

Rearrangements of Cyclohexadienones: Migratory Aptitudes
of Methyl and Ethyl Groups

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The concept of migratory aptitudes in 1,2-rearrangements of carbonium ions has proved valuable,¹ although satisfactory methods of measurement are rare.² We consider the dienone-phenol rearrangement can offer an excellent system for comparing migratory aptitudes. For example the cations (3) and (4) derived from dienones (1) and (2) differ only in the nature of the migrating group R; they are conformationally quite rigid; steric interactions in the rearrangement will be small and as close as possible to identical in the two cases; and the migration step is rate determining (see Scheme).^{3,4} Studies by the methods of ref. 3, using aqueous sulphuric acid at 25°C show (1) and (2) to be equally basic. Under these conditions dienone (2) rearranges via its cation (4) (24.9 ± 0.3) times faster than does (1) via (3), over the large range of acidity studied, and the migratory aptitude of ethyl is thus 25 times that of methyl. Stiles and Mayer² give a value 17 in the **pinacol**-pinacolone rearrangement: their determination required a simplifying assumption which ours does not need, and we are uncertain whether the difference between the values is significant. Similar studies of the migratory aptitudes of other groups are in progress.

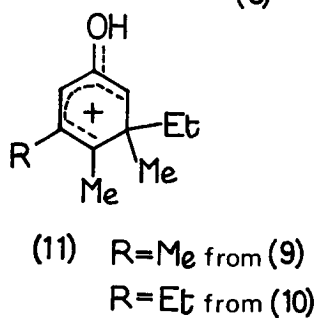
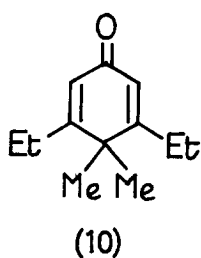
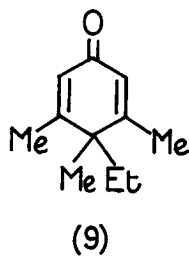
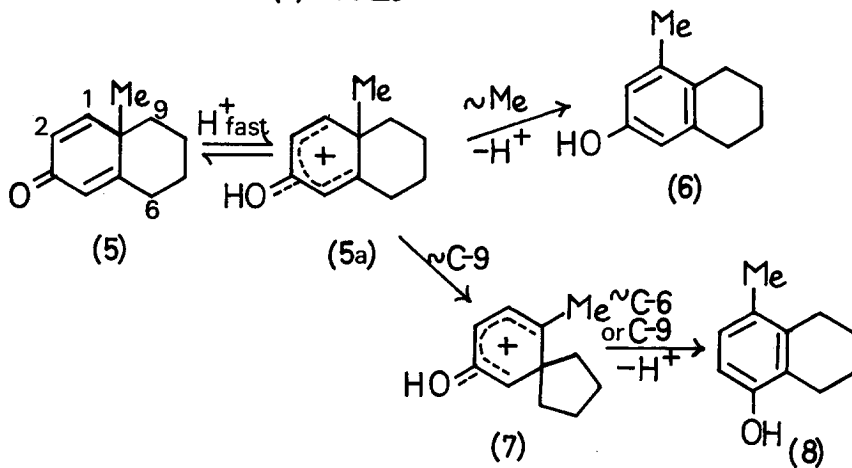
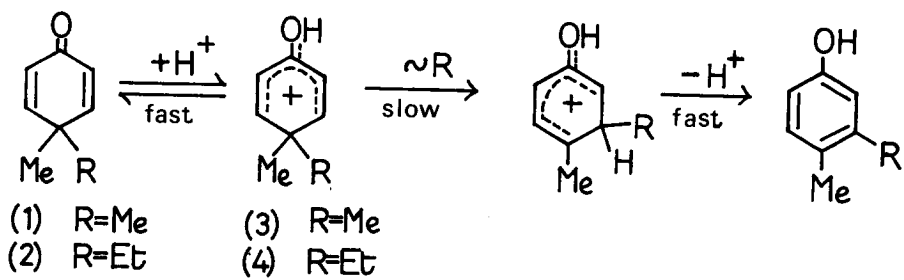
There is much qualitative evidence,⁵ based on intramolecular comparisons, that migratory aptitudes of alkyl groups in the dienone-phenol, as in the pinacol rearrangement², are in the order secondary > primary > methyl. A previous study

of (2), in which the migratory aptitudes of methyl and ethyl were compared intramolecularly,⁶ was presented in an ambiguous way but seems to show that methyl migrates in preference to ethyl. A re-investigation shows that rearrangement of (2) in 48% sulphuric acid at 25°C, or in acetic anhydride-H₂SO₄ followed by alkaline hydrolysis of the acetate, gives predominantly 3-ethyl-4-methylphenol by ethyl migration. This phenol can be distinguished with difficulty from 4-ethyl-3-methylphenol which is also formed to a small extent in the rearrangements.

Paramount among other dienone-phenol rearrangements which involve competition between migration of methyl and other alkyl groups are those of steroidal ring-A 1,4-dien-3-ones and bicyclic analogues such as (5), which give products of types (6) and (8).⁵ In connection with our studies of these reactions⁷ we needed a model which would allow the rate of migration of an alkyl chain to an occupied ring site to be estimated, free of factors such as ring strain [see (5) → (7)]. For this we used 4-ethyl-3,4,5-trimethylcyclohexa-2,5-dienone (9),[†] whose ethyl must migrate to C-3 or C-5. Significantly, the rates of this very slow reaction are virtually identical to those of (5) → (8),⁷ and to the rate of rearrangement of (10).³ This is good evidence that the cations of both (9) and (10) rearrange to (11), with (9) → (11) expected to be much the faster; (11) must then revert mainly to dienone cation by ethyl migration to C-4, and to a smaller extent rearrange to a phenol by ethyl migration to C-2. It implies that the reaction (5a) → (7) is also rapidly reversible.

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[†] This new compound has correct spectroscopic and analytical data.



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