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.

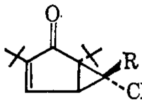
Photorearrangements of Enolizable Cyclohexadienones[1,2]

Bernard Miller

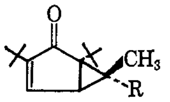
Contribution from the Chemical Research and Development Laboratories,
Agricultural Division, American Cyanamid Company,
Princeton, New Jersey 08540. *Received September 21, 1966*

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.

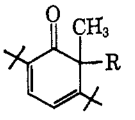
In an earlier paper it was reported that irradiation of the bicyclo[3.1.0]hex-3-en-2-ones **1** or **2** with ultraviolet light through a Pyrex filter gave the linearly conjugated cyclohexadienones **3a** and **3b**[3] as the principal products.[4] Irradiation of **1** or **2** by a low-pressure mercury 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 products and evidence regarding the mechanism by which they are formed.



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



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



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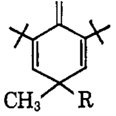

4

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).

Table I. Nmr Spectra of Bicyclo[3.1.0]hex-3-en-2-ones in Benzene

	τ values for chemical shifts of protons (J, cps)[a]					
Compd	t-Butyl	Methyl[b]	Vinyl proton[b]	Cyclopropyl	$CH_2CH{=}C{<}$	H $>C{=}CCH_3$
5a	s, 8.81 s, 8.86	s, 8.54	s, 3.06	q, 8.33 (8.3)	m, 7.96 (J_{AX} = 6.0, J_{AB} = 8.3)	...
5b	s, 8.83 s, 8.86	s, 8.59	s, 3.08	c	...	...
6a	s, 8.82 s, 8.94	s, 8.62	s, 3.00	q, 8.33 (6.9)	m, 7.95 (J_{AX} = 6.0, J_{AB} = 6.9)	...
12	s, 8.81 s, 8.86	s, 8.60	s, 3.19	c	m, *ca.* 7.85– 8.05	d, 8.40 (4.5)

[a] Abbreviations used are: s, singlet; d, doublet; m, multiplet. [b] Methyl and vinyl protons on ring. [c] Cyclopropyl absorption obscured by methylene and methyl absorptions.

sisting, initially, of two products in the ratio 1.25:1. Similarly the initial products from irradiation of **1b** and **2b** consisted, in each case, of a mixtue of two compounds (the same from each isomer) in the ratio 1.2:1. The molar ratio of the two compounds from each reaction changed as the irradiations proceeded, since the minor product from each reaction, but not the major product, was rapidly decomposed by photoirradiation. Therefore, although each "minor" product initially comprised nearly half of the products of rearrangement, none of these products could be isolated in yields greater than 15–20%. Since the bicyclo[3.1.0]hexenones **1** and **2** had themselves been prepared only in small quantities,[4] obtaining significant quantities of their photorearrangement products might have been a serious problem. Since the stereoisomers **1** and **2** in each series gave the same products, however, it was not necessary to perform the tedious task of separating **1** and **2**. Instead, solutions of the cross-conjugated cyclohexadienones **4a** and **4b**, from which **1** and **2** were prepared,[4] were irradiated until vpc analysis showed that the concentrations of the desired photoproducts of **1** and **2** had reached a maximum. The products were then isolated by chromatography on alumina.

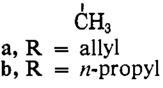
The major product from each photorearrangement was found to be the linearly conjugated cyclohexadienone **3**, identical with the products obtained from irradiation of **1** and **2** through Pyrex filters.[4]

The minor products (**5a** and **5b**) obtained from irradiation of **1** and **2** were shown by their mass spectra and elemental analyses to be isomeric with the starting compounds. Their spectra were quite similar, although the nmr and infrared spectra of **5b** lacked the peaks for terminal vinyl groups which were present in the spectra of **5a**. Hydrogenation of **5a** converted it to **5b**. Thus, **5a** and **5b** differ from one another only in the presence of an allyl group in **5a** in place of the propyl group of **5b**.

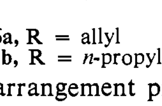
The ultraviolet spectra of **5a** and **5b** in methanol have λ_{max} 232 mμ (log ε 3.76), 272 mμ (log ε 3.45), and 330 mμ (shoulder, log ε 2.45). Their infrared spectra have carbonyl peaks at 5.91–5.92 μ. These spectra are characteristic of bicyclo[3.1.0]hex-3-en-2-ones.[4–6] The nmr spectra of **5a** and **5b** (see Table I) show the presence of two t-butyl groups in each compound. Each spectrum shows an isolated methyl group absorption at a position typical of methyls on the cyclopropane rings of bicyclo[3.1.0]hex-3-en-2-ones.[4,6] Each spectrum shows the presence of a single vinyl proton β to the carbonyl group of the α,β-unsaturated ketone.[2,4,5] Unlike the spectra of bicyclohexenones **1** and **2**, however, all of which show the vinyl protons as doublets split by the cyclopropyl protons,[4] the spectra of **5a** and **5b** show the vinyl protons as sharp singlets. The adjacent cyclopropyl position (C-5) must therefore be occupied by a group other than a proton. The cyclopropyl proton in **5a** appears about 0.4 ppm upfield from the positions of the cyclopropyl protons in **1** and **2**, thus confirming that the proton is no longer in an allylic position.

The most significant feature of the cyclopropyl absorption in **5a**, however, is that it appears as part of an AB_2 multiplet together with the methylene protons of the allyl group. (The multiplet could be analyzed in benzene or deuteriobenzene solution, but was not sufficiently resolved for analysis in carbon tetrachloride or deuteriochloroform solutions.) The cyclopropyl proton and the allyl group, in **5a**, therefore, must be on the same carbon atom, which can only be C-6. The geometry at C-6 can be deduced from the unusually high-field absorption (τ 7.96) of the allylic methylene group. This absorption appears at approximately the same position as that of the allylic methylene group of **1a**, but is about 0.4 ppm higher field than the allylic methylene absorption of **2a**.[4] The allyl group in **5a**, therefore, must be in the shielded "*endo*" position over the π electron cloud of the cyclopentenone ring.[4,5]

The spectroscopic evidence allows just two possible structures to be written for **5a**. These are the structures below labeled (presciently) **5a** and **6a**. Since the products in the **a** and **b** series differ only in the presence of a double bond, the photorearrangement product of **1b** and **2b** must have structure **5b** or **6b**.



5a, R = allyl
b, R = n-propyl



6a, R = allyl
b, R = n-propyl

Structure **6a** was independently synthesized (see below) and shown not to be identical with the product of photorearrangement of **1a**. Furthermore, the results of further photorearrangement of **5b** are consistent

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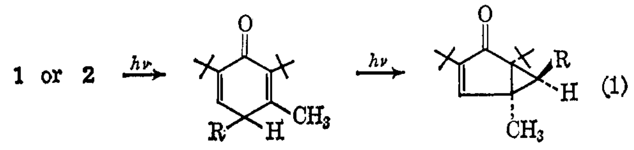
(5) T. Matsuura, *Bull. Chem. Soc. Japan*, 37, 564 (1964).

(6) J. Frei, C. Ganter, D. Kägi, K. Kocsis, M. Miljković, A. Siewinski, R. Wenger, K. Schaffner, and O. Jeger, *Helv. Chim. Acta*, 49, 1049 (1966).

with that structure, but not with structure **6b**.[7] The photorearrangement products of **1** and **2** must therefore have structures **5a** and **5b**.

A strong case for these structures could have been made on purely mechanistic grounds. Structure **6** could be formed from **1** or **2** only by a most circuitous and improbable series of rearrangements. On the other hand, formation of **5** can be accomplished in just two steps, as is shown in eq 1.

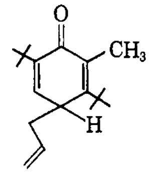


7 **5**

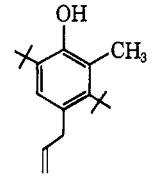
Both steps in eq 1 have ample analogy. Similar over-all sequences leading from one bicyclo[3.1.0]-hex-3-en-2-one to another have been reported by Jeger and his school[6] and by Kropp.[8]

Reaction 1 does differ from those sequences, however, since the intermediate dienone **7** has a proton at C-4, and can thus tautomerize to a phenol. Such enolizable dienones are presumably formed in many photorearrangements[9] but have never been observed to undergo rearrangements to bicyclohexenones. Instead, the tautomeric phenol is isolated.[9] The presence of two *t*-butyl groups flanking the carbonyl group in **7**, however, as well as the nonpolar solvent, might slow down the rate of tautomerization of **7** sufficiently to allow photorearrangement to **5**.

Photorearrangement of 8. To test the hypothesis that enolizable cyclohexa-2,5-dienones such as **7** can rearrange to bicyclohexenones faster than they tautomerize to phenols, a solution of the stable dienone **8**[2] in *n*-hexane was irradiated with 2537-A light. The course of the reaction was followed by vpc analysis. It was found that a single photorearrangement product was produced after short periods of irradiation. Continued irradiation gave rise to additional products, which were shown to arise from further photorearrangement of the initial product. If irradiation was continued until no further change in the intensity of the vpc peak for **8** occurred, it was found that the area of the residual peak was only $1-2\%$ of the original peak area. Since **8** tautomerizes immediately to phenol **9** on the vpc column,[2] any **9** formed during photorearrangement would appear in the vpc peak attributed to **8**. Thus, less than $1-2\%$ of **8** can have tautomerized to **9** during the photoirradiation. (Phenol **9** is, of course, unchanged by photoirradiation under these conditions.) Even this small amount of phenol need not have arisen from photocatalyzed tautomerism of **8**, since the presence of $1-2\%$ of **9** in the original sample of **8** would probably not have been detected.



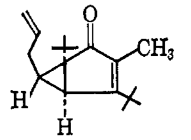
8



9

The elemental analysis and mass spectra of the photorearrangement product of **8** show that it is an isomer of **8**. Its ultraviolet spectrum in methanol had λ_{max} 236 mμ (log ε 3.79), 272 mμ (log ε 3.57), and 331 mμ (log ε 2.44) and its infrared spectrum had a carbonyl absorption at 5.90 μ, in agreement with the assumption that it is a bicyclo[3.1.0]hex-3-en-2-one.[4,6]

Of the four possible "lumi" products from photorearrangement of **8**, the two stereoisomers of **10** are excluded by the nmr spectrum of the product, which shows the presence of a vinyl proton on the ring and a methyl group which is not on the double bond of an α,β-unsaturated ketone. The nmr spectrum is completely consistent with that expected of structure **6a**.



10

In particular, the position of the allylic methylene absorption at τ 7.95 again shows that the allyl group is in the "*endo*" position over the cyclopentenone ring.[4,5]

Formation of **6a** by photorearrangement of **8** not only shows that enolizable cyclohexadienones can form bicyclohexenones on photoirradiation much more rapidly than they tautomerize to phenols, thus supporting the proposed mechanism for formation of **5**, but, by eliminating the only alternative structure, demonstrates that **5a** must be the structure of the product obtained by photoirradiation of **1** and **2**.

Migration of a *trans*-2-Butenyl Group during Photorearrangement. Migration of the allyl group during rearrangement of **1a** or **2a** to **7** might proceed by a mechanism in which the same carbon of the allyl group is joined to the ring in **7** as in **1a** or **2a** (diagram A) or by a cyclic mechanism in which C-3 of the allyl chain becomes linked to the ring in the product (diagram B). Rather limited evidence suggests that mechanism A is followed in the dienone–phenol rearrangement.[10]

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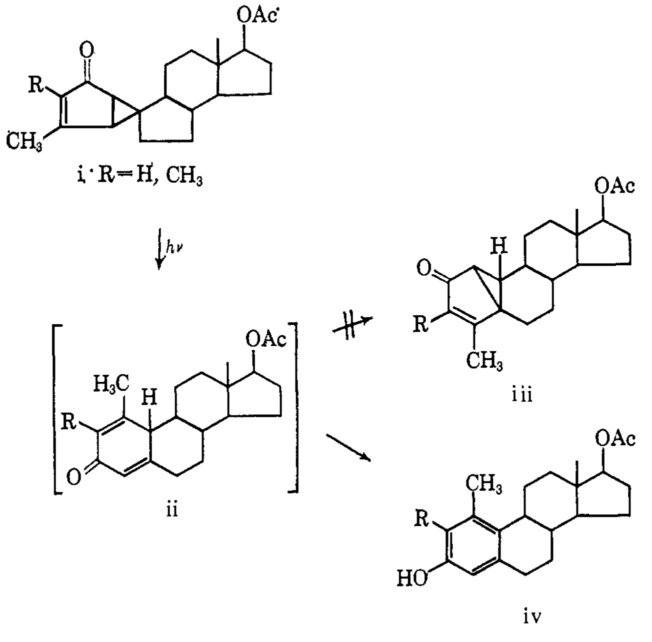
(7) B. Miller, to be published.

(8) P. J. Kropp, *J. Am. Chem. Soc.*, **86**, 4053 (1964).

(9) For instance, the careful product studies by Jeger and his coworkers[6] have given no indication that photorearrangement of i gives any iii, although phenol iv, which undoubtedly arises by enolization of the intemerdiate dienone ii, is a major product of the reaction.

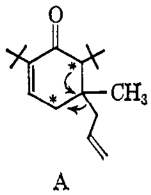


i: R = H, CH₃

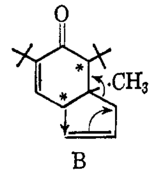
ii

iii

iv

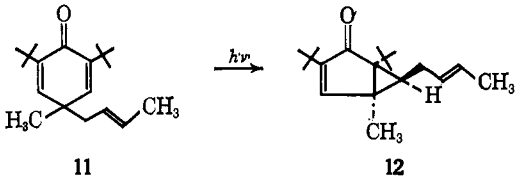


A

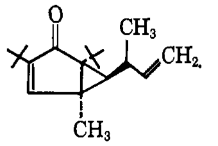


B

Nothing is known about the nature of allyl group migrations during photorearrangements. To gain some information about this point, dienone **11** was photoirradiated as usual and the reaction followed by vpc analysis. The initial products of the reaction were two compounds with very similar retention times, which were assumed to be the expected "lumi" ketones **1** and **2** ($R = CH_2CH{=}CHCH_3$). These ketones were not isolated. Instead, irradiation was continued until the concentration of a secondary product, which, from its retention time, was believed to have a structure analogous to **5**, reached a maximum. The desired product was then isolated. Its spectra (see Table I and Experimental Section) indicated that the structure of the product was indeed analogous to that of **5**. In addition, the nmr spectrum clearly showed that the *trans*-2-butenyl group of **11** remained unchanged during the reaction. Thus, the structure of the product was **12**, and it was formed by mechanism A rather than B. No evidence for formation of isomer **13** was found, but the possibility that some **13** was present in the reaction mixture cannot be eliminated.



11 12



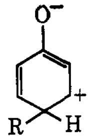
13

Discussion

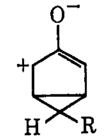
Several cyclohexa-2,5-dienones which can tautomerize to monocyclic phenols have recently been prepared.[4,11] The list of chemical reactions of these compounds is quite limited, however. The allyl group in **8** can be hydrogenated to a propyl group without affecting the cyclohexadienone ring.[2] All other nonphotochemical reactions lead to immediate aromatization of the dienones. Reaction with acids[2,11] or bases,[2] chromatography on most absorbents,[2] or simple heating[2,11] convert enolizable cyclohexadienones to their phenolic tautomers. Reaction with triethyl phosphite converts 2,6-di-*t*-butyl-4-bromocyclohexa-2,5-dienone to derivatives of the *debrominated* phenol.[12]

In contrast to the almost invariable aromatization caused by "ground-state" reactions, the selectivity with which photochemical processes avoid aromatization of enolizable cyclohexadienones is striking. It was pointed out above that no more than 1–2% of **8** could have been tautomerized to **9** during photoirradiation. The same selectivity is apparently found in the photorearrangement of **7**, since vpc analysis of the products of photorearrangement of **1** and **2** showed them to consist entirely of **3**, **5**, and the further photorearrangement products of **5**. No more than traces of the phenolic tautomers of **7a** and**7b** could have been formed during the reaction.

The absence of any aromatization during photorearrangement of **7** and **8** is particularly striking because the wavelength employed should cause a π–π^* transition in the unsaturated carbonyl group,[13] which might be expected to result in an enhanced positive charge at C-3 and C-5 (as in structure **14**).[14] The presence of a positive charge on the adjacent carbons should greatly increase the ease with which a proton is lost from C-4. Since loss of a proton from C-4 does not occur during photorearrangement of **7** and **8**, it seems probable that structures such as **14**, if they exist at all, have only short lifetimes. Either bond reorganization to structure **15** or transition of **14** to another electronic state presumably occurs more rapidly than loss of a proton.



14



15

A surprising aspect of the photorearrangements of **1** and **2** is that the initial ratio of **3** to **5** is almost the same in the **a** series as in the **b** series. Since formation of **3** does not involve participation of the allyl or propyl groups at C-6,[4] the rate of rearrangement of **3** should be about the same for the **a** and **b** series. On the other hand, formation of **5** requires migration of one of the groups at C-6. Migration of an allyl group would be expected to be much faster than that of an *n*-propyl group.[10] (The apparent absence of any products resulting from methyl migration supports the view that the normal order of migratory aptitudes is followed in the reactions of **1** and **2**.) The amount of **5** formed should be higher in the **a** series than in the **b** series if migration were part of the rate-determining process for its formation.

We may conclude, therefore, that migration of the allyl or propyl groups must follow the rate-determining step leading to **5**. Since the only step preceding migration of the allyl or propyl group is opening of the three-membered ring in **1** and **2**, it appears that opening this ring is a slow, *essentially irreversible* process, which is not simultaneous with migration of a group from C-6.

Experimental Section[15]

Photoirradiation. All photoirradiations were carried out in a Hanovia tubular shaped irradiation cell made of quartz, as pre-

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[10] B. Miller and H. Margulies, *J. Am. Chem. Soc.*, 87, 5106 (1965); B. Miller, *ibid.*, 87, 5111 (1965); B. Miller, *ibid.*, 87, 5115 (1965).

[11] A. A. Volod'kin and V. V. Ershov, *Bull. Acad. Sci. USSR, Div. Chem. Sci.*, 1931 (1962).

[12] B. Miller, *J. Org. Chem.*, 30, 1964 (1965).

[13] J. W. Sidman, *Chem. Rev.*, 58, 689 (1958).

[14] G. W. Wheland, "Resonance in Organic Chemistry," John Wiley and Sons, Inc., New York, N. Y., 1955, Chapter 6.

[15] Microanalyses by Galbraith Microanalytical Laboratories, Knoxville, Tenn.

viously described.[4] The lamp employed was a 25-w, low-pressure mercury lamp obtained from the Southern New England Ultraviolet Co., Middletown, Conn.

Vpc Analyses. Vpc analyses were carried out as described below using F & M Model 720 or 500 vapor phase chromatography units. Three columns were employed: A, a 6-ft, 10% Carbowax 20M Chromosorb Z column; B, a 6-ft, 1% Carbowax 20M on Gas Chrom P column; and C, a 6-ft, 2% XE60 on Gas Chrom Z column.

Preparation of 1,3-Di-*t*-butyl-6-*endo*-allyl-5-methylbicyclo[3.1.0]hex-3-en-2-one (5a). A solution of 7.0 g of 2,6-di-*t*-butyl-4-allyl-4-methylcyclohexa-2,5-dienone (**4a**) in 35 ml of *n*-hexane was irradiated. The reaction was followed by vpc at 145° on column A. The initial peak at a retention time of 3.5 min shrank as peaks at 9.0 and 9.8 min (**1a** and **2a**) grew. After 3 hr, the peak for **4a** was approximately one-half its original intensity, and a small peak (**5a**) had appeared at 4.5 min. After 8 hr **4a** had all reacted. The intensities of the peaks for **1a**, **2a**, and **5a** were in the ratio *ca.* 5:3.5:2. The height of the peak for **5a** reached a maximum at 26 hr (when it was about 1.5 times the height of the peak for **1a**), after which all three peaks began to decrease in height. Irradiation was stopped after 29 hr and the solvent evaporated. The residue had peaks in the infrared at 5.9, 6.1, and 6.3 μ, and an absorption maximum in methanol (ε 1100) at 321 mμ in the ultraviolet. It was chromatographed on 2 kg of Woelm neutral alumina and eluted with petroleum ether (bp 30–60°). Fractions containing 250 ml of eluent were collected. Fraction 1 contained 0.1 g of material which had no carbonyl absorption in the infrared, and was discarded. Fraction 5 contained 0.6 g of pure **5a**, $n^{25}\text{D}$ 1.4851.

Anal. Calcd for $C_{18}H_{28}O$: C, 83.1; H, 10.8. Found: C, 83.4; H, 11.1.

Fractions 6 and 7 contained an additional 0.5 g of **5a**, contaminated with 10% of **1a**. Fraction 9 contained 0.5 g of **1a** containing *ca.* 5% of **2a**. Fractions 10–15 (total 0.9 g) contained mixtures of **1a** and **2a**, and fractions 16 and 17 contained 0.4 g of pure **2a**. Elution was not continued further.

Preparation of 1,3-Di-*t*-butyl-5-methyl-6-*endo*-*n*-propylbicyclo[3.1.0]hex-3-en-2-one (5b). A solution of 6.5 g of 2,6-di-*t*-butyl-4-methyl-4-*n*-propylcyclohexa-2,5-dienone[4] in 35 ml of *n*-hexane was irradiated. The reaction was followed by vpc analysis on column A at 155°. The initial peak appeared at a retention time of 3.0 min. Peaks for **1b** and **2b** appeared after a few minutes' irradiation at retention times of 6.1 and 7.0 min. After irradiation for 1.5 hr, small peaks could be seen at 3.9 (shoulder) and 12.1 min (**3b**). The height of the peak at 3.9 min reached a maximum at 27.5 hr, after which it began to decline. The irradiation was stopped after 32 hr, and the solvent evaporated. The product had infrared peaks at 5.9, 6.1, and 6.35 μ. Its ultraviolet spectrum (in methanol had λ_{max} 319 mμ (ε 1215). The product was chromatographed on 2.5 kg of Woelm neutral alumina, eluting with petroleum ether (bp 30–60°). Fractions containing 250 ml of eluent were collected. Fractions 8 and 9 contained 0.70 g of **5b**, $n^{25}\text{D}$ 1.4764.

Anal. Calcd for $C_{18}H_{30}O$: C, 82.4; H, 11.45. Found: C, 82.8; H, 10.6.

Fractions 10 and 11 contained 0.3 g of **5b** containing small amounts of **1b**. Fractions 13–15 contained 0.6 g of pure **1b**, while fractions 16–21 contained 0.5 g of a mixture of **1b** and **2b**. Fractions 22 and 23 contained 0.2 g of pure **2b**. Elution was continued using methylene chloride. Fractions 24–28 contained 1.7 g consisting of impure **3b** (containing some **2b** and materials with higher retention times by vpc).

Photorearrangement of 1a. A solution of **1a** (0.25 g) in 35 ml of *n*-hexane was irradiated. After 5 min the irradiation was stopped, the solvent evaporated, and the mixture analyzed by temperature-programmed vpc on column B. The starting temperature was 125°, and the temperature rose 5.6° per minute. The chromatogram showed the major peak for **1a** at 143°, and two small peaks (each *ca.* 10% of total area) at 136 and 192° (**5a** and **3a**, respectively). Calibration of the chromatogram using mixtures with known concentrations of **5a** and **3a** showed the ratio of **5a** to **3a** to be 1:1.25. The reaction product was redissolved in *n*-hexane and irradiated for 10 min. The solvent was evaporated and the products were analyzed as above. Approximately 40% of **1a** was unreacted. The mole ratio of **5a** to **3a** was 1:1.4. Small traces of other materials appeared in the chromatogram. The mixture was again dissolved in *n*-hexane and irradiated for an additional 10 min, and the solvent removed. Vpc analysis showed the total amount of **5a** to have decreased slightly. Small samples of the materials appearing at 136 and 192° were collected by vpc on column B and identified by their infrared spectra as **5a** and 2,5-di-*t*-butyl-4-allyl-6-methylphenol.[2]

Photorearrangement of 2a. A solution of 0.15 g of **2a** in *n*-hexane was irradiated and analyzed, and the product isolated as described for **1a**. The initial products formed were shown to be **5a** and **3a**.

Photorearrangement of 1b. A solution of 0.5 g of **1b** in *n*-hexane was irradiated for 5 min. A 10-μl sample was injected on column C at 130°. In addition to a peak at a retention time of 5.3 min (**1b**) small peaks in the mole ratio of 1:1.2 appeared at retention times of 4.7 and 9.6 min. After irradiation for an additional 20 min, the solvent was evaporated under vacuum, and the products were isolated by vpc. The peak at 4.7 min was identified as **5b** and the peak at 9.6 min as **3b** by their infrared spectra.

Photorearrangement of 2b. A solution of 0.10 g of **2b** in *n*-hexane was irradiated and analyzed, and the products were isolated as described for **1b**. The initial products were shown to be **5b** and **3b**.

Hydrogenation of 5a. To a solution of 0.20 g of **5a** in 10 ml of benzene was added 0.1 g of platinum oxide. The mixture was shaken in a hydrogen atmosphere until absorption of hydrogen stopped. The mixture was then filtered and the solvent evaporated to give 0.20 g of **5b**, which was identified by its nmr and infrared spectra.

Photorearrangement of 4-Allyl-2,5-di-*t*-butyl-6-methylcyclohexa-2,5-dienone (8). Preparation of 6-*endo*-Allyl-3,5-di-*t*-butyl-1-methylbicyclo[3.1.0]hex-3-en-2-one (6a). A solution of 1.3 g of **8**[2] in *n*-hexane was irradiated for 1.5 hr. After evaporation of the solvent, the product was chromatographed on 200 g of Woelm neutral alumina. The product was eluted with petroleum ether (bp 30–60), and fractions containing 100 ml of eluent were collected. Fractions **7–10** contained 0.55 g of **6a**, $n^{25}\text{D}$ 1.4862.

Anal. Calcd for $C_{18}H_{28}O$: C, 83.1; H, 10.8. Found: C, 82.7; H, 10.8.

Photorearrangement of 2,6-Di-*t*-butyl-4-methyl-4-*trans*-2-butenylcyclohexa-2,5-dienone (11). A solution of 3.5 g of **11**[16] in 35 ml of *n*-hexane was irradiated and the reaction followed by temperature-programmed vpc, using column B. The starting temperature was 130°, and the temperature of the column was raised 5.6° per minute. The peak for **11** appeared at 137°. After irradiation for 0.5 hr, small peaks (area ratio *ca.* 4:3) appeared at column temperatures of 149 and 152°. After 5-hr irradiation, the sum of the areas for the two peaks at 149 and 152° roughly equalled the area of the 137° peak. Small new peaks had appeared at 141 and 200°. After irradiation for 27 hr, the intensity of the peak at 141° began to decrease. The hexane was evaporated and the residue chromatographed on 1 kg of neutral alumina, eluting with petroleum ether (bp 30–60°). Eluent fractions containing 250 ml were collected. Fractions **7–9** contained 0.4 g of 1,3-di-*t*-butyl-5-methyl-6-*endo*,*trans*-2-butenylbicyclo[3.1.0]hex-3-en-2-one (**12**), $n^{25}\text{D}$ 1.4832, λ_{max} (in methanol) 233 mμ (log ε 3.75), 273 mμ (log ε 3.46), and 332 mμ (shoulder, log ε 2.40).

Anal. Calcd for $C_{19}H_{30}O$: C, 83.25; H, 11.0. Found: C, 83.0; H, 11.2.

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