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DINITRATION STUDIES OF 2,4,5-TRIBROMO-3,6-DIMETHYLPHENOL: THE FORMATION OF AN ACYLOIN REARRANGEMENT PRODUCT

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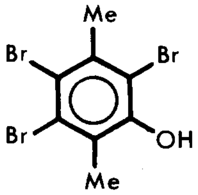
Summary: Dinitration of 2,4,5-tribromo-3,6-dimethylphenol(1) gives either the tribromodinitro-compound(2) or its acyloin rearrangement product(3), depending on the reaction conditions: X-ray crystal structure analyses are reported for compounds (2) and (3).

Zincke and Breitweiser[1] in 1911 reported the formation of two isomeric dinitration products of molecular formula $C_8H_7Br_3N_2O_6$ from the tribromophenol(1). We now report the structures of these two products.

Nitration of the tribromophenol(1) with fuming nitric acid (5.5 moles) in acetic acid (5 ml/g. phenol(1)) at 20° (or with nitric acid, d. 1.48) gave a red solution from which crystallised 2,4,5-tribromo-2,5-dinitro-6-hydroxy-3,6-dimethylcyclohex-3-enone(2;58%), m.p. 102° (d.) [Lit.[1] m.p. 104° (d.)]. This tribromodinitro-compound(2) was identified through its spectroscopic data, by comparison with data for the dibromodinitro- compound(4)[2], and by single crystal X-ray structure analysis. Crystals of the tribromodinitro- compound(2) ($C_8H_7Br_3N_2O_6$) belong to the monoclinic system, space group $P2_1/C$, with $a = 13.063(3)$, $b = 9.173(4)$, $c = 11.011(3)$ Å, $\beta = 95.04(2)^{\circ}$, $z = 4$, $D_c = 2.36$ g cm^{-3}. Intensity data, with $2\theta \leqslant 40^{\circ}$, were collected using a Hilger and Watts four-circle diffractometer and Zr filtered Mo-Kα radiation. The reflection data were corrected for absorption and, of the 1451 unique reflections, 701 were judged observed, $I > 3\sigma(I)$, and used in all refinement calculations. A three-dimensional Patterson synthesis was used to determine the bromine atom positions and the remaining non-hydrogen atoms were located using conventional difference Fourier syntheses. Full-matrix refinement of atomic positional and thermal



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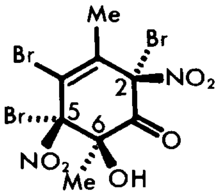

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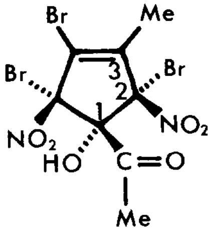

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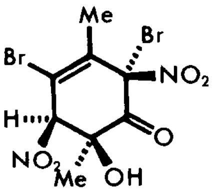


(4)

(anisotropic Br, O; isotropic N,C) parameters converged to give a conventional R-factor = 0.069. The resulting structure consists of the well-separated monomeric molecules shown in Fig.1.[3]

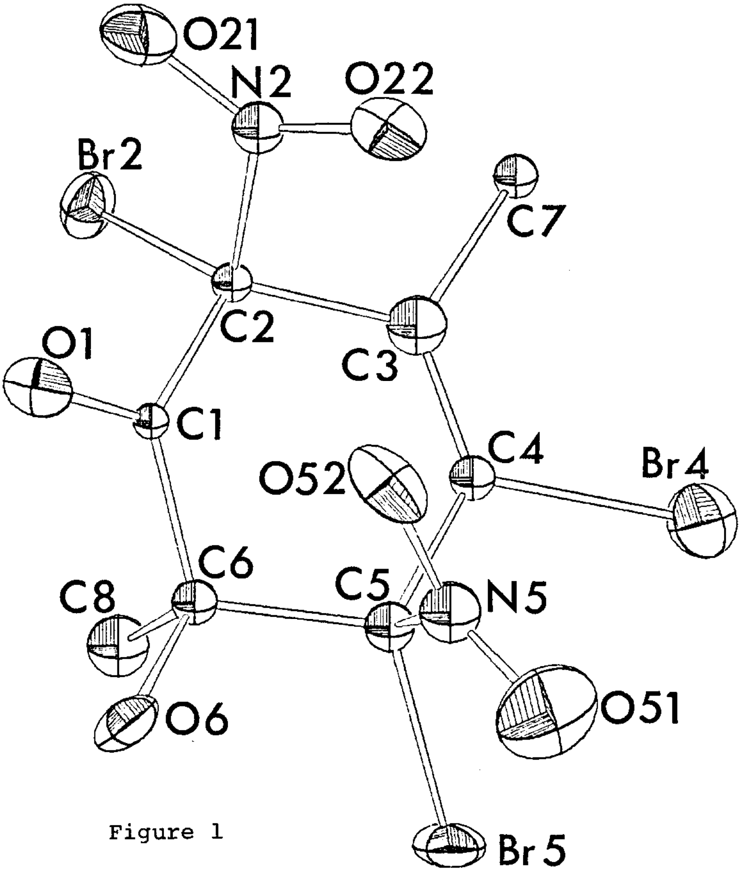


Figure 1

Nitration of the tribromophenol(1), as above except that water (1ml/5ml AcOH used) was added to the reaction mixture twenty minutes after the addition of the fuming nitric acid, gave the cyclopentenol derivative (3;47%), m.p. 141° (Lit.[1] m.p. 141°), the structure of which was determined by single crystal X-ray analysis (see below). This material (3) was also readily obtained in high yield by triturating the tribromodinitro- compound(2) with 2M aqueous sodium carbonate solution.[1] The infrared spectrum of the cyclopentenol(3) revealed the major functionality of the compound: ν_{max}(nujol) 3480(OH);1716(C=O);1620(C=C);1580,1570 (NO_2), and the magnetic resonance spectra were as follows: ^1H n.m.r.($CDCl_3$) 2.35,Me;2.36,Me;4.57,OH: ^{13}C n.m.r.(CD_3COCD_3,-25°)16.82,CO-$\underline{Me}$;26.89,C3-$\underline{Me}$;89.55, C1;101.32,C5[4];103.16,C2[4];125.13,C4;145.01,C3;181.78,$\underline{C}$O-Me[5].

The cyclopentenol derivative(3) ($C_8H_7Br_3N_2O_6$) crystallises in the triclinic space group $P\bar{1}$ with a = 8.398(4), b = 14.668(9), c = 6.363(3) Å, α = 92.34(5), β = 110.54(4), γ = 112.52(3)°, z = 2, D_c = 2.34 g cm^{-3}. Intensity data with $2\theta \leq 44^{\circ}$ were also collected using Zr filtered Mo-Kα radiation. The reflection data were corrected for absorption and, of the 1615 unique reflections, 922 were judged observed. A three-dimensional Patterson synthesis was used to determine two of the bromine atom positions and the remaining non-hydrogen atoms were located using conventional difference Fourier syntheses. On refinement, using full-matrix least-squares, it became apparent that the crystal was statistically disordered. Detailed electron density contour maps are consistent with one methyl group and one bromine atom being attached, with equal probability, to ring carbon atoms C3 and C4. Thus enantiomers, obtained by reflection in the obvious pseudo-mirror plane of symmetry (Fig.2), occur with equal probability throughout the crystal. The refined model necessarily contains half-carbon (C8) and half-bromine (Br3) atoms in near pseudo-mirror equivalent positions to the half-atoms, C9 and Br4 shown in Fig.2. Though refined separately the parameters defining the pair of half-atoms C9,Br3 and those defining C8,Br4 are correlated. Accordingly estimated standard deviations for these half-carbon atoms are high

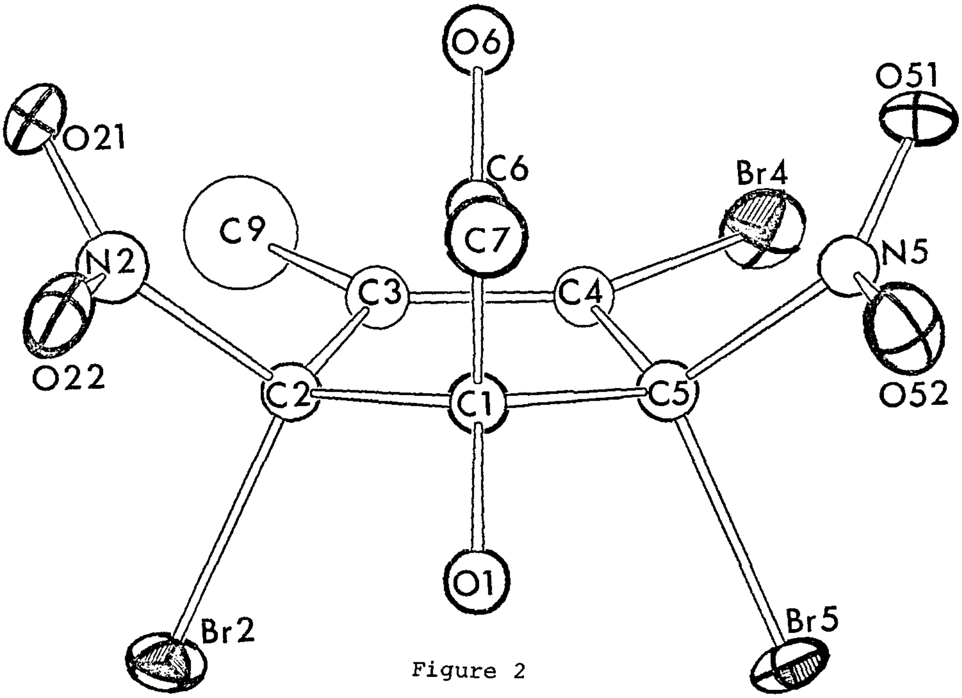
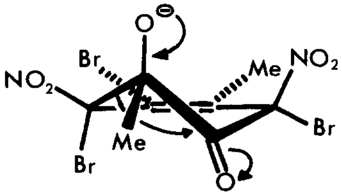


Figure 2

with respect to ordered parts of the structure. With the bromine and nitro group oxygen atoms treated anisotropically, and all other non-hydrogen atoms treated isotropically the refinement converged to give a conventional R-factor of 0.060.

Notable in the structure of the cyclopentenol derivative(3) is the relative stereochemistry of C1, C2 and C5. The formation of this stereoisomer in the acyloin rearrangement of hydroxyketone(2) requires that rearrangement occurs in the half-chair conformation(5)[6]; the alternative half-chair structure present in the solid state (Fig.1) is presumably stabilised by intramolecular hydrogen-bonding in the α-hydroxyketone system.



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REFERENCES AND NOTES

1. T. Zincke and W. Breitweiser, Chem. Ber., 1911, **44**, 176.
2. M.P. Hartshorn, Huong Tuong Ing, K.E. Richards, and W.T. Robinson, J.C.S. Chem. Commun., 1981, 225.
3. The atomic co-ordinates for this work are available on request from the Director of the Cambridge Crystallographic Data Centre, University Chemical Laboratories, Lensfield Road, Cambridge CB2 1EW.
4. These assignments may be interchanged.
5. Argument in support of these assignments will be presented elsewhere.
6. Shown for the base-catalysed acyloin rearrangement.

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