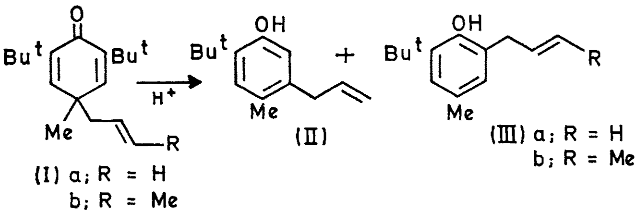
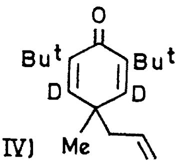
Allylic Inversion of the Migrating Group in the Acid-catalysed Rearrangement of a 2,6-Di-t-butylcyclohexa-2,5-dienone[1]

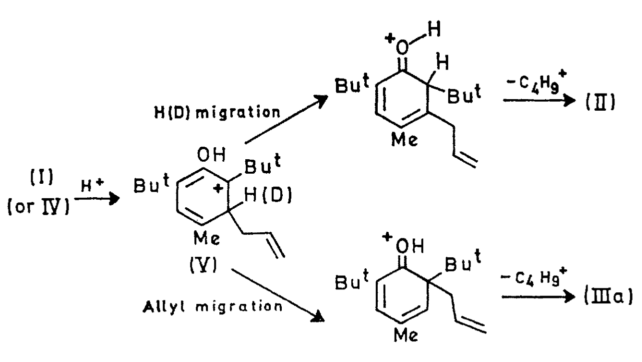
By KWO-HRONG LAI and BERNARD MILLER*
(*Department of Chemistry, University of Massachusetts, Amherst, Massachusetts* 01002)

Summary The acid-catalysed migration of an allyl group from C-4 to C-2 of a 2,6-di-t-butylcyclohexa-2,5-dienone proceeds with essentially complete allylic inversion, while migration to C-3 proceeds without inversion.

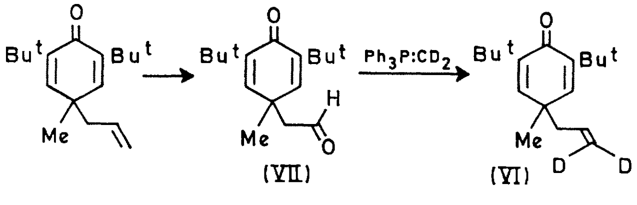
IT was reported that the rearrangement of dienone (Ia) in acid gave a mixture of phenols (II) and (IIIa).[2] Since migration of the crotyl group in dienone (Ib) proceeded without inversion to give phenol (IIIb), it was assumed that the allyl group in (Ia) similarly migrated without inversion during formation of (IIIa).[2] To distinguish between formation of (IIIa) by a direct [1,3] shift or by a sequence of [1,2] shifts, the rearrangement of the ring-deuteriated dienone (IV) was studied.[3] It was found that rearrangement of (IV) gave a mixture containing 76% of (IIIa) and 24% of (II) (both appropriately deuteriated), while undeuteriated (Ia) gave equal amounts of (II) and (IIIa). This result was taken to indicate that carbonium ion (V) was an intermediate in formation of both (II) and (IIIa), with a second migration of the allyl group in (V) to C-2 competing more successfully with migration of a deuteron to C-2 (or loss of a deuteron followed by re-protonation at C-2) than with migration or loss of a proton.[3]



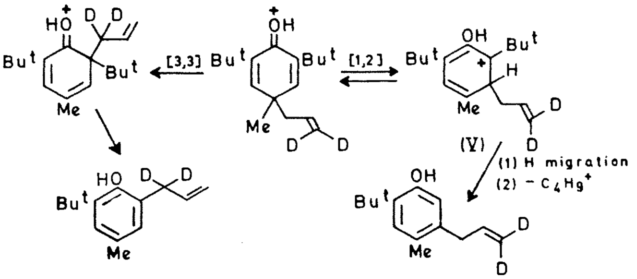

(IV)



We have now synthesized dienone (VI) by ozonolysis of (Ia) to aldehyde (VII) (m.p. 91—93°) followed by reaction of (VII) with dideuteriomethylenetriphenylphosphorane. N.m.r. analysis of (VI) showed the presence of 1·67 ± 0·03 atoms of deuterium in the vinyl position. Rearrangement of (VI) in 10% sulphuric acid in acetic acid, under the same conditions used for rearrangement of (Ia),[2] gave a 50:50 mixture of (deuteriated) (II) and (IIIa). The (II) obtained was found to retain all the deuterium at the vinyl position, demonstrating its formation by a [1,2] rather than a [2,3] migration. The n.m.r. analysis of (IIIa), however, showed the allylic methylene group to contain 1·61 ± 0·01 atoms of deuterium, demonstrating essentially complete inversion of the allyl group. Formation of (IIIa), therefore, unlike the apparently similar formation of (IIIb), proceeds by an acid-catalysed [3,3] sigmatropic shift. Undoubtedly, the strong steric repulsions between the methyl on the migrating crotyl group in (Ib) and the t-butyl group at the migration terminus prevent [3,3] migration in the rearrangement of (Ib).



The question then arises as to the reason for the marked effect of ring deuteriation on the ratios of products obtained from rearrangement of dienone (IV). This effect appears far too large to be accounted for as a secondary deuterium isotope effect.[3-5] One possible explanation is that loss of the proton or deuteron at C-3 is simultaneous with migration of the allyl group to C-3. However, the exclusive formation of phenol (IIIb) from (Ib) (a reaction which, on the basis of orbital symmetry rules,[6] must proceed by a sequence of [1,2] shifts), demonstrates that loss of the C-3 proton is *not* simultaneous with crotyl group migration in that case. It seems improbable (though not inconceivable) that [1,2] migration of an allyl group in (Ia) occurs simultaneously with loss of a proton, while [1,2] migration of a crotyl group is independent of loss of the proton. We prefer the alternative explanation that formation of carbonium ion (V) is reversible, with reverse migration of the



allyl group from C-3 to C-4 competing with loss or migration of the proton at C-3. [3,3] Migration of the allyl group from C-4 to C-2, in turn, competes with [1,2] migration of the allyl group to C-3.

It appears, therefore, that our earlier argument[3] that allyl migration in carbonium ions such as (V) can compete with loss of a proton to give an aromatic molecule is correct, although the direction of migration is the opposite of what we assumed to be the case. In retrospect, it is clear that migration of an allyl group in (V) to C-4 is more probable than its migration to C-2, both because of steric repulsion of the migrating group by the t-butyl group at C-2 and because of the stability of cross-conjugated cyclohexadienones as compared with linearly-conjugated cyclohexadienones.[7]

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[3] B. Miller, *J. Amer. Chem. Soc.*, 1965, **87**, 5111.

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