An Abnormal Dinitration Product from 4,6-Dibromo-2,5-dimethylphenol; *X*-Ray Crystal Structure of 2,4-Dibromo-6-hydroxy-3,6-dimethylcyclohex-3-enone

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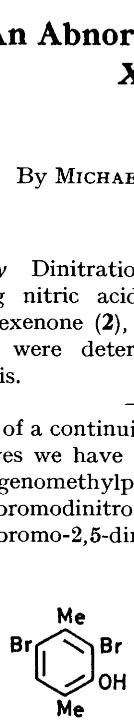
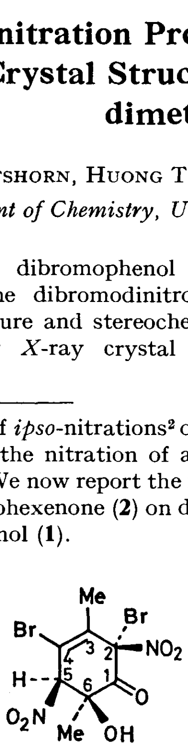
Summary Dinitration of the dibromophenol (**1**) with fuming nitric acid gives the dibromodinitrohydroxycyclohexenone (**2**), the structure and stereochemistry of which were determined by *X*-ray crystal structure analysis.

As part[1] of a continuing study of *ipso*-nitrations[2] of benzene derivatives we have examined the nitration of a series of polyhalogenomethylphenols. We now report the formation of the dibromodinitrohydroxycyclohexenone (**2**) on dinitration of 4,6-dibromo-2,5-dimethylphenol (**1**).



(**1**)



(**2**)

Addition of fuming nitric acid (1 ml/g phenol) to a stirred suspension of the dibromophenol (**1**)[3] in acetic acid at 20 °C gave a red solution from which the dinitro-compound (**2**) (36%) slowly crystallised. This compound, m.p. 117 °C (decomp.), had the molecular formula $C_8H_8Br_2N_2O_6$ [elemental analysis and *X*-ray structure analysis (see below)] and was characterised partially through its spectroscopic data. Its i.r. spectrum revealed the major functionalities of the compound: ν_{max} (Nujol) 3540 (OH), 1746 (non-conjugated C=O) 1630 (C=C), 1585, and 1573 cm^{-1} (NO_2), while its u.v. spectrum: λ_{max} (EtOH), 203 (ϵ 12,750) and 240sh (ϵ 7050) nm and its ^{2}H n.m.r. spectrum ($CDCl_3$): δ 1·83 (s, 6-Me), 2·15 (s, 3-Me), and 5·84 (s, 5-H), were consistent with the assigned $\beta\gamma$-unsaturated ketone structure. Its ^{13}C n.m.r. spectrum (CD_3COCD_3, −25 °C) exhibited the following signals: δ 21·11 (C-8), 27·89 (C-7) 77·65 (C-6), 99·80 (C-5), 119·50 (C-2), 125·54 (C-3), 139·45 (C-4), and 193·46 p.p.m. (C-1); argument in support of these assignments will be presented elsewhere.

Because of the unusual nature of the dinitration product (**2**), the determination of its structure by *X*-ray crystal-structure analysis was necessary.

Crystal data: triclinic, space group $P\bar{1}$, a = 8·932(6), b = 11·329(8), c = 6·232(5) Å, α = 83·2(1), β = 102·4(1), γ = 97·5(1)°, U = 607·97 Å^3, D_c = 1·78 g cm^{-3}, Z = 2. Intensity data were collected to 2θ = 18° on a Hilger and Watts 4-circle automatic diffractometer using Zr filtered Mo-K_α radiation; 320 reflections having $F_0 > 3\sigma(F_0)$ were used. The structure was solved by Patterson and difference Fourier methods and refined to R = 0·063 using anisotropic thermal parameters for Br atoms only. Hydrogen atoms

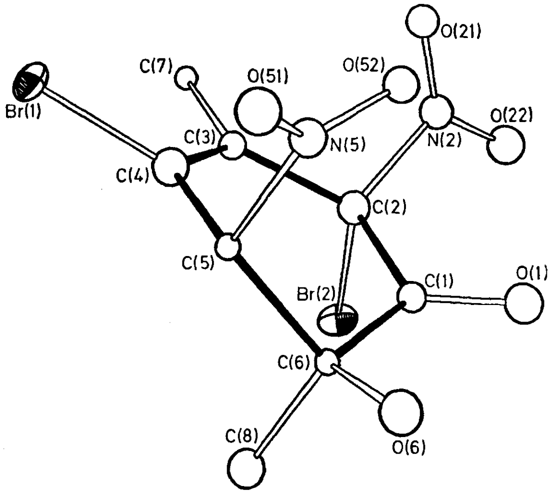


FIGURE. *X*-Ray crystal structure of compound (**2**).

were not included in these refinements and structure factor calculations. The resulting structure consists of the well separated monomeric molecules shown in the Figure.†

Notable in the formation of the dinitration product (**2**) is the introduction of the new functional groups at C-2, C-5, and C-6 in an all-*cis* relationship, including the C-5-NO_2 function at a position *meta* to the phenolic OH in the dibromophenol (**1**).

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† The atomic co-ordinates for this work are available on request from the Director of the Cambridge Crystallographic Data Centre, University Chemical Laboratory, Lensfield Road, Cambridge CB2 1EW. The structure factor table is available as Supplementary Publication No. Sup. 23020 (3 pp.) from the British Library. For details, see Notice to Authors No. 7, *J. Chem. Soc., Perkin* or *Dalton Trans.*, Index issues.

[1] Previous paper: A. H. Clemens, M. P. Hartshorn, K. E. Richards, and G. J. Wright, *Aust. J. Chem.*, 1977, **30**, 113.
[2] For a review, see R. B. Moodie and K. Schofield, *Acc. Chem. Res.*, 1976, **9**, 287.
[3] K. Auwers and J. Ercklentz, *Liebigs Ann. Chem.*, 1898, **302**, 114.