

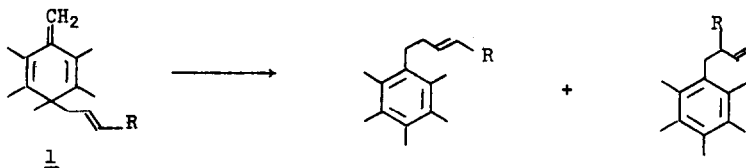
ALLYL AND BENZYL MIGRATIONS IN ORTHO-SEMIBENZENES

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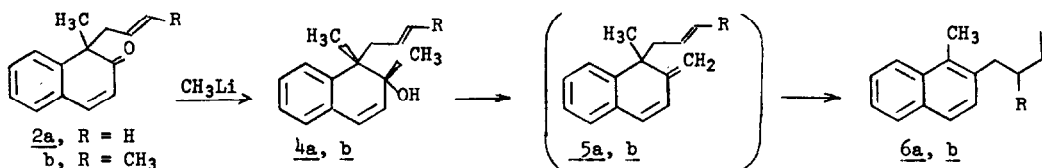
It was recently shown that allyl groups in para-semibenzenes (4-allyl-1-methylenecyclohexadienes) such as 1 readily undergo migration to the exocyclic methylene group by free



radical chain processes.¹ Aromatic products, in principle, could also be obtained from 1 by rearrangement via two successive Cope migrations. The corresponding cyclohexadienones rearrange exclusively by Cope migrations at 30-100°.² However, no evidence for such migrations could be observed in the reactions of para-semibenzenes. It was therefore of interest to examine the thermal rearrangements of ortho-semibenzenes, in which Cope rearrangements would give aromatic products, to see if concerted or free radical paths are favored.

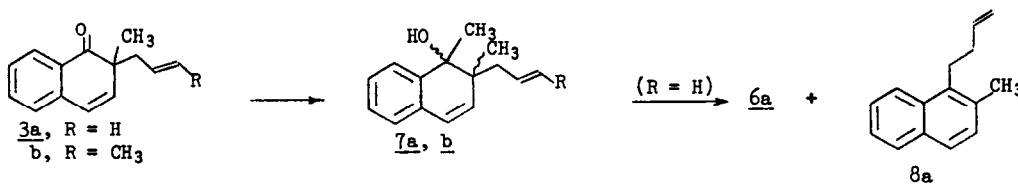
Reaction of methyl lithium with naphthalenones 2a-c gave a single alcohol in each case. Addition of the nmr shift reagent Eu(fod)₃³ resulted in larger shifts in the positions of the allylic or benzylic methylene signals than in the peaks for the methyls at C-1, suggesting that, as expected, the lithium reagent had added trans to the larger group in 2. Reaction of methyl lithium with naphthalenones 3a-c gave a mixture of isomeric alcohols in each case. Again, use of the shift reagent suggested that the Z isomers, resulting from attack of methyl lithium at the less hindered sides of the ketones, were predominant.

Despite careful monitoring of the reaction by nmr, dehydration of dienol 4a with phosphorus

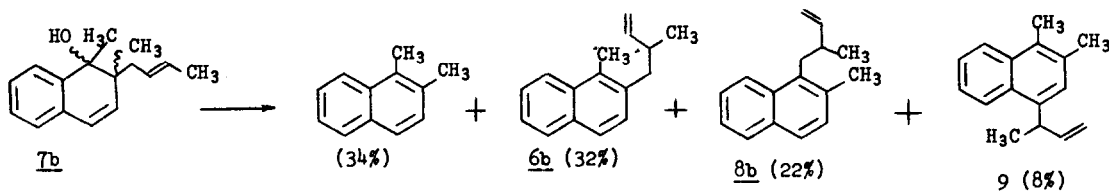


oxychloride in pyridine at 30°, or thionyl chloride in pyridine at 0°, gave no evidence for formation of the desired semibenzene **5a**. Instead, a single aromatic product was obtained and was assigned structure **6a**. Dehydration of dienol **4b** gave (in addition to 10% of the cleavage product 1,2-dimethylnaphthalene) the corresponding rearrangement product **6b**.

Dienols **7a** and **7b** reacted very slowly with phosphorus oxychloride in pyridine at temperatures below 50°. At 70°, dehydration of **7a** gave the two rearrangement products **8a** and **6a** in



an 8 to 1 ratio. Dehydration of **7b** under the same conditions gave 1,2-dimethylnaphthalene, **6b**, **8b**, and **9** in the yields shown below.



The locations of the substituents in each of the reaction products were established from their nmr spectra. In each product signals for methylene or methyl groups in α -positions (deshielded by the *peri* hydrogens) were located *ca.* 0.2 ppm downfield from signals for similar substituents in β -positions.

Formation of hydrocarbons **6a** and **6b** from **4a** and **4b** can only be explained by postulating the transient formation of the semibenzenes **5a** and **5b**, which rearrange too rapidly for detection. The regiospecific rearrangement of **5b** clearly proceeds by a [3,3] sigmatropic shift, rather than a free radical path similar to that observed in the rearrangement of **1**. Hydrocarbons

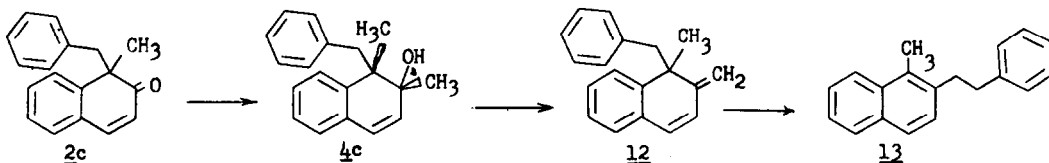
8a and 8b must similarly be formed by Cope rearrangements of the appropriate semibenzenes.⁴

Formation of 6a and 6b from dehydration of 7a and 7b can best be explained by Wagner-Meerwein shifts of allyl and crotyl groups in the α -naphthyl carbonium ions formed from 7. The more stable β -naphthyl carbonium ions formed from the rearrangement then yield semibenzenes 5a and 5b. The much higher yield of rearranged product from the crotyl derivative is in accord with this hypothesis.

Hydrocarbon 9 can also arise via a carbonium ion shift, as is shown by the fact that it is the only rearrangement product formed, together with 1,2-dimethylnaphthalene, from reaction of 4b with sulfuric acid in acetic acid or with aqueous hydrochloric acid. Under these conditions 7a similarly gives 4-allyl-1,2-dimethylnaphthalene (10).⁵ Formation of 9 but not of 10 from dehydration of the corresponding alcohols in pyridine is consistent with formation of 9 by a carbonium ion mechanism, in which a crotyl group is a much better migrator than an allyl group. The lack of any formation of 10 during dehydration of 7a in pyridine suggests that 9 is formed only via the carbonium ion path, and not from a Cope rearrangement of the semibenzene, since there seems no reason for a crotyl, but not an allyl, group to migrate to C-4 rather than the exocyclic methylene of a semibenzene.

The very rapid Cope rearrangements of allyl groups in the semibenzenes reported above suggested that benzyl groups in ortho-semibenzenes might undergo the corresponding [3,3] shifts.⁶

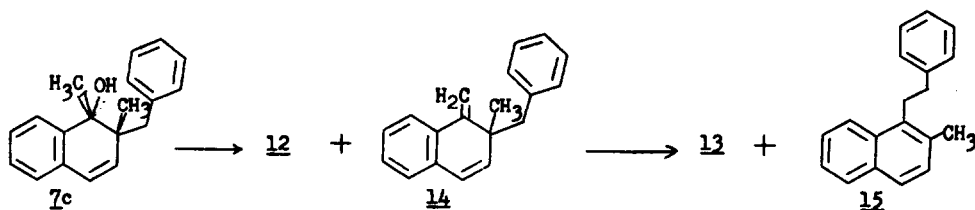
To see if this were so, semibenzene 12 was prepared by dehydration of 4c. In contrast to allyl substituted semibenzenes, 12 was easily isolated as a yellow oil which resisted rearrange-



ment at temperatures below 120°. At 165° in diglyme solution, 12 rearranged to give 13, together with a small amount of 1,2-dimethylnaphthalene.

Dehydration of dienol 7c gave an inseparable mixture which appeared to consist of 12 and 14. Rearrangement of this mixture at 165° for 16 hours gave approximately equal amounts of 13 and 15, again accompanied by a small yield of 1,2-dimethylnaphthalene. No evidence for the occurrence of any [3,3] migration could be observed.

The formation of [1,3] migration products from 12 and 14 presumably proceeds via free



radical chains similar to those responsible for [1,5] benzyl migrations in para-semibenzenes.¹

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