

The Base Catalysed Rearrangement of Catechol Mono-allyl Ethers

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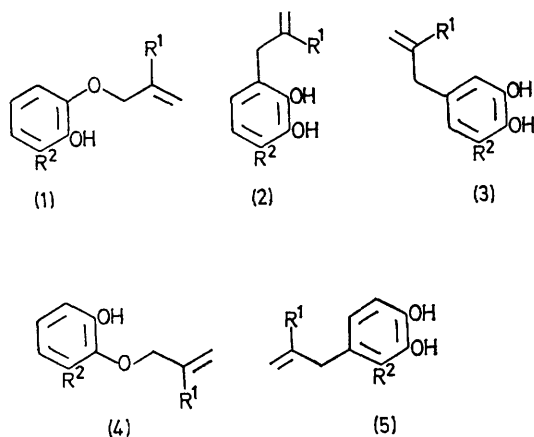
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Summary The base catalysed rearrangement of catechol mono-allyl ethers (**1**) and (**4**) at 78° involves successive sigmatropic rearrangements to give products that differ from those obtained by sigmatropic rearrangements under normal Claisen conditions.

THE thermal rearrangement of catechol mono-allyl ether (**1a**) is reported¹ to give at 160—200° a mixture of products,

(**2a**) and (**3a**), in the ratio 5:4, apparently resulting from competing *ortho*- and *para*-Claisen rearrangements.² Our investigation of this reaction shows that the ratio of the products, (**2a**) and (**3a**), and the rate of the rearrangement are sensitive to the pH at which the reaction is carried out. Thus in ethanolic HCl (2 drops HCl in 25 ml EtOH) at 180° the ratio of (**2a**):(**3a**) is 2:1 and in ethanol containing 1 equiv. of NaOEt at 78° the reaction proceeds at

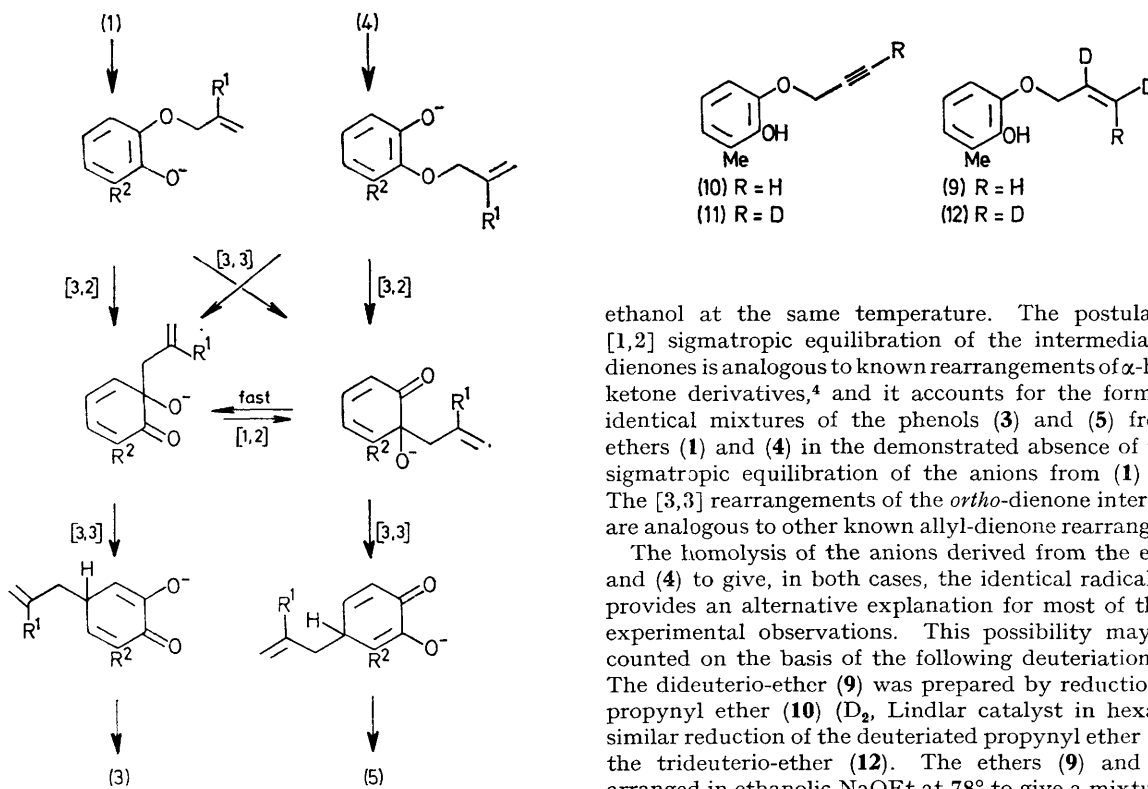
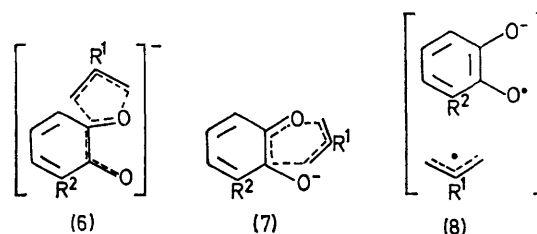
approximately the same rate and the ratio (2a):(3a) is 1:4. These preliminary observations suggested that the rearrangement of (1a) is base catalysed and that the rearrangement of the anion of (1a) takes a different course from that of the un-ionised phenol.



a; $R^1 = R^2 = H$, **b;** $R^1 = H$, $R^2 = Me$, **c;** $R^1 = R^2 = Me$.

The thermal rearrangement of the ether (1b) in dimethylaniline at *ca.* 180° gives the products (2b) (45%) and (5b) (35%), whereas the ether (4b) gives a single product (3b) as expected. Rearrangement of the same two ethers, (1b) and (4b), in ethanolic NaOEt (1 equiv.) at 78° gives, in both cases, a 1:1 mixture of the phenols (3b) and (5b) as the major reaction product, and in addition the ether (1b)

gives a little of the *ortho*-Claisen product (2b). The ethers (1b) and (4b) recovered from partial rearrangement in ethanolic NaOEt show no signs of interconversion by a [1,4] sigmatropic rearrangement of the anions; furthermore the isolated phenolic products do not rearrange under the conditions of the reaction. The nearly identical product distribution from both (1b) and (4b) must therefore result from the rearrangement of intermediate dienones. Similar results have also been obtained for the ethers (1c) and (4c). The above observations may be rationalised in terms of the allowed sigmatropic rearrangements outlined in the Scheme. It is probable that these rearrangements are initiated by a [3,2] sigmatropic rearrangement of the phenolate anions, analogous to the well known Wittig rearrangement,³ since the transition state for this process (6) would involve greater charge delocalisation than the transition state (7) for a [3,3] (Claisen) rearrangement. The latter process is however accelerated by anion formation, since whereas a small amount of the Claisen product (2b) is obtained from the ether (1b) using ethanolic NaOEt at 78° no rearrangement occurs when the ether (1b) is heated in



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ethanol at the same temperature. The postulated fast [1,2] sigmatropic equilibration of the intermediate *ortho*-dienones is analogous to known rearrangements of α -hydroxyketone derivatives,⁴ and it accounts for the formation of identical mixtures of the phenols (3) and (5) from both ethers (1) and (4) in the demonstrated absence of the [1,4] sigmatropic equilibration of the anions from (1) and (4). The [3,3] rearrangements of the *ortho*-dienone intermediates are analogous to other known allyl-dienone rearrangements.⁵

The homolysis of the anions derived from the ethers (1) and (4) to give, in both cases, the identical radical pair (8) provides an alternative explanation for most of the above experimental observations. This possibility may be discounted on the basis of the following deuteration studies. The dideuterio-ether (9) was prepared by reduction⁶ of the propynyl ether (10) (D_2 , Lindlar catalyst in hexane) and similar reduction of the deuteriated propynyl ether (11) gave the trideuterio-ether (12). The ethers (9) and (12) rearranged in ethanolic NaOEt at 78° to give a mixture of the phenols (3b) and (5b) in which the deuterium labels were

located only at positions 2' and 3' of the allyl side chain (n.m.r., mass spectra) within the limits of experimental error. This demonstrated absence of 1',3'-allylic scrambling of the deuterium labels is entirely in accord with the con-

certed sigmatropic reaction pathways outlined in the Scheme.

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