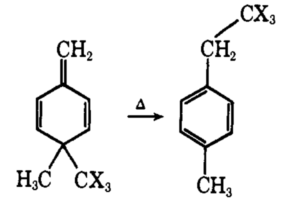
Allyl and Benzyl Migrations in the Semibenzene Rearrangement[1]

Bernard Miller* and Kwo-Hrong Lai

Contribution from the Department of Chemistry, University of Massachusetts, Amherst, Massachusetts 01002. *Received November 10, 1971*

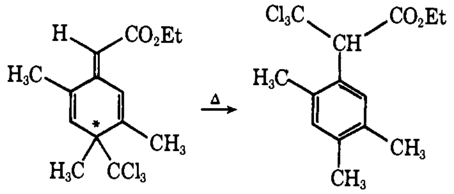
Abstract: Allyl and benzyl groups migrate rapidly from C-4 to the exocyclic methylene group of cross-conjugated methylenecyclohexadienes. Rearrangement occurs rapidly at room temperature and below, except when the exocyclic methylene group is flanked by *tert*-butyl groups. Deuterium labeling studies show that the two ends of the allyl group become equivalent during the reaction. The rearrangement rates are variable, show significant induction periods, and are affected by radical chain inhibitors and initiators. The rearrangements are best accounted for as proceeding by free-radical chains in which the substituent at C-4 forms the chain carrier.

Dichloromethyl and trichloromethyl groups have frequently been found to undergo formal 1,5 shifts in methylenecyclohexadienes ("semibenzenes") such as **1**.[2] The reactions proceed readily at temperatures as low as 80°, giving good yields of the more stable aromatic isomers. It has recently been reported that even methyl groups in **1** (X = H) will undergo similar migrations at 165°.[3]

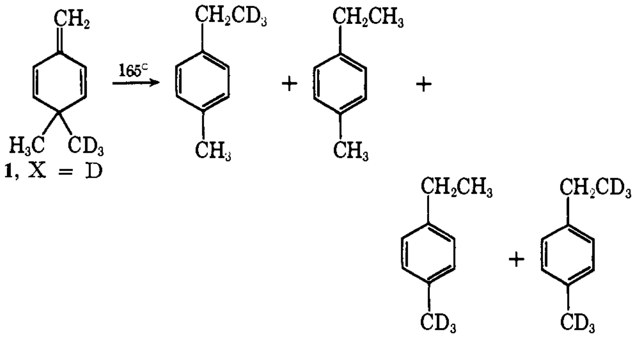


1, X = Cl, H

These rearrangements appear to proceed at least predominantly by free-radical chain mechanisms. Several studies have shown that the rearrangements are accelerated by light or by free-radical initiators, exhibit significant induction periods, and are inhibited by radical trapping agents.[3–5] Newman and Layton[5] have shown that the rearrangement of optically active **2** gives completely racemic **3**. This appears to rule out any rearrangement *via* intramolecular paths, since these should proceed suprafacially to give active products. Hart and DeVrieze have shown that pyrolysis of the labeled semibenzene **1** (X = D) gives a statistical mixture of products containing zero, one, and two trideuteriomethyl groups.[3] Again, this indicates that intramolecular paths contribute little, if anything, to the rearrangement.



2 **3**



Possible migrations of allyl and benzyl groups in methylenecyclohexadienes seemed of particular interest, since these groups have potential migration paths not available to simple alkyl groups. Allyl groups might undergo formal 1,5 shifts by a series of 3,3 migrations[6] (as well as by symmetry forbidden[7] 3,5 shifts), while a possible benzyl migration *via* a 5,5 shift can be envisaged. Several possible free radical migration paths also exist for these groups.

We were therefore encouraged to synthesize semibenzenes bearing allyl and benzyl groups at the quaternary carbons, and to investigate their rearrangements.

Preparation and Rearrangements of Polymethylsemibenzenes. Methylenecyclohexadienes have been prepared by reaction of cyclohexadienones with organometallic reagents, followed by dehydration of the resulting tertiary alcohols.[2,5] Our choice of starting ketones for this sequence was severely restricted by the difficulty in obtaining more than trace amounts of 4-allyl- or 4-benzyl-4-methylcyclohexadienones bearing hydrogens at C-2 or C-6.[8] We therefore decided to start our investigations with the more readily prepared polymethylcyclohexadienones and 2,6-di-*tert*-butylcyclohexadienones.

Reaction of cyclohexadienone **4** with methyllithium gave the desired cyclohexadienol **5** in quantitative yield. The nmr and ir spectra of the crude reaction product (see Experimental Section) clearly demonstrated its structure, except for the question of whether more than one stereoisomer had been formed, and indicated the absence of any significant impurities. Attempts to

---

[1] A preliminary account of part of this work has appeared: B. Miller and K. H. Lai, *Tetrahedron Lett.*, 1617 (1971).

[2] K. von Auwers and G. Keil, *Chem. Ber.*, **36**, 1861 (1903); **38**, 1963 (1905); K. von Auwers, *Justus Leibigs Ann. Chem.*, **352**, 219 (1907); K. von Auwers and W. Jühlicher, *Chem. Ber.*, **55**, 2167 (1922); R. C. Fuson and T. G. Miller, *J. Org. Chem.*, **17**, 316 (1952); R. L. Tse and M. S. Newman, *ibid.*, **21**, 638 (1956).

[3] H. Hart and J. D. DeVrieze, *Tetrahedron Lett.*, 4259 (1968).

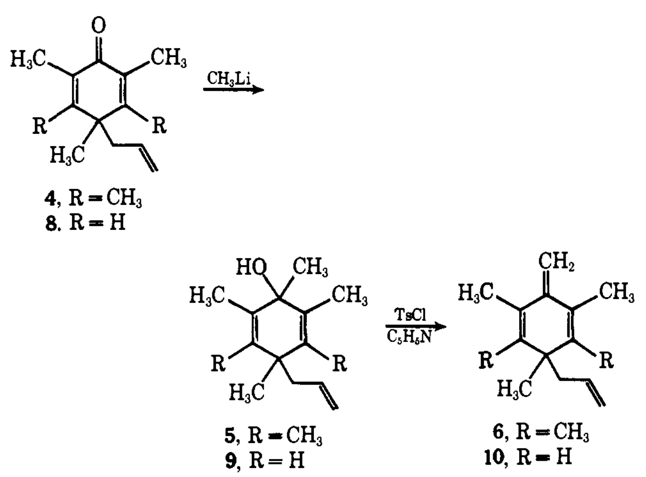
[4] C. W. Bird and R. C. Cookson, *J. Org. Chem.*, **24**, 441 (1959).

[5] M. S. Newman and R. M. Layton, *ibid.*, **33**, 2338 (1968).

[6] B. Miller in "Mechanisms of Molecular Migrations," Vol. I, B. S. Thyagarajan, Ed., Interscience, New York, N. Y., 1968, pp 249–254.

[7] R. B. Woodward and R. Hoffmann, *Angew. Chem., Int. Ed. Engl.*, **8**, 781 (1969).

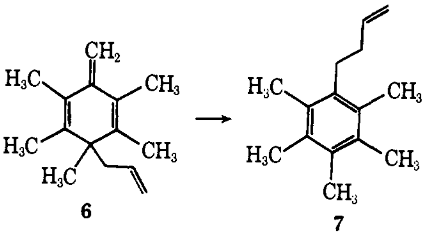
[8] R. Barner, A. Boller, J. Borgulya, E. G. Herzog, W. von Phillipsborn, C. von Planta, A. Fürst, and H. Schmid, *Helv. Chim. Acta*, **48**, 94 (1965).


4, R = CH_3
8. R = H
5, R = CH_3
9, R = H
6, R = CH_3
10, R = H

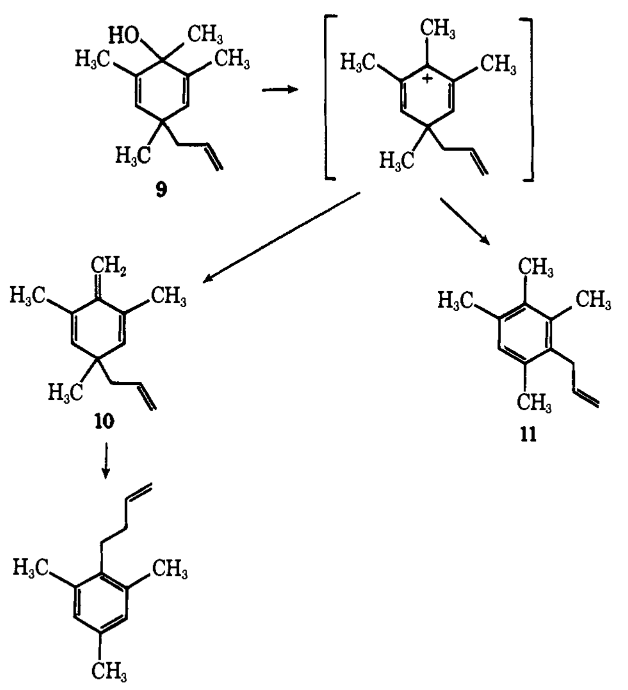
further purify the product by column chromatography on Florisil resulted in appreciable decomposition. The reaction product was therefore directly dehydrated with *p*-toluenesulfonyl chloride in pyridine.

When the reaction was carried out at room temperature, the nmr spectrum of the product suggested that it was a mixture of aromatic and nonaromatic products. On standing, the percentage of the aromatic product increased at the expense of the nonaromatic product. When the dehydration was carried out below 0°, however, and the mixture worked up quickly at low temperatures, the product appeared to consist largely of a single product which could be assigned the structure of the desired semibenzene **6** on the basis of its nmr spectrum, which is described in the Experimental Section.

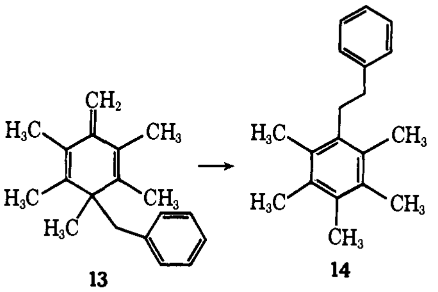
On standing, the nmr spectrum of the product changed markedly. All the peaks attributed to the semibenzene decreased in intensity while peaks attributed to aromatic methyl absorptions increased markedly. The vpc of the mixture, however, did not change with time. It showed the presence of only one major component. On isolation, this was identified as 1-(3-butenyl)-2,3,4,5,6-pentamethylbenzene (**7**) on the basis of its elemental analysis and nmr spectrum (see Experimental Section).


6
7

In contrast to formation of **6** by dehydration of **5**, dehydration of cyclohexadienol **9**, even at low temperatures, resulted in immediate formation of a product with strong aromatic methyl peaks in the nmr. Small singlets at τ 8.16 and 9.02, which faded slowly on standing at room temperature, suggested that some of the desired **10** had been formed during the reaction. The vpc showed the presence of two major products in the ratio *ca.* 1:2. The two products were isolated by preparative vpc and were found to be isomers of the formula $C_{13}H_{18}$. The nmr spectrum of the major isomer showed, in addition to aromatic methyl resonances totaling 12 hydrogens, a one-proton aromatic hydrogen singlet and a two-hydrogen multiplet around τ 6.66, attributed to a methylene group flanked by an aromatic ring and a double bond. The compound was assigned structure **11**, and presumably arose from a Wagner–Meerwein shift in the intermediate cyclohexadienyl carbonium ion. The minor isomer showed a two proton aromatic singlet and a normal benzylic multiplet around τ 7.33, as well as two singlets (in the ratio 2:1) for the three aromatic methyl groups. It was assigned structure **12**, and presumed to arise from rearrangement of the semibenzene **10**.


9
10
11
12

Benzyl Group Migration. Addition of methyllithium to 4-benzyl-2,3,4,5,6-pentamethylcyclohexa-2,5-dien-1-one gave the desired cyclohexadienol as a solid, mp 52–54°. No evidence for formation of more than one isomer could be detected. Dehydration of the dienol with *p*-toluenesulfonyl chloride in pyridine at room temperature gave a white solid, mp 93.5–94.5°, in high yield. Its elemental analysis and nmr spectrum (see Experimental Section) demonstrated its structure to be 2-pentamethylphenyl-1-phenylethane (**14**). When the dehydration was carried out below 0° and the nmr spectrum of the pyridine solution was taken immediately, a series of sharp singlets was observed (see Experimental Section). These peaks were assigned to the vinyl protons, benzylic methylene group, allylic methyls, and quaternary methyl group of semibenzene **13**. A strong aromatic methyl absorption at τ 7.85 was attributed to the *p*-toluenesulfonate group and to any **14** present in the mixture. The peaks attributed to **13** faded slowly when the solution was allowed to stand

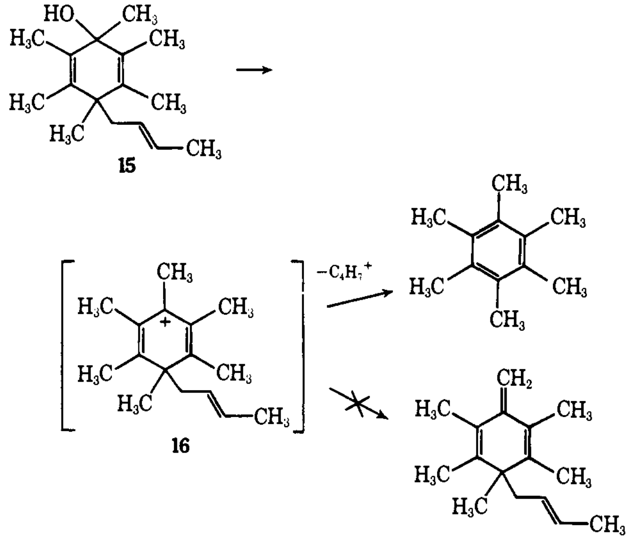

13
14

at −10° and much more rapidly at higher temperatures. The half-life of **13** at 39° was about 15 min. As the peaks for **13** decreased in intensity, the intensity of the broad singlet at τ 7.85 increased. Work-up of the mixture gave **14** in essentially quantitative yield.

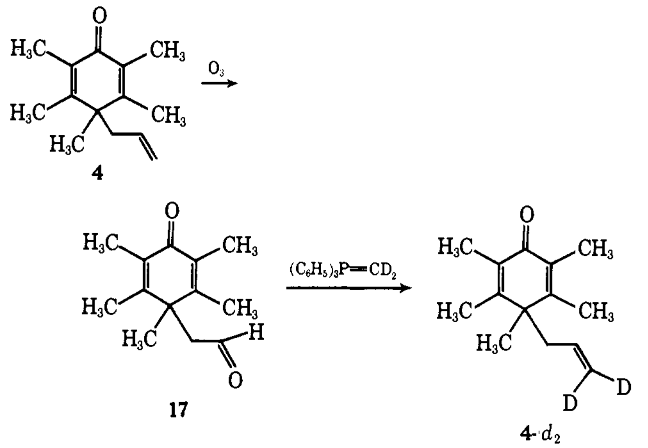
Evidence for Free-Radical Mechanisms of Allyl and Benzyl Migrations. The rate of conversion of **6** to **7** was quite variable. The half-life of different samples of **6** ranged from a few hours to several days. The slower isomerizations exhibited significant induction periods when their rates were followed by nmr analysis. The induction periods could be lengthened by addition of free-radical inhibitors such as *N*,*N*-diphenylpicrylhydrazyl, or shortened by addition of benzoyl peroxide.

Similarly, addition of *N*,*N*-diphenylpicrylhydrazyl to a pyridine solution of **13** at −10° resulted in a marked decrease in the rate of disappearance of the peaks attributed to **13**, although even at high inhibitor concentrations the rearrangement of **13** could not be completely prevented. Addition of benzoyl peroxide resulted in a moderate increase in the rearrangement rate.

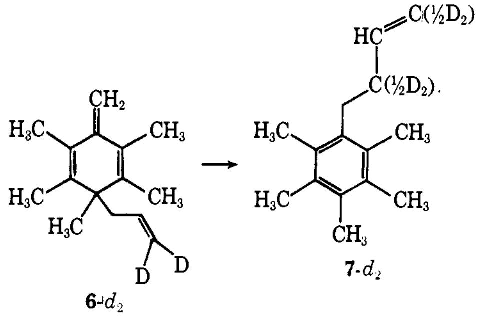
To determine whether rearrangement of **6** had proceeded with inversion or retention of the structure of the allyl group, it was necessary to investigate the migration of an unsymmetrical allyl group. An attempt to synthesize the crotyl-substituted semibenzene, however, failed. Reaction of the appropriate dienone with methyllithium appeared to proceed normally to give the desired cyclohexadienol, **15**. Attempted dehydration of **15** with *p*-toluenesulfonyl chloride in pyridine at room temperature gave a crystalline product whose nmr spectrum showed a single line at τ 7.89. The product was identified as hexamethylbenzene by comparison with an authentic sample. It is presumed that hexamethylbenzene was formed by fragmentation of carbonium ion **16**. Dehydration at lower temperatures gave mixtures whose nmr spectra suggested the presence of some of the desired semibenzene as well as aromatic products. Further work along this line, however, did not seem likely to be profitable.



The deuterium-labeled semibenzene **6**-d_2 was instead synthesized to determine the fate of the allyl group. Dienone **4** was ozonized to form the ketoaldehyde **17**, which was then treated with dideuteriomethylenetriphenylphosphorane to give **4**-d_2. Nmr analysis showed the terminal carbon of the allyl chain to contain 1.83 ± 0.01 atoms of deuterium[9] based on internal comparison with the area of the allylic methylene absorption. Reaction with methyllithium and dehydration at low temperature give **6**-d_2. Its nmr spectrum was essentially identical with that of the deuterium free analog except for decreased intensity of the vinyl peaks from τ 4 to 5.4. Unfortunately, the instability of the semibenzene and the presence of the peak for the exocyclic methylene group prevented an accurate determination of the location of the deuterium atoms in **6**-d_2. There seems little reason, however, to believe they are different from those in **4**-d_2.



On standing at room temperature for 3 days, **6**-d_2 rearranged quantitatively to form the aromatic isomer **7**-d_2. Nmr analysis of **7**-d_2 showed that the terminal methylene group contained 0.91 ± 0.07 atom of deuterium,[9] based on comparison with the area of the benzylic methylene group. The deuterium had therefore become equally distributed between the two ends of the allyl group during the migration.

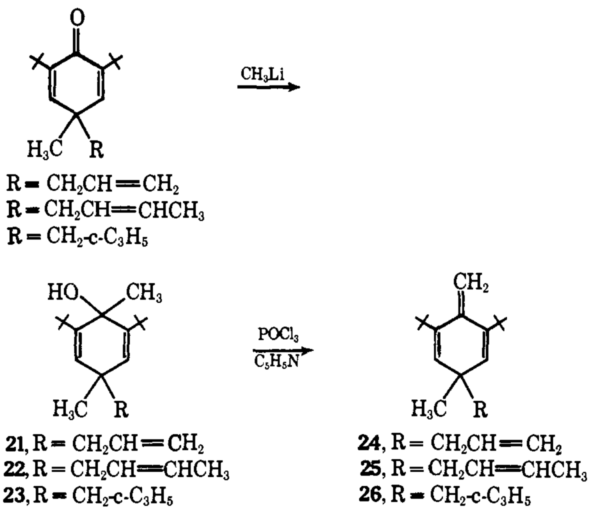


Semibenzenes Bearing *tert*-Butyl Groups. While dienones **4** and **8** reacted rapidly with methyllithium, no reaction could be observed when cyclohexadienone **18** was allowed to react with methyllithium in ether or benzene solution at room temperature. When a benzene solution of **18** and methyllithium was evaporated to dryness under vacuum with mild heating, according to the procedure of Becker,[10] however, the reaction proceeded smoothly to give cyclohexadienol **21**. The crotyl and cyclopropylmethyl-substituted dienols were similarly prepared by reaction of the corresponding dienones with methyllithium. (The previously unreported cyclohexadienone **20** was prepared in low yield by reaction of **18** with the Simmons-Smith reagent.[11])

---

(9) The precisions given for deuterium analyses represent the reproducibility of repeated integration traces. They are not intended to represent the accuracy of the deuterium analyses.

(10) H.-D. Becker, *J. Org. Chem.*, 32, 4093 (1967).



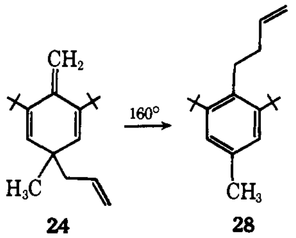
18, R = CH$_2$CH=CH$_2$
19, R = CH$_2$CH=CHCH$_3$
20, R = CH$_2$-c-C$_3$H$_5$

21, R = CH$_2$CH=CH$_2$
22, R = CH$_2$CH=CHCH$_3$
23, R = CH$_2$-c-C$_3$H$_5$

24, R = CH$_2$CH=CH$_2$
25, R = CH$_2$CH=CHCH$_3$
26, R = CH$_2$-c-C$_3$H$_5$

Attempts to purify cyclohexadienols **21–23** failed since vpc or column chromatography on alumina or Florisil resulted in partial decomposition. However, the structures of the cyclohexadienols were readily established from their nmr spectra. These spectra also suggest that mixtures of cis and trans isomers are formed in each case, since the resonances for the C-1 methyls appear as two peaks separated by about 0.05–0.1 ppm for each compound, in the ratio *ca.* 1:3 with the larger peak upfield. These peaks are considered to be due to mixtures of cis and trans isomers in the products. We do not believe that the differences in location for the peaks for the C-1 methyls are large enough to be ascribed to differences between the axial and equatorial locations for these groups, since the equatorial position should be much more crowded by the two *tert*-butyl groups. It seems more likely that the C-1 methyls maintain axial positions, and that the isomers differ in their geometries at C-4.

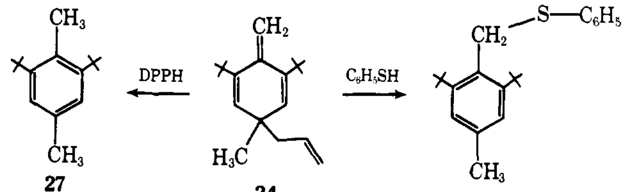
The crude dienols were dehydrated with phosphorus oxychloride in pyridine, giving the desired semibenzenes **24–26**, whose structures were confirmed by their nmr spectra. Semibenzenes **24** and **25**, in contrast to their polymethyl-substituted analogs, proved to be stable at room temperature, and could be isolated in pure form by chromatography on silica gel. Compound **26** was obtained in such small amounts that chromatography was not attempted. Its nmr spectrum clearly demonstrated its structure, but showed that it contained about 20% of 2,6-di-*tert*-butyl-1,4-dimethylbenzene (**27**) resulting from cleavage of a cyclopropylmethyl group from the molecule. No peaks not attributable to **26** or **27** were present.



24 **28**

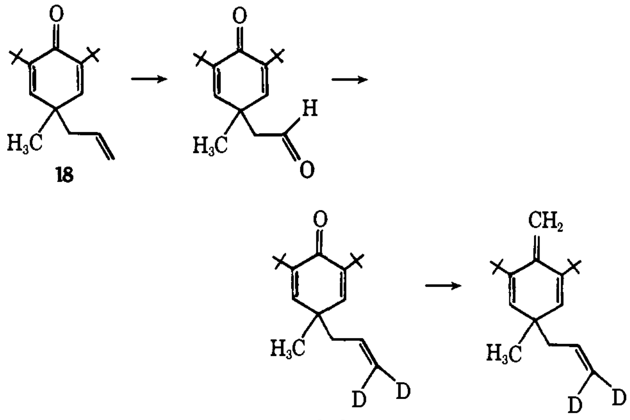
While the semibenzenes appeared quite stable at room temperature, they rearranged completely to form aromatic products in 2 hr at 160°. Rearrangement of **24** at 160°, whether neat or in alcohol, chloroform, or methyl iodide solutions, gave **28** as the only product which could be detected by vpc. Although **24** was quite stable by itself at room temperature, it did rearrange quite slowly to **28** at room temperature in methyl iodide solution. After 15 days, rearrangement was about 50% complete.

A kinetic study of the rearrangement of **24** in ethylene glycol solution at 122.0° showed that the rearrangement exhibited a significant induction period, after which the reaction proceeded at a rate which was approximately first order in **24**. The intermediacy of free radicals in the reaction was confirmed by the observation that a solution of **24** in benzene decolorized *N*,*N*-diphenylpicrylhydrazyl (DPPH) slowly at room temperature, or very rapidly at 150°. Surprisingly, the major product of this reaction was found to be 2,6-di-*tert*-butyl-*p*-xylene (**27**). No **28** was formed under these conditions. The fate of the DPPH was not determined. When thiophenol was added as a chain-trapping agent a product assigned structure **29** was obtained after 1 hr at 100° or 3 days at room temperature. The presence of *trans*-stilbene, however, did not affect the normal course of the rearrangement to **28**.



27 **24** **29**

The deuterium-labeled semibenzene **24**-d_2 was prepared in a manner similar to the preparation of **6**-d_2.



18 **18**-d_2 **24**-d_2

Ozonolysis of dienone **18** gave the desired ketoaldehyde which on reaction with dideuteriomethylenetriphenylphosphorane gave **18**-d_2, containing 1.76 ± 0.02 atoms of deuterium (by nmr) at the terminal methylene group. Conversion of the dienone to the semibenzene as usual gave **24**-d_2 with 1.79 ± 0.02 atoms of deuterium at the terminal carbon of the allyl chain.

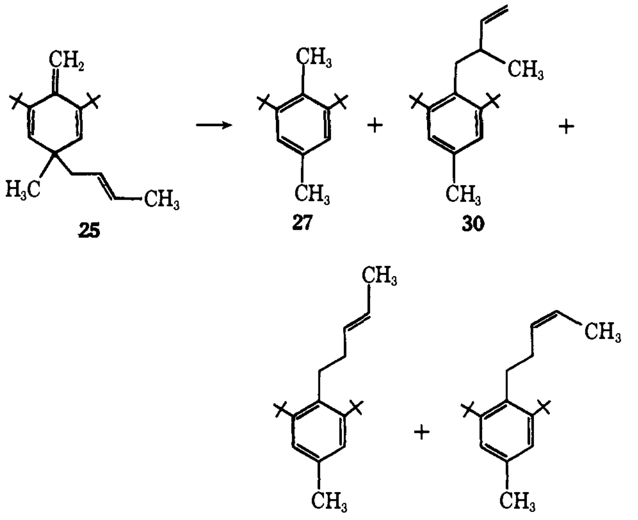
Rearrangement of **24**-d_2 at 150° gave **28**-d_2 containing 0.90 ± 0.01 atom of deuterium at the terminal vinyl carbon. Thus, exactly 50% of the deuterium appeared at the end of the allyl chain, as would be expected from a process involving equilibration of the ends of the allyl group. The allylic methylene group also appeared to contain about one atom of deuterium, although a very

---

(11) H. E. Simmons and R. D. Smith, *J. Amer. Chem. Soc.*, **80**, 5324 (1958); **81**, 4256 (1959).

accurate analysis was precluded by the overlapping methyl peak. When unreacted 24-d_2 was recovered from a reaction after one half-life for rearrangement, it was observed that no change in the position of the deuterium had occurred. This excluded the possibility that equilibration of the ends of the allyl group had preceded rearrangement

Crotyl and Cyclopropylmethyl Migrations. In contrast to the rearrangement of **24**, rearrangement of semibenzene **25** gave four products in yields of 12, 21, 44, and 23% (arranged in order of appearance in the vpc). These products were isolated by preparative vpc and identified by their elemental analysis and nmr spectra as compounds **27** and **30–32**.

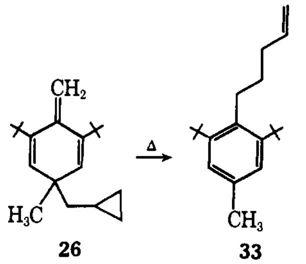


25 **27** **30**

31 **32**

A characteristic feature of the nmr spectra of these compounds, which are described in the Experimental Section, is the very low-field positions for the benzylic methylene groups of the side chains, and for one of the aromatic methyls of **27**, due to steric deshielding by the adjacent *tert*-butyl groups.[12a] Similar downfield shifts are observed in the spectra of **28** and **33** (see below). The geometries of the cis and trans isomers, **32** and **31**, were assigned on the basis of the somewhat greater width of the vinyl multiplet in **31**, expected to result from trans coupling of the vinyl protons, and of the appreciably greater yield of **31**. These assignments were supported by the infrared spectra of the two isomers. The spectrum of the product assigned structure **31** showed an intense out of plane hydrogen bending absorption at 965 cm^{-1}, appropriate for a trans-substituted double bond[12b] while the product assigned structure **18** showed a typical cis-substituted double bond peak[12b] at 690 cm^{-1}. The spectra of both compounds were essentially transparent in the region in which the other absorbed strongly.

Finally, rearrangement of semibenzene **26** gave one major product in addition to two trace products which were not isolated. The nmr spectrum of the major product showed, in addition to the three singlets for the aromatic protons, the aromatic methyl group, and the *tert*-butyl groups, the presence of a monosubstituted olefin and of benzylic and allylic methylene groups, as well as a methylene group not adjacent to a double bond. It was assigned structure **33**.



26 **33**

Discussion

Several reasonable types of migrations of allyl and benzyl groups could have been anticipated in the thermal rearrangements of semibenzenes. The evidence presented above suffices to eliminate most of these possibilities.

Either a 1,5 shift or a sequence of two 3,3 shifts of allyl groups in semibenzenes from C-4 to the exocyclic methylene groups would result in deuterium atoms at the terminal carbon of the allyl group being retained at that position in the product. A direct 3,5 shift would result in the deuterium atoms being localized on the allylic methylene group with no deuterium at the vinyl position. It is clear that our finding that exactly 50% of the deuterium is located at the terminal vinyl carbon in the products of rearrangement of **6**-d_2 and **24**-d_2 is inconsistent with any of these mechanisms. (The possibility that the rearrangements occur by combinations of two or more competing mechanisms cannot be rigorously excluded. The probability of several mechanisms proceeding at precisely the correct relative rates to locate exactly half the deuterium at the terminal vinyl position, in both **7**-d_2 and **28**-d_2, however, is exceedingly low.)

Equilibration of deuterium between the ends of the allyl chain can be explained if the semibenzenes simply dissociate into allyl and benzyl radicals, which then recombine to form the aromatic products. Such a mechanism cannot readily be excluded on energetic grounds. The dissociation energy of the bond linking an allyl (or benzyl) group to C-4 of a semibenzene would be reduced below the normal 80–85 kcal/mol[13,14a] dissociation energy of a C–C bond by the stabilization energies of the allyl and benzyl radicals (*ca.* 13 kcal/mol for each radical[14]) and by the stabilization energy of the newly formed aromatic ring (*ca.* 36 kcal/mol). (It may not be evident that both benzylic and aromatic stabilization energies should be counted. This point may be more clearly illustrated in the energy level diagram, Chart I). Thus, on the basis of normal bond energies alone, activation energies for dissociation of allyl- or benzyl-substituted semibenzenes should be around 18–23 kcal/mol.

If the rearrangements of compounds **8** and **24** proceed by simple dissociation–recombination processes, however, they should be simple first-order reactions whose rates would not be very susceptible to change by the presence of other reagents. In fact, as is shown

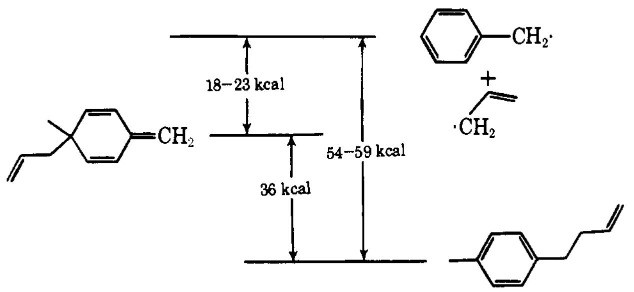
---

[12] (a) W. A. Gibbons and V. M. S. Gil, *Mol. Phys.*, **9**, 167 (1965); (b) L. J. Bellamy, "The Infra-red Spectra of Complex Molecules," 2nd ed, Wiley, New York, N. Y., 1958, pp 96–98. See also, B. Miller and H. Margulies, *J. Amer. Chem. Soc.*, **87**, 5106 (1965).

[13] T. L. Cottrell, "The Strengths of Chemical Bonds," 2nd ed, Butterworths, London, 1958.

[14] (a) S. W. Benson, *J. Chem. Educ.*, **42**, 502 (1965); (b) K. W. Egger, D. H. Golden, and S. W. Benson, *J. Amer. Chem. Soc.*, **86**, 5420 (1964).

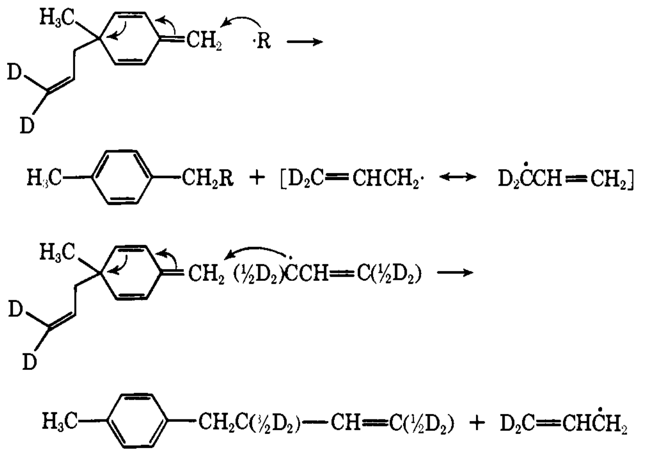
Chart I. Diagrammatic Representation of Energies in Dissociation of Semibenzenes



above, the rearrangement rates are highly variable, show significant induction periods, and are markedly affected by the presence of radical chain inhibitors and initiators. The major process involved in these rearrangements, therefore, appears to be free-radical chain mechanisms.

Several possible free-radical chain mechanisms might account for formation of **7** and **28** from **6** and **24**. However, the experiments with deuterium labeling, as well as the products obtained from rearrangement of semibenzenes **25** and **26**, require that free allylic (or cyclopropylmethyl) radicals act as chain carriers in the rearrangements. The only plausible mechanism for these rearrangements, therefore, appears to be that shown in Scheme I.

Scheme I

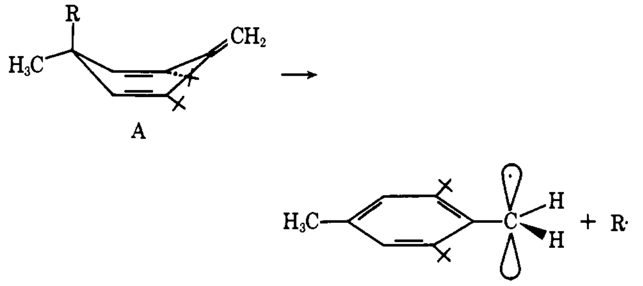


It seems probable that migration of a benzyl group similarly proceeds by a free-radical chain mechanism, but the evidence is not sufficient to exclude the possibility that a direct 1,5 shift mechanism contributes to migration of a benzyl group. The possibility that the benzyl group in **13** migrates *via* a sequence of two 3,3 shifts does, however, seem to be excluded, since the initial migration would result in disruption of the aromaticity of the aromatic ring without forming another aromatic ring. Its activation energy should therefore be greater than 36 kcal/mol. An activation energy of this magnitude is excluded by the very rapid rate of benzyl group migration.

Finally, we may consider the question as to why migration does not occur by simple dissociation–recombination processes, if the dissociation energy required is indeed as low as that we have estimated above.

The possibility was considered that dissociation does indeed occur rapidly, but that, because of the hindered nature of the benzylic methylene group, recombination of the radicals at the para position of the aromatic radical to reconstitute the semibenzene might be more rapid than recombination at the benzylic position. This phenomenon would have an analogy in the combination of triphenylmethyl radicals to form a semibenzene, rather than hexaphenylethane.[15] However, the experiment in which semibenzene **24**-d_2 recovered from partial rearrangement showed no equilibration of the ends of the allyl chain demonstrated that a dissociation–recombination process does not occur as rapidly as rearrangement.

We believe that steric factors play a major role in inhibiting dissociation of the allyl–semibenzene bonds (at least in semibenzenes bearing *tert*-butyl substituents). Formation of a 2,6-di-*tert*-butylbenzyl radical from a semibenzene would convert a boat-shaped molecule (structure A) to a planar one, thus forcing the methylene group into the same plane as the *tert*-butyl groups. Measurements on Dreiding models show that the average distances of the methylene hydrogens from hydrogens on the *tert*-butyl groups are markedly decreased when the planar aromatic radical is formed from a semibenzene. It has previously been demonstrated that very large strain energies can result from forcing substituents on an aromatic ring into positions adjacent to *tert*-butyl groups.[16]



Similar, although much smaller, effects presumably play a role in inhibiting dissociation–recombination processes in the reactions of 2,6-dimethylsemibenzenes.

Experimental Section

Nmr spectra were taken on Varian A-60 and A-60-A spectrometers in CCl_4 solution unless otherwise noted. Vpc's, unless otherwise indicated, were obtained on one of two columns: column A, 6 ft × 0.25 in., 3% SE-30 on Chromosorb W at flow rates of *ca.* 60 ml/min; column B, 5 ft × 0.38 in., 20% SE-30 at flow rates of *ca.* 160 ml/min. Melting points were corrected. Elemental analyses were carried out by the University of Massachusetts Microanalytical Laboratory, Amherst, Mass., or by Galbraith Laboratories, Knoxville, Tenn.

Preparation and Rearrangement of 4-Allyl-2,3,4,5,6-pentamethyl-1-methylenecyclohexa-2,5-diene (6). Methyllithium solution (10.0 ml, 0.0168 mol) was added to a cold solution of 4-allyl-2,3,4,5,6-pentamethylcyclohexa-2,5-dien-1-one[17] (1.50 g, 0.00735 mol) in 25 ml of ether. The immediate vigorous reaction was complete in 2 min. Water was carefully added, the two layers were separated, and the organic layer was dried and evaporated to give 1.6 g of a yellow oil. Its ir spectrum showed a strong OH band at 3450 cm^{-1} but no carbonyl absorption. Its nmr spectrum showed a multiplet in the region τ 4.3–5.4 (*ca.* 3 H, vinyl protons), a broad doublet (J = 7.0 Hz) at τ 7.74 (2 H, allylic methylene), quartets (J = 1.0 Hz) at τ 7.96 and 8.35 (6 H each, allylic methyls), and singlets at τ 8.79 (3 H, methyl at C-1) and 8.98 (3 H, methyl at C-4).

The crude dienol was dissolved in 5 ml of pyridine, and *p*-toluenesulfonyl chloride (1.50 g, 0.0078 mol) was added. The mixture was

---

(15) H. Lankamp, W. Th. Nauta, and C. MacLean, *Tetrahedron Lett.*, 246 (1968).

(16) H. C. Brown, D. Gintis, and L. Domash, *J. Amer. Chem. Soc.*, **78**, 5387 (1956).

(17) B. Miller, *ibid.*, **92**, 6246 (1970).

allowed to stand at room temperature for 1.5 hr, then poured into water, and extracted with methylene chloride. Evaporation of the solvent under vacuum at 35° left 1.2 g of yellow fluid. Its nmr spectrum indicated it to be a mixture (*ca.* 1:1) of **6** and **7**. Its vpc (column A, 150°) showed a single peak with a retention time of 8.1 min. After standing overnight, the peaks indicating the presence of **6** had largely disappeared, to be replaced by enhanced absorptions for **7**. The product was distilled under vacuum to give 0.65 g (3.2 mmol, 41%) of 4-pentamethylphenyl-1-butene (**7**), bp 111–115° (1.5 mm). Its nmr spectrum showed a multiplet (1 H, secondary vinyl proton) in the region τ 3.64–4.20, an AB quartet around τ 4.79 (J = 9.0, 2.5 Hz, 1 H, terminal vinyl proton trans to secondary vinyl proton), an AB quartet around τ 5.01 (J = 2.5, 1.0 Hz, 1 H, terminal vinyl proton cis to secondary vinyl proton), a multiplet around τ 7.32 (2 H, benzylic methylene group), and two singlets at τ 7.79 and 7.83 superimposed on a multiplet around τ 7.75 (totaling *ca.* 17 H, methyl groups and allylic methylene group). An analytical sample was prepared by preparative vpc on column B (175°, retention time 11 min). *Anal.* Calcd for $C_{15}H_{22}$: C, 89.1; H, 10.9. Found: C, 88.7; H, 10.8.

In another run, the dienol (3 mmol), prepared as above, was dissolved in pyridine and the mixture cooled to −25°. *p*-Toluenesulfonyl chloride (5 mmol) was added and the mixture kept in an ice–water bath for 6 hr. The mixture was again cooled to −20° and diluted with water. It was then extracted with methylene chloride, the organic layer washed with water, dried over magnesium sulfate while being stored in the refrigerator, and filtered, and the filtrate evaporated under vacuum without heating The product was a pale yellow oil (2.2 mmol) whose nmr spectrum showed a sharp singlet at τ 5.13 (2 H) superimposed on a multiplet (3 H) from τ 3.7 to 5.4, a multiplet (2 H) around τ 7.7, quartets at τ 8.14 and 8.22 (6 H, each, $J < 0.5$ Hz), and a singlet at τ 8.91 (3 H). The multiplet around τ 7.7 was partially obscured by peaks at τ 7.81 and 7.85, showing the presence of approximately 10% of 4-pentamethylphenyl-1-butene. This product appeared to be stable for 2 days at room temperature. After 60 hr, however, the peaks attributable to the aromatic isomer began to increase in size, and rearrangement was largely complete after 1 week.

Preparation and Acid Cleavage of 4-(*trans*-2-Butenyl)-1,2,3,4,5,6-hexamethylcyclohexa-2,5-dien-1-ol (15). 4-(*trans*-2-Butenyl)-2,3,4,-5,6-pentamethylcyclohexa-2,5-dien-1-one[17] (2.0 g, 9.2 mmol) was dissolved in 25 ml of ether. The solution was cooled in ice, and methyllithium in ether (10 ml, 16.8 mmol) was added. After 5 min, water was added cautiously and the ether layer was separated, dried, and evaporated to give 2.0 g of yellow oil. Its ir spectrum exhibited strong peaks at 3498 (OH), 2950, 1457, 1370, 1300, 1080, 965, and 896 cm^{-1}, and showed no absorption in the carbonyl region. Its nmr spectrum showed singlets at τ 8.81 (3 H, methyl at C-1), 8.98 (3 H, methyl at C-4), 8.00 and 8.18 (*ca.* 6 H each, allylic methyls on ring) overlapping a multiplet from τ 7.7 to 8.1 (allylic methyl and methylene on side chain), and a broad singlet at τ 5.9 (1 H, hydroxyl) as well as a vinyl multiplet (*ca.* 2 H) from τ 3.5 to 4.7.

Without purification, the dienol was dissolved in 10 ml of pyridine and *p*-toluenesulfonyl chloride (1.60 g, 84 mmol) was added. After 1 hr, the mixture was diluted with water and extracted with methylene chloride. The organic layer was washed with dilute hydrochloric acid, dried over magnesium sulfate, and evaporated to give 1.40 g (86 mmol, 94%) of hexamethylbenzene, mp 162–164° (from benzene). The structure of the product was confirmed by mixture melting point and spectroscopic comparisons with an authentic sample.[18]

Synthesis of 4-(2-Oxoethyl)-2,3,4,5,6-pentamethylcyclohexa-2,5-dien-1-one (17). A solution of 4-allyl-2,3,4,5,6-pentamethylcyclohexa-2,5-dien-1-one (5.3 g, 0.026 mol) in 150 ml of methylene chloride was cooled with stirring in a Dry Ice–acetone bath. Ozone was passed into the solution at the rate of 7.0 l./min. The mixture was warmed to room temperature and 50 ml of 2% aqueous sodium sulfite solution was added. The mixture was further stirred for 0.5 hr and the layers separated. The methylene chloride layer was dried over magnesium sulfate and evaporated to give 6.5 g of a yellow semisolid oil. The ir spectrum exhibited the presence of a new CO band at 5.8 μ and the absence of a C=C band at 11.0 μ. The crude product was chromatographed on 60 g of neutral alumina. Elution with 1:1 pentane–methylene chloride gave, after evaporation, 3.0 g (57%) of **17** as a white solid, mp 62–64°. Its ir spectrum showed peaks at 3030, 1725, 1653, and 1628 cm^{-1}. Its nmr spectrum showed a triplet (J = 3.0 Hz) at τ 0.75 (1 H, aldehydic proton). a doublet (J = 3.0 Hz) at τ 7.25 (2 H, methylene α to carbonyl), quartets (J = 1.0 Hz) at τ 7.94 and 8.08 (6 H each, methyls at C-3 and C-5 and at C-2 and C-6), and a singlet at τ 8.68 (3 H, methyl at C-4).

Synthesis of 4-(3,3-Dideuterioallyl)-2,3,4,5,6-pentamethylcyclohexa-2,5-dien-1-one (4-d_2). To a solution of trideuteriomethyltriphenylphosphonium bromide (2.88 g, 0.008 mol) in 100 ml of anhydrous ether was added 3.8 ml of *n*-butyllithium (2.15 *M* in hexane). The mixture was stirred for 3 hr. Then 1.2 g of aldehyde **17** (0.006 mol) was added. The resulting mixture was stirred at room temperature for 7 days and then filtered. The filtrate was washed with water, dried over magnesium sulfate, and evaporated to give 1.2 g of a brown oil. Its ir spectrum showed that the carbonyl band at 1725 cm^{-1} was absent, but the bands at 1653 and 1625 cm^{-1} remained unchanged. The product was chromatographed on 20 g of neutral alumina. Elution with 1:1 benzene–pentane gave 0.5 g (41%) of **6-d_2** as a pale yellow liquid. Its ir spectrum showed peaks at 2942 (s), 1653 (s), 1628 (s), 1460 (s), 1429 (m), 1370 (s), 1342 (m), 1299 (m), 1250 (m), 1176 (m), 1093 (m), 1058 (m), 1026 (m), 980 (w), 957 (w), 935 (w), 885 (w), 772 (m), 744 (m), 730 (m), and 697 (m) cm^{-1}. Its nmr spectrum was essentially identical with that of **4**, with the exception of the reduced areas for the vinyl protons at τ 4.5–5.3. Integration of this area showed the terminal allyl group to contain 1.83 ± 0.01 atoms of deuterium.

Synthesis of 4-(3,3-Dideuterioallyl)-1,2,3,4,5,6-hexamethylcyclohexa-2,5-dien-1-ol (5-d_2). To a solution of 0.51 g of **4-d_2** (0.0025 mol) in 10 ml of ether was added 4 ml of methyllithium (2.16 *M* in ether). After 5 min, water was added. The two layers were separated and the organic layer was washed with water, dried over magnesium sulfate, and evaporated to give 0.5 g of a yellow oil. The ir spectrum showed a peak at 3450 cm^{-1} but no carbonyl peaks. Its nmr spectrum was essentially identical with that of **5**, except for the decreased area for the vinyl protons.

Synthesis of 4-(3,3-Dideuterioallyl)-1-methylene-2,3,4,5,6-pentamethylcyclohexa-2,5-diene (6-d_2). Dienol **5-d_2** (0.050 g; 0.002 mol) was dissolved in 4 ml of pyridine and the solution was cooled to −30°. *p*-Toluenesulfonyl chloride (0.50 g, 0.003 mol) was then added and the reaction mixture was kept overnight at 0°. The mixture was again cooled in a Dry Ice–acetone bath and 2 ml of water was slowly added. The organic portion was then extracted with *n*-pentane. The extract was washed with water, dried over magnesium sulfate, and evaporated to give 0.44 g of 6-d_2 as a brown oil. Its nmr spectrum was essentially identical with that of **6**, except for the decreased vinyl proton area.

Thermal Rearrangement of 6-d_2. A solution of **6-d_2** (0.40 g) in 0.5 ml of carbon tetrachloride was placed in an nmr tube and stored at room temperature for 3 weeks. Its nmr spectrum was occasionally examined. At the end of the storage period, the singlets at τ 8.91 had disappeared. The product (**7-d_2**) was isolated by preparative vpc on column B at 175°. Its nmr spectrum was essentially identical with that of **7**, except for the decreased areas for the quartets at τ 4.50 and 4.79. Each of these quartets had areas corresponding to *ca.* 0.4–0.5 proton. The total area of the terminal vinyl absorptions showed the presence of 0.91 ± 0.07 atom of deuterium. The area for the secondary vinyl hydrogen equalled 1.0 proton.

Attempted Preparation of 4-Allyl-2,4,6-trimethyl-1-methylenecyclohexa-2,5-diene (10). A solution of 1.5 g (8.5 mmol) of 4-allyl-2,4,6-trimethylcyclohexa-2,5-dien-1-one in 15 ml of anhydrous ether was cooled in an ice bath and 10 ml of methyllithium solution (16.6 mmol) added. After 3 min, water was added cautiously and the mixture worked up as usual, giving 1.6 g (8.35 mmol, 98%) of 4-allyl-1-hydroxy-1,2,4,6-tetramethylcyclohexa-2,5-diene (**9**) as a yellow oil. Its ir spectrum showed a hydroxyl peak at 3400 cm^{-1}, but no carbonyl peak. Its nmr spectrum showed singlets at τ 8.21 (6 H, allylic methyls), 8.76 (3 H, methyl at C-1), and 9.05 and 9.08 (approximately in the ratio 1:5:1, totaling 3 H, cis and trans methyls at C-4) as well as multiplets around τ 8.0 (*ca.* 2 H, allylic methylene group) and in the region τ 4.5–5.3. Superimposed on the last multiplet were singlets at τ 4.8 (*ca.* 2 H, vinyl protons on ring) and 4.98 (*ca.* 1 H, hydroxyl proton). The peak at τ 4.98 disappeared when pyridine was added to the solution.

The crude reaction product was dissolved in 5 ml of pyridine and cooled to 0°. *p*-Toluenesulfonyl chloride (2.1 g, 11 mmol) was added and the mixture was kept at 0° for 10 min. It was then diluted with methylene chloride (cold) and washed with cold dilute hydrochloric acid. It was dried over magnesium chloride and filtered, and the solvent was evaporated under vacuum to give 1.3 g of yellow oil. Its nmr spectrum showed singlets at τ 9.01, 8.15, 7.83, 7.71, and 3.24, in addition to multiplets from τ 4.0 to 5.5 and around 6.7. The peaks at τ 9.01 and 8.15 gradually decreased in intensity over a period of several days. Its vpc (column A at 125°) showed

---

[18] Obtained from the Aldrich Chemical Co., Milwaukee, Wis.

peaks at 4.5 and 6.2 min, in the ratio *ca.* 1:1.7. The products were isolated by preparative vpc on column B at 160° (retention times 10.1 and 12.8 min). The minor (lower retention time) product was identified as **1-(3-butenyl)-2,4,6-trimethylbenzene (12)**. *Anal.* Calcd for $C_{13}H_{18}$: C, 89.6; H, 10.4. Found: C, 89.7; H, 10.4. Its nmr spectrum showed a singlet at τ 3.30 (2 H, aromatic protons), a multiplet from τ 4.0 to 5.2 (3 H, vinyl protons), a multiplet around τ 7.35 (2 H, benzylic methylene group), and two singlets in the area ratio *ca.* 2:1 at τ 7.68 and 7.75 (totaling *ca.* 10 protons, aromatic methyls superimposed on a multiplet attributed to the allylic methylene group).

The major product (higher retention time) was identified as 1-allyl-2,3,4,6-tetramethylbenzene (**11**). *Anal.* Calcd for $C_{13}H_{18}$: C, 89.6; H, 10.4. Found: C, 89.6; H, 10.2. Its nmr spectrum showed a singlet at τ 3.28 (1 H, aromatic proton), multiplets from τ 3.8 to 4.4 (1 H, secondary vinyl proton) and from 4.95 to 5.45 (2 H, primary vinyl protons), a doublet of triplets at τ 6.66 (2 H, $J_d = 5.5$ Hz, $J_t = 1.0$ Hz, benzylic methylene group), and singlets at τ 7.81 and 7.85 (approximately equal intensities totaling 12 protons, aromatic methyls).

Preparation of 4-Benzyl-1,2,3,4,5,6-hexamethylcyclohexa-2,5-dien-1-ol. Methyllithium solution (4 ml, 10 mmol) was added to a solution of 4-benzyl-2,3,4,5,6-pentamethylcyclohexa-2,5-dien-1-one[19] (1.1 g, 4.04 mmol) in 15 ml of ether. After 10 min, the solution was cooled in ice and water added cautiously. The ether layer was separated, washed with water, dried over magnesium sulfate, and evaporated to give 1.2 g (100%) of a colorless oil which solidified on standing in an ice bath. Recrystallization from pentane (caution: prolonged refluxing in pentane results in appreciable decomposition) gave 0.70 g (2.59 mmol, 64%) of the dienol as a white solid, mp 52–54°. Its infrared spectrum showed a hydroxyl peak at 3670 cm^{-1} but no carbonyl absorption. Its nmr spectrum showed singlets at τ 8.98 (3 H, methyl at C-4), 8.84 (3 H, methyl at C-1), 8.44 and 8.27 (6 H, each, allylic methyls on ring), 7.88 (1 H, hydroxyl), 7.38 (2 H, benzylic methylene), and a multiplet from τ 2.8 to 3.5 (5 H, phenyl group). *Anal.* Calcd for $C_{19}H_{26}O$: C, 84.4; H, 9.58. Found: C, 84.5; H, 9.73.

Formation and Rearrangement of 4-Benzyl-1,2,3,4,5,6-pentamethyl-1-methylenecyclohexa-2,5-diene (13). 4-Benzyl-1,2,3,4,5,6-hexamethylcyclohexa-2,5-dien-1-ol (0.55 g, 2.04 mmol) was dissolved in 5 ml of pyridine. The solution was cooled to −20° in a Dry Ice–acetone bath, and 1.0 g of *p*-toluenesulfonyl chloride added. The nmr spectrum of the pyridine solution was taken after 3 min. It showed singlets at τ 5.27 (2 H), 7.15 (2 H), 8.15 and 8.28 (totaling 12 H), and 8.77 (3 H), A strong peak at τ 7.85 was attributed to the *p*-toluenesulfonyl group and some (2-phenylethyl)pentamethylbenzene. The peak at τ 7.85 increased rapidly in intensity when the sample was kept in the nmr spectrometer at 39°. The mixture was diluted with water and extracted with methylene chloride, and the organic layer was washed with water and dried over magnesium sulfate. Evaporation of the solvent gave 0.51 g (2.02 mmol, 99%) of a yellow oil, which solidified almost immediately. Recrystallization from hexane gave 0.32 g (62%) of **(2-phenylethyl)pentamethylbenzene (14)** as white needles, mp 93.5–94.5°. Its nmr spectrum showed singlets at τ 7.82 and 7.87 (totaling 15 H, aromatic methyls), a multiplet around τ 7.28 (4 H, benzylic methylenes), and a singlet at τ 2.88 (5 H, phenyl group). *Anal.* Calcd for $C_{19}H_{24}$: C, 90.4; H, 9.58. Found: C, 90.3; H, 9.78.

Preparation of 4-Allyl-2,6-di-*tert*-butyl-1,4-dimethylcyclohexa-dien-1-ol (21). A solution of 4-allyl-2,6-di-*tert*-butyl-4-methylcyclohexa-2,5-dien-1-one (**18**)[20] (11.0 g, 0.052 mol) in 75 ml of dry benzene was cooled in an ice bath and 40 ml of a 2.07 *N* solution of methyllithium in ether was added. The solution was allowed to come to room temperature over a 10-min period, and then evaporated to dryness under vacuum, while being heated in a water bath at 50°. Aqueous methanol was then added to hydrolyze the residue and the mixture extracted with *n*-hexane. The organic layer was washed with water, dried over magnesium sulfate, and evaporated to give 11.56 g (100%) of **21** as a colorless fluid. Its ir spectrum showed no carbonyl peak but had a hydroxyl peak (w) at 3700 cm^{-1}. Its nmr spectrum showed singlets at τ 9.03 (3 H, methyl at C-4) and 8.80 (18 H, *tert*-butyl), a doublet ($J = 6.5$ Hz) at τ 7.97 (2 H, allylic methylene), two singlets in the ratio 1:3 at τ 8.47 and 8.52 (totaling 3 H, methyl at C-1), and two singlets in the ratio 1:3 at τ 4.62 and 4.65 (totaling 2 H, protons at C-3 and C-5) superimposed on a multiplet from *ca.* τ 4.0 to 5.3 (*ca.* 4 H, vinyl protons in allyl group and hydroxyl protons). Attempts to further purify this product by chromatography on neutral alumina, Fluorisil, or silica gel resulted in partial decomposition, as did attempted purification by vpc.

Preparation of 4-(*trans*-2-Butenyl)-2,6-di-*tert*-butyl-1,4-dimethylcyclohexa-2,5-dien-1-ol (22). The reaction of methyllithium and dienone **19**[20] was carried out as described above on a 0.01-mol scale. Dienol **22** was obtained as a colorless fluid in 96% yield. Its ir spectrum showed a hydroxyl peak (w) at 3700 cm^{-1}, and no carbonyl peak. Its nmr spectrum showed singlets at τ 8.79 (18 H, *tert*-butyls) and 9.00 (3 H, methyl at C-4), and two singlets in the ratio *ca.* 1:3 at τ 8.48 and 8.51 (totaling 3 H, methyl at C-1). It showed doublets at τ 8.40 ($J = 4.0$ Hz, 2 H, allylic methyl) and 7.97 ($J = 5.0$ Hz, 2 H, allylic methylene), and a pair of singlets in the ratio *ca.* 1:3 at τ 4.56 and 4.60 (totaling 2 H, hydrogens at C-3 and C-5) superimposed on a broad multiplet from *ca.* τ 4.4 to 4.9 (totaling *ca.* 3 H, vinyl and hydroxyl protons). Attempts at column chromatography or vpc resulted in decomposition of the alcohol.

Synthesis of 2,6-Di-*tert*-butyl-4-cyclopropylmethyl-4-methylcyclohexa-2,5-dien-1-one (20). Methylene iodide (1.5 g, 0.0056 mol) was added to a mixture of zinc–copper couple[21] (6.5 g, 0.10 g-atom) and 1,2-dimethoxyethane (6.75 g, 0.10 mol) in 50 ml of dry ether. A mixture of dienone **3** (13.4 g, 0.051 mol) and methylene iodide (20 g, 0.075 mol) was then added over a 1-hr period. The mixture was then refluxed while being magnetically stirred for 10 days. Vpc analysis indicated no further change in composition by prolonging the reaction. The reaction mixture was filtered and the filtrate washed with cold dilute hydrochloric acid solution, dilute sodium bicarbonate solution, and water. It was dried over magnesium sulfate and the solvent evaporated to give 10.6 g of yellow liquid. Vpc on column A showed the presence of two components, retention times 8.3 min (dienone **18**) and 15.0 min, in the area ratio 2.8:1.0. Part of the product (4.0 g) was dissolved in 150 ml of 80% aqueous *tert*-butyl alcohol. The solution was cooled to 0° and then added to a solution of potassium permanganate (3.16 g, 0.02 mol) and sodium hydroxide (0.7 g, 0.0075 mol) in 120 ml of water.[22] The mixture was stirred and the addition rate controlled so as to maintain the temperature at 0° during the addition. Stirring was continued at 0° for 5 min, and 0.02 mol of sodium sulfite then added to reduce any unreacted potassium permanganate. The resulting mixture was filtered through a filter aid to remove manganese dioxide, the filtrate was washed several times with water, and the aqueous extracts were reextracted with methylene chloride. The combined organic layers were dried over magnesium sulfate and evaporated to give 3.0 g of a brown liquid, which was chromatographed on 60 g of neutral alumina. Elution with *n*-pentane eluted 0.6 g (11% based on amount chromatographed) of dienone **20** as a pale yellow liquid. Its uv spectrum had $\lambda_{max}^{CH_3OH}$ 245 mμ (log ϵ 4.0). Its ir spectrum had peaks at 3125 and 1020 (w, cyclopropyl group), 1666 (s, conjugated carbonyl), and 1611 cm^{-1} (s, double bond conjugated with carbonyl). Its nmr spectrum showed singlets at τ 8.82 (18 H, *tert*-butyls), 8.75 (3 H, methyl at C-4), and 3.54 (2 H, vinyl protons), a doublet at τ 8.50 ($J = 7.0$ Hz, 2 H, methylene bearing cyclopropyl group) and multiplets around τ 9.63 and 10.1 (5 H, cyclopropyl hydrogens). An analytical sample was prepared by vpc on column A. *Anal.* Calcd for $C_{19}H_{30}O$: C, 83.2; H, 11.0. Found: C, 83.4; H, 10.9.

Preparation of 4-Cyclopropylmethyl-2,6-di-*tert*-butyl-1,4-dimethylcyclohexa-2,5-dien-1-ol (23). The reaction of methyllithium with dienone **20** was carried out as described for the synthesis of **21** on a 7.3 mmol scale. Dienol **23** was obtained as a clear pale yellow liquid in 91% yield. Its ir spectrum showed a hydroxyl peak (w) at 3700 cm^{-1}. Its nmr spectrum showed singlets at τ 8.73 (18 H, *tert*-butyl), 9.02 (3 H, methyl at C-4), and 5.0 (1 H, hydroxyl). Pairs of singlets in roughly the ratio 1:4 appeared at τ 4.59 and 4.62 (2 H, protons at C-3 and C-5) and at 8.43 and 8.50 (3 H, methyl at C-1). The cyclopropylmethyl absorptions appeared as a multiplet (partially obscured by *tert*-butyl and methyl absorptions) from τ 8.8 to 10.0. No attempt was made to further purify this compound.

Synthesis of 4-Allyl-2,6-di-*tert*-butyl-4-methyl-1-methylenecyclohexa-2,5-diene (24). Dienol **21** (4.0 g, 0.0145 mol) was dissolved in 18 ml of pyridine, and phosphorus oxychloride (3.0 g, 0.02 mol) was added. The resulting mixture was heated in an oil bath overnight at 70° and then poured into ice and extracted with *n*-hexane. The organic layer was washed with water, dried over magnesium sulfate, and evaporated to give 3.8 g of colorless fluid. The crude product was chromatographed on 50 g of silica gel. Elution with *n*-pentane

---

(19) B. Miller, *J. Amer. Chem. Soc.*, **92**, 6252 (1970).

(20) B. Miller and H. Margulies, *J. Org. Chem.*, **30**, 3895 (1965).

(21) E. LeGoff, *ibid.*, **29**, 2048 (1964).

(22) K. B. Wiberg and A. Saegebarth, *J. Amer. Chem. Soc.*, **79**, 2822 (1957).

gave 0.50 g (0.00194 mol, 13%) of **24** as a colorless oil. Its ir spectrum showed no hydroxyl or carbonyl absorptions. Its nmr spectrum showed singlets at τ 9.08 (3 H, methyl at C-4) and 8.77 (18 H, *tert*-butyls), a broad doublet at τ 7.95 (J = 7.0 Hz, 2 H, allylic methylene), and singlets at τ 4.44 (2 H, exocyclic methylene) and 4.65 (2 H, ring hydrogens) superimposed on a multiplet from τ 4.0 to 5.3 (*ca.* 3 H, vinyl hydrogens on allyl group). *Anal.* Calcd for $C_{19}H_{30}$: C, 88.3; H, 11.7. Found: C, 88.1; H, 11.9.

Synthesis of 4-(*trans*-2-Butenyl)-2,6-di-*tert*-butyl-4-methyl-1-methylenecyclohexa-2,5-diene (25). Dehydration of dienol **22** was carried out as described for preparation of semibenzene **24**, using 1.5 g (0.052 mol) of **22**. Work-up gave 1.45 g of pale yellow oil which was chromatographed on 20 g of silica gel. Elution with *n*-hexane gave 0.64 g (0.024 mol, 45%) of **25** as a colorless liquid. Its nmr spectrum showed singlets at τ 8.75 (18 H, *tert*-butyl) and 9.12 (3 H, methyl at C-4), doublets at τ 7.97 (J = 5.0 Hz, 2 H, allylic methylene) and 8.49 (J = 5.0 Hz, 3 H, allylic methyl), and triplets at τ 4.40 and 4.63 (J = 0.5 Hz, 2 H each, exocyclic methylene and ring hydrogens) superimposed on a multiplet from τ 4.2 to 5.4 (*ca.* 2 H, vinyl protons on side chain). *Anal.* Calcd for $C_{20}H_{32}$: C, 88.2; H, 11.8. Found C, 88.2; H, 11.9.

Synthesis of 4-Cyclopropylmethyl-2,6-di-*tert*-butyl-4-methyl-1-methylenecyclohexa-2,5-diene (26). Dehydration of dienol **23** (0.17 g) was carried out as described for preparation of **24**, giving 0.12 g (75%) of **26** as a yellow oil. Its nmr spectrum showed singlets at τ 8.75 (18 H, *tert*-butyls) and 8.99 (3 H, methyl at C-4) superimposed on a multiplet from τ 8.8 to 9.8 (cyclopropylmethyl group), and triplets (J = 0.8 Hz) at τ 4.39 (2 H, exocyclic methylene group) and 4.72 (2 H, ring hydrogens). Small peaks at τ 3.13, 7.80, 7.42, and 7.59, in the ratio 2:3:3:18, showed the presence of compound **27**, as approximately 20% of the product. No further purification of the product was carried out.

Synthesis of 2,6-Di-*tert*-butyl-4-methyl-4-(2-oxoethyl)cyclohexa-2,5-dien-1-one. A solution of dienone **18** (34.0 g, 0.131 mol) in 500 ml of methylene chloride was cooled in a Dry Ice–acetone bath and stirred while ozone was passed into the solution at the rate of 1 l./min for 2 hr. The solution was then warmed to room temperature and 200 ml of 10% sodium sulfite solution was added. After the mixture was stirred for an additional 0.5 hour, the methylene chloride layer was separated and washed with water. It was dried over magnesium sulfate and evaporated to give 38 g of a brown oil. This was stream distilled until 5 l. of distillate was collected and the distillate extracted with *n*-pentane. Evaporation of the pentane solution gave a crystalline product which was purified by sublimation at 80° (0.1 mm) to give 8.65 g of the ketoaldehyde (0.034 mol, 26%) as white crystals, mp 91–93°. Its ir spectrum showed peaks at 1740 (s, aldehyde carbonyl), 1667 (s, conjugated carbonyl), and 1625 cm^{-1} (s, double bond conjugated with carbonyl). Its nmr spectrum had a triplet at τ 0.67 (J = 3.0 Hz, 1 H, aldehyde hydrogen), a doublet at τ 7.54 (J = 3.0 Hz, 2 H, methylene α to carbonyl), and singlets at τ 3.50 (2 H, ring hydrogens), 8.72 (*ca.* 3 H, methyl), and 8.78 (*ca.* 18 H, *tert*-butyls). *Anal.* Calcd for $C_{17}H_{20}O_2$: C, 77.8; H, 9.99. Found: C, 78.0; H, 10.0.

Synthesis of 4-(3,3-Dideuterioallyl)-2,6-di-*tert*-butyl-4-methylcyclohexa-2,5-dien-1-one (18-d_2). A solution of 2.15 *M* *n*-butyllithium in hexane (18 ml, 0.039 mol) was added to a solution of trideuteriomethyltriphenylphosphonium bromide (13.5 g, 0.0375 mol) in 220 ml of anhydrous ether, and the mixture stirred at room temperature for 5 hr. 2,6-Di-*tert*-butyl-4-(2-oxoethyl)cyclohexa-2,5-dien-1-one (5.85 g, 0.0277 mol) was then added and the mixture stirred at room temperature under nitrogen for 72 hr. Water was then added cautiously, the layers were separated, and the ether layer was washed with water, dried over magnesium sulfate, and evaporated to give 6.2 g of a brown oil which was chromatographed on neutral alumina (90 g). Elution with *n*-pentane gave 4.2 g (0.0165 mol, 60%) of **18**-d_2 as a yellow liquid. Its nmr spectrum was identical with that of **18** except for the decreased intensity of the multiplet in the region τ 4.25–5.30. The deuterium content of the terminal methylene groups was found by nmr analysis to be 1.76 ± 0.02 atoms, based on the ratio of the area for those protons to that for the ring vinyl protons.

4-(3,3-Dideuterioallyl)-2,6-di-*tert*-butyl-1-methylenecyclohexa-2,5-diene (24-d_2). The synthesis of **24**-d_2 was carried out as described for **24**, starting with 3.85 mmol of **18**-d_2. The overall yield for the two steps was 31%. The nmr spectrum of **24**-d_2 was identical with that of **24**, except for the decreased area of the terminal vinyl multiplet from τ 4.75 to 5.33. The deuterium content of the terminal vinyl position was determined by nmr analysis to be 1.79 ± 0.02 atoms.

Rearrangement of 24. Compound **24** (0.50 g) was put in an nmr tube and heated in an oil bath at 150°. The nmr peak at τ 9.08 had disappeared completely after 2 hr. Vpc analysis on column A at 150° showed the presence of one significant component with a retention time of 9.6 min. An analytical sample was obtained by vpc on column B at 185°. Its spectra were essentially identical with those of the unchromatographed rearrangement product. The nmr spectrum of the product showed a singlet at τ 3.09 (2 H, aromatic protons), multiplets from τ 3.37 to 4.35 (1 H, secondary vinyl proton) and from τ 4.78 to 5.30 (2 H, primary vinyl protons), a multiplet around τ 6.80 (2 H, benzylic methylene group), a singlet at τ 7.80 superimposed on a multiplet in the same region (totaling 5 H, aromatic methyl and allylic methylene groups), and a singlet at τ 8.58 (18 H, *tert*-butyl groups). It was assigned the structure **4-(3-butenyl)-3,5-di-*tert*-butyltoluene (28)**. *Anal.* Calcd for $C_{19}H_{30}$: C, 88.3; H, 11.7. Found: C, 88.4; H, 11.6.

Thermal rearrangement of **24** in benzene, absolute ethanol, or chloroform in sealed tubes, heating at 160° for 1 hr, resulted in formation of **28**. No other products could be detected by vpc. A benzene solution of **24** and an equimolar amount of *trans*-stilbene was heated for 2 hr at 160°. The vpc showed the presence of two components in the product, which were isolated and identified as **28** and recovered *trans*-stilbene.

Kinetic Study of the Thermal Rearrangement of 24. Semibenzene **24** (30.0 mg) was dissolved in 25 ml of ethylene glycol which had been previously brought to thermal equilibrium with the thermostat bath. The solution was kept at 122.0 ± 0.5°. At varying intervals, 1-ml aliquots were withdrawn and immediately diluted to 10 ml with cold methanol. Uv spectra were recorded with a Cary 14 spectrophotometer, and the rate of the reaction followed by the change in absorption at 249 mμ. The reaction showed an induction period of about 25 min, after which a reasonably straight line was obtained. The first-order rate constant for the straight portion of the curve was calculated as 1.7×10^{-2} min^{-1}.

Thermal Reaction of 24 with Thiophenol. A mixture of semibenzene **24** (0.2 g, 0.77 mmol) and thiophenol (0.4 g, 3.6 mmol) was heated on a steam bath for 2 hr, at which time the nmr peak at τ 9.08 had disappeared. The mixture was dissolved in *n*-pentane and the solution extracted with 1 *N* sodium hydroxide solution, washed with water, dried over magnesium sulfate, and evaporated to give 0.22 g of a yellow fluid. The product was chromatographed on 10 g of silica gel. Elution with 1:2 benzene–pentane gave 0.15 g of a pale yellow liquid. Vpc analysis (column A, 217°) showed one main component with a retention time of 17.4 min, and a small peak with a retention time of 3.8 min (diphenyl disulfide). The major product was isolated by preparative vpc on a 1.5 ft × $^3/_8$ in. SE-30 on Chromo- sorb W column at 200°, flow rate 186 ml/min. Its nmr spectrum had a multiplet between τ 3.1 and 3.5 (7 H, aromatic protons), and three singlets at τ 5.77 (2 H, benzylic methylene bearing a sulfur atom), 8.22 (3 H, aromatic methyl), and 8.85 (18 H, *tert*-butyls). The product was assigned the structure **2,6-di-*tert*-butyl-*p*-tolyl phenyl sulfide (29).**

Thermal Rearrangement of 24-d_2. Semibenzene **24**-d_2 (0.20 g) was heated in an oil bath at 200° for 1 hr. The product showed one significant peak in the vpc. A sample isolated by preparative vpc on column B at 190° had an nmr spectrum identical with that of **28** except for the lower intensities of peaks in the areas τ 4.78–5.30 and 7.4–8.5. The deuterium content of the terminal vinyl group was determined to be 0.90 ± 0.01 atom by nmr analysis. In another run a sample of **24**-d_2 (0.20 g) was heated in an nmr tube at 93° until the spectrum indicated that 50% rearrangement had occurred (25 hr). The product was chromatographed on silica gel. Elution with *n*-hexane yielded recovered **24**-d_2 (0.070 g). Nmr analysis demonstrated the deuterium content at the terminal methylene group to be 1.8 ± 0.1 atoms. Further elution with *n*-hexane yielded **28**-d_2 (0.080 g). This was further purified by vpc on column B. Nmr analysis indicated the deuterium content at the terminal methylene group to be 0.9 ± 0.1 atom.

Rearrangement of 25. Semibenzene **25** was placed in an nmr tube and heated in an oil bath at 200° for 1 hr. The vpc of the product on column A at 175° showed the presence of four products. The retention times of these products (A–D) were A, 2.6 min; B, 4.3 min; C, 6.7 min; and D, 7.0 min. The four products were isolated by preparative vpc on column B at 185°. Product A (12% yield by vpc) was obtained as a white solid, mp 91–93°. It was identified as **2,6-di-*tert*-butyl-1,4-dimethylbenzene (27)** by its nmr spectrum which showed singlets at τ 3.13 (2 H, aromatic protons adjacent to *tert*-butyl groups), 7.80 (3 H, aromatic methyl), and 8.61 (18 H, *tert*-butyl groups), as well as at τ 7.42 (3 H, aromatic methyl between two *tert*-butyl groups). *Anal.* Calcd for $C_{16}H_{26}$: C, 88.0; H, 12.0. Found: C, 88.0; H, 11.8.

Product B (21% by vpc) was obtained as a pale yellow oil. It was identified as **2,6-di-*tert*-butyl-1-(2-methyl-3-butenyl)-4-methylbenzene (30)** by its nmr spectrum, which showed singlets at τ 3.14 (2 H, aromatic protons adjacent to *tert*-butyl groups), 7.80 (3 H, aromatic methyl), and 8.60 (18 H, *tert*-butyl groups), a doublet at τ 9.28 (3 H, J = 6.8 Hz, methyl group on side chain), and a doublet at τ 6.88 (2 H, J = 8.3 Hz, benzylic methylene on side chain) as well as three vinyl protons in the region τ 3.4–5.3. *Anal.* Calcd for $C_{20}H_{32}$: C, 88.2; H, 11.8. Found: C, 88.2; H, 11.8.

Product C (44% yield by vpc) was assigned the structure **2,6-di-*tert*-butyl-1-(*trans*-3-pentenyl)-4-methylbenzene (31)** on the basis of the nmr spectrum, which showed peaks for aromatic hydrogens, an aromatic methyl, and *tert*-butyl groups at essentially the same positions as those in **30**. It also showed a two proton multiplet around τ 6.9 (benzylic methylene group) and around τ 7.8 (allylic methylene group), and a doublet of doublets (J = 3.5, 1.5 Hz) at τ 8.35 (3 H, methyl group on a double bond). *Anal.* Calcd for $C_{20}H_{32}$: C, 88.2; H, 11.8. Found: C, 88.0; H, 11.9.

Product D (23% yield by vpc) was obtained as a pale yellow oil and assigned the structure **2,6-di-*tert*-butyl-1-(*cis*-3-pentenyl)-4-methylbenzene (32)** on the basis of its nmr spectrum which showed aromatic hydrogen, aromatic methyl, and *tert*-butyl groups similar to those of **30** and **31**. Its benzylic methylene and allylic methylene absorptions were also essentially identical with those of **31**, but it showed the vinyl methyl group as a doublet of doublets (J = 5.0, 1.5 Hz) at τ 8.46.

Rearrangement of Semibenzene 26. Compound **26** (0.17 g) was placed in an nmr tube and heated in an oil bath at 110° overnight. Its vpc on column A at 185° showed the presence of two major components with retention times of 2.1 and 4.7 min, in the area ratio 1:3, and two minor components with retention times of 2.8 and 6.4 min. The major components were isolated by preparative vpc on column B at 190°. The product with a retention time of 2.8 min was identified as compound **27**. The product with a retention time of 4.7 min was obtained as a yellow oil. Its nmr spectrum showed singlets at τ 8.60, 7.79, and 3.12 for the *tert*-butyl groups, aromatic methyl groups, and aryl hydrogens, respectively. It showed a multiplet from τ 3.89 to 4.69 (1 H, secondary vinyl proton), from τ 4.90 to 5.39 (2 H, primary vinyl protons), from τ 7.60–8.12 (2 H, allylic methylene group), and from τ 6.80–7.05 (2 H, benzylic methylene group). This product was assigned the structure **2,6-di-*tert*-butyl-1-(4-pentenyl)-4-methylbenzene (33).**

Acknowledgment. We thank the donors of the Petroleum Research Fund, administered by the American Chemical Society, for a grant in support of this work.

Cation–Anion Combination Reactions. VII.[1] Reactions of Aryltropylium Ions in Aqueous Solution

C. D. Ritchie* and H. Fleischhauer

Contribution from the Department of Chemistry,
State University of New York at Buffalo, Buffalo, New York 14214.
Received October 1, 1971

Abstract: The reactions of tropylium, phenyltropylium, *p*-chlorophenyltropylium, *p*-methoxyphenyltropylium, and *p*-dimethylaminophenyltropylium ions in buffered aqueous solutions have been studied by stop-flow spectrophotometry. The pK_R values and the rate constants for the reactions with water and with hydroxide ion, respectively, are as follows for the various cations: tropylium ion, 4.76, 2.6 sec^{-1}, 3.1 × 10^5 M^{-1} sec^{-1}; phenyltropylium ion, 4.84, 1.0 sec^{-1}, 7.9 × 10^4 M^{-1} sec^{-1}; *p*-chlorophenyltropylium ion, 4.55, 1.2 sec^{-1}, 1.4 × 10^5 M^{-1} sec^{-1}; *p*-methoxyphenyltropylium ion, 5.75, 0.27 sec^{-1}, 4.0 × 10^4 M^{-1} sec^{-1}; *p*-dimethylaminophenyltropylium ion, 7.35, 0.020 sec^{-1}, 1.7 × 10^3 M^{-1} sec^{-1}. Thus, although the stabilities of the cations vary over three powers of ten and the reactivities toward water and hydroxide ion vary by two powers of ten, the selectivities toward water and hydroxide ion are nearly constant.

Tropylium ions have attracted considerable attention over the past decade.[2-6] The pK_R value of the tropylium ion in aqueous solution was determined by Doering,[2] and the rate constant for the reaction of tropyl alcohol with hydronium ion has been reported by Zuman[6] and by Eigen.[7] Jutz and Voithenleitner have reported relative pK_R values for a number of aryltropylium ions in aqueous acetonitrile solution.[5]

In connection with our studies of nucleophilic reactions with cationic species,[1a] we have now studied the rates and equilibria of reactions of tropylium ion and aryltropylium ions in buffered aqueous solution.

Results

The pK_R values determined are reported in Table I. For the aryltropylium ions, spectrophotometric mea-

Table I. pK_R and Spectral Data for Tropylium Ions in Aqueous Solution at 23 ± 1° (Ionic Strength = 1.0 × 10^{-2} M)

Cation	λ_{max}, nm	ϵ, M^{-1} cm^{-1}	pK_R	Lit.	Buffer used
$C_7H_7^+$	276	4.1 × 10^3	4.76	4.75[a] 4.01[b]	Acetate
$C_6H_5C_7H_6^+$	350	1.3 × 10^4	4.84	3.88[b]	Acetate
p-$ClC_6H_4C_7H_6^+$	377	1.7 × 10^4	4.55	3.30[b]	Acetate
p-$CH_3OC_6H_4C_7H_6^+$	425	1.8 × 10^4	5.75	4.60[b]	γ-Picoline
p-$(CH_3)_2NC_6H_4C_7H_6^+$	569	3.8 × 10^4	7.35	6.90[b]	γ-Collidine

[a] Value determined in aqueous solution by Doering, ref 2. [b] Values determined in aqueous acetonitrile by Jutz, ref 5.

---

[1] (a) Previous paper in this series: C. D. Ritchie, *J. Amer. Chem. Soc.*, **93**, 7324 (1971). (b) This work was supported by Grant No. GP-29164 from the National Science Foundation and Grant No. GM-12832 from PHS-NIH.

[2] W. von E. Doering and L. H. Knox, *J. Amer. Chem. Soc.*, **76**, 3203 (1954); **79**, 352 (1957).

[3] T. Nozoe, *Progr. Org. Chem.*, **5**, 132 (1961).

[4] J. W. Wilt and D. Piszkiewicz, *Chem. Ind.*, 1762 (1963).

[5] C. Jutz and F. Voithenleitner, *Chem. Ber.*, **97**, 29 (1964).

[6] P. Zuman, J. Chodkowski, and F. Santavy, *Collect. Czech. Chem. Commun.*, **26**, 380 (1961).

[7] M. Eigen, *Angew. Chem., Int. Ed. Engl.*, **3**, 1 (1964).