Photorearrangements of 2,6-Di-*t*-butylcyclohexa-2,5-dienones[1,2]

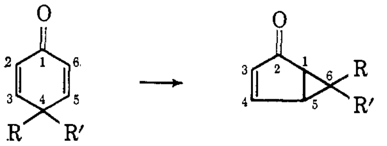
Bernard Miller and Howard Margulies

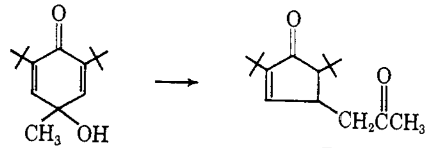
Contribution from the Chemical Research and Development Laboratories,
Agricultural Division, American Cyanamid Company,
Princeton, New Jersey 08540. *Received September 21, 1966*

Abstract: Irradiation of *n*-hexane or cyclohexane solutions of 2,6-di-*t*-butylcyclohexa-2,5-dienones through Pyrex filters gives high yields of 2,5-di-*t*-butylcyclohexa-2,4-dienones. It can be shown that 1,3-di-*t*-butylbicyclo[3.1.0]hex-3-en-2-ones are intermediates in the reaction, which requires an unusual opening of one of the "exocyclic" cyclopropane bonds of the bicyclohexenone. It is suggested that opening the "exocyclic" bond relieves steric strain in the bicyclohexenone more than would the usual opening of an "endocyclic" bond.

Recent studies of acid-catalyzed rearrangements of 2,6-di-*t*-butylcyclohexa-2,5-dienones have shown that marked changes from the normal course of dienone–phenol rearrangements are caused by the presence of the bulky *t*-butyl groups.[3] We were therefore encouraged to examine the effect of ultraviolet light on these dienones, in order to see whether steric effects similarly affect their photorearrangements.

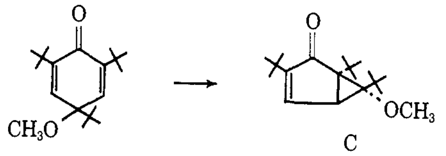
During the past decade it has been shown that the initial products of photorearrangement of cross-conjugated cyclohexadienones are bicyclo[3.1.0]hex-3-en-2-ones (the so-called "lumi" products).[4] Our initial expectation was that the quaternary carbon at C-4 would be inhibited from bonding to a carbon already bearing a *t*-butyl group, and that the reaction might thus be forced to take a different course when both carbons *ortho* to the carbonyl bore *t*-butyl groups. At the time this work was started, the only report of a photorearrangement of a 2,6-di-*t*-butylcyclohexa-2,5-dienone was the observation by Altwicker and Cook that irradiation of the hydroxy ketone A gave the cyclopentenone B.[5] Compound B might have been formed by cleavage of the cyclopropane ring of a bicyclo[3.1.0]hexenone, but might also have been formed directly from A by migration of the vinyl group. During the course of our work, Matsuura reported that photorearrangement of several 2,6-di-*t*-butylcyclohexa-2,5-dienones gave low (10–11%) yields of bicyclo[3.1.0]hexenones, including the unusually crowded compound C.[6] At the time Matsuura's work appeared, however, we had obtained quite different products from photorearrangements of 2,6-di-*t*-butylcyclohexa-2,5-dienones. Our products appear to arise by a process which rarely occurs during photorearrangements of cross-conjugated cyclohexadienones, and thus it does seem that these reactions are markedly affected by the presence of *t*-butyl groups.





A

B



C

Irradiation with Wavelengths above 2800 A. In order to avoid many of the complications possible in hydroxylic solvents[4] our initial reactions were carried out in *n*-hexane or cyclohexane solutions. No difference was observed between the two solvents. Solutions of 2,6-di-*t*-butyl-4-ethyl- (or -4-propyl-) 4-methylcyclohexa-2,5-dien-1-one (**1** or **2**) were irradiated by high-pressure mercury lamps through Pyrex or Corex filters until vpc analysis showed that little starting material remained. The products in each case consisted of 70–75% of a single material (by vpc) together with several minor products. Further irradiation did not result in significant changes in the products.

The principle products were isolated by chromatography on alumina,[7] and were found to be isomeric with the starting dienones. Their infrared spectra had strong carbonyl peaks at 6.07 μ and weaker double-bond peaks at 6.33 μ. Their ultraviolet spectra in methanol had λ_{max} 320–322 mμ (ϵ 3900–4080). These spectra are typical of linearly conjugated cyclohexadienones.[8]

Earlier studies have shown that cyclohexa-2,4-dienones with *t*-butyl groups on the quaternary carbon (C-6) immediately lose the *t*-butyl groups when they are chromatographed on alumina or silica gel, or during vapor phase chromatography.[9] In contrast, the photolysis products of **1** and **2** were isolated unchanged by vpc or column chromatography. The conclusion that these compounds do not bear *t*-butyl groups at C-6 is supported by their nmr spectra (see Table I) which

---

[1] Reactions of Cyclohexadienones. XVII. For part XVI see B. Miller, *Chem. Commun.*, 327 (1966).

[2] A preliminary report of this work has been published: B. Miller and H. Margulies, *ibid.*, 314 (1965).

[3] B. Miller and H. Margulies, *J. Am. Chem. Soc.*, **87**, 5106 (1965).

[4] (a) O. L. Chapman, *Advan. Photochem.* **1**, 323 (1963); (b) P. de Mayo and S. T. Reid, *Quart. Rev.* (London), **15**, 393 (1961).

[5] E. R. Altwicker and C. D. Cook, *J. Org. Chem.*, **29**, 3087 (1964).

[6] T. Matsuura, *Bull. Chem. Soc. Japan*, **37**, 564 (1964).

[7] The structures of the minor products will be considered in the following paper.

[8] *E.g.*, D. Y. Curtin and R. J. Crawford, *J. Am. Chem. Soc.*, **79**, 3156 (1957); H. Hart, P. M. Collins, and A. J. Waring, *ibid.*, **88**, 1005 (1966).

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

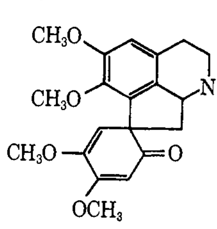
Table I. Nmr Spectra of Photorearrangement Products

Compd	Solvent	τ values for chemcial shifts of protons (J, cps)[a] t-Butyl	CH$_3$[b]	Vinyl[c]	Cyclopropyl	CH$_2$[b]
3a	CDCl$_3$	s, 8.69 s, 8.77	s, 8.61	d, 3.15 (7.1) d, 3.65 (7.1)	. . .	q, 8.05 (7.0)
4a	CDCl$_3$	s, 8.71 s, 8.80	s, 8.63	d, 3.20 (7.0) d, 3.71 (7.0)	. . .	t, 8.24 (9.0)
11	CCl$_4$	s, 8.68 s, 8.81	s, 8.62	d, 3.20 (7.5) d, 3.69 (7.5)	. . .	d, 7.36 (6.6)
12a	CDCl$_3$	s, 8.87[d]	s, 8.65	d, 2.95 (3.5)	d, 7.92 (3.5)	~8.0[e]
12b	CDCl$_3$	s, 8.84 s, 8.87	s, 8.60	d, 2.90 (3.5)	d, 7.94 (3.5)	[f]
13a	CDCl$_3$	s, 8.86[d]	s, 9.05	d, 3.02 (3.0)	d, 7.93 (3.0)	d, 7.53 (6.5)
13b	CDCl$_3$	s, 8.87	s, 9.08	d, 3.04 (3.2)	d, 7.92 (3.2)	[f]

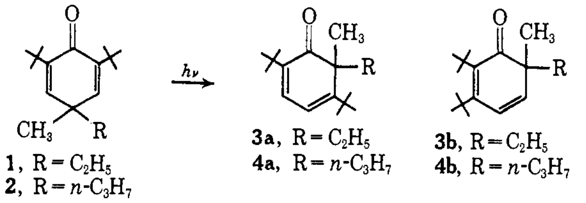
[a] Abbreviations used are: s, singlet; d, doublet,; t, triplet; q, quartet. [b] Methyl or methylene bonded to C-6 on ring. [c] Vinyl protons on ring. [d] Eighteen protons. [e] Splitting partially obscured by cyclopropyl proton. [f] Multiplet obscured by other absorptions.

show that the methyl and ethyl (or propyl) groups are on quaternary carbons, rather than on double bonds.

The photorearrangement products did not react with sodium borohydride, even in refluxing ethanol, although dienone D, for instance, is readily reduced by sodium borohydride.[10] This marked difference in reactivity suggests that attack at the carbonyl groups of the photorearrangement products is hindered by the presence of a t-butyl group at C-2. This suggestion is supported by the formation of cryptophenols from acid-catalyzed rearrangements of the photorearrangement products (see below).


D

The nmr spectra of the photoproducts each show the presence of two vinyl protons on adjacent carbon atoms. Combining this information with the information given above allows just two possible types of structures for the photorearrangement products. They must be either **3a** and **4a** or **3b** and **4b**.

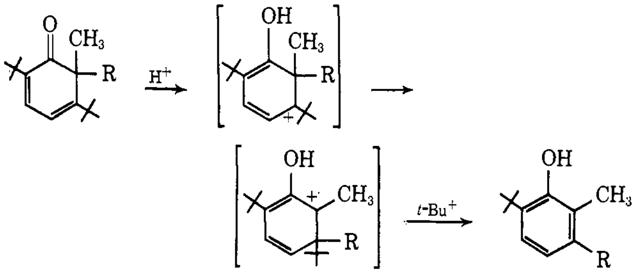


1, R = C$_2$H$_5$
2, R = n-C$_3$H$_7$
3a, R = C$_2$H$_5$
4a, R = n-C$_3$H$_7$
3b, R = C$_2$H$_5$
4b, R = n-C$_3$H$_7$

To distinguish between these possibilities, the product of photorearrangement of **1** was rearranged in a 10% solution of sulfuric acid in acetic acid. The product, a phenol (**5**) with the empirical formula $C_{13}H_{20}O$, had lost a t-butyl group during the rearrangement. The nmr spectrum of **5** (in CDCl$_3$) had a single peak (2 H) at τ 3.09 in the aromatic region. However, a solution of **5** in DMSO containing potassium t-butoxide had a pair of doublets (J = 7.5 cps) at τ 3.30 and 3.62, showing that the two aromatic protons remained on adjacent carbons.

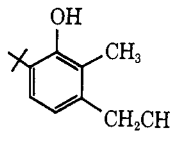
Although t-butyl groups are often easily removed by acid from *ortho* positions of phenols,[11] it was clear that a t-butyl group remained *ortho* to the hydroxyl group of **5**. Phenol **5** was insoluble in base, was readily eluted from alumina by methylene chloride, and had low retention times on polar vpc columns. The hydroxyl peak of **5** appeared at 2.76 μ in the infrared spectrum. (This may be compared with 2.78 μ for 2-t-butyl-6-methylphenol and 3.00 μ for o-cresol.) Finally, the position of the aromatic proton peak at τ 3.09 is appreciably lower than has been observed for protons *ortho* to phenolic hydroxyl groups.[3]

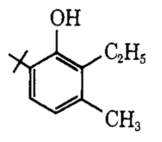
Elimination of a t-butyl group would be the expected result of acid-catalyzed rearrangement of **3a** and can readily be explained by the mechanism below.



No reasonable mechanism, however, could account for the loss of a t-butyl group from a position *meta* to the hydroxyl group of **3b**. The product of photorearrangement of **1**, therefore, must have structure **3a**.

The phenol obtained by rearrangement of **3a** could have either structure **5a** or **5b**, depending on whether the ethyl or the methyl group had migrated. Structure **5a** seems more probable, in view of the expected greater migratory aptitude of the ethyl group,[3] but sufficient information to make a definite choice between the two structures is not yet available.


5a


5b

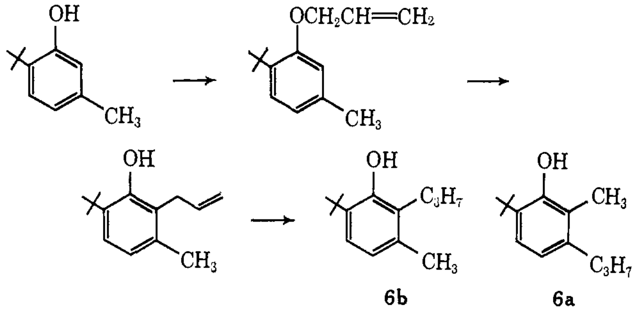
Rearrangement of **4a** in acid again resulted in loss of a t-butyl group to give a phenol whose physical properties were similar to those of **5**. Of the two possible

---

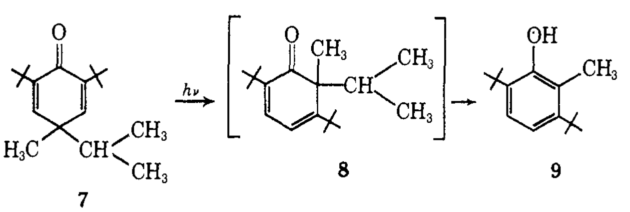
(10) A. H. Jackson and J. A. Martin, *Chem. Commun.*, 142 (1965); M. Shamma and W. A. Slusarchyk, *ibid.*, 528 (1965).

(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).

isomeric products, **6b** was synthesized by the route shown below, and was found not to be identical with the product from reaction of **4a** with acid. Rearrangement of **4a**, therefore, must result in migration of a propyl group to give **6a**. Migration of a propyl group, rather than methyl migration, is consistent with the results of other dienone–phenol rearrangements.[3]

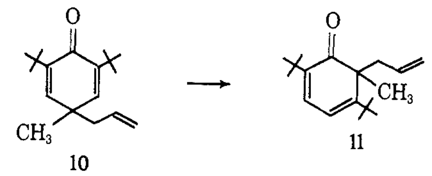


Photoirradiation of a hexane solution of 2,6-di-*t*-butyl-4-isopropyl-4-methylcyclohexa-2,5-dienone (**7**) through a Pyrex filter again gave a crude product with ultraviolet (λ_{max} 320 mμ) and infrared (λ_{max} 6.08 and 6.38 μ) spectra typical of linearly conjugated cyclohexadienones. Attempts to isolate the presumed product **8** by column chromatography on silica gel or activity III alumina, however, gave a phenol, $C_{15}H_{24}O$, mp 76–78°, resulting from loss of an isopropyl group. The infrared spectrum of the phenol showed a peak for a hindered hydroxyl group (2.77 μ), while its nmr spectrum in $CDCl_3$ showed the presence of two *t*-butyl groups (τ 8.63 and 8.67), a methyl group (τ 7.67), and two adjacent aromatic protons (τ 3.12 and 3.19, J = 8.7 cps) as well as a hydroxyl proton at τ 5.32. On the assumption that dienone **8** is the initial product of the photorearrangement, its decomposition product can be assigned structure **9**.



The loss of an isopropyl group from a carbon atom under such mild conditions appears to be unique, although *t*-butyl groups are often lost under similar conditions.[9] It may be noted that dienone **7** is readily isolated by chromatography using the same conditions in which dienone **8** loses an isopropyl group.[9] The ready decomposition of **8** can be attributed to the combined effects of steric interference between the adjacent isopropyl and *t*-butyl groups in **8** and of the normally low stability of linearly conjugated cyclohexadienones compared to cross-conjugated cyclohexadienones.[12]

It was anticipated that photorearrangement of the 4-allylcyclohexadienone **10** mignt involve participation of the double bond to give products of types different from those obtained from the saturated analogs of **10**. It was found, however, that the linearly conjugated dienone **11** was the principle product, since hydrogenation of the crude photorearrangement mixture, followed by column chromatography, gave **4a** in 68% yield. Compound **11** could be isolated in rather low yield by rapid chromatography on magnesium silicate ("Florisil"). Attempts to isolate **11** by vpc, or by chromatography on alumina or silica gel, however, led to further rearrangements. These reactions will be described in a later paper.



In an attempt to determine whether formation of the linearly conjugated dienones proceeded through ketene intermediates (see Discussion), dienone **1** was irradiated in methanol solution. The principle rearrangement product was again found to be dienone **3a**. A major by-product was phenol **5**, which was not obtained from reaction in hexane. It seemed probable that **5** was produced from **3a** by traces of acid in the methanol. To prevent this type of reaction, sodium methoxide was added to the solution before irradiation. This did, in fact, eliminate formation of **5**, but resulted in formation of several other minor products, which were not identified. Even in the presence of sodium methoxide, however, **3a** remained the principle reaction product.

Irradiation with 2537-A Light. Formation of the linearly conjugated dienones described above from cross-conjugated dienones appeared to result from linking C-3 and C-5 in the starting compounds. It seemed likely, therefore, that the first steps in the rearrangements were formation of bicyclo[3.1.0]hexenones, which could then rearrange further to give the products isolated. Vpc analysis of the reactions showed that small amounts of compounds which might be intermediates leading to the observed cyclohexa-2,4-dienones were formed, but not in sufficient quantities for isolation and identification.

Kropp[13] and Jeger[14] have observed that irradiation of cross-conjugated cyclohexadienones with light from low-pressure mercury lamps can give good yields of bicyclo[3.1.0]hexenones, while light from high-pressure lamps results in further rearrangements. The irradiation of 2,6-di-*t*-butylcyclohexa-2,5-dienones with essentially monochromatic 2537-A light was therefore investigated.

Irradiation of hexane or cyclohexane solutions of the 4-*n*-propylcyclohexadienone **2** or the 4-allyl dienone **10** gave, as the initial products in each case, a mixture of two compounds in the ratio *ca.* 1.3:1. Small amounts of each product could be isolated by vapor phase chromatography or by column chromatography on alumina.

The photorearrangement products from each reaction were isomeric with the starting dienones. Hydrogenation of the major product from rearrangement of **10** gave the major product from rearrangement of **2**, while hydrogenation of the minor product from rearrangement of **10** gave the minor product from rearrangement of **2**. The two sets of products, therefore, like the starting materials, differ only in the presence or absence of a double bond.

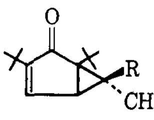
---

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

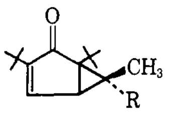
(13) P. J. Kropp, *Tetrahedron*, **21**, 2183 (1965).

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

The spectra of the two products obtained from each reaction are in excellent agreement with the assumption that they are the expected epimeric "lumi" products **12** and **13**. The infrared spectra of the products all



12a, R = allyl
12b, R = *n*-propyl



13a, R = allyl
13b, R = *n*-propyl

have carbonyl peaks at 5.90–5.92 μ, and their ultraviolet spectra (in methanol) have maxima at 232 mμ (log ϵ $\sim$3.8), 272 mμ (log ϵ $\sim$3.5), and 330 mμ (shoulders, log ϵ $\sim$2.5), as is expected of bicyclo[3.1.0]hex-3-en-2-ones.[4,6] The nmr spectra show the expected doublets in the τ-3.0 region for a vinyl proton β to the carbonyl, and cyclopropyl doublets with equal J values at *ca.* τ 7.9. The positions of the peaks for the methyl groups and the allylic methylene groups show that they are attached to quaternary carbon atoms, in agreement with structures **12** and **13**.

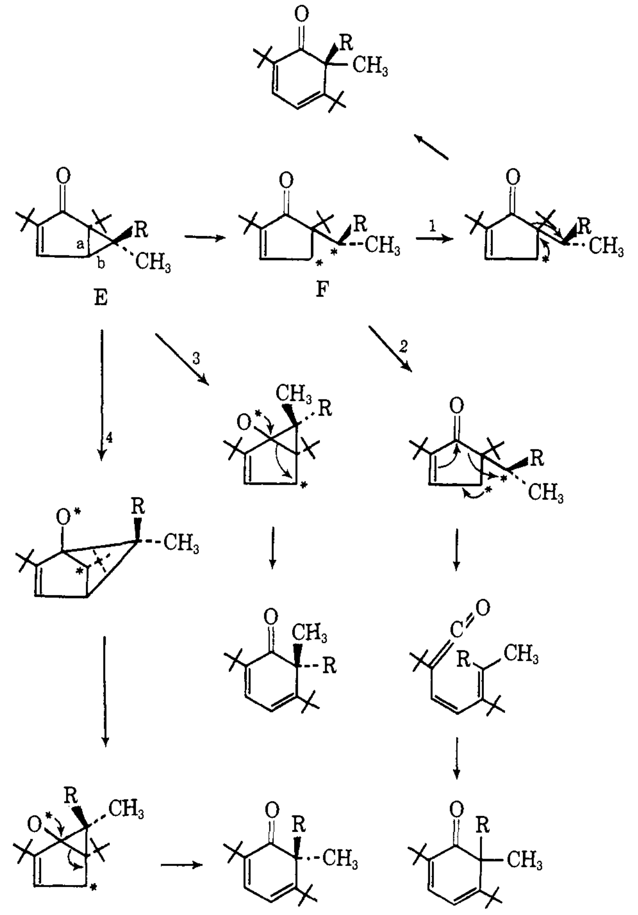
The configuration of each compound can be deduced from its nmr spectrum. The isolated methyl peaks of **13a** and **b** appear at unusually high fields, as does the allylic methylene doublet of **12a**. The shielding of these groups can be ascribed to their location over the π electrons of the cyclohexenone ring. The geometries of the four "lumi" compounds must, therefore, be as shown above.[15] The principle isomer obtained from each reaction is the more stable one, since in each case the *t*-butyl group at C-1 on the cyclopropyl ring is *trans* to the larger of the two groups at C-6.

Irradiation of Bicyclo[3.1.0]hex-3-en-2-ones. Irradiation of cyclohexane solutions of **12a** or **13a** through Pyrex filters gave product mixtures which appeared by their infrared and ultraviolet spectra and their vapor phase chromatograms to be essentially identical with those obtained by photolysis of **7**. Similarly, irradiation of **12b** or **13b** through Pyrex filters gave products identical with those obtained from irradiation of **2**. Perhaps surprisingly, no significant differences were noted between the two epimers in each pair. It thus appears that the rearrangements of 2,6-di-*t*-butylcyclohexa-2,5-dienones in nonpolar solvents proceed almost entirely, if not exclusively, by way of bicyclo[3.1.0]-hexenones as the first isolable products.

In an attempt to isolate other possible intermediates in the formation of linearly conjugated cyclohexadienones, each of the four "lumi" products was irradiated by 2537-A light. In these reactions, products other than the linearly conjugated cyclohexadienones were formed in large amounts. These reactions will be discussed in a later paper. Continued irradiation of the reaction products, however, gave no indication that any of the other products were converted to cyclohexa-2,4-dienones, which thus appear to be formed directly from **12** and **13**.

Discussion

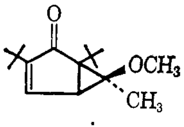
The conversion of bicyclo[3.1.0]hexenones to cyclohexa-2,4-dienones such as **3a** and **4a** requires that bond b (structure E) be broken and a new bond formed between the carbonyl carbon and the quaternary carbon at C-6. Four possible routes can be written to describe this process. (1) After (or simultaneously with) scission of bond b, the carbonyl group migrates to C-6 while a new double bond replaces the three-membered ring. (2) Electromeric bond rearrangement in E or F gives a ketene, which cyclizes to the dienone. (3) Rotation of C-6 occurs in the manner suggested by Schuster and Patel to account for formation of bicyclo-[3.1.0]hexenones,[16] and a new three-membered ring is thus formed. Cleavage of the three-membered ring then gives the cyclohexa-2,4-dienone. (4) Migration of C-6 to the carbonyl group, followed by a second migration to shrink the newly formed cyclobutane ring, gives a new cyclopropane derivative. Cleavage of the cyclopropane again gives the desired dienone. Mechanism 4 has recently been advocated by Jeger and his co-workers.[14]



The observation that **3a** was the major product formed in methanol solution led us, at first, to conclude that ketenes could not be intermediates in the formation of **3a**. Further consideration, however, suggested that the ketene which would be formed by photolysis of **1** might very well cyclize to **3a** faster than it would react with the solvent. The normal free choice of configurations of a polyolefin chain would be inhibited by steric interference between the *t*-butyl groups and group R or the

---

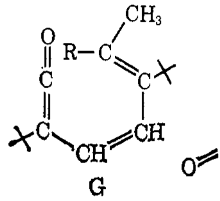
[15] Matsuura has reported that the methoxyl singlet in i appears at unusually high fields, while the methyl resonance has a normal value.[6]

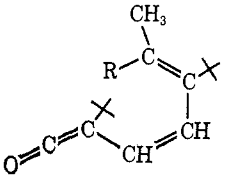


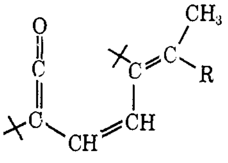
i

[16] D. I. Schuster and D. J. Patel, *J. Am. Chem. Soc.*, **88**, 1825 (1966).

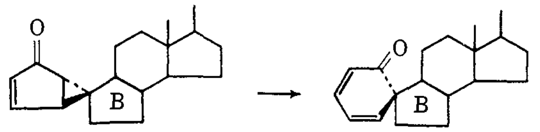
carbonyl group in configurations G′ and G″. The ketene chain should, therefore, tend to maintain a configuration close to that of G, which is the necessary configuration for cyclization to a cyclohexa-2,4-dienone. These steric effects undoubtedly account for the stability of **3a** to further irradiation in methanol.[17]


G


G′


G″

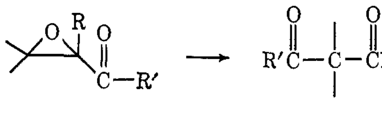
A partial decision among paths 1–4 can be based on the recent stereochemical studies of Jeger and his coworkers,[14] who have found that bicyclo[3.1.0]hexenones formed from steroids give low yields of cyclohexa-2,4-dienones (as in the equation below) by a process analogous to the conversion **1** → **2**. The process is completely stereospecific, with the carbonyl group in each case remaining on the same side of ring B in the product as in the starting material.



It is clear that mechanism 1 agrees with these results, provided that migration of the carbonyl group is concerted with cleavage of bond b. On the other hand, process 2 should lead to a mixture of isomers if the intermediate ketene has a lifetime sufficient to allow rotation of the polyolefin chain. If the lifetime of the ketene is too short to allow such rotation, there would seem to be no need to postulate its existence as an intermediate, rather than simply considering it as a possible representation of the transition state for mechanism 1.

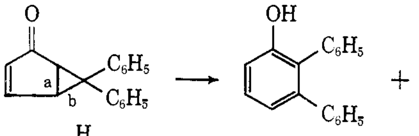
Process 3 applied to compounds in the steroid series should, in each case, result in a single product with a configuration opposite to that observed,[14] owing to the rotation of C-6 during its migration. Finally, mechanism 4 would result in the observed retention of configuration at C-6.

A clear choice cannot be made between mechanisms 1 and 4 at present. Nonetheless, we prefer mechanism 1 on the following grounds. Zimmerman and Schuster[18] have pointed out that rearrangements resulting from photoirradiation of bicyclo[3.1.0]hexenones have many of the characteristics of carbonium ion rearrangements. Mechanism 1 has ample analogy in carbonium ion reactions—in particular, the migration of acyl groups during the acid-catalyzed rearrangements of epoxy ketones[19] provides a fine analogy among three-membered ring reactions. On the other hand, migrations of the type postulated[14] in path 4 appear to have no close analogy. It is true that the carbonium ion reactions of bicyclo[3.1.0]hex-3-en-2-ones in nonpolar solvents might well have unusual features. Since path 1 does offer a satisfactory rationalization for the rearrangement, however, there seems to be no need to postulate the unusual reactions required for path 4.



At this point we have to consider another question, namely, why should either process occur? The normal result of photolysis of bicyclo[3.1.0]hex-3-en-2-ones[14,20,21] is cleavage of the "endocyclic" bond between C-1 and C-5 (bond a in structure E), followed by migration of one of the groups at C-6 to C-1 or C-5. Cleavage of bond a is presumably favored because the intermediates thus formed have more possibilities for resonance stabilization than do structures such as F.

The most favorable case for opening the exocyclic cyclopropane bonds occurs in the 6,6-diphenylbicyclohexenone H studied by Zimmerman and Schuster,[18] since cleavage of one of the exocyclic cyclopropane bonds would give a benzhydryl radical or ion. Irradiation of H in aqueous dioxane has been reported to give phenol I, resulting from opening of a,[18] and acid J, resulting from opening bond b,[22] possibly by way of a cyclohexa-2,4-dienone intermediate. Acid J was the principal product obtained. Its molar ratio to the amount of I obtained was never greater than 1.6:1, however.[22] Thus, even when the electronic factors are as favorable as they are in compound H, the probability of cleaving bond b is smaller than it is for bicyclohexenones **12** and **13**.

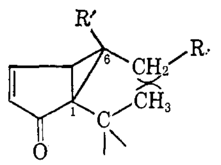


H
I

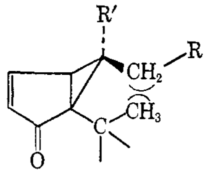
$(C_6H_5)_2C{=}CHCH{=}CHCH_2CO_2H$

J

The strong tendency for cleavage of bond b in **12** and **13** can be rationalized on the basis of steric effects. The ground states (K) in **12** and **13** exhibit severe interference between the *t*-butyl groups at C-1 and the adjacent *exo* substituents at C-6.

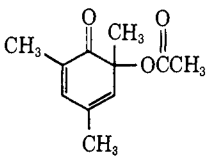


K


L

---

[17] D. H. R. Barton and G. Quinkert [*J. Chem. Soc.*, 1 (1960)] have suggested that a similar inhibition of rotation in the ketene formed from the quinol acetate ii accounts for its relative stability to photolysis.


ii

[18] H. E. Zimmerman and D. I. Schuster, *J. Am. Chem. Soc.*, **84**, 4527 (1962).

[19] R. E. Parker and N. S. Isaacs, *Chem. Rev.*, **59**, 737 (1959).

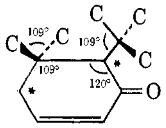
[20] J. W. Wheeler and R. H. Eastman, *J. Am. Chem. Soc.*, **81**, 236 (1959).

[21] P. J. Kropp, *Tetrahedron*, **21**, 2183 (1965).

[22] H. E. Zimmerman, R. Keese, J. Nasielski, and J. S. Swenton, *J. Am. Chem. Soc.*, **88**, 4895 (1966).

Weakening bond b to allow the *exo* substituent at C-6 to rotate slightly toward the carbonyl group, as in L, would markedly relieve the crowding, while at the same time bring the geometry at C-6 into a more favorable arrangement for migration of the carbonyl group. (It may be noticed that just one mode of rotation of C-6 is permissible if migration of the carbonyl group is concerted with the rotation.) Further relief of steric interference between the *t*-butyl group and the methylene at C-6 would result if the weakening of bond b allowed C-1 to assume the normal bond angles of a tetrahedral carbon atom. The alternative reaction mechanism 4 also can account for preferential opening of bond b, since the distance between the *exo* substituent at C-6 and the *t*-butyl at C-1 is increased if the transition state has the geometry of a four-membered ring.

On the other hand, the normal reaction path involving opening of the endocyclic bond a does not appear to offer any significant relief of steric strain. Measurements on Dreiding models show that an *exo* carbon at C-6 is 2.9–3.0 A from the carbon atoms of each of two methyl groups on the adjacent *t*-butyl group in the most favorable conformation. If the six-membered ring in the transition state for opening of bond a is assumed to be completely planar, with C–C bond lengths of 1.54 A and the bond angles shown in structure M, each of the methyl carbon atoms on the ring is 2.94 A from the carbon atom of a methyl on the adjacent *t*-butyl group.



M

Therefore, little over-all change in steric interactions occurs on going from structure K to structure M.

Thus, although the steric effects of the *t*-butyl groups do not prevent photochemical formation of bicyclo[3.1.0]hexenones, they appear to play a decisive role in determining the nature of the further reactions of the bicyclo[3.1.0]hexenones.

Experimental Section[23]

Photoirradiations. All photoirradiations were carried out in a Hanovia apparatus in which the light source and filter were placed in a quartz tube surrounded by the solution to be irradiated, which had a total volume of 35 ml. The solution was surrounded by a water jacket for cooling. A gentle stream of nitrogen was blown over the surface of the solution during irradiation. Unless otherwise specified, the light source for all irradiations was a 450-w, Hanovia high-pressure lamp.

Photorearrangement of 2,6-Di-*t*-butyl-4-ethyl-4-methylcyclohexa-2,5-dien-1-one (1). A solution of 2.0 g of **1**[9] in 35 ml of *n*-hexane was irradiated for 3.75 hr. Vpc analysis on a 20% methyl silicone oil (SF96) on a Gas Chrom Z column at 230° showed ~85% of the starting material to have reacted. The solvent was evaporated and the residual oil chromatographed on Woelm neutral alumina (activity I). Elution with petroleum ether (bp 30–60°) gave 0.2 g of starting dienone. Further elution with petroleum ether and methylene chloride gave an additional 0.15 g of material consisting of starting material and several other components with closely similar retention times (4–6 min) on the SF96 column. The infrared spectrum of the mixture had a peak at 5.90 μ. This fraction was discarded. Elution with chloroform yielded 1.25 g (62.5%) of 2,5-di-*t*-butyl-6-ethyl-6-methylcyclohexa-2,4-dien-1-one (**3a**), λ_{max} (MeOH) 322 mμ (ϵ 3900).

Anal. Calcd for $C_{17}H_{28}O$: C, 82.3; H, 11.3. Found: C, 81.9; H, 11.3.

Rearrangement of 2,5-Di-*t*-butyl-6-ethyl-6-methylcyclohexa-2,4-dien-1-one (3a) in Acid. A solution of 0.500 g of **3a** in 20 ml of glacial acetic acid was cooled in an ice bath while 2 ml of concentrated sulfuric acid was slowly added. The mixture was stirred at room temperature for 7 hr, poured into water, and extracted with methylene chloride. The methylene chloride layer was washed with sodium bicarbonate solution, dried over magnesium sulfate, filtered, and evaporated to give 0.35 g of brown oil. Vpc analysis on a 2% silicone gum (XE60) on Gas Chrom Z column at 185° showed a single major component at a retention time of 9.6 min, together with several minor peaks. The mixture was chromatographed on alumina (activity III). Elution with petroleum ether (bp 30–60°) gave 0.05 g of oil which was discarded. Further elution with CH_2Cl_2 gave 0.20 g of pale yellow oil, whose properties were consistent with the structure of 2-*t*-butyl-5-ethyl-6-methylphenol.

Anal. Calcd for $C_{13}H_{20}O$: C, 81.2; H, 10.45. Found: C, 81.2; H, 10.4.

Preparation of 2,6-Di-*t*-butyl-4-methyl-4-*n*-propylcyclohexa-2,5-dien-1-one (2). A solution of 5.0 g of 4-allyl-2,6-di-*t*-butyl-4-methylcyclohexa-2,5-dien-1-one[24] in 20 ml of benzene was hydrogenated using 0.20 g of Pd on $CaCO_3$ as the catalyst, until absorption of hydrogen stopped. The solution was filtered free of catalyst and the solvent evaporated to give 5.2 g of fluid in which the allyl peak at 11.0 μ was essentially gone. The last traces of the starting dienone were removed by chromatography on neutral alumina, to give 4.0 g of pure 2,6-di-*t*-butyl-4-methyl-4-*n*-propylcyclohexa-2,5-dien-1-one. Its nmr spectrum (in $CDCl_3$) showed singlets at τ 8.75 (two *t*-butyls), 8.83 (methyl at C-4), and 3.60 (two ring vinyl protons) and triplets at τ 9.10 (J = 4.5 cps, methyl on propyl group) and 8.45 (J = 4.8 cps, methylene at C-4).

Anal. Calcd for $C_{18}H_{30}O$: C, 82.4; H, 11.45. Found: C, 82.7; H, 11.8.

Photorearrangement of 2,6-Di-*t*-butyl-4-methyl-4-*n*-propylcyclohexa-2,5-dien-1-one (2). A solution of 1.0 g of **2** in 35 ml of cyclohexane was irradiated through a Corex filter for 2.5 hr. Evaporation of the solvent and chromatography on neutral alumina (activity III) gave 0.76 g (76%) of 2,5-di-*t*-butyl-6-methyl-6-*n*-propylcyclohexa-2,4-dien-1-one (**4a**), λ_{max} (in CH_3OH) 321 mμ (ϵ 4080).

Anal. Calcd for $C_{18}H_{30}O$: C, 82.4; H, 11.45. Found: C, 82.1; H, 11.3.

Rearrangement of 4a in Acid. A solution of **4a** (0.50 g) in 10 ml of glacial acetic acid was cooled in ice and 1 ml of concentrated sulfuric acid added slowly. The solution was kept at room temperature for 18 hr and then poured into water. The aqueous mixture was extracted with methylene chloride. The organic layer was washed with sodium bicarbonate, dried over magnesium sulfate, and evaporated to give 0.30 g of brown oil. Chromatography on neutral alumina (activity III) and elution with methylene chloride gave 0.15 g of 2-*t*-butyl-6-methyl-5-*n*-propylphenol, $n^{25}\text{D}$ 1.5153.

Anal. Calcd for $C_{14}H_{22}O$: C, 81.5; H, 10.7. Found: C, 81.6; H, 10.9.

Preparation of Allyl 2-*t*-Butyl-5-methylphenyl Ether. 2-*t*-Butyl-5-methylphenol (50.0 g) was dissolved in 300 ml of dimethyl sulfoxide. Sodium methoxide (16.5 g) was added and the mixture shaken until it was homogeneous (5 min). Allyl bromide (37.0 g) was added, resulting in an immediate exotherm and precipitation of sodium bromide. After 5 min the reaction mixture was poured into water and the mixture extracted with methylene chloride. The methylene chloride layer was washed three times with water, dried over magnesium sulfate, and evaporated to give 68.0 g of yellow fluid. The product was distilled to give 60.4 g (97%) of allyl 2-*t*-butyl-5-methylphenyl ether, bp 112–115° (5.0 mm), $n^{25}\text{D}$ 1.4844.

Anal. Calcd for $C_{14}H_{20}O$: C, 82.4; H, 9.79. Found: C, 82.5; H, 9.91.

Preparation of 2-Allyl-6-*t*-butyl-3-methylphenol. Allyl 2-*t*-butyl-5-methylphenyl ether (50.0 g) was heated at 225–235° for 3.5 hr. The reaction was then 95% complete by vpc on a 2% silicone oil (SE30) column at 155°. Distillation gave 38.1 g (76%) of 2-allyl-6-*t*-butyl-3-methylphenol, bp 103–107° (1.75 mm), $n^{25}\text{D}$ 1.5220.

Anal. Calcd for $C_{14}H_{20}O$: C, 82.4; H, 9.79. Found: C, 82.6; H 9.85.

Preparation of 2-*n*-Propyl-3-methyl-6-*t*-butylphenol (6b). 2-Allyl-3-methyl-6-*t*-butylphenol (7.5 g) was dissolved in 100 ml of

---

[23] Elemental analyses by Galbraith Microanalytical Laboratories, Knoxville, Tenn. Nmr spectra were taken on a Varian A-60 and ultraviolet spectra on a Cary Model 11 spectrophotometer. Vpc analyses were done on an F & M Model 720 chromatograph using the columns described below.

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

n-hexane, and 1.0 g of 10% Pd on C catalyst was added. After being shaken in a hydrogen atmosphere until absorption of hydrogen stopped, the mixture was filtered and evaporated. The product was distilled to give 7.0 g (92%) of **6b**, bp 111-113° (2.5 mm), $n^{25}\text{D}$ 1.5107.

Anal. Calcd for $C_{14}H_{22}O$: C, 81.5; H, 10.7. Found: C, 81.6; H, 10.6.

Photoirradiation of 2 at 2537 A. A solution of 8.0 g of **2** in 35 ml of *n*-hexane was irradiated by a 25-w, low-pressure mercury lamp[25] through a quartz tube. The reaction was monitored by injecting samples of the solution onto a 6-ft, 10% polyethylene glycol (Carbowax 20M) column at 145°. The peak for **2** appeared at 3.7 min. After 30-min irradiation, small peaks at 7.2 and 8.1 min appeared in the ratio 4:3. Continued irradiation resulted in increases in the intensity of the 7.2- and 8.1-min peaks, and the appearance of small peaks at 4.8 and 13.3 min. The 13.3-min retention time was identical with that of **4a**. After 3 hr, the starting material was almost gone. The solvent was evaporated and the product chromatographed on 2 kg of Woelm neutral alumina. The column was eluted with petroleum ether (bp 30-60°) and 250-ml fractions were taken. The first five fractions contained no products. Fractions 6-8 contained 0.3 g of a material which was largely the component with a retention time of 4.8 min. It was later identified as 1,3-di-*t*-butyl-5-methyl-6-*endo*-*n*-propylbicyclo[3.1.0]hex-3-en-2-one.[7] Fractions 12 and 13 contained 1.2 g of 1,3-di-*t*-butyl-6-*endo*-*n*-propyl-6-*exo*-methylbicyclo[3.1.0]hex-3-en-2-one (**12b**), $n^{25}\text{D}$ 1.4778, retention time 7.2 min.

Anal. Calcd for $C_{18}H_{30}O$: C, 82.4; H, 11.45. Found: C, 82.80; H, 11.6.

Fractions 14-16 contained an additional 1.5 g of **12b** containing some **13b**. Fractions 17-20 contained 0.8 g of 1,3-di-*t*-butyl-6-*endo*-methyl-6-*exo*-*n*-propylbicyclo[3.1.0]hex-3-en-2-one (**13b**), $n^{25}\text{D}$ 1.4784, retention time 8.1 min.

Anal. Calcd for $C_{18}H_{30}O$: C, 82.4; H, 11.45. Found: C, 82.3; H, 11.2.

Photorearrangement of 2,6-Di-*t*-butyl-4-methyl-4-isopropylcyclohexa-2,5-dien-1-one (7). A solution of 1.8 g of **7**[9] in 35 ml of cyclohexane was irradiated through a Pyrex filter for 2.5 hr. The ultraviolet spectrum of the oil obtained by evaporating the solvent had $\lambda_{\max}$ 320 mμ [ϵ (based on mol wt 262) 3100]. Several attempts to chromatograph the product on activity III alumina resulted in partial decomposition to a phenol. The product was, therefore, chromatographed on activity I alumina. Elution with petroleum ether (bp 30-60°) gave 1.10 g (73%) of 2,5-di-*t*-butyl-6-methylphenol, mp 65-67°.

Anal. Calcd for $C_{15}H_{24}O$: C, 81.9; H, 11.0. Found: C, 82.0; H, 11.0.

Photorearrangement of 2,6-Di-*t*-butyl-4-allyl-4-methylcyclohexa-2,5-dienone (10). A solution of 3.8 g of **10** in 35 ml of cyclohexane was irradiated for 3 hr, after which the solvent was evaporated under vacuum. The ultraviolet spectrum in methanol had a strong band at 320 mμ (ϵ 3100), indicating that *ca.* 70% of the product was a linearly conjugated cyclohexadienone. The product was chromatographed on "Florisil" magnesium silicate. Elution with petroleum ether (bp 30-60°) gave 0.5 g of material which showed little absorption at 320 mμ and was discarded. Elution with a 1:1 mixture of petroleum ether and methylene chloride gave 1.1 g (29%) of 2,5-di-*t*-butyl-6-allyl-6-methylcyclohexa-2,4-dienone (**11**), $\lambda_{\max}$ 319 mμ (ϵ 4120).

Anal. Calcd for $C_{18}H_{28}O$: C, 83.1; H, 10.8. Found: C, 83.1; H, 11.0.

In a second run the product from irradiation of 2.0 g of **10** was dissolved in a 20 ml of benzene. Platinum oxide catalyst (0.10 g) was added, and the mixture hydrogenated until no more hydrogen was absorbed. Chromatography of the product gave 1.38 g (68%) of **4a**.

Photorearrangement of 10 at 2537 A. A solution of 6.0 g of **10** in *n*-hexane was irradiated by a low-pressure mercury lamp until vpc analysis on a 6-ft, 10% polyethylene glycol (Carbowax 20M) column at 145° showed 90% of the starting material to be gone. The solvent was evaporated and the residue chromatographed on 3 kg of Woelm neutral alumina. The initial elution was with petroleum ether (bp 30-60°) and 250-ml fractions were taken. Fractions 7-8 contained 0.4 g of material which was largely **10**. Fractions 12 and 13 contained 1.3 g of 1,3-di-*t*-butyl-6-*endo*-allyl-6-*exo*-methylbicyclo[3.1.0]hex-3-en-2-one (**12a**), $n^{25}\text{D}$ 1.4833.

Anal. Calcd for $C_{18}H_{20}O$: C, 82.4; H, 11.45. Found: C, 81.8; H, 11.6.

Fractions 14-17 (1.4 g) contained mixtures of **12a** and **13a**. Fractions 18-22 (0.6 g) contained pure 1,3-di-*t*-butyl-6-*exo*-allyl-6-*endo*-methylbicyclo[3.1.0]hex-3-en-2-one (**13a**), $n^{25}\text{D}$ 1.4843.

Anal. Calcd for $C_{18}H_{20}O$: C, 82.4; H, 11.45. Found: C, 82.1; H, 11.6.

Hydrogenation of 12a. To a solution of 0.100 g of **12a** in 15 ml of benzene was added 0.05 g of platinum oxide catalyst. The mixture was shaken with hydrogen until absorption of hydrogen ceased. The solution was filtered free of catalyst and evaporated to give 0.100 g of clear yellow fluid, identical in its nmr and infrared spectra with **12b**.

Hydrogenation of 13a. A solution containing 0.060 g of **13a** was hydrogenated as above, to give 0.061 g of **13b**, identified by its nmr and infrared spectra.

Photorearrangements of 1,3-Di-*t*-butylbicyclo[3.1.0]hex-3-en-2-ones. A solution of 0.200 g of **12b** in 35 ml of *n*-hexane was irradiated through a Pyrex filter until vpc analysis on a 3-ft, 1% polyethylene glycol (Carbowax 20M) on Gas Chrom Z column showed less than 5% of **12b** remained unreacted (*ca.* 25 min). Evaporation of the solvent left 0.200 g of yellow oil with $\lambda_{\max}$ (in CH_3OH) 321 mμ (ϵ 3190) and with strong bands at 6.1 and 6.35 μ in the infrared spectrum. Similar irradiation of a solution containing 0.150 g of **13b** gave a product with essentially identical ultraviolet and infrared spectra. Each product was analyzed by temperature-programmed, vapor phase chromatography on the Carbowax column. The starting temperature was 125°, and the temperature was increased 5° per minute. In addition to the principal peak for **4a** (constituting *ca.* 75% of the total product) at 156°, small peaks (in order of intensity) appeared at 187, 141, and 171°. Trace peaks appeared at 160, 175, and 183°. The vapor phase chromatograms were essentially identical for **13a** and **13b**, and were essentially identical with the chromatogram obtained by irradiation of **2** under the same conditions. No changes occurred in the chromatograms on irradiation of the samples for an additional 30 min, except that the peak at 141° was greatly reduced in intensity.

A solution of 0.150 g of **12b** in *n*-hexane was irradiated by the low-pressure mercury lamp until less than 5% of **12b** remained unreacted (1.5 hr). Vapor phase chromatography showed large peaks (in order of intensity) at 156 (**4a**) and 141°, and small peaks at 187 and 183°. Further irradiation decreased the intensity of the 141° peak and raised the intensity of the 187 and 183° peaks, but did not change the intensity of the 156° peak. After 3.5 hr, the 141° peak had essentially disappeared. Further irradiation for 2.0 hr did not change the chromatogram.

Photoirradiation of 1 in Methanol. a. In Absence of Base. A solution of 0.500 g of **1** in 35 ml of methanol was irradiated through a Pyrex filter for 1.5 hr. The solution was dissolved in water and extracted with methylene chloride. The methylene chloride layer was washed with water, dried over magnesium sulfate, and evaporated to give 0.410 g of yellow oil. Vpc analysis on a 6-ft, 2% silicone gum (XE60) column at 200° showed the presence of two major products, with retention times of 7.0 and 10.0 min, in the approximate ratio 3:1. Small amounts of each product were isolated by vpc on the same column and identified by their retention times and infrared spectra as **3a** (major product) and **5**.

b. In Presence of Base. A solution of 1.00 g of **1** in 35 ml of a 0.1 *N* solution of KOH in methanol was irradiated and worked up as above to give 0.684 g of yellow oil, $\lambda_{\max}$ (in CH_3OH) 321 mμ (ϵ 2800). Vpc on the same column as a showed the principle product to have a retention time of 9.6 min. Smaller peaks appeared at 4.7, 11.2, and 14.8 min. The principal product was isolated by vpc and identified by its infrared spectrum as **3a**.

---

(25) Obtained from the Southern New England Ultraviolet Co., Middletown, Conn.