The Reaction of Tropoids and Quinone Derivatives. VI. On the Structures of the Reaction Products of *p*-Benzoquinonedibenzenesulfonimide with Phenol or Tropolone

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Adams and Blomstrom[1] reported that the reaction of *p*-benzoquinonedibenzenesulfonimide (I) with phenols in the presence of triethylamine yielded the products exemplified by formula II.[2] The present authors[5] then applied this reaction to tropolone and reported that the product thereby obtained, which corresponded to an adduct of one molecule of I and one molecule of tropolone, would have structure III, as determined by analogy to the case of phenol.[1] Thereafter, as an extension of this reaction, the reaction of *o*-benzoquinonedibenzimide (IV) with phenol[6,7] or tropolone[8] was carried out, giving an adduct of one molecule of IV and one molecule of phenol or tropolone. The investigation of the structures of these adducts revealed that they were the *N*-(4-hydroxyphenyl)- and *N*-(tropolon-5-yl)-*o*-phenylenediamine derivatives V and VI respectively. Since this fact threw doubt upon the structures of the reaction products of I with phenol and tropolone, which had been previously assumed to be II and III respectively, the present authors attempted to reexamine these structures. This paper will present evidence showing that the structures previously assumed are erroneous and should be revised to the *N*-substituted derivatives VII and VIII.

The reaction of I with phenol in the presence of a catalytic amount of triethylamine gives colorless crystal (A), m. p. 227—228°C (decomp.). Adams et al. reported the melting points of 228.5—229.5°C (decomp.)[1] or 227—228°C (decomp.).[3] The methylation of A with diazomethane affords a methyl derivative (A), m. p. 136°C, which does not exhibit any absorption band due to the OH and NH groups in its infrared spectrum. In the NMR spectrum of B,[9] the signals for the protons of NCH_3 and OCH_3 groups appear at 6.85 and 6.21 τ, respectively and have almost equal intensities. These facts show that B is not IX, but X. *N*-Methyl-*N'*-(4-methoxyphenyl)-*N*, *N'*-dibenzenesulfonyl-*p*-phenylenediamine (X) was then synthesized for purposes of comparison by an unequivocal route; the diamine obtained by the catalytic reduction of known 4-nitro-4'-methoxydiphenylamine[10] gives X on benzenesulfonylation followed by methylation. The compound X synthesized thus was found to be identical with the methyl derivative (B) through a mixed fusion test and by a comparison of the ultraviolet and infrared spectra. This evidence firmly establishes that, on the reaction of *p*-benzoquinonedibenzenesulfonimide (I) with phenol, the bond formation between the nitrogen atom of I and the carbon atom at the 4-position of phenol occurs, as in the case of the reaction with the *o*-benzoquinone derivative IV,[6] and that, consequently, the product is not 2-(4'-hydroxyphenyl)-*N*, *N'*-dibenzenesulfonyl-*p*-phenylenediamine (II), as was reported by Adams et al.,[1,3] but *N*-(4-hydroxyphenyl)-*N*, *N'*-dibenzenesulfonyl-*p*-phenylenediamine (VII). Adams and Braun[11] reported an example of such C–N bond formation by the reaction of the quinoneimide derivatives; the reaction of 2, 3, 5, 6-tetrachloro-*p*-benzoquinonedibenzenesulfonimide (XI) with aromatic amines, e. g., aniline and *N*-dimethylaniline, gave as products XII and XIII without a catalyst. The present authors carried out the reaction of XI with phenol in the presence of triethylamine and obtained a products XIV analogous to XII. On methylation with diazomethane, XIV affords a methyl derivative

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1) R. Adams and D. C. Blomstrom, *J. Am. Chem. Soc.*, **75**, 3405 (1953).

2) It has been reported that the same types of products were obtained by the reaction of phenols with I, naphthoquinonedibenzenesulfonimide[1,3] or *p*-benzoquinonedibenzimide[4] in the presence of aluminum chloride or boron trifluoride.

3) R. Adams and K. R. Eilar, *J. Am. Chem. Soc.*, **73** 1149 (1951).

4) R. Adams and D. S. Acker, ibid., **74**, 5872 (1952).

5) S. Seto, H. Yamazaki and Y. Nishiyama, This Bulletin, **33**, 1081 (1960).

6) S. Seto and Y. Nishiyama, *J. Pharm. Soc. Japan.* (*Yakugaku Zasshi*), **82**, 590 (1962).

7) Y. Nishiyama, *Bull. Chem. Research Inst. of Non-Aqueous Solutions, Tohoku Univ.*, **12**, 55 (1963).

8) S. Seto and Y. Nishiyama, This Bulletin, **35**, 1010 (1962).

9) The NMR spectra were measured in deuteriochloroform, using a Varian 4301 high resolution NMR spectrometer (60 Mc.), by Assistant Professor Tsuneo Ikenoue of this Institute; to him the authors are indebted.

10) F. Ullmann and K. K. Jüngel, *Ber.*, **42**, 1077 (1909).

11) R. Adams and B. H. Braun, *J. Am. Chem. Soc.*, **74**, 5869 (1952).

(XV) whose NMR spectrum exhibits the signal at 6.78 and 6.20 τ, due to the protons of the NCH_3 and OCH_3 groups respectively, with almost equal intensities.

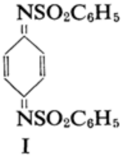
The reaction product (C)[12] of I with *o*-cresol was also methylated to a methyl derivative (D). The NMR spectrum of D shows the signals for the protons of NCH_3, OCH_3 and CH_3 at the position at 6.87, 6.21 and 7.84 τ respectively; their intensities are almost the same. These facts indicate that compounds C and D are XVI and XVII respectively, analogous to the case of the reaction product of I with phenol.

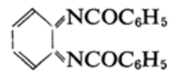
In the case of the reaction product (E)[5] of I with tropolone, the situation is very similar to that with phenols. The methylation of E with diazomethane gives a methyl derivative (F)[13], m. p. 190—191°C, whose infrared spectrum does not show any absorption band due to the OH or NH groups. To compound E, the introduction of two or three methyl groups may be expected, but the analytical figures do not permit the selection of the number of methyl groups in the case of a compound with a large molecular weight, such as F. Hence, the benzylation of E was undertaken; a monobenzyl derivative (XVIIIa) was thereby obtained. Its infrared spectrum shows the band due to the OH group, but it lacks that due to the NH group. The NMR spectrum of F shows the signals for the protons of NCH_3 and OCH_3 attached to the tropone nucleus at 6.84 and 6.04 τ respectively;[14] they have almost equal intensities. These facts suggest that product E is not III, but VIII.

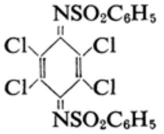
In order to confirm the structure further, the rearrangement of the tropolone ring in F into benzoic acid was attempted. The heating of F with sodium ethoxide in absolute ethanol, followed by hydrolysis, gave a benzoic acid derivative which was then converted into a methyl ester (G) by treatment with diazomethane. If product E is VIII and, consequently, F is XVIII, methyl ester G should be XIX. Therefore, the synthesis of XIX by an unequivocal route was carried out.

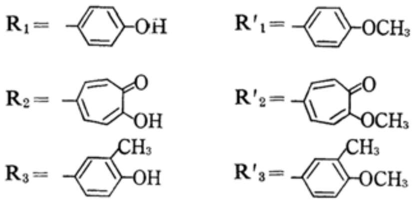
The treatment of known 4-amino-4′-methyldiphenylamine[15] with benzenesulfonyl chloride in pyridine gave XX, whose oxidation with potassium permanganate, followed by methylation with diazomethane, gave XIX. Methyl ester G showed no depression of its melting point on admixture with XIX, and the ultraviolet and infrared spectra of these two substances were in good agreement. Consequently, product E must be *N*-(tropolon-5-yl)-*N*, *N*′-dibenzenesulfonyl-*p*-phenylenediamine (VIII).

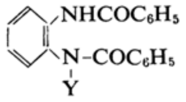
The reaction of XI with tropolone gave the tetrachloro-derivative XXI. The NMR spectrum of the methyl derivative of XXI shows the


I

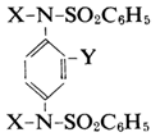

IV


XI

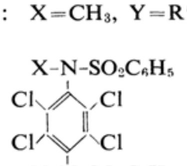


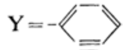
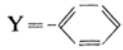


V : $Y=R_1$
VI : $Y=R_2$



II : $X=H$, $Y=R_1$
III : $X=H$, $Y=R_2$
IX : $X=CH_3$, $Y=R'_1$



XII : $X=H$, $Y=$  $-NH_2$
XIII : $X=H$, $Y=$  $-N(CH_3)_2$
XIV : $X=H$, $Y=R_1$
XV : $X=CH_3$, $Y=R'_1$
XXI : $X=H$, $Y=R_2$
XXII : $X=CH_3$, $Y=R'_2$

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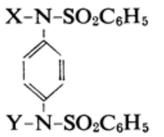
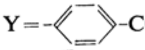
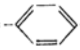
[12] Adams and Blomstrom reported that this product also had a structure of type II.[1]

[13] The authors previously described F as a monomethyl compound,[5] although its analytical values agreed rather with those of a dimethyl compound.

[14] The proton signals of the OCH_3 group in 2-methoxytropones appear at a field lower by about 0.12—0.17 p.p.m. than those in methoxyphenyl groups, as a result of the magnetic anisotropy effect of the neighboring carbonyl group.

[15] F. Ullmann and R. Dahmen, *Ber.*, **41**, 3751 (1908).



VII : $X=H$, $Y=R_1$
VIII : $X=H$, $Y=R_2$
X : $X=CH_3$, $Y=R'_1$
XVI : $X=H$, $Y=R_3$
XVII : $X=CH_3$, $Y=R'_3$
XVIII : $X=CH_3$, $Y=R'_2$
XVIIIa : $X=CH_2C_6H_5$, $Y=R_2$
XVIIIb : $X=CH_2C_6H_5$, $Y=R'_2$
XIX : $X=CH_3$, $Y=$--$COOCH_3$
XX : $X=H$, $Y=$--CH_3

signals for the protons of the NCH_3 and OCH_3 groups at 6.83 and 6.08 τ respectively, and they have almost equal intensities all indicating that the methyl derivative is XXII.

Experimental[16]

***N*-(4-Hydroxyphenyl)-*N*, *N'*-dibenzenesulfonyl-*p*-phenylenediamine (VII).** — a) VII was prepared in the manner reported by Adams and Blomstrom,[1] using 1 g. of I and 600 mg. of phenol. Colorless crystals m. p. 227—228°C (decomp.) were obtained. Yield, 780 mg.

b) To a solution of 0.5 g. of I in 20 ml. of chloroform, a solution of 0.3 g. of phenol in 3 ml. of chloroform was added. The addition of 3 drops of boron trifluoride etherate changed the color of the solution temporarily to dark violet, but colorless crystals began to separate after a few minutes. The mixture was allowed to stand for 1 hr., and then the crystals were collected to give 530 mg. of VII. This compound was found to be identical with that prepared by method a) through a mixed fusion test and by a comparison of the ultraviolet and infrared spectra.

***N*-(4-Methoxyphenyl)-*N'*-methyl-*N*, *N'*-dibenzenesulfonyl-*p*-phenylenediamine (X).** — a) An ether solution of diazomethane was added to 100 mg. of VII suspended in 4 ml. of methanol; thereby, with the evolution of nitrogen the crystals dissolved once, and after a few minutes new colorless crystals began to separate out. After the mixture had been allowed to stand overnight, the crystals were collected and recrystallized from a mixture of methanol and chloroform to afford 65 mg. of X, m. p. 163—164°C.

Found: C, 61.19; H, 4.85; N, 5.54. Calcd. for $C_{26}H_{24}O_5N_2S_2$: C, 61.43; H, 4.72; N, 5.51%.

b) A suspension of 500 mg. of 4-nitro-4'-methoxydiphenylamine[10] in 40 ml. of ethanol, with 300 mg. of 5% palladium-carbon added, was shaken in a hydrogen atmosphere at an ordinary temperature. After the absorption of hydrogen had ended, a small amount of sodium dithionite was added to the mixture and the catalyst was removed by filtration. The filtrate was then evaporated to dryness under reduced pressure. The solid which formed on the addition of a small amount of water to the residue was collected to afford 400 mg. of 4-amino-4'-methoxydiphenylamine m. p. 98°C. To a solution of 200 mg. of this compound in 1 ml. of pyridine, 300 mg. of benzenesulfonyl chloride was added drop by drop. The color of the mixture changed to dark red and then to dark violet. After heating on a water bath for 3 hr., pyridine was evaporated under reduced pressure. The addition of ice water to the residue gave a solid which was recrystallized from ethanol to give 410 mg. of *N*-(4-methoxyphenyl)-*N*, *N'*-dibenzenesulfonyl-*p*-phenylenediamine, m. p. 187—188°C.

Found: C, 60.90; H, 4.44; N, 5.91. Calcd. for $C_{25}H_{22}O_5N_2S_2$: C, 60.74; H, 4.45; N, 5.66%.

To a suspension of 100 mg. of the *p*-phenylenediamine derivative obtained above in 5 ml. of ethanol, an ether solution of dizomethane was added. After the mixture had been allowed to stand overnight, the crystals were collected and recrystallized from methanol to give 95 mg. of colorless crystals, m. p. 163—164°C. The crystals thereby obtained did not show any depression of melting point on admixture with the compound obtained by method a), and the infrared spectra of the two were in good agreement.

***N*-(4'-Hydroxyphenyl)-*N*, *N'*-dibenzenesulfonyl-2, 3, 5, 6-tetrachloro-*p*-phenylenediamine (XIV).** — To 200 mg. of 2,3,5,6-tetrachloro-*p*-quinonedibenzenesulfonimide (XI) suspended in 4 ml. of chloroform, a solution of 130 mg. of phenol in 2 ml. of chloroform was added. On the addition of 2 drops of triethylamine to the mixture, the crystals of XI dissolved immediately, and then colorless crystals separated out. After the mixture had been allowed to stand overnight, the crystals were collected and recrystallized from chloroform to give 200 mg. of XIV as colorless crystals, m. p. 232—233°C.

Found: C, 46.72; H, 2.48; N, 4.70. Calcd. for $C_{24}H_{16}O_5N_2S_2Cl_4$: C, 46.64; H, 2.56; N, 4.53%.

Dimethyl Derivative (XV) of XIV. — An ether solution of diazomethane was added to 100 mg. of XIV suspended in 1 ml. of methanol. After the mixture had been allowed to stand for 1 hr., the crystals that separated out were collected and its solution in ethyl acetate was purified through an alumina column to give 30 mg. of XV, m. p. 228°C.

Found: C, 48.36; H, 2.78; N, 4.62. Calcd. for $C_{26}H_{20}O_5N_2S_2Cl_4$: C, 48.33; H, 3.09; N, 4.33%.

***N*-(4-Methoxy-3-methylphenyl)-*N'*-methyl-*N*, *N'*-dibenzenesulfonyl-*p*-phenylenediamine (XVII).**— To 150 mg. of XIV (the reaction product[1] of I with *o*-cresol) suspended in 5 ml. of methanol, an ether solution of diazomethane was added. After 24 hr. the solvent was evaporated and the residue was recrystallized from methanol to afford 135 mg. of colorless crystals (XVII), m. p. 158—160°C. The infrared spectrum of this compound did not show

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[16] All melting points are uncorrected. Microanalyses were carried out by the Misses Yoko Endo and Yukiko Endo in this Institute. Measurements of ultraviolet and infrared spectra were made, respectively, with a Hitachi EPU-2A type spectrophotometer and with a Perkin-Elmer 21 infrared spectrophotometer using a potassium bromide disk.

any absorption band due to the OH and NH groups.

Found: C, 62.31; H, 5.02; N, 5.51. Calcd. for $C_{27}H_{26}O_5N_2S_2$: C, 62.09; H, 4.98; N, 5.36%.

N-(2-Methoxytropon-5-yl)-N′-methyl-N, N′-dibenzenesulfonyl-*p*-phenylenediamine (XVIII).—To 1 g. of VIII (the reaction product[5]) of I with tropolone) suspended in 10 ml. of methanol, an ether solution of diazomethane was added. After the mixture had been allowed to stand overnight, the crystals that separated out were collected and recrystallized from a mixture of methanol and chloroform to give 950 mg. of XVIII, m. p. 190—191°C.

Found: C, 60.44; H, 4.35; N, 5.18. Calcd. for $C_{27}H_{24}O_6N_2S_2$: C, 60.46; H, 4.47; N, 5.22%.

The Rearrangement Reaction of XVIII with Sodium Ethoxide.—A mixture of 150 mg. of XVIII and sodium ethoxide prepared from 100 mg. of sodium and 2.5 ml. of absolute ethanol was heated at 120°C; thereby the crystals of XVIII once dissolved once, and after a while a solid separated out. After being heated for 1 hr., the mixture was cooled. The solid was collected by filtration and washed with ethanol. The solid (50 mg.) was heated in 2 ml. of 6 N hydrochloric acid on a water bath for 1 hr. After being cooled, the solid was collected, suspended in 2 ml. of methanol, and treated with an ether solution of diazomethane. After standing overnight, the solvent was evaporated. The residue was chromatographed on an alumina column, and elution with ethyl acetate afforded 20 mg. of colorless needles (XIX), m. p. 182—183°C.

Found: C, 60.69; H, 4.64; N, 5.51. Calcd. for $C_{27}H_{24}O_6N_2S_2$: C, 60.46; H, 4.47; N, 5.22%.

N-(4-Methoxycarbonylphenyl)-N′-methyl-N, N′-dibenzenesulfonyl-*p*-phenylenediamine (XIX).—To a solution of 250 mg. of 4-amino-4′-methyldiphenylamine[14]) in 2 ml. of pyridine, 390 mg. of benzenesulfonyl chloride was added drop by drop in a nitrogen atmosphere; the color of the mixture thereupon changed to a red dish purple and then, after 5 min., faded. The mixture was heated on a water bath for 30 min., and pyridine was removed under reduced pressure. The residue solidified on the addition of water. The solid thereby formed was collected and recrystallized from ethanol to give 400 mg. of *N*-(4-methylphenyl)-*N*,*N*′-dibenzenesulfonyl-*p*-phenylenediamine (XX) as colorless crystals, m. p. 175°C.

Found: C, 62.73; H, 4.27; N, 5.93. Calcd. for $C_{25}H_{22}O_4N_2S_2$: C, 62.77; H, 4.59; N, 5.85%.

To 50 mg. of XX suspended in a solution of 100 mg. of potassium hydroxide in 10 ml. of water, a solution of 50 mg. of potassium permanganate in 10 ml. of water was added. The mixture was then heated at 100°C for 1.5 hr. After the remaining potassium permanganate had been decomposed by the addition of methanol, the mixture was filtered to remove any manganese dioxide. The filtrate was then acidified, and the precipitate thereby formed was collected. The precipitate was added to an aqueous solution of sodium carbonate (30 mg. in 5 ml. of water), and an insoluble substance was removed by filtration. When the filtrate was acidified again, 35 mg. of the precipitate was collected. A solution of this precipitate in methaol was treated with an ether solution of diazomethane. The evaporation of the solvent gave 20 mg. of colorless needles, m. p. 183°C. This substance was identical with the compound (XIX) derived from the rearrangement reaction mentioned above.

Found: C, 60.61; H, 4.34; N, 5.04%.

N-(Tropolon-5′-yl)-N, N′-dibenzenesulfonyl-2, 3, 5, 6-tetrachloro-*p*-phenylenediamine (XXI).—To 200 mg. of XI suspended in 4 ml. of chloroform, a solution of 100 mg. of tropolone in 2 ml. of chloroform was added. On the addition of one drop of triethylamine to the mixture, the orange crystals of XI dissolved immediately and colorless crystals separated out. After they had stood for 3 hr., the crystals (200 mg.) were collected. Recrystallization from a mixture of ethanol and chloroform gave 190 mg. of XXI as colorless crystals, m. p. 208—210°C (decomp.).

Found: C, 45.97; H, 2.73; N, 4.49. Calcd. for $C_{25}H_{16}O_6N_2S_2Cl_4$: C, 46.47; H, 2.48; N, 4.33%.

N-(2′-Methoxytropon-5′-yl)-N′-methyl-N, N′-dibenzenesufonyl-2, 3, 5, 6-tetrachloro-*p*-phenylenediamine (XXII).—This compound was prepared by the treatment of 100 mg. of XXI with an ether solution of diazomethane in the same manner as in the case of XV. Colorless crystals; m. p. 228°C (decomp.).

Found: C, 47.96; H, 3.14; N, 4.21. Calcd. for $C_{27}H_{20}O_6N_2S_2Cl_4$: C, 48.10; H, 2.97; N, 4.15%.

N-(Tropolon-5-yl)-N′-benzyl-N, N′-dibenzenesulfonyl-*p*-phenylenediamine (XVIIIa).—Into a solution of 300 mg. of VIII in aqueous potassium hydroxide (400 mg. in 12 ml. of water), 265 mg. of benzyl chloride was stirred at 30—40°C. After the treatment had been continued for 6 hr., the solid thereby formed was collected by filtration, suspended in a small amount of water, and acidified with dilute sulfuric acid. After the mixture had been stirred for a while, 160 mg. of the solid was collected; the recrystallization of this from a mixture of ethyl acetate and ethanol gave 120 mg. of the desired compound as colorless crystals, m. p. 220—222°C (decomp.). This compound showed a positive color reaction with ferric chloride.

Found: C, 64.78; H, 4.67; N, 4.82. Calcd. for $C_{32}H_{26}O_6N_2S_2$: C, 64.23; H, 4.35; N, 4.68%.

N-(2-Methoxytropon-5-yl)-N′-benzyl-N, N′-dibenzenesulfonyl-*p*-phenylenediamine (XVIIIb).—The treatment of 50 mg. of the benzyl derivative prepared above with an ether solution of diazomethane gave 39 mg. of the methyl derivative; colorless needles, m. p. 204—205°C.

Found: C, 64.97; H, 4.65; N, 4.53. Calcd. for $C_{33}H_{28}O_6N_2S_2$: C, 64.72; H, 4.57; N, 4.57%.

N,N′-Dimethyl-N,N′-dibenzenesulfonyl-*p*-phenylenediamine.—To 300 mg. of *p*-phenylenedibenzenesulfonamide suspended in 5 ml. of methanol, an ether solution of diazomethane was added. After the mixture had been allowed to stand overnight, the solvent was removed by evaporation. The residue was recrystallized from a mixture of chloroform and ethanol to afford 220 mg. of colorless crystals, m. p. 193—195°C.

Found: C, 58.43; H, 4.95; N, 6.84. Calcd. for $C_{20}H_{20}O_4N_2S_2$: C, 57.70; H, 4.80; N, 6.74%.

In its NMR spectrum, a singnal for the protons of NCH_3 appears at 6.84 τ.

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