The Reaction of Tropoids with Quinone Derivatives. VIII. The Reaction of Several Tropolones with *p*-Benzoquinonemonobenzenesulfonimide

By Yukio NISHIYAMA

(Received January 11, 1965)

The reactions of tropolones with quinone derivatives have been investigated in our laboratory several times. For example, in one earlier paper of this series[1], it was reported that the reactions of *p*-benzoquinonedibenzenesulfonimide with tropolone and its bromo derivatives in the presence of a catalytic amount of triethylamine gave *N*-(tropolon-5-yl)-*N,N'*-dibenzenesulfonyl-*p*-phenylenediamine and its bromo derivatives in comparatively good yields.[2,3]

The present paper will describe the determination of the structure of the products of the reaction of *p*-benzoquinonemonobenzenesulfonimide (I)[4] with tropolone and its bromo derivatives without a catalyst.

The addition of tropolone to *p*-benzoquinonemonobenzenesulfonimide (I) dissolved in a mixture of methanol and benzene resulted in an orange solution. When this mixture had been allowed to stand overnight at room temperature, colorless crystals (II) were precipitated out. The analytical values of II corresponded to the molecular formula $C_{19}H_{15}O_{55}\cdot NS$, and its ultraviolet and infrared absorption spectra revealed that the tropolone ring was retained. Furthermore, from an analogy to the reaction of quinonediimide derivatives,[5-8] it was assumed that the *N*-benzenesulfonyl-*p*-aminophenol moiety entered into the 5-position of the tropolone ring. The experimental results described below support this assumption.

In order to ascertain the position where the tropolone ring links, a similar reaction was carried out with 3-bromotropolone and 3,7-dibromotropolone in place of tropolone itself; pale yellow crystals III and yellow crystals IV were obtained respectively. The analytical values of III and IV agreed with the formulae for the monobromo and dibromo derivatives of II respectively.

The hydrogenolysis of III and IV in the presence of palladium-carbon afforded II. Since the electrophilic substitution of tropolone is

---

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

2) See also Y. Nishiyama, Y. Ikegami and S. Seto, ibid., **38**, 72 (1965).

3) It was reported in an earlier paper of this series[1] that the structures of the reaction products of *p*-benzoquinonedibenzenesulfonimide with tropolone and its bromo derivatives were 5-(2',5'-dibenzenesulfonamidophenyl)tropolone and its bromo derivatives. However, further examination of these reaction products has revealed that they were *N*-(tropolon-5-yl)-*N, N'*-dibenzenesulfonyl-*p*-phenylenediamine and its bromo derivatives.[2]

4) R. Adams and J. H. Looker, *J. Am. Chem. Soc.*, **73**, 1145 (1951).

5) S. Seto and H. Sato, This Bulletin, **35**, 349 (1961).

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

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

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

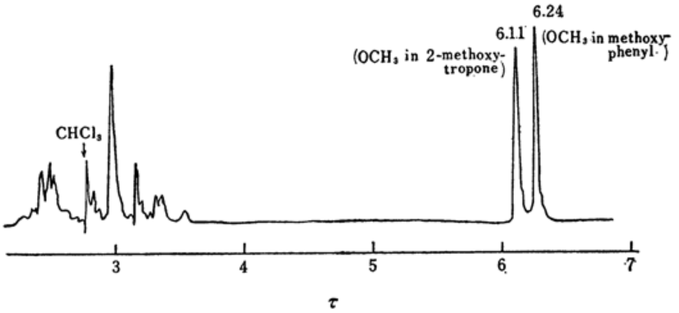
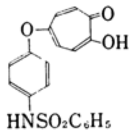
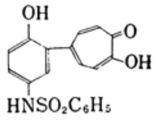


Fig. 1. The NMR spectrum of X.

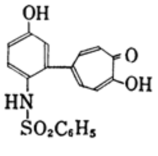
known to occur at the 3, 5, and 7-position, these facts clearly indicate that the *N*-benzenesulfonyl-*p*-aminophenol moiety in II, III and IV is situated in the 5-position of the tropolone ring. Accordingly, formulae A, B, C and D have been taken into consideration in determining the structure of II.



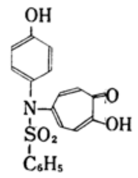
A



B



C



D

The heating of II in a sealed tube with concentrated hydrochloric acid afforded the *p*-aminophenol derivative V.

The acetylation of II and V afforded diacetyl derivative VI and triacetyl derivative VII respectively, these acetyl derivative did not exhibit any absorption band due to the NH and OH groups in their infrared spectra.

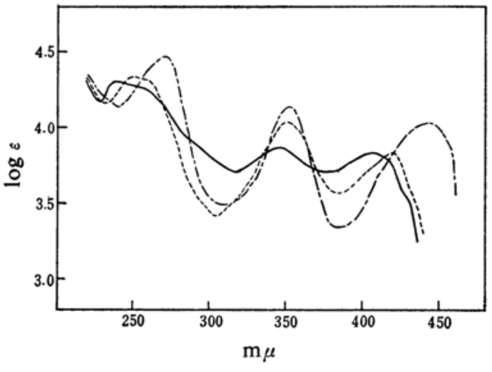


Fig. 2. Ultraviolet absorption spectra of II (——), III(----) and IV(—-—) in methanol.

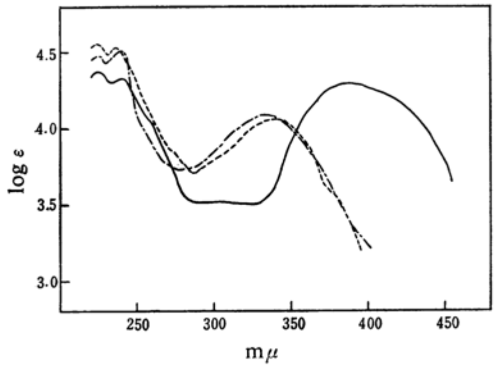


Fig. 3. Ultraviolet absorption spectra of V (——), VI(----) and VII(—-—) in methanol.

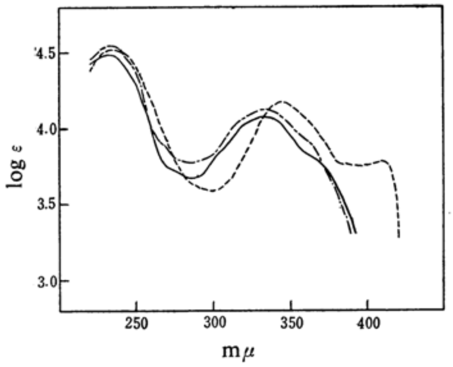
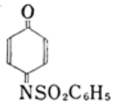
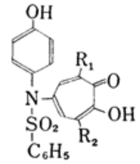


Fig. 4. Ultraviolet absorption spectra of VIII (——), IX(----) and X(—-—) in methanol.

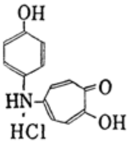
The reaction of II with diazomethane afforded a methyl ether, the analytical values of which corresponded to those of the monomethyl compound VIII. Its ultraviolet absorption spectrum and the absence of coloration with ferric chloride revealed that VIII was a 2-methoxytropone derivative. The methylation of II with dimethyl sulfate in the presence of potassium hydroxide gave another monomethyl ether derivative, IX, which showed coloration with ferric chloride. The further methylation of IX with diazomethane afforded a dimethyl compound, X, that showed no coloration with ferric chloride. The infrared spectrum of X does not show any absorption band due to the NH and OH groups, and in the NMR spectrum[9] the signals for the protons of the OCH_3 groups in methoxyphenyl and 2-methoxytropone appear at 6.24 and 6.11 τ[2] respectively, with almost equal intensities. If X had the NCH_3 group, the signal for the NCH_3 group would appear near 6.8—6.9 τ.[2] Therefore, X, was identified as *N*-benzenesulfonyl-*N*-(2-methoxytropon-5-yl)-*p*-anisidine.



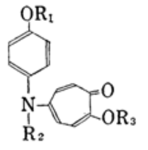
I



II: $R_1=R_2=H$
III: $R_1=Br$, $R_2=H$
IV: $R_1=R_2=Br$



V



VI: $R_1=R_3=COCH_3$, $R_2=SO_2C_6H_5$
VII: $R_1=R_2=R_3=COCH_3$
VIII: $R_1=H$, $R_2=SO_2C_6H_5$, $R_3=CH_3$
IX: $R_1=CH_3$, $R_2=SO_2C_6H_5$, $R_3=H$
X: $R_1=R_3=CH_3$, $R_2=SO_2C_6H_5$

From these facts, formulae A, B and C must be excluded for structure of II; thus it may be concluded that the reaction product of *p*-benzoquinone-monosulfonimide (I) with tropolone is *N*-benzenesulfonyl-*N*-(tropolon-5-yl)-*p*-aminophenol (II), and that III and IV are monobromo and dibromo derivatives of II respectively.

Experimental[10]

***N*-Benzenesulfonyl-*N*-(tropolon-5-yl)-*p*-aminophenol (II).**—A solution of *p*-benzoquinonemonobenzenesulfonimide (I) (200 mg.) and tropolone (180 mg.) in 9 ml. of a mixture (3 : 1 by volume) of benzene and methanol was allowed to stand at room temperature. After 24 hr., the colorless crystals (120 mg.) which precipitated were collected by filtration. Recrystallization from ethanol afforded 110 mg. of II; m. p. 228°C.

Found: C, 61.90; H, 4.27; N, 3.74. Calcd. for $C_{19}H_{15}O_5NS$: C, 61.81; H, 4.06; N, 3.79%.

UV λ_{max}^{MeOH} mμ (log ε): 235 (4.28), 345 (3.84), 403 (3.82).

***N*-Benzenesulfonyl-*N*-(3-bromotropolon-5-yl)-*p*-aminophenol (III).**—To a solution of I (300 mg.) in 7 ml. of benzene-methanol (3 : 1 by volume) was added a solution of 3-bromotropolone (490 mg.) in 2 ml. of the same solvent; the mixture was then allowed to stand at room temperature. After 2 days, the solvent was evaporated under reduced pressure. To this residue, a small amount of ethanol was added, whereupon pale yellow crystals (270 mg.), m. p. 240°C (decomp.) were obtained.

Found: C, 51.22; H, 3.96. Calcd. for $C_{19}H_{14}O_5NSBr$: C, 50.89; H, 3.13%.

UV λ_{max}^{MeOH} mμ (log ε): 250 (4.32), 350 (4.04), 420 (3.83).

The filtrate left after the separation of III was evaporated under reduced pressure. When the residue was sublimed at 2 mmHg in a bath of 130°C, 130 mg. of 3-bromotropolone was recovered.

***N*-Benzenesulfonyl-*N*-(3,7-dibromotropolon-5-yl)-*p*-aminophenol (IV).**—When treated in the same way as above, I (400 mg.) and 3, 7-dibromotropolone (480 mg.) afforded 670 mg. of yellow crystals, m. p. 197°C (decomp.).

Found: C, 43.47; H, 2.79; N, 2.39. Calcd. for $C_{19}H_{13}O_5NSBr_2$: C, 43.26; H, 2.47; N, 2.66%.

UV λ_{max}^{MeOH} mμ (log ε): 270 (4.47), 353 (4.13), 445 (4.02).

The Hydrogenolysis of III.—A solution of the monobromo derivative III (50 mg.) in water (6 ml.) and ethanol (2 ml.) containing potassium hydroxide (100 mg.) was shaken in a hydrogen atmosphere over palladium-carbon (50 mg.) at room temperature. When the absorption of hydrogen had ceased, the catalyst was filtered off, the filtrate was acidified with diluted sufuric acid, and the precipitate thereby formed was collected by filtration. Recrystallization from ethanol afforded 30 mg. of colorless crystals, m. p. 227—228°C, undepressed on admixture with II. The ultraviolet and infrared absorption spectra of these two substances were also in complete agreement.

The Hydrogenolysis of IV.—A solution of the dibromo derivative IV (150 mg.) in water (6 ml.) and ethanol (4 ml.) containing potassium hydroxide (200 mg.) was added to palladium-carbon (50 mg.). The mixture was then treated as in the foregoing example. The recrystallization of the precipitate gave 70 mg. of crystals with a m. p. of 227—228°C, undepressed on admixture with II. The

---

[9] The NMR spectrum was measured in deuteriochloroform, using a Varian 4301 high-resolution NMR spectrometer (60 Mc.); the measurements were performed by Assistant Professor Tsuneo Ikenoue of this Institute, to whom the author is indebted.

[10] All melting points are uncorrected. The microanalyses were carried out by Misses Yoko Endo and Yukiko Endo in this Institute. The measurements of the ultraviolet and infrared spectra were made, respectively, with a Hitachi EPI-2A-type spectrophotometer in methanol and with a Hitachi EPI-S2-type infrared spectrophotometer using a potassium bromide disk.

ultraviolet and infrared absorption spectra of this product were also in agreement with those of II.

The Reaction of II with Concentrated Hydrochloric Acid. —A mixture of II (100 mg.) and concentrated hydrochloric acid (2 ml.) was heated in a sealed tube at 130°C for 5 hr. When it had cooled, the tube was opened and the orange red crystals that separated out were collected by filtration. Recrystallization from dilute hydrochloric acid gave 20 mg. of the hydrochloride of *N*-(tropolon-5-yl)-*p*-aminophenol (V) as orange red crystals, m. p. 265—266°C (decomp.).

Found: C, 58.04; H, 4.34; N, 5.44. Calcd. for $C_{13}H_{10}O_3NCl$: C, 59.20; H, 4.55; N, 5.31%.

UV λ_{max}^{MeOH} mμ (log ε): 225 (4.37), 240 (4.32), 390 (4.26).

***N*-Benzenesulfonyl-*N*-(2-acetoxytropon-5-yl)-*p*-acetoxyaniline (VI).**—A mixture of II (200 mg.) and acetic anhydride (4 ml.) was heated at 130°C for 1 hr. The mixture was then evaporated under reduced pressure, and the residue was crystallized from ethanol to give 60 mg. of colorless crystals, melting at 139—140°C.

Found: C, 60.57; H, 4.33; N, 3.15. Calcd. for $C_{23}H_{19}O_7NS$: C, 60.95; H, 4.19; N, 3.09%.

UV λ_{max}^{MeOH} mμ (log ε): 225 (4.54), 235 (4.48), 340 (4.05).

***N*-Acetyl-*N*-(2-acetoxytropon-5-yl)-*p*-acetoxyaniline (VII).**—A mixture of the hydrochloride V (150 mg.), anhydrous sodium acetate (50 mg.) and acetic anhydride (2 ml.) was heated at 130°C for 2 hr. The mixture was then evaporated under reduced pressure, and the residue was washed with water. The crystalline residue was recrystallized from ethyl acetate to give 80 mg. of colorless crystals, m. p. 173—174°C.

Found: C, 65.08; H, 5.04; N, 4.38. Calcd. for $C_{19}H_{17}O_6N$: C, 64.26; H, 4.79; N, 3.94%.

UV λ_{max}^{MeOH} mμ (log ε): 225 (4.48), 240 (4.50), 335 (4.09).

***N*-Benzenesulfonyl-*N*-(2-methoxytropon-5-yl)-*p*-aminophenol (VIII).**—An ether solution of diazomethane was added to a suspension of II (150 mg.) in methanol (10 ml.). The mixture was then allowed to stand overnight, and the crystals that separated out were collected by filtration. Recrystallization from a methanol and chloroform mixture afforded 400 mg. of colorless needles, m. p. 160—162°C.

Found: C, 62.97; H, 5.04; N, 3.32. Calcd. for $C_{20}H_{17}O_5NS$: C, 62.68; H, 4.44; N, 3.65%.

UV λ_{max}^{MeOH} mμ (log ε): 232.5 (4.48), 332 (4.07).

This product does not show any coloration with ferric chloride.

The Methylation of II with Dimethyl Sulfate.—A solution of II (300 mg.) in 2 N sodium hydroxide (16 ml.) was stirred at room temperature. To this solution, dimethyl sulfate (1 ml.) was added. A colorless solid began to separate after a few minutes. After 30 min., the solid was collected by filtration and suspended in a small amount of water. The mixture was then acidified with dilute sulfuric acid, and the solid that remained was collected and recrystallized from ethanol to give 130 mg. of *N*-benzenesulfonyl-*N*-(tropolon-5-yl)-*p*-methoxyaniline (IX) as colorless needles, m. p. 169—170°C.

Found: C, 63.62; H, 4.63; N, 3.89. Calcd. for $C_{20}H_{17}O_5NS$: C, 62.68; H, 4.44; N, 3.65%.

UV λ_{max}^{MeOH} mμ (log ε): 235 (4.51), 345 (4.17), 407 (3.76).

This compound showed a positive color reaction with ferric chloride.

The filtrate left after the separation of IX was acidified with dilute sulfuric acid, and the solid that precipitated was collected. Recrystallization from ethanol gave 120 mg. of colorless crystals m. p. 228°C, undepressed on admixture with II.

The Reaction of IX with Diazomethane.—An ether solution of diazomethane was added to a suspension of IX (100 mg.) in methanol (4 ml.). After the mixture had been allowed to stand overnight, the crystals that separated were collected. Recrystallization from ethanol afforded 40 mg. of *N*-benzenesulfonyl-*N*-(2-methoxytropon-5-yl)-*p*-methoxyaniline as colorless crystals, m. p. 175—176°C.

Found: C, 63.91; H, 4.89; N, 3.64. Calcd. for $C_{21}H_{19}O_5NS$: C, 63.49; H, 4.78; N, 3.52%.

UV λ_{max}^{MeOH} mμ (log ε): 235 (4.54), 332 (4.15).

Compound X did not show any coloration with ferric chloride.

The author wishes to express his gratitude to Professor Shuichi Seto for his kind guidance and encouragement throughout this work. A part of the expenses was defrayed by the Sankyo Co., Ltd., to which the author is deeply indebted.

The Chemical Research Institute of
Non-Aqueous Solutions
Tohoku University
Katahira-cho, Sendai