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5-Bromo-2,3-benzotropone and its Maleic Anhydride Adduct[1]

Seiji EBINE, Masamatsu HOSHINO, and Takahisa MACHIGUCHI

Department of Chemistry, Faculty of Science and Engineering, Saitama University, Urawa, Saitama

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5,7-Dibromo-2,3-benzotropone (I),[2,3] obtained by the dehydrobromination of a tetrabromo derivative of 2,3-benzocycloheptenone, was debrominated on heating with a mixture of acetic and hydrobromic acids at 160°C to give 5-bromo-2,3-benzotropone (II). The position of the bromo substituent in II was established by the following NMR data. The spectrum of II (Fig. 1) contains an AB-type pattern consisting of H-7 at 6.67 ppm (d, $J_{7,6}$=12.8 Hz) and H-6 at 7.19 ppm (dd, $J_{6,7}$=12.8 and $J_{6,4}$=2.05 Hz), with perturbation arising from H-4 at 7.72 ppm (d, $J_{4,6}$=2.05 Hz). 7-Bromo-2,3-benzotropone (III),[4] prepared from 7,7-dibromo-2,3-benzocycloheptenone on treatment with lithium chloride, showed an entirely different NMR spectrum.[5a]

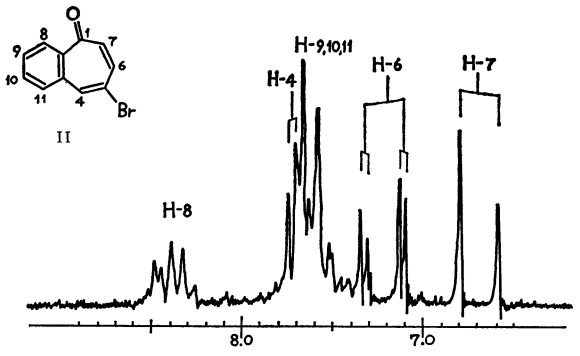
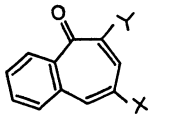
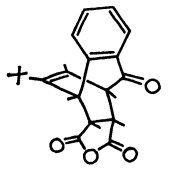


Fig. 1. NMR spectrum in deuteriochloroform at 60 MHz with TMS internal reference.

Chloro-2,3-benzotropone (IV), obtained by the reaction of 1-methoxynaphthalene with dichlorocarbene, has previously been assumed to be a 5- or 7-chloro compound.[6] The NMR spectrum of IV has an AB-type pattern consisting of H-7 at 6.88 ppm (d, $J_{7,6}$=13.0 Hz) and H-6 at 7.15 ppm (dd, $J_{6,7}$=13.0 and $J_{6,4}$=1.9 Hz) perturbed by H-4 at 7.81 ppm (d, $J_{4,6}$=1.9 Hz). The pattern is very similar to that of II, suggesting that IV is also 5-substituted. The dipole moment measurement of II and IV in a benzene solution has supported the above conclusion.[7] The X-ray crystal structure analysis of II and related compounds has also recently been undertaken.[5b]



I, X=Y=Br II, X=Br, Y=H
III, X=H, Y=Br IV, X=Cl, Y=H



V, X=Br VII, X=Cl

The Diels-Alder reaction of monocyclic troponoids has been studied,[8] and that of benzotroponoids has been briefly reported.[2,9] II underwent a Diels-Alder reaction with maleic anhydride on heating at 160—165°C to give an adduct (V). V was hydrolyzed, on standing in a dilute acetone solution at room temperature, to give the corresponding dicarboxylic acid (VI) which was, in turn, dehydrated with ease on refluxing in a benzene solution to give the original V, proving

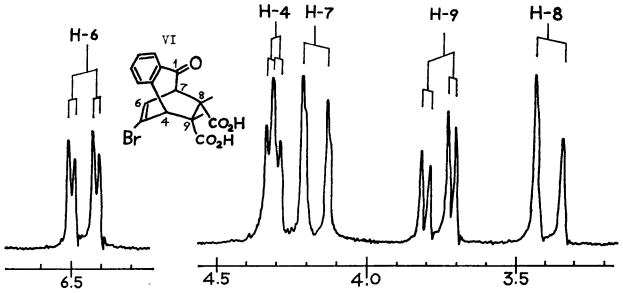


Fig. 2. NMR spectrum in acetone at 100 MHz with TMS internal reference.

1) a) Part IX in a series on 3,4-benzotropolone and related compounds: for Part VIII, see M. Hoshino and S. Ebine, This Bulletin, **43**, 1778 (1970). b) Presented at the 22nd Annual Meeting of the Chemical Society of Japan, Tokyo, April 2, 1969. Preprints III, p. 1468 (No. 16206).

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8) T. Nozoe, S. Seto, and T. Ikemi, *Proc. Japan Acad.*, **27**, 655 (1951); E. Sebe, and C. Osako, *ibid.*, **28**, 281 (1952); E. Sebe, and Y. Itsuno, *ibid.*, **29**, 107, 110 (1953); J. Meinwald, S. L. Emerson, N. C. Yang, and G. Büchi, *J. Amer. Chem. Soc.*, **77**, 4400 (1955); O. L. Chapman, and D. J. Pasto, *ibid.*, **81**, 3696 (1959); T. Nozoe, T. Mukai, T. Nagase, and Y. Toyooka, This Bulletin, **33**, 1247 (1960); T. Nozoe, and Y. Toyooka, *ibid.*, **34**, 623 (1961); Y. Kitahara, I. Murata, and T. Nitta, *Tetrahedron Lett.*, **1967**, 3003; S. Ito, H. Takeshita, Y. Shoji, Y. Toyooka, and T. Nozoe, *ibid.*, **1968**, 3215; **1969**, 443; S. Ito, K. Sakan, and Y. Fujise, *ibid.*, **1969**, 775.

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that VI is a *cis*-dicarboxylic acid. The stereochemistry of VI has now been established on the basis of the following NMR spectral analysis (Fig. 2). An apparent triplet at 4.31 ppm and a doublet at 4.17 ppm collapse to simpler signals on irradiation at an olefinic proton, H-6 at 6.45 ppm, and, alternately, a double doublet ($J_{6,7}$=8.1 and $J_{6,4}$=1.9 Hz) of H-6 collapses to a doublet ($J_{6,7}$=8.1 Hz) on irradiation at 4.31 ppm and to a doublet ($J_{6,4}$=1.9 Hz) on irradiation at 4.17 ppm. The aforementioned triplet and doublet, therefore, are ascribable to H-4 and H-7 respectively. By the use of a similar double-resonance method, an AB-type pattern in the higher field can be assigned to H-8 at 3.40 ppm (d, $J_{8,9}$=9.0 Hz) and H-9 at 3.75 ppm (dd, $J_{9,8}$= 9.0 and $J_{9,4}$=2.6 Hz) perturbed by H-4 (d, $J_{4,9}$=2.6 Hz). It follows, therefore, that, in agreement with the above chemical evidence, VI should be a *cis*-dicarboxylic acid based upon a large value of $J_{8,9}$ and should have an *endo*-configuration based upon a small value of $J_{4,9}$. The *endo-cis*-configuration of VI is further supported by the Nuclear Overhauser Effect (10.4%) observed between H-8 and H-9, and by a small value of $J_{7,8}$ ($\leq$1) not obserbable even in the 100 MHz spectrum, but evidenced by the sharpening of the H-7-doublet on irradiation at H-8, and *vice-versa*. The stereochemistry of V could not be concluded from the NMR spectrum because V failed to give a satisfactory chart because of its difficut solubility, but a facile interconversion between V and VI suggests that V assumes the same *endo*-configuration as VI. V and VI, however, did not undergo Alder-Stein bromolactonization,[10] presumably because of the presence of the 5-bromo substituent. IV reacted with maleic anhydride to afford an adduct (VII), which again failed to give detailed NMR spectral data.

Experimental

5-Bromo-2,3-benzotropone (II). A solution of 200 mg of I[2] in 20 m*l* of 47% hydrobromic acid and 25 m*l* of acetic acid was heated in a sealed tube at 160—165°C for 5 hr. The solution gave a positive potassium iodide-starch test, indicating the presence of free bromine. The hydrobromic and acetic acids were removed by evaporation *in vacuo*, and the residue was recrystallized from methanol to yield 100 mg (76% yield) of II as pale yellow needles melting at 102—103.5°C.

Found: C, 55.99; H, 3.20%. Calcd for $C_{11}H_7OBr$: C, 56.20; H, 3.00%.

I remained unchanged on treatment with hydrochloric acid in the same manner as above.

A solution of 100 mg of II and 70 mg of bromine in 10 m*l* of acetic acid was refluxed for 40 min; the product was then recrystallized from methanol to give 90 mg (67% yield)of I.

Diels-Alder Reaction of 5-Halo-2,3-benzotropones with Maleic Anhydride. The Adducts (V and VII): A mixture of 440 mg of II and 220 mg of maleic anhydride was heated at 160—165°C for 30 min. The mixture was treated with anhydrous ether to remove the excess maleic anhydride, and the crude product (570 mg; 91% yield; mp 220°C dec.) was recrystallized from benzene to give colorless granular crystals of the 5-bromo-2,3-benzotropone-maleic anhydride adduct (V); mp 242°C (dec.).

Found: C, 54.32; H, 2.97%. Calcd for $C_{15}H_9O_4Br$: C, 54.08; H, 2.72%.

A similar treatment of 100 mg of IV[6] with 150 mg of maleic anhydride gave 130 mg (87% yield) of colorless granular crystals of the 5-chloro-2,3-benzotropone-maleic anhydride adduct (VII); mp 217.5—218.5°C.

Found: C, 62.62; H, 3.31%. Calcd for $C_{15}H_9O_4Cl$: C, 62.40; H, 3.14%.

Derivatives of V. a) Dicarboxylic Acid (VI): A solution of 340 mg of V in dilute acetone (35 m*l* of acetone and 20 m*l* of water) was allowed to stand at room temperature for 3 days. On the subsequent evaporation of the solvent below 30°C *in vacuo*, there remained 330 mg (91% yield) of colorless prisms of VI melting at 241—242°C (dec.). The hydrolysis of V with dilute alkali at room temperature gave the same result. VI gave the original V in 90% yield on refluxing in a benzene solution for 1.5 hr.

Found: C, 51.31; H, 3.19%. Calcd for $C_{15}H_{11}O_5Br$: C, 51.30; H, 3.16%.

b) Monomethyl Ester: A solution of 300 mg of V in 160 m*l* of methanol was allowed to stand at room temperature for a day. The subsequent evaporation of the solvent and recrystallization of the residue from dilute acetone (1: 1) gave 290 mg (88% yield) of the monomethyl ester as colorless needles; double mp 112°C and 238°C.

Found: C, 50.15; H, 3.94%. Calcd for $C_{16}H_{13}O_5Br \cdot H_2O$: C, 50.15; H, 3.95%.

c) Dimethyl Ester: The methylation of 200 mg of VI with diazomethane in an ether solution afforded 120 mg (55% yield) of the dimethyl ester as colorless granular crystals; mp 113—113.5°C.

Found: C, 53.84; H, 4.07%. Calcd for $C_{17}H_{15}O_5Br$; C, 53.84; H, 3.99%.

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