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AN ABNORMAL FRIES REARRANGEMENT INDUCED BY A PERI-METHOXYL GROUP IN MONOACETATES OF NAPHTHOHYDROQUINONES.

Trevor A. Chorn, Robin G.F. Giles,* Ivan R. Green, Victor I. Hugo, and Peter R.K. Mitchell
Department of Organic Chemistry, University of Cape Town, Rondebosch, Cape, 7700, South Africa.

Abstract. The acetyl group of two 1-acetoxy-4-hydroxy-5-methoxynaphthalenes migrates to C-3 on treatment with boron trifluoride etherate.

Several recent syntheses of analogues of naturally occurring naphthoquinones lacking oxygen(s) in the aromatic ring have used 2-acetyl-1,4-naphthoquinone as starting material.[1,2] While investigating routes to the isomeric 2- and 3-acetyljuglone methyl ethers and their 7-methoxy derivatives, an unusual "meta-Fries rearrangement" was observed.

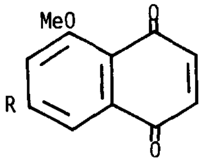
Juglone methyl ether (1) could be reductively monoacetylated exclusively at the less hindered oxygen to afford (2)[3] (72%). Rearrangement of (2) (BF_3) gave (3), in which the acetyl had migrated to the meta position (no ortho found), together with (4). The crude mixture was acetylated to convert (4) into starting material (2) (35%) while (3) was trapped as its monoacetate (5)[3], (37%, or 56% based on unrecovered (2)). Quinone (6) could likewise be converted to the monoacetate (7)[3] (80%). This, too, underwent a meta migration of acetyl to afford, after acetylation, the acetylnaphthol (8)[3] (74% based on unrecovered (7)) together with acetate (7) (31%).

Acetates (5) and (8) afforded the target quinones (9)[4] (91%) and (10)[3] (90%), respectively, on oxidation with ceric ammonium nitrate (CAN).

That meta rearrangements had occurred was shown by reductive monomethylation of quinones (1) and (6) to naphthols (11)[5] (90%) and (12)[3] (81%) ($Na_2S_2O_4$ then $K_2CO_3/Me_2SO_4/Me_2CO$). Fries rearrangement of the corresponding acetates (13) (92%) and (14) (85%) gave the ortho-acetylnaphthols (15)[3] (88%) and (16)[3] (68%)[6], which were in turn oxidised to the same quinones (9) (86%) and (10) (86%). Reductive monoacetylation of these quinones thus derived gave the naphthols (5) and (8) respectively. This provided further evidence that these compounds arose from acetates (2) and (7) through meta migration of acetyl.

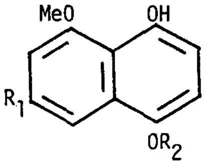
That acetylation of the hydroquinones of (1) and (by extrapolation) of (6) had occurred to give, respectively, (2) and (7), was confirmed by methylation of (2) to 1-acetoxy-4,5-dimethoxynaphthalene, isomeric with (13).

The <u>meta</u> rearrangement is presumably exclusively intermolecular.



1. R = H

6. R = OMe



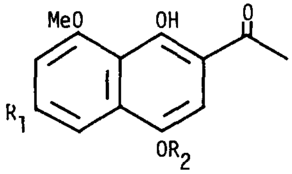
2. R_1 = H, R_2 = Ac

4. R_1 = R_2 = H

7. R_1 = OMe, R_2 = Ac

11. R_1 = H, R_2 = Me

12. R_1 = OMe, R_2 = Me



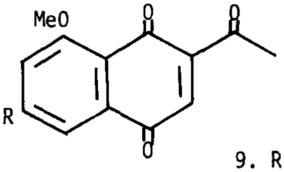
3. R_1 = R_2 = H

5. R_1 = H, R_2 = Ac

8. R_1 = OMe, R_2 = Ac

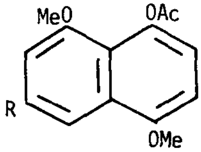
15. R_1 = H, R_2 = Me

16. R_1 = OMe, R_2 = Me



9. R = H

10. R = OMe



13. R = H

14. R = OMe

<u>References</u>.

1. G.A. Kraus and B. Roth, <u>J. Org. Chem.</u>, 1978, <u>43</u>, 4923.
2. T.A. Chorn, R.G.F. Giles, P.R.K. Mitchell, and I.R. Green, <u>J.C.S.</u>, <u>Chem. Comm.</u>, 1981, 534.
3. All new compounds gave correct elemental analyses and spectroscopic data.
4. Compound (9) is known; P. Bosshard, S. Fumagalli, R. Good, W. Trueb, W.v Philipsborn, and C.H. Eugster, <u>Helv. Chim. Acta</u>, 1964, 47, 769. However the yield (34%) in the final step made an alternative route to (5) desirable for further syntheses.
5. Also prepared by other methods; (a) R.L. Hannan, R.B. Barber, and H. Rapoport, <u>J. Org. Chem.</u>, 1979, <u>44</u>, 2153; (b) H. Laatsch, <u>Liebig's Ann. Chem.</u>, 1980, 140.
6. Yields based on unrecovered starting materials. By-products (11) (24%) and (12) (33%) were reacetylated to (13) and (14).

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