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MECHANISMS OF THERMAL MIGRATIONS OF ALLYL AND BENZYL GROUPS IN METHYLENECYCLOHEXADIENES

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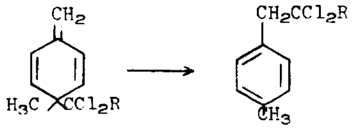
Polyhalomethyl groups at the quaternary carbons of cross-conjugated methylenecyclohexadienes ("semibenzenes" [1a]) undergo formal 1,5-shifts to the exocyclic methylene groups when heated to temperatures near 100° (e.g., 1 → 2).[1] A methyl group in semibenzene 3 undergoes a similar migration at 165° in decalin solution.[2] These reactions have been shown to proceed by free radical chain mechanisms, although the nature of the chain carriers have not been demonstrated.[2-4]



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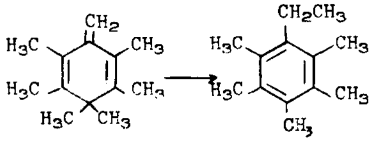
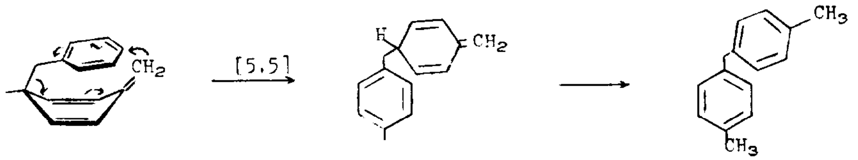


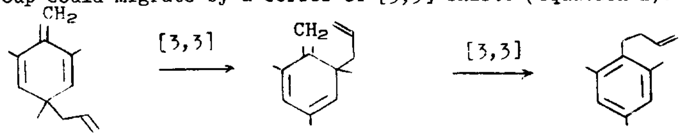
3

Rearrangements of semibenzenes bearing allyl or benzyl groups should be of particular interest, since migration of these groups by concerted paths might compete with free radical reactions. In addition to the possibility of concerted [1,5] sigmatropic shifts, a benzyl group could conceivably migrate via a thermally allowed[5] [5,5] sigmatropic shift, as in equation 1, while an



(1)

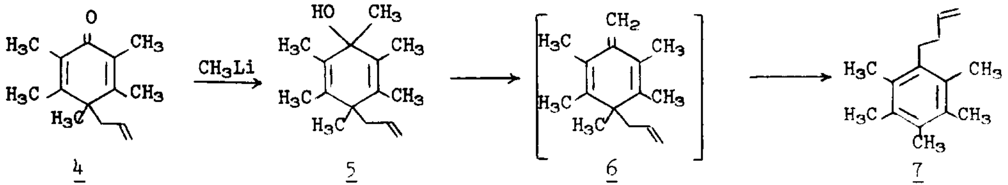
allyl group could migrate by a series of [3,3] shifts (equation 2).



(2)

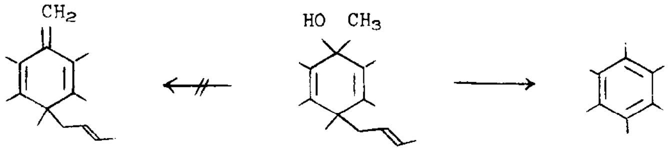
In this paper we report a study of the mechanisms of aromatization of 4-allyl and 4-benzyl-2,3,4,5,6-pentamethyl-1-methylenecyclohexa-2,5-dienes (6 and 10).

Addition of methyl lithium to dienone 4[6] gave the tertiary alcohol 5 (presumably a mixture of stereoisomers) as a viscous oil, which was dehydrated with p-toluenesulfonyl chloride in pyridine at 0°. When the reaction mixture was worked up at temperatures below 20°, the product appeared to be almost entirely the desired methylenecyclohexadiene 6. Its nmr spectrum (in CCl_4)



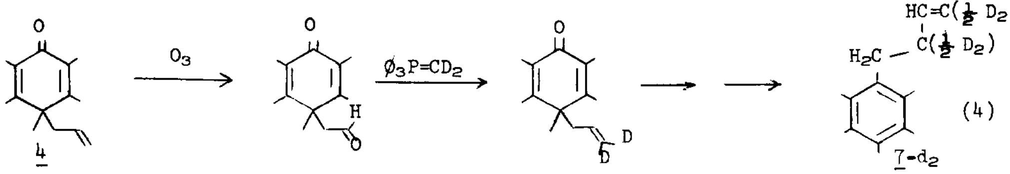
showed a sharp singlet (2H) at τ 5.13 ($\underline{CH_2}=C<^{C}_{C}$), quartets (6H apiece, $J < 0.5$Hz) at τ 8.14 and 8.22 ($\underline{CH_3}$-C=C), a singlet (3H) at τ 8.91 (-$\overset{|}{\underset{|}{C}}$-$\underline{CH_3}$), a multiplet (2H) around τ 7.7 (-$\underline{CH_2}$-C=C), and a multiplet (3H) from τ 3.7 to 5.4 (-$\underline{CH=CH_2}$). When the product was allowed to stand at room temperature, either neat or in methylene chloride solution, its spectrum changed, developing strong peaks in the aromatic methyl region (τ 7.86-7.92). After several days at room temperature, the semibenzene was largely converted to 4-pentamethylphenyl-1-butene (7), b.p. 111-115/15mm.

The rate of rearrangement of 6 was quite variable, and often showed an appreciable induction period. The rate was significantly slowed by addition of free radical inhibitors. The major rearrangement path therefore appeared to be a free radical chain process. To determine the nature of the chain involved, we desired to label the ends of the allyl group. An attempt to prepare the crotyl analog of 6 failed when attempted dehydration of the tertiary alcohol gave the cleavage product, hexamethylbenzene, rather than the desired methylenecyclohexadiene (equation 3).



(3)

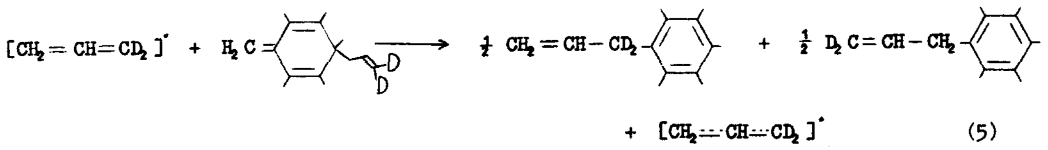
The deuterated analog of dienone 4 was therefore prepared as shown in equation 4. Nmr analysis showed the terminal methylene group to contain 1.83±0.01 atoms of deuterium. The dienone was



(4)

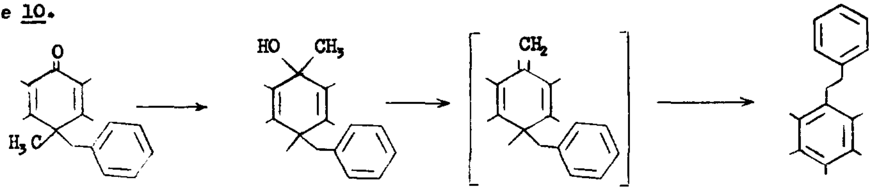
converted to 7-d_2 as described for the undeuterated analog. The terminal methylene group in the 7-d_2 obtained was found to contain 0.91± 0.07 atoms of deuterium. Complete equilibration of the ends of the allyl group had therefore taken place.

This observation eliminates any significant formation of 7 via [1,5] or [3,3] shifts. It also eliminates a free radical chain mechanism in which pentamethylphenyl radicals attack the terminal methylene of the allyl group of 6. A radical chain involving allyl radicals as the chain carriers (equation 5) appears to be the only mechanism which fits the data presented above.



(5)

We next attempted to prepare a methylenecyclohexadiene bearing a benzyl group at the quaternary carbon. Addition of methyl lithium to dienone 8 [7] gave dienol 9 as a single stereoisomer, m.p. (from pentane) 52-54°. However, dehydration of 9 with p-toluenesulfonyl chloride in pyridine, followed by working up the reaction in the usual manner, did not give the desired semibenzene 10.



8 9 10 11

Instead, 1-phenyl-2-pentamethylphenylethane, 11, m.p. (from hexane) 93.5-94.5°, was obtained in quantitative yield. Its nmr spectrum (in CCl_4) showed a broad singlet (5H, aromatic ring) at τ 2.4, a multiplet (4H, methylene groups) centered at τ 7.2, and three singlets in height ratios roughly 1:2:2 (totalling 15H, aromatic methyls) at τ 7.78, 7.81, and 7.83. In pyridine solution the three high field peaks merged to a moderately broad singlet at τ 7.86. No evidence could be observed for the formation of p-pentamethylbenzyltoluene, the product which would result from a [5,5] benzyl migration.

When p-toluenesulfonyl chloride was added to a cold (-20-0°) solution of 9 in pyridine and the nmr spectrum of the solution taken immediately, a series of sharp singlets were observed. These peaks were assigned to the terminal vinyl group (τ5.27,2H), benzylic methylene group (τ7.15,2H), methyl groups on the ring (τ8.15 and τ8.28, 6H apiece), and quaternary methyl group (τ8.77, 3H) of semibenzene 10. In addition, a strong peak at τ7.85 indicated the presence of 11. When the solution was allowed to stand in the nmr spectrometer, the peaks assigned to 10 rapidly decreased in intensity, while the peak for 11 increased. In a 0.3 M solution, the concentration of 10 was approximately halved in 15 minutes at 39°.

The rate of disappearance of 10 in pyridine solution was markedly decreased by the addition of trace amounts of diphenylpicrylhydrazyl and increased by the addition of benzoyl peroxide, indicating that a free radical chain mechanism was again occurring. Presumably, the mechanism is similar to that for rearrangement of 6, with benzyl radicals acting as chain carriers. Even quite high concentrations of diphenylpicrylhydrazyl, however, did not completely prevent isomerization of 10. It is not yet clear whether this indicates the occurrence of an intramolecular rearrangement competing with the free radical path.

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