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RING OPENING OF 3-METHOXYACENAPHTHYLENE-1,2-DIONE. APPLICATION OF ^{13}C-2D-*INADEQUATE*-N.M.R. SPECTROSCOPY TO STRUCTURE ASSIGNMENT OF SOME SUBSTITUTED NAPHTHALENES.

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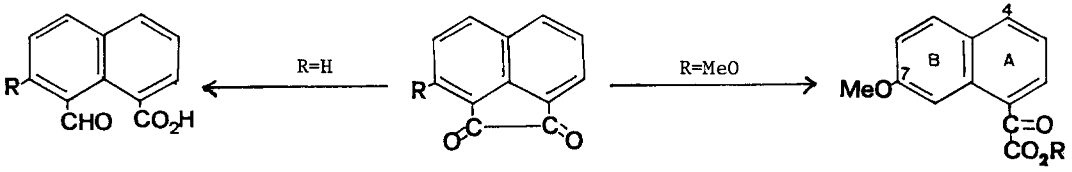
Summary: Oxidative alkaline cleavage of the title compound 3 gave unexpectedly in high yields the α-keto acid 9a instead of the aldehyde acid 5 (or its tautomer 7). The latter could be prepared via regioselective mono-ketalisation of compound 3. The structure assignment of 9, and differentiation between 5/7 and the isomer 10, were effected using natural abundance ^{13}C-^{13}C coupling techniques.

For a synthetic project we were investigating suitable routes for obtaining in quantity 7-methoxynaphthalene-1-carboxylic acid 1, and/or a compound containing an additional potential carboxyl group in ring B such as 5. The conversion of acenaphthylene-1,2-dione 2 into the aldehyde acid 4 with conc. aqueous KOH has been known for a long time[1]; and more recently a two-phase method has been found for effecting this reaction at room temperature[2]. The methoxy-analogue 3 is easily available in high yield[3], and this prompted us to subject this to the same reaction conditions, which resulted in the formation of a single acidic product in 80% yield. This and its methyl ester (MeOH/H$^+$) showed ^{1}H-N.M.R. spectra incompatible with either an aldehyde acid/ester or their cyclic forms, e.g. 7 or 8 (absence of -C(H)=O or O-C(Ar)(H)-O signals), though 2 carbonyl bands were evident in the i.r. (at 1740 and 1673 cm^{-1} in the ester).

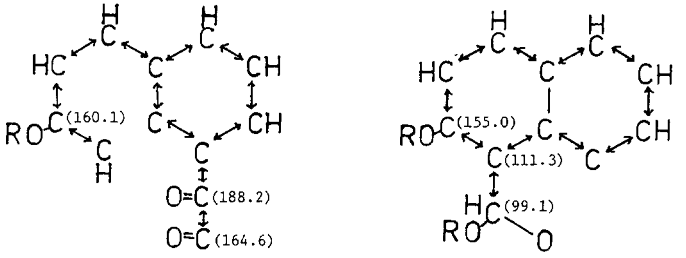


4 R=H
5 R=MeO

2 R=H
3 R=MeO

9a R=H
9b R=Me

Examination of the ^{13}C-^{1}H-coupled spectrum of the ester showed six aromatic doublets (J_{C-H} 160 Hz) indicating that the compound is a disubstituted naphthalene. Next, the ^{13}C-2D-*INADEQUATE* technique was applied to this compound[4] to reveal the exact C-C sequence; the result is summarised schematically in Fig. 1 (reference carbons were chosen on the basis of their chemical shifts in relation to well-established literature values[5,6]). The surprising conclusion was that the product was the α-keto-acid 9a[7], a result fully confirmed by oxidation (OH^-/H_2O_2) in almost theoretical yield to give acid 1, providing an excellent method of preparation of the latter. Incidentally, careful examination of the total product of this reaction with compound 2 failed to reveal any trace of naphthalene-1-glyoxylic acid.



Compound 9b

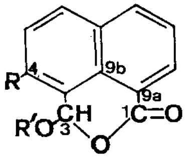
Compound 8

Fig. 1: Connectivity diagrams showing C-H bonds from $^1H-^{13}C$ -coupled spectra; and C-C vicinality (arrows) from *INADEQUATE* measurements; chemical shifts in p.p.m. downfield from TMS shown in parentheses for reference carbons.

6 R=R'=H

7 R=MeO, R'=H

8 R=R'= MeO



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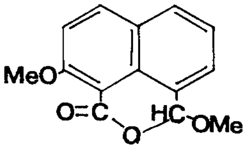
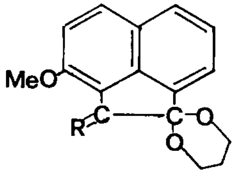


From the dione 3 a single monoketal could be obtained using Noyori's method[8]. Reduction, ketal cleavage and *in situ* periodate oxidation gave an acidic product in 61% overall yield.



11 R=O

12 R=H, OH

Scheme: 3 — a → 11 — b → 12 — c → 5/7 — d → 8

Conditions: a: $Me_3SiO(CH_2)_3OSiMe_3$[9] (1.1 equiv.), $ClCH_2CH_2Cl$, CF_3SO_3H (catal.), 60°/1 hr.

b: $NaBH_4$/EtOH, R.T.

c: $EtOH/H_2O/H_2SO_4$, then $NaIO_4$, R.T.

d: $MeOH/CH_3COCl$, 0°→R.T.

The derived ester ($MeOH/H^+$) was clearly a "pseudo" ester (^1H-singlet at 6.4 p.p.m., one carbonyl band at 1726 cm^{-1}). That this was compound 8 (and hence that the monoketal was 11) was indicated again by $^1H-^{13}C$-coupled spectra and *INADEQUATE* measurement, also summarised in Fig. 1. In particular, the found sequence $C_3 \leftrightarrow C_{3a} \leftrightarrow C_4$ (note Chem. Abstr. numbering!) is incompatible with the alternative structure 10.

These results would appear to be another useful illustration of the effectiveness of the 2D-*INADEQUATE* technique in structure elucidation[10] without the need for recourse to X-ray crystallographic analysis, in particular for substituted naphthalenes where orientation problems[11] can still arise on occasion.

REFERENCES AND FOOTNOTES

1. C. Graebe and E. Gfeller, Annalen, 1893, 276, 1.
2. H. Bader and Y.H. Chiang, Synthesis, 1976, 249.
3. H. Staudinger, H. Goldstein and E. Schlenker, Helv. Chim. Acta, 1921, 4, 342.
4. Bruker 400 MHz instrument, 1.5 g substance in $CDCl_3$, 10 mm probe, 16 hrs.
5. J. Seita, J. Sandstroem and T. Drakenberg, Org. Magn. Res., 1978, 11, 239.
6. J.B. Stothers, "Carbon-13 NMR Spectroscopy", Academic Press, 1972, pp. 303, 461.
7. To our knowledge this would appear to be the first instance of such a specific Haller-Bauer type cleavage under the mild conditions used (see ref. 2).
8. T. Tsunoda, M. Suzuki and R. Noyori, Tetrahedron Lett., 1980, 21, 1357.
9. Prepared by heating under reflux propane-1,3-diol, hexamethyldisilazane (0.6 equiv.) and imidazole (catal.), followed by fractionation, b.p. 75-77°/15 mm Hg.
10. Cf., A.N. Abdel-Sayed and L. Bauer, Tetrahedron Let., 1985, 26, 2841, and refs. there cited
11. Cf., H. Kessler, W. Bermel, C. Griesinger, P. Hertl, E. Streich and A. Rieker, J. Org. Chem., 1986, 51, 596.

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