The Effect of Methyl Groups on the Photolysis of Dienones: Pentamethylcyclohexa-2,4-dienones

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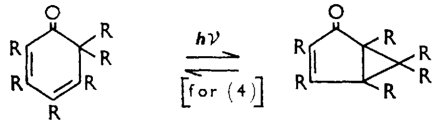
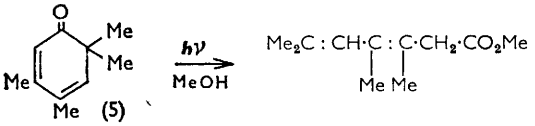
Pentamethylbenzene has been oxidised with peroxytrifluoroacetic acid–boron fluoride in methylene chloride to give mainly a mixture of pentamethylcyclohexa-2,4-dienones. The 2,4,5,6,6,- and 2,3,4,6,6-pentamethyl isomers were formed in yields of 33 and 37%, respectively, and the 3,4,5,6,6-pentamethyl isomer was formed in 7% yield. The 2,3,5,6,6-pentamethyl isomer was not isolated. The oxidation mechanism suggested is consistent with these results. The three dienones all gave Diels–Alder adducts with maleic anhydride, and these assist in the structure elucidation. Duroquinone, 2,3,4,4,6-pentamethylcyclohexa-2,5-dienone, and *p*-hydroxytetramethylbenzaldehyde have all been isolated from the oxidation in yields of about 7%. Irradiation of 2,3,4,6,6-pentamethylcyclohexa-2,4-dienone in ether or methanol afforded a bicyclo[3,1,0]hexane derivative. This reaction is thermally reversible. The 2,4,5,6,6- and 3,4,5,6,6-pentamethyl isomers were photochemically inert in ether, but in methanol the latter underwent ring opening to give a methyl dienoate while the former compound gave two major products—a bicyclo[3,1,0]hexane derivative and a second methyl dienoate.

HEXAMETHYL- and HEXAETHYLCYCLOHEXA-2,4-DIENONES (1) and (2) undergo photoisomerisation, in ether or methanol, to bicyclo[3,1,0]hexanones (3) and (4) respectively.[1,2] The mechanism has been shown, by suitable labelling experiments,[2] to involve "bond-crossing," rather than alkyl migration. On the other hand, the tetramethyldienone (5) was photochemically inert in anhydrous or moist ether but gave the usual Barton–Quinkert[3,4] type of photochemical ring opening in methanol.[5]



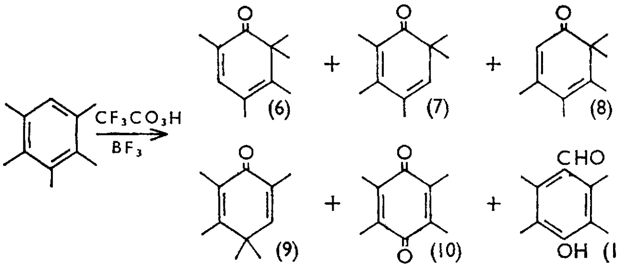
(1) R = Me (3) R = Me
(2) R = Et (4) R = Et



Since the presence or absence of methyl groups in positions 2 and/or 5 seemed critical in determining the photochemical path taken by the dienone, it was desirable to study the photolysis of dienones in which only one or the other of these two positions was substituted. This Paper describes the synthesis and photolysis of pentamethylcyclohexa-2,4-dienones in which position 2, 3, or 5 is substituted.

Oxidation of Pentamethylbenzene.—The most reasonable synthetic approach to the desired dienones appeared to be the electrophilic oxidation of pentamethylbenzene. It has already been shown that oxidation of completely substituted benzenes (*i.e.*, hexamethylbenzene) affords the corresponding dienones in excellent yields.[2,6] Indeed, even less substituted benzenes, such as prehnitene[7] and durene,[5] were oxidised with peroxytrifluoracetic acid and boron fluoride, to dienones, the yield in the latter case being quite respectable.

Accordingly pentamethylbenzene was oxidised at −5 to 0° with a mole equivalent of peroxytrifluoroacetic acid in methylene chloride. Boron trifluoride etherate was added at an equal molar rate to that of the oxidant. This oxidised 75% of the pentamethylbenzene. More forcing conditions such as higher reaction temperature or an excess of oxidant achieved greater conversions, without an increase in concentration of the primary oxidation products. The products (6—11) were separated by a combination of distillation and vapour-phase chromatography (v.p.c.).



The composition of the crude reaction mixture was determined by v.p.c. and is calculated on a 75% conversion of pentamethylbenzene. The two major components were 2,4,5,6,6-pentamethylcyclohexa-2,4-dienone (6) 33% and the 2,3,4,6,6-pentamethyl isomer (7) 37%. The other compound in this class was 3,4,5,6,6-pentamethylcyclohexa-2,4-dienone (8), formed in 7% yield. Thus the two dienones (7) and (8) required for photolysis became available. The remaining possible dienone (12) was not detected. Three other products were identified, the cross-conjugated dienone (9) (7%), duroquinone (10) (7%), and *p*-hydroxytetramethylbenzaldehyde (11) (7%).

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[1] H. Hart and A. J. Waring, *Tetrahedron Letters*, 1965, 325.

[2] H. Hart, P. M. Collins, and A. J. Waring, *J. Amer. Chem. Soc.*, 1966, **88**, 1005.

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

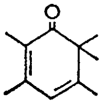
[4] For a Review, see G. Quinkert, *Angew. Chem. Internat. Edn.*, 1965, **4**, 211; P. deMayo and S. T. Reid, *Quart. Rev.*, 1961, **15**, 393; O. L. Chapman, *Adv. Photochem.*, 1963, **1**, 344.

[5] H. Hart and R. M. Lange, *J. Org. Chem.*, 1966, **31**, 3776.

[6] H. Hart and A. J. Waring, *J. Amer. Chem. Soc.*, 1964, **86**, 1454.

[7] H. Hart and C. A. Buehler, *J. Org. Chem.*, 1964, **29**, 2397.

Structures of the Dienones.—The structures of the cyclohexa-2,4-dienones (6—8) follows from their mode of formation, spectral properties, and chemical reactions. Their infrared and ultraviolet spectra are typical of cyclohexa-2,4-dienones.[2,8] This is illustrated in Table 1. The compounds do not appear to dimerise, although they all readily form crystalline Diels–Alder adducts with maleic anhydride which differ from each other. Thus this evidence supports that the three compounds are cyclohexa-2,4-dienone isomers.



(12)

Table 1

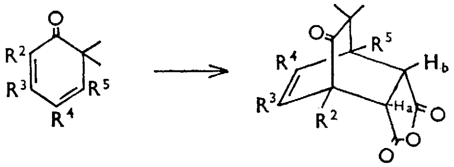
N.m.r. ultraviolet, and infrared spectral parameters for cyclohexa-2,4-dienones

Dienone	Position of H attachment [a] 3	5	2	Position of Me attachment [b] 3	2	4	5	6	$\lambda_{max.}$ (mμ)	$\nu_{max.}$ (cm.$^{-1}$)
(6)	3·40 h_w3	—	—	—	8·18[9H]			8·88[6H]	318 (3850)	1675 1660 1640
(7)	—	4·22 h_w4·5	—	8·00b, q	8·18	8·08d J = 1·6	—	8·93[6H]	309 (4800)	1690 1665 1645
(8)	—	—	4·30q h_w = 3·6	7·95d J = 1·5	—	8·13[6H]		8·88[6H]	310 (5300)	1655 1635
(1)[2]	—	—	—	7·97q	8·14b[9H]			8·89[6H]	330 (4500)	1647 1567
(5)[5]	—	4·10b	4·26	7·96d J = 1·8	—	8·08d J = 1·8	—	8·93[6H]	316 (2300)	1656 1568

d = Doublet, q = quartet, m = multiplet, b = broad; J and h_w given in c./sec.

[a] All signal one proton intensity. [b] All signal three protons intensity unless otherwise stated.

The question concerning the position of methyl attachment in these isomers was simplified as follows. N.m.r. examination of the maleic anhydride Diels–Alder adducts (**13**—**15**) formed from these isomers



(6) R^3 = H, other R's = Me
(7) R^5 = H, ,,
(8) R^2 = H, ,,
(12) R^4 = H, ,,

(13) R^3 = H, R^2 = R^4 = R^5 = Me
(14) R^5 = H, R^2 = R^3 = R^4 = Me
(15) R^2 = H, R^3 = R^4 = R^5 = Me
(16) R^4 = H, R^2 = R^3 = R^5 = Me

allowed them to be grouped into two types, those whose adduct would show a vinylic proton (**13**) and (**16**) formed from dienones (**6**) and (**12**) and those whose adduct would not show a vinylic proton (**14**) and (**15**) formed from dienones (**7**) and (**8**). Only one of the three dienones isolated gave a Diels–Alder adduct with a vinylic proton and this was the material which emerged first from the v.p.c. column (R_t 16·3 min.). Therefore this dienone had either structure (**6**) or (**12**). The choice in favour of (**6**) was made by examination of the data presented in Table 1. Compound (**6**) showed a vinylic proton at τ 3·40 which is the position expected[7,9] for a β-enone proton. Therefore a hydrogen at C-3 is indicated. The three allylic methyls appeared in one signal at τ 8·18. The importance of this observation is that it corroborates that there is no allylic methyl at C-3, since a methyl attached to the β-carbon of a cyclic dienone exhibits a signal at lower field, close to τ 8·00.[2,5,10] The adduct (**13**) formed from this dienone had m. p. 108—109°. The spectral properties are presented in Table 2. The i.r. spectrum showed features that are typical for these adducts. The most important feature of the n.m.r. spectrum was the diagnostic vinylic proton signal at τ 4·18. This appeared as a poorly resolved quartet (h_w 4·5 c./sec.), caused by coupling with the allylic methyl group R^4, which appeared as a doublet at τ 8·17 (J = 1·5 c./sec.).

The dienone with the longest retention time on the v.p.c. column (R_t = 35·7 min.) could have either structure (**7**) or (**8**) since its maleic anhydride adduct showed no vinylic proton. It was assigned structure (**8**) on the following grounds. Consistent with either structure, the n.m.r. spectrum of the dienone showed one low-field allylic methyl at τ 7·95 due to the methyl at C-3.[2,5,10] Significantly this three-proton signal was split into a doublet, J = 1·5 c./sec., which indicated that there was a hydrogen at C-2 coupled to it allylically. The C-2 proton appeared at τ 4·30 as the expected poorly resolved quartet (h_w 3·6 c./sec.). Other signals in this spectrum were consistent with the assigned structure as can be seen by examination of Table 1.

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[8] See A. J. Waring in " Advances in Alicyclic Chemistry," vol. 1, ed. H. Hart and G. J. Karabatsos, Academic Press, New York, 1967, p. 131.

[9] J. N. Schoolery and M. T. Rogers, *J. Amer. Chem. Soc.*, 1958, **86**, 5121.

[10] P. J. Kropp, *J. Amer. Chem. Soc.*, 1964, **86**, 4053.

The long retention time of this dienone compared with those of its isomers (6) and (7) is also consistent with having a hydrogen, rather than a methyl group, adjacent to the carbonyl function. The Diels–Alder adduct (15) formed from this dienone had m. p. 116—117°. Its characteristic infrared maxima are shown in Table 2. The n.m.r. spectrum showed two allylic methyl groups and, accordingly, no vinylic proton. The assignment of the complex multiplet centred between τ 6·70 and 6·53 to a bridgehead proton (R^2) and two anhydride protons H^a and H^b is quite reasonable since at these positions each hydrogen is α to a carbonyl. The chemical shifts of the three remaining protons support structure (15).

The second dienone to emerge from the v.p.c. column (R_t 17·3 min.) could have been assigned structure (7) or (8) since its maleic anhydride adduct had no vinylic proton. Because structure (8) has already been assigned, this compound must have the structure (7). However, apart from this inference, the n.m.r. spectrum of this material fully supports this conclusion. A signal for the methyl at C-3 was present at τ 8·00 as a poorly resolved quartet, presumably caused by homoallylic coupling. This indicated that there was a methyl at C-2. Another allylic methyl signal appeared at τ 8·08 as a doublet (J = 1·6 c./sec.). This is assigned to the methyl at C-4 coupled to the vinylic proton at C-5, which was present as a broad signal (h_w 4·5 c./sec.) at τ 4·22. The other assignments can be seen in Table 1. The crystalline Diels–Alder adduct (14) had m. p. 131—132°. This material showed the usual i.r.-spectral characteristics. These are given in Table 2 along with the n.m.r. spectral assignments. It is noteworthy that the three methine protons were strongly coupled. This would be expected for protons R^5, H^b, and H^a. They appear, respectively, at τ 7·13 as a doublet (J = 4 c./sec.), 6·40 as a quartet (J = 9 and 4 c./sec.), and 7·07 as a doublet (J = 9 c./sec.). Of these three protons the environment of the one at R^5 indicates that it should appear at the highest field. It is known from compound (13) and earlier work [2] that the coupling constant for protons H^a and H^b is 9 c./sec. Therefore, the signal at τ 7·13 must be the R^5 proton and this is consistent with the structure assigned.

TABLE 2

N.m.r. and infrared spectral data for cyclohexa-2,4-dienone–maleic anhydride Diels–Alder adducts

Diels–Alder adduct	Position of H attachment [a]				Position of Me attachment [b]						CCl$_4$ $\nu_{max.}$ (cm.$^{-1}$)
	R^3	R^2	H^a and H^b	R^5	R^4	R^3	R^5	R^2	R^6	R^6	
(13)	4·48q h_w 4·5	—	AB quartet 7·04 and 6·67 J = 9	—	8·17d J = 1·5	—	8·43	8·58	8·95	9·00	1725 * 1775 1855 †
(14)	—	—	7·07d 6·40q J = 9 J = 9 and 4	7·13d J = 4	8·18	8·37	—	8·55	8·89	8·92	1720 * 1775 † 1857
(15)	—	6·70 to 6·53m[3H]		—	8·23[6H]		8·45	—	8·97	9·00	1723 * 1775 † 1860
Adduct formed from (1)	—	—	AB quartet 6·77 and 7·07 J = 9·0	—	8·23	8·32	8·43	8·50	8·97	9·00	—

* Ketone (C=O). † Five-membered-ring anhydride (C=O). See footnotes to Table 1.

Structures of the Other Oxidation Products.—Of the other products formed in this oxidation, duroquinone (10) was easily identified by comparison with authentic material. The crystalline cyclohexa-2,5-dienone (9) was identified from its empirical formula, molecular weight, and i.r. spectrum, which showed absorption maxima at 1675 and 1630 cm.$^{-1}$ suggestive of an unsaturated ketone. The u.v. spectrum with an absorption maximum at 235 mμ (ε 10,500) in hexane was highly indicative of a cyclohexa-2,5-dienone. The structure was confirmed by the n.m.r. spectrum, which had one vinylic proton at τ 3·62 (J = 1·4 c./sec.). This is reasonable for the proton at C-5 allylically coupled to the methyl group at C-6. Two allylic methyl groups appeared at τ 8·18 (6H) and a third was at a lower field at τ 8·10. These signals are due to the methyls at C-2, C-6, and C-3 respectively. The lower-field signals consist, as expected, of a poorly resolved quartet, caused by homoallylic coupling with the methyl at C-2. The *gem*-dimethyls appeared at τ 8·83 (6H).

The structure of *p*-hydroxytetramethylbenzaldehyde (11) was deduced as follows. The empirical formula and molecular weight agreed with the structure. The i.r. spectrum had $\nu_{max.}$ at 3450, 1650, and 1550 cm.$^{-1}$ in KBr and 3650, 1690, and 1585 cm.$^{-1}$ in CCl$_4$, and the u.v. spectrum had $\lambda_{max.}$ at 233 and 292 mμ which is consistent with this type of compound. *p*-Hydroxybenzaldehyde, for example, has $\nu_{max.}$ 3150, 1660, and 1600 cm.$^{-1}$ in KBr [12a] and $\lambda_{max.}$ 221 and 284 mμ in ethanol.[12b] The n.m.r. spectrum showed that the structure must be highly symmetrical. Four allylic methyl groups appeared in two very sharp singlets at τ 7·87 (6H) and 7·58 (6H). A one-proton signal at τ 4·57 was readily exchangeable with D$_2$O and this was assigned to the phenolic hydroxyl. A one-proton signal, which appeared at very low field (τ —0·5) was assigned to the aldehydic

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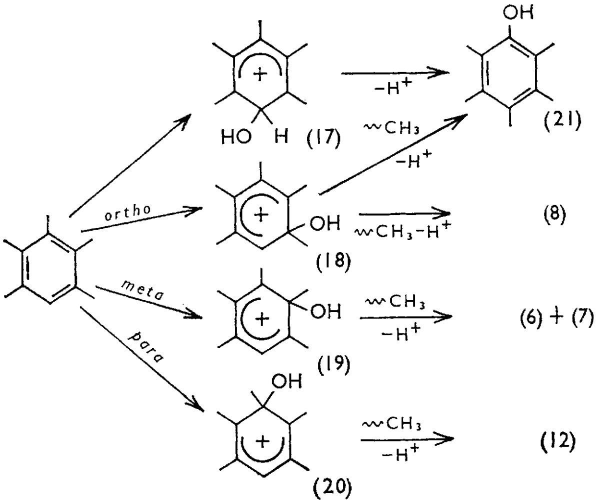
[12] (*a*) The Sadtler Standard Spectra, Sadtler Research Laboratories, Vine St., Philadelphia 2, Pennsylvania, U.S.A.; (*b*) N. J. Leonard, R. T. Rapala, H. L. Herzog, and E. R. Blout, *J. Amer. Chem. Soc.*, 1949, **71**, 2997.

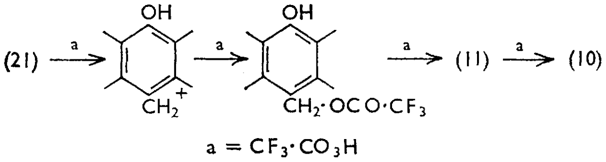
proton. The presence of an aldehyde group was further indicated by the formation of a 2,4-dinitrophenylhydrazone derivative and the rapid formation of a silver mirror with Tollens' reagent.

Mechanism of the Oxidation.—All the products can be rationalised by electrophilic [13] attack of peroxytrifluoracetic acid on the aromatic nucleus as shown in the scheme. The preferred formation of dienones (6) and (7) in fairly good yields and in similar amounts can be easily rationalised by inspection of the four possible intermediate carbonium ions (17—20) produced by electrophilic attack on pentamethylbenzene. Ions (17) and (19), with three methyl groups stabilising the classical contributing structures to the resonance hybrid, are much preferred over ions (18) and (20), where there are only two such methyl groups. Of the two preferred ions, (19) is favoured over (17) not only for statistical reasons, but probably much more important because of relief of steric strain due to eclipsing and buttressing adjacent methyl groups. Methyl migration in ion (19) can occur in two directions, to yield either (6) or (7). One direction should not be highly preferred to the other, accounting for the nearly equal amounts of both products.

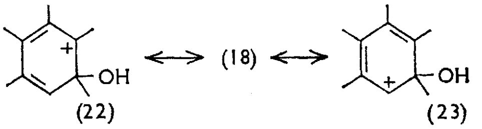


The cross-conjugated dienone (9) must come from an acid-catalysed rearrangement of a 2,4-dienone, probably (6). Treatment of a mixture of (6) and (7) under the reaction conditions afforded a product with the same retention time as (9), showing that this explanation is plausible. Thus approximately 77% of the product arises from ion (19).

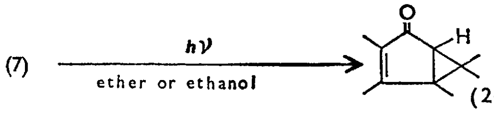
Although no pentamethylphenol (12) was detected among the oxidation products, it seems likely that two of the products, (10) and (11), amounting to 14% of the observed products, arose from further oxidation of (21). A separate experiment showed that (21) is rapidly oxidised in the reaction medium. Hydride abstraction from the methyl group *para* to the hydroxyl would lead to a resonance-stabilised benzyl cation, a type of reaction encountered previously in similar oxidations.[7,14] This cation could react with trifluoracetic acid giving the ester of the substituted benzyl alcohol, which would be readily oxidised to (11). The oxidation of compounds of the type (11) to duroquinones is known [15] to occur under very similar conditions.



Less than 10% of the oxidation products arise from carbonium ions stabilised by only two *ortho*- or *para*-methyls (18) and (20). Of these, (18) is favoured statistically. Also, ion (18) is stabilised by one methyl in an *ortho*-position and one in a *para*-position, a stabilisation which may be more effective [2,5] than that derived from two methyls both *ortho*, as in (20). Rearrangement of (18) to dienone (8) is much preferred over that to form pentamethylphenol (21), since (22) should be more important than (23) as a contributor to the resonance hybrid (18). Dienone (12) should not be present in amounts over about 3·5% [assuming only the statistical difference between (18) and (20)], and has not been isolated; if present, it is not likely to be obtained in over 1% yield.



Photolysis of the Pentamethylcyclohexa-2,4-dienones.—The two dienones of immediate interest were (7) and (8), to decide whether the methyl at C-2 or C-5 was responsible for directing the course of photolysis. Irradiation of (7) in dry ether or methanol with light from a 450 w Hanovia lamp filtered through Pyrex or uranium glass converted it into bicyclic ketone (24). Other products were formed due to over photolysis and consequently about 70% was the optimum yield of (24). It is noteworthy that no esters, formed by ring opening, could be found in the methanol solution after photolysis. The structure of (24) is based on the following facts. Its molecular weight (mass spec.) is 164. Its u.v. maxima (225, 270, and 321 mμ) and i.r. maxima (1690 and 1640 cm.$^{-1}$) were very similar to those reported [2] for bicyclic ketone (3). The n.m.r. spectrum showed all the features expected for a compound formed from (7) by a bond



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[13] Evidence has been presented that the electrophile is cationic; see A. H. Davidson and R. O. C. Norman, *J. Chem. Soc.*, 1964, 5404.

[14] H. Hart, C. A. Buehler, A. J. Waring, and S. Meyerson, *J. Org. Chem.*, 1965, **30**, 331.

[15] A. von Wacek and A. von Bezard, *Ber.*, 1941, **74***B*, 845; C. D. Logan, R. M. Husband, and C. B. Purves, *Canad. J. Chem.*, 1955, **33**, 82.

cross-over mechanism. For example, there were signals for two allylic methyl groups, the one at C-3 at τ 8·42 and the one at C-4 at τ 8·10, both poorly resolved quartets (h_w 3 c./sec.) caused by homoallylic coupling to each other. This pattern is very similar to that formed by the two allylic methyls in (3) (*e.g.*, 8·45 and 8·12). The three remaining methyl groups appeared as singlets at τ 8·76, 8·58, and 8·97 and tentative assignments can be made (see Experimental section). The remaining single proton appeared as a singlet at τ 8·87. This product is thermally labile, and is converted back into dienone (7) in the absence of light even at 0° on prolonged storage. In this respect it is similar to (4) which we reported earlier[2] to be thermally labile.

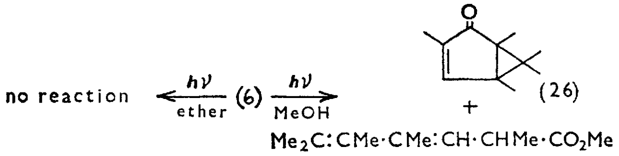
In contrast with (7), irradiation of dienone (8) in dry ether through Pyrex with light from the 450 w lamp for 8 hr. caused no change in the composition of the solution that could be detected by u.v. spectroscopy or v.p.c. However, a similar irradiation of a methanolic solution of (8) caused 95% photolysis in 2 hr. One product was isolated and shown to be the methyl dienoate (25) from its spectral properties. In particular, the i.r. spectrum showed an ester carbonyl band at 1735 cm.$^{-1}$ and the n.m.r. spectrum showed a singlet at τ 6·42 (3H) due to the methyl ester, a singlet at τ 7·07 (2H) due to the lone methylene group, and a multiplet between τ 8·28—8·53 (15H) due to the five allylic methyl groups.*

$$\text{no reaction} \xleftarrow[\text{ether}]{h\nu} (8) \xrightarrow[\text{MeOH}]{h\nu} \text{Me}_2\text{C:CMe·CMe:CMe·CH}_2\text{·CO}_2\text{Me}$$

(25)

Although not immediately pertinent to the question of which methyl group (at C-2 or C-5) directs the photolysis, the availability of appreciable quantities of dienone (6) from the oxidation of pentamethylbenzene led us to also study its photolysis. Since the results were interesting and unpredicted, they are reported here.

A solution of (6) in dry ether was irradiated through Pyrex using the 450 w source for 4·5 hr. This caused no change in the solution composition as determined by u.v.-spectroscopic and v.p.c. analysis. The starting material was recovered unchanged. However, irradiation of this dienone in methanol, through the uranium glass filter with light from the 200 w lamp led to photolysis, giving an optimum yield of products in 3·5 hr. Product analysis by v.p.c. showed 24% of the bicyclic ketone (26), 9% of the methyl dienoate (27) and 50% of the unphotolysed dienone. Prolonged photolysis increased the concentration of (27) and secondary photolysis products. The two products were isolated by v.p.c. and their structures established as follows. The bicyclic ketone had a molecular weight of 164 (mass spec.). Its i.r.-spectral properties were again very similar to those reported for (3) with $\nu_{max.}$ at 1690 and 1640 cm.$^{-1}$. The u.v. spectrum, with $\lambda_{max.}$ 210, 240, and 335 mμ is also consistent with structure (26). The n.m.r. spectrum is only consistent with the arrangement of methyl groups that would be expected for the bicyclic ketone formed by the bond crossover mechanism. It showed only one allylic methyl and this occurred as a doublet (J = 1·6 c./sec.) centred at τ 8·32. This chemical shift indicates that this allylic methyl is at C-3 rather than C-4 and that it is coupled allylically with the vinylic proton adjacent to it. The chemical shift of the vinylic proton (τ 3·20, h_w 4·5 c./sec.) is in agreement with this assignment. The four other methyls appeared at τ 8·73 (3H), 8·98 (3H), and 8·88 (6H), and these have been tentatively assigned (see Experimental section). The structure of the dienoate (27) has been determined from its spectral properties. In particular, it had a carbonyl band at 1735 cm.$^{-1}$, and its n.m.r. spectrum showed one vinyl proton at τ 4·88, coupled with the adjacent C-2 proton (J = 10 c./sec.). The ester methyl group appeared as a singlet at τ 6·43, and the lone aliphatic methyl as a doublet at τ 8·89 (J = 7·5 c./sec.). The spectrum also had a broad multiplet at τ 8·32 (12H) due to the allylic methyls, and a poorly resolved multiplet at τ 6·93 (1H) due to the single aliphatic proton on C-2.*



(26)

(27)

Photolysis Rates and Mechanism.—In order to obtain some idea of the relative rates of bicyclo[3,1,0]hexenone formation as against Barton–Quinkert ring opening, a few competitive photolyses were run. The results are summarised in Table 3.

TABLE 3

Approximate relative photolysis rates[a]

Compound	Relative rate Methanol	Ether	Product type
(1)	1	0·2	Bicyclic
(7)		0·2	Bicyclic
(8)	0·03		Ring-opened
(6)	0·01		Both

[a] The values reported are ratios of times for 50% photolysis, compound (1) being used as the reference.

Although we cannot yet suggest a mechanism that will satisfactorily rationalise these rate data or predict what structural requirements determine whether a given 2,4-dienone will give bicyclic or ring-opened product, several features of the reactions do emerge from our results. The photolysis rates of (1) and (8) in methanol show that formation of bicyclic product is much faster (and is probably a lower-energy process) than ring-opening. Even when both product types arose from one dienone [*i.e.*, (6)] the ratio favoured bicyclic product.

A methyl group at C-5 seems to have little influence on the reaction, regardless of its path [*i.e.*, (1) and (7) both give bicyclic product at comparable rates, (5) and (8) both give ring-opened product]. Methyl (or

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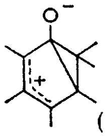
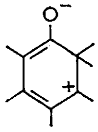
* The ultraviolet spectrum of (25) and similar compounds will be discussed in a separate Paper.

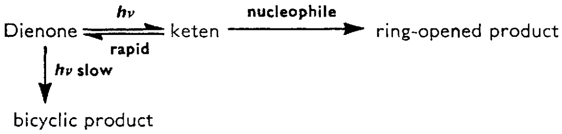
other) substitution at C-2 may be a necessary (but is not a sufficient [3]) condition for bicyclic product formation.

Both reactions proceed faster in methanol than in ether, but formation of bicyclic product is less solvent-sensitive than is ring opening. Since bicyclic product was formed faster in methanol than in ether, it seemed desirable to see if irradiation in a solvent of high polarity but low nucleophilicity might induce dienones (5) or (8) to yield bicyclic ketones. However, these dienones were inert to 4·5 hours' irradiation in acetonitrile (450 w, Pyrex) whereas (1) was completely isomerised in this solvent in less than 45 min. Attempts to quench the conversions (1) ⟶ (3) in piperylene failed as did the attempt to quench either conversion (6) ⟶ (26) or (6) ⟶ (27) in a solvent composed of equal amounts of methanol and piperylene. Thus the question of singlet or triplet remains open for both types of photoisomerisation. If a dipolar intermediate is involved in the formation of bicyclic product, a structure such as (28) would seem favoured over (29) in view of the lack of effect of a methyl at C-5 on the rate.


(28)

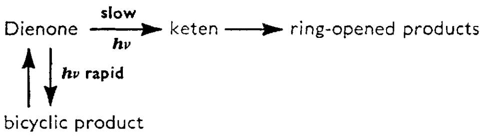

(29)

Certain mechanisms can probably be rejected. For example, one might suggest *a priori* a scheme such as:

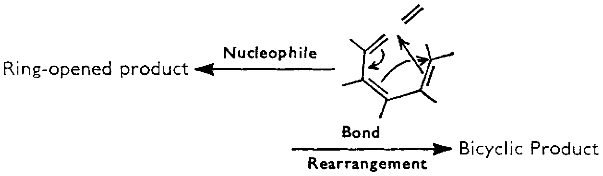


However, in this case one would expect those reactions which give bicyclic products to be slower than those which give ring-opened products. This is not the case.

An alternative route in which bicyclic product is formed reversibly, seems also to be untenable. For example, in the case of dienone (6) where both types of product were obtained, separate irradiation of the bicyclic product did not lead to the formation of any ring-opened product.



A third alternative, in which both types of product are formed from the keten also seems unlikely since once again one would expect the reaction of a keten with nucleophile to be very rapid.



At present we are inclined to prefer the view that two alternative routes with two different types of transition states are operative, but clearly additional work is needed to delineate the nature of the excited states for each reaction.

EXPERIMENTAL

Unless stated to the contrary, u.v. spectra were measured in ethanol solution with a Unicam spectrometer SP 800, the infrared spectra were measured in carbon tetrachloride solution with a Unicam SP 200 spectrometer, and the n.m.r. spectra were measured in carbon tetrachloride solution, using tetramethylsilane as an internal standard, with a Varian A-60 spectrometer. The mass spectra were obtained with a Consolidated Electrodynamic Corp. 21-103C instrument operating at an ionising potential of 70 v. Microanalysis were performed by Spang Laboratory, Ann Arbor.

The Oxidation of Pentamethylbenzene.—Pentamethylbenzene (44·4 g.) (3×10^{-1} mole), which had been recrystallised twice from ethanol to remove the 1—2% hexamethylbenzene that contaminated most commercial samples, was dissolved in methylene chloride (500 ml.) and oxidised in the presence of 47% boron trifluoride etherate (87 ml.) with peroxytrifluoroacetic acid, prepared from trifluoroacetic anhydride (63 g.) and 90% hydrogen peroxide (9·1 ml.) (3×10^{-1} mole). The oxidant and BF_3 etherate were cooled to 0° and added dropwise at the same rate during 15 min. The reaction was continued for a further 25 min., the temperature being maintained throughout between 0 and −5°. The reaction was worked up by adding methylene chloride (200 ml.) and washing the mixture with water (150 ml. × 3) and then extracting with 10% aqueous sodium hydroxide (100 ml. × 3). The aqueous basic fraction and the methylene chloride fractions were investigated separately as follows.

Back-extraction of the aqueous base with methylene chloride afforded a yellow solution which gave crystalline duroquinone (0·25 g.) (2%), m. p. 110—112°, $\lambda_{\text{max.}}$ 268 and 260 mμ, ε 20,000 and 20,000; $\nu_{\text{max.}}^{\text{KBr}}$ 1630 cm.$^{-1}$; the n.m.r. spectrum shows a sharp singlet at τ 8·03. The aqueous base was then acidified and again extracted with methylene chloride, which yielded on evaporation 2·5 g. (5%) of crude crystalline *4-hydroxy-*2,3,5,6-*tetramethylbenzaldehyde* (11). After two further recrystallisations, the white crystals had m. p. 144—145°, $\lambda_{\text{max.}}$ 233 and 292 mμ, ε 12,000 and 12,100; $\nu_{\text{max.}}$ 3650 (OH), 1685, and 1585 cm.$^{-1}$ (aromatic aldehyde C=O), $\nu_{\text{max.}}^{\text{KBr}}$ 3450 (broad), 1655, 1560 cm.$^{-1}$. The n.m.r. spectrum indicated a molecule with a high degree of symmetry. In particular the allylic methyls appeared as two sharp peaks at τ 7·87 (6H) and 7·58 (6H) due to the methyl α to the aldehyde or hydroxy-group. The signal at τ 4·57 (1H), which was readily exchangeable with D_2O, was assigned to the phenolic hydroxyl and the very low-field signal at τ −0·5 (1H), was assigned to the aldehyde proton. The mass spectrum of this material showed a parent peak at *m*/*e* 178. This compound reduced Tollens' reagent and gave a 2,4-dinitrophenylhydrazone derivative indicative of the aldehyde grouping (Found: C, 74·0; H, 7·8. $C_{11}H_{14}O_2$ requires C, 74·2; H, 7·9%).

The methylene chloride containing the major product was washed with water and evaporated to afford a deep red oil.

This deposited crystals during two weeks at 0°. The crystals (1·5 g.), which had m. p. 202—204° and an i.r. spectrum showing no carbonyl, were not investigated further. Chromatography of the oily product on silica gel in a column measuring 5·5 × 40·0 cm. afforded crystalline starting material (10 g.) 25% from the first 4 l. of pentane eluant. The removal of the pentamethylbenzene at this stage is essential, since it sublimes and interferes with distillation; also it has a v.p.c. retention time identical with that of dienone (6). Further elution with methylene chloride (6 l.) gave a yellow oil (22·1 g.) and finally, elution with ethanol removed all the material adsorbed on the column which was a yellow-brown oil (8·1 g.). Analysis of these two oily fractions by v.p.c. on Carbowax 20 ft. × $\frac{1}{4}$ in. at 202° with a helium gas flow of 60 ml. $min.^{-1}$ showed that the total crude oil (30·2 g.) had components with the following retention times: 16·6 min. (25%), 17·3 min. (28%), 18·7 min. (3%), 22·3 min. (3%), 35·7 min. (5%). The material, eluted with ethanol, was richer in materials with longer retention times and was therefore kept separate. Product separation was simplified by distillation through a Nester–Faust spinning band column. The crude oil (22·1 g.) was fractionated into four 4 g. lots of pale yellow liquid, all having b. p. 81°/3·5 mm. Hg. V.p.c. analysis of these showed that the first fraction was rich (~60%) in dienone (6) (R_t 16·6 min.) and the fourth cut was rich (~70%) in dienone (8) (R_t 17·3 min.). The pot residue from this distillation was then combined with the oil (8·1 g.) from the silica gel column. This material was then fractionally distilled at 3·5 mm. Hg giving a pale yellow liquid (3 g.), b. p. 81°, a yellow liquid (1·5 g.), b. p. 85—91°, and a further fraction of a yellow liquid (1·5 g.), b. p. 91—103°. V.p.c. analysis showed that the fraction with b. p. 85—91° was the best source of the cyclohexa-2,5-dienone (9) with R_t 22·3 min. and the fraction with b. p. 91—103° was rich in dienone (8) (R_t 35·7 min.). Final purification of all these compounds was achieved by v.p.c. The purity of all liquids was checked by v.p.c. on at least three different stationary phases and always found to be at least 98% homogeneous.

Product Identification:

2,4,5,6,6-*Pentamethylcyclohexa*-2,4-*dienone* (6).—This had a retention time of 16·6 min. (identical to that of pentamethylbenzene). It showed the spectral properties presented in Table 1. This compound (80 mg.) readily afforded a crystalline Diels–Alder adduct, after heating under reflux with an equimolar mixture of maleic anhydride in ether for 10 hr. The white crystalline product (13) (50 mg.) had m. p. 108—109°, and the spectral properties shown in Table 2 (Found: C, 68·3; H, 6·9. $C_{15}H_{18}O_4$ requires C, 68·68; H, 6·91%).

2,3,4,6,6-*Pentamethylcyclohexa*-2,4-*dienone* (7).—This had a retention time of 17·3 min. Its u.v., i.r., and n.m.r. spectra are presented in Table 1. This dienone (85 mg.) gave the Diels–Alder maleic anhydride adduct (14) (60 mg.), m. p. 131—132° (Found: C, 68·53; H, 6·82. $C_{15}H_{18}O_4$ requires C, 68·68; H, 6·91%). The u.v., i.r., and n.m.r. spectral properties are collected in Table 2.

3,4,5,6,6-*Pentamethylcyclohexa*-2,4-*dienone* (8).—This had a retention time of 35·7 min., and it showed u.v., i.r., and n.m.r. spectral properties presented in Table 1. This dienone (150 mg.) afforded a pure adduct (15) with maleic anhydride (50 mg.), m. p. 116—117° (Found: C, 68·65; H, 6·88. $C_{15}H_{18}O_4$ requires C, 68·68; H, 6·91%). The u.v., i.r., and n.m.r. spectral properties for this adduct are recorded in Table 2.

2,3,4,4,6-*Pentamethylcyclohexa*-2,5-*dienone* (9).—This was a white crystalline solid, m. p. 58—59°, with R_t 22·3 min., $\lambda_{max.}$ (hexane) 235 mμ, ε 10,500, and $\nu_{max.}$ 1630 (strong), 1650 (shoulder), and 1675 $cm.^{-1}$ (C=O conj.). The mass spectrum showed a parent peak at *m/e* 164. The n.m.r. spectrum showed a sharp singlet at τ 8·83 (6H) due to the *gem*-dimethyl group at C-4 and a multiplet at τ 8·18 (6H) due to the C-2 and C-6 allylic methyl groups. The C-3 allylic methyl group appears, as expected, at lower field τ 8·10 (3H) as a broad quartet, due to coupling with the methyl at C-2. The vinylic proton at C-5 appears at lowest field 3·62 (1H) as a quartet (*J* = 1·4 c./sec.) caused by allylic coupling with the adjacent methyl group (Found: C, 80·38; H, 9·71. $C_{11}H_{16}O$ requires C, 80·50; H, 9·83%).

Test of Product Stability Under Reaction Conditions:—*Pentamethylphenol*.—Pentamethylphenol (0·49 g.) (3 × 10^{-3} mole) was oxidised in methylene chloride (5 ml.) in the presence of boron trifluoride etherate (2·5 ml.) with the usual oxidant composed of trifluoroacetic anhydride (1·8 g.) and 90% hydrogen peroxide (0·27 mg.) (9 × 10^{-3} mole) in methylene chloride (2 ml.). The reaction was examined after 5 and 15 min. at 0°. V.p.c. analysis, after 5 min., showed that 80% of the phenol had been consumed and after 15 min. no phenol could be detected. The products were not investigated.

Rearrangement of the Dienones (6) *and* (7).—Approximately equal amounts of dienones (6) and (7) (0·1 g.) (6·1 × 10^{-4} mole) were treated in methylene chloride (5 ml.) containing boron trifluoride etherate (0·17 ml.) with the oxidant, made from perfluoracetic anhydride (0·13 g.) and hydrogen peroxide (90%) (0·018 ml.) at 0° for 30 min. The reaction mixture was worked up and examined by v.p.c. One of the rearranged products was shown to have a retention time identical to that of cyclohexa-2,5-dienone (9).

General Photolysis Procedure.—All solvents used were distilled under an atmosphere of dry nitrogen. Either a Hanovia mercury arc, type S (200 w) or type L (450 w), was used and the light was filtered through a Pyrex or Corning 3320 uranium borosilicate glass sleeve.

Method 1 *for Photolysis*.—The dienones were dissolved in solvent and irradiated in the annular space formed between a water-cooled Hanovia immersion well and an outer Pyrex vessel, whose dimensions were such that, when filled with 130 ml. of solution, the mercury arc was covered. This solution could be agitated by bubbling nitrogen gas through it.

Method 2 *for Photolysis*.—The solution to be irradiated was placed in a Pyrex test tube, sealed with a serum cap, and attached to the outside of the Hanovia water-cooled immersion well, 2·5 cm. from the centre of the mercury arc. This set-up was then placed in an ice bath, which maintained the temperature of the solution during irradiation between 3 and 8°.

In every case a control experiment showed that no reaction occurred under similar conditions in the dark.

Irradiation of Dienone (7) *in Ether*.—Dienone (7) (0·31 g.) of 95% purity was dissolved in ether (22 ml.) and photolysed by method 2 with light from the 450 w lamp filtered through Pyrex. The photolysis was monitored by v.p.c., aliquots being removed at intervals of 10 min. during a period of 50 min. Examination of the samples on Carbowax 5 ft. × $\frac{1}{4}$ in. at 175° with a gas flow of 90 ml. $min.^{-1}$ showed a progressive decrease in concentration of (7) (R_t 3·8 min.) and a corresponding increase in the concentration of bicyclic ketone (24) R_t 4·2 min.). The concentrations of (7) and (24) were equal after 31 ± 2 min., and after 51 min. 70% of the bicyclic ketone (24) was present.* In an identical experiment using hexamethylcyclohexa-2,4-dienone (1) 50% of it had been photolysed after 29 ± 2 min.

3,4,5,6,6-*Pentamethyl*[3,1,0]*bicyclohex*-3-*en*-2-*one* was isolated by v.p.c. and the oily product showed $\lambda_{max.}$ 225, 270, and 321 mμ, ε 5800, 3400, and 1250; $\nu_{max.}$ 1690 (strong) and 1640 cm.$^{-1}$ typical for these bicyclic ketones. The n.m.r. spectrum showed two allylic methyl groups as two poorly resolved multiplets, the one at C-3 at τ 8·42 (3H), (h_w 3 c./sec.) and the one at C-4 at 8·10, (3H), (h_w 3 c./sec.). The three remaining methyl groups at C-5 and C-6 appear as fairly sharp singlets at 8·76 (3H) and 8·58 (3H) and 8·97 (3H); the last two are probably the *gem*-dimethyls at C-6, but this is only a tentative assignment. The single proton appears as a singlet at 8·87 (1H).

Irradiation of Dienone (7) *in Methanol*.—Dienone (7) (0·33 g.) in methanol (3·4 ml.) was irradiated by method 2 with light from the 200 w lamp filtered through Pyrex. The photolysis was monitored as described above and was 50% complete in 23 ± 3 min. The only product that could be detected on the chromatogram was (24) even though unsaturated esters were looked for.

Irradiation of Dienone (6) *in Ether*.—Dienone (6) (80 mg.) in ether (8·0 ml.) was irradiated by method 2 with light from the 450 w lamp filtered through Pyrex and the reaction monitored by v.p.c. and u.v. spectroscopy. Neither technique revealed any photolysis during 4½ hr. and starting material was recovered, as shown by the i.r. and n.m.r. spectra.

Irradiation of Dienone (6) *in Methanol*.—Dienone (6) (1·0 g.) in methanol (1·50 ml.) was photolysed with light from the 200 w lamp, filtered through the uranium glass sleeve, by method 2. Monitoring the experiment by v.p.c. on Carbowax 10 ft. × ¼ in. at 175° with a gas flow 75 ml. min.$^{-1}$ showed that after 3½ hr. 50% of the dienone (6) with R_t 8·4 min. remained, accompanied by 24% of bicyclic ketone (26), R_t 5·8 min., 9% of dienoate (27), R_t 4·0 min., and 17% of three other compounds with longer retention times. This seemed to be the optimum photolysis time for this experiment. Shorter photolysis gave less of the compounds with longer retention times but little of (26) and (27), whereas longer irradiation periods increased the amount of (27) and products with long retention times but not of (26). Isolation of bicyclic ketone (26) and dienoate (27) was achieved by v.p.c. In experiments where more than 1 g. of dienone (6) was photolysed, chromatography was simplified by concentrating the two products (26) and (27). This was achieved by vaporising them at room temperature at 10^{-1} mm. Hg and condensing the vapour at −70° over a period of 20 hr. The product with R_t 5·8 min. was shown to be 1,3,5,6,6-*pentamethylbicyclo*[3,1,0]-*hex*-3-*en*-2-*one* (26). It had $\lambda_{max.}$ 210, 240, and 335 mμ, ε 3000, 4670, and 655; $\nu_{max.}$ 1690 (strong) and 1640 cm.$^{-1}$ (shoulder) (typical for this system). The n.m.r. spectrum showed one allylic methyl group as a doublet at τ 8·32 (3H) (J = 1·6 c./sec.). This must be the methyl at C-3, split by the vinyl proton at C-4, which appears at τ 3·20 (1H) (h_w 4·5 c./sec.). The sharp signal at τ 8·73 (3H) is tentatively assigned to the methyl group at C-5 and of the three remaining methyls, at C-1 and C-6, two have similar chemical shifts and appear as the six-proton signal at τ 8·88 and the other at τ 8·98 (3H). The mass spectrum of this compound had a parent peak at *m/e* 164. The product with R_t 4·0 min. was shown to be *methyl* 2,4,5,6-*tetramethylhepta*-3,5-*dienoate* (30). It showed $\lambda_{max.}$ 212, 4740; $\nu_{max.}$ 1735 cm.$^{-1}$, and its n.m.r. spectrum showed the following features: a doublet at τ 4·88 (1H) (J = 10 c./sec.) due to the vinyl proton at C-3, coupled with the hydrogen at C-2; a methyl ester signal at τ 6·43, a broad peak at about τ 8·32 (12H) due to the four allylic methyls and a doublet at τ 8·98 (3H) (J = 7·5 c./sec.) due to the methyl at C-2 coupled to the proton at C-2. This single proton appeared as a very broad poorly resolved multiplet centred at τ 6·93 (1H). The mass spectrum had a parent peak at *m/e* 196.

The relative rate of photolysis of this dienone was estimated in a separate experiment as follows: Dienone (6) (9 mg.) in methanol (0·7 ml.) and dienone (1) (9 mg.) in methanol (0·7 ml.) were irradiated at the same time by method 2, using the same light source and filter described above. V.p.c. analysis of each photolysate showed 50% of dienone (1) had disappeared in 6 ± 1 min., whereas 50% of dienone (6) was photolysed only after 430 ± 25 min.

Irradiation of Bicyclic Ketone (26) *in Methanol*.—Bicyclic ketone (26) (5 mg.) in methanol (5 ml.) was irradiated by method 2 with light from the 200 w lamp filtered through the uranium glass sleeve. The reaction was followed by v.p.c. and after 1·75 hr. irradiation no dieonoate (27) could be detected. The chromatogram from Carbowax 10 ft. × ¼ in. at 180° and helium flow 55 ml. min.$^{-1}$ showed (26) with R_t 6·4 min., and a product with R_t 3·6 min. as well as material with R_t >8 min. Authentic (27) was then mixed with the photolysate and this showed a peak with R_t 4·2 min. in addition to those cited above.

Irradiation of Dienone (8) *in Ether*.—Dienone (8) (0·1 g.) in ether (6 ml.) was photolysed by method 2 with light from the 450 w lamp filtered through Pyrex. No reaction could be detected after 8 hr. by v.p.c. or by u.v. spectroscopy, and the starting material was recovered.

Irradiation of Dienone (8) *in Methanol*.—Dienone (8) (0·17 g.) in methanol (120 ml.) was irradiated by method 1 with light from the 450 w lamp filtered through Pyrex. After 2 hr. the v.p.c. showed that 95% of the dienone had reacted, and one product, whose retention time was 1/3 that of the dienone, was produced. The product was concentrated by the " sublimation " technique described above and the white liquid *methyl* 3,4,5,6-*tetramethylhepta*-3,5-*dienoate* (25) (0·1 g.) thus obtained was finally purified by v.p.c. This material showed $\lambda_{max.}$ 220 mμ, ε 2950; $\nu_{max.}$ 1735 cm.$^{-1}$. The n.m.r. spectrum showed a singlet at τ 6·42 (3H) due to the methyl ester, a singlet at 7·07 (2H) due to the C-2 methylene, and a multiplet between τ 8·53 and 8·28 (15H), which must be due to the five allylic methyl groups.

The relative rate of this photolysis was estimated as follows: Dienone (1) (98 mg.) in methanol (7 ml.) and dienone (8) (98 mg.) in methanol (7 ml.) were simultaneously photolysed by method 2 with light filtered through uranium glass. Both reactions were followed by v.p.c.; 50% of dienone (1) had been photolysed after 24 min., and 50% of dienone (8) had been photolysed after 15 hr.

Solvent Effect on Photolysis.—Dienones (1) and (5) (20 mg. each) in acetonitrile (2 ml.) and dienone (6) (4 mg.) in acetonitrile (0·5 ml.) were photolysed at the same time by

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* Further photolysis was undesirable, since products with longer retention times begin to appear in significant amounts.

method 2 with light from the 200 w lamp filtered through uranium glass. The reaction progress was monitored by v.p.c. This showed that in less than 45 min. all of dienone (1) had been photolysed to bicyclic ketone (3). However, irradiation for 4·5 hr. showed no change in the composition of the other solutions containing dienone (6) and dienone (5). This conclusion was checked for (6) by adding authentic (26) to the photolysate. This showed that 1% of (26) as product would have been easily detected.

Quenching Experiments.—(*A*) Samples of dienone (1) (50 mg.) were dissolved in the following solvents: ether (1 ml.), hexane (1 ml.), methanol (1 ml.), and piperylene (1 ml.). These solutions were then irradiated by method 2 with light from the 200 w lamp filtered through uranium glass. The reactions were followed by v.p.c. The approximate periods of irradiation required to photolyse 50% of the dienone were 20 min., 1·4 hr., 1·7 hr., and 2·2 hr. in methanol, piperylene, ether, and hexane respectively. The major product in all experiments had the same retention time as bicyclic ketone (3).

(*B*) Two 25 mg. samples of dienone (6) were weighed, one was dissolved in a solvent composed of methanol (0·5 ml.) and hexane (0·5 ml.), the other was dissolved in methanol (0·7 ml.) and piperylene (0·7 ml.). The two solutions were irradiated and monitored as described in *A*. After about 20 hr., irradiation the chromatogram showed very similar product composition for each experiment, 50% of the dienone remained, accompanied by dienoate (27) and bicyclic ketone (26).

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