SHORT COMMUNICATIONS

p-Quinols from the Nitration Product of Dihaloprehnitenes

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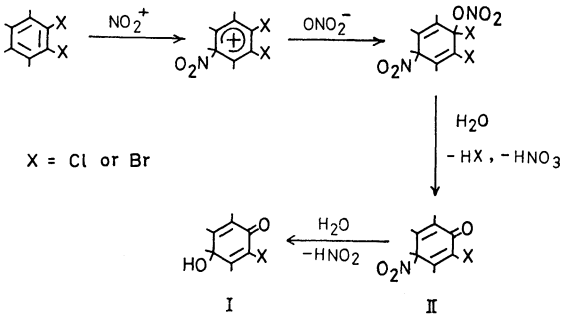
Nitration of halopentamethylbenzenes and dihalotetramethylbenzenes with fuming nitric acid gives, as a major product, benzyl nitrate or bis(nitro-oxymethyl)-benzene.[1,2] The crude product usually contains small amounts of carbonyl by-products arising from the oxidation of the nitro-oxymethyl compounds.[3] In a previous paper,[2] it was reported that 5,6-dihaloprehnitenes (5,6-dihalo-1,2,3,4-tetramethylbenzenes) are unusual in their ability to form a substantial amount (*ca.* 10—15%) of carbonyl compounds, the major component of which is now identified as 6-halo-4-nitro-2,3,4,5-tetramethyl-2,5-cyclohexadien-1-one (II), a new class of anomalous nitration product.

When 5,6-dichloroprehnitene was treated with fuming nitric acid (d=1.5) in dichloromethane at −5—0°C and the product mixture was subjected to chromatographic separation over alumina, using light petroleum, benzene and diethyl ether as eluents, the fractions eluted with a mixture of benzene and diethyl ether gave a carbonyl compound melting at 178—179°C as large prisms. The result of elemental analysis was consistent with the composition $C_{10}H_{13}ClO_2$ (Found: C, 60.0; H, 6.8; Cl, 17.3; O, 16.0%. Calcd for $C_{10}H_{13}ClO_2$: C, 59.8; H, 6.5; Cl, 17.5; O, 16.2%), and its infrared spectrum (in Nujol) showed prominent peaks at 766, 774, 902, 1073, 1083 (C–OH), 1224, 1270 (C–C=O), 1612 (C=C), 1636 (C=O), and 3400 cm^{-1} (OH). The possibility that the product is benzaldehyde or benzoic acid was immediately ruled out by its ^1H NMR spectrum (100 MHz, $CDCl_3$), which exhibited signals of four methyl groups (8.61, 8.19, 7.94, and 7.80 τ) and a hydroxyl group (*ca.* 7.0 τ). Ultraviolet spectrum (in CH_3OH) showed absorptions at 246—247 nm (log ε=4.08) and 286—287 nm (log ε= 3.34), which are characteristic of cross-conjugated cyclohexadienones. Comparison of the chemical shifts of its methyl groups with those of known polymethylcyclohexadienones readily revealed the presence of chlorine atom at a position next to the carbonyl group. The mass spectrum had a molecular ion peak at m/e 200, and fragment ion peaks at m/e 185 (M−CH_3), 165 (M−Cl), 157 (M−CH_3−CO), and 137 (M−Cl−CO). These spectral evidences permit the formulation of the ketonic product as *6-chloro-4-hydroxy-2,3,4,5-tetramethyl-2,5-cyclohexadien-1-one* (I, X=Cl). Since the infrared and ^1H NMR spectra of the original mixture had no indication of the presence of I, the quinol seems to be derived from the initially formed *6-chloro-4-nitro-2,3,4,5-tetramethyl-2,5-cyclohexadien-1-one* (II, X=Cl) through hydrolysis during the chromatographic treatment over alumina. The nitro group at 4-position of these systems is known to be subject to a facile hydrolysis.[4]

6-Bromo-4-hydroxy-2,3,4,5-tetramethyl-2,5-cyclohexadien-1-one (I, X=Br; mp 190—191°C) was similarly obtained from 5,6-dibromoprehnitene. IR: 739, 1070, 1085, 1216, 1260, 1607, 1637, and 3420 cm^{-1}; NMR: 8.64, 8.20, 7.98, 7.80 (CH_3), and *ca.* 7.3 τ (OH); UV: 248—249 (log ε=4.06) and 284—287 nm (log ε=3.30). Found: C, 49.0; H, 5.4%. Calcd for $C_{10}H_{13}BrO_2$: C, 49.0; H, 5.4%.

We suggest that the unusual product I is formed by the reaction sequence depicted in the Scheme. As the reaction seems to possess some synthetic potentials, the scope of the anomaly is being investigated.



1) L. I. Smith and J. W. Horner, *J. Amer. Chem. Soc.*, **62**, 1349 (1940); H. Suzuki, This Bulletin, **43**, 481 (1970).

2) H. Suzuki, K. Nakamura, and M. Takeshima, *ibid.*, **44**, 2248 (1971).

3) H. Suzuki and K. Nakamura, *ibid.*, **43**, 473 (1970); H. Suzuki, *ibid.*, **43**, 879 (1970).

4) E. Müller, A. Schick, and K. Scheffler, *Chem. Ber.*, **92**, 474 (1959).