1,3-dimethoxy-1,3-diphenylcyclopropane according to glc analysis (20% Se-30, 225°).

B. Dimethoxyethane–Water.—To 2.036 g (11 mmol) of *trans*-1,2-diphenylcyclopropane in 132 ml of 1,2-dimethoxyethane and 48 ml of water was added in one portion 4.1 g (23 mmol) of NBS. The resulting solution was kept at room temperature for 5 days in the dark. Thereafter the solution was poured into 1 l. of water and the mixture was extracted with ether (3 × 250 ml). The ether extract was washed with water and dried (anhydrous $MgSO_4$). Vacuum evaporation of the ether left a white solid whose glc analysis (Se-30, 225°) showed a single peak in addition to solvent. Two recrystallizations from ethanol–water gave 2.4 g of *trans*-1,2-*p*-bromophenylcyclopropane whose spectral properties were identical with those given above.

Registry No.—**1a**, 873-49-4; **1c**, 34733-61-4; **2a**, 1124-14-7; **2c**, 34733-62-5; **3a**, 1138-48-3; (±)-**3c**, 34733-63-6; *meso*-**3c**, 34733-64-7; **3e**, 34712-58-8; **4a**, 1138-47-2; **5a**, 34733-66-9; NBS, 128-08-5.

Rearrangement and Cleavage Processes in Crowded Cyclohexadienyl Carbonium Ions

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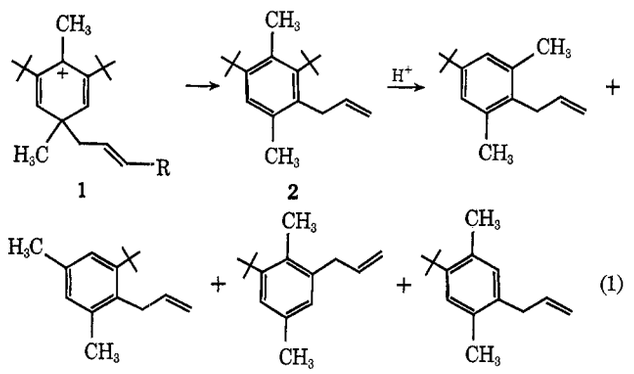
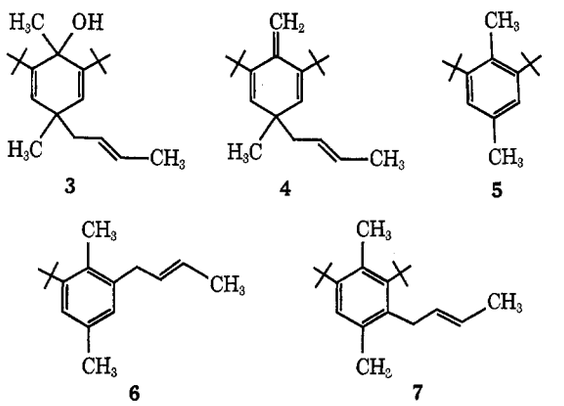
In an earlier paper[1a] we reported that carbonium ion **1** (R = H) rearranges to give the normal [1,2] migration product **2**. Rearrangement of **2**, in turn,



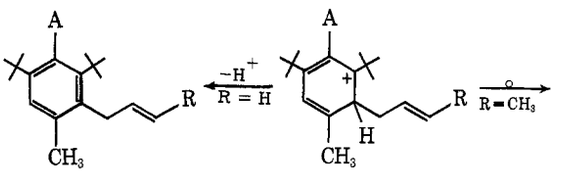
(1)

proceeds in surprisingly mild acid conditions to give the products shown in eq 1. The ease of rearrangement of **2** and the unusual nature of its rearrangement products were attributed to steric effects favoring protonation at the most hindered position on the ring.[1] We have now prepared several additional highly crowded cyclohexadienyl carbonium ions, in order to compare their reactions with those of **1**.

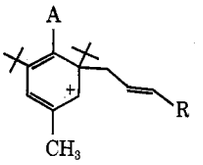
We first substituted a crotyl group (a better migrating group[2]) for the allyl group in **1**. Reaction of cyclohexadienol **3**[3] with 10% sulfuric acid in acetic acid gave two products in the ratio 6:1. These products were isolated by preparative vpc. The major product was identified as 2,6-di-*tert*-butyl-*p*-xylene (**5**),[3] while the minor product was assigned the structure 2-(*trans*-2-butenyl)-6-*tert*-butyl-*p*-xylene (**6**). (Evidence for structural assignments is discussed below.) When either **3** or the semibenzene **4**[3] was refluxed in benzene solution in the presence of Florisil (magnesium fluorosilicate), a mildly acidic heterogeneous catalyst,[4] **5** was again the major product, constituting from 60 to 75% of the total product, while **6** was obtained in 8–10% yield. A third component, constituting 20–30% of the product, was obtained under these conditions, however, and was assigned structure **7**. Compound **7** was found to be unchanged on prolonged refluxing in the presence of Florisil. Furthermore, on prolonged standing in sulfuric acid in acetic acid, **7** reacted to give a complex mixture of products. These were not isolated due to the small amount of **7** available. Vpc analysis, however, showed that **6** was only a minor component of the mixture. Thus, formation of **6** in the Florisil catalyzed reaction occurs predominantly during the initial rearrangement of carbonium ion **1** (R = CH_3) rather than as a result of further rearrangement of **7**.



The products obtained from carbonium ion **1** closely resemble those obtained from reactions of 2,6-di-*tert*-butylcyclohexadienones in acid.[2] With either the dienone or **1**, no cleavage of an allyl group from the ring takes place,[1,2] while crotyl groups undergo appreciable cleavage.[2] That a higher yield of cleavage product is obtained from **1** than from the cyclohexadienone may be attributed to the fact that the energy gained by formation of an aromatic ring from **1** is greater than that resulting from formation of a phenol from a protonated cyclohexadienone. With either the dienone or cyclohexadienyl carbonium ion, initial [1,2] migration of a crotyl group to form **8** is immediately



8, A = CH_3, OH



followed, in sulfuric acid–acetic acid solution, by a second [1,2] migration of the crotyl group to the carbon

(1) (a) K.-H. Lai and B. Miller, *Tetrahedron Lett.*, 3575 (1971); (b) K.-H. Lai and B. Miller, *Tetrahedron*, **28**, 2221 (1972).

(2) B. Miller and H. Margulies, *J. Amer. Chem. Soc.*, **87**, 5106 (1965); B. Miller, *ibid.*, **87**, 5115 (1965).

(3) B. Miller and K.-H. Lai, *ibid.*, **94**, 3471 (1972).

(4) M. J. Gentles, J. B. Moss, H. L. Herzog, and E. B. Hershberg, *ibid.*, **80**, 3702 (1958).

TABLE I

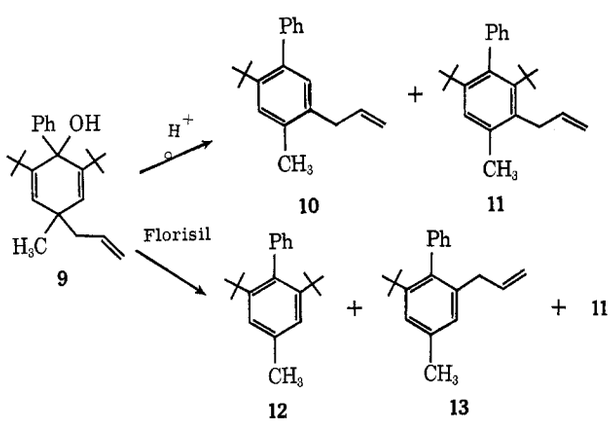
MAJOR PEAKS IN NMR SPECTRA (CHEMICAL SHIFTS IN UNITS OF δ)

Compd	ArH	*t*-Bu (s)	$-CH_2CH=C$	$ArCH_3$ (s)	$C=CHCH_3$
7	7.00 (s)	1.52 (9 H)	3.59 (d, J = 6.0 Hz)	2.51 (3 H)	1.65 (d, J = 6.0 Hz)
		1.41 (9 H)		2.23 (3 H)	
6	6.99 (d, J = 2 Hz)	1.44 (9 H)	3.22 (d, J = 5.5 Hz)	2.40 (3 H)	1.68 (d, J = 5.0 Hz)
	6.75 (d, J = 2 Hz)			2.25 (3 H)	
9	5.44 (s, 2 H)[a]	0.87 (18 H)	2.05 (d, J = 7.0 Hz)[b]	1.16 (3 H)[b]	
	7.1 (m, 5 H)				
10	7.1 (m, 7 H)	1.20 (9 H)	3.20 (b d, J = 6.0 Hz)	2.24 (3 H)	
11[c]	7.06 (s, 7 H)	0.99 (9 H)	3.72 (m)	2.28 (3 H)	
	7.14 (s, 5 H)	1.04 (9 H)			
12[c]	7.1 (b s, 7 H)	1.02 (18 H)		2.31 (3 H)	
13[c]	7.1 (m, 7 H)	1.11 (9 H)	2.73 (d, J = 6.0 Hz)	2.29 (3 H)	
14	5.45 (s, 2 H)[a]	0.92 (18 H)	2.02 (d, J = 6.0 Hz)[b]	1.19 (3 H)[b]	1.63 (d, J = 4.5 Hz)
	7.1 (m, 5 H)				
15[c]	7.12 (s, 1 H)	0.99 (9 H)	3.71 (m)	2.28 (3 H)	1.67 (d, J = 5.0 Hz)
	7.17 (b s, 5 H)	1.04 (9 H)			

[a] Vinyl protons on ring. [b] Substituents at C-4. [c] The chemical shifts for these compounds are slightly different from those previously reported,[5] due to recalibration of the instrument.

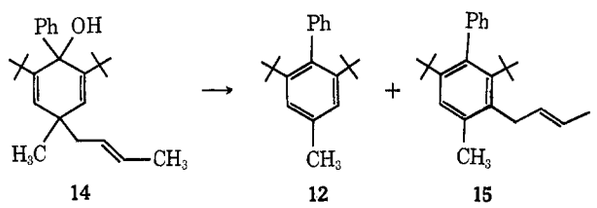
bearing the *tert*-butyl group. In contrast, migration of an allyl group in either case is sufficiently slow so that loss of a proton from **8** competes effectively with allyl migration.

The effect of substituting a phenyl group for the methyl at C-1 in **1** seemed of interest. Reaction of 4-allyl-2,6-di-*tert*-butyl-4-methylcyclohexadienone with phenyllithium gave the corresponding cyclohexadienol **9**, apparently as a single isomer. Reaction of **9** with 10% sulfuric acid for 18 hr gave rise to two products, in the ratio 5:95.[5] The products were isolated by preparative vpc and assigned structures **10** and **11** (see below). In contrast, rearrangement of **9** in refluxing benzene in the presence of Florisil gave three products in the ratio 7:20:73. These were isolated by preparative vpc. The major product was found to be **11**. The product present in lowest yield was assigned the structure **12**, and the product obtained in 20% yield was assigned structure **13**.



Reaction of **11** with 20% sulfuric acid in acetic acid for 24 hr gave rise to a very complex mixture containing at least six significant components. These had very similar vpc retention times, and could not be separated or identified. It could be determined, however, that the peak with retention time equal to that of **10** accounted for no more than 20% of the total area. Since **10** was the sole product other than **11** obtained from rearrangement of **9**, it could not have arisen as a secondary product from further reaction of **11**, but must have been formed directly from **9** by migration of a proton in carbonium ion **8** (R = H, A = C_6H_5). Similarly, formation of **13** during the Florisil-catalyzed rearrangement of **9** must have occurred during the initial rearrangement process, since **11** was unchanged by prolonged refluxing in the presence of Florisil.

Finally, rearrangement of dienol **14** in 10% sulfuric acid in acetic acid gave rise to **12** and a to new compound assigned structure **15**, in the ratio 89:11, respectively. Rearrangement of **14** in refluxing benzene



in the presence of Florisil gave **12** and **15** in the ratio 2:1.

The absence of any product analogous to **13** from rearrangement of **14** is presumptive evidence that **13** is formed by a [3,3] shift of the allyl group in the carbonium ion derived from **9**, rather than by two [1,2] shifts, since the crotyl group should undergo [1,2] shifts more readily than an allyl group. That a crotyl group in **8** (R = CH_3) apparently undergoes further migration more readily when A = CH_3 than when A = C_6H_5 can be accounted for by destabilization of **8** by the inductive effect of the phenyl group. Resonance stabilization of the carbonium ion by the phenyl substituent would presumably be minor, since the two rings are nearly perpendicular to one another.

Structural Assignments.—Most of the rearrangement products were assigned structures on the basis of their nmr spectra. The salient features of these spectra are outlined in Table I. (In addition to the resonances listed in the table, all compounds showed appropriate absorptions for vinyl protons of the allyl and crotyl groups. These absorptions were not of appreciable use for identifying products, and are therefore not listed in Table I.)

As has previously been pointed out,[1,6] resonances for

(5) A preliminary account of the formation of 2,6-di-*tert*-butylbiphenyls has been reported: B. Miller and K.-H. Lai, *Tetrahedron Lett.*, 2957 (1971).

(6) W. A. Gibbons and V. M. S. Gil, *Mol. Phys.*, **9**, 163, 167 (1965).

aromatic substituents (including hydrogen) ortho to *tert*-butyl groups exhibit significant downfield shifts compared to "normal" positions for resonances of these substituents when they are not located ortho to *tert*-butyl groups. Similarly, the resonances for *tert*-butyl groups ortho to groups other than hydrogen atoms exhibit slight downfield shifts. On the basis of these downfield shifts it can be seen that one methyl group in **7** is ortho to two *tert*-butyl groups and one methyl group in **6** is ortho to one *tert*-butyl group, while the other methyl groups in these molecules and in the other products are not ortho to *tert*-butyl groups. Similarly, the positions of the resonances for the allylic methylene groups demonstrate that the allyl group in **11** and the crotyl groups in **7** and **15** are ortho to *tert*-butyl groups, while those in **6**, **10**, and **13** are not. The aromatic hydrogen in **7** and *one* of the two aromatic hydrogens in **6** must be ortho to *tert*-butyl groups, while the coupling between the aromatic hydrogens in **6** demonstrates that they are meta to each other.

Further useful structural evidence is provided by the marked upfield shifts of substituents ortho to a phenyl group. As has been noted above, the two aromatic rings in the biphenyl derivatives are essentially perpendicular to one another, and ortho substituents will thus lie in the shielding cone of the unsubstituted phenyl ring. The high field locations of the resonances for the *tert*-butyl groups in **10**–**13** and **15** show that they remain ortho to the phenyl group. Similarly, the allyl group in **13** is clearly ortho to the *tert*-butyl group, while that in **10** is not.

Thus, the nmr spectra serve to unequivocally identify most of the rearrangement products. The only remaining ambiguity concerns the relative positions of the crotyl group and one of the methyl groups in **6**, and of the allyl group and the methyl group in **10**. In view of the strong evidence that allyl and crotyl groups are far better migrators than methyl groups,[2] it has been assumed that the methyl groups in **6** and **10** remain at C-4, and that these structures result from "normal" sequences of [1,2] migrations of the allyl and crotyl groups.

Experimental Section

All nmr spectra were taken in $CDCl_3$ solution on a Varian A-60 spectrometer, except where otherwise indicated. Ir spectra were taken on a Perkin-Elmer Model 237 spectrometer, using films of oils and liquids, and mineral oil mulls of solids. Vpc analyses were carried out on a Varian 202c chromatographic instrument equipped with a thermal conductivity detector, using the following columns: column A, 6 ft × 0.25 in., 3% SE-30 on Chromosorb W, at a He flow rate of 64 ml/min; column B, 5 ft × 0.375 in., 20% SE-30 on Chromosorb W, at a He flow rate of 155 ml/min; and column C, 1.5 × 0.375 in., 30% SE-30 on Chromosorb W, at a He flow rate of 186 ml/min. Elementary analyses were carried out by the University of Massachusetts Microanalytical Laboratory.

Synthesis of 4-Allyl-2,6-di-*tert*-butyl-4-methyl-1-phenylcyclohexa-2,5-dien-1-ol (9).—To a solution of 4-allyl-2,6-di-*tert*-butyl-4-methylcyclohexa-2,5-dien-1-one[2] (3.9 g, 0.015 mol) in 20 ml of benzene was added with stirring 15 ml of phenyllithium solution (2.11 *M* in 3:7 ether–benzene). After 0.5 hr, the solvent was evaporated under reduced pressure, and the residue was heated at 50° for 1 hr. The residue was shaken with 3:1 methanol–water solution and extracted with methylene chloride. The organic layer was washed with water, dried over magnesium sulfate, and evaporated under vacuum to give 5.6 g of a colorless fluid. Its ir spectrum showed a sharp OH peak at 2.7 μ, and no carbonyl peak. Vpc on column A at 200° showed three peaks with retention times of 1.1, 4.1, and 6.2 min, in the relative areas 1:1:13. These three products were isolated by preparative vpc on column B at 175°. The component with the lowest retention time was identified by its ir and nmr spectrum as biphenyl. The component with intermediate retention time was obtained as a white solid, mp 121–123°. Its ir spectrum showed peaks at 3.4 (s), 6.25 (m), 7.0 (m), 7.1 (m), 8.1 (w), 8.4 (m), 8.55 (w), 9.35 (m), 11.6 (s), 12.8 (w), 12.9 (s), 13.5 (s), and 14.0 μ (s). On the basis of its nmr spectrum (see Table I) it was assigned the structure **3,5-di-*tert*-butyl-4-phenyltoluene (12)**.

Anal. Calcd for $C_{21}H_{28}$: C, 89.9; H, 10.1. Found: C, 90.2; H, 10.2.

The component with highest retention time was obtained as a pale yellow oil. Its ir spectrum showed peaks at 2.7 (m), 3.35 (s), 6.05 (w), 6.2 (w), 6.75 (s), 6.9 (s), 7.18 (m), 7.35 (s), 7.55 (m), 8.1 (m), 8.35 (m), 8.45 (w), 8.65 (m), 9.15 (w), 9.65 (s), 9.85 (m), 10.05 (m), 10.75 (s), 10.9 (s), 11.5 (m), 12.9 (s), 13.7 (s), 14.2 (s), and 14.5 μ (m). On the basis of its nmr spectrum (see Table I) it was assigned the structure **4-allyl-2,6-di-*tert*-butyl-4-methyl-1-phenylcyclohexa-2,5-dien-1-ol (9)**. The presence of small peaks around δ 1.5, however, suggested the presence of aromatic impurities, to the extent of 2–3%.

The crude reaction product remaining (4.6 g) was chromatographed on silica gel (66 g). Elution with 5% benzene in *n*-pentane gave 3.2 g of oil. Vpc analysis on column A at 200° showed the presence of one major component, with a retention time of 9.5 min, as well as traces of biphenyl and **12**. The major component was isolated as a colorless oil by vpc on column B at 215°. Its ir spectrum showed peaks at 3.37 (s), 5.08 (w), 5.22 (w), 5.43 (w), 6.05 (w), 6.2 (w), 6.71 (w), 6.9 (s), 7.05 (m), 7.15 (m), 7.33 (s), 7.90 (w), 8.09 (w), 8.3 (s), 8.4 (m), 8.59 (w), 9.1 (w), 9.3 (w), 9.7 (m), 10.04 (m), 10.35 (w), 10.65 (w), 10.95 (s), 11.43 (m), 12.5 (w), 12.88 (s), 13.55 (w), and 14.1 μ (s). On the basis of its nmr spectrum (see Table I) it was assigned the structure **2-allyl-3,5-di-*tert*-butyl-4-phenyltoluene (11)**, yield 0.01 mol (73%).

Anal. Calcd for $C_{24}H_{32}$: C, 89.9; H, 10.1. Found C, 89.7; H, 10.2.

Further elution with 1:1 ether–pentane gave 0.8 g (2.2 mmol, 16%) of **9** as a colorless oil.

Synthesis of 4-(*trans*-2-Butenyl)-2,6-di-*tert*-butyl-4-methyl-1-phenylcyclohexa-2,5-dien-1-ol (14).—Phenyllithium solution (20 ml, 2.11 *M*) in 3:7 ether–benzene was added to 4-(*trans*-2-butenyl)-2,6-di-*tert*-butyl-4-methylcyclohexa-2,5-dien-1-one[2] (5.0 g, 0.0182 mol) in 20 ml of benzene. The mixture was stirred for 0.5 hr and then evaporated to dryness under reduced pressure, while being heated in a water bath at 50°. A mixture of water and methanol was then added, and the resulting mixture was extracted with *n*-pentane. The organic layer was washed with water, dried over magnesium sulfate, and evaporated to give 6.3 g (0.0179 mol, 98%) of **14** as a yellow oil. Its ir spectrum showed peaks at 2.73 (w), 3.35 (s), 6.2 (w), 6.75 (s), 6.9 (s), 7.15 (m), 7.35 (m), 7.65 (w), 8.1 (m), 8.35 (m), 8.65 (m), 9.15 (w), 9.65 (s), 9.86 (m), 10.35 (s), 10.8 (s), 11.5 (w), 12.4 (m), 13.7 (m), 14.2 (s), and 14.5 μ (m). Its nmr spectrum (see Table I) showed it to be essentially pure **14**.

Reaction of 4-(*trans*-2-Butenyl)-2,6-di-*tert*-butyl-1,4-dimethylcyclohexa-2,5-dien-1-ol (3) with Acid.—A solution of dienol **3** (0.14 g) in 2 ml of 10% sulfuric acid (by volume) in glacial acetic acid was kept at room temperature for 15 hr. Water was then added, and the mixture was extracted with *n*-pentane. The organic layer was washed with water, then with sodium bicarbonate solution, again with water, and then dried over magnesium sulfate and evaporated under vacuum to give 0.11 g of a brown oil. Vpc analysis on column A at 155° showed the presence of two components with retention times of 4.4 and 5.1 min, in the area ratio 6:1. The products were isolated by preparative vpc on column B at 175°. The major product was a white solid, mp 91–93°, which was identified as **2,6-di-*tert*-butyl-*p*-xylene (5)** by comparison of its ir and nmr spectra and vpc retention times with those of an authentic sample.[3] The minor component showed peaks at 3.4 (s), 6.2 (m), 6.85 (s), 6.92 (s), 7.35 (m), 9.55 (w), 8.2 (w), 8.4 (w), 9.5 (w), 9.7 (w), 9.95 (w), 10.4 (s), 11.7 (s), 13.5 (w), and 13.7 μ (w) in its ir spectrum. On the basis of its nmr spectrum, it was assigned the structure **2-(*trans*-2-butenyl)-6-*tert*-butyl-*p*-xylene (6)**.

Anal. Calcd for $C_{16}H_{24}$: C, 88.8; H, 11.2. Found: C, 88.7; H, 11.1.

Reactions of 4-(*trans*-2-Butenyl)-2,6-di-*tert*-butyl-1,4-dimethylcyclohexa-2,5-dien-1-ol (3) and 4-(*trans*-2-Butenyl)-2,6-di-*tert*-butyl-4-methyl-1-methylenecyclohexa-2,5-diene (4) in the Pres-

ence of Florisil.—Florisil (0.50 g) was added to a solution of **3** (0.20 g) in 10 ml of benzene, and the mixture was refluxed for 15 hr. The mixture was then cooled and filtered, and the solvent was evaporated to give 0.15 g of a pale yellow oil. Vpc on column A at 175° showed the presence of three peaks with retention times of 2.6, 3.0, and 8.3 min, with relative areas in the ratio 10:52, respectively. The three products were isolated by preparative vpc on column B at 200°. The two components with lower retention times were identified as **5** and **6** by comparison of their nmr and ir spectra and vpc retention times with those of samples previously prepared.

The component with the highest retention time showed maxima in its ir spectrum at 3.35 (s), 6.3 (w), 6.8 (s), 6.9 (s), 7.05 (m), 7.17 (m), 7.3 (m), 7.35 (s), 7.98 (m), 8.25 (s), 8.4 (m), 8.75 (w), 9.45 (w), 9.7 (w), 10.05 (m), 10.35 (s), 10.55 (m), 11.5 (m), 12.7 (w), and 12.9 μ (w). On the basis of its nmr spectrum (see Table I) it was assigned the structure **3-(*trans*-2-butenyl)-2,6-di-*tert*-butyl-*p*-xylene (7)**.

A suspension of Florisil (0.20 g) in a solution of **4**[3] (0.20 g) in 10 ml of benzene was refluxed for 24 hr. Work-up as above gave 0.18 g of pale yellow oil. Vpc analysis on column A at 150° showed the presence of three components, with retention times of 2.6, 3.0, and 8.2 min, with relative areas of 9:3:1 The three products were isolated by preparative vpc on column B, and identified as **5**, **6**, and **7** by their ir and nmr spectra.

Rearrangement of 4-Allyl-2,6-di-*tert*-butyl-4-methyl-1-phenylcyclohexa-2,5-dien-1-ol (9) in Acid.—Dienol **9** (0.20 g) was dissolved in 4 ml of a 10% (by volume) solution of sulfuric acid in acetic acid. An insoluble layer immediately separated above the acetic acid layer. The mixture was allowed to stand at room temperature overnight, and the two layers then separated. The upper layer was dissolved in *n*-pentane, washed with water, sodium bicarbonate solution, and water, and dried over magnesium sulfate. The mixture was filtered and the filtrate was evaporated to give 0.16 g of a clear oil. Vpc analysis on column A at 200° showed the presence of only one peak with a retention time of 9.5 min. The ir and nmr spectra and vpc retention time of the product showed it to be 2-allyl-3,5-di-*tert*-butyl-4-phenyltoluene (**11**). The acetic acid layer was extracted with *n*-pentane, and the pentane layer was washed with water and sodium bicarbonate solution. It was dried over magnesium sulfate and the solvent was evaporated to give 0.05 g of brown oil. Vpc on column A at 200° showed the presence of two components with retention times of 3.6 and 9.6 min, with relative areas in the ratio 1:4. The two products were isolated by preparative vpc on column C at 175°. The major product was again shown to be **11**. The low retention time component had peaks in its ir spectrum at 3.4 (s), 6.1 (m), 6.2 (m), 6.75 (s), 6.85 (s), 6.95 (s), 7.15 (w), 7.35 (m), 8.05 (m), 8.3 (m), 9.35 (m), 9.7 (m), 10.5 (m), 11.0 (s), 11.4 (m), 13.0 (s), and 14.35 μ (s). On the basis of its nmr spectrum (see Table I) it was assigned the structure **2-allyl-5-*tert*-butyl-4-phenyltoluene (10)**.

Rearrangement of 9 in the Presence of Florisil.—A mixture of **9** (0.20 g) and Florisil (0.20 g) in 10 ml of benzene was refluxed overnight. After filtration evaporation of the solvent gave 0.17 g of a clear oil. Vpc analysis on column A at 200° showed the presence of three peaks with retention times of 3.4, 4.1, and 9.8 min, with relative areas in the ratio 3:1:11. The products were isolated by preparative vpc on column C at 175°. The product with lowest retention time was a pale yellow oil with ir peaks at 3.35 (s), 6.05 (m), 6.2 (m), 6.4 (w), 6.85 (w), 6.95 (s), 7.1 (w), 7.2 (w), 7.35 (m), 8.2 (m), 8.3 (m), 8.5 (w), 8.7 (w), 9.35 (m), 9.7 (w), 9.9 (m), 10.05 (w), 10.95 (s), 11.65 (s), 12.6 (w), 13.1 (s), and 14.2 μ (s). On the basis of its nmr spectrum (see Table I) it was assigned the structure **3-allyl-5-*tert*-butyl-4-phenyltoluene (13)**.

Anal. Calcd for $C_{20}H_{24}$: C, 90.9; H, 9.15. Found: C, 90.9; H, 9.17.

The other two products were identified by their ir and nmr spectra and vpc retention times as **12** and **11**.

Reaction of 4-(*trans*-2-Butenyl)-2,6-di-*tert*-butyl-4-methyl-1-phenylcyclohexa-2,5-dien-1-ol (14) with Acid.—Dienol **14** (0.20 g) was dissolved in 10% sulfuric acid in glacial acetic acid solution. A white solid formed immediately. Water was added and the mixture was extracted with *n*-pentane. The pentane solution was washed with water and sodium bicarbonate solution, dried over magnesium sulfate, and evaporated to give 0.18 g of oily crystals. Vpc on column A at 200° showed the presence of two components with retention times of 4.1 and 11.0 min, in the area ratio 10:1. Recrystallization from methanol gave white crystals, mp 122–124°, which were identified by their vpc retention time and ir and nmr spectra as **12**. The oil obtained from the mother liquor after recrystallization showed two peaks with the same retention times as before recrystallization. The peak with the higher retention time was isolated as a pale yellow oil by preparative vpc. The ir spectrum of the product had peaks at 3.35 (s), 5.8 (w), 6.22 (m), 6.3 (w), 6.75 (s), 6.95 (s), 7.1 (m), 7.2 (m), 7.65 (w), 7.9 (w), 8.15 (w), 8.3 (s), 8.4 (m), 8.6 (w), 9.3 (m), 9.7 (m), 9.85 (m). 10.3 (s), 10.7 (w), 10.8 (w), 11.4 (m), 12.75 (s), 13.55 (w), and 14.05 μ (s). On the basis of its nmr spectrum (see Table I) this compound was assigned the structure **2-(*trans*-2-butenyl)-3,5-di-*tert*-butyl-4-phenyltoluene (15)**.

Anal. Calcd for $C_{25}H_{34}$: C, 89.7; H, 10.2. Found: C, 89.9; H, 9.86.

Reactions of 14 in the Presence of Florisil.—A mixture of **14** (0.20 g) and Florisil (0.20 g) in 10 ml of benzene was refluxed overnight and then filtered. The filtrate was evaporated to give 0.15 g of colorless oil. Vpc on column A at 200° showed the presence of two components with retention times of 4.1 and 10.1 min, with areas in the ratio 2:1. The two components were isolated by preparative vpc on column C at 175°. Comparison of their vpc retention times and ir spectra with those of the products previously showed them to be **12** and **15**, respectively.

Registry No.—**3**, 34731-37-8; **6**, 34731-38-9; **7**, 34731-39-0; **9**, 34712-56-6; **10**, 34731-40-3; **11**, 34014-53-4; **12**, 34014-54-5; **13**, 34014-56-7; **14**, 34712-57-7; **15**, 34731-44-7.

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The Reaction of 1-Azirines with 1,3-Diphenylisobenzofuran. Ring Expansion to Isoquinoline, Dihydroisoquinoline, and Azanorcarane Derivatives

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Under appropriate reaction conditions advantage can be taken of the inherent reactivity of the rigid C=N bond of 1-azirines to effect cycloadditions. The 2-π electrons of this system can participate in thermally allowed [$_\pi 4 + {}_\pi 2$] reactions as dienophiles[1,2] or as dipolarophiles.[3-5] Thus, reaction of 1-azirines with cyclopentadienones proceeds *via* the cycloadduct to furnish after decarbonylation, valence tautomerism, and 1,5-sigmatropic shift, 3*H*-azepine derivatives. 1,3-Dipolar cycloaddition to the three-orbital 4-π electron system of diazomethane and nitrile oxides transforms these 1-azirines into allylic azides and carbodiimides, respectively. The apparent photochemical [2 + 2] cycloaddition with electron-deficient olefins actually proceeds through thermal addition of a 1,3-dipolar species generated by cleavage of the electronically excited singlet state of the appropriate azirine.[6]

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