frared spectrum identical with that of the principal product from competitive amination of *t*-butylbenzene and toluene.

Water Cocatalytic Studies with *sec*-Butylbenzene. A. Dry. Aluminum chloride (Fisher sublimed), freshly opened in a dry nitrogen atmosphere, was weighed and placed in a 1-l. three-neck flask, equipped with stirrer, condenser, thermometer, and drying tube, containing freshly distilled *sec*-butylbenzene at 10° under nitrogen. To this was added a trichloramine solution dried for 3 hr over magnesium sulfate before use. The standard reaction procedure was followed.[5]

B. Wet. The dried trichloramine solution (200 ml) was shaken with 50 ml of water. After standing for 5 min, the layers were separated and the volumes were measured. The amount of water absorbed was 2.0 ml (0.11 mole). The wet trichloramine solution was added to the aluminum chloride-*sec*-butylbenzene mixture at 10°. The standard reaction procedure was followed.[5]

Acknowledgment. We are grateful to the National Science Foundation for support of this work.

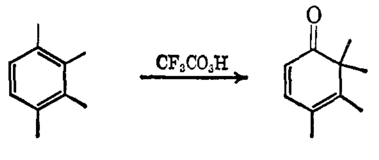
Preparation, Chemistry, and Photochemistry of Hexaalkyl-2,4-cyclohexadienones[1-3]

Harold Hart, Peter M. Collins, and Anthony J. Waring

Contribution from the Department of Chemistry, Michigan State University, East Lansing, Michigan 48823. *Received October 27, 1965*

Abstract: Hexamethyl- and hexaethylbenzene are oxidized by peroxytrifluoroacetic acid–boron fluoride to hexaalkyl-2,4-cyclohexadienones **1** and **2**, respectively. The dienones do not dimerize, but **1** gives Diels–Alder adducts with maleic anhydride and other dienophiles. The enolate anion of **1** is much more easily formed at the C-3 methyl than at the C-5 methyl, which enables these methyls to be selectively deuterated. Reaction of **1** with methylmagnesium iodide leads to 1,2,3,3,4,5-hexamethyl-6-methylene-1,4-cyclohexadiene (**8**). Reduction of **1** or **2** with lithium aluminum hydride gives the secondary alcohols **11** and **13** which, on treatment with acid, are converted either to cross-conjugated trienes or to hexaalkylbenzenes, depending on controllable conditions. Factors which affect this partition of the intermediate carbonium ion are discussed. Catalytic reduction of **1** gave a conjugated and nonconjugated enone, the latter being formed by "1,4" addition of hydrogen. Irradiation of **1** or **2** leads to bicyclo[3.1.0]hexanes **18** or **22**. These are a novel type of photorearrangement product, not previously obtained from 2,4-cyclohexadienones. Labeling experiments show that a "bond-crossing" mechanism, not alkyl migration, is involved.

Earlier reports[3] from this laboratory have illustrated the use of peroxytrifluoroacetic acid–boron fluoride as a reagent for the oxidation of aromatic compounds. With a partially substituted aromatic ring, phenols were obtained, the yield being quite good if positions *ortho* or *para* to the entering hydroxyl group were blocked, to retard further oxidation. When the oxidation was applied to prehnitene (1,2,3,4-tetramethylbenzene), one of the products, isolated in very low yield, was 4,5,6,6-tetramethyl-2,4-cyclohexadienone.[4]



This could be accounted for by attack of the cationic oxidant at an already substituted position (C-1) of the hydrocarbon, followed by a Wagner–Meerwein methyl migration and proton loss. This result suggested to us that if the original hydrocarbon were entirely alkylated, conversion to dienone might become the dominant reaction path. This hope was fulfilled,[5] and the present paper reports the oxidation of hexamethyl- and hexaethylbenzene to dienones, as well as some of the interesting ground state and photochemistry of these products.

Results and Discussion

Synthesis of Dienones and Structure Proof. Oxidation of hexamethylbenzene with peroxytrifluoroacetic acid and boron fluoride in methylene chloride at 0° afforded hexamethyl-2,4-cyclohexadienone (**1**) in excellent yield. Similarly, hexaethylbenzene gave the ethyl analog (**2**).[6] The oxidation can also be accomplished with 90% hydrogen peroxide in a mixture of acetic and sulfuric acids, although the reaction is less clean and the yield somewhat lower. The latter reagent is of the type used by Waters and Derbyshire[7] to convert mesitylene to mesitol. Epoxidation of the dienones is probably suppressed because of the lower reactivity of conjugated systems[8] and because only a limited excess of oxidant was used.

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(1) We gratefully acknowledge support by the National Science Foundation (GP-71). P. M. C. thanks the Board of Governors of Birkbeck College, London, for a leave of absence.

(2) Portions of this work have been reported in preliminary form in the following communications: (a) A. J. Waring and H. Hart, *J. Am. Chem. Soc.*, **86**, 1454 (1964); (b) H. Hart and A. J. Waring, *Tetrahedron Letters*, No. **5**, 325 (1965).

(3) Paper V in a series on Oxidations with Peroxytrifluoroacetic Acid–Boron Fluoride. For paper IV, see H. Hart, C. A. Buehler, A. J. Waring, and S. Meyerson, *J. Org. Chem.*, 30, 331 (1965).

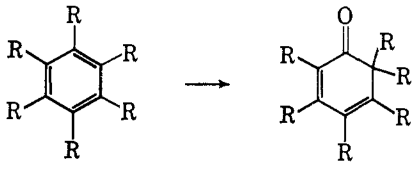
(4) H. Hart and C. A. Buehler, *J. Org. Chem.*, **29**, 2397 (1964).

(5) It turns out, however, that it is not necessary that all positions be blocked; pentamethylbenzene and durene give predominantly dienones with peroxytrifluoroacetic acid. These results will be reported in detail later.

(6) Professor E. M. Arnett advises us that application of our reaction to hexaisopropylbenzene did not lead to dienones.

(7) W. A. Waters and D. H. Derbyshire, *Nature*, **165**, 401 (1950); no experimental details were given.

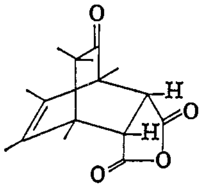
(8) H. O. House, "Modern Synthetic Reactions," W. A. Benjamin, Inc., New York, N. Y., 1965, p 115. A mass spectrum of **1** does show



1, R = CH_3
2, R = C_2H_5

The structures of the dienones follow from their spectral properties and reactions. The infrared spectrum of **1** shows carbonyl absorption at 1642 (CCl_4) or 1647 cm^{-1} (liquid film) and C=C absorption at 1567 cm^{-1} (liquid film).[9] The dienones are yellow, with absorption maxima at 330 mμ and 339 mμ, respectively. It is perhaps surprising that the spectrum of **1** shows scarcely any bathocromic shift from that of 4,5,6,6-tetramethyl-2,4-cyclohexadienone,[4] despite the additional α- and β-methyl substituents. The expected effect of additional substitution may be counterbalanced by twisting of the ring caused by four adjacent methyls in **1**.[13] The nmr spectrum of **1** will be discussed in more detail below, but its gross features are consistent with the structure, consisting of three bands at τ 8.89, 8.14, and 7.97, with relative areas 2:3:1.[14] The nmr spectrum of **2** is complex but reasonable in terms of the assigned structure (see Experimental Section). It does have one very interesting feature, a triplet centered at τ 9.52 ($J \cong 7.0$ cps), corresponding to six protons. It is thought that these peaks are due to the methyls of the *gem*-diethyl group, and that they occur at unusually high field because severe molecular crowding brings these methyls into the shielding region of the carbonyl group. The infrared and ultraviolet spectra of **2** are consistent with its structure.

Dienones **1** and **2** are very stable. Lack of dimerization contrasts markedly with the behavior of less substituted dienones.[10] Maleic anhydride and ethyl azodicarboxylate react with **1** under mild conditions to form adducts **3** and **4**, respectively, but **2** could not be induced to react with maleic anhydride. The structures of **3** and **4** follow from analytical and spectroscopic data.



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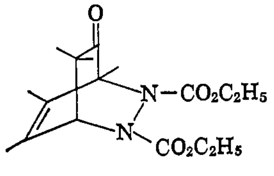

4

Enolization. In connection with photochemical experiments described below, it was necessary to prepare **1** with a CD_3 group at C-5 or C-6, and the easiest approach seemed to be base-catalyzed exchange of the hydrogens at the C-5 methyl. Treatment of **1** at 30° with CH_3OD and approximately 1 equiv of sodium caused trideuteration (nmr peak at τ 7.97 disappeared) in a few minutes. Prolonged standing at room temperature showed no further exchange. More drastic conditions (heating a CH_3OD solution which was 10 *M* in sodium methoxide and 1 *M* in dienone at 60° for 48 hr) gave a 50% yield of hexadeuterated dienone, and an unidentified by-product. The same dienone-d_6 was obtained in nearly quantitative yield by allowing a 1 *M* solution of dienone to react with 0.6 *M* potassium *t*-butoxide in dimethyl sulfoxide-d_6 at room temperature for 6 hr.[15]

It was shown that the product of rapid exchange had deuterium at the C-3 methyl, and that the hexadeuteriodienone had deuterium at the C-3 and C-5 methyls.[16] Dienone labeled only at C-5 was prepared by following the hexadeuteration with a rapid back exchange with sodium methoxide in ordinary methanol.

The nmr spectra of these dienones are summarized in Table I. The six-proton high-field signal at τ 8.89 is due to the *gem*-dimethyls at C-6. The low-field signal at τ 7.97 is due to the methyl at C-3.[17] The

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traces of contaminant at M + 16, possibly epoxide (S. Meyerson, unpublished results).

[9] The high-frequency band (1650–1675 cm^{-1}) present in most 2,4-cyclohexadienones (for examples, see ref 4 and 10) is absent from the spectrum of **1** or **2**. Most 2,4-cyclohexadienones have a second carbonyl band at 1625–1665 cm^{-1}, and **1** and **2** are no exception. The low-frequency band, at 1560–1570 cm^{-1}, is reported for relatively few cyclohexadienones;[10b,11] its frequency is lower than the usual range found for conjugated dienes[12] and seems characteristic of the 2,4-cyclohexadienone system.[13]

(10) (a) D. Y. Curtin and R. R. Fraser, *Chem. Ind.* (London), 1358 (1957); (b) K. Alder, F. H. Flock, and H. Lessenich, *Ber.*, **90**, 1709 (1957); (c) D. Y. Curtin, R. J. Crawford, and M. Wilhelm, *J. Am. Chem. Soc.*, **80**, 1391 (1958); (d) J. D. McClure, *J. Org. Chem.*, **28**, 69 (1963).

(11) (a) L. Mandell, D. Caine, and G. E. Kilpartick, *J. Am. Chem. Soc.*, **83**, 4457 (1961); (b) P. J. Kropp, *ibid.*, **86**, 4053 (1964).

(12) K. Nakanishi, "Infrared Absorption Spectroscopy," Holden-Day, Inc., San Francisco, Calif., 1962, p 24.

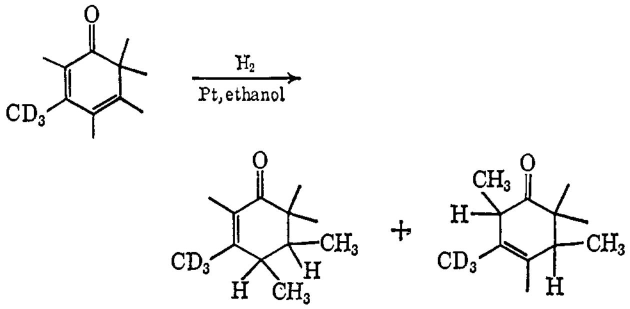
(13) The spectral properties of dienones are discussed in greater detail in a chapter by A. J. W. to appear in "Advances in Alicyclic Chemistry," Vol. 1, H. Hart and G. J. Karabatsos, Ed., Academic Press Inc., New York, N. Y., in press.

(14) In our original communication,[2a] the band at τ 7.96 was assigned to the C-2 methyl; this assignment was in error, and the band is now known to be due to the C-3 methyl (*vide infra*).

(15) The nmr spectra are consistent with the amounts of label indicated. Mass spectrometry, however, which gives a much more accurate picture, shows for a typical example that a sample of dienone, exchanged at room temperature with methoxide and which appears from the nmr to be labeled at the C-3 methyl, is in fact a complex mixture containing 1.3%-d_0, 4.0%-d_1, 24.8%-d_2, 68.3%-d_3, and 1.6%-d_4 components. This calculates to 88.3% labeling, calculated as d_3. The mass spectra of these compounds are being investigated in greater detail, and results will be published separately. We are grateful to S. Meyerson, American Oil Company, Whiting, Ind., for these preliminary results.

(16) Base-catalyzed labeling of **1** should occur only at the C-3 and C-5 methyls. Nevertheless, since assignment of the label was critical to evaluation of the photochemical results described later in this paper (and to other unpublished results), it was felt necessary to establish the positions of labeling with certainty. The details are to be found in the experimental part of this paper, but the results are summarized here.

Catalytic reduction of **1**, using platinum, gave two enones, one conjugated and one not. Reduction of trideuterio-**1**, obtained from rapid exchange of **1** with CH_3OD-$NaOCH_3$ at room temperature, gave the same enones; in each case, one of the allylic methyls was labeled, as judged by the absence of a peak from that region of the nmr spectrum. This result can only be explained if the label in **1** is at C-3, and if the nonconjugated enone is the Δ^3 isomer.



Catalytic reduction of hexadeuterio-**1**, prepared as described above, gave conjugated and nonconjugated enone each of which still showed one unlabeled allylic methyl group. This is only possible if the remaining label is at C-5. It is therefore unequivocally established that the easily exchanged protons in **1** are at the C-3 methyl, and the more difficultly exchanged protons are at the C-5 methyl.

(17) See ref 11b, footnote 19 and text, for additional examples of enones or dienones with a low-field β-methyl group.

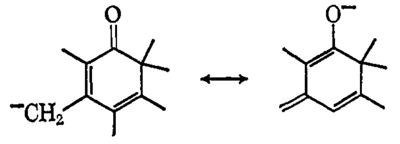
remaining allylic methyls appear in the region τ 8.13–8.17. When the C-3 and C-5 methyls are labeled, the remaining methyl bands are resolved into two singlets at τ 8.13 and 8.17 which can be assigned to the C-4 and C-2 methyls, respectively. This choice can be made because, when only the C-5 methyl is deuterated, the band at τ 8.13 remains a singlet, whereas that at τ 8.17 is a quartet. This is due to homoallylic coupling with the C-3 methyl, which is most easily seen by examining the latter, since it stands apart from the other methyls and is a quartet, $J = 0.8$ cps.[18]

Table I. Nmr Parameters of Hexamethyl-2,4-cyclohexadienone (**1**)[a]

Deuterated methyl at	τ 7.97	τ 8.13	τ 8.17	τ 8.89
C-3 and C-5	Nil	s(3)	s(3)	s(6)
C-5	q(3), $J = 0.8$	s —(6)—q		s(6)
C-3	Nil	–2 peaks (9)–		s(6)
Fully protonated	q(3), $J = 0.8$	— m(9) —		s(6)

[a] s = singlet, q = quartet, m = multiplet; J = peak separation in cps; numbers in parentheses are proton signal strength.

The large difference in rates of exchange at C-3 and C-5 must be due to a difference in the energy of the corresponding enolate anions **5** and **6**. One might have expected **6** to be favored over **5**, because of greater charge delocalization. But if one examines the contributing forms of **5** and **6** which place the negative charge on oxygen, **5** takes the form of a 1,4-cyclohexadiene and **6**, a 1,3-cyclohexadiene. It has been shown[19] that these systems have comparable energies when the rings are unsubstituted. The observation,[20] confirmed and extended in the present work, that heptamethylbenzenonium ion (**7**) loses a proton to give only cross-conjugated (**8**) rather than completely conjugated triene (**9**) is probably a related phenomenon.



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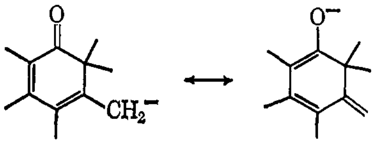

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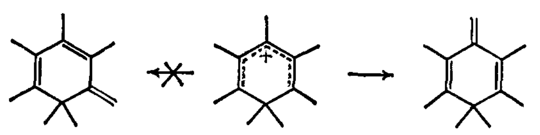
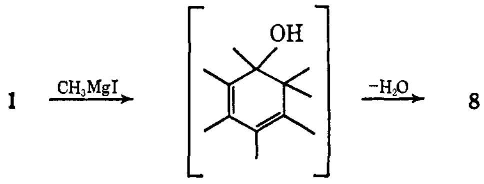


9 **7** **8**

Reactions at the Carbonyl Group. Treatment of **1** with methylmagnesium iodide failed to give the alcohol **10**, but led directly to triene **8** in good yield. The properties of the triene and its carbonium ion **7**, agree well with those previously reported[20] (see Experimental Section, however, for differences in nmr chemical shifts).



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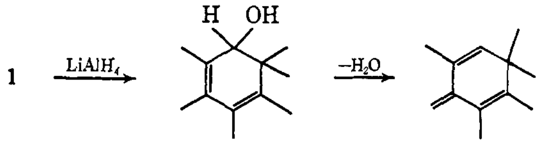
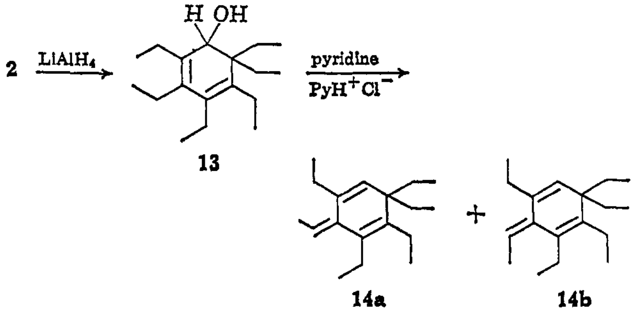
Lithium aluminum hydride reduction of **1** gave the expected alcohol **11** as an unstable crystalline solid which could be stored for as long as 2 weeks in a non-acidic atmosphere. The ultraviolet spectrum of **11**, λ_{max} 262 mμ (ϵ 9380), is in the right range for 1,3-cyclohexadienes, but perhaps at somewhat shorter wavelength than might have been expected[21] considering the alkyl substitution. This may again be due to twisting of the ring (*vide supra*) because of so many vicinal substituents. The absorption maximum is nevertheless at sufficiently long wavelength to exclude the allylic isomer of **11** in which the double bonds are not conjugated. The nmr spectrum (see Experimental Section) is consistent with the structure.



11 **12**

Dehydration of **11** to triene **12** was readily achieved in pyridine solution containing acid, or simply by allowing the dienol prolonged exposure to laboratory air at room temperature. The structure of **12** follows from its method of formation, facile conversion to hexamethylbenzene in acid, and physical properties. The ultraviolet absorption spectrum of **12** was superimposable on that of **8** (for infrared and nmr spectra, see Experimental Section). The cross-conjugated triene structure is once again preferred over the completely conjugated triene (which could have been formed by 1,6-elimination).

The hexaethyldienone **2**, on reduction with lithium aluminum hydride, afforded dienol **13**, which was considerably more stable than the methyl analog; it



13 **14a** **14b**

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(18) Such five-bond couplings have been discussed: N. S. Bhacca and D. H. Williams, "Applications of NMR Spectroscopy in Organic Chemistry," Holden-Day, Inc., San Francisco, Calif., 1964, p 110; see also S. Sternhill. *Rev. Pure Appl. Chem.*, **14**, 15 (1964).

(19) R. B. Bates, R. H. Carnighan, and C. E. Staples, *J. Am. Chem. Soc.*, **85**, 3030 (1963).

(20) W. von E. Doering, M. Saunders, H. G. Boynton, H. W. Earhart, E. F. Wadley, W. R. Edwards, and G. Laber, *Tetrahedron*, **4**, 178 (1958).

(21) 273 mμ: H. H. Jaffe and M. Orchin, "Theory and Applications of Ultraviolet Spectroscopy," John Wiley and Sons, Inc., New York, N. Y., 1962, p 200.

could be distilled at 105° (0.07 mm) without dehydrating. The nmr spectrum of **13** in pyridine or dimethyl sulfoxide-d_6, showed the hydroxyl proton and C-1 proton as an AB quartet.[22]

By heating the hexaethyldienol **13** with pyridine containing acid, a product was obtained to which structures **14a** and **14b** were assigned. In acid it afforded hexaethylbenzene, showing that the gross structure is correct. It has λ_{max} at 259 mμ (ϵ 11,900) similar to **8** (λ_{max} 256 mμ (ϵ 21,400)), and its nmr spectrum had a complex signal at high field for 28 protons (five ethyl groups and one allylic methyl) and at low field another complex signal of two vinyl protons. This is consistent with the over-all structure, but the complexity of the vinyl signal requires that two isomers be present.

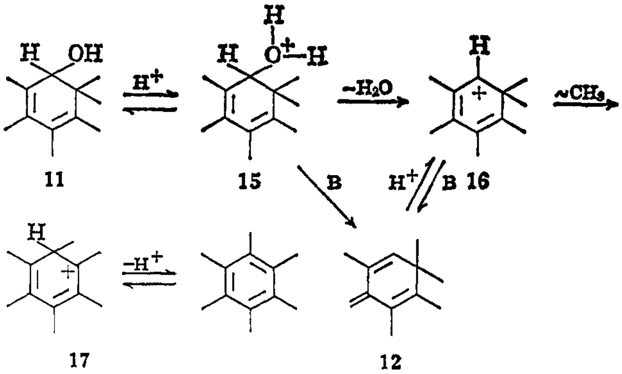
The acid-catalyzed dehydration of **11** and **13** to trienes was a somewhat unexpected result, since the anticipated carbonium ion intermediate could undergo alkyl group migration, thus forming an aromatic product. Indeed, protonation of the trienes led to these aromatic products. An exploratory study was therefore made of the dehydration of dienols **11** and **13** in various solvents; the product composition ranged from exclusively triene to exclusively hexaalkylbenzene (see Table II).

Table II. Dehydration of Dienols **11** and **13** in Various Solvents

Solvent	Conditions[a]	Dienol **11**		Dienol **13**	
		% triene **12**	% HMB[b]	% triene **14**	% HEB[c]
CCl_4	3 hr, 30°	95	5	No dehydration	
CCl_4	0.002 *M* NaOMe in MeOH, 20 hr	No dehydration		...	
CCl_4	Satd HCl gas, <1 min	50	50	0	100
CCl_4	0.02 *M* in HCl–EtOH, 1 min	75	25	...	
EtOH	0.02 *M* HCl, 1 min	95	5	...	
Pyridine	3 hr	No dehydration		No dehydration	
Pyridine	HCl, 1.5 hr, 60°	>95	...	>95	...
DMSO-d_6	10 min	>95	<5	No dehydration in 3 hr	

[a] Room temperature, unless otherwise stated. [b] Hexamethylbenzene. [c] Hexaethylbenzene.

The dienols are stable in alkaline solution (pyridine, or CCl_4 containing some sodium methoxide in methanol). However, in a solvent which can function as a base, but which also contains a proton source (such as pyridine containing pyridinium chloride, or ethanolic hydrogen chloride), dehydration to triene is rapid. As the basicity of the solvent is decreased (for example, using ethanolic hydrogen chloride in carbon tetrachloride, or HCl gas in carbon tetrachloride), the amount of hexaalkylbenzene in the product increases. Perhaps the most striking example is the dehydration of **13** by hydrogen chloride exclusively to triene in pyridine, and exclusively to hexaethylbenzene in carbon tetrachloride. Thus there is a competition between proton removal and alkyl migration (followed by proton removal), the former being favored in solvents with basic properties.



The scheme, shown for **11**, can be used to rationalize the data. The conversion of triene to hexaalkylbenzene must proceed *via* a carbonium ion such as **16**.[23] The dehydration can partition between triene and aromatic at this same point, proton removal competing favorably with alkyl migration when the solvent is sufficiently basic. Alternatively, the protonated alcohol **15** could proceed directly to **12** in basic solvents, but to **16** in less basic solvents. It should be noted, however, that even in acidified solutions of relatively nonpolar solvents (*i.e.*, carbon tetrachloride containing HCl), loss of water from **15** is rapid, as indicated by the high yield of aromatic product. Thus it seems most likely that the partitioning comes at the carbonium ion stage.

Some differences in the behavior of the methyl and ethyl dienols and trienes are worthy of comment. The ethyl dienol **13** is more resistant to dehydration than the methyl analog. Thus it can be distilled without dehydration, its nmr spectrum can be measured in DMSO, whereas **11** is rapidly dehydrated in this solvent[24] (Table II), and its conversion to triene in pyridine–pyridinium chloride requires more vigorous conditions than those needed for **11** (Table II). Thus the transition state for dehydration of **13** seems to have a higher energy than that of **11**. On the other hand, kinetic studies showed that in ethanolic hydrogen chloride, the ethyl triene **14** is converted to hexaethylbenzene at least three times faster than is the methyl triene **12** converted to hexamethylbenzene.[25] This is due to the higher energy of **14** (relative to **12**), since the methyl group on the exocyclic double bond will interact unfavorably with the adjacent ethyl group.

One can rationalize the observation that in carbon tetrachloride saturated with hydrogen chloride, **11** gives a 50–50 mixture of triene and aromatic, whereas **12** gives aromatic exclusively. This result is consistent with the slower rate of proton abstraction and greater instability of the triene for the ethyl compound.

Photochemistry of Hexaalkyl-2,4-cyclohexadienones. Three types of photochemical transformations of 2,4-cyclohexadienones were elucidated in the classical work of Barton and Quinkert:[26,27] (a) ring fission to a

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[22] *Cf.* O. L. Chapman and R. W. King, *J. Am. Chem. Soc.*, **86**, 1256 (1964).

[23] For simplicity, only one form of ions **16** and **17** is shown.

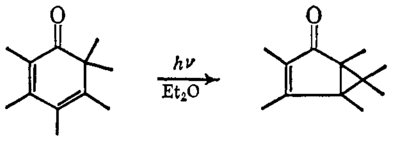
[24] *Cf.* V. J. Traynelis, W. L. Hergenrother, H. T. Hanson, and J. A. Valicenti, *J. Org. Chem.*, **29**, 123 (1964).

[25] Although the conversion **12** → HMB followed clean first-order kinetics, the first-order "constant" for the conversion of **14** → HEB decreased during the reaction. This could be due to **14** being a mixture of **14a** and **14b** which differ in reactivity. Probably **14a** would have lower energy and be less reactive than **14b**, because the ethyl group toward which the allylic methyl group is directed is less restricted in its motions in **14a** (neighboring H rather than neighboring ethyl).

[26] D. H. R. Barton and G. Quinkert, *J. Chem. Soc.*, 1 (1960).

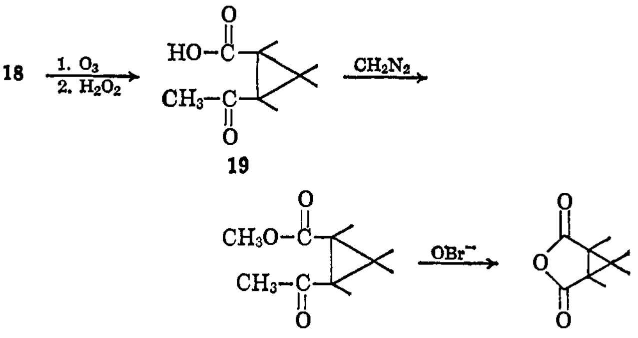
cis-diene ketene (which is subsequently isomerized to the *trans* isomer and also reacts at the ketene function with nucleophiles present); (b) expulsion of an acetoxyl group from C-6, followed by aromatization to a phenol; and (c) migration of an acetoxyl group from C-6 to C-5, if unsubstituted, again with concomitant aromatization to a phenol. Because of the marked effect which alkyl groups may have on the photochemical transformations of dienones,[11b,24,28] it seemed worthwhile to study the photochemistry of dienones **1** and **2**.

Irradiation of an approximately 1% solution of **1** in either anhydrous or water-saturated ether with a Hanovia S 200-w lamp was carried out in Pyrex under a nitrogen atmosphere. The reaction was monitored using vpc or by ultraviolet spectroscopy (decrease in dienone absorption at 330 mμ and appearance of a new maximum at 270 mμ was observed). The major product, produced within a few hours and obtained in over 80% yield,[29] was a crystalline ketone shown to be 1,3,4,5,6,6-hexamethylbicyclo[3.1.0]hex-3-en-2-one (**18**). This was based on the following evidence. The empirical formula showed it to be isomeric with its precursor. The infrared spectrum showed expected bands[30] at 1690 and 1640 cm^{-1}, and the ultraviolet spectrum, with maxima at 235 mμ (ϵ 6270), 274 (3240), and 320 (605) was also consistent[30] with the structure. The nmr spectrum of **18** showed five singlets at τ 8.12, 8.45, 8.78, 8.90, and 9.08 with relative areas 1:1:1:2:1. The two low-field signals, on expanded scale were, in fact, each quartets, J = 1.0 cps, and are ascribed to the two allylic methyls which split each other.[18]

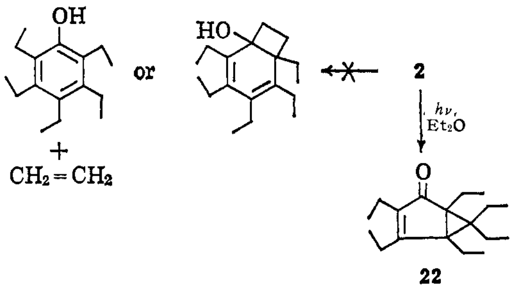


1 **18**

The structure of **18** was proved unequivocally by ozonolytic degradation. Oxidative hydrolysis of the ozonide gave a crystalline ketoacid **19** which showed $\nu_{\max}^{\mathrm{KBr}}$ at 1760 cm^{-1} due to acid carbonyl, 1855, 1810, and 3400 (broad) due to OH. The acid was esterified without further purification to give the methyl ester **20**, $\nu_{\max}^{\mathrm{CCl_4}}$ 1720 and 1705 cm^{-1}, due to ester and ketone carbonyl, respectively. The nmr of **20** showed the ester methyl at τ 6.34, ketone methyl at τ 7.90, and three other signals at τ 8.73, 8.80, and 8.90 for six, three, and three protons. Either **19** or **20**, when subjected to a bromoform reaction, afforded crystalline tetramethylcyclopropane-1,2-dicarboxylic anhydride (**21**) in good yield. The structure of **21** followed from its empirical formula and nmr spectrum, which in acetone-d_6 showed three singlets at τ 8.63 (six protons, due to the two equivalent methyls on the ring juncture), 8.70 (three protons, probably due to the geminal methyl *cis* to the anhydride ring[31]), and 8.77 (three protons due to the remaining geminal methyl). The infrared spectrum of **21** showed anhydride carbonyl bonds, $\nu_{\max}^{\mathrm{CCl_4}}$ at 1875, 1825 and 1775 cm^{-1}.



Dienone **2** was irradiated to determine whether the rearrangement was general. In this case, the ethyl groups provide hydrogens in a γ position relative to the carbonyl, which might allow hydrogen-transfer reactions to occur.[32] It was found, however, that **2** afforded **22**, the ethyl analog of **18**, as the principal photoproduct. No pentaethylphenol was produced, nor was there evidence for a cyclobutanol. The structure of **22** rests on spectroscopic data (see Experimental Section).



The conversion of **1** to **18** can be formulated as a 1,2 methyl migration (path A), or the methyls may retain their original positions and the reaction may be of the "bond-crossing" type (path B). These alternatives are shown in Scheme I, using ionic intermediates for convenience, and not necessarily as valid representations of the reactive species. It is seen that the two alternatives can readily be distinguished if the C-5 methyl is labeled.

Hexadeuterio-**1** containing deuterium at the C-3 and C-5 methyls was irradiated. This yielded hexadeuterio-**18**, the nmr spectrum of which lacked the peak at τ 8.12 (due to the allylic methyl at C-4; the other allylic methyl, τ 8.45, was now a singlet rather than a quartet). The peak at τ 8.90 was reduced in area to only three protons. Ozonolytic degradation led to a trideuterated anhydride **21**, whose nmr spectrum had three singlets, each corresponding to three protons, at τ 8.63, 8.70, and 8.77. This proved that the CD_3 originally at C-5 in **1** must have been at a ring juncture in **18** and ex-

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(27) For reviews, see (a) G. Quinkert, *Angew. Chem., Intern. Ed. Engl.*, **4**, 211 (1965); (b) P. deMayo and S. T. Reid, *Quart. Rev.* (London), **15**, 393 (1961); (c) O. L. Chapman, *Advan. Photochem.*, **1**, 344 (1963).

(28) H. Dutler, C. Ganter, H. Ryf, E. C. Utzinger, K. Weinberg, K. Schaffner, D. Arigoni, and O. Jeger, *Helv. Chim. Acta*, **45**, 2346 (1962); C. Ganter, E. C. Utzinger, K. Schaffner, D. Arigoni, and O. Jeger, *ibid.*, **45**, 2403 (1962); P. J. Kropp and W. F. Erman, *J. Am. Chem. Soc.*, **85**, 2456 (1963).

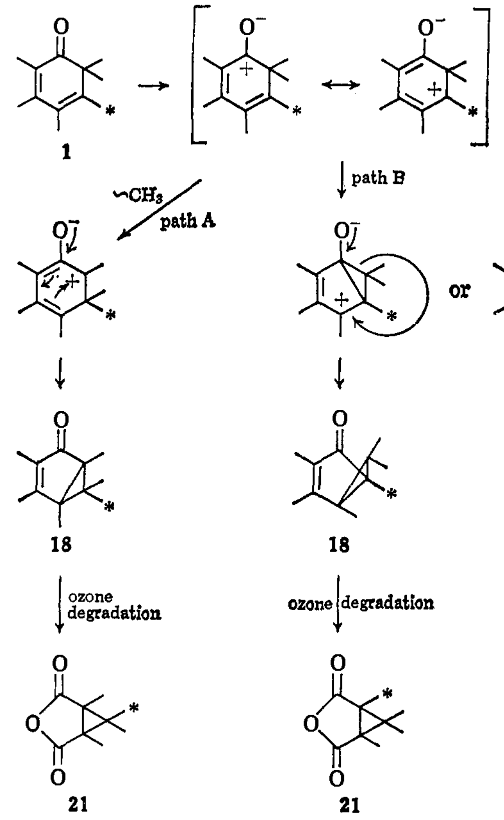
(29) The minor products, and products of over-irradiation in ether and in other solvents, will be discussed in detail in a separate paper (with D. Swatton and R. M. Lange).

(30) *Cf.* umbellulone, 1695 and 1620 cm^{-1}: $\lambda_{\max}$ 220 mμ (ϵ 5900), 265 3290), and 308 (200); R. H. Eastman, *J. Am. Chem. Soc.*, **76**, 4115 (1954); see also the first reference in footnote 28, and ref 11b for other examples.

(31) P. S. Wharton and T. I. Bair, *J. Org. Chem.*, 30, 1681 (1965).

(32) See ref 27c, p 371.

Scheme I



cludes the mechanism involving methyl migration. That the label was at the ring juncture α (and not β) to the carbonyl group is suggested by the plausible mechanisms which can be written for this transformation, and is proved by further work.[29]

The conversion of a 2,4-cyclohexadienone to a bicyclo[3.1.0]hexane (*i.e.*, **1** → **18**, **2** → **22**) is novel;[33] indeed, the reverse process has been established in several cases. Bicyclo[3.1.0]hexanes are frequently obtained on irradiation of 2,5-cyclohexadienones; further irradiation gives 2,4-cyclohexadienones and ultimately, *via* a ketene intermediate, open-chain unsaturated acid derivatives.[34]

It has been shown[26] that a 2,4-cyclohexadienone which is so heavily substituted that it will not undergo photolysis to a *trans*-diene–ketene sometimes undergoes slower photolytic rearrangement to different products. Thus our observations might be interpreted as follows: since the *trans*-diene–ketene from **1** would have an unfavored structure (due to 1,3-methyl interactions), the conversion to a bicyclic enone (*i.e.*, **18**) becomes energetically more favorable. However, this does not always appear to be so, since Kropp[11b] has claimed that bicyclic ketone **23c** is readily converted to dienone **23d**, but the latter is converted, on prolonged irradiation, to **23e**. The photoexcited state of **23d** should have a choice[35] between the transition state involved in the transformation of **23c** → **23d**, or the higher-energy transition state for the **23d** → **23e** conversion. The failure[36] to obtain bicyclic ketone **23c** when dienone **23d** was irradiated appears to be due to its photochemical instability. Therefore it might be that some 2,4-cyclohexadienones that appear to give diene–ketenes by a preferred route do so only because the bicyclic enones, formed in a more facile process, are photochemically reconverted to starting material.

Finally, it should be pointed out that rearrangements of the type herein reported have been observed with hydrocarbon analogs of 2,4-cyclohexadienones (*i.e.*, compounds in which the carbonyl oxygen is replaced by carbon); for example, irradiation of dehydroergosterol gives photodehydroergosterol.[37] In such triene rearrangements, a $\pi \rightarrow \pi^*$ transition must certainly be involved in the excitation. The analogous behavior of highly alkylated dienones suggests that either the type transition may be altered from the usual,[38] or that the multiplicity of the excited state may be altered. An investigation of hydrocarbon analogs of certain dienones is in progress.[39]

Experimental Section

The nmr spectra were obtained with a Varian A-60 spectrometer. The chemical shifts are τ values measured from tetramethylsilane as an internal standard. Analysis by vpc was carried out on columns of 5- or 10-ft lengths, packed with SE 30, 20% on Chromosorb W, at ~170°.

2,3,4,5,6,6-Hexamethyl-2,4-cyclohexadienone (1). Peroxytrifluoroacetic acid,[40] prepared from 9.75 ml of trifluoroacetic anhydride and 1.63 ml (0.06 mole) of 90% hydrogen peroxide in 30 ml of methylene chloride at 0°, was added dropwise to a stirred solution of 9.7 g (0.06 mole) of hexamethylbenzene in 100 ml of methylene chloride at 0 to 5° during 45 min. Boron trifluoride (0.06 mole) was bubbled into the reaction mixture at the same rate as the oxidant addition, the gas volume being determined with a flowmeter. After stirring for 35 min, 30 ml of ice-water was added and the organic layer washed with aqueous sodium bicarbonate and water and then dried. Evaporation afforded a crude product, which was dissolved in 70 ml of ethanol and cooled at 0° for several hours. Any hexamethylbenzene which crystallized was then filtered off. The ethanol solution was then evaporated to an oil which was distilled, bp 85° (1.0 mm), 9.7 g, 88%. On storage at 0° the distillate solidified: $\lambda_{\max}^{\mathrm{EtOH}}$ 330 mμ (ϵ 4500); $\nu_{\max}^{\mathrm{CCl_4}}$ 1642, liquid film 1647 and 1567 cm^{-1} (C=O and C=C, conjugated). The nmr spectrum consisted of three signals, τ 8.89 (s), 8.14 (broad), and 7.97 (q) with relative areas 2:3:1. The peaks were assigned, respectively, to the *gem*-dimethyl at C-6, the three allylic methyls at C-2, C-4, and C-5, and the methyl on C-3. The low-field signal was

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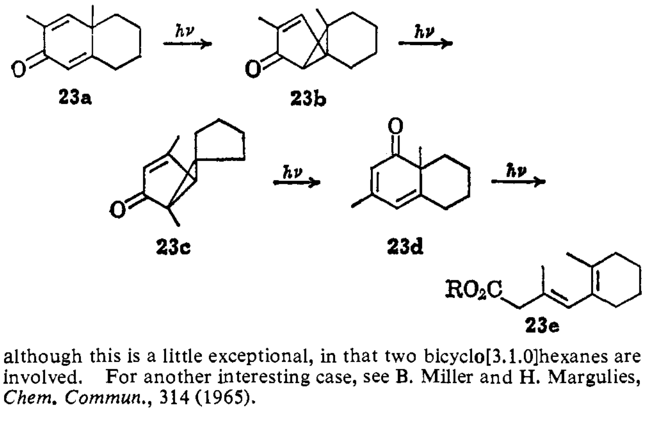
(33) See, for example, ref 11b, footnote 22.

(34) An example[11b] would be



although this is a little exceptional, in that two bicyclo[3.1.0]hexanes are involved. For another interesting case, see B. Miller and H. Margulies, *Chem. Commun.*, 314 (1965).

(35) This choice should be available since most mechanistic explanations in dienone photochemistry are based on a continuous electron redistribution in the photoexcited state; see H. Zimmerman, ref 27c, p 188.

(36) The ester **23e** (R = CH_3) was obtained[11b] in 43% yield from **23d** in methanol. The possible presence of **23c** in the photoproduct was not mentioned.

(37) D. H. R. Barton and A. S. Kende, *J. Chem. Soc.*, 688 (1958).

(38) M. H. Fisch and J. H. Richards, *J. Am. Chem. Soc.*, **85**, 3029 (1963).

(39) For some preliminary results, see H. Hart, A. J. Waring, P. Collins, and R. Lange, Abstracts, 149th National Meeting of the American Chemical Society, Detroit, Mich., April 1965, p 51P.

(40) W. D. Emmons, *J. Am. Chem. Soc.*, 76, 3468 (1954).

shown, when examined at a sweep width of 100 cycles, to be a poorly resolved quartet with peak separation of 0.8 cps.

Anal. Calcd for $C_{12}H_{18}O$: C, 80.86; H, 10.18. Found: C, 80.76; H, 10.03.

An Alternative Preparation. Hexamethylbenzene (31.2 g, 0.2 mole) in a slurry with 300 ml of acetic acid, 200 ml of sulfuric acid, and 50 ml of methylene chloride was stirred while the oxidant, 7 ml (0.23 mole) of 90% hydrogen peroxide in a solution of 45 ml of acetic acid and 30 ml of sulfuric acid, was added during 15 min. The reaction temperature did not exceed 30°. After 2.5 hr the acid solution was poured onto 2 l. of ice and extracted into 2 l. of methylene chloride. The organic layer was worked up in the usual way. Evaporation yielded an oil, 34.2 g (99%), which on distillation gave 23 g (73%) of dienone contaminated with 2% of hexamethylbenzene. The pot residue afforded an additional 2 g (6%) of hexamethylbenzene.

Diels–Alder Adduct 3. The dienone **1** (0.45 g) in 5 ml of anhydrous ether was heated under reflux with 0.25 g of maleic anhydride for 5 hr. Work-up gave crystals which, after recrystallization from 5 ml of petroleum ether (bp 60–90°), had mp 140–141°.

Anal. Calcd for $C_{16}H_{20}O_4$: C, 69.5; H, 7.3. Found: C, 69.17; H, 6.79.

The infrared spectrum (Nujol mull) showed $\nu_{\max}$ at 1770 and 1852 cm^{-1} (five-membered ring anhydride) and at 1695 cm^{-1} (six-membered ring ketone). The nmr spectrum showed two singlets at τ 9.00 and 8.97 (*gem*-dimethyl), singlets at τ 8.50 and 8.43 (bridgehead methyls), quartets at τ 8.32 and 8.23 (J = 1 cps, allylic methyls), and an AB quartet at τ 7.07 and 6.77 (J = 9.0 cps, hydrogens derived from maleic anhydride).

Hexadeuterio-**1**, labeled at C-3 and C-5 (see footnote 16), was also converted to its maleic anhydride adduct. The nmr spectrum differed from that of unlabeled **3** in the following ways: the bands at τ 8.43 and 8.32 were absent, and the band at τ 8.23 was a singlet. Thus the high-field allylic and bridgehead methyls are adjacent to the carbonyl group, a somewhat unexpected result.

Ethyl Azodicarboxylate Adduct 4. A mixture of 2 g each of dienone **1** and ethyl azodicarboxylate was warmed at 45° (water bath) for 36 hr, then cooled. The crystalline product was recrystallized from hexane, yielding 3.3 g (83%) of white cubic crystals, mp 109–110.5°.

Anal. Calcd for $C_{16}H_{28}N_2O_5$: C, 61.4; H, 8.02; N, 7.96. Found: C, 61.35; H, 8.06; N, 7.88.

The infrared spectrum showed broad carbonyl absorption from 1700 to 1740 cm^{-1}.

2,3,4,5,6,6-Hexaethyl-2,4-cyclohexadienone (2). Hexaethylbenzene (34.1 g) was oxidized by the peroxytrifluoroacetic acid–boron fluoride method reported above for the methyl analog. After recovery of hexaethylbenzene (4 g, 12%), the crude product was distilled, giving an oil which crystallized (29.6 g, 82%). Recrystallization from *n*-hexane gave material which had mp 44–45°; $\lambda_{\max}^{\mathrm{EtOH}}$ 339 mμ (ϵ 11,000); $\nu_{\max}^{\mathrm{KBr}}$ 1635 and 1560 cm^{-1} (C=O and C=C, conjugated). The nmr spectrum consisted of a multiplet at τ 7.28–8.00 (eight allylic methylenes), a quartet at τ 8.00–8.30 (four methylenes of the *gem*-diethyl group, J = 7.0 cps), a multiplet at τ 8.30-9.20 (12 methyl protons), and a triplet centered at τ 9.52 (J = 7.0 cps, two methyls of the *gem*-diethyl group).

Anal. Calcd for $C_{18}H_{30}O$: C, 82.5; H, 11.55. Found: C, 82.34; H, 11.35.

2,4,5,6,6-Pentamethyl-3-methyl-*d*$_3$-2,4-cyclohexadienone. The dienone **1** (2.0 g) was dissolved in 10 ml of methanol-*d* containing ~0.2 g of sodium.[41] Monitoring the solution by examination of its nmr spectrum showed that the methyl signal at τ 7.95 disappeared in less than 10 min at room temperature. During this time a gain, equivalent to three protons, was observed in the hydroxyl signal. No further change in the nmr spectrum occurred after several hours. The trideuterio dienone was isolated by pouring the solution into 200 ml of methylene chloride and washing with ice water (three 25-ml portions). Any residual base was removed with solid CO_2. After drying, the solution was evaporated to an oil, which was purified by distillation, yielding 1.7 g (85%), bp 100–105° (2 mm). A forerun boiling at a lower temperature was rejected. The vpc retention time of the product was identical with that of undeuterated dienone. The nmr spectrum consisted of two signals at τ 8.89 (s) and 8.14 (slightly split) with relative areas 2:3. These were assigned respectively to the *gem*-dimethyls and the allylic methyls at C-2, C-4, and C-5.

2,4,6,6-Tetramethyl-3,5-dimethyl-*d*$_6$-2,4-cyclohexadienone. C-3 trideuterated dienone (1.1 g) was added to a solution of 0.32 g of potassium *t*-butoxide in 5 ml of dimethyl sulfoxide-*d*$_6$. The solution became deep red immediately and remained so. The nmr spectrum of the solution changed during 6 hr at room temperature. The red-brown solution was poured into 300 ml of methylene chloride and worked up in the usual way. Analysis by vpc of the crude oil showed it contained an impurity with a short retention time. This was removed by heating the crude oil at 80° for 20 min at 0.3 mm. Analysis of the residual oil showed it to be 98% dienone, whereas the condensed vapor was mainly the material with the short retention time. The infrared spectrum of the deuterated dienone was similar to that of the protonated dienone except for a weak broad peak at 2500 cm^{-1} and minor differences in the 850–1100-cm^{-1} region. The nmr spectrum was consistent with the structure, showing peaks which had relative areas 2:1:1 at τ 8.87 (singlet, *gem*-dimethyl) and 8.13 and 8.17 (singlets, allylic methyls).

A lower yield of product was obtained when 0.07 g of the trideuterio dienone was heated in 0.8 ml of methanol-1-*d* containing 0.1 g of sodium for 48 hr at 60°. Vpc analysis of the crude product indicated a 50% recovery of dienone which, after purification, was shown by its nmr spectrum to be hexadeuterated.

2,3,4,6,6-Pentamethyl-5-methyl-*d*$_3$-2,4-cyclohexadienone. The hexadeuterated dienone (0.1 g) was treated with unlabeled methanol and sodium in the manner reported above. After purification by vpc the nmr spectrum showed the following features: a three-proton signal at τ 7.97, which at a sweep width of 100 cps was shown to be a poorly resolved quartet with a peak separation of 0.8 cps, due to the methyl at C-3. At τ 8.13 there was a peak joined to the broad signal centered at τ 8.17 (six protons altogether). The visible part of this last signal was shown, at a sweep width of 100 cps, to have a shape similar to the signal at τ 7.97. The singlet due to the *gem*-dimethyls appeared at τ 8.89.

Catalytic Reduction of 1. A solution of 2.3 g of **1** in 50 ml of ethanol was added to 0.2 g of prereduced Adams platinum oxide catalyst. After 1 mole of hydrogen was consumed, the solvent was evaporated to yield a mixture of products which were separated by vpc on a 10-ft column packed with 20% SE-30 on 60–80 Chromosorb W. The two components, formed in 70–80% and 20–10% yield, respectively, were collected.

The major component showed $\lambda_{\max}^{\mathrm{EtOH}}$ 245 mμ (ϵ 8500); $\nu_{\max}^{\mathrm{CCl_4}}$ 1665 cm^{-1} (very strong) with shoulders at 1630 and 1640 cm^{-1}; a liquid film showed $\nu_{\max}$ 1660 cm^{-1} (very strong) and a shoulder at 1630 cm^{-1} (conjugated C=O).

Anal. Calcd for $C_{12}H_{20}O$: C, 79.93; H, 11.18. Found: C, 80.08; H, 11.04.

The compound is considered to be 2,3,4,5,6,6-hexamethyl-2-cyclohexenone. The nmr spectrum showed a doublet centered at τ 9.15, J = 7.0 cps (three protons), due to the C-5 methyl coupled to a proton at lower field, two singlets at τ 9.00 (three protons) and 8.92 (three protons) due to the geminal methyls at C-6, and a doublet centered at τ 8.87, J = 7.0 cps (three protons), due to the methyl at C-4 coupled with a lower field proton. Two multiplets centered at τ 8.28 (three protons; six peaks visible) and 8.12 (three protons; four peaks visible) were due to the allylic methyls at C-2 and C-3, respectively. All the peaks comprising the two single protons at C-4 and C-5 were not completely visible, but integration showed one proton between the limits τ 9.00 and 8.50 and the other between τ 8.50 and 7.67. The latter was undoubtedly the allylic proton at C-4. Further interpretation of this spectrum becomes possible from a study of deuterated analogs (*vide infra*).

The second component showed $\lambda_{\max}^{\mathrm{EtOH}}$ 285 mμ (ϵ 43); $\nu_{\max}^{\mathrm{CCl_4}}$ 1705 cm^{-1} (C=O) with a shoulder at 1670 cm^{-1} (C=C).

Anal. Calcd for $C_{12}H_{20}O$: C, 79.93; H, 11.18. Found: C, 79.88; H, 11.23.

The compound is considered to be 2,3,4,5,6,6-hexamethyl-3-cyclohexenone. The nmr spectrum shows a doublet centered at τ 9.17, J = 7.5 cps (three protons), due to the C-5 methyl coupled with a lower field proton, two singlets at τ 9.17 (three protons) and 8.87 (three protons) due to the geminal methyls at C-6, and a doublet centered at τ 8.87, J = 7.5 cps, due to the methyl at C-2 coupled with a lower field proton. The two allylic methyls at C-3 and C-4 exhibit a complex multiplet (at least nine peaks), $W_h \leqq$ 7 cps, centered at τ 8.32 (six protons). The two allylic protons exhibit two distinct, broadened quartets. The one at C-5 is centered at τ 8.25, J = 7.5 cps, whereas the proton at C-2, which

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[41] F. W. Hobden, E. F. Johnston, L. H. P. Weldon, and C. L. Wilson, *J. Chem. Soc.*, 61 (1939). The methanol-*d* had bp 65–78° because of D_2O present which, however, was of no inconvenience. The isotopic purity was always better than 97% as ascertained by comparing the OH signal with the ^{13}C satellites.

is both allylic and α to the carbonyl group, is at lower field, centered at τ 7.43, J = 7.5 cps.

Reduction of 2,4,5,6,6-Pentamethyl-3-methyl-d_3-2,4-cyclohexadienone. Dienone obtained by exchange of **1** with CH_3OD–$NaOCH_3$ at room temperature, as described above, was reduced with H_2–Pt, and the two products were separated by vpc as with the unlabeled material. The nmr spectrum of the Δ^2-enone showed the following differences from unlabeled material. The multiplet at τ 8.12 was missing, and the multiplet at τ 8.28 was now a doublet centered at τ 8.32, J = 2.0 cps. This splitting is due to homoallylic coupling with the proton at C-4. The *trans* arrangement of the C-2 methyl and C-4, and the approximately 90° angle between the C–H bonds and the plane of the double bond are well arranged to give strong coupling. It should be noted that the methyls at C-4 and C-5 are probably *cis* in the Δ^2-enone.

The nmr spectrum of the Δ^3-enone showed the following differences from unlabeled material. The six-proton multiplet at τ 8.32 was now a doublet centered at τ 8.28, J = 1.7 cps (three protons), due to coupling of the C-4 methyl group with the proton at C-2.

Reduction of 2,4,6,6-Tetramethyl-3,5-dimethyl-d_6-2,4-cyclohexadienone. Dienone obtained by exchange of trideuterio-**1** with potassium *t*-butoxide in dimethyl sulfoxide-d_6 as described above, was reduced with H_2–Pt, and the two products were separated by vpc as with the unlabeled material. The nmr spectrum of the Δ^2-enone was like that of its trideuterio analog, except that the doublet at τ 9.15 ascribed to the C-5 methyl was missing. Similarly, the doublet at τ 9.17 was missing from the spectrum of the Δ^3-enone.

2,3,4,5,6,6-Hexamethyl-2,4-cyclohexadien-1-ol (11). Hexamethyldienone **1** (4.0 g) in 110 ml of anhydrous ether was heated under reflux with 0.8 g of lithium aluminum hydride for 3 hr. After cooling, water was added and the ethereal solution filtered. The hydroxide residue was twice extracted with 100 ml of ether. Evaporation afforded 3.83 g (95%) of an oil, which solidified: λ_{max}^{hexane} 262 mμ (ϵ 9380), ν_{max}^{KBr} 3350 (broad) (OH) 1660 cm^{-1} (C=C conjugated). The nmr spectrum of a pyridine solution showed six peaks with relative areas 1:1:3:9:3:3 at τ 5.03 (s, hydroxyl proton), 6.40 (s, proton at C-1), 8.0 (s, $W_h \cong$ 4.5 cps), 8.33 (s, $W_h \cong$ 8 cps) (four allylic methyls), 8.77 and 9.0 (singlets, two *gem*-dimethyls). Addition of D_2O caused the signal at τ 5.03 to shift to τ 4.83. In carbon tetrachloride signals appeared at τ 6.87 (1 H), 7.82 and 7.97 (12 H), 8.60 and 8.63 (4 H), 8.85 (3 H), the respective assignment being the C-1 proton, four allylic methyls, hydroxyl, and *gem* dimethyls.

2,3,4,6,6-Hexaethyl-2,4-cyclohexadien-1-ol (13). The hexaethyldienone **2** (5.5 g) was treated with lithium aluminum hydride as reported above. The oily product (5.25 g, 89%) had bp 105° (0.07 mm); λ_{max}^{EtOH} 262 mμ (ϵ 2700); $\nu_{max}^{CCl_4}$ 3620 (sharp), 3500 (weak, monomeric and bonded OH), 1695, 1645 cm^{-1} (C=C, conjugated); the liquid film infrared spectrum showed bands at 3600 (weak), 3495 (strong), 1690, and 1640 cm^{-1}. The nmr spectrum showed an AB quartet (τ 5.98 and 6.28, J = 8 cps) in pyridine and (τ 6.58 and 6.85, J = 8 cps) in dimethyl sulfoxide-d_6. Addition of D_2O to the pyridine solution produced two sharp singlets at τ 5.17 and 6.27. Accordingly, the low-field component of the quartet was assigned to the hydroxyl proton and the high-field component to the proton on C-1. In both these solvents a complex signal appeared at high field, owing to the ethyl protons.

1,2,4,5,6,6-Hexamethyl-3-methylene-1,4-cyclohexadiene (8). Hexamethyldienone **1** (1.78 g) in 5 ml of ether was added dropwise to a stirred methyl Grignard solution at 25°. This was prepared from 1.56 g of methyl iodide and 0.27 g of magnesium in 35 ml of ether. The solution was then heated under reflux for 30 min. After using aqueous ammonium chloride to decompose the Grignard reagent and working up, a crude oil was obtained. This was purified by dissolving it in 30 ml of pentane and extracting the heptamethylbenzenonium chloride into concentrated hydrochloric acid (three 20-ml portions). The acid extract was then poured onto 50 g of ice, neutralized with sodium bicarbonate, and reextracted with *n*-pentane. This yielded a partially crystalline material (1.1 g) which upon sublimation gave crystals: mp 36–44°; $\lambda_{max}^{isooctane}$ 256 mμ (ϵ 21,400); λ_{max}^{HCl} 400 and 288 mμ (ϵ 11,000 and 7230); $\nu_{max}^{CCl_4}$ 1680, 1613, and 1560 cm^{-1} (C=C, conjugated). The nmr spectrum in carbon tetrachloride exhibited signals at τ 5.23 (s), 8.22 (s), and 8.91 (s), the relative areas being 1.8:12:6.4, respectively. In concentrated hydrochloric acid, the nmr spectrum showed τ 6.49 (s), 6.69 (s), 6.99 (s), and 7.80 (s), with relative areas 2.6:5.9:6.3:6.1, respectively. The reported[20] constants are mp 47°, λ_{max} 257 mμ (ϵ 18,600) in isooctane, λ_{max} 397 and 287 mμ (ϵ 8520 and 6760) in concentrated hydrochloric acid. The chemical shifts of the signals in carbon tetrachloride obtained in this work are at 0.77 ppm higher field from those calculated from the earlier results, although the relative positions and areas of the peaks are identical. The discrepancy could be due to the difference in chemical shifts between an internal standard and one in a capillary. It can be seen that the chemical shifts reported here are much closer to those expected for a compound with structure **8** than the values in the earlier report[20] (*e.g.*, terminal methylene at τ 5.23 compared with 4.46). In concentrated hydrochloric acid the chemical shifts from TMS in a capillary, observed in this work, were all about 0.34 ppm upfield from those reported earlier.[20]

1,2,4,6,6-Pentamethyl-3-methylene-1,4-cyclohexadiene (12). Hexamethyldienol (**11**) (1.0 g) in 30 ml of pyridine containing 0.4 ml of concentrated hydrochloric acid was heated at 60° for 1 hr. The solution was poured into methylene chloride and worked up, yielding a yellow oil. Alternatively, if the crude dienol, formed in the lithium aluminum hydride reduction of the dienone, is allowed prolonged contact with laboratory air, the triene **12** is formed, contaminated with water. The crude oil obtained by either route was distilled, bp 55–60° (0.1 mm). Distillation of this material was always accompanied by sublimation of hexamethylbenzene, which was presumably formed by thermal rearrangement of the triene. The triene had λ_{max} 253 mμ (ϵ 19,700) in isooctane; $\nu_{max}^{CCl_4}$ 1680, 1613 (C=C, conjugated), 1390, 1350 (*gem*-dimethyl), and 862 cm^{-1} (terminal methylene).

Anal. Calcd for $C_{12}H_{18}$: C, 88.8; H, 11.2. Found: C, 88.63; H, 11.38.

The nmr spectrum, in pyridine, showed bands centered at τ 4.48 (s), 5.04 (m, $W_h \cong$ 5 cps), 8.15 (m, $W_h \cong$ 15 cps), and 8.93 (s) with areas 1:2:9:6, respectively. In carbon tetrachloride the band positions were centered at τ 4.55 (s), 5.16 (m), 8.17 (m), and 8.93 (s). The relative areas were the same as those for the pyridine solution. The interpretation of the spectra from both solutions is similar and the bands can be assigned, respectively, commencing at low field, to a ring vinyl proton, two methylene protons, three allylic methyls, and the *gem*-dimethyls.

1,2,4,6,6-Pentaethyl-3-ethylidene-1,4-cyclohexadiene (14). Hexaethyldienol **13** (1.5 g) was treated with pyridine containing hydrochloric acid in the same way as outlined above. This gave an oil (1.3 g) contaminated with some hexaethylbenzene, which was best removed by allowing it to crystallize and decanting the supernatant oil. (Distillation, bp 80° (0.07 mm), vpc, and tlc, on silica gel with *n*-hexane were not successful methods or purification, owing to the ease of rearrangement of the triene to hexaethylbenzene.) The residual oil had λ_{max} 259, 233 (shoulder), and 213 mμ (ϵ 11,900, 5500, and 10,700); $\nu_{max}^{CCl_4}$ 1700, 1660, 1630 (C=C, conjugated), and 950 cm^{-1} (terminal vinyl). The nmr spectrum showed a complex multiplet between τ 4.77 and 5.17 and at high field there was a complex signal. The relative areas are 1:14. The low-field signals must be due to the vinyl ring proton and the exocyclic vinyl proton, the latter split by the terminal methyl.

Dehydration of Dienols in Various Solvents. The dienol, about 100 mg, was dissolved in 0.4 ml of the solvent and the nmr spectrum measured. In some cases acid was added and the effect of the rate of dehydration and the product composition was studied. The results are collected in Table II.

Kinetics of Triene Aromatization. The rearrangement of trienes **12** or **14** to hexaalkylbenzenes was followed spectrophotometrically (ultraviolet), by measuring the decrease in absorbance of the triene at 255 mμ. A solution of triene in ethanol at 32.00 ± 0.04°, the temperature at which all reactions were run, was added to an ethanolic hydrogen chloride solution at the same temperature. The concentrations of the stock solutions were such that the initial absorbance was 0.95 and the acid concentration was either 0.022 or 0.041 *M*. The reactions were followed to at least 60% completion and first-order rate constants determined at periods throughout the reaction. Good rate constants were obtained for the methyl triene **12**; 10^4k was 3.9 and 7.7 sec^{-1} in 0.022 and 0.041 *M* acid, respectively. For the ethyl triene **14**, however, the rate constants decreased as the reaction proceeded; *e.g.*, 10^3k was 2.4 sec^{-1} at 10% reaction and 1.2 sec^{-1} at 70% reaction in 0.022 *M* acid and similarly 4.6 sec^{-1} at 10% reaction and 2.2 sec^{-1} at 60% reaction in 0.041 *M* acid.

Photolysis Procedure. Apparatus. Irradiations were carried out using a Hanovia Type S 200-w lamp. This was placed in a quartz water jacket which fitted into a Pyrex vessel of slightly larger diameter. The annular space so formed held about 450 ml of solution which could be agitated by a flow of nitrogen gas.

(a) **Hexamethyldienone 1.** Dienone (3 g) in 400 ml of anhydrous ether agitated with a nitrogen gas flow was irradiated with a

Hanovia Type S 200-w lamp through a Pyrex filter until ultraviolet or vpc analysis of the irradiated solution showed maximum product formation (about 5 hr). The retention time of the photo product on a 10-ft vpc column was 6.3 min and for the dienone, 7.8 min. After solvent removal the crude oil obtained was distilled, bp 60° (0.5 mm), to give 1.5 g (50%) of a crystalline product **18** which on further purification by vpc or sublimation had mp 50–52°; λ_{max}^{EtOH} 235, 274, and 320 mμ (shoulder) (ε 6270, 3240, and 605, respectively); $\nu_{max}^{CCl_4}$ 1690 and 1640 cm^{-1}.

Anal. Calcd for $C_{12}H_{18}O$: C, 80.86; H, 10.18. Found: C, 81.11; H, 10.15.

The nmr spectrum showed five singlets at τ 8.12, 8.45, 8.78, 8.90, and 9.08, with relative areas 1:1:1:2:1. Measurement of the spectrum at a sweep width of 100 cycles showed the two signals at low field to be quartets with peak separation equal to 1 cps.

(b) **Hexaethyldienone 2.** The photolysis procedure was similar to that reported above. The reaction was monitored only by ultraviolet analysis, since the product was shown to be reconverted to starting material by repeated passages through the vpc column or by prolonged heating. Purification of the crude material was best achieved by vpc, since decomposition occurring after the detector stage of the instrument would be small. This yielded material **22** with λ_{max}^{EtOH} 239, 270, and 332 mμ (ε 5300, 2660, and 850); ν_{maz} 1638 and 1680 cm^{-1} liquid film. The nmr spectrum consisted of two complex multiplets running approximately from τ 7.4 to 8.0 (four allylic methylenes) and τ 8.67 to 9.35 (remaining 24 protons).

Degradation of Hexamethylbicyclo[3.1.0]hex-3-en-2-one. The bicyclo derivative **18** (1.2 g) in 170 ml of methylene chloride was treated at −20° with ozone gas for 1 hr. The blue solution was evaporated to an oil, which was then refluxed for 2 hr with 150 ml of water, 1.5 ml of 30% hydrogen peroxide, and 3 ml of 1 *M* sodium hydroxide. The aqueous solution was then filtered from any residual gum (<50 mg), and 1 *N* sulfuric acid was added to adjust the pH to 4.0. The product was extracted into ether, which upon evaporation afforded a crystalline keto acid **19** (0.85 g, 82%) showing ν_{maz}^{KBr} 3400 (broad, OH), 1855, 1810, and 1760 cm^{-1}. Esterification of this acid was accomplished with diazomethane. Vpc analysis of the crude ester showed it to be at least 80% one compound. A sample, which was purified by vpc, had $\nu_{max}^{CCl_4}$ at 1720 and 1705 cm^{-1} and bands in the nmr spectrum at τ 6.34 (ester methyl), 7.90 (ketone methyl), 8.73, 8.80, and 8.90 with relative areas 1:1:2:1:1.

The methyl keto ester **20** was dissolved in 12 ml of dioxane and added dropwise during 30 min to an aqueous solution of sodium hypobromite at 0°. This was prepared from 3.0 g of sodium hydroxide in 4 ml of water and 1.2 ml of bromine. The aqueous dioxane solution was then heated at 35° for 15 min, and after cooling the excess hypobromite was removed with sodium bisulfite. The solution was extracted with ether which removed material (80 mg) that was shown to contain only 10% of the required product. This was discarded. The acidified aqueous solution was then extracted with ether and this afforded crude crystalline anhydride **21** (0.45 g, 65%). After recrystallization from ether the crystals had mp 144–145°; $\nu_{max}^{CCl_4}$ 1875, 1825, and 1775 cm^{-1}.

Anal. Calcd for $C_9H_{12}O_3$: C, 64.3; H, 7.20. Found: C, 64.87; H, 7.51.

The nmr spectrum in acetone-d_6 had singlets at τ 8.63, 8.70, and 8.77 with relative areas 2:1:1. These can be assigned to the equivalent methyls at the ring junctions, the *cis* and then the *trans gem*-methyls. The spectrum in carbon tetrachloride, however, showed only two peaks at τ 8.65 and 8.83 with relative areas 3:1.

Reactions of Carbodiimides. I. The Mechanisms of the Reactions of Acetic Acid with Dicyclohexylcarbodiimide[1,2]

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Received March 27, 1965

Abstract: The mechanisms of the reactions of dicyclohexylcarbodiimide (DCC) and of diisopropylcarbodiimide with acetic acid in acetonitrile and in carbon tetrachloride have been studied. Previously reported products for the reaction of acetic acid with DCC are acetic anhydride, dicyclohexylurea, and acetyldicyclohexylurea, and these have now been shown to account quantitatively for reactants. Furthermore, it has been found that the relationship between product yields and initial concentrations of acetic acid and of DCC can be predicted accurately from eq 1–3 with a k_2/k_3 ratio of about 60 mole^{-1} l. in acetonitrile and about 400 in carbon tetrachloride. The ratios may be regarded as empirical parameters. The possibility has been investigated that the acylurea might arise in part from reaction of acetic anhydride with carbodiimide or from acylation of urea, but both of these have been excluded. In acetonitrile the reaction is first order in carbodiimide and somewhat higher than first order in acetic acid. The reaction is about 30 times faster in carbon tetrachloride than in acetonitrile. This unusual result, the order with respect to acetic acid, and several trends of product yields can be accounted for on the basis that acetic acid dimer reacts more rapidly with carbodiimide than does the monomer. Predictions based on a mechanism consisting of eq 1–5 are quantitatively in accord with product data in acetonitrile at 30° with $k_1 = 0.013$ mole^{-1} l. sec^{-1}, $k_2/k_3 = 60$ mole^{-1} l., $K_4 = 0.5$ mole^{-1} l., $k_5/k_1 = 10$. The monomer–dimer equilibrium constant for acetic acid in acetonitrile has been found to be 0.5 mole^{-1} l.

Carbodiimides have a cumulative double-bond system which reacts with many types of functional groups.[4] They have been particularly valuable in the synthesis of peptides[5,6] and of nucleotides[7] because of their capability of effecting acylations under mild conditions.

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(1) This work received principal support from Research Grant RG 7828 of the Public Health Service.

(2) This work was also supported in part by Contract No. AT-(40-1)-2690 under the Division of Biology and Medicine, U. S. Atomic Energy Commission.

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