Dienone–Phenol Rearrangements of 2,6-Di-*t*-butylcyclohexadien-1-ones[1,2]

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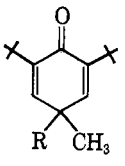
The rearrangements of several 2,6-di-t-butylcyclohexadienones in 9% H_2SO_4 in acetic acid were studied. 2,6-Di-t-butyl-4-ethyl-4-methylcyclohexadien-1-one (**3**) *gave 2-t-butyl-5-ethyl-4-methylphenol* (**4**), *which on reaction with excess bromine gave 2-t-butyl-4,6-dibromo-5-ethylphenol. 4-Allyl-2,6-di-t-butyl-4-methylcyclohexadien-1-one* (**7**) *gave a mixture of the 1,2- and 1,3-rearrangement products, 3-allyl-6-t-butyl-4-methylphenol* (**9**) *and 2-allyl-6-t-butyl-4-methylphenol* (**8**), *on treatment with acid. 4-(trans-2-Butenyl)-2,6-di-t-butyl-4-methylcyclohexadien-1-one* (**10**) *gave a mixture of 2,6-di-t-butyl-4-methylphenol and 2-(trans-2-butenyl)-6-t-butyl-4-methylphenol* (**12**), *while 2,6-di-t-butyl-4-isopropyl-4-methylcyclohexadien-1-one* (**13**) *gave only 2,6-di-t-butyl-4-methylphenol in acid solution. The 1,3-rearrangements were shown to be intramolecular reactions.*

Introduction

Transformations of *p*-cyclohexadienones to phenols in the presence of acidic catalysts have been known for many years and have been extensively studied.[3] This is particularly true of those cyclohexadienones which are derived from steroids and other natural products. The emphasis on the rearrangements of these readily obtained cyclohexadienones, however, has limited the range of structures which have been studied. Comparatively little is known about the effects which substituents on the cyclohexadienone ring or on the migrating group exert on the rearrangements.

We recently reported the preparation of a series of 2,6-di-*t*-butylcyclohexadienones (**1**).[4,5] Several features



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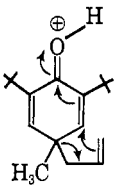

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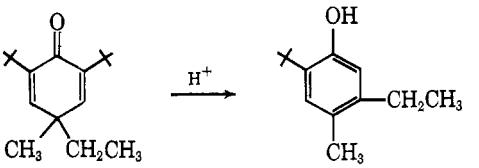
of these molecules suggested that their behavior in acid solution might differ from that of other dienones.[3] The normal migration of a substituent from the 4-position to the 3-position of the dienone should be subject to appreciable steric interference from the adjacent *t*-butyl group.[6] This effect should increase as the size of the migrating group increases. We might expect, therefore, to find the over-all rearrangement rates of 2,6-di-*t*-butylcyclohexadienones to be slower than those of other dienones, and to find anomalies in the order of "migratory aptitudes" of substituents. Furthermore, the availability of dienones with allyl and crotyl groups in the 4-position raises the possibility of interaction between the double bond of the side chain and a positive charge at the adjacent 3-position.[7] A possible form of such interaction, giving rise to dienone–phenol rearrangements of a novel type, is shown in structure **2**.

Although these possibilities were only partially realized, it was found that rearrangements of **1** in acid did have several unusual features, which are reported in this paper.

Results

Rearrangements of 2,6-di-*t*-butyl-4-ethyl-4-methylcyclohexadien-1-one (**3**) in a 9% (by volume) solution of sulfuric acid in acetic acid gave a single phenol in 90% yield. This phenol was assigned the structure 2-*t*-butyl-5-ethyl-4-methylphenol (**4**) on the basis of the



3 **4**

following evidence. The elemental analysis of **4** fit the empirical formula $C_{13}H_{20}O$, indicating that a *t*-butyl group had been lost in the course of the reaction. This was confirmed by the n.m.r. spectrum of **4** (in CCl_4) which showed the presence of a single *t*-butyl group (τ 8.69), as well as hydroxyl (τ 5.52), methyl (τ 7.82), and ethyl (quartet around τ 7.55, triplet around τ 8.88) groups. The aromatic proton region showed the presence of two isolated protons, which exhibited no spin–spin coupling and therefore appeared to be *para* to each other. The position of one peak at τ 3.12 suggested that one aromatic hydrogen was *meta* to the hydroxyl group. (The aromatic hydrogens in 2,6-di-*t*-butyl-4-methylphenol appear at τ 3.17, and the isolated proton in 2-*t*-butyl-*p*-cresol at τ 3.05.) The second aromatic proton would necessarily be *ortho* to the hydroxyl group, if it is *para* to the first proton,

(1) Reactions of Cyclohexadienones. XI. Part X: B. Miller and H. Margulies, *Chem. Commun.* (London), 314 (1965).

(2) Part of this work has been reported as a preliminary report: B. Miller and H. Margulies, *Tetrahedron Letters*, **No. 22**, 1727 (1965).

(3) See (a) R. B. Woodward and T. Singh, *J. Am. Chem. Soc.*, **72**, 494 (1950); (b) S. M. Bloom, *Tetrahedron Letters*, **No. 21**, 7 (1959), for leading references.

(4) B. Miller, *J. Org. Chem.*, **30**, 1964 (1965).

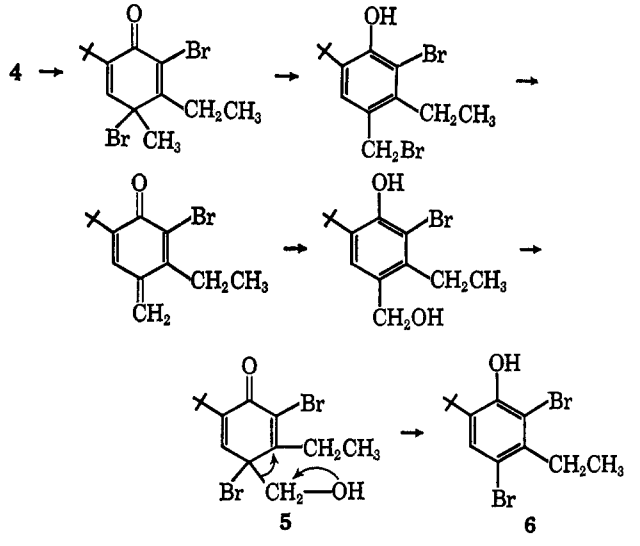
(5) B. Miller and H. Margulies, *ibid.*, **30**, 3895 (1965).

(6) It has been suggested that the steric influence of a *methyl* group in the 2-position can be sufficient to prevent migration to the adjacent position: P. J. Kropp, *Tetrahedron Letters*, **No. 25**, 1671 (1963).

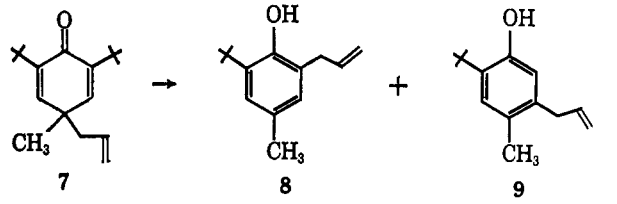
(7) Interaction of a carbonium ion with the π cloud of the double bond should be more favorable than for the analogous acyclic cases (P. D. Bartlett, W. D. Closson, and T. J. Cogdell, *J. Am. Chem. Soc.*, **87**, 1308 (1965)), since both the bulk of the substituents around the 3-position and the necessity for final conversion to an aromatic system should eliminate serious competition from the solvent.

and this was supported by the position of its n.m.r. peak at τ 3.70.[8] It would require an extraordinary rearrangement indeed to place a substituent other than a *t*-butyl group at the second *ortho* position. That this did not occur was indicated by the relative lack of polarity of **4** (*e.g.*, its ease of elution from alumina) and the position of its infrared peak at 2.79 μ. (The hydroxyl peaks of 2,6-di-*t*-butylphenol, 2-*t*-butylphenol, 2,6-dimethylphenol, and *o*-cresol appear at 2.70, 2.81, 2.91, and 3.00 μ, respectively.)

Just one question about the structure of **4** remained for consideration—the relative positions of the methyl and ethyl groups. To resolve this question, **4** was reacted with 3 moles of bromine in aqueous acetic acid. 2,6-Disubstituted *p*-cresols are normally oxidized to the corresponding 4-hydroxybenzaldehydes under these conditions.[9] If the methyl group of **4** were in the *para* position, a *p*-hydroxybenzaldehyde should have been the product, while a *p*-hydroxyacetophenone would be expected if the methyl group had migrated and the ethyl group were in the *para* position. The only product isolated from the reaction, however, was a phenol (**6**) which exhibited no carbonyl absorption in the infrared. The n.m.r. spectrum of **6** (in $CDCl_3$) showed only the presence of a hydroxyl (τ 4.05), a *t*-butyl (τ 8.60), and an ethyl group (quartet at τ 7.02, triplet at τ 8.82) as well as a single aromatic proton (τ 2.60). No methyl peak or any transformation product of the methyl group could be observed. Apparently the methyl group had been replaced by a bromine atom. That this had occurred was confirmed by the elemental analysis of **6**, which fit the formula $C_{12}H_{16}OBr_2$. Elimination of the methyl group presumably follows a course such as that shown. The sequence of reactions leading to **5** has many analogies.[9b] The conversion of **5** to **6** will be considered further in the Discussion section. It is certain, however, that the elimination of the methyl group can have occurred only from the *para* position of **4**.[10] The structure of **4** must be that shown above, therefore, rather than the isomer with the positions of the methyl and ethyl groups reversed.

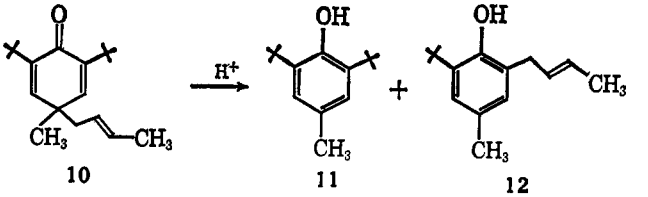


In contrast to the formation of a single product from rearrangement of **3**, a mixture of two isomeric phenols was obtained when the 4-allylcyclohexadienone **7** was dissolved in a 9% solution of sulfuric acid in acetic acid. The products were separated by chromatography on alumina. The first phenol eluted was identified as 2-allyl-6-*t*-butyl-4-methylphenol (**8**) by comparison of its infrared and n.m.r. spectra and retention time on v.p.c. with those of an authentic sample.[4] The more polar isomer was assigned structure **9**, since its n.m.r. spectrum and physical properties were very similar to those of **4**. In particular, its n.m.r. spectrum showed two sharp, one-hydrogen singlets at τ 3.10 and 3.77 (in CCl_4). In contrast, the n.m.r. spectrum of **8** showed aromatic peaks at τ 3.16 and 3.36, which exhibited typical *meta* coupling.[4]



Several arguments support the assumption that the allyl group, rather than the methyl group, of **7** had migrated during formation of **9**. V.p.c. analysis of the products of rearrangement of a mixture of **3** and **7** showed that **7** had completely reacted before more than 2–3% of **4**, resulting from rearrangement of **3**, had been formed. It would be difficult to rationalize the marked increase in rearrangement rate caused by changing a substituent from ethyl to allyl unless the allyl group were directly involved in the reaction as a migrating group. The demonstration that the ethyl group, rather than the methyl group, of **3** migrates shows that the steric effect of an adjacent *t*-butyl group is not sufficient to cause a reversal of the normal order of migratory aptitudes, and suggests that the allyl group, which can so readily bear a positive charge, should migrate in preference to a methyl group. The final evidence for the migration of the allyl group is derived from a study of deuterium substitution in **7**. It will be considered in the following paper.

Just as **7** rearranged much faster than **3**, the 4-*trans*-2-butenylcyclohexadienone **10** rearranged much more rapidly than **7**. V.p.c. analysis of a mixture of **7** and **10** showed that **10** had reacted completely by the time 3–5% of the rearrangement products of **7** had appeared. Rearrangement of **10** gave an equimolar mixture of two phenols, which were identified by their infrared and n.m.r. spectra and their v.p.c. retention times as 2,6-di-*t*-butyl-4-methylphenol (**11**) and 2-(*trans*-2-butenyl)-6-*t*-butyl-4-methylphenol (**12**).[4] Except for a trace peak at high-retention times in the v.p.c.,



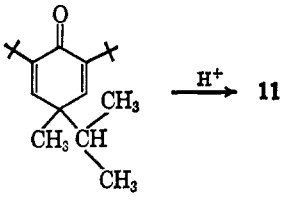
(8) The *ortho* protons in alkylphenols appear between τ 3.4 and 3.8 in CCl_4 solution.

(9) (a) G. M. Coppinger and T. W. Campbell, *J. Am. Chem. Soc.*, **75**, 734 (1953); (b) V. V. Ershov, A. A. Volod'kin, G. A. Nikiforov, and K. M. Dyumaev, *Izv. Akad. Nauk SSSR Otd. Khim. Nauk*, 1839 (1962).

(10) E. M. Arnett and G. B. Klingensmith, *J. Am. Chem. Soc.*, **87**, 1023, 1032, 1038 (1965).

no evidence for any products of a normal 1,2-migration could be detected.

Finally, dienone **13** gave a 73% yield of **11** on treatment with acid.



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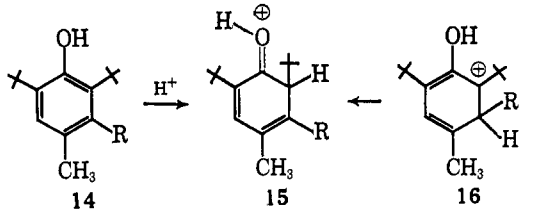
Discussion

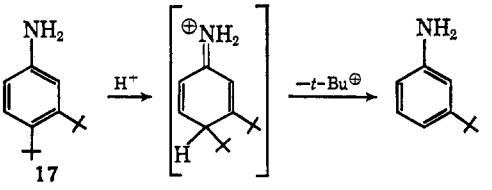
The results of the rearrangement studies described above show that 2,6-di-*t*-butylcyclohexadienones can undergo three types of reactions in acidic solution. Substituents in the 4-position can undergo 1,2- or 1,3-migrations, or can be eliminated from the molecule entirely, presumably in the form of carbonium ions.

Even the "normal" 1,2-migrations, however, have the unusual feature that a *t*-butyl group is eliminated in the course of the reaction. Two possible paths for elimination of a *t*-butyl group can be envisaged. In the first route, 1,2-migration of substituent R occurs in the normal manner to give phenol **14**. Protonation of **14** gives the protonated dienone **15**, which can give **8**



14 **15** **16**

and **12** by loss of a *t*-butyl carbonium ion. It is true that elimination of *t*-butyl groups from the *ortho* positions of phenols in acid normally occurs only under more rigorous conditions than those used in these rearrangements,[11] and that both 2,6-di-*t*-butyl-*p*-cresol and 2,6-di-*t*-butylphenol are stable indefinitely under these conditions. Steric interference between the *t*-butyl group and group R in **14**, however, should facilitate protonation at the *ortho* position, since the crowding would be reduced as the *t*-butyl group is moved from the plane of the ring. An extreme example of steric strain aiding "ketonization" of aromatic systems has recently been reported by Burgstahler and his co-workers, who found that a *t*-butyl group could be eliminated from 3,4-di-*t*-butylaniline (**17**) simply by prolonged refluxing in *ca.* 1% sulfuric acid solution.[12]



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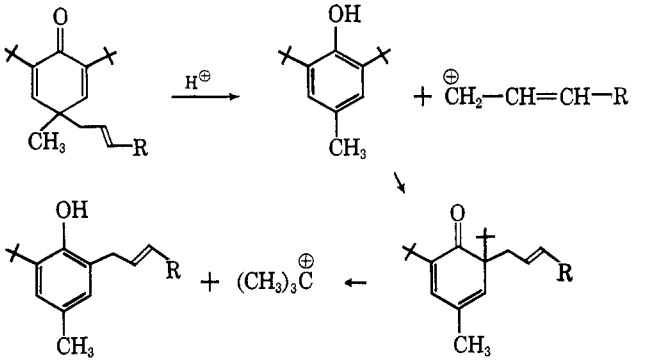
Similarly, bromination of 3,4-di-*t*-butylphenol resulted in elimination of a *t*-butyl group to give 2,4-dibromo-5-*t*-butylphenol.[12] It is difficult to compare the steric strain present in **14** and in **17**, but it does not seem unlikely that **14** would similarly be quite labile in acid.

Phenol **14**, however, need not be an intermediate in the formation of **8** and **12**. Migration of a hydride ion from the *meta* to the *ortho* position of the carbonium ion (**16**) formed initially by migration of R would give **15** without **14** ever being formed.

An attempt to distinguish between these two mechanisms by deuterium labeling of the *meta* protons of **7** failed, since exchange of the *ortho* proton of **9** with solvent was appreciably more rapid than rearrangement of **7**.[13] No clear decision between these two mechanisms, therefore, can be made at present. However, we prefer the first mechanism, on the grounds that hydride transfer, like loss of a proton from **16**, would force R and the *t*-butyl group into the same plane at some time. This being so, we can see no reason why simple loss of a proton from **16**, with the concomitant gain of an aromatic system, should not be preferred to migration of a hydride ion.

The most intriguing aspect of the rearrangements of 2,6-di-*t*-butylcyclohexadienones is the occurrence of 1,3-migrations of the allyl and crotyl groups. The 1,3-migration of the *trans*-2-butenyl group of **10** without inversion of the butenyl group to a 1-methylallyl group shows that the rearrangement does not occur by a cyclic path resembling the Cope or Claisen rearrangements.[14]

One likely mechanism for the 1,3-rearrangements is dissociation of the dienone into 2,6-di-*t*-butyl-4-methylphenol (**11**) and an allyl carbonium ion, which then realkylates the phenol at the *ortho* position. The



possibility of an intermolecular mechanism of this type occurring is supported by the isolation of **11** from the reactions of **10** and **13**. The higher percentages of 1,3-rearrangement from those dienones whose dissociation would yield the most stable carbonium ions is quite consistent with this idea.

Several observations, however, eliminate this route from consideration. Attempts to react **11** with carbonium ions formed from allyl alcohol, *trans*-2-buten-1-ol, or 1-buten-3-ol under the conditions used in the rearrangements failed. The 2,6-di-*t*-butyl-4-methylphenol was quantitatively recovered. Even more convincing was the result of a run in which **7** was rearranged in the presence of a 50-mole excess of phenol. The phenol should trap any allyl carbonium ions produced before they can react with **11**. No change in

(11) G. H. Stillson and J. B. Fishel, British Patent 591,547 (1947); D. M. W. Anderson and J. L. Duncan, *Chem. Ind.* (London), 457 (1959).

(12) A. W. Burgstahler, P. L. Chien, and M. O. Abdel-Rahman, *J. Am. Chem. Soc.*, **86**, 5281 (1964).

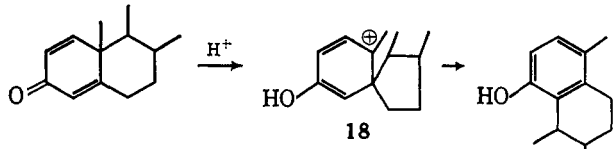
(13) Succeeding paper: B. Miller, *ibid.*, **87**, 5111 (1965).

(14) S. J. Rhoads in "Molecular Rearrangements," P. de Mayo, Ed., Interscience Publishers, Inc., New York, N. Y., 1963, pp. 660–672.

the nature or composition of the rearrangement products of **7** was observed, however. No evidence for the presence of **11**, nor of any products of alkylation of phenol by allyl or butenyl carbonium ions, could be detected by v.p.c. However, the *t*-butyl carbonium ions liberated in formation of **7** and **8** reacted with phenol to give *o*-*t*-butylphenol.

The 1,3-migrations of allyl and butenyl groups, therefore, appear to be true intramolecular rearrangements.

Intramolecular 1,3-migrations during dienone–phenol rearrangements, particularly of steroids, are quite common.[3,15] In all known examples of such rearrangements, however, the presence of substituents at the 3-position of the dienone eliminated the possibility of isolating products of 1,2-migration. Woodward,[16] Bloom,[17a] and Futaki[17b] have shown that these 1,3-migrations are actually sequences of two 1,2-migrations, proceeding, in rearrangements of steroid dienones, through the spiro carbonium ion **18**. A similar path for formation of **8** and **12**, however, would require



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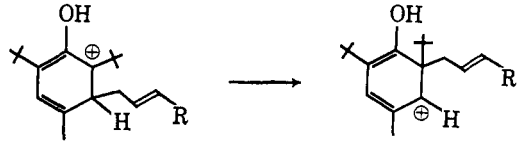
that carbonium ion **19** undergo a second migration of the allyl group to give the more stable carbonium ion **20**, rather than simply lose a proton to give an aromatic

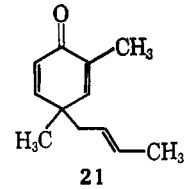


19 **20**

molecule. Loss of a proton from **19** might be hindered by the necessity of forcing the *t*-butyl group and allyl group into the same plane. Nonetheless, the possibility of direct 1,3-migrations of the allyl and butenyl groups, must be eliminated before this mechanism can be accepted.

Various procedures have been developed in the steroid field to convert cyclohexadienones to phenols by elimination of substituents from the 4-position.[18] Simple solution in acid, however, has not previously sufficed to cleave off such substituents.[19] Two factors might account for the ready elimination of substituents from **10** and **13**. The isopropyl and butenyl carbonium ions might be sufficiently more stable than cyclohexyl carbonium ions,[20] which would be formed from ring **B** of steroid cyclohexadienones, to account for the differences in ease of elimination. The importance of carbonium-ion stability in determining the extent of cleavage is shown by the absence of any cleavage in the reactions of **3**. Alternatively, the presence of the bulky *t*-butyl groups in the 2-positions could markedly hinder a substituent from migrating to an adjacent carbon, and thus favor an elimination reaction.

Several arguments support the view that elimination of substituents from **10** and **13** is largely due to the steric effects of the *t*-butyl groups. First, the elimination of the isopropyl group of **13**, to the complete exclusion of any rearrangement, seems clearly to be due to steric factors. The isopropyl carbonium ion is far less stable than allyl or butenyl carbonium ions,[21] yet no ejection of allyl carbonium ions from **7** occurs, and **10** undergoes equal amounts of elimination and rearrangement. The situation is, to be sure, complicated by the occurrence of 1,3-rearrangements of the allyl and crotyl groups. In the following paper however, it will be shown that the initial step in all the rearrangements is a simple 1,2-shift.[13] The ratios of elimination to rearrangement products, therefore, represent direct comparisons of the rates of elimination and 1,2-rearrangement. Further evidence for the importance of the *t*-butyl groups in determining the extent to which elimination of substituents occurs is found in the observation that no elimination of the crotyl group occurs during the rearrangement of dienone **21** in acid.[22]



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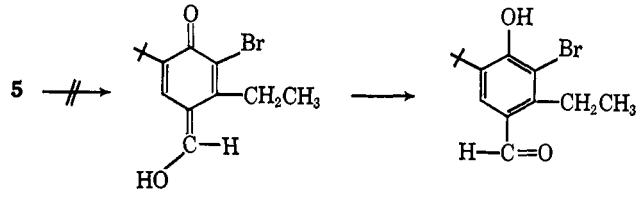
Finally, the replacement of a methyl group by a bromine atom in the attempted oxidation of **4** deserves consideration. It was suggested above that oxidation of **4** to a *p*-hydroxybenzyl alcohol, and then to the 4-bromocyclohexadienone **5** occurs without incident. Rearrangement of **5** to the aldehyde, presumably *via* the quinone methide **22**, would be the normal reaction path.[9b] Instead, cleavage to **6** is the principal reaction



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path. This sort of cleavage occurs extensively in the bromination of *p*-alkoxy[10,23a] and *p*-aminobenzyl alcohols,[23b] presumably due to the instability of the intermediate cations **23** and **24**. Similar cleavage on bromination of *p*-hydroxybenzyl alcohols does occasionally occur in low yield.[10,23a]

(15) *E.g.*, A. S. Dreiding, W. J. Pummer, and A. J. Tomasewski, *J. Am. Chem. Soc.*, **75**, 3160 (1953); C. Djerassi and T. T. Grossnickle, *ibid.*, **76**, 1741 (1954); E. Caspi, P. K. Grover, and Y. Shimizu, *ibid.*, **86**, 2463 (1964); R. Villotti, A. Cervantes, and A. D. Cross, *J. Chem. Soc.*, 3621 (1964).

(16) R. B. Woodward in "Perspectives in Organic Chemistry," A. Todd, Ed., Interscience Publishers, Inc., New York, N. Y., 1956, p. 178.

(17) (a) S. M. Bloom, *J. Am. Chem. Soc.*, **80**, 6280 (1958); (b) R. Futaki, *Tetrahedron Letters*, **No. 41**, 3059 (1964).

(18) (a) L. F. Fieser and M. Fieser, "Steroids," Reinhold Publishing Corp., New York, N. Y., 1959, Chapter 15.14; (b) H. L. Dryden, Jr., G. M. Webber, and J. L. Wieczorek, *J. Am. Chem. Soc.*, **86**, 743 (1964); (c) M. Heller, R. L. Lenhard, and S. Bernstein, *ibid.*, **86**, 2309 (1964).

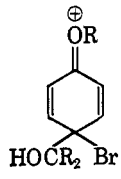
(19) Ref. 18a, Chapter 9.8.

(20) H. C. Brown and M. Borkowski, *J. Am. Chem. Soc.*, **74**, 1894 (1952).

(21) A. Streitwieser, Jr., *Chem. Rev.*, **56**, 571 (1956).

(22) B. Miller, *J. Am. Chem. Soc.*, **87**, 5115 (1965).

(23) (a) E. P. Kohler and R. H. Patch, *ibid.*, **38**, 1205 (1916); (b) L. Clarke and G. J. Esselen, Jr., *ibid.*, **33**, 1135 (1911); L. Clarke and R. H. Patch, *ibid.*, **34**, 912 (1912); G. J. Esselen, Jr., and L. Clarke, *ibid.*, **36**, 308 (1914).



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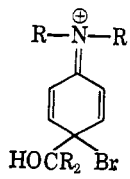

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It seems probable that the large amount of cleavage of **5** is due to the presence of the adjacent ethyl group. Dehydrobromination of **5** to **22** would be hindered by steric interference between the ethyl group and the vinyl proton, allowing the competing cleavage reaction to take preference.

Experimental Section[24]

Rearrangement of 2,6-Di-t-butyl-4-ethyl-4-methylcyclohexadien-1-one (**3**).[5] A solution of **3** (1.0 g., 0.00404 mole) in 20 ml. of glacial acetic acid was stirred and 2 ml. of concentrated sulfuric acid added slowly. After stirring at room temperature for 16 hr., the solution was dissolved in water and extracted with methylene chloride. The methylene chloride layer was washed with sodium bicarbonate solution, dried over magnesium sulfate, and evaporated to give 0.90 g. of a dark brown oil. V.p.c. analysis at 165° showed the presence of one major peak (retention time, 8.8 min.) along with trace components. The product was chromatographed on Woelm neutral alumina (activity III). Elution with chloroform gave 0.70 g. (0.00365 mole, 90%) of 2-*t*-butyl-5-ethyl-4-methylphenol (**4**) as a pale yellow oil.

Anal. Calcd. for $C_{13}H_{20}O$: C, 81.3; H, 10.5. Found: C, 81.4; H, 10.7.

When the rearrangement was carried out in a solution of 20 ml. of concentrated H_2SO_4 in 60 ml. of glacial acetic acid, there was obtained, together with **4**, about an equal amount of a carbonyl-containing material which was not isolated, but was assumed to be 2-*t*-butyl-5-ethyl-4-methylphenyl acetate, since refluxing the crude product mixture with a 10% solution of potassium hydroxide in ethanol converted it all to **4**. Reaction of **4** with acetic anhydride gave an acetate with the same v.p.c. retention time (7.6 min. at 165°) as the rearrangement product.

Bromination of 2-t-Butyl-5-ethyl-4-methylphenol. To a solution of **4** (1.0 g., 0.00521 mole) in 20 ml. of glacial acetic acid and 5 ml. of water was added a solution of bromine (2.50 g., 0.0157 mole) in 5 ml. of glacial acetic acid. After 15 hr. at room temperature, the solution was diluted with methylene chloride, washed several times with water and finally with sodium bicarbonate solution, dried over magnesium sulfate, and evaporated to give 1.65 g. of a dark oil. Chromatography on Florisil gave 0.90 g. (0.00268 mole, 51%) of 2,4-dibromo-6-*t*-butyl-5-ethylphenol. The analytical sample, obtained by v.p.c. (retention time, 8.5 min. at 195°) was identical with the chromatographed product in its infrared and n.m.r. spectra.

(24) All melting points are corrected. Microanalyses were by Galbraith Microanalytical Laboratories, Knoxville, Tenn. All v.p.c. analyses were carried out on a 6-ft., 2% XE60 on Gas Chrom Z column at the temperatures indicated.

Anal. Calcd. for $C_{12}H_{16}Br_2O$: C, 42.8; H, 4.76; Br, 47.6. Found: C, 43.2; H, 4.86; Br, 46.8.

Rearrangement of 4-Allyl-2,6-di-t-butyl-4-methylcyclohexadien-1-one (**7**).[4] Concentrated sulfuric acid (2 ml.) was added drop by drop to a solution of **7** (1.0 g., 0.00385 mole) in 20 ml. of glacial acetic acid, which was stirred constantly and cooled in ice during the addition. When all the acid was added, the mixture was stirred at room temperature for 5 hr., and the reaction then was worked up as described for **3**. A black oil was obtained (0.90 g.) which was found by v.p.c. to be a mixture of equal amounts of two components, with v.p.c. retention times of 5.3 and 12.9 min. at 165°. The mixture was chromatographed on 200 g. of Fisher neutral alumina (activity III). Elution with pentane gave 0.35 g. (0.00172 mole, 46%) of 2-allyl-6-*t*-butyl-4-methylphenol.[4] Elution with methylene chloride gave 0.20 g. (0.00098 mole, 25%) of the component with the higher retention time, 3-allyl-6-*t*-butyl-4-methylphenol.

Anal. Calcd. for $C_{14}H_{20}O$: C, 82.3; H, 9.85. Found: C, 81.8; H, 10.1.

Intermediate chromatography fractions (0.20 g.), consisted principally of 3-allyl-6-*t*-butyl-4-methylphenol.

Rearrangement of **7** *in the Presence of Phenol.* Phenol (10.0 g., 0.106 mole) and **7** (0.50 g., 0.00192 mole) were dissolved in 20 ml. of glacial acetic acid. The solution was cooled in ice and stirred while 2 ml. of concentrated H_2SO_4 was added. After being stirred at room temperature for 4 hr., the solution was poured into water and extracted with methylene chloride. The methylene chloride solution was washed with 6 *N* sodium hydroxide solution and the solvent was evaporated. The residue was dissolved in alcoholic potassium hydroxide solution and the mixture was refluxed for 30 min., cooled, and diluted with methylene chloride. The methylene chloride layer was washed with water, dried over magnesium sulfate, and evaporated to give 0.70 g. of reddish oil, which was shown by v.p.c. to be completely free of 2,6-di-*t*-butyl-*p*-cresol. The v.p.c. analysis of the product showed it to contain **8** (36%), **9** (33%), and 28% of a third component which was isolated by v.p.c. and shown by its infrared and n.m.r. spectra to be *o*-*t*-butylphenol.

Rearrangement of 4-(trans-2-Butenyl)-2,6-di-t-butyl-4-methylcyclohexadien-1-one (**10**).[4] Concentrated H_2SO_4 (3 ml.) was added drop by drop to a stirred, ice-cooled solution of **10** (3.0 g., 0.0109 mole) in 40 ml. of glacial acetic acid. The mixture was then stirred at room temperature for 3 hr. and worked up as usual to give 2.8 g. of a yellow liquid, which was shown by v.p.c. (188°) to contain two components (retention times, 2.35 min. and 3.5 min.) in the ratio 47:53, as well as a trace component with a retention time of 7.35 min. The product was chromatographed on Woelm acidic alumina (activity I). Elution with petroleum ether (b.p. 39–55°) yielded 1.1 g. (0.0050 mole, 46%) of 2,6-di-*t*-butyl-*p*-cresol. Further elution with methylene chloride and then with methanol yielded 0.9 g. of 2-(*trans*-2-butenyl)-6-*t*-butyl-*p*-cresol[4] (0.00413 mole, 38%).

Rearrangement of 2,6-Di-t-butyl-4-isopropyl-4-methylcyclohexadien-1-one (**13**). Sulfuric acid (3.0 ml.) was added slowly to an ice-cooled, stirred solution of

13 (1.0 g., 0.00382 mole) in 30 ml. of glacial acetic acid. The solution was stirred for 6 hr. at room temperature and worked up as usual. The product was chromatographed on Woelm neutral alumina (activity III) to give 0.1 g. of recovered **13**, and 0.6 g. (0.00273 mole, 73%) of 2,6-di-*t*-butyl-*p*-cresol.

The Mechanism of 1,3-Migrations of Allyl Groups in the Dienone–Phenol Rearrangements of 2,6-Di-*t*-butylcyclohexadienones[1,2]

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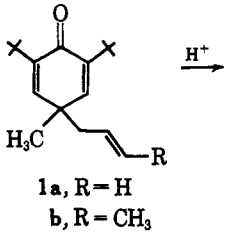
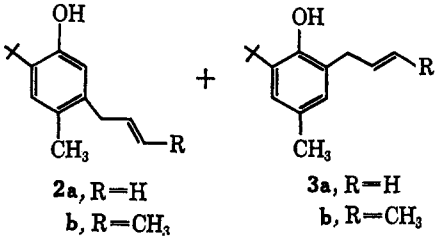
4-Allyl-2,6-di-t-butyl-4-methylcyclohexadien-1-one-3,5-d_2 was prepared and rearranged in acid. The ratio of the 1,3-rearrangement product to the 1,2-rearrangement product was much higher than in rearrangement of the undeuterated dienone. The hydrogen–deuterium kinetic isotope ratio was greater than 4. The mechanism of the 1,3-rearrangement was thus shown to involve two successive 1,2-shifts of the allyl group. The large isotope effect supports, but does not prove, the deprotonation–reprotonation mechanism for loss of a t-butyl group during the 1,2-rearrangement.

In the preceding paper,[1] it was reported that rearrangement of 2,6-di-*t*-butylcyclohexadienones (**1**) in acid gave both the products of 1,2- (**2**) and of 1,3-rearrangements (**3**), provided that an allyl or 2-butenyl group was present at the 4-position of **1**. Both 1,2- and 1,3-rearrangements resulted in loss of a *t*-butyl group from **1**.



1a, R=H
b, R=CH_3

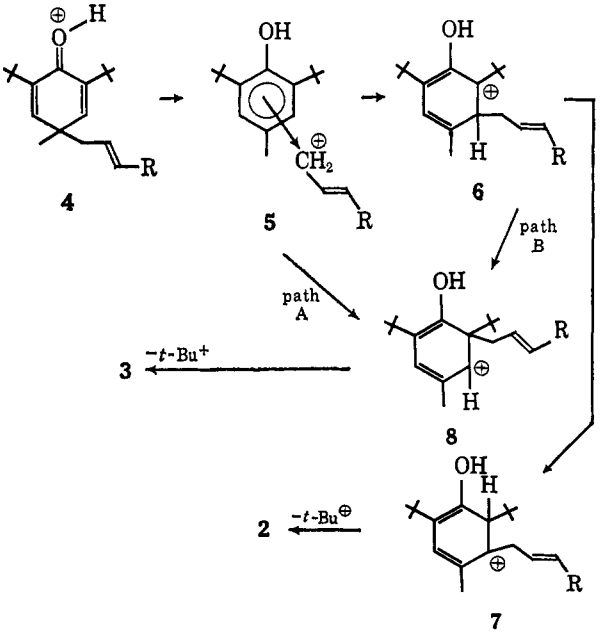


2a, R=H
b, R=CH_3

3a, R=H
b, R=CH_3

It was found[1] that both 1,2- and 1,3-rearrangements were intramolecular, and that both rearrangements occurred without allylic rearrangement of the *trans*-2-butenyl group. The percentage of 1,3-migration appeared to depend on the ability of the migrating group to bear a positive charge, since no 1,3-migration occurred when the migrating substituent was an ethyl group, approximately equal amounts of 1,2- and 1,3-migration took place when an allyl group migrated, and only 1,3-rearrangement of the *trans*-2-butenyl (crotyl) group could be demonstrated. Rearrangement of **1b** to **3b**, however, was accompanied by loss of the crotyl group to give 2,6-di-*t*-butyl-4-methylphenol in approximately equal amounts.

Two general types of mechanisms, which we will call the single-migration and the double-migration mechanisms, can be written to account for the 1,3-rearrangements. In the single migration mechanism the protonated dienone **4** is converted to an intermediate π-complex (**5**), in which the migrating group is not



linked to any one carbon of the ring by a σ-bond. Collapse of the π-complex to a "classical" carbonium ion will result in formation of a σ-bond between the migrating group and an adjacent ring carbon.

(1) Reactions of Cyclohexadienones, XII. Preceding paper, part XI: B. Miller and H. Margulies, *J. Am. Chem. Soc.*, 87, 5106 (1965).
(2) Part of this work has been published as a preliminary communication: B. Miller, *Tetrahedron Letters*, No. 22, 1733 (1965).