Chemical Bond," second edition, Cornell University Press, Ithaca, N. Y., 1940, pp. 189, 190.

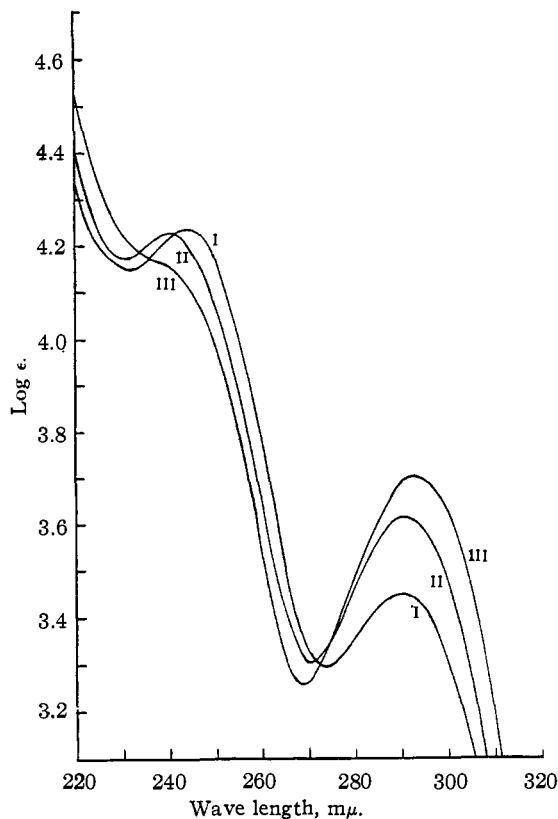


Fig. 5.—Ultraviolet absorption spectra of I, 2,2',6,6'-tetramethylbenzidine (IV); II, 2,2',4,6'-tetramethyldiphenylene (VII); III, 2,2',4,4'-tetramethyl-6,6'-diaminobiphenyl (X) (95% ethanol).

concept which is also supported by some recently reported¹⁶ rate studies. However, this evidence should not be interpreted to mean that the reaction of one or two protons with a hydrazobenzene is a slow, rate-determining step in the rearrangement reactions. Dewar¹⁶ has pointed out that such reactions would probably be too rapid to be rate-determining.

Medium Effects.—A change in medium from 10% aqueous hydrochloric acid to 2:1 sulfuric acid brought about the following changes in the reactions of the tetramethylhydrazobenzene I: (1) a great increase in the total rate of rearrangement; (2) an increase from less than 2% to about 15% of disproportionation of I; and (3) a profound change in rearrangement product ratios. The first effect is well known and was to be expected. That the effect on disproportionation is substantially a medium effect is supported by the fact that reaction conditions other than medium, such as temperature and concentration, were quite comparable. With regard to the effect upon product ratios, comparison of the two right-most columns of Table I shows that the change from the weaker to the stronger acid medium changes the major rearrangement product from the benzi-

(16) Dewar, *J. Chem. Soc.*, 777 (1946).

dine IV to the diphenylene VII. In addition, the 2,2'-diaminobiphenyl (X) was not detected among the rearrangement products of I in 10% aqueous hydrochloric acid.⁴

The results of the investigations reported in this and the preceding paper serve to emphasize the comparative scarcity of knowledge of the effects of structure, environment and temperature on the course of the benzidine and related rearrangements. Further work, including kinetics studies, directed toward providing more information about these effects, is now in progress.

Experimental¹⁷

3,5-Dibromonitrobenzene.—The procedure given by Meyer, Meyer and Taeger⁵ was modified in the following manner. To a stirred, boiling mixture of 2,6-dibromo-4-nitroaniline,⁵ 500 ml. of ethanol and 55 ml. of concentrated sulfuric acid, 50 g. of pulverized sodium nitrite was added in portions as rapidly as foaming would permit. Boiling was continued for a half-hour after the sodium nitrite addition was complete. The mixture was allowed to cool, and the solids were collected by filtration and washed with water. The 3,5-dibromonitrobenzene was separated from remaining inorganic salts by dissolving it in boiling ethanol and filtering the hot solution, from which 86.3 g. (91%) of the product, m. p. 104–105°, crystallized on cooling. Recrystallization from ethanol gave orange needles, m. p. 106°; reported m. p. 106°.⁵

3,5-Dichloronitrobenzene.—Application of the above procedure to 20 g. of 2,6-dichloro-4-nitroaniline,¹⁸ 200 ml. of ethanol, 15 ml. of concentrated sulfuric acid and 13.4 g. of sodium nitrite gave a crude solid mixture from which inorganic salts were removed by slurring with water and filtering. It was not necessary to recrystallize the 15.6 g. (84%) of crystalline product obtained in this way, for it had the m. p. 62–63.5°. Korner¹⁹ gives the m. p. 65.4°.

This preparation of pure 3,5-dichloronitrobenzene in good yield from the dichloroaniline, using ethanolic sulfuric acid and sodium nitrite, contrasts with the experience of Ridge, who recently reported²⁰ that these reagents produced no more than 60% yields of a product which, under some conditions, was frequently contaminated with 2,2',6,6'-dichloro-4,4'-dinitrobiphenyl. The results described in this paper are, however, in agreement with those of other investigators who have carried out this reaction.²¹

3,3',5,5'-Tetrabromoazobenzene.—To a stirred, boiling suspension of 32 g. of zinc dust in a solution of 40 g. of 3,5-dibromonitrobenzene in 160 ml. of ethanol, 80 ml. of 30% aqueous sodium hydroxide was added as rapidly as foaming would permit (about ten minutes). It was found that the more rapidly the sodium hydroxide solution is added, the better the yield of product from the reaction. The mixture was boiled for an hour after the base had been added; then about 75% of the ethanol was removed by distillation, and the residue was diluted with 100 ml. of water and permitted to cool. The solids were removed by filtration, dried and extracted with portions of boiling toluene until the extracts were no longer colored. On concentrating the toluene extracts to 150 ml. and cooling, the solution deposited 28.3 g. (80%) of the tetrabromoazobenzene as orange needles, m. p. 231–236.5°. After recrystallization from toluene, a sample had the m. p. 246.5–247°. The m. p. 244° has been reported.⁵

3,3',5,5'-Tetrachloroazobenzene was prepared in 85% yield by applying the foregoing procedure to 3,5-dichloronitrobenzene. The only modifications found to be necessary were in the quantities of solvents used. Several re-

crystallizations of the crude product, m. p. 161–180°, from toluene gave orange needles, m. p. 194–194.5°.

Anal. Calcd. for C₁₂H₈N₂Cl₄: C, 45.03; H, 1.89. Found: C, 44.84; H, 2.01.

3,3',5,5'-Tetrabromohydrazobenzene (II).—To a stirred, boiling suspension of 40 g. of finely powdered 3,3',5,5'-tetrabromoazobenzene in 400 ml. of ethanol and 20 ml. of glacial acetic acid, 28 g. of zinc dust was added in small portions until the insoluble azo compound disappeared and the solution became nearly colorless. The mixture was cooled and filtered, and the filtrate was poured cautiously into about 500 ml. of boiling water. The sludge from the filtration was extracted with two portions of boiling ethanol, and the extracts were also poured into the boiling water. Boiling was continued until sufficient agglomeration of the precipitated hydrazo compound had occurred to permit its filtration. The mixture was cooled, and 38.2 g. (95%) of II was collected as tiny white needles, m. p. 179.5–181°. The m. p. 182–183° has been reported.⁵

3,3',5,5'-Tetrachlorohydrazobenzene (III) was obtained in 96% yield from 3,3',5,5'-tetrachloroazobenzene by means of essentially the same procedure used for the preparation of II. Recrystallization of the precipitated product, m. p. 128.5–130°, from petroleum ether (b. p. 65–110°) gave colorless prisms or plates, m. p. 131–132°.

Anal. Calcd. for C₁₂H₈N₂Cl₄: C, 44.75; H, 2.50. Found: C, 44.81; H, 2.49.

Procedures for the Rearrangements of the 3,3',5,5'-Tetrasubstituted Hydrazobenzenes.—A 15.0-g. sample of the tetrabromohydrazobenzene II was treated with 450 ml. of 2:1 sulfuric acid which had been preheated to 85–90°, and the mixture was stirred and maintained within that temperature range for four hours, then cooled and filtered through a sintered glass funnel. The insoluble 3,3',5,5'-tetrabromoazobenzene (1.40 g., 9.3%), after washing with water, had the m. p. 244.5–247°; and no melting point depression was observed when a sample of this material and one of authentic azo compound were mixed. The sulfuric acid filtrate was cooled and neutralized slowly with cold 40% aqueous sodium hydroxide. The organic material which precipitated was dissolved in benzene.

Application of precisely the same procedure to 16.2 g. of the tetrachlorohydrazobenzene III (with the exception that the sulfuric acid mixture was warmed for eighteen hours) gave 1.3 g. (8%) of 3,3',5,5'-tetrachloroazobenzene m. p. 189–193°, and 14.5 g. of a brown powder, m. p. 106–145°, which was precipitated by the base from the sulfuric acid solution.

Similarly, 10.5 g. of the tetramethylhydrazobenzene I⁴ was treated cautiously (since the reaction was vigorous) with 150 ml. of 2:1 sulfuric acid at 85–90°. The mixture was stirred for five minutes, diluted with 200 ml. of water and filtered. The insoluble material consisted of 0.81 g. (7.7%) of 3,3',5,5'-tetramethylazobenzene, m. p. 137.5–139° (reported m. p. 138–139°⁴). The solid material formed by neutralizing the filtrate with 30% sodium hydroxide was dissolved in benzene.

Separation of Products from Sulfuric Acid-Soluble Fractions. A. From the Tetrabromohydrazobenzene (II).—The benzene solution obtained as described above was dried and allowed to flow through a 2-in. column of activated alumina to remove highly colored tars. The pale yellow solution was then concentrated to 50 ml. and treated with petroleum ether (b. p. 77–93°) at the boiling point until small needles began to appear. On cooling, the solution deposited 7.46 g. of mixed crystalline bases. Concentration of the filtrate gave a red oil, from which 1.3 g. (8.7%) of 3,5-dibromoaniline, m. p. 53.5–56°, distilled when the oil was evacuated to 0.01 mm. at room temperature in a sublimation apparatus. The identity of the dibromoaniline was confirmed by preparing the crystalline acetyl derivative in the usual way, m. p. 227–228°.²²

(22) Vorländer and Seibert, *Ber.*, **52**, 293 (1919), reported the m. p. 57° for 3,5-dibromoaniline. Chattaway and Orton, *ibid.*, **33**, 2397 (1900), gave the m. p. 231° for 3,5-dibromoacetanilide.

(17) Melting points are corrected.

(18) Witt, *Ber.*, **8**, 144 (1875).

(19) Korner, *Gazz. chim. ital.*, **4**, 377 (1874).

(20) Ridge, *J. Chem. Soc.*, 734 (1947).

(21) Holleman, *et al.*, *Rec. trav. chim.*, **23**, 366 (1904); **35**, 8 (1915); Willstätter and Schudel, *Ber.*, **51**, 782 (1918).

The residual oil after removal of the dibromoaniline was heated to 125° (0.001 mm.) until no more yellow, pasty condensate formed. This material was treated as described below.

The 7.47 g. of mixed crystalline bases was subjected to a countercurrent extraction procedure,⁷ using in each of nine separatory funnels 150 ml. each of benzene and 3 *N* hydrochloric acid. Separation into 2.83 g. of 2,2',6,6'-tetrabromobenzidine (V), 3.87 g. of 2,2',4,6'-tetrabromodiphenylene (VIII) and a brown glass occurred. The glass was dissolved in 100 ml. of benzene and the solution was extracted with two 100-ml. portions of 4 *N* hydrochloric acid. When the extracts were made alkaline with sodium hydroxide, an additional 0.22 g. of the diphenylene VIII was obtained. The yellow pasty distillate from the red oil was dissolved in the benzene solution remaining after extraction with 4 *N* acid, and the new solution was extracted with 6 *N* hydrochloric acid. Neutralization of the extract with sodium hydroxide gave 1.08 g. of brown powder from which 0.73 g. of crude 2,2'-diamino-4,4',6,6'-tetrabromobiphenyl (XI) was isolated by recrystallization from petroleum ether-benzene. The remaining 0.35 g. of the brown powder was considered as "mixed bases," and no attempt at further separation was made. The benzene solution remaining after the 6 *N* acid extraction was shaken with concentrated hydrochloric acid. A solid salt, insoluble in both liquid phases, was formed. Neutralization of this salt and of the acid solution gave 1.04 g. of brown powder, from which 0.26 g. of the "semidine" (XIII or XIV, R = Br) was isolated as a first crop of crystals from petroleum ether-benzene. Concentration of the filtrate from this crop of crystals gave 0.49 g. of a second crop, which proved to be more XI. The remaining 0.29 g. of material from which these two crops of crystals were obtained was classed as "mixed bases," and no further attempt at separation was made. Total yields of the isomeric rearrangement products were as follows: benzidine (V), 2.83 g. (18.9%); diphenylene (VIII), 4.09 g. (27.2%); 2,2'-diaminobiphenyl (XI), 1.22 g. (8.2%); "semidine," 0.26 g. (1.7%); mixed bases, 0.63 g. (4.2%). Total yield of all reaction products, 11.73 g. (78.2%).

The 2,2',6,6'-tetrabromobenzidine (V) formed white needles from petroleum ether-benzene, m. p. 249-250°. The m. p. 242° has been reported.⁵

2,2',4,6'-Tetrabromodiphenylene (VIII) formed white needles from petroleum ether-benzene, m. p. 183-184°. The m. p. 180° has been reported.⁵

Anal. Calcd. for 2,2'-diamino-4,4',6,6'-tetrabromobiphenyl (XI), small white prisms, m. p. 161-162°, from petroleum ether-benzene, C₁₂H₈N₂Br₄: C, 28.83; H, 1.61. Found: C, 29.39; H, 1.77.

The "semidine" (XIII or XIV, R = Br) formed short, white needles, m. p. 177.5-178.5°, after sublimation in high vacuum and two recrystallizations from petroleum ether-benzene. Mixtures of this compound with a sample, m. p. 178-180° of the diphenylene VIII and with a sample, m. p. 180-181°, of the tetrabromohydrazobenzene II, melted at 145-165° and at 148-162°, respectively.

Anal. Calcd. for C₁₂H₈N₂Br₄: C, 28.83; H, 1.61. Found: C, 28.95; H, 1.14.

The "semidine," of XIV (R = Br), should form a mono-salicylal derivative; if XIII (R = Br), it should form either a dihydrobenzimidazole derivative isomeric with a monosalicylal derivative, or the related benzimidazole derivative. The derivative actually formed with salicylaldehyde (general procedure to be given presently) formed white needles, m. p. 211-211.5° from petroleum ether-benzene.

Anal. Calcd. for mono salicylal derivative or dihydrobenzimidazole, C₁₉H₁₂N₂OBr₄: C, 37.78; H, 2.00. Calcd. for benzimidazole, C₁₉H₁₀N₂OBr₄: C, 37.91; H, 1.67. Found: C, 37.88; H, 1.74.

B. From the Tetrachlorohydrazobenzene (III).—The benzene solution of mixed bases was dried, decolorized by passing through a 3-in. column of activated alumina, and the solute divided into three fractions through a series of recrystallizations from petroleum ether-benzene: (1), an

8.0-g. fraction melting above 135°; (2), a 4.4-g. fraction melting below 135°; and (3), a red oil from which 1.21 g. (7.5%) of 3,5-dichloroaniline, white needles, m. p. 50-51°, were obtained by evacuating the oil to 0.01 mm. at room temperature in a sublimation apparatus. Its structure was confirmed by preparing 3,5-dibromoacetanilide, m. p. 187.5-188.5°, from it in the usual way. The m. p. 50.5° has been reported for the dichloroaniline,¹⁸ and that of its acetyl derivative is stated to be 186-187°.²³

Crystallization fraction (1) was subjected to countercurrent extraction, using nine separatory funnels, each of which contained 150 ml. each of benzene and 1 *N* hydrochloric acid. This extraction gave 5.15 g. of 2,2',6,6'-tetrachlorobenzidine (VI), 0.88 g. of a crystalline mixture, m. p. 157-179° and 1.94 g. of a crystalline mixture, m. p. 126-136°.

The 1.94-g. fraction was combined with crystallization fraction (2) and the mixture submitted to a second nine-funnel counter-current extraction, using 150 ml. each of benzene and 3 *N* hydrochloric acid in 10% acetic acid in each funnel. A separation into 2.55 g. of 2,2',4,6'-tetrachlorodiphenylene (IX), 2.59 g. of 2,2'-diamino-4,4',6,6'-tetrachlorobiphenyl (XII), and 1.11 g. of a mixture m. p. 150-170°, was accomplished. The 1.11 g. fraction from the second extraction procedure and the 0.88 g. fraction from the first procedure were combined and submitted to a third counter-current extraction. This time only three funnels were employed, and benzene and 1 *N* hydrochloric acid constituted the solvent pair. A separation was effected into an additional 0.75 g. of the benzidine VI, an additional 0.90 g. of the diphenylene IX, and 0.31 g. of a mixture upon which no further separation procedure was attempted. The total yields of the isomeric rearrangement products were as follows: benzidine VI, 5.90 g. (36.4%); diphenylene IX, 3.45 g. (21.3%); 2,2'-diaminobiphenyl XII, 2.59 g. (16.0%); mixture (probably of VI and IX), 0.31 g. (1.9%); total yield of all reaction products, 14.76 g. (91.1%).

Anal. Calcd. for 2,2',6,6'-tetrachlorobenzidine, white needles, m. p. 212.5-213.5°, from petroleum ether-benzene, C₁₂H₈N₂Cl₄: C, 44.75; H, 2.50. Found: C, 44.73; H, 2.62.

Anal. Calcd. for 2,2',4,6'-tetrachlorodiphenylene (IX), white needles, m. p. 141-141.5° from petroleum ether-benzene, C₁₂H₈N₂Cl₄: C, 44.75; H, 2.50. Found: C, 45.17; H, 2.50.

Anal. Calcd. for 2,2'-diamino-4,4',6,6'-tetrachlorobiphenyl (XII), white prisms, m. p. 120-121°, from aqueous ethanol, C₁₂H₈N₂Cl₄: C, 44.75; H, 2.50. Found: C, 45.00; H, 2.76.

C. From the Tetramethylhydrazobenzene (I).—The benzene solution of the crude mixture of rearranged bases was concentrated to 150 ml. and submitted to a countercurrent distribution procedure, in which 150 ml. each of benzene and of 10% aqueous acetic acid was used in each of nine separatory funnels. The procedure gave 2.82 g. of 2,2',6,6'-tetramethylbenzidine (IV), 3.18 g. of 2,2',4,6'-tetramethyldiphenylene (VII), 0.16 g. of a mixture of these two compounds, and a benzene solution of another mixture. This solution was extracted with 150 ml. each of 0.1 *N* and 0.2 *N* hydrochloric acid. When the extracts were made alkaline with sodium hydroxide, 1.44 g. of brownish solid was obtained. Recrystallization of this material from 4:1 petroleum ether-benzene gave 1.14 g. of 2,2'-diamino-4,4',6,6'-tetramethylbiphenyl (X). The remaining 0.30 g. of precipitated material was regarded as "mixed bases" and was not further examined. Extraction with stronger acids of the benzene solution remaining after treatment with 0.2 *N* hydrochloric acid gave only red oils from which no crystalline solids could be isolated. The total yields of isomeric rearrangement products was as follows: benzidine IV, 2.82 g. (26.8%); diphenylene VII, 3.18 g. (30.3%); 2,2'-diaminobiphenyl X, 1.14 g. (10.9%); "mixed bases," 0.46 g. (4.4%); total yield of all reaction products, 8.41 g. (80.1%).

(23) Beilstein and Kurbatov, *Ann.*, **196**, 219 (1879).

2,2',6,6'-Tetramethylbenzidine (IV) formed white needles, m. p. 167.5° from petroleum ether-benzene. The m. p. 167-168° has been reported.⁴

2,2',4,6'-Tetramethyldiphenylene (VII) formed clusters of short white needles, m. p. 146.5-147.5°, from petroleum ether-benzene. The m. p. 143° has been reported.⁴

Anal. Calcd. for 2,2'-diamino-4,4',6,6'-tetramethylbiphenyl (X), short white needles, m. p. 180-181°, from petroleum ether-benzene, C₁₆H₂₀N₂: C, 79.95; H, 8.39. Found: C, 80.06; H, 8.12.

Preparations of Derivatives of Rearrangement Products IV-XII.—The N,N'-diacetyl derivatives of these compounds were prepared in at least 90% yields from the diamines and acetic anhydride, by means of the procedure given by Meyer, Meyer and Taeger⁵ for the acetylation of the tetrabromobenzidine (V). All of the compounds formed white needles.

All but one of the N,N'-disalicylal derivatives were prepared by warming a sample of the diamine with ten to fifteen times its weight of salicylaldehyde at 100° for thirty minutes. Each mixture was dissolved in three to five times its weight of boiling petroleum ether (b. p. 65-110°). On cooling, the solutions deposited the disalicylal derivatives in the form of yellow or orange needles. Yields were 75% or better. The derivative with one equivalent of salicylaldehyde of the "semidine" from the rearrangement of II was also prepared by this general procedure, except that the reaction mixture was dissolved in ethanol; yield, 0.022 g. from 0.070 g. of "semidine." The disalicylal derivative of VI was obtained by boiling 0.5 g. of VI and 0.5 g. of salicylaldehyde in 5 ml. of ethanol for three hours. The derivative was precipitated by pouring the reaction mixture into water. Petroleum ether-benzene was the solvent used for recrystallization of all salicylal derivatives except that of VI, which was recrystallized from nitrobenzene. Table II gives the properties and analytical data for the diacetyl and disalicylal derivatives which were prepared during the course of this work.

TABLE II

Diacetyl ^{a,b} Deriv. of	M. p., °C.	Carbon, %		Hydrogen, %	
		Calcd.	Found	Calcd.	Found
VI	317-318	47.32 ^c	47.42	2.98 ^c	2.79
IX	238-243	47.32 ^c	47.23	2.98 ^c	3.06
XII	180-181	47.32 ^c	47.02	2.98 ^c	2.93
Disalicylal Deriv. of					
VI	317-319	58.90 ^d	58.86	3.04 ^d	2.90
IX	266-167	58.90 ^d	59.48	3.04 ^d	3.28
XII	247-249	58.90 ^d	59.04	3.04 ^d	3.12
X	205-206	80.32 ^e	80.60	6.29 ^e	6.23

^a Diacetyl derivative of V, m. p. 329-341°; reported 331°. ^b Diacetyl derivative of VIII, m. p. 272-273°; reported 269-270°. ^c For C₁₆H₁₂O₂N₂Cl₄. ^d For C₂₈H₁₆O₂N₂Cl₄. ^e For C₃₀H₂₈O₂N₂.

Hydrogenolysis of Rearrangement Products of II and III.—For hydrogenolysis of each of the bromo compounds, a solution of one of these and sufficient sodium hydroxide to neutralize the theoretical amount of liberated hydrogen bromide in enough ethanol to maintain the solids in solution at room temperature was treated with Raney nickel, and the resulting mixture was subjected to the action of hydrogen under a pressure of 45-50 lb./sq. in. for about ten hours. The catalyst was removed by filtration, extracted two or three times with portions of boiling ethanol, and the extracts were added to the filtrate. The ethanol solution was concentrated to 20-50 ml. and diluted with about ten times its volume of water. At this point, N,N'-diacetylbenzidine could be removed by filtration and recrystallized from aqueous ethanol. N,N'-Diacetyldiphenylene was soluble in this slightly alcoholic water solution, and the solution had to be concentrated under diminished pressure to a small volume before the compound could be obtained. It was recrystallized from ethanol. 2,2'-Diaminobiphenyl was precipitated at this point in the

procedure as a gum. It was extracted with benzene, the benzene solution was concentrated to a small volume and diluted with petroleum ether. The diaminobiphenyl crystallized and was recrystallized from this solvent.

Identical procedures were used for the chloro compounds, except that hydrogenolysis was carried out at 75° under hydrogen at 550 lb./sq. in. for three hours.

By means of these methods, the N,N'-diacetyl derivatives of V and VI were converted to N,N'-diacetylbenzidine in 84 and 66% yields, respectively. The N,N'-diacetyl derivatives of VIII and IX were converted to N,N'-diacetyldiphenylene in 62 and 80% yields, respectively; and 2,2'-diaminobiphenyl was formed from XI and XII in 37 and 65% yields, respectively. The hydrogenolysis of XI gave a comparatively poor yield of product because a small sample was used, and the considerable losses thereby incurred can be ascribed to the solubility of the product in water. The diacetyl derivatives of the tetrahalobenzidines and diphenylenes, rather than the diamines themselves, were selected for hydrogenolysis because their products, unlike the corresponding diaminobiphenyls, have sharp and constant melting points and are stable in air.

N,N'-Diacetylbenzidine samples, m. p. 331-332.5°, from the hydrogenolysis of V and VI, were mixed with samples obtained by acetylation²¹ of an authentic specimen of benzidine. There was no melting point depression in either case. However, a mixture of the compound with a sample of the N,N'-diacetyl derivative of VIII, m. p. 339-341°, had the m. p. 288-312°.

N,N'-Diacetyldiphenylene and 2,2'-diaminobiphenyl were synthesized from 2,4'-dinitrobiphenyl²⁵ and from 2,2'-dinitrobiphenyl,²⁶ respectively, by hydrogenation of the dinitro compounds in absolute ethanol solutions at room temperature under about 50 lb./sq. in. pressure of hydrogen, in the presence of Adams catalyst. After removal of the catalyst, the solutions were concentrated to a small volume. The diphenylene solution was treated with excess acetic anhydride, permitted to stand overnight, and then diluted with water. Diacetyldiphenylene was obtained in 84% yield in the form of white prisms, m. p. 199-201° alone or when mixed with specimens formed by hydrogenolysis of the tetrachloro and tetrabromo derivatives.²⁶ The solution of 2,2'-diaminobiphenyl in a small volume of ethanol was treated with water at the boiling point until a slight turbidity became evident. On cooling, the solution deposited large leaflets, surface-colored yellow, of product in 80% yield. It had the m. p. 78-79°, alone or when mixed with samples of the hydrogenolysis products of XI and XII.²⁷ The N,N'-dibenzoyl derivative of this product was prepared by means of the Schotten-Baumann procedure. It had the m. p. 189-190.5°, alone or when mixed with samples prepared in a similar way from the hydrogenolysis products of XI and XII.²⁸

2,4,5,7-Tetramethylcarbazole (XV).—A mixture of 0.327 g. of the diaminotetramethylbiphenyl X and 40 ml. of 25% aqueous sulfuric acid was heated in an autoclave at 200° for sixteen hours. The reaction mixture was diluted with water and extracted with toluene. The toluene solution was concentrated to 5 ml. and diluted with 10 ml. of petroleum ether. On cooling, the solution deposited 0.170 g. (56%) of XV in the form of small white plates, m. p. 206-207°. After two recrystallizations from the same solvent mixture, the substance had the m. p. 207-207.5°.

Anal. Calcd. for C₁₆H₁₇N: C, 86.05; H, 7.68. Found: C, 86.44; H, 7.51.

Ultraviolet absorption spectra were determined in purified ethanol²⁹ solutions by means of a Beckmann Quartz

(24) Sachs and Whittaker, *Ber.*, **35**, 1435 (1902), give the m. p. 330-331°.

(25) Gull and Turner, *J. Chem. Soc.*, 494 (1929).

(26) Schultz, Schmidt and Strasser, *Ann.*, **207**, 355 (1881), give the m. p. 202°.

(27) Tauber, *Ber.*, **24**, 198 (1891), gives the m. p. 81°.

(28) Niementowski, *ibid.*, **34**, 3330 (1901), gives the m. p. 184°.

(29) Leighton, Cray and Schipp, *THIS JOURNAL*, **53**, 3017 (1931).

Spectrophotometer, Model DU. Analytical samples of all compounds were used for spectroscopic study.

Summary

1. The rearrangements of three 3,3',5,5'-tetra-substituted hydrazobenzenes, in which the substituents are methyl, bromine and chlorine, respectively, are reported. In each case, rearrangements to a benzidine, a diphenylene, and a 2,2'-diaminobiphenyl occur in 2:1 sulfuric acid medium; and disproportionation in considerable amount ac-

companies the rearrangements. A semidine may have been formed in one case.

2. Certain assessments of the polar and steric effects of the substituents and of medium effects upon the rates of rearrangements, the product ratios and degree of disproportionation are made.

3. The ultraviolet absorption spectra of the rearrangement products are reported and compared.

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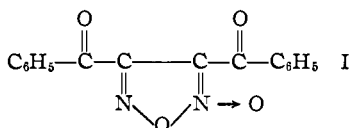
[CONTRIBUTION FROM THE NOYES CHEMICAL LABORATORY, UNIVERSITY OF ILLINOIS]

A Mechanism for the Formation of Dibenzoylfurazane Oxide from Phenylmethylcarbinol

BY ELLIOT R. ALEXANDER, MARK R. KINTER¹ AND JOHN D. MCCOLLUM

During another investigation, an attempt was made to carry out the nitration of phenylmethylcarbinol with fuming nitric acid in acetic acid solution. A violent reaction occurred. From the reaction mixture, benzoic acid was isolated and in addition a yellow, crystalline substance which had the molecular formula $C_{16}H_{10}O_4N_2$. Analysis by infrared spectroscopy showed a characteristic absorption in the region of a conjugated carbonyl group and of a conjugated carbon-carbon or carbon-nitrogen double bond, but none in the region to be expected of nitro, hydroxyl, amino, nitrile or nitroso groups. It formed a 2,4-dinitrophenylhydrazone and on oxidation with potassium dichromate it gave benzoic acid.

A search of the literature revealed that this compound was identical in its properties with dibenzoylfurazane oxide (I), a compound which also



has been prepared by dissolving acetophenone in fuming nitric acid and allowing it to stand at approximately 50° for several days.² We then became interested in the mechanism of this unusual transformation. Dibenzoylfurazane oxide, it will be observed, *does not have the carbon skeleton which might be expected from a preliminary self-condensation of acetophenone or phenylmethylcarbinol*. In this paper a mechanism is proposed for the formation of dibenzoylfurazane oxide from phenylmethylcarbinol or acetophenone and experiments are described in support of the intermediates which are suggested.

(1) Present address: Department of Chemistry, Massachusetts Institute of Technology, Cambridge, Massachusetts.

(2) Holleman, *Ber.*, **20**, 3359 (1887). For a number of references pertinent to the structure of the furazane oxide ring, see "Beilstein's Handbuch der organischen Chemie," Vol. 27, Julius Springer, Berlin, 1937, p. 562.

Experimental³

A. Preparation of Dibenzoylfurazane Oxide from Phenylmethylcarbinol.—Phenylmethylcarbinol (61.0 g., 0.5 mole) was dissolved in glacial acetic acid (65 ml.). This solution was placed in a one-liter three-neck flask equipped with a mechanical stirrer, a condenser and a dropping funnel. The mixture was then heated to 100°, stirring was commenced, the heating bath was removed and a solution of red fuming nitric acid (85 ml., d. = 1.59) in glacial acetic acid (50 ml.) was added dropwise. The reaction was exothermic and the heat evolved was sufficient to maintain the reaction mixture at a gentle boil. After addition was complete, stirring was continued until the flask was just warm to the touch. The contents were then poured with stirring into 500 ml. of water. A yellow oil separated and soon solidified. It was collected on a filter, washed with water and dried.

The granular solid was then ground in a mortar with excess 10% aqueous sodium carbonate solution and the resulting thin suspension was filtered. The solid material was washed with water and dried *in vacuo*. Acidification of the filtrate gave 7.3 g. (12.3%) of benzoic acid, m. p. 120–121°. A mixture of this material with an authentic sample of benzoic acid melted at 122–123°.

In order to purify the dry solid which was insoluble in sodium carbonate solution, it was taken up in a slight excess of warm ether, filtered to remove a small amount of insoluble material and evaporated until crystals began to form. On cooling, the product separated as pale yellow crystals, m. p. 82–84°. After one recrystallization from ether, 17.9 g. (24.3%) of almost white dibenzoylfurazane oxide, m. p. 85–86°,² was obtained.

*Anal.*⁴ Calcd. for $C_{16}H_{10}O_4N_2$: C, 65.31; H, 3.43; N, 9.52. Found: C, 65.08; H, 3.60; N, 9.79.

By infrared analysis, our sample of dibenzoylfurazane oxide showed absorption in the region characteristic of a conjugated carbon-carbon or carbon-nitrogen double bond.⁵ The absorption curve also suggested the absence of nitro, hydroxyl, amino, imino, nitrile or nitroso groups in the molecule. When a solution of the compound in methanol was refluxed with hydrazine hydrochloride, an orange crystalline azine was formed, m. p. 206–207°.⁶ A 2,4-dinitrophenylhydrazone was also prepared.⁷ It crys-

(3) All melting points and boiling points are uncorrected.

(4) We are indebted to Miss Theta Spoor for the microanalyses reported in this paper.

(5) We are indebted to Dr. Foil A. Miller and Mrs. J. L. Johnson for the determination and interpretation of the infrared spectra mentioned in this paper.

(6) Widman and Virgin, *Ber.*, **42**, 2794 (1909).

(7) Shriner and Fuson, "Identification of Organic Compounds," John Wiley and Sons, Inc., New York, N. Y., 1940, p. 143.