

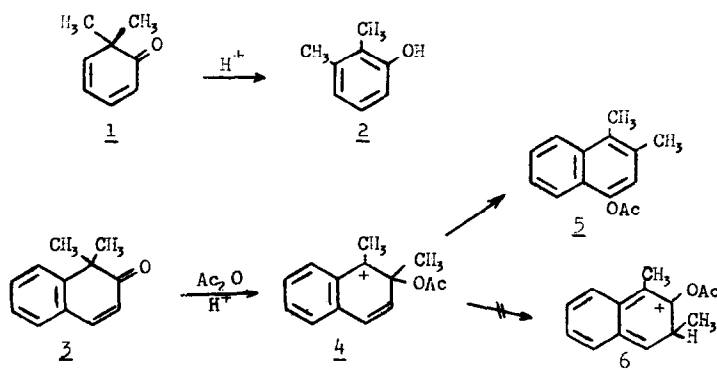
Novel Acid Catalyzed Migrations in β -Naphthalenones

Bernard Miller and Mohammed R. Saidi

Department of Chemistry, University of Massachusetts, Amherst, Mass., 01002

(Received in USA 16 August 1972; received in UK for publication 22 September 1972)

The normal dienone-phenol rearrangements of linearly-conjugated cyclohexadienones (e.g., 1 \rightarrow 2) are prevented in the β -naphthalenone 3.² Instead, a methyl group in 3 migrates to the carbonyl carbon to give carbonium ion 4, which then gives rise to the naphthyl acetate 5. No further migration of a methyl group to give 6 occurs, since formation of 6 would require disruption of the aromaticity of the second ring.

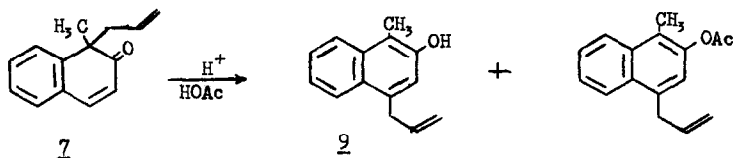


We have now investigated the migrations of allyl groups in β -naphthalenones. In these molecules the normal major rearrangement pathways - [3,3] migration of the allyl group to the position "para" to the oxygen atom, or [1,5] migration to the second ortho position if the para position is occupied³ - would both disrupt the aromaticity of the second ring. It seemed likely, therefore, that other, novel, reactions might occur in these compounds.

We have found that the acid-catalyzed migration of an allyl group in a β -naphthalenone does indeed occur by a novel [3,4] shift - a type of migration which has not previously been observed in the dienone-phenol rearrangement. In addition, a crotyl group undergoes both a [3,4] and an effective [1,5] sigmatropic shift, in spite of the apparent necessity for disruption of the aromatic ring during the rearrangement.

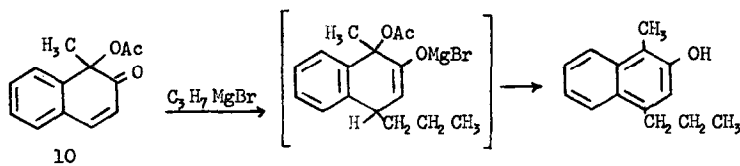
Naphthalenones 7 and 8 were prepared by Claisen alkylation of 1-methyl-2-naphthol. In comparison with migrations of allyl groups in monocyclic cyclohexadienones,³ rearrangement of 7 proceeded extremely slowly, requiring ca. 48 hours in a solution of 10% sulfuric acid (by volume) in acetic acid at room temperature for essentially complete disappearance of the starting material. The only products of the reaction were naphthol 9 and its acetate.

When the reaction was interrupted after one half-life, the yield of the acetate was only 3%

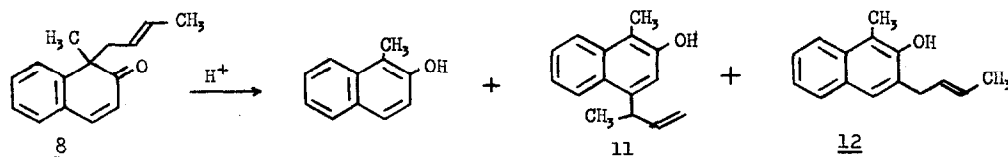


of that of 9, but the ratio of acetate to naphthol increased with increasing reaction time.

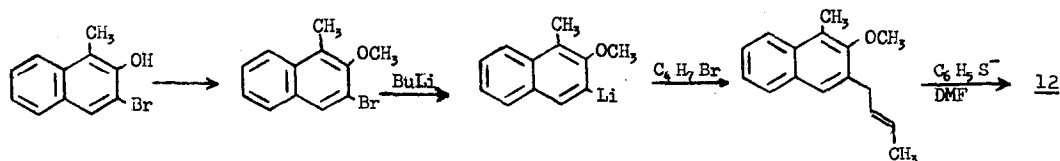
The structure of 9 was indicated by its nmr spectrum, which showed a singlet for the proton at C-3 at δ 6.8 and two distinct sets of aromatic multiplets around δ 7.25 and δ 7.8 ppm - a pattern characteristic of 1,4-disubstituted naphthalenes.⁴ Its structure was confirmed by reduction to 1-methyl-4-propyl-2-naphthol, which was independently synthesized by reaction of n-propyl magnesium bromide with the acetoxy ketone 10.⁵



Formation of 9 (assuming it to be a single step reaction) could proceed by either a [1,4] migration (without inversion of the allyl group) or a [3,4] migration (with inversion of the allyl group). To distinguish between these two possibilities, the rearrangement of the crotyl-substituted naphthalenone 8 was studied. Rearrangement of 8 proceeded readily in 1% sulfuric acid-acetic acid at room temperature to give (after 24 hours) three naphthols



identified as the cleavage product, 1-methyl-2-naphthol, and the rearrangement products 11 and 12 in yields (vpc) of 45, 24, and 31%, respectively. Naphthol 11 was identified by its nmr spectrum and by reduction to 4-*sec*-butyl-1-methyl-2-naphthol, which was synthesized by the method used for the n-propyl analog. The structure of naphthol 12 was suggested by its nmr spectrum, which showed the absence of a proton at C-3, and was confirmed by independent synthesis from 3-bromo-1-methyl-2-naphthol,⁶ as is shown below.



The two types of rearrangements thus appear completely regioselective, migration to C-4 proceeding with inversion of the allyl group and migration to C-3 without inversion. As indicated above, the simplest description of these processes is as [3,4] and [1,5] sigmatropic shifts, respectively. Both migrations could proceed by multistep processes however - the [3,4] migration by a [1,2] migration followed by a [3,3] migration, and the [3,5] migration by two [1,2] migrations. No distinction between these paths is yet possible. Two other multistep mechanisms appear to be ruled out. 1-Methyl-2-naphthol undergoes electrophilic substitution predominantly at C-6.⁶ Thus, neither rearrangement product could arise via a cleavage-realkylation process. We have found that allyl 1-methyl-2-naphthyl ethers in acid give rise to the same products obtained from rearrangement of the naphthalenones, but these rearrangements are appreciably slower than those reported above, and appear to proceed via the naphthalenones as intermediates, rather than the reverse.

Previous observations of acid-catalyzed rearrangements of cyclohexadienones indicated that effective migrating groups tend to give reactions which resemble thermal migrations, while poorer migrating groups undergo reactions resembling those which occur in carbonium ion rearrangements.⁷ The observation that a crotyl group (the better migrator, since it can bear a positive charge more easily) undergoes both a [1,5] shift⁸ and a [3,4] shift in a β -naphthalenone, while an allyl group undergoes only a [3,4] shift⁹, is consistent with our earlier generalization. One of us has suggested that "thermal" types of migrations proceed from the normal n -protonated cyclohexadienones, while the "carbonium-ion" migrations proceed from the higher energy η -protonated species. While our present results are consistent with this hypothesis, other interpretations are not excluded.

Acknowledgments: We thank the donors of the Petroleum Research Fund, administered by the American Chemical Society, for a grant in support of this work.

- 1) Reactions of Cyclohexadienones, XXX, Part XXIX: B. Miller, Tetrahedron Letters, 1010 (1972)
- 2) E.N. Marvell and J.L. Stephenson, J. Amer. Chem. Soc., 77, 5177 (1955).
- 3) B. Miller, ibid., 92, 6246 (1970).
- 4) e.g., Sadtler Standard Spectrum No. 13910.
- 5) F. Wessery and F. Sinwel, Monats., 81, 1055 (1950).
- 6) K. Fries and K. Schimmelschmidt, Ann., 484, 245 (1930).
- 7) B. Miller, J. Amer. Chem. Soc., 92, 6252 (1970).
- 8) Allyl groups do not undergo [1,5] shifts in cyclohexadienones, since [3,3] shifts are much more rapid [B. Miller, J. Org. Chem., 35, 4262 (1970)]. However, cyclopropylmethyl groups [B. Miller and K.-H. Lai, Tetrahedron Letters, 519 (1972)] and benzyl groups (unpublished work from this laboratory) do readily undergo such reactions. The thermal rearrangements of β -naphthalenones are presently under investigation.
- 9) Allyl groups undergo [3,4] migrations in simple cyclohexadienyl carbonium ions [H.-J. Hansen, B. Sutter and N. Schmid, Helv. Chim. Acta, 51, 828 (1968)].