Tetrahedron Letter Vol. 21, pp 1163 - 1164
©Pergamon Press Ltd. 1980. Printed in Great Britain

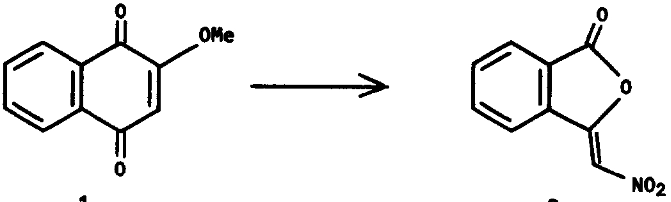
0040-4039/80/0315-1163$02.00/0

A NOVEL REARRANGEMENT OF 2-METHOXY-1,4-NAPHTHOQUINONE TO 3-NITROMETHYLENE PHTHALIDE

Balawant S. Joshi* and Vinod R. Hegde
CIBA-GEIGY Research Centre, Goregaon, Bombay 400063
and
Donald Rogers and David J. Williams
Chemical Crystallography Laboratory, Imperial College, London SW7 2AY

2-Methoxynaphthoquinone under nitrating conditions afforded 3-nitromethylene phthalide, the structure of which was solved by an X-ray crystallographic analysis.

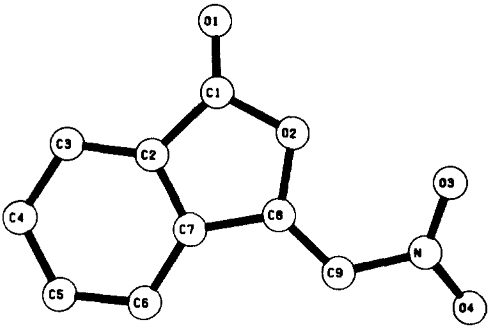
We report here the nitration of 2-methoxy-1,4-naphthoquinone 1 with potassium nitrate and conc. sulphuric acid to afford 3-nitromethylene phthalide 2.



1 2

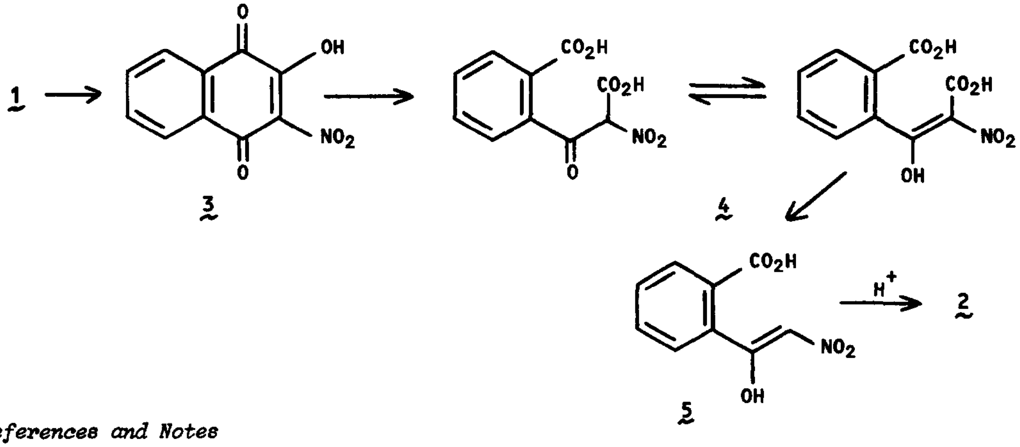
The quinone 1 (10.0g) in conc. sulphuric acid (60ml) was stirred at 30° in a three-necked flask and powdered potassium nitrate (50g) was added in small portions during 1hr. The solution was stirred for 1hr more and poured into crushed ice. The yellow precipitate was collected, washed with water and crystallized from ethylacetate to give yellow needles, m.p. 226-228° dec., $C_9H_5NO_4$; UV(EtOH) λ_{max} 277 (infl.), 282 and 330nm (logε 3.19, 3.21 and 2.93); IR (nujol) ν_{max} 1805, 1660, 1640cm^{-1}. NMR ($CDCl_3/CD_6SOCD_6$) 8.28 (s, 1H), 8.0 (m, 4H); MS $^m/e$ 191 (M^+, 100%), 161 (45), 133 (85). The compound 2 was also obtained by nitration of 2-hydroxy-1,4-naphthoquinone or 2-hydroxy-3-nitro-1,4-naphthoquinone 3 under identical conditions.[1]

The structure 2 was established by X-ray analysis. The crystals are orthorhombic; a = 17.413(1), b = 5.832(1), c = 7.945(1)Å; U = 806.6Å^3. Space-group $P2_12_12_1$; Z = 4. $F(000)$ = 392; $\mu(Cu\text{-}K_\alpha)$ = 9.8cm^{-1}. 936 independent reflections were measured on a diffractometer with Cu-K_α radiation to θ = 71°. The structure (Figure) was solved by use of the program MULTAN and refinement, based on 914 reflections (20 unobserved, 2 suffering from extinction) gave R = 0.039.[2] No absorption corrections were applied. The bond lengths are consistent with 2. The molecule is closely planar except for the two nitro-group oxygens. This group is twisted by 10.5° about the C-N bond and prevented from coplanarity with the rest of the molecule by a short non-bonded intramolecular contact (2.668(4)Å) between O(2) and O(3). A short intermolecular



contact (2.99Å) occurs between screw related carbonyl oxygen atoms. The geometry of this contact closely resembles that of the carbonyl dipole-dipole interactions found in several of the crystalline barbiturates.[3]

The rearranged product is probably formed by demethylation followed by nitration to give 2-hydroxy-3-nitro-1,4-naphthoquinone **3** and oxidatively cleaved to afford **4**. This keto carboxylic acid would readily decarboxylate to the nitro ketone **5**. The enolic form on cyclisation under acidic conditions would lead to 3-nitromethylene phthalide **2**. The intermediacy of **4** is supported by its isolation as water-soluble silky orange needles, m.p. 340° dec., on nitration of **1** at 0° under identical conditions. This reaction is closely analogous to the one recently published for the conversion of chromone-3-carboxaldehyde to 5-nitro-2,3-benzofurandione-(2)-2-oxime.[4]



References and Notes

1. A. Inoue, N. Kuroki and K. Konishi, *Yuki Gosei Kagaku Kyokaishi*, **17**, 1959, 711; *Chem. Abs.*, **54**, 1960, 4504.
2. The atomic coordinates have been deposited with the Cambridge Crystallographic Data Centre, University Chemical Laboratory, Lensfield Road, Cambridge, CB2 1EW, U.K.
3. W. Bolton, *Acta Cryst.*, **17**, 1964, 147.
4. W. V. Curran, F.M. Lovell and N.A. Perkinson, *Tetrahedron Letters*, 1979, 2221.

(Received in UK 4 January 1980)