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# THE MECHANISM OF 1-3 ALLYL MIGRATIONS IN THE DIENONE-PHENOL REARRANGEMENT[1]

Bernard Miller

American Cyanamid Company, Agricultural Center
Princeton, New Jersey

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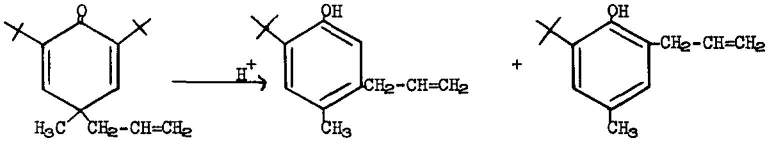
The preceding paper[1] reported that rearrangement of the 4-allylcyclohexadienone I in a sulfuric acid-acetic acid mixture gives a mixture of the 1-2 rearrangement product II and the 1-3 rearrangement product III.



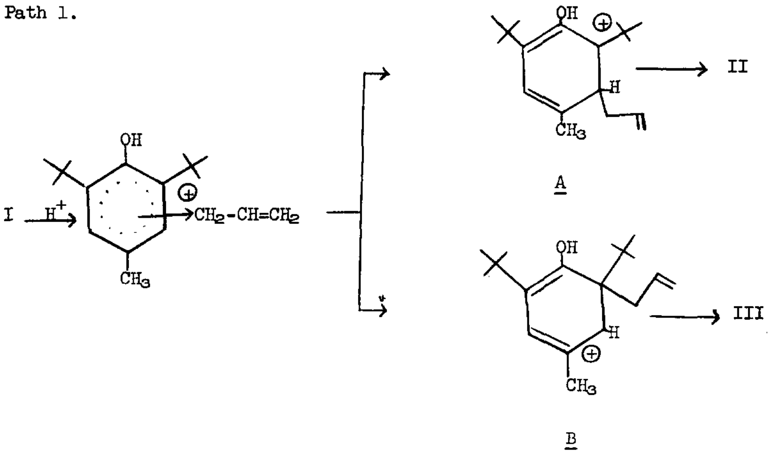
I II III

The 1-3 rearrangement was found to be intramolecular and to occur without inversion of the allyl group. Furthermore, the amount of 1-3 migration occurring appeared to depend on the ability of the migrating group to bear a positive charge, since the percentages of 1-3 migration products increased as the migrating group changed from ethyl to allyl to 2-butenyl[1].

Two possible mechanisms are consistent with these observations.

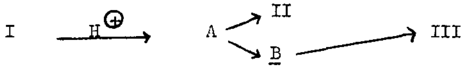
1. The migrating group may form a π-complex with the phenol ring. The π-complex may then collapse to form carbonium ion A, or, if the π-complex is sufficiently stable, the energetically favored carbonium ion B.

Path 1.



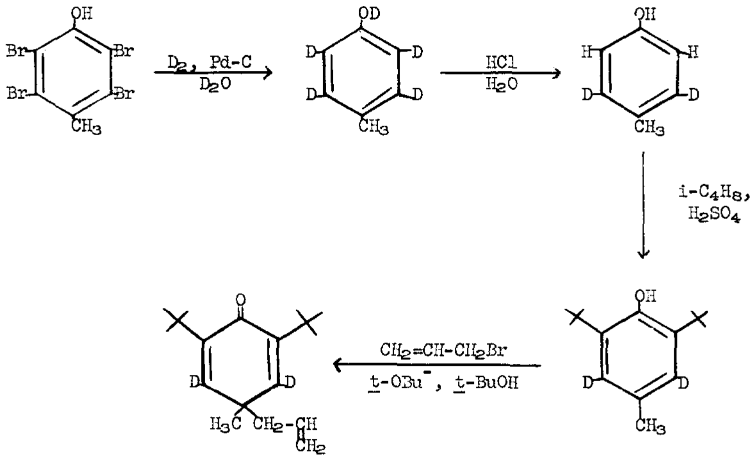
2. Carbonium ion A may be formed initially and subsequently rearrange to B.

Path 2.



In either path, loss of a t-butyl group from B would yield III, while transfer of a hydride ion to the ortho position of A, or loss of a proton and reprotonation at the ortho position, would precede loss of a t-butyl group to give II. The nature of the products obtained by Path 1. would be determined by the mode of collapse of the intermediate π-complex, while the nature of the products obtained by Path 2. would be determined by the competition between loss of a proton from A (or migration of a hydride ion in A) and further migration of the allyl group to give B.

To distinguish between these two possible paths, the deuterated dienone IV was synthesized as shown below:



IV

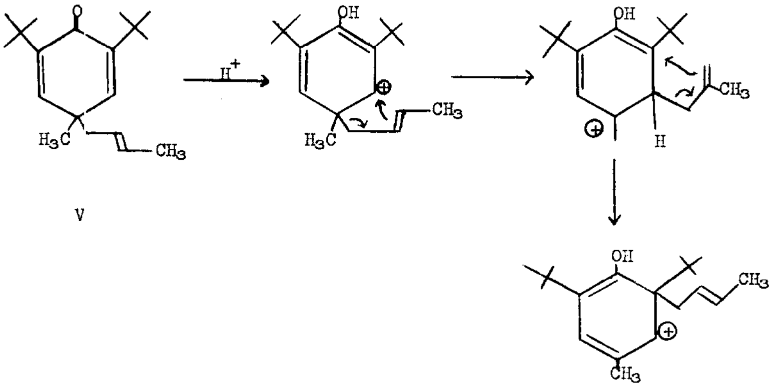
NMR analysis of IV indicated that 85-90% of the vinyl protons on the ring were replaced by deuterium. The mass spectrum of IV showed it to contain 6.9% of undeuterated and 27.4% of monodeuterated ketone.

Samples of I and IV were dissolved in 10% solutions of sulfuric acid in acetic acid for five hours, and the products analyzed by VPC on a six foot, 2% silicone gum (XE 60) column at 160°. Rearrangement of I gave a mixture of II and III in the ratio 50:50. Rearrangement of IV gave II and III in the ratio 26:75.

The large isotope effect observed requires that the product-determining step of the rearrangement involve the loss or migration of a deuterium atom. The 1-3 migration of the allyl group, therefore, must proceed by two successive 1-2 shifts.

Two consecutive allyl shifts may occur without resulting inversion of the allyl group either by a sequence of two allyl inversions (as in Path 2a) or by two rearrangements without inversion.

Path 2a



V

The observation that dienone V rearranges appreciably faster than dienone I[1] suggests that both allyl migrations occur without inversion, since attack by the methyl-substituted double bond of V on an atom adjacent to a *t*-butyl group should be significantly retarded by steric strain.

The unexpected second shift of the migrating group from the *meta* to the *ortho* position is undoubtedly due, in part, to the high migratory aptitudes of the allyl and butenyl groups. In addition, loss of a proton from *A* should be unusually difficult, since it would force the allyl and *t*-butyl groups into close proximity in the same plane. The relative importance of these two factors in determining the extent of 1-3 migration is now being studied.

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## REFERENCES

1. Reactions of Cyclohexadienones, VIII. Part VII, Preceding paper.