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

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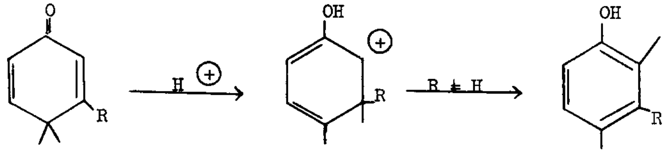
Acid catalyzed rearrangements of 1,4 cyclohexadienones normally result in 1-2 shifts of alkyl groups to give phenols[2]. While 1-3 migrations of substituents are common, particularly in rearrangements of steroid cyclohexadienones[3, 4], these processes have been shown to proceed by way of intermediate carbonium ions such as I[5-7], and occur only when I

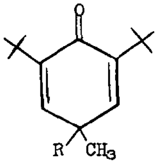


I

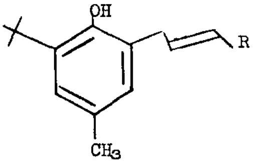
cannot lose a proton to give a phenol without further rearrangement.

We now wish to report that 1-3 migration of allyl groups can occur during dienone-phenol rearrangements even when the absence of substituents in the 3 position of the cyclohexadienone makes a 1-2 rearrangement quite feasible.

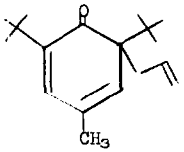
Dienone II[1], when dissolved in a nine per cent solution of sulfuric acid in acetic acid for five hours, was completely converted to an approximately equimolar mixture of two products, which were isolated by chromatography on alumina. The first component eluted was identified as 2-allyl-6-t-butyl-4-methylphenol (V) by comparison of its IR and NMR spectra and VPC retention times with those of a previously prepared sample[1]. This product, therefore, results from a 1-3 migration of the allyl group. The conjugated dienone VII, which must be an intermediate in the rearrangement, has been shown to lose a t-butyl group very rapidly under these conditions to give V[8].



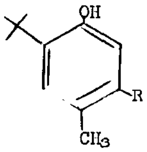
II R = CH_2-CH=CH_2
III R = C_2H_5
IV R = CH_2-CH=CH-CH_3



V R = H
VI R = CH_3



VII



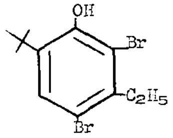
VIII R = CH_2-CH=CH_2
IX R = C_2H_5

The second product of the rearrangement of II was an oily phenol, isomeric with V (Anal. Calc'd. for $C_{14}H_{20}O$: C, 82.3; H, 9.85. Found: C, 81.8; H, 10.1). This phenol was assigned the structure 3-allyl-6-*t*-butyl-4-methylphenol (VIII) on the basis of the following evidence. Its NMR spectrum showed a hydroxyl hydrogen, a single *t*-butyl group, an allyl group and a methyl group attached to the aromatic ring. In addition, two aromatic hydrogen atoms were present which exhibited no detectable coupling and therefore appeared to be *para* to each other. While one aromatic hydrogen peak was at 3.10τ, which is typical of *meta* hydrogens in a series of phenols related to VIII, the second aromatic hydrogen peak appeared at 3.77τ, which is typical of hydrogen atoms *ortho* to the hydroxyl group. The presence of a free *ortho* position was confirmed by the physical properties of the phenol, which had longer retention times on alumina and VPC columns than V, and by its IR spectrum, which showed a stronger and broader hydroxyl peak than that of V. Furthermore, competitive reactions in a ten per cent solution of sulfuric acid in acetic acid showed that dienone II was consumed more than one hundred times as rapidly as III (although less than one-hundreth as rapidly as IV). This observation suggested that the allyl group of II, rather than the methyl group, had migrated during the rearrangement.

The elimination of a *t*-butyl group which accompanies formation of VIII appears to be general in dienone-phenol rearrangements of 2,6-di-*t*-butylcyclohexadienones. The 4-ethylcyclohexadienone III[8], when dissolved in a twenty-five per cent solution of sulfuric acid in acetic acid, rearranged quantitatively to a mixture of IX and its acetate, which was converted to IX by alkaline hydrolysis. The structure assigned to IX was supported by its elemental analysis (Calc'd. for $C_{13}H_{20}O$: C, 81.3; H, 10.5. Found: C, 81.4; H, 10.71) and its IR and NMR spectra, which showed features (in particular, the positions and the lack of splitting of the aromatic hydrogen peaks) similar to those of VIII.

The only structural question left unresolved by the spectra of IX is that of the relative positions of the ethyl and methyl groups. Reaction of a solution of IX in an acetic acid-water mixture with three moles of bromine gave, instead of the expected aldehyde or methyl ketone[9], a phenol with the formula $C_{12}H_{16}OBr_2$ (Anal. Calc'd.: C, 42.8; H, 4.76; Br, 47.6. Found: C, 43.2; H, 4.86; Br, 46.8.) The NMR spectrum of this phenol showed only a hydroxyl group, a t-butyl group, an ethyl group, and a single aromatic proton (τ=2.60).

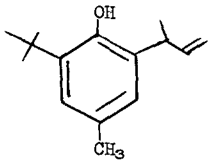
Since elimination of the methyl group must have taken place at the para position rather than the meta position, structure X is assigned to the brominated phenol, and the positions of the methyl and ethyl groups before bromination must be that shown in formula IX.



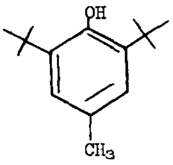
X

Migration of the ethyl group, rather than the methyl group, during the rearrangement of III shows that the ability of the migrating group to bear a positive charge, rather than steric effects, determines the choice of migrating groups in the 1-2 shift. This lends support to the assignment of structure VIII to the product of 1-2 rearrangement of dienone III.

Conversion of the *para*-dienone II to the *ortho*-dienone VII formally resembles a Cope rearrangement, despite the differences in reaction conditions. However, when the butenylcyclohexadienone IV[1] was dissolved in a seven per cent solution of sulfuric acid in acetic acid for three hours, the product of its rearrangement was VI[1], rather than the isomeric phenol XI which would result from a Cope rearrangement.



XI



XII

Rearrangement of IV gave, in addition to VI, about an equal yield of 2,6-di-*t*-butyl-4-methylphenol (XII). The fate of the butenyl group eliminated in the formation of XII was not determined. Elimination of an alkyl group from the *4*-position of a cyclohexadienone in acid has not previously been observed, but Kropp has reported the cleavage of an alkyl group from the *meta* position of a carbonium ion similar to I[10].

No evidence for the formation of products of 1-2 rearrangement of IV could be detected.

The simplest path for transfer of allyl groups from the *4* to the *2* positions of II and IV would be cleavage of the dienones to XII and allyl or butenyl carbonium ions, which could then realkylate XII at the *ortho* position. The rearrangements do not appear to follow intermolecular routes of this sort, however, since, under the conditions employed in the rearrangements, allyl alcohol, 2-buten-1-ol, and 1-buten-3-ol did not react with XII. Furthermore, rearrangement of II in the presence of six equivalents of phenol, which would be expected to trap any carbonium ions formed, did not change the nature or yields of the rearrangement products. No allylphenol could be detected, but a mixture of t-butylphenols was obtained in good yield.

The 1-3 migrations of allyl groups, therefore, appear to be true intramolecular rearrangements. Their mechanism will be considered further in the following paper.

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