Allylic Migrations in Acid-catalyzed Dienone–Dienone Rearrangements†

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ALLYL groups at the angular positions of cyclohexadienones have been shown to undergo very rapid acid-catalyzed Cope rearrangements to give phenols.[1] The rearrangements of similar dienones in which methyl groups are located at the positions to which the allyl groups would migrate have now been studied, in the expectation that the presence of substituents at the migration terminus would inhibit migration to that carbon. The actual results were however, quite different.

Rearrangement of the dienone (I) at room temperature in 0·1N-HCl–MeOH gave an almost quantitative yield of the *para*-dienone (II). The mechanism is not clear, since (II) could be formed

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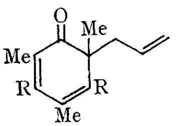
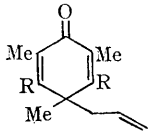
† Part of the series, "Reactions of Cyclohexadienones". For Part XIX, see B. Miller, *J. Amer. Chem. Soc.*, 1967, 89, 1690.

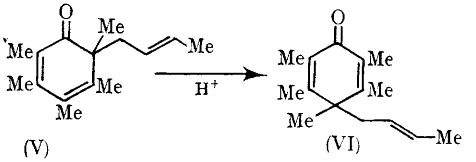
either by a single acid-catalyzed Cope migration or by a sequence of two Wagner–Meerwein shifts. The rearrangement of the dienone (III) was therefore studied. Surprisingly, rearrangement of (III) in $0\cdot1$N-HCl–MeOH gave the *para*-dienone (IV) and the Wagner–Meerwein rearrangement product, 3-allyl-2,4,6-trimethylphenol, in the ratio 6 : 1. "Blocking" the migration terminus with a methyl group therefore markedly increases the extent of migration to that position, since rearrangement of a dienone lacking the methyl group at C-4 gives a much higher ratio of 1,2- to 1,3-rearrangement products.[1b] This effect is presumably due to inhibition of the "normal" dienone–phenol rearrangement, rather than facilitation of the Cope rearrangement.



(I) R=Me
(III) R=H

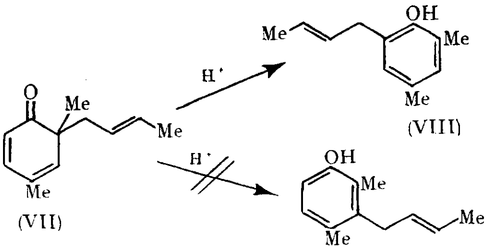


(II) R=Me
(IV) R=H



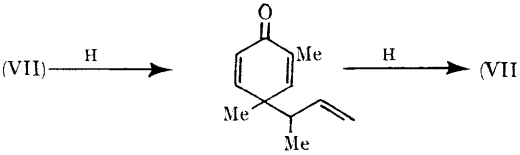
(V) (VI)

Migration of *trans*-2-butenyl groups was then examined, since steric interference between the migrating group and substituents at the migration terminus should be much greater than for migration of an allyl group. This was apparently the case for the acid-catalyzed rearrangement of the dienone (V), which gave approximately equal amounts of dienone the (VI) and the fragmentation product, pentamethylphenol. The dienone (VI) clearly results from two successive Wagner–Meerwein rearrangements, rather than from an acid-catalyzed Cope rearrangement.



(VII) (VIII) (IX)

That the rearrangement of (V) in acid is more complex than appears at first glance, however, is suggested by the results of rearrangement of the dienone (VII) in acid. The major product from this reaction was the phenol (VIII), which was accompanied by a small amount of 2,4-dimethylphenol. The structure of (VIII) was indicated by its n.m.r. spectrum, and was confirmed by comparison with a sample of (VIII) prepared by Claisen alkylation of 2-4-dimethylphenol with 1-bromobut-2-ene. No evidence for the presence of the "normal" dienone–phenol rearrangement product (IX) could be observed.



Rearrangement of (VII) in the presence of a large excess of phenol or of *para*-cresol did not reduce the yield of (VIII). This observation eliminates the possibility that (VIII) is formed by intermolecular alkylation of 2,4-dimethylphenol by the protonated dienone (VII) or by free butenyl carbonium ions. The hypothesis that (VIII) is formed by a sequence of two acid-catalyzed Cope rearrangements, giving first the cross-conjugated dienone (X) and then (VIII), is consistent with the results of other rearrangements of allyl-substituted cyclohexadienones reported in this and previous papers.[1] It is probable that the 2-butenyl group in (V) similarly undergoes a series of Cope migrations between the *ortho-* and *para-*positions before finally undergoing a Wagner–Meerwein rearrangement to form (VI).‡

Finally, it may be noted that preparation of cross-conjugated cyclohexadienones by acid-catalyzed rearrangement of linearly-conjugated cyclohexadienones is a useful synthetic reaction which, when applicable, gives appreciably better yields and fewer side-reactions than other methods.[1a,2]

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‡ The possibility that the 2-butenyl group in (VII) undergoes a direct *ortho–ortho'* migration cannot yet be eliminated. This type of rearrangement lacks close analogues, however, and seems less probable than a sequence of acid-catalyzed Cope migrations.

[1] (a) B. Miller, *J. Amer. Chem. Soc.*, 1965, **87**, 5115; (b) P. Fahrni, A. Habich, and H. Schmid, *Helv. Chim. Acta.*, 1960, **43**, 448; (c) J. Leitich, *Monatsh.*, 1960, **92**, 1167.

[2] R. Barner, A. Boller, J. Borgulya, E. G. Herzog, W. von Philipsborn, C. von Planta, A. Fürst, and H. Schmid, *Helv. Chim. Acta*, 1965, **48**, 94.