The Reaction of Tropoids and Quinone Derivatives. I. Reaction of Several Tropolones and p-Benzoquinone-dibenzenesulfonimide[*]

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Several processes have been reported for the synthesis of tropolones having an aryl group[1]. For example, as a method of introducing an aryl group into the 5-position of the tropolone ring, one by the decomposition of the diazonium salt obtained from 5-aminotropolone in benzene, anisole or allied compounds has been described, but the yield is generally not good. Based on the work of Admas and others[2] that aryl phenylenediamide derivatives are obtained in good yields from quinonimide derivatives by their reactions with aromatic compounds, an attempt was made to apply this reaction to tropolones.

This reaction appears to be the action of quinonimide, acting as a kind of a cationoid reagent, on the aromatic compounds and it seems possible to apply this to tropoids other than tropolones.

Mixing of the chloroform solutions of tropolone and *p*-benzoquinonedibenzenesulfonimide (I) results in orange red solution. Addition of a small amount of triethylamine to this solution results in change of color of the solution to yellow and after some time, a colorless solid (II) separates.

This behavior is similar to the formation of 2-(4′-hydroxyphenyl)-*p*-phenylenedibenzenesulfonamide from phenol and I[3].

It is clear from its ultraviolet absorption spectrum, and coloration with ferric chloride that II possesses a tropolone ring, and its analytical values agree with those calculated for 2′,5′-dibenzenesulfonamidophenyltropolone.

From an analogy, to the reaction of phenol, the 2′, 5′-dibenzenesulfonamidophenyl-group is considered to have entered the *para*- or 5-position of the tropolone ring and the experimental results described below supports this assumption.

The same reaction carried out with 3-bromotropolone and 3, 7-dibromotropolone in place of tropolone respectively affords colorless crystals (III) and pale yellow crystals (IV), although the reaction velocity is somewhat slower than that in the case of tropolone itself. The analytical values of III and IV agree respectively with those for the monobromo and dibromo derivatives of II.

Hydrogenolysis of III and IV in the presence of palladium-charcoal affords II, and bromination of II and III in chloroform affords IV. These fact can be understood by assuming that the 2′, 5′-dibenzenesulfonamidophenyl group in II, III and IV is situated in the 5-position of the tropolone ring.

The reaction of I and 4-isopropyltropolone (hinokitiol) is likely to be affected by steric hindrance of the isopropyl group in the 4-position, but the reaction actually progressed smoothly, giving colorless crystals (V). Further, reaction of I with 3-bromo-6-isopropyltropolone and 3, 7-dibromo-4-isopropyltropolone respectively afforded colorless crystals (VI) and pale yellow crystals (VII).

Hydrogenolysis of VI and VII gave V.

From the foregoing experimental facts, and from analytical values and ultraviolet absorption spectra of V, VI and VII, it is clear, that V is 4-isopropyl-5-(2′, 5′-dibenzenesulfonamidophenyl)tropolone, and VI and VII are respectively its monobromo and dibromo derivatives. The fact, that the aryl group enters the 5-position without interference of such a bulky group in 4-position suggests, that this reaction might be applied to the syntheses of tricyclic tropolone derivatives.

3-Isopropyltropolone (α-thujaplicin) also reacts easily with I to form 3-isopropyl-5-(2′, 5′-dibenzenesulfonamidophenyl)tropolone (VIII).

The reaction of tropolone derivatives with a substituent in the 5-position with I was then carried out. Addition of triethylamine to the chloroform solution of 5-methyltropolone and I resulted in gradual blackening of the solution. This color change is different from that observed, when the reaction is progressing as anticipated.

Colorless crystals separated on standing this reaction mixture and this substance was found to be the reduction product of I, i. e. *p*-phenylenedibenzenesulfonamide.

A part of the starting 5-methyltropolone was recovered from the filtrate.

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[1] Cf. T. Nozoe, Festschrift Arthur Stoll, Birkhäuser A. G., Basel (1957) p. 746.

[2] R. Adams and W. Reifschneider, *Bull. Soc. chim. France*, **1958**, 23.

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

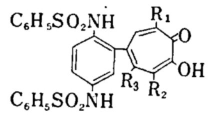

TABLE I. SOME PROPERTIES OF THE REACTION PRODUCTS

	R_1	R_2	R_3	M. p. °C (decomp.)	UV λ_{max}^{MeOH} mμ(log ε)
II	H	H	H	233～235	241(4.49), 345(4.15), 390(3.79)
III	Br	H	H	210～213	257(4.65), 351(4.29), 418(3.99)
IV	Br	Br	H	211～213	272(4.60), 356(4.31), 435(4.18)
V	H	H	isoPr	254～256	250(4.60), 344(4.24)
VI	Br	H	isoPr	242～243	263(4.58), 349(4.24), 413(3.93)
VII	Br	Br	isoPr	195～197	265(4.44), 355(4.06), 430(3.84)
VIII	isoPr	H	H	207～215	243(4.58), 340(4.28), 390(3.84)

The reaction of 5-bromotropolone and I also took the same course. It is known, that when the *para* position of phenol is blocked, as in *p*-cresol, the same reaction affords the reduction product, *p*-phenylenedibenzenesulfonamide[3,4].

I specifically attacks the *para* position of phenols and it is interesting, that it also attacks the 5-position of tropolones, corresponding to the *para* position, showing the similarity of phenols and tropolones.

Experimental[5]

5-(2′, 5′-Dibenzenesulfonamidophenyl) tropolone (II).—To a solution of 1 g. of *p*-benzoquinonedibenzenesulfonimide (I) dissolved in 25 ml. of chloroform, a solution of 0.8 g. of tropolone in 2 ml. of chloroform was added, by which the color of the solution changed to orange red. Addition of 3 drops of triethylamine to it further changed the color of the solution to yellow and colorless crystals began to separate after a few minutes. The mixture was allowed to stand for 1 hr. and the crystals were collected by filtration to 1.27 g. of the first crop of crystals, m. p. 228～232°C (decomp.). The filtrate was evaporated under a reduced pressure, 5 ml. of benzene and 2 ml. of 1 N sulfuric acid were added to the residue, and the crystals that separated out were collected by filtration. The crystals were washed with benzene and water, and amounted to 70 mg. of the second crop of m. p. 228～230°C (decomp.). The combined first and second crops of crystals were recrystallized from a mixture of chloroform and benzene to yield 1.30 g. of II of m. p. 233～235°C (decomp.).

Found: C, 59.20; H, 3.64; N, 5.30. Calcd. for $C_{25}H_{20}O_6N_2S_2$: C, 59.02; H, 3.97; N, 5.51%.

The filtrate left after separation of the second crop of crystals was combined with the washings, the benzene layer was separated, and evaporated under a reduced pressure. The residue was sublimed at 1 mmHg in a bath of 60°C, and 0.46 g. of tropolone was recovered.

II was dissolved in ethyl acetate and aqueous solution of ferric chloride was added by which the organic layer colored red.

2-Acetoxy-5-(2′, 5′-dibenzenesulfonamidophenyl)-tropone.—A mixture of 100 mg. of II and 0.5 ml. of acetic anhydride was heated at 140°C for 20 min., by which II dissolved completely. The mixture was evaporated under a reduced pressure and the crystalline residue was recrystallized from chloroform to 60 mg. of crystals melting at 200～201°C.

Found: C, 58.85; H, 4.18; N, 5.03. Calcd. for $C_{27}H_{22}O_7N_2S_2$: C, 58.87; H, 4.03; N, 5.09%.

U. V. λ_{max}^{MeOH} mμ (log ε): 231(4.56), 330(4.11).

2-Methoxy-5-(2′, 5′-dibenzenesulfonamidophenyl)-tropone.—An ether solution of diazomethane was added to 100 mg. of II suspended in 4 ml. of methanol by which an active reaction set in with evolution of nitrogen. After standing the mixture over night, the crystals were collected and recrystallized from methanol, affording 70 mg. of colorless needles, m. p. 190～191°C.

Found: C, 60.36; H, 4.36; N, 5.27. Calcd. for $C_{26}H_{22}O_6N_2S_2$: C, 59.73; H, 4.24; N, 5.36%.

U. V. λ_{max}^{MeOH} mμ (log ε): 226(4.47), 330(4.11).

3-Bromo-5-(2′, 5′-dibenzenesulfonamidophenyl)-tropolone (III).—One drop of triethylamine was added to the solution of 130 mg. of 3-bromotropolone and 100 mg. of I dissolved in 5 ml. of chloroform and the mixture was allowed to stand for 2 days. The first crop of crystals that separated was collected by filtration to 50 mg. of crystals of m. p. 210～213°C (decomp.). The filtrate was evaporated under a reduced pressure, 2 ml. of benzene and 1 ml. of 1 N sulfuric acid were added and 90 mg. of the second crop of crystals, m. p. 205～212°C (decomp.), was obtained. The first and second crops of crystals were combined and recrystallized from chloroform-ethanol mixture to 135 mg. of crystals of m. p. 210～213°C (decomp.).

Found: C, 50.76; H, 3.26; N, 4.70. Calcd. for $C_{25}H_{19}O_6N_2BrS_2$: C, 51.08; H, 3.26; N, 4.77%.

The benzene layer was separated from the filtrate left after removal of the second crop of crystals, the solvent was evaporated, and the residue was sublimed at 1 mmHg in a bath of 100°C, by which 70 mg. of 3-bromotropolone was recovered.

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4) R. Adams and K. R. Eilar, ibid., 73, 1149 (1951).

5) All melting points are uncorrected. The microanalyses were carried out by Mr. S. Ohyama and Miss Y. Endo of this Institute.

3, 7-Dibromo-5-(2′, 5′-dibenzenesulfonamidophenyl)tropolone (IV).—One drop of triethylamine was added to the solution of 180 mg. of 3, 7-dibromotropolone and 100 mg. of I dissolved in 5 ml. of chloroform and the mixture was allowed to stand for 5 days. The first crop of 160 mg. of crystals, m. p. 207~210°C (decomp.), was collected by filtration, the filtrate was evaporated, and 5 ml. of benzene and 1 ml. of 1 N sulfuric acid were added to its residue. The second crop of 10 mg. of crystals, m. p. 206~210°C (decomp.), thereby obtained was collected by filtration, combined with the first crop, and recrystallized from ethanol-chloroform mixture, affording 165 mg. of pale yellow crystals, m. p. 211~213°C (decomp.).

Found: C, 45.48; H, 2.71; N, 3.97. Calcd. for $C_{25}H_{18}O_6N_2Br_2S_2$: C, 45.03; H, 2.72; N, 4.20%.

The benzene layer was separated from the filtrate left after removal of the second crop of crystals, the solvent was evaporated, and the residue was sublimed at 1 mmHg and 120°C, from which 85 mg. of 3, 7-dibromotropolone was recovered.

Hydrogenolysis of III.—A solution of 90 mg. of III dissolved in 20 ml. of 0.1 N sodium hydroxide, added with 200 mg. of 5% palladium-charcoal, was shaken in hydrogen atomsphere at ordinary temperature. After the absorption of hydrogen ended, the catalyst was filtered off, the filtrate was acidified, and the precipitate thereby formed was crystallized from a mixture of ethanol and chloroform to 25 mg. of crystals, m. p. 230~233°C (decomp.), undepressed on admixture with II. The ultraviolet absorption spectra of these two substances were also in complete agreement.

Hydrogenolysis of IV.—A solution of 50 mg. of IV dissolved in 20 ml. of 0.1 N sodium hydroxide was added with palladium-charcoal. The mixture was treated as in the foregoing example. Recrystallization of the precipitate gave 15 mg. of crystals of m. p. 233~234°C (decomp.), undepressed on admixture with II. The ultraviolet absorption of this product was also in agreement with that of II.

Bromination of II. — A mixture of 60 mg. of bromine added to a suspension of 70 mg. of II in 5 ml. of chloroform was allowed to stand for 2 days and crystals were collected. This substance was found to be the unreacted II. The filtrate was evaporated under a reduced pressure and the oily residue solidified on being added with methanol. This solid was recrystallized from a chloroform-ethanol mixture to 10 mg. of pale yellow crystals, m. p. 207~210°C (decomp.), undepressed on admixture with IV. The ultraviolet absorption spectra of these two substances were also in good agreement. Admixture of this product with III melted at 195~200°C.

Bromination of III.—A suspension of 50 mg. of III in 5 ml. of chloroform, added by 60 mg. of bromine, was allowed to stand for 2 days. The reaction mixture was filtered to collect 30 mg. of crystals which was proved to be the unreacted III. The filtrate was treated as in the foregoing example and 10 mg. of pale yellow crystals, m. p. 207~209°C (decomp.), was obtained. This showed no depression of m. p. on admixture with IV.

4-Isopropyl-5-(2′,5′-dibenzenesulfonamidophenyl)-tropolone (V).—One drop of triethylamine was added to the reddish orange solution formed by dissolving 110 mg. of 4-isopropyltropolone and 100 mg. of I in 4 ml. of chloroform and the color of the solution changed immediately to yellow, gradually separating colorless crystals. After allowing the mixture to stand for 30 minutes, the crystals were collected by filtration, affording 130 mg. of colorless crystals, m. p. 253~256°C (decomp.). The filtrate was evaporated under a reduced pressure, 5 ml. of benzene and 1 ml. of 1 N sulfuric acid were added to the residue, and 10 mg. of the second crop of crystals, m. p. 247~251°C (decomp.), was collected. The first and second crops of crystals were combined and recrystallized from a chloroform-ethanol mixture to 135 mg. of crystals, m. p. 254~256°C (decomp.).

Found: C, 60.36; H, 4.67; N, 4.90. Calcd. for $C_{28}H_{26}O_6N_2S_2$: C, 61.06; H, 4.76; N, 5.09%.

The benzene layer was separated from the filtrate left after removal of the second crop of crystals, the solvent was evaporated from it, and the residue was sublimed under a reduced pressure, from which 60 mg. of 4-isopropyltropolone was recovered.

3-Bromo-6-isopropyl-5-(2′, 5′-dibenzenesulfonamidophenyl)tropolone (VI).—An orange solution formed on dissolving 170 mg. of 3-bromo-6-isopropyltropolone and 100 mg. of I in 4 ml. of chloroform was added with one drop of triethylamine and the solution turned yellow but there was no precipitation of crystals. After allowing this mixture to stand for 7 days, the solvent was evaporated under a reduced pressure, leaving a mixture of crystals and oil. To this residue, 5 ml. of benzene and 1 ml. of 1 N sulfuric acid were added and crystals that separated out were collected to 150 mg. of colorless crystals, m. p. 242~243°C (decomp.).

Found: C, 53.21; H, 3.67; N, 4.10. Calcd. for $C_{28}H_{25}O_6N_2BrS_2$: C, 53.39; H, 4.00; N, 4.45%.

The benzene layer was separated from the filtrate left after removal of crystals, the solvent was evaporated from this layer, and sublimation of the residue under a reduced pressure gave 85 mg. of the recovered 3-bromo-6-isopropyltropolone.

3, 7-Dibromo-4-isopropyl-5-(2′, 5′-dibenzenesulfonamidophenyl)tropolone (VII).—To the yellow solution formed on dissolving of 400 mg. of 3, 7-dibromo-4-isopropyltropolone and 200 mg. of I in 8 ml. of chloroform, one drop of triethylamine was added and the solution changed transitrally red but returned immediately to the original yellow color. There was no precipitation of crystals after standing the mixture for 10 days. The solvent was evaporated under a reduced pressure from this mixture, 6 ml. of benzene and 1 ml. of 1 N sulfuric acid were added to the residue, and the crystallized residue was recrystallized from a chloroform-ethanol mixture to 330 mg. of pale yellow crystals, m. p. 195~197°C (decomp.).

Found: C, 47.62; H, 3.26; N, 3.73. Calcd. for $C_{28}H_{24}O_6N_2Br_2S_2$: C, 47.44; H, 3.42; N, 3.96%.

Evaporation of the benzene layer separated from the filtrate and low-pressure sublimation of its residue afforded 210 mg. of recovered 3, 7-dibromo-4-isopropyltropolone.

Hydrogenolysis of VI.—Hydrogenolysis of 50 mg. of VI in the same manner as for III afforded 30 mg. of crystals, m. p. 251~253°C (decomp.), undepressed on admixture with V.

Hydrogenolysis of VII.—Treatment of 100 mg. of VII as in the foregoing examples afforded 50 mg. of crystals of m. p. 251~253°C (decomp.), undepressed on admixture with V.

3-Isopropyl-5-(2′,5′-dibenzenesulfonamidophenyl)-tropolone (VIII).—Treatment of 110 mg. of 3-isopropyltropolone and 100 mg. of I in the same manner as for V afforded 140 mg. of crystals of m. p. 207~215°C (decomp.).

Found: C, 61.92; H, 4.59; N, 4.84. Calcd. for $C_{28}H_{26}O_6N_2S_2$: C, 61.05; H, 4.76; N, 5.09%.

There was recovered 60 mg. of 3-isopropyltropolone.

Reaction of 5-Methyltropolone and I.—One drop of triethylamine was added to the solution of 40 mg. of 5-methyltropolone and 50 mg. of I dissolved in 2 ml. of chloroform by which the solution turned dark brown and crystals began to form after some time. The mixture was allowed to stand for 2 hr. and 20 mg. of colorless crystals, m. p. 240~241°C, were obtained. This showed no depression of m. p. on admixture with *p*-phenylenedibenzenesulfonamide and the ultraviolet absorption spectra of the two substances were identical.

Evaporation of the filtrate left an oily substance to which benzene and 1 N sulfuric acid were added, and the benzene layer was separated. The benzene solution was chromatographed over silica gel and 20 mg. of 5-methyltropolone was recovered from it.

Reaction of 5-Bromotropolone and I.—One drop of triethylamine was added to the solution of 30 mg. of 5-bromotropolone and 20 mg. of I dissolved in 2 ml. of chloroform by which the color of the solution changed through dark green to dark brown. The reaction mixture was treated as above, and 15 mg. of *p*-phenylenedibenzenesulfonamide and 15 mg. of 5-bromotropolone were obtained.

Summary

The reaction of tropolones with *p*-benzoquinonedibenzenesulfonimide was carried out and the following points were observed.

1) The 2′, 5′-dibenzenesulfonamidophenyl group enters the 5-position of the tropolone ring, similar to the case of phenol.

2) The reaction proceeds in the same way in the case of 4-isopropyltropolone, without interference of the isopropyl group.

3) In the case of tropolones with a substituent in 5-position, reduction of *p*-benzoquinonedibenzenesulfonimide takes place.

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