Ring Opening and Rearrangement in Spirocyclic Quinol Ethers

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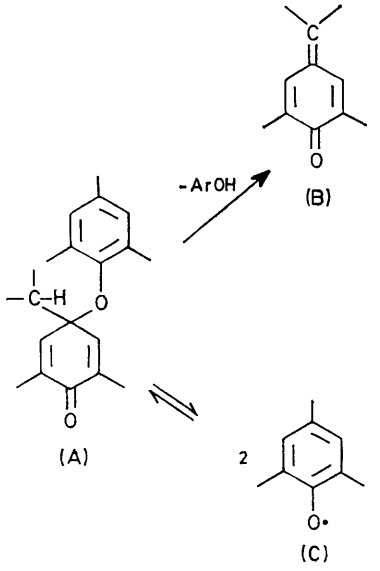
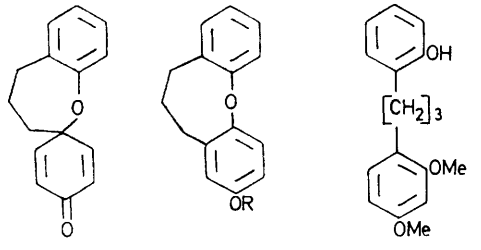
Summary A spirocyclic quinol ether undergoes ring opening in dilute acid and dienone–phenol rearrangement leading to ring enlargement in more concentrated acid.

THE acid-catalysed reactions of cyclohexadienones are complicated but, since these compounds are probable intermediates in many important biosynthetic pathways, their reactivity continues to be of interest. In enzymatic and



other phenol oxidations, quinol ethers of type (A) have been proposed[1] as intermediates in the formation of quinone methides (B) from phenoxyl radicals (C). A similar quinone methide is a likely intermediate in the rearrangement of sterically hindered quinol ethers to benzyl ethers.[2]



a; R = COMe
b; R = Me
c; R = H

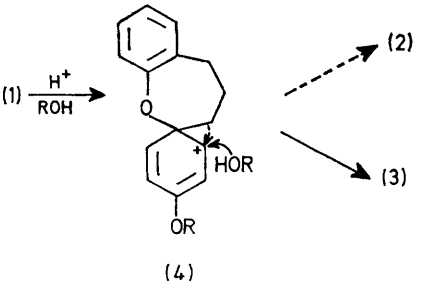
In the course of an investigation into the mechanism of phenol oxidation a model for the intermediate of the type (A), the spirocyclic quinol ether (**1**), was synthesized and subjected to acid hydrolysis. It was found that the dienone undergoes dienone–phenol rearrangement to (**2**) or ring opening to (**3**) depending on the concentration of the acid used in the hydrolysis.

TABLE. Yields of hydrolysis products of (**1**) in methanolic sulphuric acid.

	Yields/%		
H_2SO_4 % (v/v)	(**2b**)	(**2c**)	(**3**)
1	4·7	—	95·3
3	6·3	—	93·7
5	7·0	—	93·0
10	12·0	—	88·0
20	29·5	3·1	67·4
30	92·5	5·1	2·4

In acetic anhydride with a trace of sulphuric acid compound (**1**) rearranged almost quantitatively to (**2a**), m.p. 44—45 °C. In 1% methanolic sulphuric acid the ring-opening product (**3**) is formed in 95% yield and only 5% of the ring-expansion product is obtained at this concentration. Increasing the sulphuric acid concentration to 30% causes almost exclusive formation of (**2b**). A small amount of the rearrangement product (**2c**) is also obtained along with (**2b**) at higher acid concentrations (Table). The structure of (**3**) was confirmed by synthesis and that of (**2b**) by a combination of ^{13}C and ^1H n.m.r. analysis. The yields given in the Table were determined by g.l.c.

Both the ring opening[3] and the ring expansion[4] reactions have been encountered before in similar quinol ethers, but the effect of the acidity of the solvent on the course of the reaction has not, to our knowledge, been observed before.



From the structures of the products formed, the cation (**4**) seems to be the primary intermediate in both cases.[5] In dilute methanolic sulphuric acid the nucleophilic attack of the solvent is apparently more rapid than the migration of the alkyl group.

(*Received, 28th June* 1976; *Com.* 719.)

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[2] G. Brunow and S. Sumelius, *Acta Chem. Scand. B*, 1975, **29**, 499.
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[5] A. J. Birch, A. H. Jackson, P. V. Shannon, and G. W. Stewart, *J.C.S. Perkin I*, 1975, 2492.