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

Quinone Imides. XLI. Orientation in the Addition of Thiophenol and Benzenesulfinic Acid to 2-Substituted-*p*-quinonedibenzimides

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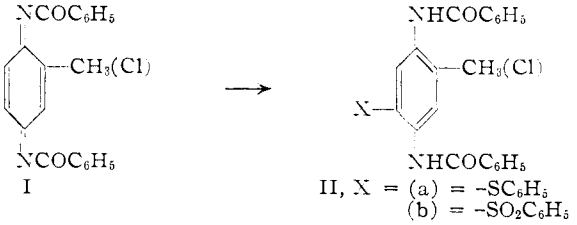
Thiophenol and benzenesulfinic acid have been added to *p*-quinonedibenzimides holding methyl-, chloro-, phenylmercapto- and benzenesulfonyl groups as substituents. The methyl and chloro imides give products with 1,2,4,5-orientations while the phenylmercapto- and benzenesulfonyl-imides yield mixtures of adducts with 1,2,3,4- and 1,2,4,6-orientations. The amount of the latter isomer was larger, the greater the steric influence at the 3-position. These and the results on orientation in adducts of dibenzenesulfonimides are summarized and general conclusions drawn regarding the effect on the orientation in the final adducts of (1) alteration of groups on the nitrogen of the imide, (2) the nature of the substituent on the ring, and (3) the influence of the entering group.

The addition of hydrogen chloride to a variety of 2-substituted-*p*-quinonedibenzimides was reported in the previous paper in this series.[2] The work has now been extended to determine the effects of alteration of the added reagent on the orientation of groups in the final adducts. Thiophenol and benzenesulfinic acid have been added to 2-methyl-, 2-chloro-, 2-phenylmercapto- and 2-benzenesulfonyl-*p*-quinonedibenzimides and the constitution of the resulting products studied.

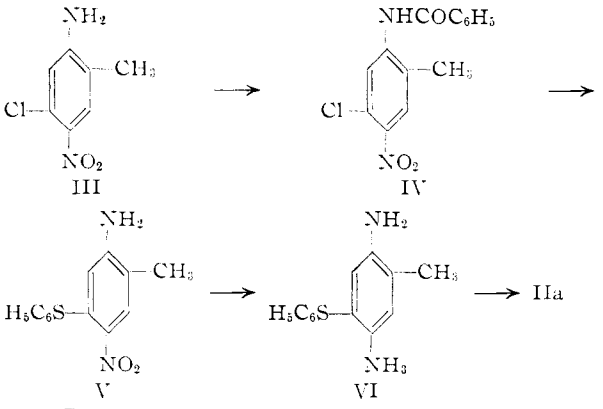
Thiophenol and benzenesulfinic acid were added to 2-methyl-*p*-quinonedibenzimide (I) to give in both instances 5-substituted diamides, 2-methyl-5-phenylmercapto-*p*-phenylenedibenzamide (IIa) and 5-benzenesulfonyl-2-methyl-*p*-quinonedibenzamide (IIb).



I

II, X = (a) = $-SC_6H_5$
(b) = $-SO_2C_6H_5$

The thiophenol adduct was shown to have the 1,2,4,5-orientation by an unequivocal synthesis, as designated in formulas III to VI. The benzenesulfinic acid adduct IIb has the same orientation since it is also obtained by the hydrogen peroxide oxidation of the thiophenol adduct IIa.



III IV V VI

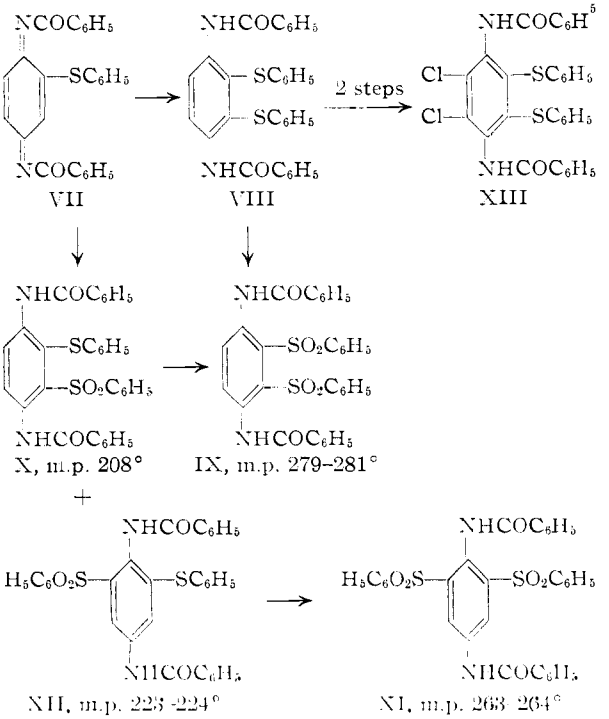
(1) An abstract of a thesis submitted by M. D. Nair to the Graduate College of the University of Illinois in partial fulfillment of the degree of Doctor of Philosophy, 1956.

(2) R. Adams and M. D. Nair, THIS JOURNAL, **78**, 5927 (1956).

Thiophenol and benzenesulfinic acid add to 2-chloro-*p*-quinonedibenzimide (I) to give 2-chloro-5-phenylmercapto-*p*-phenylenedibenzamide (IIa) and 5-benzenesulfonyl-2-chloro-*p*-phenylenedibenzamide (IIb), respectively. Both compounds have been sythesized previously and their structures determined unequivocally.[2]

Thiophenol adds to 2-phenylmercapto-*p*-quinonedibenzimide (VII) to give exclusively 2,3-diphenylmercapto-*p*-phenylenedibenzamide (VIII). This orientation might have been anticipated in view of the fact that hydrogen chloride has been shown to add in the same manner.[2] Further evidence for this 2,3-structure was revealed when oxidation to the corresponding dibenzenesulfonyl derivative IX was attempted and proceeded with great difficulty. The yield was small owing to steric factors and was in contrast to the good yields ordinarily obtained in the oxidation of unhindered diphenyl sulfides to diphenyl sulfones by hydrogen peroxide.

The disulfone IX thus formed was identical with the isomer in lesser amount of the two obtained by the addition of benzenesulfinic acid to 2-benzenesulfonyl-*p*-quinonedibenzimide; it was also iden-



VII VIII XIII

X, m.p. 208° IX, m.p. 279–281°

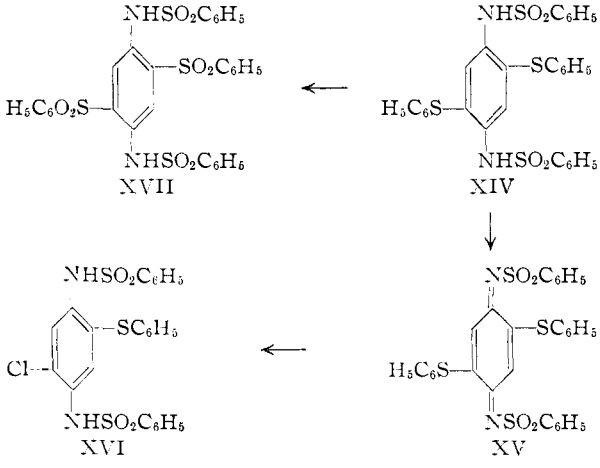
XII, m.p. 223–224° XI, m.p. 263–264°

tical with the oxidation product of the isomer in lesser amount obtained by addition of benzenesulfinic acid to 2-phenylmercapto-*p*-quinonedibenzimide (X). These facts lend support to the 2,3-configuration of the product under discussion.

The infrared spectrum of the dibenzenesulfonyl derivative also substantiates the 2,3-orientation, for there is present a relatively strong band at about 804 cm.$^{-1}$ characteristic of benzene derivatives possessing two adjacent hydrogen atoms.

Addition of benzenesulfinic acid to 2-phenylmercapto-*p*-quinonedibenzimide gives a mixture of isomers (X and XII) which may be separated by crystallization and chromatography. Oxidation of these compounds yields the corresponding disulfones (IX and XI) which are identical with those made by other routes and for which the 2,3- and 2,6-configurations have been proposed. The higher melting adduct and major product XII yields upon oxidation a disulfone XI identical with that obtained as the lower melting major product from the addition of benzenesulfinic acid to 2-benzenesulfonyl-*p*-quinonedibenzimide; the lower melting adduct X obtained in small yield, upon oxidation gives a disulfone IX identical with the higher melting product in the addition of benzenesulfinic acid to 2-benzenesulfonyl-*p*-quinonedibenzimide and with the disulfone from the oxidation of the previously discussed 2,3-diphenylmercapto-*p*-phenylenedibenzamide.

Oxidation of 2,3-diphenylmercapto-*p*-phenylenedibenzamide with lead tetraacetate converts it to the corresponding quinone to which hydrogen chloride readily adds. Oxidation of this adduct and addition of hydrogen chloride results in the completely substituted 5,6-dichloro-2,3-diphenylmercapto-*p*-phenylenedibenzamide (XIII).



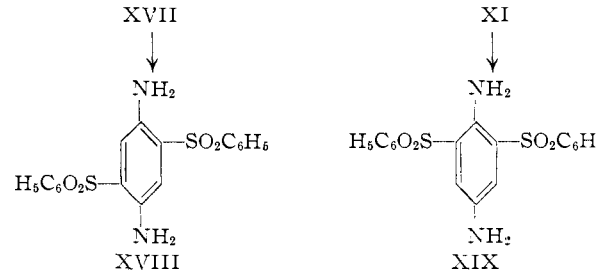
The addition of benzenesulfinic acid to 2-benzenesulfonyl-*p*-quinonedibenzimide gives a mixture of two isomers IX, m.p. 279–281° (6.2% yield), and XI, m.p. 263–264° (35% yield). They were separated by chromatography. Unequivocal syntheses for these two products failed so that it was necessary to resort to indirect methods to determine their constitutions. Advantage was taken of the previous study of certain dibenzenesulfonamides.

2-Phenylmercapto-*p*-quinonedibenzenesulfonimide adds thiophenol to form a compound deduced as 2,5-bis-(phenylmercapto)-*p*-phenylenedibenzenesulfonamide (XIV) on the basis of the structure of related adducts.[3] The 2,5-orientation of groups has now been established unequivocally.

Upon oxidation with lead tetraacetate, XIV is converted to the corresponding quinone XV. When XV is treated with hydrogen chloride, the expected adduct, which was to be used in another projected method of constitutional proof, is not formed but instead the product is the known 5-chloro-2-phenylmercapto-*p*-phenylenedibenzenesulfonamide[3] (XVI).

This type of replacement of nuclear substituents is well-known among 2,5-disubstituted-*p*-benzoquinones.[4,5] The analogy between the above reactions and that observed when 2,5-bis-(phenylmercapto)-*p*-quinonedibenzenesulfonimide is treated with hydrogen chloride fails only in that the final product in the latter case is not 5-chloro-2-phenylmercapto-*p*-quinonedibenzenesulfonimide but the corresponding amide XVI. This apparent anomaly is probably due to the reducing power of the thiophenolate ion. The reaction, however, serves to confirm the postulated 1,2,4,5-orientation of the addition product of 2-phenylmercapto-*p*-quinonedibenzenesulfonimide with thiophenol.

Upon oxidation of the 2,5-bis-(phenylmercapto)-*p*-phenylenedibenzenesulfonamide with hydrogen peroxide, 2,5-dibenzenesulfonyl-*p*-phenylenedibenzenesulfonamide (XVII) results. By means of concentrated sulfuric acid, the benzenesulfonyl groups are hydrolyzed from product XVII and 2,5-dibenzenesulfonyl-*p*-phenylenediamine (XVIII) is formed.



When the dibenzenesulfonyl-*p*-phenylenedibenzamide (XI), the isomer in major yield from the addition of benzenesulfinic acid to 2-benzenesulfonyl-*p*-quinonedibenzimide, is hydrolyzed with hot concentrated sulfuric acid the resulting dibenzenesulfonyl-*p*-phenylenediamine (XIX) is not identical with the 2,5-dibenzenesulfonyl-*p*-phenylenediamine (XVIII) described above. It follows then that it must be either the 2,3- or 2,6-derivative and this orientation applies as well to the dibenzamide from which the diamine is formed. Since steric factors would favor the predominance of the 2,6-isomer in the addition reaction, the compound obtained in larger amounts is assigned this structure.

Moreover, the diamine XIX proved to be identical with that resulting from hydrolysis of the

(3) R. Adams, E. F. Elslager and T. E. Young, THIS JOURNAL, **75**, 663 (1953).

(4) W. K. Anslow and H. Raistrick, *J. Chem. Soc.*, 1446 (1939).

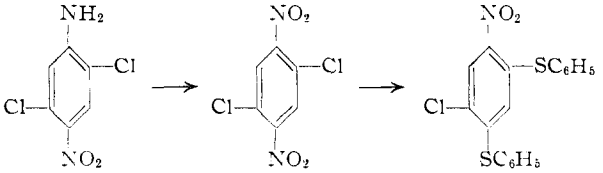
(5) J. Hoffmann, *Ber.*, **34**, 1557 (1901).

single adduct of benzenesulfinic acid to 2-benzenesulfonyl-*p*-quinonedibenzenesulfonimide. The 2,6-configuration was assigned to this product because it was formed in 90% yield and was not identical with the 2,5-isomer. Steric factors would certainly inhibit the formation of a 2,3-derivative in good yield.

From the above discussion, it follows that the isomer obtained in low yield in the reaction of benzenesulfinic acid with 2-benzenesulfonyl-*p*-quinonedibenzimide must have the 2,3-configuration as shown in IX. Thus the structures of the various isomeric phenylmercapto- and benzenesulfonyl-*p*-phenylenedibenzamides have been clarified.

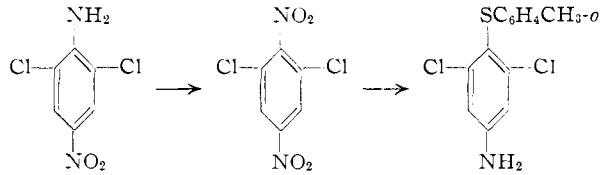
Correlations between –CH absorption frequency and orientation in tetrasubstituted aromatic systems have already been mentioned in a previous paper.[2] Attempts to correlate the data in this investigation with those previously reported reveals various complications. Owing to the complexity of bands occurring in the 800–900 cm.$^{-1}$ region, differentiation between 1,2,4,5- and 1,2,4,6-tetrasubstituted benzenes is often difficult. However, 2-chloro-3-phenylmercapto-*p*-phenylenedibenzamide, 2,3-dibenzenesulfonyl-*p*-phenylenedibenzamide and 3-benzenesulfonyl-2-phenylmercapto-*p*-phenylenedibenzamide, all of which have a 1,2,3,4 orientation, show bands around 804 cm.$^{-1}$. This is in keeping with earlier observations[2] that the isomers possessing two adjacent hydrogen atoms on the aromatic nucleus exhibit a band at this frequency.

Early experiments which were directed toward the synthesis of 2,6- and 2,5-dibenzenesulfonyl-*p*-phenylenedibenzamide failed. Several facts of interest were uncovered during these unsuccessful experiments. A contemplated procedure was the replacement of the two chlorines in 2,5-dichloro-1,4-dinitrobenzene (XXI) by phenylmercapto groups followed by reduction, benzoylation and oxidation. Compound XXI is readily prepared by the hydrogen peroxide–trifluoroacetic acid method from 2,5-dichloro-4-nitroaniline (XX). Attempts to replace the two chlorine atoms by phenylmercapto groups, however, led to the replacement of one nitro group and one chlorine atom with the formation probably of compound XXII. The relative positions of the groups in this molecule were not determined.



XX XXI XXII

2,6-Dichloro-4-nitroaniline (XXIII) is likewise readily converted to 2,6-dichloro-1,4-dinitrobenzene (XXIV). Upon treatment with *o*-thiocresol in dioxane, one nitro group was replaced and the other was reduced. The structure XXV is proposed on the basis of elemental analysis, infrared spectrum and analogy with similar abnormal nucleophilic displacement reactions.

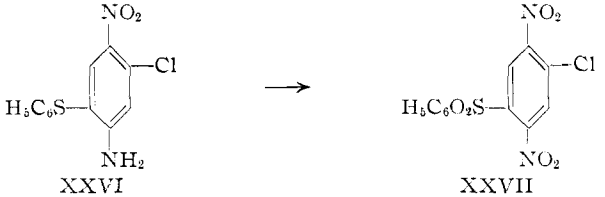


XXIII XXIV XXV

While no attempt was made to prove the relative positions of the amino and tolylmercapto groups, it is safe to assume that the nitro flanked by the two chlorine atoms in the *ortho* positions is the one replaced. This is supported by the studies on the action of sodium methoxide and ammonia on 2,6-dichloro-1,4-dinitrobenzene.[6] The reduction of the second nitro group can be explained as due to the reducing power of the thiocresolate ion. The above results substantiate the earlier observations on the greater mobility of an activated nitro group in preference to a similarly activated chlorine.[7]

2,6-Dibromo-1,4-dinitrobenzene made in a manner similar to the dichloro compound would not react with thiophenol to give an identifiable product. It is possible that this failure to react may be due to lack of activation of the bromine atoms because of their size which throws the nitro group out of the plane of the ring and thus inhibits resonance.

5-Benzenesulfonyl-2-chloro-1,4-dinitrobenzene (XXVII), prepared by oxidation of 5-phenylmercapto-2-chloro-4-nitroaniline (XXVI), did not give an identifiable product when reacting with the sodium salt of thiophenol in dioxane.



XXVI XXVII

The results of investigations on the orientation in addition of reagents to substituted *p*-quinonedibenzimides are summarized in Table I.

TABLE I

ORIENTATION OF GROUPS IN ADDUCTS FROM *p*-QUINONEDIBENZIMIDES

Substituent in the 2-position	Entering group –Cl	–SC6H5	–SO2C6H5
–OCH3[8]	1,2,4,6 and 1,2,4,5	....	....
–CH3	1,2,4,6	1,2,4,5	1,2,4,5
–OCOCH3[8]	1,2,4,6	....	....
–Cl	1,2,4,6[9]	1,2,4,5	1,2,4,5
–SC6H5	1,2,3,4	1,2,3,4	1,2,3,4
–SO2C6H5	1,2,3,4 and 1,2,4,6	None	1,2,4,6

It is obvious that in *p*-quinonedibenzimides (Table I) with an electron-donating substituent, represented by methoxyl, methyl, acetoxy and

(6) A. F. Hollemann and A. J. den Hollander, *Rec. trav. chim.*, **39**, 435 (1920).

(7) J. F. Bunnett and R. E. Zahler, *Chem. Revs.*, **49**, 273 (1951).

(8) H. J. Neumiller, Ph.D. Thesis, 1956, University of Illinois.

(9) R. Adams and D. S. Acker, THIS JOURNAL, **74**, 3029 (1952).

chloro groups, in the 2-position, the orientation of reagent fragments in the products depends upon the character of the added reagent. Thus, the chlorine of hydrogen chloride enters primarily in the 6-position, the phenylmercapto and benzenesulfonyl groups in the 5-position.

With the electron-attracting benzenesulfonyl group in the 2-position, the orientation of the groups in the products is different. The 3- or 6-position is favored by the entering group; the relatively small chlorine atom goes primarily to the 3-position, but the relatively bulky benzenesulfonyl group enters the 6-position. It is significant that the presence of a 2-phenylmercapto group leads to 1,2,3,4-orientation in the addition products. From this fact it might be concluded that, if electrical effects are important, the phenylmercapto group in these molecules is acting like an electron-attracting group. Mangini and co-workers[10] have studied the ultraviolet spectra of diphenyl sulfides and, indeed, have found evidence that the phenylmercapto group is capable of acting as an electron-attracting group. The results of studies on orientations in substituted *p*-quinonedibenzenesulfonimides are represented in Table II.

TABLE II

ORIENTATION OF GROUPS IN ADDUCTS FROM *p*-QUINONEDIBENZENESULFONIMIDES

Substituent in 2-position	Entering group -Cl	-SC_6H_5	-$SO_2C_6H_5$
-OCH_3	1,2,4,5[11]	1,2,4,5[11]	1,2,4,5[11]
-Cl	1,2,4,5[12] and 1,2,3,4	1,2,4,5[11]	1,2,4,5[11] and 1,2,4,6
-CH_3	1,2,4,5[12]		
-SC_6H_5	1,2,4,5[3]	1,2,4,5	1,2,4,5[13]
-$SO_2C_6H_5$	1,2,3,4[13]		1,2,4,6

The results indicate that an electron-donating group in the 2-position leads predominantly to 1,2,4,5-orientation in the adducts. The electron-attracting benzenesulfonyl group, on the other hand, causes 1,2,3,4- and 1,2,4,6-orientation, the latter when a bulky entering group is involved. The 2-phenylmercapto group in this series acts exclusively as an electron-donating group.

Acknowledgment.—The authors are indebted to Mr. J. Nemeth and Mrs. M. Benassi for the microanalyses and to Mr. J. Brader for the determination and interpretation of the infrared spectra.

Experimental

All melting points are corrected.

2-Methyl-5-phenylmercapto-*p*-phenylenedibenzamide.—A solution of 1.0 g. of 2-methyl-*p*-quinonedibenzimide in 15 ml. of dioxane was added to a solution of 1 ml. of thiophenol in 15 ml. of dioxane containing 3 drops of concd. sulfuric acid. The mixture was shaken well and allowed to stand for 24 hours and then filtered to give 0.95 g. (75.5%) of white crystals. Recrystallization from ethanol gave white needles, m.p. 232–233°.

Anal. Calcd. for $C_{27}H_{22}N_2O_2S$: C, 73.94; H, 5.06; N, 6.39. Found: C, 73.82; H, 4.86; N, 6.30.

5-Benzenesulfonyl-2-chloro-*p*-phenylenedibenzamide. Method A.—A mixture of 0.3 g. of 2-methyl-5-phenylmercapto-*p*-phenylenedibenzamide, 2 ml. of 30% hydrogen peroxide and 20 ml. of glacial acetic acid was heated under reflux for one hour, cooled and poured into cracked ice and water, which precipitated a white product. It was filtered and dried to give 0.3 g. (95%) of crude product. Recrystallization from dilute ethanol gave white needles, m.p. 208–208.5°. This compound did not depress the melting point of the benzenesulfinic acid adduct of 2-methyl-*p*-quinonedibenzimide and their infrared spectra are identical.

Method B.—To a solution of 0.55 g. of 2-methyl-*p*-quinonedibenzimide in 40 ml. of dry thiophene-free benzene was added 0.4 g. of benzenesulfinic acid. On shaking the mixture the color faded to a pale yellow in 5 minutes. The clear solution was distilled under vacuum to give a yellow oil which, when mixed with 10 ml. of ethanol and scratched, turned into a white mass. The slurry was poured into 100 ml. of water and the precipitated product collected by filtration to give 0.7 g. (89%) of adduct. Two recrystallizations from ethanol gave white crystals, m.p. 208°.

Anal. Calcd. for $C_{27}H_{22}N_2O_4S$: C, 68.91; H, 4.71; N, 5.96. Found: C, 68.91; H, 4.76; N, 5.90.

N-Benzoyl-5-chloro-2-methyl-4-nitroaniline.—A mixture of 2.0 g. of 5-chloro-2-methyl-4-nitroaniline,[14] 2 ml. of benzoyl chloride and 30 ml. of pyridine was shaken well for 5 minutes and then heated on a steam-bath for 10 minutes. The solution was poured into cracked ice and concd. hydrochloric acid, filtered, washed and dried to give 2.8 g. (90%) of white product. Recrystallization from ethanol gave white needles, m.p. 212°.

Anal. Calcd. for $C_{14}H_{11}ClN_2O_3$: C, 57.84; H, 3.81. Found: C, 57.74; H, 4.00.

2-Methyl-5-phenylmercapto-4-nitroaniline.—To a mixture of 2.0 g. of N-benzoyl-5-chloro-2-methyl-4-nitroaniline and 1 ml. of thiophenol in 75 ml. of redistilled dioxane was added a solution of 5 g. of sodium hydroxide in 30 ml. of water. After heating under reflux for 16 hours the dark solution was poured into cracked ice and water, which precipitated a yellow product. Filtration yielded 1.4 g. (78%) of yellow powder. It was recrystallized from ethanol–water mixture to give shining platelets, m.p. 164–165°.

Anal. Calcd. for $C_{13}H_{12}N_2O_2S$: C, 59.98; H, 4.64; N, 10.66. Found: C, 60.16; H, 4.54; N, 10.58.

2-Methyl-5-phenylmercapto-*p*-phenylenedibenzamide.—To a solution of 0.5 g. of 2-methyl-5-phenylmercapto-4-nitroaniline in 20 ml. of hot methanol was added 1 g. of wet Raney nickel in 10 ml. of methanol. The solution was heated on the water-bath and 3 ml. of hydrazine hydrate added in drops. The solution was warmed on the water-bath for an additional period of 10 minutes and then filtered. The filtrate was evaporated to dryness and the residue mixed with 10 ml. of pyridine and 1 ml. of benzoyl chloride. After heating the mixture under reflux for 1 hour, it was poured into cracked ice and concd. hydrochloric acid, which precipitated 0.4 g. (48%) of product. After two recrystallizations the compound melted at 232–233°. It did not depress the melting point of the thiophenol adduct of 2-methyl-*p*-quinonedibenzimide and their infrared spectra are identical.

2-Chloro-5-phenylmercapto-*p*-phenylenedibenzamide.—To a solution of 0.6 g. of 2-chloro-*p*-quinonedibenzimide[15] in 15 ml. of dioxane was added 0.5 ml. of thiophenol in 15 ml. of dioxane. Two drops of triethylamine was added. The color faded immediately. The solution was allowed to stand at room temperature for 2 hours and then poured into 100 ml. of cold water. The precipitated material was filtered and dried to give 0.74 g. (93%) of crude product. Three recrystallizations from glacial acetic acid gave white crystals, m.p. 197.5–198°. One recrystallization from ethanol (cooled in ice-box) gave a pure compound, m.p. 202–203° (lit.[2] m.p. 202.5°).

This compound did not depress the melting point of an authentic sample of 2-chloro-5-phenylmercapto-*p*-phenylenedibenzamide.

(10) A. Mangini and R. Passerini, *Bull. sci. facolta chim. ind. Bologna*, **8**, 12 (1950); *J. Chem. Soc.*, 1168 (1952); private communication.

(11) R. Adams and T. E. Young, THIS JOURNAL, **75**, 3235 (1953).

(12) R. Adams, E. F. Elslager and K. F. Heumann, *ibid.*, **74**, 2608 (1952).

(13) R. Adams, T. E. Young and R. W. P. Short, *ibid.*, **76**, 1114 (1954).

(14) J. Kenner, C. W. Tod and E. Witham, *J. Chem. Soc.*, **127**, 2343 (1925).

(15) R. Adams and J. L. Anderson, THIS JOURNAL, **72**, 5154 (1950).

Anal. Calcd. for $C_{26}H_{19}ClN_2O_2S$: C, 68.04; H, 4.17; N, 6.10. Found: C, 67.81; H, 4.19; N, 6.15.

5-Benzenesulfonyl-2-chloro-*p*-phenylenedibenzamide.—To a solution of 0.6 g. of 2-chloro-*p*-quinonedibenzimide in 10 ml. of glacial acetic acid was added 0.3 g. of sodium benzenesulfinate in 10 ml. of glacial acetic acid. The mixture was shaken for 5 minutes, then heated to boiling, cooled and poured into 100 ml. of cold water. A pale tan precipitate separated which was collected by filtration and dried. The yield of crude product was 0.8 g. (94%). Two recrystallizations from methanol gave pure white crystals, m.p. 219° (lit.[2] m.p. 219.5–220°).

The compound did not depress the melting point of 2-benzenesulfonyl-5-chloro-*p*-phenylenedibenzamide, synthesized by an unequivocal method.

Anal. Calcd. for $C_{26}H_{19}ClN_2O_4S$: C, 63.60; H, 3.90; N, 5.71. Found: C, 63.76; H, 4.04; 5.78.

2,3-Dibenzenesulfonyl-*p*-phenylenedibenzamide.—A mixture of 0.6 g. of 2,3-bis-(phenylmercapto)-*p*-phenylenedibenzamide,[16] 4 ml. of 30% hydrogen peroxide and 20 ml. of glacial acetic acid was heated under reflux for 2 hours. At the end of this period the solution was poured into cracked ice and water and the precipitated material collected by filtration, washed and dried. The amount of product was less than 0.1 g. Recrystallization from glacial acetic acid gave white shining platelets, m.p. 278–280°.

Anal. Calcd. for $C_{32}H_{24}N_2O_6S_2$: C, 64.42; H, 4.05; N, 4.68. Found: C, 64.50; H, 4.03; N, 4.69.

The infrared spectrum of the compound shows a band at 798 cm.$^{-1}$ indicating presence of a 1,2,3,4-tetrasubstituted benzene system.

Addition of Benzenesulfinic Acid to 2-Phenylmercapto-*p*-quinonedibenzimide: 6-Benzenesulfonyl-2-phenylmercapto-*p*-phenylenedibenzamide and 3-Benzenesulfonyl-2-phenylmercapto-*p*-phenylenedibenzamide.—A mixture of 2.5 g. of 2-phenylmercapto-*p*-phenylenedibenzamide,[16] 2.65 g. of lead tetraacetate and 300 ml. of reagent chloroform was stirred at room temperature for 3 hours, filtered and the filtrate reduced in volume to 100 ml. by distillation under vacuum. To the clear red solution thus obtained was added 1.45 g. of dry benzenesulfinic acid. The color faded in 10 minutes. The solution was allowed to stand at room temperature for 12 hours, filtered and the filtrate evaporated to dryness. The oily residue was triturated with 10 ml. of ethanol and filtered to give 2.3 g. (70%) of product. This crude product melted over a wide range. It was boiled with ethanol, filtered and cooled, depositing 0.3 g. (13% of the total yield) of white crystals. One recrystallization gave white plates, m.p. 208°.

Anal. Calcd. for $C_{32}H_{24}N_2O_4S_2$: C, 68.06; H, 4.28. Found: C, 68.34; H, 4.42.

The filtrate, when poured into water, caused precipitation of a gummy solid. This was dissolved in hot benzene and cooled to give 1.6 g. of crystals, m.p. 190–220°. These crystals were dissolved in the minimum amount of chloroform and chromatographed on a column of alumina. Four 25-ml. portions of a 1:1 mixture of chloroform and ethyl acetate was used as the eluant. Most of the pure compound was obtained in the third and fourth fractions. The solvents were evaporated off and the residues recrystallized from ethanol to give a total yield of 1.1 g. of white needles, m.p. 223–224°.

Oxidation of Adducts with Hydrogen Peroxide: 2,3-Dibenzenesulfonyl-*p*-phenylenedibenzamide.—The lower melting isomer (m.p. 208°) was oxidized to the dibenzenesulfonyl derivative as previously described. The yield was 46% of white crystals, m.p. 283°.

This compound did not depress the melting point of the product obtained by addition of benzenesulfinic acid to 2-benzenesulfonyl-*p*-quinonedibenzimide or that of the oxidation product of 2,3-bis-(phenylmercapto)-*p*-phenylenedibenzamide. Their infrared spectra are identical.

2,6-Dibenzenesulfonyl-*p*-phenylenedibenzamide.—The higher melting isomer was oxidized in a similar manner to give 95% yield of 2,6-dibenzenesulfonyl-*p*-phenylenedibenzamide. After crystallization from glacial acetic acid, it melted at 264°.

This compound did not depress the melting point of the major product obtained by addition of benzenesulfinic acid to 2-benzenesulfonyl-*p*-quinonedibenzimide.

(16) R. Adams and D. S. Acker, THIS JOURNAL, **74**, 5872 (1952).

Anal. Calcd. for $C_{32}H_{24}N_2O_6S_2$: C, 64.42; H, 4.05; N, 4.68. Found: C, 64.11; H, 3.93; N, 4.69.

Addition of Hydrogen Chloride to 2,3-Bis-(phenylmercapto)-*p*-quinonedibenzimide.—A mixture of 1.0 g. of 2,3-bis-(phenylmercapto)-*p*-phenylenedibenzamide,[9] 0.6 g. of lead tetraacetate and 100 ml. of reagent chloroform was stirred at room temperature for 2 hours. Stirring was continued for one more hour after addition of 5 drops of ethylene glycol. The dark red solution was filtered to remove inorganic salts and into the filtrate was passed a current of hydrogen chloride. The color faded to a pale yellow in 30 minutes. The solution was evaporated to dryness under vacuum and the residual oil triturated with ethanol to give a white precipitate. The yield was 0.7 g. (67%). Two recrystallizations from ethanol gave white crystals, m.p. 189–189.5°.

Anal. Calcd. for $C_{32}H_{23}ClN_2O_2S_2$: C, 67.77; H, 4.08; N, 4.94. Found: C, 67.60; H, 4.06; N, 4.92.

Addition of Hydrogen Chloride to 2,3-Bis-(phenylmercapto)-5-chloro-*p*-quinonedibenzimide: 5,6-Dichloro-2,3-bis-(phenylmercapto)-*p*-phenylenedibenzamide.—A mixture of 2.0 g. of 2,3-bis-(phenylmercapto)-5-chloro-*p*-phenylenedibenzamide, 1.8 g. of lead tetraacetate and 200 ml. of reagent chloroform was stirred at room temperature for one hour. Stirring was continued for 30 minutes after addition of 6 drops of ethylene glycol. At the end of this time the solution was filtered and into the dark red solution was passed a current of hydrogen chloride. The color faded to a pale red at the end of 30 minutes. After permitting the solution to stand at room temperature for 2 hours, it was filtered to remove any inorganic material. The pale yellow solution was distilled under vacuum to dryness and the residue triturated with 20 ml. of ethanol. It was cooled and filtered to give 1 g. of white product. On reducing the volume of the filtrate and cooling, 0.6 g. more of product deposited bringing the total yield to 1.6 g. (74%). Three recrystallizations from glacial acetic acid gave pale tan crystals, m.p. 298°.

Anal. Calcd. for $C_{32}H_{22}Cl_2N_2O_2S_2$: C, 63.88; H, 3.68; N, 4.60. Found: C, 64.08; H, 3.45; N, 4.31.

Addition of Benzenesulfinic Acid to 2-Benzenesulfonyl-*p*-quinonedibenzimide: 2,3-Dibenzenesulfonyl-*p*-phenylenedibenzamide and 2,6-Dibenzenesulfonyl-*p*-phenylenedibenzamide.—A mixture of 1.0 g. of 2-benzenesulfonyl-*p*-phenylenedibenzamide,[2] 1.2 g. of lead tetraacetate and 70 ml. of reagent chloroform was heated under reflux for 3 hours, cooled and filtered. To the filtrate was added 0.35 g. of benzenesulfinic acid. The mixture was allowed to stand at room temperature for 36 hours and filtered. The residue weighing 0.15 g. was found to be 2-benzenesulfonyl-*p*-phenylenedibenzamide. The filtrate was evaporated to dryness and dissolved in 15 ml. of boiling ethanol and cooled. The precipitated product was collected by filtration and recrystallized from glacial acetic acid to give 0.1 g. (6.2%) of white crystals, m.p. 279–281°. This compound did not depress the melting point of 2,3-dibenzenesulfonyl-*p*-phenylenedibenzamide prepared by oxidation of 2,3-bis-(phenylmercapto)-*p*-phenylenedibenzamide.

The filtrate was evaporated to dryness yielding a red oily gum. This was dissolved in a minimum amount of chloroform and chromatographed on a column of alumina. Elution with benzene, then a mixture of benzene and ether, yielded some 2-benzenesulfonyl-*p*-phenylenedibenzamide. When ether and then ether and chloroform were used next, the desired product was obtained.

To 0.45 g. (35%) of the adduct, eluted by the last solvents, was purified by recrystallization from glacial acetic acid to give white needles, m.p. 263–264°.

This compound did not depress the melting point of the product obtained by oxidation of the principal adduct of benzenesulfinic acid to 2-phenylmercapto-*p*-quinonedibenzimide.

Reaction of 2,5-Bis-(phenylmercapto)-*p*-quinonedibenzenesulfonimide with Hydrogen Chloride: 2-Chloro-5-phenylmercapto-*p*-phenylenedibenzenesulfonamide.—To a solution of 0.8 g. of 2,5-bis-(phenylmercapto)-*p*-quinonedibenzenesulfonimide[3] in 100 ml. of reagent chloroform was passed a stream of hydrogen chloride. After 5 minutes the color began to fade and in 20 minutes the solution was very pale yellow and remained so without change. The residue, after evaporation of the solution to dryness, was dissolved in hot glacial acetic acid (Darco) and filtered to

give 0.48 g. (53%) of product. One recrystallization gave pure white crystals, m.p. 204–205° (lit.[3] m.p. 206–207.5°).

The infrared spectrum of this compound is identical to the spectrum of authentic 2-chloro-5-phenylmercapto-*p*-phenylenedibenzenesulfonamide.

Anal. Calcd. for $C_{24}H_{19}ClN_2O_4S_3$: C, 54.27; H, 3.61; N, 5.28. Found: C, 54.15; H, 3.38; N, 5.01.

Oxidation of the product gave 5-benzenesulfonyl-2-chloro-*p*-phenylenedibenzenesulfonamide.[11]

2,5-Dibenzenesulfonyl-*p*-phenylenediamine.—A mixture of 0.5 g. of 2,5-dibenzenesulfonyl-*p*-phenylenedibenzenesulfonamide[11] and 25 ml. of concentrated sulfuric acid was allowed to stand at room temperature for 24 hours. At the end of this period the brown solution was poured into cracked ice and water. The resulting suspension was made basic with 10% aqueous sodium hydroxide and filtered. The residue was washed with water repeatedly. Recrystallization from ethanol gave 0.15 g. (52%) of yellow crystals. It exhibited strong fluorescence (green and yellow). One recrystallization from glacial acetic acid gave pure crystals, m.p. 287°.

Anal. Calcd. for $C_{18}H_{16}N_2O_4S_2$: C, 55.65; H, 4.15. Found: C, 55.51; H, 4.11.

The infrared spectrum of this compound shows $-NH_2$(def.) at 1636 cm.$^{-1}$ and −CH(wag) at 828 cm.$^{-1}$ corresponding to a 1,2,4,5-orientation. The non-splitting of the $-NH_2$ (def.) also indicates a symmetrical structure.

Hydrolysis of 2,6-Dibenzenesulfonyl-*p*-phenylenedibenzenesulfonamide: 2,6-Dibenzenesulfonyl-*p*-phenylenediamine.—A mixture of 5.00 g. of 2,6-dibenzenesulfonyl-*p*-phenylenedibenzenesulfonamide made by addition of benzenesulfinic acid to 2-benzenesulfonyl-*p*-quinonedibenzenesulfonimide[13] and 40 ml. of concentrated sulfuric acid was allowed to stand at room temperature for 48 hours. It was worked up as described in the previous experiment except for extraction with ether after treatment with alkali. The residual oil from the ether was dissolved in hot ethanol and water added to turbidity. On cooling 0.65 g. (23%) of material separated. One recrystallization from ethanol, followed by two from glacial acetic acid, gave yellow needles, m.p. 221–222°.

Anal. Calcd. for $C_{18}H_{16}N_2O_4S_2$: C, 55.65; H, 4.15; N, 7.21. Found: C, 55.91; H, 4.21; H, 6.99.

The melting point of this compound did not depress the melting point of 2,6-dibenzenesulfonyl-*p*-phenylenediamine and their infrared spectra are identical.

Hydrolysis of 2,6-Dibenzenesulfonyl-*p*-phenylenedibenzamide: 2,6-Dibenzenesulfonyl-*p*-phenylenediamine, Method A.—The lower melting product (m.p. 263–264°) of oxidation of the benzenesulfinic acid adduct of 2-phenylmercapto-*p*-quinonedibenzimide was hydrolyzed by means of concentrated sulfuric acid as previously described. The product from the ether extract was dissolved in 15 ml. of hot glacial acetic acid and cooled. The precipitate weighed 0.27 g. (82%). Recrystallization from glacial acetic acid gave yellow crystals, m.p. 220–222°.

It did not depress the melting point of the diamine obtained by hydrolysis of the major product from addition of benzenesulfinic acid to 2-benzenesulfonyl-*p*-quinonedibenzimide. The infrared spectra of the two compounds are identical.

Anal. Calcd. for $C_{18}H_{16}N_2O_4S_2$: C, 55.65; H, 4.15; N, 7.21. Found: C, 55.60; H, 4.23; N, 7.03.

Method B.—The lower melting (m.p. 263–264°) benzenesulfinic acid adduct of 2-benzenesulfonyl-*p*-quinonedibenzimide was hydrolyzed in a similar manner and the same product obtained as in Method A.

The infrared spectrum of this compound shows the presence of primary amino groups −NH(def.) 1627 and 1615 cm.$^{-1}$. The split −NH(def.) indicates that the amino groups are different and that the molecule is not symmetrical. A band at 895 cm.$^{-1}$ represents a 1,2,4,6-tetrasubstituted benzene nucleus.

2,5-Dichloro-1,4-dinitrobenzene.—To a solution of 0.5 g. of 2,5-dichloro-4-nitroaniline[17] in 20 ml. of trifluoroacetic acid[18] heated under reflux was added with stirring 6 ml. of 30% hydrogen peroxide over a period of 15 minutes. The color of the solution turned yellow. After stirring under reflux for an additional 15 minutes, the solution was cooled and poured into cracked ice and water. A very pale yellow precipitate appeared which was filtered, washed with water and dried to give 0.45 g. (71%) of product. Two recrystallizations from ethanol gave yellow crystals, m.p. 119°. The compound was readily sublimed to give yellow needles of the same melting point.

Anal. Calcd. for $C_6H_2Cl_2N_2O_4$: C, 30.40; H, 0.85; N, 11.82. Found: C, 30.64; H, 1.01; N, 12.06.

The infrared spectrum of this compound does not exhibit a band corresponding to a primary amino group.

Reaction of 2,5-Dichloro-1,4-dinitrobenzene with Thiophenol.—A mixture of 1.0 g. of 2,5-dichloro-1,4-dinitrobenzene, 1 ml. of thiophenol, 40 ml. of dioxane and 10 ml. of 10% aqueous sodium hydroxide was heated under reflux for 8 hours. The cooled solution was then poured into cracked ice and water. On standing in the ice-box a dark red powder was deposited which was separated by filtration to give 1.1 g. (70%) of product. It was recrystallized from dilute methanol and then from ethanol, m.p. 184.5°. Analysis of this compound indicates replacement of one nitro group and one chlorine with phenylmercapto groups.

Anal. Calcd. for $C_{18}H_{12}ClNO_2S_2$: C, 57.82; H, 3.23; N, 3.74. Found: C, 57.85; H, 3.26; N, 3.51.

The infrared spectrum of this compound shows the presence of $-NO_2$(str.) at 1543 and 1328 cm.$^{-1}$, and of monosubstituted benzene at 755, 708 and 693 cm.$^{-1}$.

2,6-Dichloro-1,4-dinitrobenzene.—2,6-Dichloro-4-nitroaniline[19] was oxidized under the same conditions used in the preparation of 2,5-dichloro-1,4-dinitrobenzene. The product was obtained in 79% yield. Several recrystallizations from ethanol gave yellow crystals, m.p. 113°.

The infrared spectrum of the compound does not show a band corresponding to a primary amino group.

Reaction of 2,6-Dichloro-1,4-dinitrobenzene with *o*-Thiocresol.—To a mixture of 2.0 g. of 2,6-dichloro-1,4-dinitrobenzene and 3 ml. of *o*-thiocresol in 100 ml. of dioxane was added a solution of 8 g. of sodium hydroxide in 48 ml. of water. After heating the dark solution under reflux for 22 hours, it was cooled and poured into cracked ice and water. The red precipitate which appeared was collected by filtration and dried to give 2.6 g. of red powder. Two recrystallizations from petroleum ether (b.p. 80–110°) gave yellow crystals, m.p. 139°.

Analysis indicates replacement of one nitro group by a tolylmercapto group and reduction of the second nitro group to an amine.

Anal. Calcd. for $C_{13}H_{11}Cl_2NS$: C, 54.94; H, 3.90; N, 4.92. Found: C, 55.33; H, 3.90; N, 4.86.

The compound gives a positive Beilstein test indicating presence of halogen. The infrared spectrum of the compound shows strong bands for a primary amino group at 3300 and 3390 cm.$^{-1}$.

2,6-Dibromo-1,4-dinitrobenzene.—2,6-Dibromo-4-nitroaniline[20] was oxidized under conditions described for the preparation of 2,5-dichloro-1,4-dinitrobenzene. The product was formed in 82% yield. Two recrystallizations from ethanol gave yellow crystals, m.p. 131°.

Anal. Calcd. for $C_6H_2Br_2N_2O_4$: C, 22.11; H, 0.61; N, 8.59. Found: C, 22.50; H, 0.79; N, 8.32.

The infrared spectrum of this compound shows no −NH(str.) or $-NH_2$(def.) bands while the presence of two nitro groups is indicated by bands at 1552, 1541 and 1350 cm.$^{-1}$.

No product could be isolated from the reaction with the sodium salt of thiophenol under the same conditions that were used in the reaction of thiocresol with the 2,6-dichloro-1,4-dinitrobenzene.

5-Benzenesulfonyl-2-chloro-1,4-dinitrobenzene.—2-Chloro-5-phenylmercapto-4-nitroaniline[2] was oxidized in a similar manner to give practically a quantitative yield of product. Three recrystallizations from dilute ethanol gave a pure product; yellow crystals, m.p. 177°.

Anal. Calcd. for $C_{12}H_7ClN_2O_6S$: C, 42.05; H, 2.05; N, 8.17. Found: C, 42.27; H, 1.95; N, 8.06.

The infrared spectrum of the compound shows no −NH(str.) bands, while the presence of two nitro groups is

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(18) W. D. Emmons, THIS JOURNAL, **76**, 3470 (1954).

(19) A. Leulier, *Bull. soc. chim. France*, [4] **35**, 1327 (1924).

(20) C. Wurster and E. Noelting, *Ber.*, **7**, 1564 (1874).

indicated by bands at 1559, 1540, 1377 and 1328 cm.$^{-1}$. The SO_2(str.) at 1358 and 1158 cm.$^{-1}$ is indicative of the presence of a sulfone.

No pure product could be isolated from the reaction of this compound with the sodium salt of thiophenol.

URBANA, ILLINOIS

[CONTRIBUTION FROM HAVEMEYER LABORATORY, COLUMBIA UNIVERSITY]

The Benzilic Ester Rearrangement[1]

BY W. VON E. DOERING[2] AND R. S. URBAN

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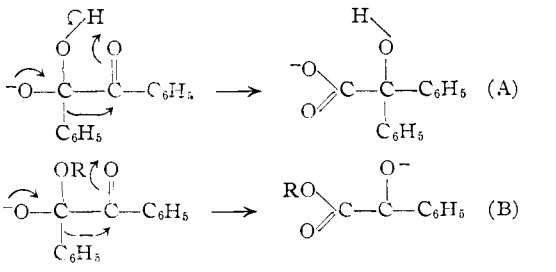
The benzilic ester rearrangement has been realized in the conversions of benzil to *t*-butyl benzilate and methyl benzilate with potassium *t*-butylate and methylate, respectively. The rearrangement of benzil with oxidizable alkoxide ions generally competes with the Meerwein–Ponndorf–Verley–Oppenauer equilibration and the subsequent cleavage of benzoin with alkoxide ions. So, for example, with ethoxide ion these competitions are unfavorable and no benzilic ester rearrangement can be detected. With this limitation the rearrangement is probably a general one. In benzene solution where, from freezing point measurement, it appears to be present as the tetramer, potassium *t*-butylate effects the rearrangement very rapidly in high yield in a clearly second-order reaction with a heat of activation of 19 ± 2 kcal. The condition of "specific hydroxide-ion catalysis," previously accepted as a characteristic of the benzilic rearrangement, is invalid and its mechanistic formulation as a simultaneous proton transfer is no longer *necessary* and may be incorrect. Another example of the mechanistically related, but relatively rare, alkaline tertiary ketol rearrangement has been uncovered in the reaction of benzil with mesitylmagnesium bromide to give *mesitoyl*diphenylcarbinol instead of the expected *benzoyl*phenylmesitylcarbinol.

The benzilic acid rearrangement has come to be considered a reaction specifically effected by hydroxide-ion.[3] This conviction has rested on several pieces of evidence: the formation from benzil and potassium *hydroxide* of an addition product which rapidly proceeds to benzilic acid on warming[4]; the rapid *hydroxide*-ion catalyzed exchange of oxygen-18 in benzil[5] by H_2O^{18}; the demonstrations by Westheimer[6] that the rearrangement is second order, first order each in benzil and *hydroxide* ion,[6a] that two other bases, phenolate and *p*-chlorophenolate ions, are neither catalysts nor reagents[6a] and that the intermediate is a negatively charged species[6b]; and the failure of alkoxide ion to effect the rearrangement. Illustrations of this last type are to be found in the reaction of benzil and sodium ethoxide which, alone, gives an adduct without rearrangement[4] and which, in ethanol, gives benzoic acid, ethyl benzoate, benzaldehyde and traces of benzilic acid[7]; in the reaction of the benzil–sodium methoxide adduct in benzene to give benzoin (13%) and sodium benzilate (6%)[4]; in the reaction of benzil and sodium ethoxide to give, in addition to the products isolated by Lachmann, ethyldibenzoin[5] later shown to be 1-hydroxy-3,4-diphenyl-4-benzoyltetrahydrofuran,[9] a condensation product of benzaldehyde, acetaldehyde and benzoin; and in the observation of Swan that benzil and potassium *t*-butylate in ether gives benzilic acid.[10]

The apparent failure of alkoxides to effect the benzilic acid rearrangement has been denied,[11] thought mysterious[12] and considered to support the hypothesis of "specific hydroxide-ion catalysis."[13] However, as a generally accepted characteristic of the benzilic rearrangement, specific hydroxide-ion utilization (scarcely catalysis in any sense) represented one of the conditions to be satisfied by a mechanistic hypothesis. One satisfying this condition is the Michael hypothesis[14] (restated in contemporary language here and by Clark, Hendley and Neville[15e] who, however, make reference in this connection only to Doering, Taylor and Schoenewaldt[16]) that the transition state involves simultaneously rearrangement of phenyl and neutralization of the incipient carboxyl group by a migration of a proton (A). This exothermic step can only contribute to the reaction when hydroxide ion is the rearranging base and would be precluded were alkoxide ion the rearranging agent (B).



(1) Taken from a dissertation submitted April 1, 1949, by Richard Stephen Urban in partial fulfillment of the requirements for the degree of Doctor of Philosophy in the Faculty of Pure Science of Columbia University.

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