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THE REARRANGEMENT OF SOME 2-SUBSTITUTED-4-BROMO-2,5-DINITRO-6-HYDROXY-3,6-DIMETHYLCYCLOHEX-3-EN-1-ONES

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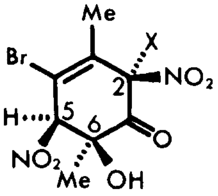
Summary: In chloroform at 20°, or in tetrachloroethylene at 120°, the title compounds(1) rearrange to give the α-diketone(2), the structure of which was determined by X-ray crystal structure analysis; a possible rearrangement mechanism is outlined.

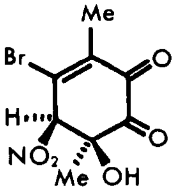
Recently we reported[1] the formation of the dibromodinitro-compound(1a) on nitration of 4,6-dibromo-2,5-dimethylphenol with fuming nitric acid in acetic acid. We now report a rearrangement displayed by this compound in halocarbon solvents.

The dibromodinitro- compound(1a) on heating in tetrachloroethylene solution at 120° for 1 hour, or more slowly (16 days) in chloroform at 20°, gave the α-diketone(2), m.p. 150°(d.) and molecular formula $C_8H_8BrNO_5$[2], the structure of which was determined by single crystal X-ray analysis (see below). The bromochlorodinitro- compound(1b)[2,3] also gave the α-diketone(2) on similar treatment. The infrared spectrum of the α-diketone(2) revealed the major functionality of the compound: ν_{max}(nujol) 3480(-OH);1755(C=O);1692(conjugated C=O);1604(C=C);1586cm^{-1}(NO_2), while its ultraviolet spectrum, $\lambda_{max}^{CHCl_3}$ 280nm(ε 8530) confirmed the presence of the conjugated ketone chromophore. The magnetic resonance spectra for the α-diketone(2) were as follows: p.m.r.($CDCl_3$) 1.57,s,C6-Me;2.18,s,C3-Me;5.68,s,H5: c.m.r.(CD_3COCD_3) 17.04,C7;23.01,C8;79.35,C6; 101.2,d,C5;134.5,C3;147.34,C4;179.63,C2;190.82,C1.[4]



(1) (a) X = Br

(b) X = Cl



(2)

Because of the established structural complexity of the dibromodinitro- compound(1a), and the consequent need for definitive stereochemical information for rearrangement product its X-ray crystal structure analysis is reported. Crystals of the α-diketone ($C_8H_8BrNO_5$) belong to the orthorhombic system, space group $P2_12_12_1$, with a = 9.548(3), b = 12.830(5), c = 8.340(5)Å; U = 1022Å^3, Z = 4 and d_{calc} = 1.81 g cm^{-3}. Intensity data with 2θ < 134° were collected using a Hilger and Watts four-circle diffractometer, nickel filtered Cu Kα (λ = 1.541 8Å) radiation and the θ-2θ scan technique. Of the 943 reflections measured, 478 were judged observed (I ⩾ 3σ(I). A three-dimensional Patterson synthesis was used to determine the bromine position and the remaining non-hydrogen atoms were located using difference Fourier syntheses. Full-matrix least-squares refinement of atomic positional and thermal (anisotropic Br, O; isotropic N,C) parameters converged to give a conventional R-factor of 0.063. Figure 1 is a perspective drawing of the molecule generated from the final coordinates[5]. Notable in the structure of the α-diketone(2) is that the relative stereochemistry of C5 and C6 in the dinitroketones(1) is retained during the rearrangement.

The progress of the rearrangement of the dinitroketone(1) in deuterochloroform to give the α-diketone(2) was followed by repeatedly recording the p.m.r. of a solution of (1). Comparison of the sets of p.m.r. spectra for each compound(1) revealed that two intermediates were formed in the transformation and that the first reaction step probably involved C2-halogen bond cleavage. A possible rearrangement mechanism is outlined in the Scheme.

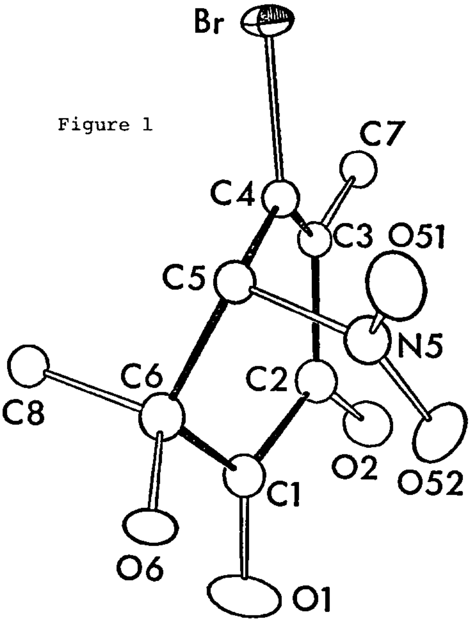
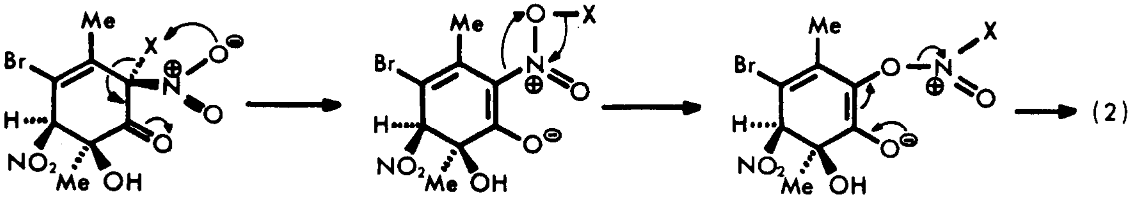


Figure 1



(1)

REFERENCES AND NOTES

1. M.P. Hartshorn, Huong Tuong Ing, K.E. Richards, and W.T. Robinson, J.C.S.Chem.Commun., *in press*.
2. Satisfactory elementary analysis data were obtained for new compounds.
3. The preparation of the bromochlorodinitro- compound(lb) will be reported later.
4. Argument in support of these assignments will be presented elsewhere.
5. 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 lEW.

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