*3,4-Benzotropolone and Related Compounds. I. Bromo Derivatives of 3,4-Benzotropolone**

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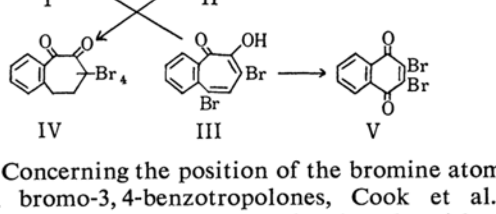
3,4-Benzotropolone (I) was synthesized first by Cook et al.[1], later by Moroe et al.[2], and some of its substitution products were reported on by Nozoe et al.[3] Some other benzologs of tropolone and hydroxytropones, such as 4,5-benzotropolone[4], 4-hydroxy-2,3-benzotropone[5], and hydroxydibenzotropone[6,7], have recently been reported on. Of these compounds, I is most closely related to the parent tropolone. It seems, therefore, of interest to compare the chemical behavior of I with that of monocyclic tropolone and thereby to examine how the condensed benzene ring influences the character of the tropolone nucleus of I. From this point of view, the present author has undertaken a more detailed study of I and its derivatives. As a part of this work, this paper deals with bromo-3,4-benzotropolones and their brominated products.

I and its monobromo- and dibromo-derivatives, II and III, the materials for this study, were prepared according to Cook's method[1] starting with 3,4-benzocycloheptene-1,2-dione. I, II and III gave ultraviolet spectra characteristic of troponoid compounds (Fig. 1)[8] and exhibited infrared absorption bands of their carbonyl groups within the same region as other troponoid carbonyl groups (as given in the experimental section).



Concerning the position of the bromine atoms in bromo-3,4-benzotropolones, Cook et al.[1] have reasonably suggested, though without any experimental evidence, that II is 7-substituted and that III is 5,7-disubstituted. Their prediction is now proved to be true by studies of the oxidation of II and III with alkaline

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1) J. W. Cook and A. R. Sommerville, *Nature*, **163**, 410 (1949); J. W. Cook, A. R. Gibb, R. A. Raphael and A. R. Sommerville, *J. Chem. Soc.*, **1952**, 603.

2) T. Moroe, T. Matsushima and O. Miyamoto, *J. Pharm. Soc. Japan* (*Yakugaku Zasshi*), **72**, 1238 (1952).

3) T. Nozoe, Y. Kitahara and T. Ando, *Proc. Japan Acad.*, **27**, 107 (1951).

4) D. S. Tarbell, G. P. Scott and A. D. Kemp, *J. Am. Chem. Soc.*, **72**, 379 (1950); D. S. Tarbell and J. C. Bill, ibid., **74**, 1234 (1952); G. A. Nicholls and D. S. Tarbell, ibid., **74**, 4935 (1952); H. Fernholz, E. Hartwig and J. -C. Salfeld, *Ann.*, **576**, 131 (1952).

5) a) G. L. Buchanan, *J. Chem. Soc.*, **1954**, 1060; b) G. L. Buchanan and J. K. Sutherland, ibid., **1956**, 2620.

6) T. Sakan and M. Nakazaki, *J. Inst. Polytech. Osaka City Univ.*, **I**, No. 2, 23 (1950): *Chem. Abstr.*, **46**, 5036 (1952).

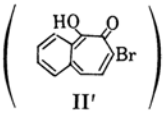
7) J. Rigaudy and L. Nédélec, a) *Compt. rend.*, **236**, 1287 (1953); b) *Bull. soc. chim. France*, **1959**, 638, 659.

8) The ultraviolet spectrum of I was given previously. J. W. Cook et al., loc. cit.

hydrogen peroxide to *o*-carboxycinnamic acid and phthalic acid respectively. An attempt was made to obtain 5-bromo-3, 4-benzotropolone by catalytic hydrogenolysis of III with one mole of hydrogen. However, this resulted only in the formation of one-half an equivalent of I, the remainder being recovered unchanged and no monobromo derivative being obtained.

I, II and III are less acidic than monocyclic tropolone and bromotropolones. I formed an unstable amine salt which was decomposed readily to its components on recrystallization from solvents. II and III formed stable salts with aliphatic amines but did not with aromatic amines, whereas monocyclic bromotropolones were known to combine firmly with both aliphatic and aromatic amines[9]. The lesser acidity of benzotropolones may be ascribed to the fact that the condensed benzene ring restricts the resonance of the tropolone nucleus. On the other hand, I, II and III behaved as weak bases and dissolved in concentrated sulfuric acid, from which they were recovered unchanged on dilution with water. Such an amphoteric property is characteristic of troponoid compounds.

As reported by Nozoe et al.[10], 3-bromotropolone exists as a tautomeric mixture with 7-bromotropolone, and is methylated to produce the two corresponding isomeric methyl ethers. However, II, a benzolog of 3-bromotropolone, was methylated to give only one methyl ether, 6-bromo-7-methoxy-2, 3-benzotropone, indicating that II exists in only one form, unlike the monocyclic bromotropolones. A tautomeric form (II′) of II could not exist because its benzene ring is not aromatic but quinonoid.



II′

III was similarly methylated, affording 4, 6-dibromo-7-methoxy-2, 3-benzotropone as the sole product. These methyl ethers, like II and III, exhibited ultraviolet spectra characteristic of troponoid compounds (Fig. 1). As compared with monocyclic bromotropolone methyl ethers, bromobenzotropolone methyl ethers were more stable towards hydrolysis and were not affected when heated with hydrobromic acid in a methanolic solution for an hour, but hydrolyzed when heated with 47% hydrobromic acid without methanol for two hours. The methyl ether of II was debrominated by catalytic hydrogenolysis to give an oily methyl ether of I, which failed to crystallize[11]. The methyl ether of I afforded a picrate and a 2, 4-dinitrophenylhydrazone. II and III gave acetates which were readily hydrolyzed when their methanolic solutions containing a little hydrochloric acid, were refluxed for 5 min.

II was brominated in acetic acid solution to yield III as previously described[1]. In contrast, II was brominated in chloroform solution to yield an addition product assumed to be tetrabromo-3, 4-benzocycloheptene-1, 2-dione (IV) based upon its spectrum (Fig. 1), which was crystallized unchanged from petroleum ether but was decomposed to yield III on crystallization from acetic acid. III and bromine in chloroform gave an unstable addition product, from which III was regenerated on crystallization from solvents.

III was subjected to exhaustive bromination by heating its acetic acid solution with excess bromine on a water bath for fifteen hours, 2, 3-dibromo-1, 4-naphthoquinone (V) being unexpectedly produced. V was identified by mixed melting point determination and by agreement in ultraviolet and infrared spectra with an authentic sample. An anilino derivative of V also showed no melting point depression on admixture with an authentic 2-bromo-3-anilino-1, 4-naphthoquinone. The structure of V was further elucidated by converting it to 2-bromo-3-*p*-toluidino-1, 4-naphthoquinone, 2-bromo-3-hydroxy-1, 4-naphthoquinone, 2-bromo- and 2,

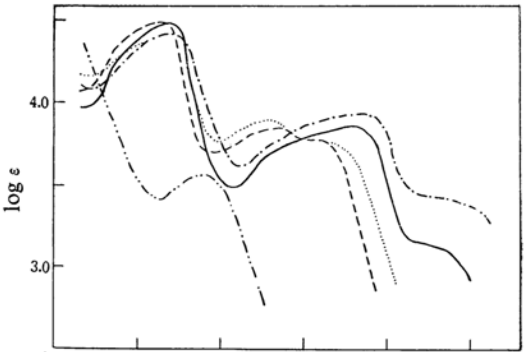


Fig. 1. Ultraviolet spectra of 7-bromo-3, 4-benzotropolone (II) (——), 5, 7-dibromo-3, 4-benzotropolone (III) (-·-·), the methyl ether of II (----), the methyl ether of III (······) in methanol and tetrabromo-3, 4-benzocycloheptene-1, 2-dione (IV) (-··-) in cyclohexane.

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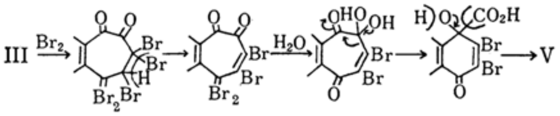
[9] T. Nozoe, T. Mukai and K. Takase, *Proc. Japan Acad.*, **26** No. 8, 22 (1950); T. Nozoe, E. Sebe, S. Mayama and S. Iwamoto, *Sci. Repts. Tohoku Univ., Ser. I*, **36**, 194 (1952).

[10] T. Nozoe, Y. Kitahara and S. Masamune, *Proc. Japan Acad.*, **27**, 649 (1951); T. Sato, *J. Chem. Soc. Japan, Pure Chem. Sec.* (*Nippon Kagaku Zasshi*), **80**, 1340 (1959).

[11] Nozoe et al. (Ref. 3) have obtained the methyl ether of I, m. p. 82.5~83.5°C, by the action of ethereal diazomethane on I, while Cook et al. (Ref. 1) have reported that I reacts very sluggishly with diazomethane and smoothly with methyl *p*-toluenesulfonate to yield an oily methyl ether of I.

3-dibromo-1, 4-diacetoxynaphthalenes. The tentative mechanism of this transformation may be represented by the following scheme:



Closely related ring contractions of hydroxytropones into quinones have been reported: 5, 7-dibromo-4-hydroxy-2, 3-benzotropone is transformed on heating with alkali to 2-hydroxy-1, 4-naphthoquinone[5b)], and 4-hydroxy-2, 3:6, 7-dibenzotropone in alkaline solution is oxidized by air to anthraquinone[7b)].

Experimental

7-Bromo- and 5, 7-Dibromo-3, 4-benzotropolones (II and III). — Prepared according to Cook and others' method[1)]. 7-Bromo-3, 4-benzotropolone (II), yellow prisms from ethanol, m. p. 149°C (reported m. p.'s 143~144[1)] and 148~149°C[3)]), (Found: C, 52.72; H, 3.02. Calcd. for $C_{11}H_7O_2Br$: C, 52.61; H, 2.81%), infrared ν(KBr): 1612, 1600, 1547 cm^{-1}.

5, 7-Dibromo-3, 4-benzotropolone (III), yellow needles, m. p. 127°C (reported m. p. 119~121°C[1)]), (Found: C, 40.31; H, 2.08. Calcd. for $C_{11}H_6O_2Br_2$: C, 40.03; H, 1.83%), infrared ν(KBr): 1612, 1585, 1550 cm^{-1}.

The Amine Salts.—A solution of a 50-mg. sample and 0.2 g. of an amine in 1 ml. of ethanol was warmed on a water bath for 5 min. The solution was concentrated, and the product which separated on cooling was collected and recrystallized from ethanol. The amine salts thus obtained were decomposed to regenerate bromobenzotropolones when dissolved in ethanol containing a little hydrochloric acid.

Amine Salts of II. — Diethylamine salt, yellow scales, m. p. 130.5~131.5°C.

Found: C, 55.30; H, 5.57; N, 4.53. Calcd. for $C_{11}H_7O_2Br\cdot C_4H_{11}N$: C, 55.57; H, 5.60; N, 4.32%.

Ethylenediamine salt, yellow scales decomposing at 157°C.

Found: C, 50.86; H, 3.95; N, 5.03. Calcd. for $(C_{11}H_7O_2Br)_2\cdot C_2H_8N_2$: C, 51.26; H, 3.94; N, 4.98%.

Benzylamine salt, yellow, silky needles, m. p. 143°C.

Found: C, 60.36; H, 4.32; N, 4.29. Calcd. for $C_{11}H_7O_2Br\cdot C_7H_9N$: C, 60.36; H, 4.50; N, 3.91%.

Amine Salts of III. — Diethylamine salt, yellow needles, m. p. 146~147°C.

Found: C, 44.58; H, 4.25; N, 3.71. Calcd. for $C_{11}H_6O_2Br_2\cdot C_4H_{11}N$: C, 44.69; H, 4.25; N, 3.48%.

Ethylenediamine salt, a yellow crystalline powder, m. p. above 300°C.

Benzylamine salt, yellow, silky needles, m. p. 142°C (decomp.).

Found: C, 49.65; H, 3.40; N, 3.41. Calcd. for $C_{11}H_6O_2Br_2\cdot C_7H_9N$: C, 49.46; H, 3.46; N, 3.21%.

The Methyl Ethers.—Prepared by methylation of II and III with ethereal diazomethane in the usual manner. Methyl ether of II, colorless needles from dilute methanol, m. p. 86~87°C (reported m. p. 84~85°C[1)]), infrared $\nu(CCl_4)$: 1635, 1598, 1565 cm^{-1}.

Found: C, 54.54; H, 3.56. Calcd. for $C_{12}H_9O_2Br$: C, 54.36; H, 3.42%.

Methyl ether of III, pale yellow needles, m. p. 120°C, infrared $\nu(CCl_4)$: 1650, 1589, 1565 cm^{-1}.

Found: C, 42.19; H, 2.56. Calcd. for $C_{12}H_8O_2Br_2$: C, 41.89; H, 2.34%.

The Acetates.—A solution of a 50-mg. sample in 1 ml. of acetic anhydride containing a trace of concentrated sulfuric acid was heated on a water bath for 5 min., the excess acetic anhydride was decomposed with ice, and the product was crystallized from methanol. Acetate of II, colorless crystals, m. p. 91°C.

Found: C, 52.96; H, 3.13. Calcd. for $C_{13}H_8O_3Br$: C, 53.27; H, 3.10%.

Acetate of III, colorless crystals, m. p. 92°C.

Found: C, 41.90; H, 2.33. Calcd. for $C_{13}H_8O_3Br_2$: C, 41.97; H, 2.17%.

3, 4-Benzotropolone Methyl Ether. — A solution of 500 mg. of the methyl ether of II in 10 ml. of ethanol was shaken with hydrogen in the presence of 0.5 ml. of diethylamine and 50 mg. of 10% palladium-on-charcoal at ordinary temperature and pressure. After uptake of 1 mol. equivalent of hydrogen, the catalyst was removed and the solvent was evaporated. The crude product thus obtained was converted to its picrate, orange prismatic needles from carbon tetrachloride, m. p. 84~85°C.

Found: C, 52.24; H, 3.23; N, 9.97. Calcd. for $C_{12}H_{10}O_2\cdot C_6H_3O_7N_3$: C, 52.05; H, 3.16; N, 10.12%.

The picrate was decomposed by passing its chloroform solution through an alumina column to yield 130 mg. (37%) of 3, 4-benzotropolone methyl ether, a pale yellow oil, which gave a 2, 4-dinitrophenylhydrazone[1)], m. p. 238~240°C. In this experiment, there was produced a solid by-product, presumably a more hydrogenated product, which was not studied.

Attempted Monodebromination of III.—A solution of 500 mg. of III in 10 ml. of ethanol containing 0.3 ml. of 33% aqueous dimethylamine was shaken with hydrogen over 50 mg. of 10% palladium-on-charcoal until 1 mol. equivalent of hydrogen had been absorbed. The catalyst was removed, the solution was diluted with water, and the crystalline precipitate which separated was recrystallized from ethanol to yield 220 mg. (44%) of unchanged II, m. p. and mixed m. p. 125~126°C. The mother liquor from the above recrystallization was evaporated, and the residue was crystallized from petroleum ether to afford 80 mg. (30%) of I, pale yellow crystals, m. p. and mixed m. p. 84~85°C. No monobromo derivative could be obtained.

Oxidation of II and III.—To a stirred suspension of 200 mg. of II in 40 ml. of 0.2 N sodium hydroxide was added dropwise 2 ml. of 35% hydrogen peroxide, and the resulting mixture was set aside under continued stirring at room temperature. The suspension went into solution in 10 min. and the yellow color of the solution disappeared in an hour. Acidification with 6 N sulfuric acid produced a precipitate which was collected and crystallized from dilute acetic acid to yield 70 mg. (46%) of colorless needles of *o*-carboxycinnamic acid. Found: C, 62.48; H, 4.33. Calcd. for $C_{10}H_8O_4$: C, 62.50; H, 4.20%), m. p. 187∼189°C.

The melting point was undepressed on admixture with an authentic sample[12].

Oxidation under the same conditions was applied to 200 mg. of III, affording 74 mg. (74%) of phthalic acid, m. p. and mixed m. p. 199∼201°C (decomp.).

Addition of Bromine to II and III.—A solution of 100 mg. of II and 0.1 ml. of bromine in 3 ml. of chloroform was left to stand for 10 min., the chloroform and excess bromine were evaporated, and the solid residue was crystallized from petroleum ether to give 140 mg. (72%) of tetrabromo-3,4-benzocycloheptene-1,2-dione (IV), a pale yellow, crystalline powder, decomposing at 115∼118°C.

Found: C, 27.36; H, 1.45. Calcd. for $C_{11}H_6O_2\cdot Br_4$: C, 26.98; H, 1.24%.

The product was insoluble in alkali, showed no ferric chloride coloration, and was decomposed to III, m. p. and mixed m. p. 126°C, on recrystallization from acetic acid.

A similar bromination of III gave an addition product, decomposing at 111°C, which could not be purified owing to its facile decomposition to regenerate III on crystallization from solvents.

Exhaustive Bromination of III.—A solution of 1 g. of III and 0.5 ml. of bromine in 15 ml. of acetic acid was heated on a water bath for 5 hr., and to this were added two additional 0.5-ml. portions of bromine at intervals of 5 hr. under continued heating. Dilution with water caused precipitation of the product, which was collected and crystallized from acetic acid, affording 775 mg. (81%) of yellow needles of 2,3-dibromo-1,4-naphthoquinone (V), melting at 218.5°C. (Found: C, 38.27; H, 1.38. Calcd. for $C_{10}H_4O_2Br_2$: C, 38.01; H, 1.28%). The melting point was not depressed on admixture with an authentic sample[13].

Derivatives of V.—2-Bromo-3-anilino-1,4-naphthoquinone[13], 2-bromo-3-hydroxy-1,4-naphthoquinone[13] and 2,3-dibromo-1,4-diacetoxynaphthalene[14] derived from V showed no melting point depression on admixture with authentic samples. 2-Bromo-3-*p*-toluidino-1,4-naphthoquinone was prepared by warming 50 mg. of V and 170 mg. of *p*-toluidine in 2 ml. of ethanol for 5 min. Dark red plates from ethanol, m. p. 190.5°C.

Found: C, 59.83; H, 3.46; N, 4.35. Calcd. for $C_{17}H_{12}O_2NBr$: C, 59.66; H, 3.53; N, 4.09%.

2-Bromo-1,4-diacetoxynaphthalene was prepared by heating a mixture of 200 mg. of V, 600 mg. of zinc powder, 400 mg. of fused sodium acetate and 3 ml. of acetic anhydride on a water bath for 10 min. Colorless, granular crystals from ethanol, m. p. 146°C.

Found: C, 52.11; H, 3.62. Calcd. for $C_{14}H_{11}\cdot O_4Br$: C, 52.03; H, 3.43%.

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