

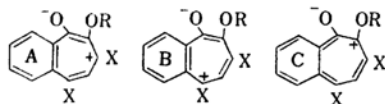
*Anionoid Substitution of Bromo-
3, 4-benzotropolones**

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(Received April 15, 1961)

It was recently reported that 3, 4- and 4, 5-benzotropolones failed to react with thionyl chloride¹⁾. The present author has studied on anionoid substitution of bromo-3, 4-benzotropolones in detail and the results are summarized herein.

7-Bromo-3, 4-benzotropolone (I) reacts with thionyl chloride to yield an adduct, m. p. 147°C (Found: C, 35.77; H, 1.80. Calcd. for $C_{11}H_7O_2Br \cdot SOCl_2$: C, 35.69; H, 1.91%), which, on recrystallization from ethanol, gives 5, 7-dichloro-3, 4-benzotropolone, m. p. 137°C (Found: C, 54.97; H, 2.40. Calcd. for $C_{11}H_6O_2Cl_2$: C, 54.80; H, 2.51%). 5, 7-Dibromo-3, 4-benzotropolone (II) with thionyl chloride affords the same dichlorobenzotropolone. The methyl ethers of I and II react with dilute hydrochloric acid in methanol at reflux temperature to give 7-chloro-3, 4-benzotropolone methyl ether, m. p. 97°C (Found: C, 65.30; H, 4.06. Calcd. for $C_{12}H_9O_2Cl$: C, 65.31; H, 4.11%) and 5, 7-dichloro-3, 4-benzotropolone methyl ether, m. p. 106°C (Found: C, 56.46; H, 3.11. Calcd. for $C_{12}H_8O_2Cl_2$: C, 56.49; H, 3.16%), respectively. The methyl ether of I, on treatment with dilute alkali in methanol at room temperature, affords 6-hydroxy-7-methoxy-2, 3-benzotropone, m. p. 115~116°C (Found: C, 71.56; H, 5.06. Calcd. for $C_{12}H_{10}O_3$: C, 71.28; H, 4.99%). In these reactions, the hydroxyl groups of bromobenzotropolones and the methoxyl groups of their methyl ethers remained unaffected, whereas the bromine atoms at 5- and 7-positions of these compounds were replaced with ease.



These behaviors of bromobenzotropolones and their methyl ethers are different from those of monocyclic bromotropolones and their methyl ethers; bromotropolones react with

thionyl chloride to yield chlorotropones²⁾ and their methyl ethers, on treatment with dilute alkali are hydrolyzed or further rearranged into aromatic compounds, bromines remaining unreplaced³⁾. Such a difference in behavior may be ascribed to the resonance structures of bromobenzotropolones and their methyl ethers. The contribution of the formulas A and B are great but that of the formula C is to a limited extent because its benzene ring is not aromatic but quinonoid, hence the bromines at 5- and 7-positions are highly susceptible to but the 1-hydroxyl and 1-methoxyl groups are almost inert towards the anionoid substitution.

II is reduced with hydriodic acid at 100°C to 5-bromo-3, 4-benzotropolone, m. p. 140°C (Found: C, 52.86; H, 2.67. Calcd. for $C_{11}H_7O_2Br$: C, 52.61; H, 2.81%). The methyl ether of II reacts with hydriodic acid in methanol under reflux to afford 5-bromo-7-iodo-3, 4-benzotropolone methyl ether, m. p. 130~131°C (Found: C, 36.69; H, 2.07. Calcd. for $C_{12}H_8O_2BrI$: C, 36.86; H, 2.06%) and rearranges with dilute alkali in methanol under reflux into 1-hydroxy-4-bromo-2-naphthoic acid, m. p. and mixed m. p. 237°C (decomp.). Coupling of II with diazotized *p*-toluidine produces 2-(*p*-tolylazo)-4-bromo-1-naphthol, m. p. and mixed m. p. 183~184°C. In these reactions, the bromine at 5-position of II or its methyl ether remained unreplaced, presumably because the action of iodide, hydroxide and diazonium ions on the 5-position is sterically hindered due to being the *peri* position of the condensed benzene ring. This fact seems to be another characteristic of bromobenzotropolones.

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

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