Effects of Steric Interference between Substituents on the Stabilities and Rearrangements of Cyclohexadienones[1,2]

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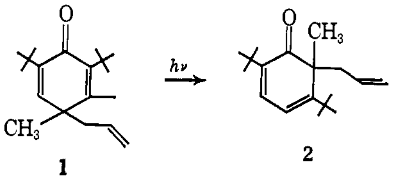
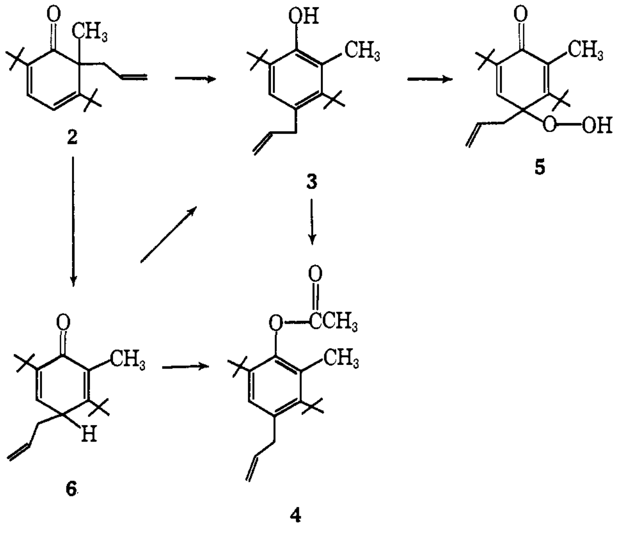
Abstract: Thermal rearrangement of dienone **2** gave the cross-conjugated dienone **6**. Compound **6** could be hydrogenated to **7** without undergoing aromatization and was quite stable at temperatures below 100° in the absence of acidic or basic catalysts. In the presence of catalysts, or at high temperatures, **6** was tautomerized to phenol **3**. Phenol **3** was very rapidly autoxidized to **5**. Dienone **10** rapidly lost methyl bromide and was converted to **12** at temperatures slightly above room temperature. These reactions are interpreted as the result of the steric effects of the *t*-butyl groups at C-3 in **3** and **6** and at C-5 in **2** and **10**.

In the preceding paper it was reported that photoirradiation of 4-allyl-2,6-di-*t*-butyl-4-methylcyclohexa-2,5-dienone (**1**) through a Pyrex filter gave a mixture which consisted principally of 6-allyl-2,5-di-*t*-butyl-6-methylcyclohexa-2,4-dienone (**2**).[1] Although the presence of **2** could be demonstrated by its hydrogenation to the known 6-propyl derivative, attempts to isolate **2** by vpc or by chromatography on alumina or silica gel resulted in the rapid disappearance of the characteristic ultraviolet band of **2** at 320 $m\mu$. This band was replaced by aromatic absorption. It was later found that **2** could be isolated by rapid chromatography on "Florisil" magnesium silicate, but the over-all yield was much lower than the amount of **2** known to be present in the photolysis product.[1] Investigation of the causes for the difficulty in isolating **2** disclosed several intriguing reactions, including the formation of an unusually stable ketonic tautomer of a phenol and the exceptionally rapid formation of an oxonium salt from a ketone. A unifying feature of these rather diverse reactions is that they all appear to be dependent on the steric influence of the *t*-butyl group at C-5 in **2** and its products. These reactions are reported in this paper.



Rearrangement of 2 to 3. Attempted isolation of **2** by chromatography on alumina or silica gel or by vpc gave a colorless oil, **3**. Chromatography of pure **2** under the same conditions again yielded **3**, which could also be obtained almost instantly by dissolving **2** in a 1% solution of sulfuric acid in acetic acid or by heating **2** for a short time at 220°. Isolation of **3** in pure form was quite difficult, since it was rapidly autoxidized in air, but when care was taken to exclude air, **3** could be obtained pure, preferably by vpc.

Compound **3** was isomeric with **2** but showed no carbonyl bands in its infrared spectrum. Its ultraviolet and infrared spectra indicated that it was a phenol. Since 6-allylcyclohexa-2,4-dienones are readily rearranged to 4-allylphenols under the conditions in which **2** is converted to **3**,[3,4] the structure 4-allyl-2,5-di-*t*-butyl-6-methylphenol was tentatively assigned to **3**. This structure was consistent with the infrared spectrum of **3**, which had a hydroxyl peak at 2.84 μ, suggesting the presence of a *t*-butyl group at one of the carbons *ortho* to the hydroxyl group.[1,5] The nmr spectrum of **3** (see Table I) is also consistent with the proposed structure, although it does not distinguish it from possible isomers. Of particular interest in the nmr spectrum of **3** is the marked separation between the positions of the two *t*-butyl absorptions, and especially the very low-field position of one of the two absorptions, which is assigned to the sterically crowded *t*-butyl group at C-3. The positions of the aromatic methyl and of the allyl methylene doublet also appear at unusually low fields.[6] The same downfield shifts are found in the spectrum of the acetate **4** which may be prepared from **3** or directly from **2** by reaction with acetic anhydride and sulfuric acid.



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(1) Reactions of Cyclohexadienones. XVIII. For part XVII, see the preceding paper.

(2) Parts of this work have been published as preliminary communications: B. Miller, *J. Am. Chem. Soc.*, 87, 5515 (1965); B. Miller, *Chem. Commun.*, 327 (1966).

(3) D. Y. Curtin and R. J. Crawford, *J. Am. Chem. Soc.*, 79, 3156 (1957).

(4) B. Miller, *ibid.*, 87, 5115 (1965).

(5) B. Miller and H. Margulies, *ibid.*, 87, 5106 (1965).

(6) *E.g.*, the methyl peaks in the spectra of 2-allyl-4,6-dimethylphenol and 5-allyl-2,4-dimethylphenol[4] appear at τ 7.84–7.87, and the methylene doublets at τ 6.73–6.75: B. Miller, unpublished observations.

Table I. Nmr Spectra (in $CDCl_3$)

	τ values for chemical shifts of protons (J, cps)[a]					
Compd	Aromatic or vinyl proton on ring	*t*-Butyl	Methyl	Allylic methylene	Hydroxyl	Others
3	s, 3.12	s, 8.62 s, 8.49	s, 7.63	d, 6.39 (5.3)	5.25	*b*
4	s, 2.98	s, 8.69 s, 8.49	s, 7.71	d, 6.37 (5.5)	...	s, 7.78 (acetyl methyl) *b*
5	s, 3.41	s, 8.74 s, 8.51	s, 7.89	dd, 7.40 (4.2)	1.90	*b*
6	d, 3.21 (4.9)	s, 8.75 s, 8.62	s, 7.91	m, 7.0–7.9	...	*b*
7[c]	d, 3.19 (5.0)	s, 8.77 s, 8.64	s, 7.93	...	...	*d*
12	d, 2.98 d, 3.22 (8.5)	s, 8.67[e]	...	*f*	...	*f*

[a] Abbreviations used are: s, singlet; d, doublet; dd, doublet of doublets; m, multiplet. [b] Vinyl multiplet at *ca.* τ 3.8–5.2. [c] Spectrum taken in CCl_4. [d] Broad absorption at *ca.* τ 8–9 for propyl group. [e] Eighteen-proton singlet. [f] See Figure 1.

Similar downfield shifts of the resonances for alkyl groups in very sterically crowded positions on benzene rings have previously been reported for *o*-di-*t*-butylbenzene[7] and 2,4,6-tri-*t*-butyltoluene.[8]

Although its acetate **4** was stable and easily handled, exposure of phenol **3** to air for only a few minutes resulted in the appearance of white crystals, and the entire sample solidified after a few hours' exposure. The solid product **5**, mp 123–124.5°, liberated iodine immediately from potassium iodide solution or starch iodide paper, suggesting that **3** had been oxidized to a keto hydroperoxide. This was confirmed by the elementary analysis of **5**, which agreed with the empirical formula, $C_{18}H_{28}O_3$, and by its infrared spectrum, which showed intense peaks at 3.00 μ for the hydroperoxyl group and at 6.18 μ for the carbonyl. The ultraviolet spectrum of **5** in methanol showed the intense band at 242 mμ (ϵ 10,600) typical of cross-conjugated cyclohexadienones.[4]

The nmr spectrum of **5** shows that the allyl group is located on the quaternary carbon at C-4 in **5**, and was, therefore, located at C-4 in **3**. This confirms the formation of **3** by a normal Cope rearrangement of the allyl group in **2**.[3,4] The unusually rapid autoxidation of **3** provides additional evidence for the presence of a *t*-butyl group at C-3 in **3**, since the steric interference between the alkyl groups at **3** is relieved by its oxidation to **5**. This point will be considered at greater length in the Discussion.

Rearrangement of 2 to 6. 6-Allylcyclohexa-2,4-dienones are normally readily converted to 4-allylphenols by heating at 100–125°.[3,4] When we attempted to rearrange **2** to **3** by heating at 110°, the characteristic ultraviolet absorption of **2** at 320 mμ and its infrared absorptions at 6.05 and 6.35 μ did indeed almost completely disappear after just 5 min, or after 1 hr at 70°. The product, however, showed no evidence for the presence of a phenol. Its infrared spectrum had an intense carbonyl peak at 6.18 μ and its ultraviolet spectrum had a maximum at 244 mμ, typical of cross-conjugated cyclohexadienones.[4]

Attempts to isolate the ketonic product by chromatography on alumina or silica gel, as well as by prolonged chromatography on Florisil, apparently converted it quantitatively to **3**. Rather low yields of the pure ketone could be isolated as an oil by rapid chromatography on Florisil. It was found to be isomeric with **2** and **3**. On heating to 200° or on being dissolved in a 1% solution of sulfuric acid in glacial acetic acid, or in 1 *N* sodium methoxide in methanol, the ketone was rapidly isomerized to **3**. In contrast, dienone **2** was unchanged after prolonged periods in sodium methoxide solution.

The properties of the new ketone are only compatible with structure **6**, the dienone which would be the first product formed by Cope rearrangement of **2** on its way to **3**. This structure is completely confirmed by the nmr spectrum of **6** (see Table I) which shows that the allyl group has migrated to C-4, and that the vinyl proton on the α,β-unsaturated ketone and the doubly allylic proton at C-4 are on adjacent carbon atoms.

Reactions of 6. Dienone **6**, as mentioned above, is rapidly isomerized to **3** in the presence of acidic or basic catalysts. In the absence of acids or bases, however, **6** is a reasonably stable compound, as might be expected of the product of a thermal rearrangement. A sample of **6** which has been kept at room temperature for over a year has exhibited no changes in its infrared spectrum. The spectrum of **6** is also unchanged after 6 hr at 70°, but does show the presence of some phenol after 3 hr at 100°.

The stability of **6** suggested that it would undergo chemical reactions without tautomerizing to **3**. No such reactions of ketonic tautomers of phenols were known at the time this work was done.[9]

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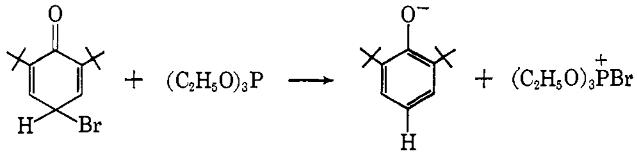
(7) A. W. Burgstahler, P. Chien, and M. O. Abdel-Rahman, *J. Am. Chem. Soc.*, **86**, 5281 (1964).

(8) W. A. Gibbons and H. Fischer, *Tetrahedron Letters*, 43 (1964).

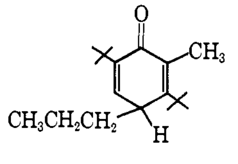
(9) The reaction of 2,6-di-*t*-butyl-4-bromocyclohexa-2,5-dienone (i) with triethyl phosphite is a formal exception, since the phosphite ab-



i

stracts a positive bromine atom rather than the proton at C-4[10] Since

Hydrogenation of the terminal double bond in **6** using a palladium on barium sulfate catalyst proceeded smoothly to give a quantitative yield of the *n*-propyl derivative **7**. There was no evidence of any tautomerization of **6** or **7** to phenols during the reaction. On the other hand, addition of 1 equiv of bromine to a solution of **6** in chloroform resulted in the immediate liberation of hydrogen bromide in large amounts. The product was a black oil which was not characterized, but which exhibited a strong hydroxyl peak but no absorption peaks for carbonyl groups or terminal vinyl groups in its infrared spectrum. It may be noted (see Experimental Section) that there is no evidence for elimination of hydrogen bromide during addition of bromine to the allyl group of **1**. It seems probable that attack of a bromide on the initially formed bromonium ion[11] **8** is hindered by the adjacent *t*-butyl group, so that loss of a proton from the side chain of **8** (presumably giving **9**) becomes the principal process. The presence of hydrogen bromide, of course, will isomerize **6** or **9** to the corresponding phenol.



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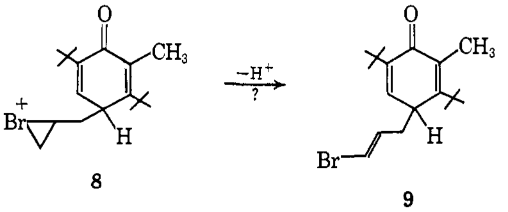
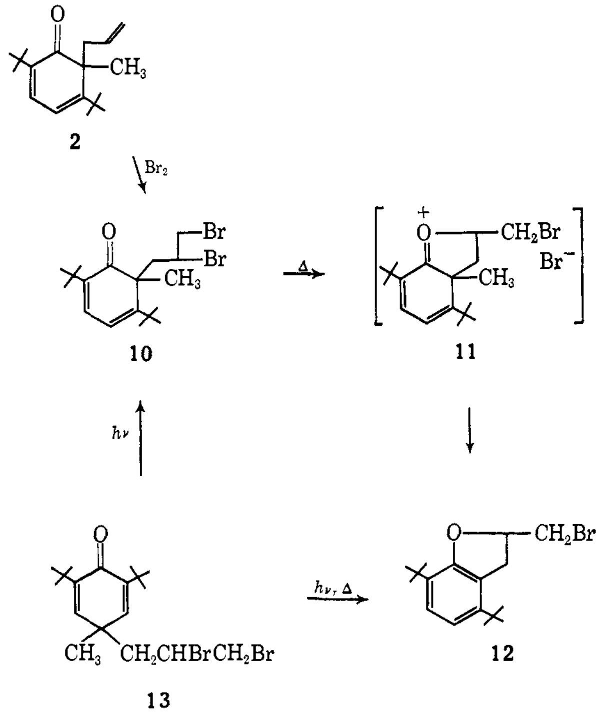


Although hydrogenation of **6** to **7** represents the first known reaction of an enolizable cyclohexadienone other than conversion to an aromatic compound, it was accomplished only by carefully avoiding any reaction with the sensitive cyclohexadienone ring system. It seems unlikely that any "ground-state" reactions can be carried out directly on the cyclohexadienone ring without aromatizing the ring. It has been found, however, that photoirradiation of **6** leads to formation of a bicyclo[3.1.0]hex-3-en-2-one rather than aromatization. This reaction will be reported in a later paper.[12]

Cyclization and Demethylation of 10. While attempting to confirm the structure of **2**, we tried to characterize it as its bromine addition product **10**. A solution of **2** in methylene chloride appeared to absorb bromine immediately, although some hydrogen bromide was evolved. The solvent was then removed on a rotary evaporator under vacuum, in a water bath at 50–60°. As the evaporation of the solvent neared its end, a rather vigorous emission of gas occurred. The gas evolved in a second reaction was collected and was identified by its nmr spectrum as methyl bromide. The infrared spectrum of the residual material was essentially free of both hydroxyl and carbonyl absorptions. Chromatography on alumina gave a white solid, mp 66–67°, with the empirical formula $C_{17}H_{25}BrO$. Its ultraviolet spectrum in methanol [λ_{max} 286 and 277 mμ (log ϵ 2.9)] showed only aromatic absorptions. Its nmr spectrum showed the presence of two *t*-butyl groups and two adjacent aromatic protons, suggesting that the arrangement of groups on the ring remains the same as in **2**. The remaining five protons consisted of a one-proton multiplet at τ 5.1, which was attributed to a hydrogen on a carbon attached to oxygen, and a four-proton multiplet around τ 6.5, which was considered to be the combined signals of a benzylic methylene group and a bromomethyl group.[13] A complete analysis of the spin–spin couplings is shown in Figure 1.



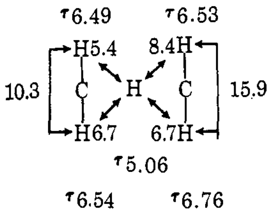


Figure 1. Analysis of nmr signals for three-carbon chain of **12**. Numbers associated with arrows are *J* values in cps.

The spectra of the solid product combined with its mode of formation allow structure **12** to be assigned to it. This structure was confirmed by the independent synthesis of **12** from 2,5-di-*t*-butylphenol, as is shown below.

The tetrahydrofuran **12** could also be prepared by photorearrangement of 2,6-di-*t*-butyl-4-methyl-4-(2,3-dibromopropyl)cyclohexa-2,5-dienone (**13**). If care is taken to keep the temperature of the solution below

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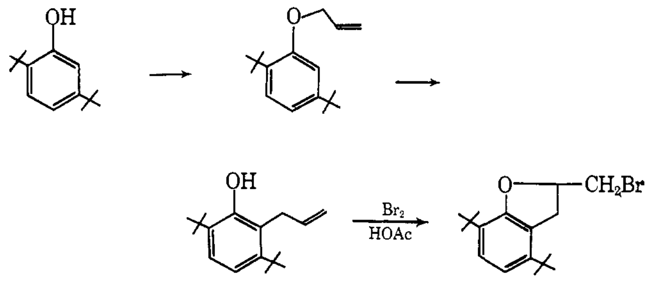
this reaction does result in immediate conversion of i to an aromatic compound, it is not different in principle from a simple tautomerization.

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

(11) E. S. Gould, "Mechanism and Structure in Organic Chemistry," Henry Holt and Co., New York, N. Y., 1959, pp 521–527.

(12) B. Miller, *J. Am. Chem. Soc.*, **89**, 1690 (1967) (following paper).

(13) L. M. Jackman, "Applications of Nuclear Magnetic Resonance in Organic Chemistry," Pergamon Press Inc., New York, N. Y., 1959.



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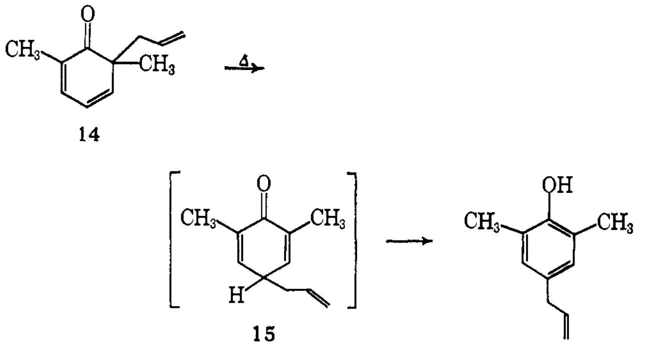
35° during irradiation of **13**, and if the solvent is evaporated at low temperatures, the ultraviolet spectrum of the crude photolysis product has a strong band at 309 mμ (in hexane), and its infrared spectrum has peaks at 6.15 and 6.4 μ, as would be expected of structure **10**. Heating the crude sample of **10** on the steam bath for 2 min results in the evolution of methyl bromide and in complete loss of the carbonyl peaks in the spectra of **10**. Chromatography of the residue again gave **12** in high yield.

If the temperature of the solution during photorearrangement is allowed to rise above 50°, or the solvent is evaporated at temperatures significantly above room temperatures, the first product isolated from the reaction is **12**, which thus would appear at first to be a (very mystifying) photorearrangement product of **13**.

Discussion

In previous papers we reported that the products of acid-catalyzed[5] and photochemical[1] rearrangements of cyclohexadienones are markedly affected by the presence of *t*-butyl groups on the dienone ring. In this paper we have reported evidence which indicates that the thermal conversion of cyclohexadienones to phenols can be either greatly accelerated or inhibited by the steric effects of *t*-butyl groups, depending upon the structures of the molecules involved.

The degree to which *t*-butyl groups can affect the relative stabilities of cyclohexadienones and phenols is shown by the isolation and relative lack of lability of dienone **6**. Curtin and Crawford[3] have studied the thermal rearrangement of dienone **14**. At 70–100°, **13** is smoothly converted to **16**. No evidence for the presence of the dienone **15**, which must have been at least a transient intermediate, was observed. In contrast, under the same conditions **2** is isomerized solely to **6**, and tautomerization to the phenol does not occur until much higher temperatures are reached.



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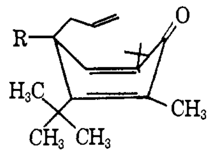
The unusual stability of dienone **6** can be ascribed to the fact that the dienone is relatively free of steric strain compared to phenol **3**. In **3**, the adjacent allyl, *t*-butyl, and methyl groups are either all in one plane or the bond angles of at least one carbon atom are severely distorted when one of the groups is forced out of the common plane. Examination of molecular models clearly indicates that both the allyl and methyl groups in **3** are pressed against hydrogen atoms on the *t*-butyl group. It has previously been pointed out that the nmr spectra of **3** and **4** suggest such compression. On the other hand, molecular models show that dienone **6** exists in a boat form (structure **17**, R = H) in which the allyl group can assume an "axial" position well away from any contact with the *t*-butyl group. Furthermore, the freedom of the *t*-butyl group in **6** from any constraint by the allyl group allows it to assume a conformation in which contact with the methyl group is eliminated. Similarly, the relatively small size of an oxygen atom allows the *t*-butyl group in the keto hydroperoxide **5** to assume a conformation in which it avoids contact with any of the three neighboring groups.



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Once phenol **3** is formed, it is unusually easily reconverted, by air oxidation, to a cyclohexadienone. We are not aware of any other simple, monohydroxy phenol that is as readily oxidized, in the absence of base or other catalysts, as is **3**. In this respect, oxidation of **3** more closely resembles the oxidation of 9-anthranols to keto hydroperoxides[14] than it does the oxidation of monocyclic phenols.

The steric effect of the *t*-butyl at C-3, as discussed above, can readily explain why the over-all energy change leading from **3** to **5** is unusually favorable. The mechanism by which the oxidation occurs is far from clear, however. It seems unlikely that oxidation of **3** to a free radical, which would normally be the first step in formation of a keto hydroperoxide,[15] would be significantly accelerated by steric effects, since the radical would presumably maintain a planar configuration. It is possible that the initial oxidation occurs by a molecular mechanism. The initially formed hydroperoxide might serve to catalyze further free radical oxidation.

The rapidity with which the normally not very nucleophilic carbonyl group displaces a bromide ion from a secondary carbon in **10** is unique. This effect again appears to be due to steric effects caused by the presence of an adjacent *t*-butyl group.

Examination of molecular models shows that a 2,3-dibromopropyl group at C-6 in a cyclohexa-2,4-dienone is normally free to assume a large number of conformations. The most favorable conformations appear to be those in which the brominated carbons are as far as possible from the carbonyl group (structure **18**). In **10**, however, the presence of the adjacent

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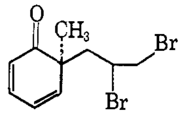
[14] P. L. Julian and A. Magnani, *J. Am. Chem. Soc.*, **56**, 2174 (1934); P. L. Julian and W. Cole, *ibid.*, **57**, 1607 (1935); P. L. Julian, W. Cole, and G. Diemer, *ibid.*, **67**, 1721 (1945). See also C. Dufraise, A. Etienne, and J. Rigaudy, *Bull. Soc. Chim. France*, **15**, 804 (1948), for structural corrections.

[15] H. R. Geismann and A. F. Bickel, *J. Chem. Soc.*, 2711 (1959).



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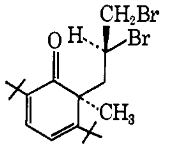

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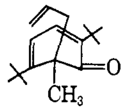
t-butyl group constrains the dibromopropyl group to assume essentially a single conformation. In that conformation (**19**), the carbonyl oxygen is brought very close to the rear of the center carbon of the dibromopropyl group. The oxygen, carbon, and bromine atoms form nearly a straight line, so that almost the perfect geometry for an SN2 displacement of the bromide ion exists. Formation of the transition state for the displacement leading to oxonium salt **11**, therefore, requires only a very slight change in the normal structure of **10**.

After being displaced from the propyl chain, the bromide ion attacks the most available site in **11**—the methyl group at C-6. Since elimination of methyl bromide will both neutralize the positive charge on the carbonyl oxygen and convert the ring to an aromatic molecule, the displacement of a methyl group from carbon occurs under exceptionally mild conditions.[16]

Finally, a comparison of the reactions **2** → **6** and **14** → **16** is of interest. Although the rate constant for the reaction **2** → **6** has not been measured, a rough comparison of the apparent half-lives for the two reactions suggests that rearrangement of **2** is at least one power of ten faster than rearrangement of **14**. A possible explanation for this is that the preferred conformation of **2** is that shown as **20**, in which the allyl group occupies the "axial" position away from the plane containing the *t*-butyl group at C-5. In **14**, on the other hand, either the methyl or allyl group at C-6 could occupy the axial position, with little reason to prefer one over the other. Since it is only the axial allyl group which can migrate to C-4, the difference in reactivity between **2** and **14** can be accounted for.



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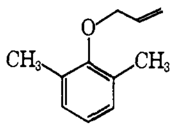

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Rearrangement of **14**, however, gives not only phenol **16**, but about 27% of the allyl ether **21**. Careful examination failed to show the formation of the comparable ether from **2**. Molecular models suggest that rearrangement of **2** to an allyl phenyl ether should be quite unhindered by either *t*-butyl group. We cannot, as yet, explain this difference between the rearrangements of **2** and **13**.

Experimental Section[17]

All photoirradiations were carried out as previously described,[1] using a 450-w, Hanovia high-pressure mercury lamp through a Pyrex filter.

Preparation of 4-Allyl-2,5-di-*t*-butyl-6-methylphenol (3). A solution of 6.0 g of 4-allyl-2,6-di-*t*-butyl-4-methylcyclohexa-2,5-dienone (**1**) in 35 ml of *n*-hexane was irradiated for 2.5 hr. The infrared spectrum of the solution indicated that **1** had largely been consumed. The solvent was evaporated, and the residue was chromatographed on activity III alumina. Elution with petroleum ether (bp 30–60°) gave 0.3 g of a material with an infrared peak at 5.8 μ. It was discarded. Elution with methylene chloride gave 0.5 g of **1**. Finally, elution with chloroform gave 3.3 g (55%) of **3** as a colorless oil, $n^{25}\text{D}$ 1.5140. An analytical sample was prepared by vpc chromatography on a 6-ft, 2% silicone gum (XE 60) on Gas Chrom Z column at 190°.

Anal. Calcd for $C_{18}H_{28}O$: C, 83.1; H, 10.75. Found: C, 82.6; H, 10.6.

Preparation of 4-Allyl-2,5-di-*t*-butyl-4-hydroperoxy-6-methylcyclohexa-2,5-dienone (5). A beaker containing **3** (1.4 g) was left open overnight at room temperature. The white solid produced was recrystallized three times from *n*-hexane to give 0.8 g (54%) of **5** as white needles, mp 123–124.5°.

Anal. Calcd for $C_{18}H_{28}O_3$: C, 73.9; H, 9.59; mol wt, 292. Found: C, 73.7; H, 9.50; mol wt (camphor), 280.

Preparation of 4-Allyl-2,5-di-*t*-butyl-6-methylphenyl Acetate (4). a. From 2. To a solution of 2.0 g of **2** in 5 ml of acetic anhydride was added three drops of concentrated sulfuric acid. The solution immediately turned black. After 30 min, 20 ml of water was added, and the mixture was stirred for 10 min. The mixture was then extracted with methylene chloride. The methylene chloride layer was washed with dilute sodium bicarbonate solution and dried over magnesium sulfate. Evaporation of the solvent left 1.85 g of dark green oil, which was chromatographed on alumina to give 1.10 g of **4** (48%) as a yellow oil, $n^{25}\text{D}$ 1.5111.

Anal. Calcd for $C_{20}H_{30}O_2$: C, 79.5; H, 9.94. Found: C, 80.3; H, 10.3.

b. From 3. To a solution of 1.0 g of **3** in 5 ml of acetic anhydride was added 0.2 ml of concentrated H_2SO_4. After 3 hr, the reaction was worked up as in part a to give 1.0 g of dark brown oil. Chromatography on alumina gave 0.70 g (60%) of **4** as a pale oil, identical in infrared and nmr spectra with the product from part a.

Preparation of 4-Allyl-3,6-di-*t*-butyl-2-methylcyclohexa-2,5-dienone (6). 6-Allyl-2,5-di-*t*-butyl-6-methylcyclohexa-2,4-dienone (**2**)[1] (1.70 g) was heated in an oil bath at 100–105° until the infrared spectrum of the product indicated that very little **2** remained unreacted (*ca.* 6–7 min). The product was cooled to room temperature, chromatographed on Florisil, and eluted with petroleum ether (bp 30–60°). Fractions 6–7 (150 ml each) of the eluent contained 0.90 g of **6**, $n^{25}\text{D}$ 1.5050, λ_{max} (in methanol) 244 mμ (ε 13,470).

Anal. Calcd for $C_{18}H_{28}O$: C, 83.1; H, 10.8. Found: C, 82.6; H, 10.7.

Preparation of 3,5-Di-*t*-butyl-2-methyl-4-*n*-propylcyclohexa-2,5-dienone (7). To a solution of **7** (0.20 g) in 15 ml of benzene was added 0.1 g of palladium on barium sulfate. The mixture was shaken in a hydrogen atmosphere until absorption of hydrogen stopped. The mixture was then filtered and the solvent evaporated to give 0.30 g of a colorless oil which appeared to be pure **7**. Chromatography on Florisil gave 0.15 g of recovered **7**, $n^{25}\text{D}$ 1.4977, λ_{max} (in methanol) 243 mμ (ε 13,410). The infrared and nmr spectra of **7** were not changed by chromatography.

Anal. Calcd for $C_{18}H_{30}O$: C, 82.4; H, 11.45. Found: C, 82.5; H, 11.7.

Preparation of 2,6-Di-*t*-butyl-4-methyl-4-(2,3-dibromopropyl)cyclohexa-2,5-dienone (13). A solution of bromine (4.58 g) in 20 ml of methylene chloride was slowly added to a solution of **1** (7.00 g) in 25 ml of methylene chloride. At the end of the reaction the solvent was evaporated to give 11.6 g of yellow oil, which crystallized on standing overnight at room temperature. Recrystallization from *n*-hexane gave 8.0 g (69%) of **13** as white crystals, mp 85–86°.

Anal. Calcd for $C_{18}H_{28}Br_2O$: C, 51.4; H, 6.67; Br, 38.1. Found: C, 51.8; H, 6.82; Br, 38.1.

Photorearrangement of 13. A solution of 5.0 g of **13** in 35 ml of *n*-hexane was irradiated until the 244-mμ peak in the ultraviolet spectrum of the solution had almost disappeared (*ca.* 1.5 hr). The spectrum of the solution (in methanol) showed a strong band at 320 mμ, and a shoulder at 290 mμ. The solvent was evaporated under vacuum on a rotary evaporator in a water bath at 35°. The ultraviolet spectrum of the product showed a somewhat decreased intensity peak at 320 mμ and a peak at 280 mμ. The infrared spectrum showed peaks at 6.1 and 6.35 μ. The product was heated for 2 min on a steam bath. Gas was evolved almost immediately, and its evolution continued for about 1.5 min. The

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[16] Compare M. Heller, R. H. Lenhard, and S. Bernstein, *J. Am. Chem. Soc.*, **86**, 2310 (1964).

[17] Microanalyses by Galbraith Microanalytical Laboratories, Knoxville, Tenn. Nmr spectra were taken on a Varian A-60 and ultraviolet spectra on a Cary Model 11 spectrometer. Melting points are corrected. Boiling points are not corrected.

spectra of the residue showed a strong band at 280 mμ, but no peaks at 320 mμ, 6.1 μ, or 6.35 μ. The residue was chromatographed on activity I neutral alumina and eluted with petroleum ether (bp 30–60°). The first fraction contained 3.0 g (77%) of 2-bromomethyl-4,7-di-*t*-butyl-2,3-dihydrobenzofuran as a white solid, mp 66–67°. Recrystallization from methanol did not change the melting point.

Anal. Calcd for $C_{17}H_{25}BrO$: C, 62.9; H, 7.70; Br, 24.6. Found: C, 62.8; H, 7.63; Br, 24.9.

Formation of 12 by Bromination and Cyclization of 2. A solution of 5.5 g of **1** was photoirradiated as usual to give a mixture consisting largely of **2**.[1] The product was dissolved in 25 ml of methylene chloride and cooled in ice, while a solution of bromine (3.4 g) in 10 ml of methylene chloride was slowly added. Absorption of bromine appeared to be almost instantaneous. Some white fumes, suggesting the formation of hydrogen bromide, appeared above the solution. After 10 min, the methylene chloride was evaporated under vacuum on a rotary evaporator in a water bath at 30°. When most of the solvent had evaporated, the water bath was replaced by a bath at 50–60°. Immediate vigorous bubbling occurred, continuing for about 1 min after all traces of solvent appeared to have evaporated. The residue weighed 7.9 g, and showed no hydroxyl or conjugated carbonyl peaks in its infrared spectrum. It was chromatographed on 100 g of activity I neutral alumina and eluted with petroleum ether (bp 30–60°) which was collected in 200-ml fractions. Fractions 2–4 contained 3.3 g (47%) of an oil which crystallized after scratching and standing for 3 days, to give a white solid, mp 54–58°. Recrystallization from methanol raised the melting point to 64–66°. A mixture melting point with **12** was 65–67°. Its infrared spectrum was identical with that of **12**.

Preparation of Allyl 2,5-Di-*t*-butylphenyl Ether. To a solution of 2,5-di-*t*-butylphenol[18] (48.0 g) in 500 ml of dimethyl sulfoxide was added 26.5 g of solid potassium *t*-butoxide. The mixture was shaken for 5 min until the solid had dissolved, and then allyl bromide (28.5 g) was added. After 2 min the solution was neutral. Water (1 l.) was added and the mixture extracted with methylene chloride. The methylene chloride layer was washed with water, dried, filtered, and evaporated to give 54.0 g of a yellow fluid, which was distilled at 5-mm pressure. Allyl 2,5-di-*t*-butylphenyl ether (42.3 g, 73%) was obtained, bp 152–154°, $n^{25}D$ 1.5023.

Anal. Calcd for $C_{17}H_{26}O$: C, 82.9; H, 10.6.. Found: C, 82.8; H, 10.9.

Preparation of 2-Allyl-3,6-di-*t*-butylphenol. Allyl 2,5-di-*t*-butylphenyl ether was heated at 238° for 4 hr. Vpc analysis on a 2-ft, 20% silicone oil (DC 550) column to 200° showed the reaction to be *ca.* 90% complete. In addition to a principal peak with a retention time of 6.4 min, two smaller product peaks with retention times of 4.7 and 5.1 min appeared. The mixture was distilled at 0.1-mm pressure through a 6-in. column packed with stainless steel gauze. 2-Allyl-3,6-di-*t*-butylphenol (6.2 g), $n^{25}D$ 1.5157, was obtained at a boiling range of 108–110°. An additional 8.3 g of less pure product was obtained with a boiling range of 100–108°.

Anal. Calcd for $C_{17}H_{26}O$: C, 82.9; H, 10.6. Found: C, 82.8; H, 10.7.

Formation of 12 by Bromination of 2-Allyl-3,6-di-*t*-butylphenol. To a solution of 2-allyl-3,6-di-*t*-butylphenol (3.0 g) in 15 ml of glacial acetic acid was added a solution of bromine (1.95 g) in 10 ml of acetic acid. After 5 min the solution was diluted with water and extracted with methylene chloride. The methylene chloride layer was washed with sodium bicarbonate solution, dried, filtered, and evaporated to give 3.90 g of yellow oil, which crystallized on seeding with **12**. Recrystallization from *n*-hexane gave 2.93 g of **12** (74%), mp 66–67°.

Acknowledgments. I wish to thank Mr. Richard Wayne and Dr. John Lancaster for assistance with interpretation of the nmr spectra.

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

Photorearrangements of Enolizable Cyclohexadienones[1,2]

Bernard Miller

Contribution from the Chemical Research and Development Laboratories,
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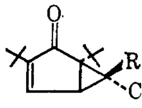
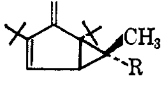
Abstract: Irradiation of **1a** or **2a** with 2537-A light gives **5a**, in addition to the previously reported **3a**. Similarly, irradiation of **1b** or **2b** gives **5b** as well as **3b**. It is proposed that formation of **5** proceeds by a mechanism involving photorearrangement of an intermediate enolizable cyclohexadienone, **7**. This mechanism is supported by the observation that irradiation of dienone **8** gives **6a**. There is no evidence that either **7** or **8** undergoes any tautomerism to phenols during photoirradiation. Irradiation of **11** gives **12**, showing that the butenyl group migrates without allylic inversion.

In an earlier paper it was reported that irradiation of the bicyclo[3.1.0]hex-3-en-2-ones **1** or **2** with ultraviolet light through a Pyrex filter gave the linearly conjugated cyclohexadienones **3a** and **3b**[3] as the principal products.[4]

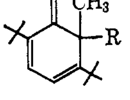


1a, R = allyl
b, R = *n*-propyl



2a, R = allyl
b, R = *n*-propyl

Irradiation of **1** or **2** by a low-pressure mercury lamp (emitting almost pure 2537-A light) gave, in addition to **3**, appreciable yields of a second product from each reaction. This paper reports the structures of those



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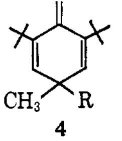

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products and evidence regarding the mechanism by which they are formed.

Photoirradiation Products of 1 and 2. Solutions of **1** and **2** in *n*-hexane were irradiated with 2537-A light, and the course of the reactions was followed by vpc analysis. Irradiation of **1a** and **2a** gave identical mixtures con-

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[1] Reactions of Cyclohexadienones. XIX.

[2] Part XVIII: B. Miller, *J. Am. Chem. Soc.*, **89**, 1685 (1967) (preceding paper).

[3] In all compounds of the **a** series, R is $CH_2CH{=}CH_2$ and in all compounds of the **b** series, R is $CH_2CH_2CH_3$. When the series is not specified, reactions are the same for both series.

[4] Part XVII: B. Miller, *J. Am. Chem. Soc.*, **89**, 1678 (1967).