Oxidation of Naphthols by Ruthenium Tetroxide

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Summary Selective oxidation of naphthols by ruthenium tetroxide with retention of one of the fused rings has been demonstrated.

Suitable conditions for the type of reaction discussed herein were first described by Djerassi and Engle.[1] General applications of the reagent have been reviewed,[2] and the oxidation of benzenoid compounds has been described[3] although this is the first report of the degradation of a fused aromatic system. The observed preference for attack of the electron-rich ring in the substrates studied indicates further synthetic applications.

α- and β-Naphthols were oxidised to phthalic acid which was characterised as its diethyl ester (55% overall) by i.r. spectroscopy and comparative g.l.c. The yields were similar when either the periodate–ruthenium dioxide procedure or the hypochlorite–ruthenium trichloride method[4] was used, but the latter two-phase system was more economical and time was saved by separation of the aqueous and CCl_4 layers before destruction of excess of tetroxide with propan-2-ol; this avoids emulsification of the precipitated ruthenium dioxide. In oestradiol derivatives[5] ring A is protected by *O*-acetylation but in contrast to this the naphthol acetates were oxidised completely to phthalic acid at a comparable rate to that for the naphthols themselves; the reactions were complete within 15 min at ambient temperature and were controlled by the rate of diffusion into the organic layer. Methylenedioxybenzene was used as a model and the ring was evidently activated by the substituent since degradation to acidic fragments occurred at a rate comparable to that of the naphthols. Conversely, methyl α-naphthyl ether reacted more slowly under comparable conditions and was converted into phthalic acid (50% yield as the diester) during 2·5 h. It was subsequently shown that controlled oxidation of 5-methoxy-1-naphthol[6] was possible despite the additional oxy-substituent, for diethyl methoxyphthalate was obtained (50%) by preparative g.l.c. (characterised by i.r. and mass spectroscopy). Another major component of similar retention time is as yet unidentified.

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[1] C. Djerassi and R. R. Engle, *J. Amer. Chem. Soc.*, 1953, **75**, 3838.
[2] P. N. Rylander, 'Engelhard Technical Bulletin', 1969, **9**, 135 (*Chem. Abs.*, 1969, **71**, 33770).
[3] J. A. Caputo and R. Fuchs, *Tetrahedron Letters*, 1967, 4729.
[4] S. Wolfe, S. K. Hasan, and J. R. Campbell, *Chem. Comm.*, 1970, 1420.
[5] D. M. Piatak, G. Herbst, J. Wicha, and E. Caspi, *J. Org. Chem.*, 1969, **34**, 116.
[6] M. Gates, *J. Amer. Chem. Soc.*, 1950, **72**, 228.

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