Tetrahedron Letters No. 46, pp 4073 - 4074, 1975. Pergamon Press. Printed in Great Britain.

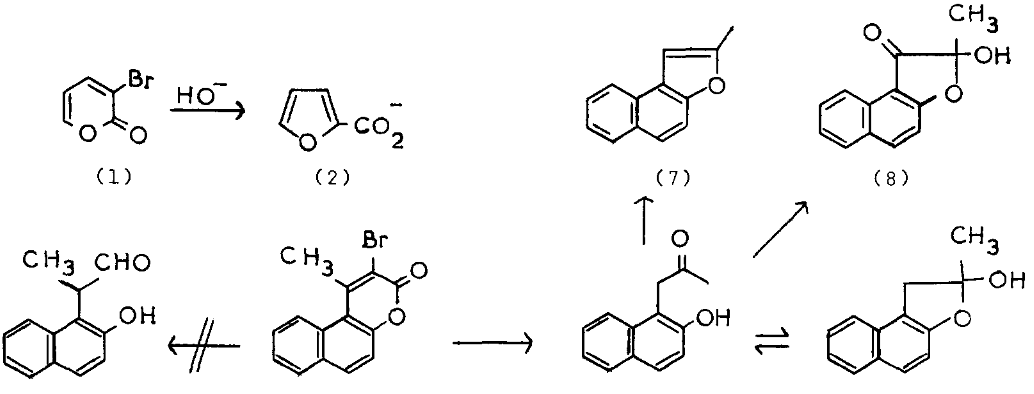
ARYL MIGRATION IN THE EXCEPTIONAL HYDROLYSIS OF A BROMOPYRONE

J. Carnduff* and R.B. Marks

Chemistry Department, University of Glasgow, Glasgow, G12 8QQ.

The alkaline hydrolysis of 3-bromo-α-pyrones (1) to furan-2-carboxylic acids (2) is a standard reaction. The mechanism is not known but there are very few cases where an alternative reaction path is followed. We report such an exception involving skeletal rearrangement.

Dey reported[1] that 1-methyl-2-bromonaphtho[2,1-b]pyran-3-one (3) on alkaline hydrolysis gives as the major product a phenol containing a carbonyl group. Because this phenol was instantly oxidised by Tollens' and Fehling's reagents it was assigned an aldehyde structure (4). It gave a methylnaphthofuran on dehydration, and on oxidation with Ag_2O it gave an 'acid' of MW about 220 determined by titration. Structures were deduced for these solely from the structure assigned to the phenol.



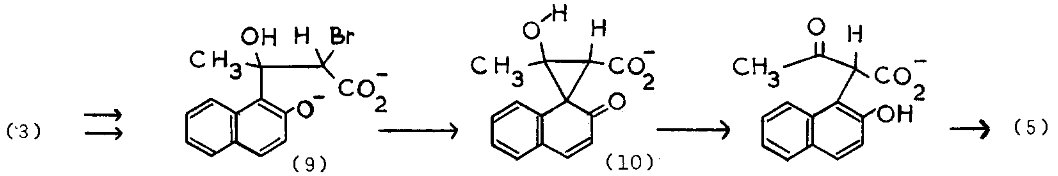
(1) (2) (7) (8)

(4) (3) (5) (6)

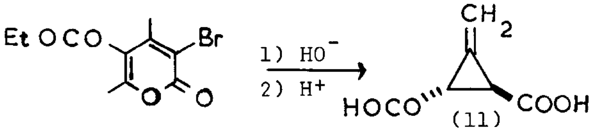
In our hands the hydrolysis yields as major product a phenol apparently identical to Dey's to which we assign the isomeric structure (5). The phenol is very sensitive to air and acids. By conducting the hydrolysis under nitrogen and then reducing the pH with carbon dioxide the phenol could be precipitated in 78% yield. Its m.p. (151-2°) is higher than reported, but its oxime, semicarbazone and acetate melt at the temperatures found by Dey. The keto phenol exists in solution as a 2:1 mixture with its hemiacetal isomer (6). This mixture shows ν_{max} 3220, 1695 cm^{-1} and n.m.r. bands at δ 2.27 ($\underline{Me}CO$), 4.14 ($ArC\underline{H}_2CO$), 1.58 ($Ar\underline{OH}$), 1.85($\underline{Me}C\overset{O}{\underset{O}{<}}$) 3.50 ($Ar\underline{CH}_2C\overset{}{\underset{}{<}}$), and 3.15 ($O\underline{H}$). Dehydration with methanolic HCl gives a methylnaphthofuran, m.p. 56-57° as Dey said, but proved by its n.m.r. spectrum to be 2-methylnaphtho[2,1-b]furan (7) 1-Methylnaphtho[2,1-b]furan, m.p. 59-60°, has a significantly different spectrum.[2]

Oxidation of the ketophenol by Cu(II) and Ag(I) does occur rapidly. Ammoniacal silver oxide in water under mild conditions gives a silver mirror and a quantitative yield of 1-pyruvyl-2-naphthol m.p. 172-5° which exists entirely in the hemiacetal form (8). This is soluble in aq. NaOH and the structure is supported by analysis and spectra, ν_{max} 3290 and 1673 cm^{-1}, δ 1.68 (s) (Me-$\overset{|}{\mathrm{C}}{<}^{\mathrm{O}}_{\mathrm{O}}$, 4.1 (br) (OH), 6.9-8.0 (m) (ArH), and 8.35 (dd) (H-9).

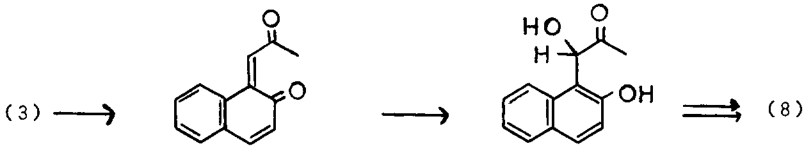
We rationalise the formation of the rearranged skeleton of (5) by a mechanism involving addition of water (which may also be the first step in the normal hydrolysis to furan acids), bromide displacement by C-1 of the naphthoxide ion and cleavage of the spirocyclopropanol.



It is not clear why rearrangement occurs in the case of (3) while the analog of (3) without the methyl group apparently[3] gives only the normal furancarboxylic acid product, plausibly by bromide displacement by the oxygen of the naphthoxide analogous to (9). The formation of the spirocyclopropane (10) has analogy in the formation[4] of Feist's acid (11), one of the few other exceptions.



The curious oxidation by silver oxide may involve dehydration to an o-quinonemethide, addition of water and repetition of this sequence.



Just such a sequence, leading to introduction of OH or OR groups, has recently been reported[5] in the DDQ oxidation of molecules containing a p-hydroxyphenylacetone moiety.

References and notes.

1. B.B. Dey and A.K. Lakshminarayanan, J. Ind. Chem. Soc., 1934, 11, 373.
2. M. Mülly, J. Zsindely and H. Schmid, Helv. Chim. Acta, 1975, 58, 610. We thank Dr. Mülly (University of Zurich) for a sample and spectra of the two methylnaphthofurans.
3. B.B. Dey, R.H.R. Rao and Y. Sankanarayanan, J. Ind. Chem. Soc., 1932, 9, 280.
4. F. Feist, Berichte, 1893, 26, 747. For later references see M. Smith in Rodd's Chemistry of Carbon Compounds, 2nd Edn., Vol. IIA, p.60.
5. G.M. Buchan, J.W.A. Findlay and A.B. Turner, J.C.S. Chem. Comm., 1975, 126.
6. We thank the S.R.C. for a research grant.