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[1,4] MIGRATIONS IN ACID CATALYZED REARRANGEMENTS OF β-NAPHTHALENONES[1]

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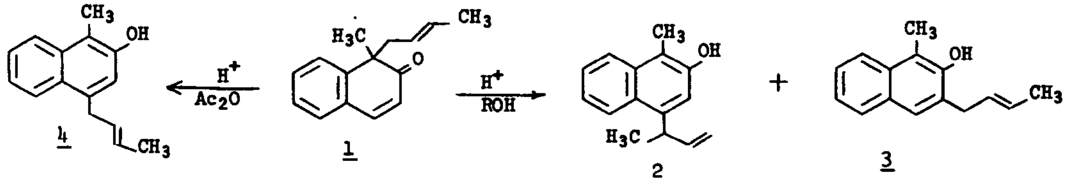
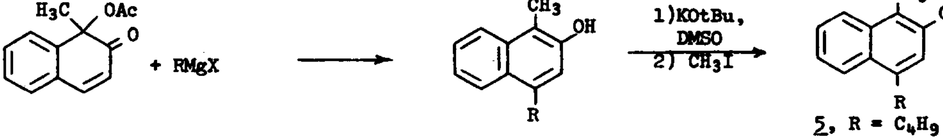
Reaction of naphthalenone 1 with protic acids (such as sulfuric acid in acetic acid or water) gives approximately equal yields of the [3,4] rearrangement product 2 and the [1,5] rearrangement product 3.[2] These products can both be formed by symmetry allowed suprafacial sigmatropic shifts.[3]

We have now observed that when 1 is reacted with a 0.2 M solution of sulfuric acid in acetic anhydride for two hours, it gives products corresponding to neither 2 nor 3. Instead, the rearrangement product 4 is obtained in 60% yield, accompanied by the cleavage product 1-methyl-2-naphthyl acetate.



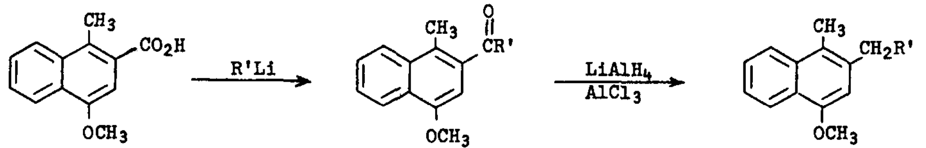
The structure of 4 was suggested by its nmr spectrum, which demonstrated the presence of an unrearranged crotyl group and showed a singlet (upfield from the other aromatic signals) for the hydrogen ortho to the acetoxy group. The structure was proved by hydrolysis of 4 to its phenol, conversion of the phenol to its methyl ether, and catalytic hydrogenation to form 1-methyl-2-methoxy-4-butylnaphthalene (5). Compound 5 was independently synthesized as shown in equation (1).



5, R = C_4H_9
13b, R = $CH_2C_6H_5$

(1)

To confirm that the reaction between the Grignard reagent and the quinol acetate had proceeded by the expected[4] conjugate addition, 7a, the product which should arise from [1,2] addition, was synthesized as shown in equation (2), starting with 6 [5]. Compound 7a was indeed



(2)

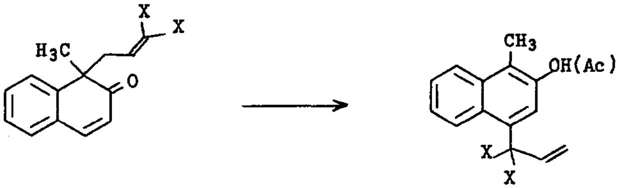
6

7a, R = $CH_2CH_2CH_3$

b, R = CH_2CH_3

different from 5. Its nmr spectrum showed a triplet at δ 7.25 ppm for the methylene group at the β-position of the ring. This signal was ca. 0.3 ppm upfield from the signal for the α-methylene group in 5, in accordance with the assigned structures.

In view of the effect of a change in solvent on the rearrangement of 1, we reinvestigated the rearrangement of naphthalenone 8,[2,6] to see if a change in solvent from protic acids to acetic anhydride would result in a change in reaction mechanism.



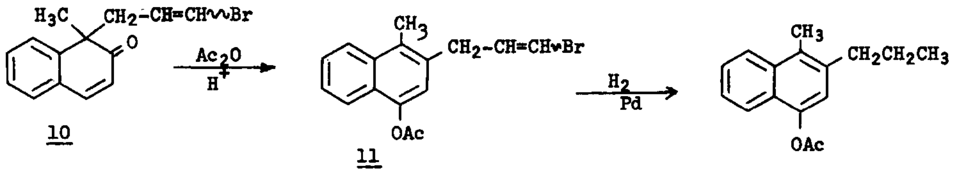
8, X = H
8-d_2, X = D

9, X = H
9-d_2, X = D

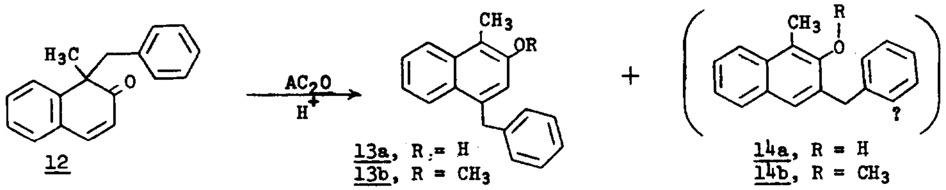
Naphthalenone 8-d_2, bearing 1.2 atoms of deuterium at the terminal vinyl positions, was rearranged in 0.5 M sulfuric acid in acetic acid for three days, in 0.3 M sulfuric acid in acetic anhydride for two hours, and in 20% BF_3 in diethyl ether for 2.5 hours. In each case, within experimental error, nmr analysis showed the presence solely of the [3,4] rearrangement product 9-d_2 or its acetate, with the deuterium located entirely on the benzylic methylene.[7]

In contrast to the [1,4] and [3,4] migrations observed in the rearrangements of 1 and 8, rearrangement of naphthalenone 10 (a mixture of cis and trans isomers) in 1.2 M sulfuric acid in acetic anhydride for three days gave solely the [1,2] rearrangement product 11.[8] The structure of 11 was demonstrated by its hydrogenation to 1-acetoxy-3-propyl-4-methylnaphthalene, which was synthesized by demethylation of 7b with potassium thiophenoxide in DMF and acetylation of the resulting phenol.

Rearrangement of the benzyl-substituted naphthalenone 12 in acetic acid gave a complex mixture of products which could not be identified. Rearrangement in 1.2 M sulfuric acid in

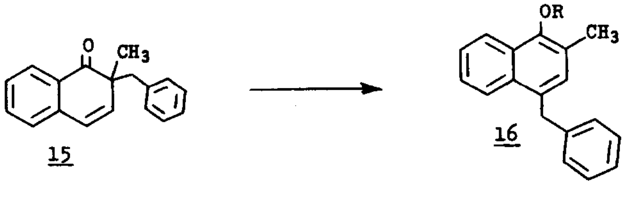


acetic anhydride gave a mixture of two acetates, in the ratio 4:1. The acetates, without being separated, were hydrolyzed to phenols, which were converted to the methyl ethers. The ether obtained from the major product was isolated and shown to be 13b by comparison with a sample independently prepared as shown in equation (1). The minor rearrangement product could



not be completely separated from the major product. Its methyl ether had vpc retention times on several columns identical with those of 14b, which was prepared by an independent route starting with 3-bromo-1-methyl-2-naphthol. Comparison of the nmr and ir spectra of a mixture of 13b and 14b with those of the mixture of ethers obtained from the products of rearrangement of 12b strongly suggested that the minor component was 14b, but a definitive structural assignment could not be made.

Finally, rearrangement of 15 in acetic anhydride-sulfuric acid or in ether containing boron trifluoride gave the [1,3] rearrangement product, 16,[9] accompanied by small amounts of a second unidentified product.



The most surprising aspect of these reactions is the remarkable difference in the products obtained from rearrangement of 1 in protic solvents as compared to acetic anhydride. A possible explanation is that "forbidden" suprafacial [1,4] (or [1,3])[10] shifts are favored by the greater positive charge on the ring resulting from acetylation rather than protonation of the carbonyl group. The increased difference in polarity between the migrating group and the framework on which it migrates should increase the probability of observing formally forbidden reactions.[11] The fact that the crotyl group undergoes [1,4] migration while the allyl group does not is in accord with this interpretation, although the relative importance of polar and steric effects in these reactions cannot yet be determined.

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References

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(7) The boron trichloride catalyzed rearrangement of 8 has also been shown to proceed by a [3,4] shift.[6]

(8) The rearrangement of 1,1-dimethyl-2-naphthalenone proceeds similarly to give 3,4-dimethyl-1-naphthyl acetate. [E.N. Marvell and A.O. Geiszler, J. Amer. Chem. Soc., 74, 1259 (1952)]. We suggest that this type of reaction is characteristic of rearrangements requiring shifts of poor migrating groups.

(9) [1,3] Benzyl migrations (of unknown stereochemistry) have been observed in acid-catalyzed rearrangements of cyclohexadienones: B. Miller, ibid., 96, 7155 (1974).

(10) Formation of 4 and 13 may actually proceed by [1,2] migrations to the carbonyl carbon, followed by [1,3] migrations to C-4. Like the [1,4] path, these processes would require suprafacially forbidden migration.

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