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REARRANGEMENTS IN POLYSUBSTITUTED CYCLOHEXADIENYL CARBONIUM IONS

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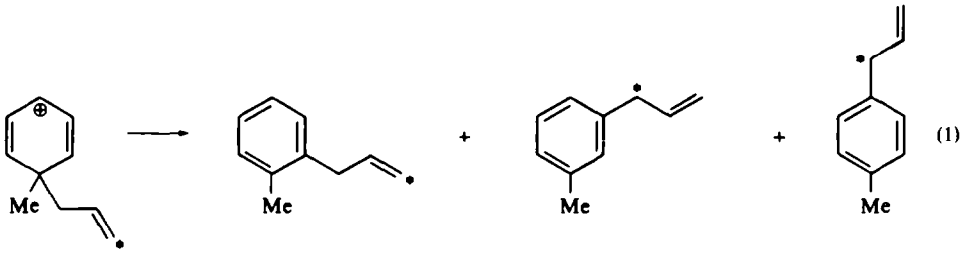
Abstract—Allyl migration in the 2,6-di-t-butyl-1.4-dimethylcyclohexadienyl carbonium ion initially proceeds by an apparently normal [1,2] shift to give the expected aromatic product. In moderately concentrated acid, however, the initial rearrangement product undergoes further rearrangements in which migration of a methyl group rather than an allyl group is the major process. This is accounted for by assuming that protonation occurs most rapidly at the position between the two t-butyl groups, thus minimizing steric strain between the substituents on the aromatic ring. Studies on migration of a deuterium labelled allyl group indicate that the allyl group can undergo processes involving allylic inversion as well as [1,2] shifts.

"DIENOL-BENZENE" rearrangements of cyclohexadienols are among the most facile of carbonium ion rearrangements.[1] A new dimension has recently been added to this area of research by the elegant work of Schmid and his group,[2] who showed that migrations of allyl groups in cyclohexadienyl carbonium ions could proceed not only by classical [1,2] shifts, but also by [3,3] and [3,4] sigmatropic shifts (eq. 1).



(1)

In earlier work, we found that allyl groups in several 2,6-di-*t*-butylcyclohexadienones underwent rather atypical migrations in the presence of acid, due to the steric effects of the bulky t-butyl groups.[3] It therefore appeared to be of interest to examine the rearrangements of similarly substituted cyclohexadienols in acid, in order to determine the effects of the t-butyl groups on the nature of the allyl group migrations.

Our studies on the rearrangements of the 4-allyl-2,6-di-t-butyl-1,4-dimethylcyclohexadienyl carbonium ion have resulted in isolation of a series of unexpected rearrangement products. The identification of these products and evidence as to the mechanism of their formation will be discussed in this paper.[4]

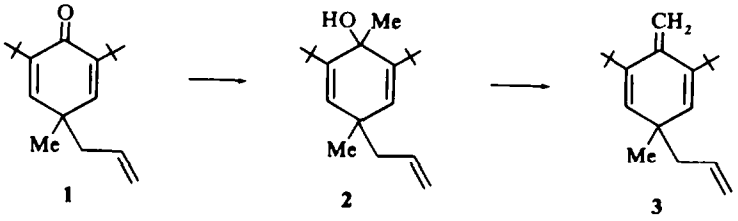
Formation and rearrangement of the 4-*allyl*-2,6-*di-t-butyl*-1,4-*dimethylcyclohexadienyl carbonium ion*

Our initial attempts to prepare 4-allyl-4-methyl-2,6-di-t-butylcyclohexadienols by

reduction of the readily available 4-allyl-4-methyl-2,6-di-t-butylcyclohexadienone (**1**) were unsuccessful. No reduction could be achieved with $NaBH_4$ in MeOH. LAH did reduce the dienone, but a complex mixture of products was obtained, which contained carbonyl, hydroxyl, and aromatic absorptions in its IR spectrum. Apparently both normal and conjugate addition had taken place as well as rearrangement to aromatic products. Efforts to prepare this dienol were therefore abandoned.

In contrast to the failure of the attempted reductions, addition of MeLi to **1** proceeded smoothly to give a mixture of stereoisomeric cyclohexadienols (**2**) which were readily dehydrated to give the methylenecyclohexadiene **3**. These reactions have been prescribed in an earlier paper.[5]

Reaction of **3** with a 10% solution of H_2SO_4 in glacial AcOH gave a mixture



1 **2** **3**

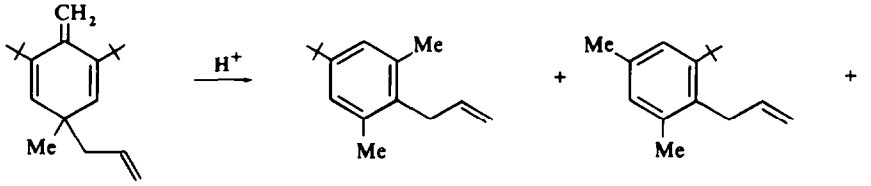
containing five components. An identical mixture was obtained from the rearrangement of a mixture of the *cis* and *trans* isomers of cyclohexadienol **2** under similar conditions. Three of the five products obtained from these reactions (the two products with lowest VPC retention times and the one with the highest retention time) could be isolated by preparative VPC. The other two products could not be completely separated from one another even by repeated VPC. However, as is discussed below, the minor component of this pair of products could be readily prepared by rearrangement of **2** in the presence of Florisil. Minor peaks assigned to this component in the NMR spectra of mixtures of the two inseparable products could therefore be discounted, and the NMR spectrum of the major component thus obtained.

The NMR spectra of the five products were described in Table 1. In addition to the resonances listed in the Table, all the products showed multiplets from τ 3·8–4·4 and τ 4·8–5·3 for the vinyl protons on the allyl group.

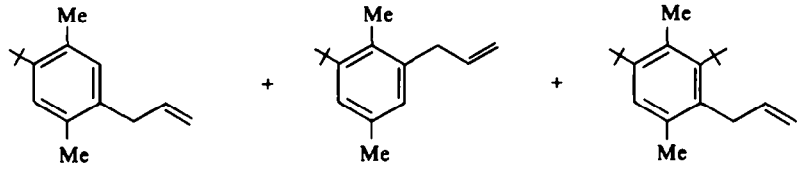
The structures of all the products isolated from this reaction can be assigned on the basis of their elemental analyses and NMR spectra. The interpretation of the spectra is greatly assisted by the presence of at least one aromatic t-butyl group in all these products. The resonances for aromatic Me groups *ortho* to t-butyl groups have been shown to be shifted significantly downfield from their normal positions at *ca.* τ 7·7–7·8, due to steric compression by the t-butyl group.[5,6] The resonances for the t-butyl groups are similarly shifted downfield, to a smaller extent, by the presence of *ortho*-substituents.[5,6] In examining the spectra in the Table, therefore, we can assign those groups which have resonances at low fields, compared to similar resonances in other products, to positions *ortho* to t-butyl groups.

The first product eluted by prep VPC, a hydrocarbon with the formula $C_{15}H_{22}$, was assigned the structure 2-allyl-5-t-butyl-*m*-xylene (**4**). As can be seen in the Table, the resonances for the t-butyl group, the Me groups, and the allyl methylene group

show no downfield shifts compared to any of the other products. This implies that neither the allyl group nor either of the Me's are *ortho* to the t-butyl group. The two aromatic protons must therefore be in those positions, and this assignment is confirmed by the location of the aromatic hydrogen resonance at τ 3·13, *ca.* δ 0·15 downfield from the aromatic hydrogen resonances in several of the other products. The sharp singlets observed for the aromatic Me and aromatic hydrogen absorptions indicate that the two Me groups must be in equivalent environments, as must the two aromatic hydrogens. Structure **4** is the only structure consistent with this data.



3 **4** **5**



6 **7** **8**

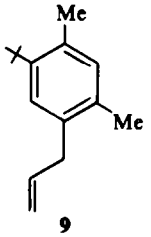
The second product isolated, **5**, an isomer of **4**, has a quite different NMR spectrum. The marked downfield shift of the multiplet for the allylic methylene group, combined with the moderate downfield shift for the t-butyl resonance, shows that the allyl group must be *ortho* to the t-butyl group. One of the aromatic hydrogens must be in some other position, therefore, and this is confirmed by the shift of the resonance for one of the two aromatic protons to τ 3·28, significantly upfield from the position of the comparable peak in **4**. The coupling between the two aromatic hydrogens demonstrates that they are in the *meta* position relative to each other. The only structure consistent with this data is 4-allyl-5-t-butyl-*m*-xylene (**5**).

The NMR spectrum of the third rearrangement product, the major component of the mixture of two difficultly separable products, shows that, like **4** and **5**, it has one t-butyl group, two Me groups, and an allyl group on the aromatic ring.

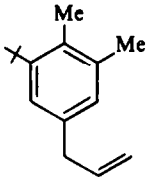
The t-butyl group is clearly flanked by one Me group and one aromatic hydrogen, in view of the low field position for the resonances for these groups. The two aromatic hydrogens are clearly in the *para*-position relative to each other, in view of the lack of any coupling between them. Two conceivable structures, **6** and **9**, are consistent with this spectrum. While no decision between them can be made simply on spectroscopic grounds, mechanistic considerations strongly favour structure **6**. Compounds **6** and **9** are the products which would be expected to arise by allyl and Me migration, respectively in the dienol–benzene rearrangement of **2**, followed by loss of t-butyl

groups from the products. That **6** is, indeed, formed by this mechanism is demonstrated below. All our evidence indicates that allyl migrations in systems similar to those under investigation here are very much faster than Me migrations.[3] This is conclusively confirmed by the work of Schmid's group.[2] Formation of **6** would therefore be readily explicable, while formation of **9** would be without precedent. We therefore assign the structure 3-allyl-6-t-butyl-*p*-xylene (**6**) to this product.

The minor component in the mixture of two difficultly separable products from the acid-catalyzed rearrangement of **3** was isolated in pure form by rearrangement of **2** in the presence of Florisil (see below). It was assigned the structure 2-allyl-6-t-butyl-*p*-xylene (**7**) on the basis of the following evidence. Its elemental analysis and NMR spectrum showed it to be isomeric with compounds **4–6**. Its NMR spectrum was similar to that of **6**, and showed that the t-butyl group is flanked by one Me group and one aromatic hydrogen atom. However, the aromatic proton signals in **7** appear as doublets, showing typical *meta*-coupling. Again, two structures **7** and **10**, are consistent with the NMR spectrum. Formation of structure **10**, however, would require a very unlikely series of Me migrations, while formation of **7** from **2** could



9



10

readily be accounted for as proceeding through either two [1, 2] migrations of the allyl group, or one [3,3] migration. The assignment of structure **7** to the rearrangement product is confirmed by the evidence, presented below, that **7** is formed largely with inversion of the allyl group. No reasonable mechanism for formation of **10** would result in inversion.

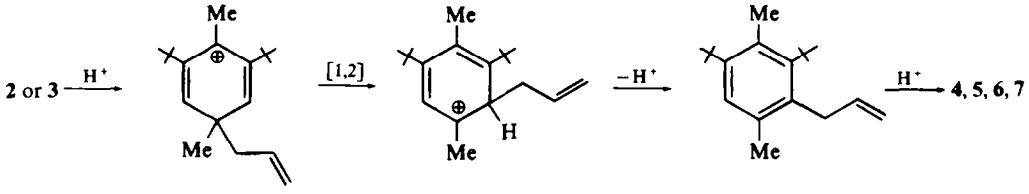
The final product isolated from rearrangement of **3** in acid had the formula $C_{19}H_{30}$. Its NMR spectrum demonstrates that the allyl group and the aromatic proton are *ortho* to t-butyl groups. While the resonance for one Me group is at a normal field, the resonance for the second Me group is significantly downfield even from that of other Me's *ortho* to t-butyl groups. We can therefore place this Me group *ortho* to both t-butyl groups, which means that the two t-butyl groups, as expected, have not moved from their initial [1,3] orientation. The only structure which fits this spectrum is **8**, the "normal" product from dienol-benzene rearrangement of **3**.

During purification of dienol **2** by column chromatography on Florisil (magnesiumfluorosilicate), we found that some aromatic materials were obtained along with pure **2**. Since Florisil has previously been employed as a mild acid catalyst in other rearrangements,[7] we considered it of interest to compare the results of rearrangement using this heterogeneous catalyst with those using homogeneous acid solutions. When **2** was heated in a refluxing benzene solution in the presence of Florisil, two products were obtained in approximately equal amounts. These products were isolated by prep VPC and identified as **7** and **8**. No other products could be detected by VPC analysis.

Effects of reaction conditions on product ratios

Compounds **4**, **5**, **6** and **7** were obtained in the molar ratios 0·9:1:1:0·3 from reaction of **3** or of a mixture of the *cis* and *trans* isomers of **2** with H_2SO_4 in AcOH. These ratios remained essentially unchanged as the concentration of H_2SO_4 was increased from 1% to 10%, and did not change significantly when the reaction time was increased. In contrast, the yield of **8** was markedly dependent upon both the concentration of acid and the reaction time. When **3** was dissolved in a solution of AcOH containing 1% of H_2SO_4 for 3 min, and the reaction then immediately quenched by pouring it into water, a 97% yield of **8** was obtained. The yield of **8** decreased, and that of the other products increased, as either the concentration of H_2SO_4 or the reaction time increased. If the solution of **3** in 10% H_2SO_4 in AcOH was allowed to stand for 48 hr, essentially no **8** was detectable in the product.

Rearrangement of **8** in 10% H_2SO_4 in AcOH gives products **4**–**7** in the same ratios obtained from rearrangement of **2** or **3**. Thus, formation of carbonium ion **11** is apparently followed by a "normal" [1,2] migration of the allyl group to give **8**, from which all the other products are formed.



11 **8**

In contrast to the rearrangements of **2** and **3** in acidic solutions, rearrangement of **2** in benzene in the presence of Florisil appears to give both **7** and **8** as primary rearrangement products, since the ratio of products is unchanged on prolonged refluxing in the presence of Florisil.

Migration of a deuterated allyl group

The apparent observation that the allyl group in carbonium ion **11** undergoes

TABLE 1. MAJOR PEAKS IN NMR SPECTRA (CCl_4)
(Chemical Shifts in Units of τ)

Compound	Ar-H	Ar-Me (s)	Ar-CH_2—CH=CH_2 (m)	Ar-t-Bu (s)
4	3·13 (s, 2H)	7·77 (6H)	6·70	8·72 (9H)
5	3·07 (d, J = 1, 1H) 3·28 (d, J = 1, 1H)	7·78 (3H) 7·82 (3H)	6·43	8·62 (9H)
6	3·06 (s, 1H) 3·25 (s, 1H)	7·57 (3H) 7·82 (3H)	6·77	8·62 (9H)
7	3·07 (d, J = 1, 1H) 3·27 (d, J = 1, 1H)	7·62 (3H) 7·77 (3H)	6·72	8·62 (9H)
8	3·13 (s, 1H)	7·44 (3H) 7·85 (3H)	6·43	8·52 (9H) 8·60 (9H)

only a [1,2] shift is quite different from the observations of Schmid on the migrations of an allyl group in the 4-allyl-4-methylcyclohexadienylcarbonium ion (eq. 1).[2] It also differs from our own observations on the dienone-phenol rearrangements of 2,6-di-t-butylcyclohexadienones, in which [3,3] shifts of an allyl group were found to be competitive with [1,2] shifts.[3] To further test the apparent absence of other types of migrations of the allyl group in **11**, methylenecyclohexadiene **3**-d_2, bearing 1·76 ± 0·02 atoms of deuterium at the terminal methylene group,* was rearranged in a 10% solution of H_2SO_4 in AcOH. Partially deuterated **4**, **5** and **8** and a mixture of **6** and **7**, were isolated by prep VPC, and the deuterium content at the methylene groups of the allylic chain determined by integration of the NMR absorptions for these hydrogens. The results are shown in Table 2.

TABLE 2. DISTRIBUTION OF DEUTERIUM ATOMS IN ALLYL GROUPS

Compounds	No. of Deuterium Atoms* at terminal vinyl position	at benzylic methylene
3-d_2	1·76 ± 0·02[a]	——
4-d_2	1·45 ± 0·10[b]	0·28 ± 0·05[b]
5d_2	1·44 ± 0·04	0·24 ± 0·08[b]
6-d_2	(1·3)[c]	0·56 ± 0·05[b]
7-d_2[d]	0·61 ± 0·09[b]	0·92 ± 0·04[b]
8-d_2	1·47 ± 0·03[b]	0·22 ± 0·03[b]

[a] Determined by internal comparison with area of allylic methylene group
[b] Determined by internal comparison with areas of aromatic hydrogens
[c] Area uncertain due to overlap with secondary vinyl protons in mixture
[d] From rearrangement of **2** in presence of Florisil

It can be seen that formation of compounds **4**, **5** and **8** proceeds with *ca.* 15% inversion of the allyl group. Within experimental error, the degree of inversion of the allyl group in these molecules is identical. Unfortunately, the deterium distributions in **6** and **7** cannot be determined, since these molecules could not be separated. It is clear, however, that at least one of these molecules is formed with much greater inversion of the allyl group than occurs in the formation of the other products.

DISCUSSION

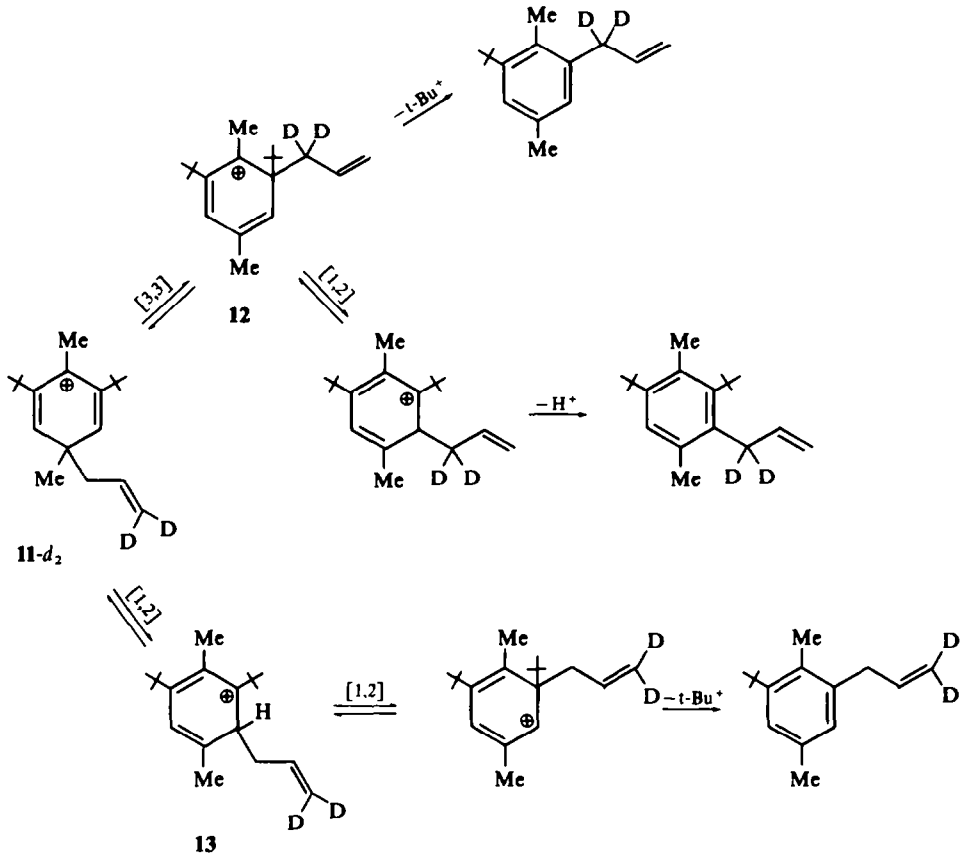
A rather complex reaction scheme appears necessary to account for the formation of such a large number of rearrangement products, with such varying degrees of allylic inversion in their formation.

The observation that **8**, the initial product of acid-catalyzed rearrangement of **2** or **3**, is formed with *ca.* 15% inversion of the allyl group shows that the simplest assumption, that **8** is formed only by a direct [1,2] migration of the allyl group, is insufficient. Formation of **8** with partial inversion can most readily be explained as proceeding by a combination of a [1, 2] migration to C-3 (the major path) and [3,3] migration to C-2, followed by a [1,2] migration of C-3 (see Scheme 1). More complex schemes

* The precisions reported for deuterium analyses represent the reproducibility of repeated integrator traces, and not the accuracy of deuterium determinations.

(e.g., [3,4] migration to C-1 followed by two [1,2] migrations) are also possible, but are not required by any of our results.

Since no more than traces of **7** are formed during formation of **8** under mild acidic conditions, it follows that loss of a t-butyl group from carbonium ion **12** must be much slower than [1,2] migration of an allyl group. In contrast, the observation that

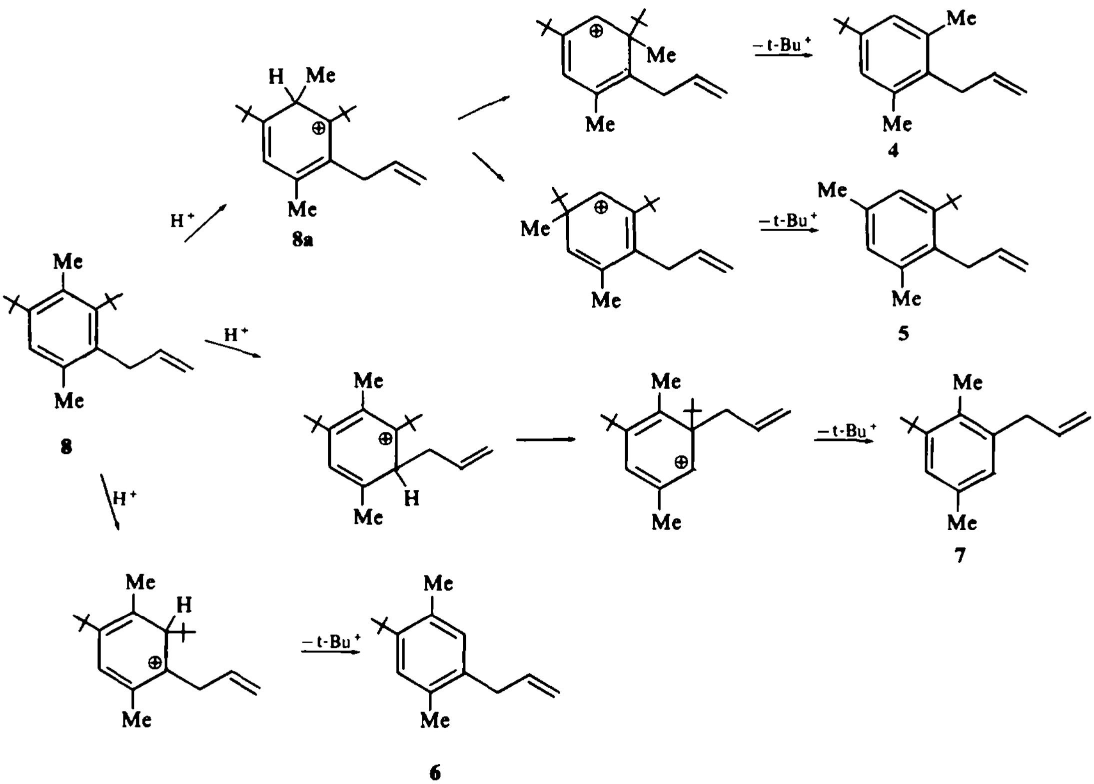


SCHEME 1

rearrangement of **2** in the presence of Florisil in benzene solution leads to appreciable formation of **7** as a primary rearrangement product indicates that loss of a t-butyl group under these conditions must be a more rapid process than migration of an allyl group. Since **7** is formed with less than 60% inversion, it must arise by both [3, 3] and two [1, 2] migrations. [1, 2]-Migration of an allyl group in carbonium ion **13** is therefore apparently able to compete with loss of a proton in benzene solution in the presence of Florisil, but not in H_2SO_4–AcOH acetic acid solution. The apparent difference, between reactions under these two sets of conditions, however, may also be explained solely by the differences in rates of t-butyl loss in **12** mentioned above, if the allyl group in **13** can undergo rapid, reversible migration between C-2 and C-3.

The rearrangements of **8** in acid are, at first glance, surprising. The major rearrange-

ment products 4 and 5 arise by migration of a Me group rather than of an allyl group, although allyl is normally much the better migrator.[3] If the question of allyl inversion is ignored for the moment, these observations can be rationalized on the basis of the reaction paths shown in Scheme 2.



SCHEME 2

The products obtained from these reaction sequences should be essentially independent of the migratory abilities of the migrating groups, since the position at which the ring is protonated will determine which group can then undergo migration.

It may appear surprising that the principal point of protonation should be the carbon atom between the two t-butyl groups—the most hindered site in the molecules. However, inspection of molecular models clearly demonstrates that protonation at this position results in net relief of steric strain in the molecule, since the appreciable steric interference between the Me group and the two t-butyl groups, which is readily visible in the NMR spectrum of 8, is relieved when the Me group is moved out of the plane in which the t-butyl groups lie.

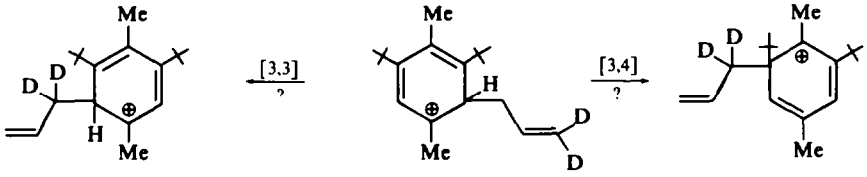
Similarly, protonation of a carbon atom bearing a t-butyl group occurs solely at the position between the Me and allyl groups, rather than at the position *ortho* only to a Me group. This can again be explained on steric grounds, since protonation at this position will move the t-butyl group out of the plane bearing the adjacent Me

and allyl groups. This would result in greater relief of steric strain than would protonation at the carbon bearing the other t-butyl group.

Protonation at the carbon bearing the allyl group would result in less relief of strain than would protonation at the other positions. Much less migration of the allyl group occurs, therefore, than migration of the Me at C-1, in spite of the presumed greater migratory aptitude of the allyl group. The actual ratio of protonation at C-1 to protonation at C-3 may, in fact, be appreciably higher than is indicated by the ratio of allyl to Me migration, since it seems unlikely that every protonation at C-1 will lead to migration of a Me group, while each protonation at C-3 is more likely to lead to migration of an allyl group.

Attempts to predict the direction of migration of a Me group in carbonium ion **8a** give ambiguous results. Migration of a Me toward the allyl group will move the t-butyl group out of the plane of the allyl group, but would place both a Me and a t-butyl group on the carbon atom adjacent to that bearing the allyl group. It is not clear whether this would result in formation of a more strained carbonium ion than that which would be formed by migration of a Me group to the carbon bearing the other t butyl group. Not surprisingly, almost equal amounts of the two types of migrations occur.

The mechanism proposed in Scheme 2 would require that the deuterium distribution in labelled **4**, **5** and **6** be identical with that in **8**, since the allyl group bearing the deuterium atoms is not involved in the reactions proposed to lead to **4**–**6**. Clearly, the deuterium distributions in **4** and **5** are consistent with this hypothesis. Unfortunately, it cannot be determined whether the locations of the deuterium atoms in **6** are the same as those in **8**. It is clear, however, that Scheme 2 must be modified to account for the excess deuterium distribution at the benzylic methylene groups in the mixture of **6** and **7**.



15 **13** **14**

Several possible paths can account for this result. Perhaps the most likely is that carbonium ion **13** reverts to carbonium ion **11** (Scheme 1) in which the allyl group then undergoes a [3, 3] migration to form **7** with inversion, as well as a [1,2] shift to reform **13**. Two other possibilities are that the allyl group in **13** can undergo a [3, 4] migration to give **14**, or a [3,3] migration to give **15**. (Presumably, in the strong acid conditions in which the rearrangements of **8** occur, loss of a proton from **13** to give **8** is slow, so that appreciable scrambling of deuterium does not occur). A choice among these mechanisms is not now possible.

EXPERIMENTAL

NMR spectra were taken in a Varian A-60 spectrometer in CCl_4 solutions. IR spectra were taken on a Perkin-Elmer model 237 spectrometer using liquid films of all compounds. Elementary analyses were by

the University of Massachusetts Microanalytical Laboratory. VPC analyses were carried out on a Varian model 202c instrument with a thermal conductivity detector, using one of two columns: Column A, 6′ × ¼″, 3% SE30 on Chromasorb W, at a He flow rate of 64 ml/min, and Column B, 5′ × ⅜″ 20% SE30 on Chromosorb W, at a flow rate of 1 6 ml/min.

Rearrangement of 4-*allyl*-2,6-*butyl*-4-*methyl*-1-*methylenecyclohexa*-2,5-*diene with sulfuric acid in acetic acid*

Semibenzene 3[5] (0·40 g) was dissolved in 6 ml of a 10% (by volume) solution of conc H_2SO_4 in glacial AcOH. The resulting solution was allowed to stand at room temperature for 5 hr, poured into water and the mixture extracted with CH_2Cl_2. The organic extract was washed with $NaHCO_3$aq and then with water, dried ($MgSO_4$), and the solvent evaporated to give 0·36 g of a brown oil. VPC on column A at 150° showed the presence of peaks with retention times of 3·6, 4·0, 4·4 and 15·2 min. These products were isolated by prep VPC on Column B at 160°. The first component was identified as 2-*allyl*-5-t-*butyl*-m-*xylene* (4). Its IR spectrum showed peaks at 3·35 (s), 6·1 (m), 6·2 (w), 6·35 (w), 6·75 (s), 6·9 (s), 7·1 (w), 7·4 (m), 7·75 (m), 8·1 (m), 8·4 (m), 9·0 (w), 9·7 (w), 10·2 (m), 11·0 (s), 11·5 (s), 12·9 (w) and 13·9 (w) μ.

The second component eluted was identified as 4-*allyl*-5-t-*butyl*-m-*yxlene* (5). Its IR spectrum showed peaks at 3·35 (s), 6·1 (m), 6·2 (m), 6·8 (s), 7·2 (w), 7·35 (m), 7·8 (s), 7·95, 8·15 (w), 8·55 (w), 8·85 (w), 9·7 (w), 10·05 (n), 10·25 (w), 10·65 (w), 10·95 (s), 11·7 (s), 12·55 (w), 13·6 (w) and 13·7 (w) μ.

The third component isolated was found from its NMR spectrum to be a mixture of two components, in the ratio 3·6 : 1. The two components had similar retention times on SE-30, DC-550 and DEGS columns. The minor component was identified by comparison of its VPC retention times and NMR peaks with that of the sample isolated from reaction of 2 with Florisil (see below) to be 2-*allyl*-6-t-*butyl*-p-*xylene* (7). The major component was shown by its NMR spectrum to be 3-*allyl*-6-t-*butyl*-p-*xylene* (6). The IR spectrum of the mixture had peaks at 3·35 (s), 6·1 (m), 6·7 (m), 6·85 (s), 7·2 (m), 7·35 (m), 7·95 (w), 8·1 (w), 8·35 (s), 8·7 (w), 9·66 (w), 10·05 (s), 10·95 (s), 11·35 (s) μ.

The fourth component was identified as 3-*allyl*-2,6-*di*-t-*butyl*-p-*xylene* (8) by its NMR spectrum and elemental analysis.

Compound	Formula	Elemental analyses Calc composition	Found
4	$C_{15}H_{22}$	89·0; 11·0	88·7; 10·7
5	$C_{15}H_{22}$	89·0; 11·0	88·9; 10·8
6	$C_{15}H_{22}$	89·0; 11·0	88·7; 11·0
7	$C_{15}H_{22}$	89·0; 11·0	88·9; 10·8
8	$C_{19}H_{30}$	88·3; 11·7	88·1; 11·9

Its NMR spectrum had peaks at 3·35 (s), 6·05 (m), 6·30 (w), 6·80 (s), 7·05 (w), 7·20 (m), 7·35 (s), 7·95 (m), 8·2 (s), 8·4 (m), 8·7 (w), 9·7 (w), 10·05 (w), 10·95 (s), 11·5 (m), 12·9 (w) and 14·1 (w) μ.

Reaction of 4-*allyl*-2,6-*di*-t-*butyl*-*dimethyleyclohexa*-2,5-*dien*-1-*ol* (2) *with Acid.* (a) Dienol 2[5] (0·20 g) was dissolved in 5 ml of a solution of H_2SO_4 (1% by volume) in glacial AcOH. After 10 min, water was added and the mixture extracted with hexane. The hexane extract was washed with water, $NaHCO_3$ aq, and again with water, dried ($MgSO_4$), and evaporated to give a yellow oil. VPC analysis on Column A at 150° showed the presence of two components, in the area ratio 1 : 42, at retention times of 4·4 and 15·2 min. The minor component was present in too small amounts to be identified. The major component was identified by its VPC retention time and IR and NMR spectra as compound 8.

(b) Dienol 2 was dissolved in a solution of H_2SO_4 (5% by volume) in glacial AcOH. The solution was allowed to stand overnight at room temp and worked up as described above. VPC analysis on column A showed the presence of 4 peaks, with retention times of 3·6, 4·0, 4·4 and 15·2 min, in the relative areas 10 : 12 : 14 : 36. The products were isolated by prep VPC and shown to be compounds 4–8 by their VPC retention times and IR spectra.

(c) Dienol 2 (0·40 g) was dissolved in 6 ml of a solution of H_2SO_4 (10% by volume) in glacial AcOH. The solution was kept for 50 hr at room temp and worked up as described above. VPC analysis of the product (0·35 g of yellow oil) on column A at 150° showed three peaks, in the area ratio 10 : 12 : 15, at retention times of 3·6, 4·0 and 4·4 min. These were identified as compounds 4, 5 and a mixture of 6 and

7, respectively. Reaction of **2** in a 3% solution of H_2SO_4 in glacial AcOH for 11 days gave essentially the same results.

Reaction of 3-*allyl*-2,6-*di*-t-*butyl*-p-*xylene* (**8**) *with acid.* A solution of **8** (0·40 g) in 6 ml of 10% (by volume) H_2SO_4 in glacial AcOH was allowed to stand at room temp for 20 hr. The reaction was worked up as described above to give 0·32 g of a brown liquid. VPC on column A at 150° showed the presence of equal amounts of three components with retention times of 3·6, 4·0 and 4·4 min. Reaction of **8** in 3% H_2SO_4 in AcOH at room temp for 11 days gave the same products, in the ratio 10:12:15. The products were isolated by prep VPC and identified as compounds **4**, **5** and a mixture of **6** and **7**.

Reaction of 4-*allyl*-2,6-*di*-t-*butyl*-4-*dimethylcyclohexa*-2,5-*dien*-1-*ol* (**2**) *with Florisil.* Dienol **2** (1·20 g) was dissolved in 10 ml of benzene and Florisil (magnesium fluorosilicate, 0·50 g) added. The mixture was refluxed for 30 min, and the Florisil removed by filtration. The filtration was evaporated to give 1·2 g of pale yellow oil. VPC on column A at 150° showed two components, in the area ratio 1:1, with retention times of 4·4 and 15·2 min. These were separated by prep VPC on column B at 190°. The product with the lower retention time was assigned the structure 2-allyl-6-t-butyl-*p*-xylene (**7**). Its IR spectrum showed peaks at 3·35 (s), 6·15 (m), 6·7 (s), 7·35 (m), 7·9 (w), 8·2 (w), 8·3 (w), 9·6 (w), 9·85 (w), 10·05 (m), 10·35 (w), 10·95 (s), 11·65 (s) and 13·35 (w) μ.

The product with the higher retention time was identified as **8** by comparison of its VPC retention time and IR and NMR spectra with those of samples previously prepared.

Reaction of 4-(3,3-*Dideuterioallyl*)-2,6-*di*-t-*butyl*-4-*methyl*-1-*methylenecyclohexa*-2,5-*diene* (**3**-d_2) *with acid.* A solution of **3**-d_2[5] (0·50 g) in 10 ml of 10% H_2SO_4 in glacial AcOH was kept overnight at room temp. It was worked up as described above to give 0·40 g of pale yellow oil, which showed four components with retention times of 3·6, 4·0, 4·4 and 15·2 min, relative areas 10:12:14:5, on VPC on column A at 150°. These components were isolated by prep VPC on column B at 165°. They were identified as the deuterated analogs of compounds **4**, **5**, a mixture of **6** and **7** and **8**, respectively, by their NMR and IR spectra and VPC retention times. The deuterium distributions obtained from NMR analysis are listed in Table 2.

Rearrangement of 4-(3,3-*Dideuterioallyl*)-2,6-*di*-t-*butyl*-1,4-*dimethylcyclohexa*-2,5-*dien*-1-*ol* (**2**-d_2) *in the Presence of Florisil.* Florisil (0·2 g) was added to a solution of **2**-d_2,[5] bearing 1·67 ± 0·02 atoms of deuterium at the terminal vinyl position of the allyl group, in 10 ml of benzene. The mixture was refluxed for 24 hr, cooled and filtered. Evaporation of the filtrate gave 0·15 g of yellow oil, which showed two components with retention times of 4·4 and 15·2 min on VPC analysis on Column A at 150°. The components were isolated by prep VPC on Column B at 190°, and identified by their retention times and NMR and IR spectra as the deuterated analogs of **7** and **8** The deuterium distributions are listed in Table 2.

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