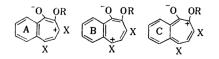
Anionoid Substitution of Bromo-3, 4-benzotropolones*

By Seizi EBINE

(Received April 15, 1961)

It was recently reported that 3, 4- and 4, 5benzotropolones 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 C₁₁H₆O₂Cl₂: 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 $C_{12}H_9O_2C1$: C, 65.31; H, 4.11%) and 5, 7dichloro-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 1hydroxyl 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 $C_{11}H_7$. $O_2Br: C, 52.61; H, 2.81\%$). The methyl ether of II reacts with hydriodic acid in methanol under reflux to afford 5-bromo-7-iodo-3, 4benzotropolone methyl ether, m. p. $130 \sim 131^{\circ}C$ (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. $183 \sim 184^{\circ}$ 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.

> Department of Chemistry Saitama University Urawa, Saitama-ken

^{*} Presented at the 14th Annual Meeting of the Chemical Society of Japan, Tokyo, April, 1961. 1) W. E. Parham, D. A. Bolon and E. E. Schweizer, J.

W. Le, Soc., 83, 603 (1961).
W. von E. Doering and L. H. Knox, ibid., 74, 5683 (1952);
B. J. Abadir, J. W. Cook, J. D. Loudon and D. K. V. Steel, J. Chem. Soc., 1952, 2350.

³⁾ T. Nozoe, Y. Kitahara and S. Masamune, Proc. Japan Acad., 27, 649 (1951).