Elimination of an Allyloxy-group During the Claisen Rearrangement of 1,2-Diallyloxyanthraquinone

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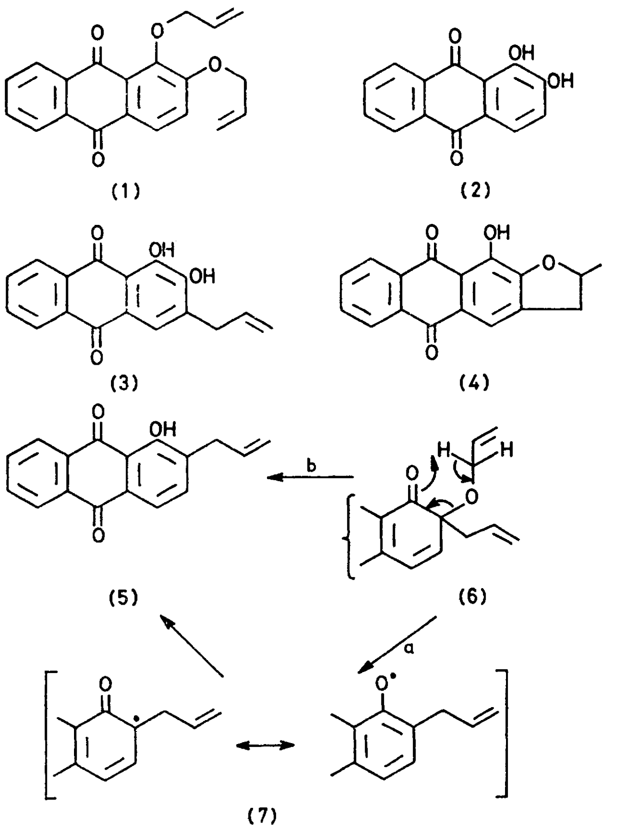
Summary Thermal Claisen rearrangement of 1,2-diallyloxyanthraquinone gives, among other products, 2-allyl-1-hydroxyanthraquinone.

AROMATIC Claisen rearrangements have been extensively studied,[1] but there are only a few examples where an *ortho* substituent has been expelled or displaced. These include elimination of carbon dioxide in the rearrangement of allyl ethers of salicylic acid and its derivatives,[2] the migration of an *o*-allyl substituent,[3] and the displacement of halogen in the allyl ethers of *o*-halogenophenols[4] and 2,3,5,6-tetrachloro-4-hydroxypyridine.[5] We now report an unexpected elimination of the 2-allyloxy-group from the Claisen rearrangement of 1,2-diallyloxyanthraquinone (**1**).

Rearrangement of 1,2-diallyloxyanthraquinone (**1**) in boiling decalin led to the isolation of three compounds. Two of the products were identified as 1,2-dihydroxyanthraquinone (**2**; 10·7%), and 3-allyl-1,2-dihydroxyanthraquinone (**3**; 72·2%), m.p. 147—148 °C, which cyclised on treatment with acid to its furan derivative (**4**), m.p. 184—185 °C, and are derived from expected ether cleavage and Claisen rearrangement. These products are also obtained from the Claisen rearrangement of 2-allyloxy-1-hydroxyanthraquinone. The third product (16% crude) was considerably less polar than the others on silica and was not easily purified by chromatography until dimethyl sulphoxide was used instead of decalin for the rearrangement. It was identified as 2-allyl-1-hydroxyanthraquinone (**5**; 4·3%), m.p. 120—121 °C, by spectral methods and by synthesis. Thus the i.r. spectrum shows two carbonyls, one hydrogen-bonded at 1630 cm^{-1} (C-9) and the other at 1670 cm^{-1} (C-10). The ^{1}H n.m.r. spectrum shows the H-bonded hydroxy group (C-1) at τ $-2{\cdot}7$, only one allyl group with the methylene protons resonating at τ 6·65 (2H, d, J 6 Hz) and olefin protons appearing as three sets of signals in the region of τ 4—5.

Two *ortho* split aromatic signals (J 8 Hz) at τ 2·75 and 2·50 are assigned to the protons at C-3 and C-4. These assignments were confirmed by europium shift studies and spin decoupling experiments at 220 MHz which show that in the presence of the lanthanide shift reagent $Eu([^2H_9]fod)_3$, the protons at C-4 and C-5 undergo appreciable downfield shifts whereas the allyl group is not influenced. Accurate mass measurement of the molecular ion at *m/e* 264 gave the molecular formula as $C_{17}H_{12}O_3$ and confirmed that an allyloxy-group had been eliminated. The structure of the product was confirmed as 2-allyl-1-hydroxyanthraquinone (**5**) by its synthesis from thermal rearrangement of 1-allyloxyanthraquinone.

Two pathways are under consideration to account for the formation of (**5**) and both require the intermediacy of the Claisen dienone (**6**). Path (a) (Scheme) involves formation of the resonance stabilised dienone radical (**7**) followed by abstraction of a hydrogen atom from, *e.g.*, the solvent, whereas in path (b) a retro-ene reaction would give (**5**) and acrolein. Previous work[6] has shown that an aromatic Claisen rearrangement of an *ortho* diallyloxy-derivative can also lead to formation of a bicyclo[2.2.2]octenone by intramolecular Diels–Alder reaction of an intermediate dienone.



Scheme

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