SHORT COMMUNICATIONS

p-Quinols from the Nitration Product of Dihaloprehnitenes

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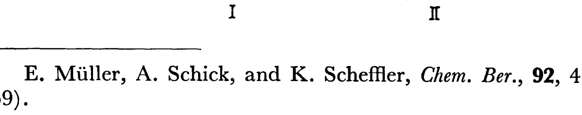
Nitration of halopentamethylbenzenes and dihalotetramethylbenzenes with fuming nitric acid gives, as a major product, benzyl nitrate or bis(nitro-oxymethyl)-benzene.[1,2] The crude product usually contains small amounts of carbonyl by-products arising from the oxidation of the nitro-oxymethyl compounds.[3] 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 ^{1}H 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 ($\log \varepsilon$=4.08) and 286—287 nm ($\log \varepsilon$=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 ^{1}H 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 ($\log \varepsilon$=4.06) and 284—287 nm ($\log \varepsilon$=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.



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[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).