Quinol Nitrates from the Reaction of Tetrachloroxylenes with Fuming Nitric Acid

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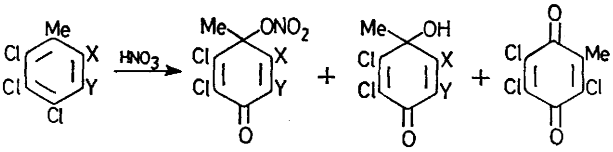
Summary Treatment of tetrachloro-*o*- and *m*-xylenes with fuming nitric acid gives 3,5,6-trichloro-1,2-dimethyl-4-oxocyclohexa-2,5-dienyl nitrate and 2,5,6-trichloro-1,3-dimethyl-4-oxocyclohexa-2,5-dienyl nitrate, respectively, as the major products.

SIDE-CHAIN substitution and formation of unsaturated cyclic ketones are the major, unexpected, reactions of polymethylbenzenes and their derivatives on treatment with conc. HNO_3. Products so far obtained include benzyl nitrates, phenylnitromethanes, benzaldehydes, nitrocyclohexenones, and nitrocyclohexadienones. In view of the current interest in the unusual 'nitration' products,[1] we report a further example, the quinol nitrate (I), which to our knowledge is the first nuclear nitrate ester isolated from the nitration mixtures.

Treatment of tetrachloro-*o*-xylene with a large excess of fuming nitric acid (*d* 1·50) at room temperature for several hours, followed by quenching with water, washing the precipitate with aqueous $NaHCO_3$ and water, and fractional crystallization from ethanol gave the nitrate (Ia), m.p. 145—146° (decomp.), as the principal product (30—35%), identified on the basis of the following evidence; *m/e* 285 (M^+, $C_8H_6Cl_3NO_4$), 239 ($M^+ - NO_2$), 223 ($M^+ - NO_3$), and 221 ($M^+ - NO_2 - CO$); ν_{max} (Nujol) 1683 (C=O), 1646 (ONO_2), 1600 (C=C), 1292 (ONO_2), 1188, 1140, and 1042 cm^{-1};

δ ($CDCl_3$) 1·71 and 2·27; λ_{max} (MeOH) 254—255 (log ε 4·05) and 286—290 nm (3·44). Compound (Ia) was not readily hydrolysed. Other products were the dienone (IIa; 18—25%), m.p. 166—167°, and the known quinone (III; < 5%). No side-chain substitution product was obtained.



(I) (II) (III)

a; X = Me, Y = Cl
b; X = Cl, Y = Me

When dissolved in nitric acid, (IIa) was converted into (Ia), which on prolonged contact with the nitrating agent was further converted into (III). Reduction of (IIa) with Zn–AcOH yielded 2,5,6-trichloro-*o*-xylen-4-ol.

Similar treatment of tetrachloro-*m*-xylene gave a mixture of carbonyl compounds, the major components being (Ib), m.p. 135—136°, and (IIb), m.p. 151—152°, although yields were lower under comparable conditions (25—30 and 15—24%, respectively). In contrast, and as expected from our earlier work,[2] tetrachloro-*p*-xylene was simply converted into 2,3,5,6-tetrachloro-4-methylbenzyl nitrate in 82% yield, m.p. 80—82°.

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[1] For reviews, see S. R. Hartshorn, *Chem. Soc. Rev.*, 1974, **3**, 167; H. Suzuki, *Bull. Inst. Chem. Res. Kyoto Univ.*, 1972, **50**, 407.

[2] H. Suzuki, O. Yagiu, and T. Hanafusa, *Bull. Chem. Soc. Japan*, 1974, **47**, 2260, and other papers in the series.