

*3,4-Benzotropolone and Related Compounds. II<sup>1)</sup>. Chloro and Iodo Derivatives of 3,4-Benzotropolone\**

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Nozoe and collaborators<sup>2)</sup> have presented a short communication on the substitution of 3,4-benzotropolone (I) describing how I can be chlorinated to yield monochloro-3,4-benzo-

tropolone. The chlorination and the iodination of I have now been studied in more detail and are described herein.

When treated with one molar equivalent of chlorine, I afforded 5,7-dichloro-3,4-benzotropolone (V) in a low yield besides the recovery of unchanged material, no monochloro derivative being isolated. Treatment of I with two molar equivalents of chlorine afforded V in a

\* Presented at the 14th Annual Meeting of the Chemical Society of Japan, Tokyo, April, 1961.

1) Part I: This Bulletin, 35, 114 (1962).

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

TABLE I. M. P. AND MIXED M. P. OF CHLORO- AND BROMO-3,4-BENZOTROPOLONES

Chloro deriv.	M. p., °C	Bromo deriv.	M. p., °C	Mixed m. p., °C
7-Chloro-	151	7-Bromo-	148	148~149
methyl ether	97	methyl ether	87	87~ 89
acetate	101.5	acetate	91	90~ 91
5,7-Dichloro-	136	5,7-Dibromo-	126	122~126
methyl ether	106	methyl ether	120	104~109
5-Chloro-7-bromo-	111~114	5-Bromo-7-chloro-	122.5	116~119

fair yield. The monochlorination of 7-bromo-3,4-benzotropolone (II) gave 5-chloro-7-bromo-3,4-benzotropolone (VI). The passage of the excess chlorine into an acetic acid solution of II furnished 5,6,7-trichloro-7-bromo-3,4-benzocycloheptene-1,2-dione (VIII), which exhibited two infrared carbonyl absorption bands at 1753 and 1700  $\text{cm}^{-1}$  and an ultraviolet spectrum closely similar to that of the parent 3,4-benzocycloheptene-1,2-dione (Fig. 2). When treated with a large excess of chlorine, 5,7-dibromo-3,4-benzotropolone (III) was transformed into 2,3-dichloro-1,4-naphthoquinone, identified by comparison with an authentic sample<sup>3</sup>. This ring contraction is analogous to that observed in the exhaustive bromination of III described in the preceding paper<sup>1</sup>.

Heating II with concentrated hydrochloric acid gave 7-chloro-3,4-benzotropolone (IV) in a good yield which could not be obtained by the direct chlorination of I. A similar treatment of III gave V. The bromination of IV furnished 5-bromo-7-chloro-3,4-benzotropolone (VII). On slight warming with hydrochloric acid in methanol, 5-bromo- and 5,7-dibromo-3,4-benzotropolone methyl ethers, II' and III', easily underwent a halogen-exchange reaction to afford 5-chloro and 5,7-dichloro-3,4-benzotropolone methyl ethers, IV' and V', respectively. Under the same conditions, II and III remained unchanged and their acetates suffered hydrolysis their bromine atoms remaining intact. The ultraviolet spectra of IV, V, IV' and V' are analogous to those of general troponeid compounds as given in Fig. 1. II was allowed to react with thionyl chloride, producing an adduct which decomposed to give V on recrystallization from ethanol. The adduct, to which the structure IX was tentatively assigned, gave no coloration with ferric chloride and exhibited an ultraviolet spectrum entirely different from that of a troponeid compound (Fig. 2). III and thionyl chloride afforded the same V. It should be noted that, although monocyclic tropolones and their bromo derivatives react with thionyl chloride to form chlorotropolones<sup>4</sup>, II and III react with

the same reagent to afford chlorobenzotropolones their hydroxyl groups remaining unreplaced<sup>5</sup>. The susceptibility of the bromine atoms at 5- and 7-positions and the inertness of hydroxyl and methoxyl groups at 1-position of bromobenzotropolones and their methyl ethers towards anionoid substitution may be ascribed to the resonance structures of these compounds to which formula A contributes mainly and formula B contributes only to a less extent because the benzene ring of formula A is aromatic, whereas that of formula B is quinonoid.

Bromo- and chloro-3,4-benzotropolones, like monocyclic halotropolones<sup>6</sup>, possess melting points close to each other and show obscure mixed melting point depression, as is shown in Table I.

I was treated with sodium iodide and sodium iodate in an acetic acid solution to yield 7-iodo-3,4-benzotropolone (X). X was produced even when an excess of iodinating reagent was employed. Under the same conditions, II was not iodinated. II and III were heated with hydriodic acid to produce I and 5-bromo-3,4-benzotropolone (XII) respectively, instead of the expected iodobenzotropolones. The bromination of XII gave III. Analogously with the reaction of bromobenzotropolone methyl ethers with hydrochloric acid, II' and III' reacted with hydriodic acid in methanol to give 7-iodo-3,4-benzotropolone methyl ether (X') and 5-bromo-7-iodo-3,4-benzotropolone methyl ether (XI) respectively. XI was identified by converting it into methyl 1-hydroxy-4-bromo-2-naphthoate<sup>7</sup>. In these reactions, the 5-position of I and II was not iodinated, and 5-bromine atom of III and III' remained unaffected, presumably because the action of an iodide ion on the 5-position was sterically hindered by the *peri* position of the condensed benzene ring.

It has been found that, as in the benzenoid compounds, the out-of-plane CH deformation

3) A. Berthelm, *Ber.*, **34**, 1554 (1901).

4) W. von E. Doering and L. H. Knox, *J. Am. Chem. Soc.*, **74**, 5683 (1952); B. J. Abadir, J. W. Cook, J. D. Loudon and D. K. V. Steel, *J. Chem. Soc.*, 1952, 2350.

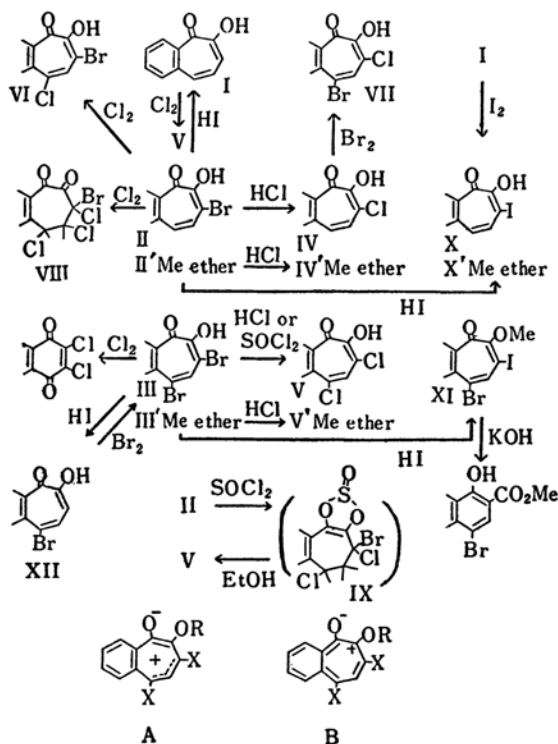
5) It has recently been reported that 3,4- and 4,5-benzotropolones fail to react with thionyl chloride. W. E. Parham, D. A. Bolon and E. E. Sweizer, *J. Am. Chem. Soc.*, **83**, 603 (1961).

6) E. Sebe, T. Nozoe, P. -Y. Yeh and S. Iwamoto, *Sci. Repts. Tohoku Univ.*, **1**, 36, 307 (1952).

7) Part IV: This Bulletin, to be published.

TABLE II. OUT-OF-PLANE CH DEFORMATION VIBRATIONS OF HALO-3,4-BENZOTROPOLONES

Compound	One isolated troponoid H 910~850 $\text{cm}^{-1}$	Two adjacent troponoid H 845~790 $\text{cm}^{-1}$	Four adjacent benzenoid H 770~735 $\text{cm}^{-1}$
7-Chloro-methyl ether		802	747
acetate		795	742
7-Bromo-methyl ether		806	740
acetate		807	753
5-Bromo-methyl ether		794	742
acetate		808	739
5-Bromo-methyl ether		832	754
7-Iodo-methyl ether		840	750
		795	737
5,7-Dichloro-	854		742
5,7-Dibromo-	907		745
methyl ether	858		760
			756
5-Bromo-7-iodo-, methyl ether	866		756



vibrations of troponoid compounds are correlated to the positions of their substituents<sup>8)</sup>. A similar correlation is also found in halo-benzotropolones, as is shown in Table II.

#### Experimental

**7-Chloro-3,4-benzotropolone (IV).**—A mixture of 300 mg. of 7-bromo-3,4-benzotropolone (II), 3 ml. of

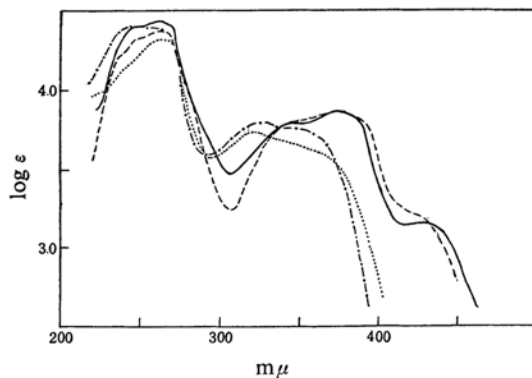


Fig. 1. Ultraviolet spectra of 7-chloro-3,4-benzotropolone (IV) (—), its methyl ether (IV') (---), 5,7-dichloro-3,4-benzotropolone (V) (----) and its methyl ether (V') (.....) in methanol.

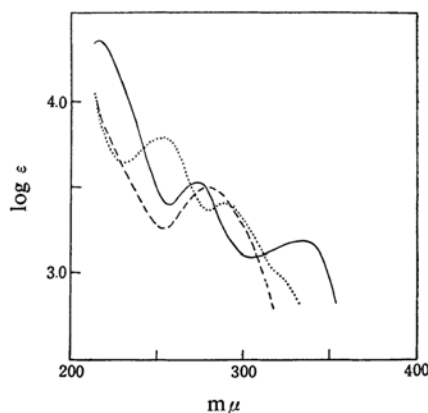


Fig. 2. Ultraviolet spectra of 3,4-benzocycloheptene-1,2-dione (.....), its 5,6,7-trichloro-7-bromo derivative (VIII) (—) in methanol and 7-bromo-3,4-benzotropolone-thionyl chloride adduct (IX) (----) in cyclohexane.

concentrated hydrochloric acid and 9 ml. of acetic acid was heated in a sealed tube at 120~130°C for 5 hr. The product deposited on cooling. Concentration of the filtrate gave a further crop of the product. The combined products were recrystallized from ethanol to give yellow prisms of m. p. 151°C. Yield, 215 mg. (88%). IV gave a brown coloration with ferric chloride in amyl alcohol solution.  $\nu(\text{KBr})$ : 1617, 1605, 1583  $\text{cm}^{-1}$ .  $\lambda(\text{MeOH})$ ,  $m\mu$  (log  $\epsilon$ ): 245(4.40), 262(4.44), 345(3.80), 370(3.85).

Found: C, 63.84; H, 3.29. Calcd. for  $\text{C}_{11}\text{H}_7\text{O}_2\text{Cl}$ : C, 63.94; H, 3.42%.

IV was also obtained in an 84% yield by refluxing a mixture of 100 mg. of 7-bromo-3,4-benzotropolone methyl ether (II'), 3 ml. of acetic acid and 15 ml. of concentrated hydrochloric acid for 5 hr.

**The Acetate of IV.**—Colorless prisms from methanol, m. p. 101.5°C.

Found: C, 62.62; H, 3.54. Calcd. for  $\text{C}_{13}\text{H}_9\text{O}_3\text{Cl}$ : C, 62.79; H, 3.65%.

8) Y. Kitahara, *Sci. Repts. Tohoku Univ.*, **1**, 39, 275 (1956).

**5, 7-Dichloro-3, 4-benzotropolone (V).**—From 3, 4-Benzotropolone (I).—To 100 mg. of I dissolved in 1.5 ml. of acetic acid was added an acetic acid solution of 82 mg. (2 mol. equiv.) of chlorine\*. After standing for an hour at room temperature, the acetic acid was removed under reduced pressure below 30°C, leaving a crystalline residue which was washed with water and recrystallized from methanol to give 85 mg. (61%) of V, yellow needles, m. p. 135~136°C. V gave a brown coloration with ferric chloride in amyl alcohol solution.  $\nu$ (Nujol): 1630, 1580  $\text{cm}^{-1}$ .  $\lambda$ (MeOH),  $m\mu$ (log  $\epsilon$ ): 266(4.40), 352(3.85), 376(3.87).

Found: C, 54.85; H, 2.40. Calcd. for  $\text{C}_{11}\text{H}_6\text{O}_2\text{Cl}_2$ : C, 54.80; H, 2.51%.

Treatment of 100 mg. of I with 41 mg. (1 mol. equiv.) of chlorine in an acetic acid solution at room temperature gave 45 mg. (32%) of V and 30 mg. of an unidentified product with a m. p. 120~126°C, besides the recovery of 15 mg. of unchanged material.

**From 7-Bromo-3, 4-benzotropolone (II).**—A 300-mg. sample of II was dissolved in 3 ml. of thionyl chloride, and the solution was allowed to stand overnight at room temperature. Removal of the thionyl chloride under reduced pressure left an oily residue which solidified on trituration with ligroin. Recrystallization of the product from ligroin gave 320 mg. (73%) of yellow prisms of the addition product, m. p. 148°C (mixed m. p. with II, 107~111°C).

Found: C, 35.77; H, 1.80. Calcd. for  $\text{C}_{11}\text{H}_7\text{O}_2\text{Br}\cdot\text{SOCl}_2$ : C, 35.69; H, 1.91%.

On recrystallization from ethanol the adduct changed into V, m. p. 137°C. Yield, 190 mg. (66% based on II).

**From 5, 7-Dibromo-3, 4-benzotropolone (III) and Hydrochloric Acid.**—A mixture of 150 mg. of III, 1.5 ml. of concentrated hydrochloric acid and 6 ml. of acetic acid was heated in a sealed tube at 110~120°C for 5 hr. and worked up as described above for the preparation of IV, affording 100 mg. (90%) of V, m. p. 136°C.

V was also obtained by refluxing a mixture of 100 mg. of 5, 7-dibromo-3, 4-benzotropolone methyl ether (III'), 3 ml. of acetic acid and 15 ml. of concentrated hydrochloric acid for 5 hr., followed by recrystallization of the product from methanol.

**From III and Thionyl Chloride.**—A treatment of 300 mg. of III with 3 ml. of thionyl chloride similar to that described above afforded 140 mg. (64%) of V, m. p. 137°C.

**7-Chloro-3, 4-benzotropolone Methyl Ether (IV') and 5, 7-Dichloro-3, 4-benzotropolone Methyl Ether (V').**—From IV and V.—IV', colorless needles, m. p. 96~97°C.  $\nu$ (Nujol): 1625, 1597, 1560  $\text{cm}^{-1}$ .  $\lambda$ (MeOH),  $m\mu$ (log  $\epsilon$ ): 243(4.40), 330(3.81).

Found: C, 65.30; H, 4.06. Calcd. for  $\text{C}_{12}\text{H}_9\text{O}_2\text{Cl}$ : C, 65.31; H, 4.11%.

V', pale yellow needles, m. p. 106°C.  $\lambda$ (MeOH),  $m\mu$ (log  $\epsilon$ ): 262(4.34), 318(3.75).

Found: C, 56.46; H, 3.11. Calcd. for  $\text{C}_{12}\text{H}_8\text{O}_2\text{Cl}_2$ : C, 56.49; H, 3.16%.

**From 7-Bromo- and 5, 7-Dibromo-3, 4-benzotropolone Methyl Ethers (II' and III').**—A mixture of 50 mg. of II', 5 ml. of methanol and 2 ml. of concentrated hydrochloric acid was refluxed for 15 min. The product separated on dilution with water. This was then recrystallized from dilute methanol to yield 35 mg. (83%) of IV', m. p. 96°C. A similar treatment of III' with hydrochloric acid in methanol gave V', m. p. 106°C, in an 80% yield.

**5-Chloro-7-bromo-3, 4-benzotropolone (VI).**—II (200 mg.) dissolved in 15 ml. of acetic acid was treated with an acetic acid solution of 56 mg. (1 mol. equiv.) of chlorine at room temperature for an hour. The solution was then concentrated to 5 ml. in vacuo and diluted with an equal volume of water, forming a precipitate (190 mg.) of a crude product, which on recrystallization from methanol yielded 110 mg. (48%) of VI as yellow needles, m. p. 111~115°C, besides 25 mg. of unchanged material. VI gave a brown coloration with ferric chloride in amyl alcohol solution.

Found: C, 46.37; H, 2.27. Calcd. for  $\text{C}_{11}\text{H}_6\text{O}_2\cdot\text{BrCl}$ : C, 46.27; H, 2.12%.

**5-Bromo-7-chloro-3, 4-benzotropolone (VII).**—A solution of 100 mg. of IV and 80 mg. (1 mol. equiv.) of bromine in 1 ml. of acetic acid was heated on a water bath for 2 hr. The crystalline product which separated on cooling was collected and recrystallized from methanol to give V as yellow needles, m. p. 122.5°C. Yield, 115 mg. (83%). VII gave a brown coloration with ferric chloride in amyl alcohol solution.

Found: C, 46.07; H, 2.08. Calcd. for  $\text{C}_{11}\text{H}_6\text{O}_2\cdot\text{BrCl}$ : C, 46.27; H, 2.12%.

**5, 6, 7-Trichloro-7-bromo-3, 4-benzocycloheptene-1, 2-dione (VIII).**—Chlorine gas was bubbled into a solution of 400 mg. of II in 25 ml. of acetic acid at room temperature for an hour, the excess chlorine removed under reduced pressure, and 50 ml. of water added. A crude product (420 mg., m. p. 113~117°C) separated after standing overnight. This was collected and recrystallized from methanol to yield yellow prisms of VIII, m. p. 124~125°C. VIII gave no coloration with ferric chloride.  $\nu$ ( $\text{CHCl}_3$ ): 1753, 1700  $\text{cm}^{-1}$ .  $\lambda$ (MeOH),  $m\mu$ (log  $\epsilon$ ): 215(4.14), 275(3.32), 340(3.02).

Found: C, 37.12; H, 1.72. Calcd. for  $\text{C}_{11}\text{H}_6\text{O}_2\cdot\text{BrCl}_3$ : C, 37.06; H, 1.70%.

**2, 3-Dichloro-1, 4-naphthoquinone from III.**—Into a solution of 250 mg. of III in 15 ml. of acetic acid was passed chlorine gas for 1.5 hr. at room temperature. After the removal of excess chlorine under diminished pressure, the solution was concentrated to 5 ml. and diluted with water to produce a precipitate. Sublimation at 110~120°C/7mmHg, followed by recrystallization from ethanol, gave yellow needles of 2, 3-dichloro-1, 4-naphthoquinone, m. p. 196~197°C, the melting point of which was undepressed on admixture with an authentic sample<sup>3)</sup> prepared by chlorination of  $\alpha$ -naphthoquinone. Yield, 60 mg. (35%).

**3, 4-Benzotropolone (I) from 7-Bromo-3, 4-benzotropolone (II) and Hydriodic Acid.**—A solution of 400 mg. of potassium iodide in 0.5 ml. of water was added to a suspension of 200 mg. of II in 5 ml. of acetic acid, and the mixture was heated in a

\* The content of chlorine in acetic acid solution was determined by iodometric titration.

sealed tube at 120~130°C for 2 hr. Dilution of the reaction mixture with water gave a brown precipitate, which was collected and dissolved in ether. The ethereal solution was shaken with sodium thiosulfate solution, the ether removed, and the residue recrystallized from petroleum ether to give 100 mg. (73%) of I, m. p. and mixed m. p. 83.5~84°C.

**5-Bromo-3,4-benzotropolone (XII).**—A solution of 300 mg. of potassium iodide in 0.5 ml. of water was added to a suspension of 200 mg. of 5,7-dibromo-3,4-benzotropolone (III) in 5 ml. of acetic acid, and the mixture was heated on a water bath for 5 hr. The product which separated on cooling was collected and recrystallized from methanol to yield 130 mg. (85%) of yellow needles, m. p. 140°C.  $\nu(\text{Nujol})$ : 1635, 1588, 1558  $\text{cm}^{-1}$ .  $\lambda(\text{MeOH})$ ,  $m\mu$  (log  $\epsilon$ ): 238(4.41), 263(4.33), 350(3.97), 375(3.99), 430(2.90).

Found: C, 52.86; H, 2.67. Calcd. for  $\text{C}_{11}\text{H}_7\text{O}_2\text{Br}$ : C, 52.61; H, 2.81%.

**5-Bromo-3,4-benzotropolone Methyl Ether.**—Colorless needles, m. p. 69~70°C.  $\nu(\text{Nujol})$ : 1623, 1600, 1572  $\text{cm}^{-1}$ .  $\lambda(\text{MeOH})$ ,  $m\mu$ (log  $\epsilon$ ): 240(4.18), 325(3.82), 360~370(3.65).

Found: C, 54.02; H, 3.23. Calcd. for  $\text{C}_{12}\text{H}_9\text{O}_2\text{Br}$ : C, 54.36; H, 3.42%.

**7-Iodo-3,4-benzotropolone (X).**—A mixture of 220 mg. of sodium iodide and 60 mg. of sodium iodate was added to a solution of 100 mg. of I in 5 ml. of acetic acid and 1.6 ml. of 2 N sulfuric acid. After standing for 10 min., the solution was diluted with water to produce a precipitate. An ethereal solution of the precipitate was shaken with sodium thiosulfate solution and the ether evaporated. The residue was recrystallized from methanol to give orange yellow crystals, m. p. 124~127°C. Yield, 70 mg. (40%).  $\nu(\text{Nujol})$ : 1612, 1590, 1550  $\text{cm}^{-1}$ .  $\lambda(\text{MeOH})$ ,  $m\mu$ (log  $\epsilon$ ): 268(4.32), 345(3.69), 360(3.90), 380(3.75).

Found: C, 44.57; H, 2.50. Calcd. for  $\text{C}_{11}\text{H}_7\text{O}_2\text{I}$ : C, 44.31; H, 2.37%.

**7-Iodo-3,4-benzotropolone Methyl Ether (X').**—A mixture of 100 mg. of 7-bromo-3,4-benzotropolone methyl ether (II'), 2 ml. of hydriodic acid and 2 ml. of methanol was heated for 10 min. on a water bath. Dilution with water gave a solid product.

An ethereal solution of the product was shaken with sodium thiosulfate solution. The ether was evaporated and the residue recrystallized from dilute methanol. Yellow scales, m. p. 99~100°C. Yield, 100 mg. (85%).  $\nu(\text{Nujol})$ : 1622, 1598, 1562  $\text{cm}^{-1}$ .  $\lambda(\text{MeOH})$ ,  $m\mu$ (log  $\epsilon$ ): 268(4.32), 350~355(3.66).

Found: C, 46.14; H, 3.18. Calcd. for  $\text{C}_{12}\text{H}_9\text{O}_2\text{I}$ : C, 46.17; H, 2.91%.

**5-Bromo-7-iodo-3,4-benzotropolone Methyl Ether (XI).**—A mixture of 100 mg. of 5,7-dibromo-3,4-benzotropolone methyl ether (III'), 2 ml. of hydriodic acid and 10 ml. of methanol was refluxed for 5 hr., and then the resulting solution was worked up in the same way as above. Yellow scales, m. p. 130~131°C. Yield, 80 mg. (68%).  $\nu(\text{Nujol})$ : 1631, 1602, 1582, 1560  $\text{cm}^{-1}$ .  $\lambda(\text{MeOH})$ ,  $m\mu$ (log  $\epsilon$ ): 267(4.40), 320(3.88).

Found: C, 36.69; H, 2.07. Calcd. for  $\text{C}_{12}\text{H}_9\text{O}_2\text{BrI}$ : C, 36.86; H, 2.06%.

**Methyl 1-Hydroxy-4-bromo-2-naphthoate from XI.**—To a solution of 200 mg. of XI in 18 ml. of methanol was added a solution of 280 mg. of potassium hydroxide in 0.8 ml. of water; the resulting solution was heated for 5 hr. on a water bath. The solution was acidified with 6 N hydrochloric acid, the methanol evaporated and the residue recrystallized from methanol to yield 100 mg. (70%) of colorless needles, m. p. 119.5~120.5°C, the melting point of which was undepressed on admixture with an authentic sample<sup>7</sup>.

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