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A [3,4] ALLYL SHIFT IN A THERMAL REARRANGEMENT OF A β-NAPHTHALENONE[1]

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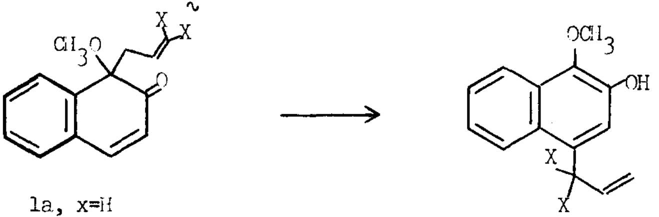
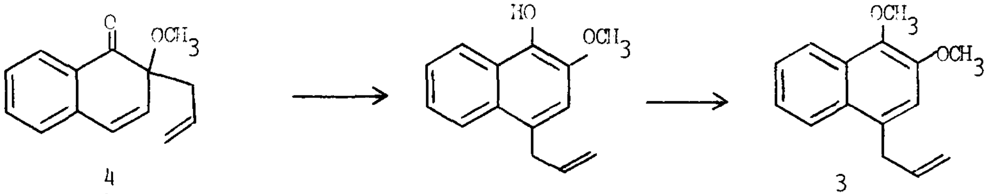
Migrations of allyl groups in acid catalyzed rearrangements of cyclohexadienones give products resulting from [1,2], [1,3], [1,4], [1,5], [3,3], and [3,4] shifts.[2] In contrast, only Cope and Claisen ([3,3]) migrations of allyl groups have been observed in thermal rearrangements of cyclohexadienones or naphthalenones.[2]

We have now observed that heating 1-allyl-1-methoxy-2-naphthalenone (1) in refluxing N,N-dimethylaniline for 30 hours gives naphthol 2, accompanied by ca. 5% of the reduction product, 1-allyl-2-naphthol. Naphthol 2 was also obtained by rearrangement of 1 in a 1% solution of sulfuric acid in acetic acid at room temperature. The structure of 2 was established from its spectra and analysis, and by methylation to form 3. Ether 3 was independently prepared by methylation of 4-allyl-2-methoxy-1-naphthol, which was obtained by a normal [3,3] shift from either thermal or acid catalyzed rearrangement of naphthalenone 4.



1a, x=H
1b, x=D

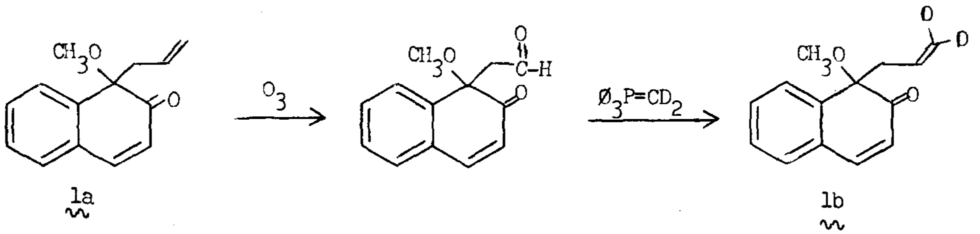
2, x=H,D



4

3

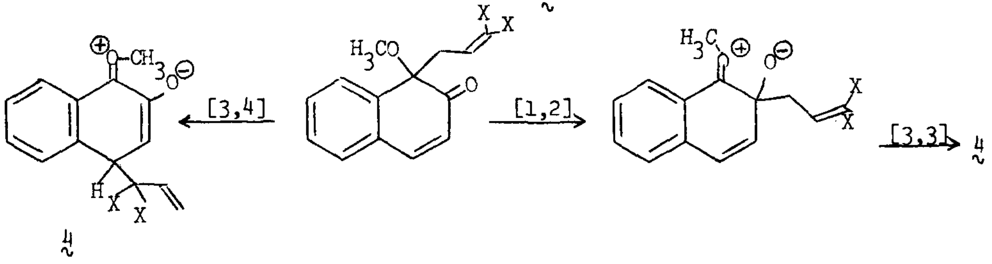
To determine the mechanism of the rearrangement of 1 to 2, the deuterated derivative 1-d_2 was synthesized as shown below. A sample of 1-d_2 containing 0.49±0.03 atoms of residual hydrogen (by nmr analysis) at the terminal methylene of the allyl group was rearranged on heating to give 2-d_2 containing 0.51±0.06 atoms of hydrogen at the benzylic methylene. Thus, the



rearrangement proceeds by an overall [3,4] shift of the allyl group. Acid-catalyzed rearrangement of a sample of 1-d$_2$ containing 0.70±0.05 atoms of residual hydrogen gave 2-d$_2$ containing 0.62±0.05 atoms of hydrogen at the benzylic methylene, confirming that the acid catalyzed reaction also proceeds by a [3,4] shift, as do acid-catalyzed rearrangements of naphthalenones lacking methoxy groups at C-1.[3]

The [3,4] shift of the allyl group of 1 under thermal conditions is clearly dependent on the presence of the methoxy group at C-1, since naphthalenones corresponding to 1a but with methyl or allyl groups in place of methoxy at C-1 undergo only the expected equilibration, via reverse Claisen migrations, with the corresponding allyl naphthyl ethers. Prolonged heating finally results in some decomposition to 1-allyl-2-naphthol or 1-methyl-2-naphthol, but no [3,4] migration is observed.[4]

The effect of a methoxy group at C-1 in facilitating the [3,4] allyl migration in 1 can be accounted for by the assumption that the dipolar ion 4 (which may be formed either by a single [3,4] shift or by successive [1,2] and [3,3] allyl shifts) is an intermediate in the rearrangement. The electron donating methoxy group should stabilize 4 much more effectively than would



an alkyl group at C-1.

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