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PHOTOISOMERIZATIONS—VI[1]

CYCLOBUTENE FORMATION AND DIENE MIGRATION IN SIMPLE 1,3-DIENES[2]

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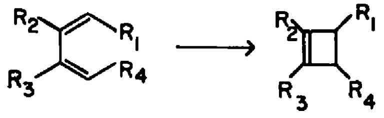
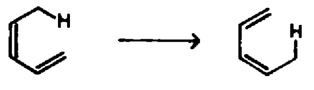
Abstract—Non-homoannular 1,3-dienes have been shown to undergo photochemical valency isomerization to cyclobutenes and/or diene migration involving 1,5-hydrogen transfer. The preparative value of these reactions is examined for eleven dienes. A single example of photochemical cyclobutane formation, involving a synthesis of β-pinene, is described.

Despite the amount of work published on the photoisomerizations of homoannular conjugated systems,[3] little has been done on the photochemistry of acyclic analogues. The latter might, *a priori*, be expected to undergo a wider variety of isomerizations owing to their greater molecular flexibility. However, until recently, the only recognized photoisomerizations of acyclic conjugated dienes were geometrical. We have found that, in dilute solution in a non-polar solvent, conjugated acyclic dienes can undergo either or both of the photoisomerizations illustrated in equations (a) and (b).[4] When a non-conjugated double bond is also present in the molecule, another reaction (c), involving cyclobutane formation, might be expected, and has been shown to occur in the one case examined. Only compounds containing the 1,3-diene system not conjugated with other unsaturated groups are considered here.



.......(a)



.........(b)

........(c)

Cyclobutane formation. Many examples of photochemical cyclobutane formation

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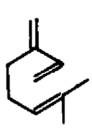
[1] Refs. 2a, 2b, 8, 2c, and 13 are considered to be Parts I–V respectively.

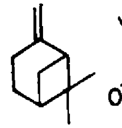
[2] Preliminary communications describing portions of this work have been published: K. J. Crowley, *Proc. Chem. Soc.* [a] 245 (1962); [b] 334 (1962); [c] 17 (1964).

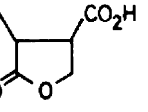
[3] For a review and leading Refs. see O. L. Chapman, *Advances in Photochemistry* (Edited by W. A. Noyes, G. S. Hammond and J. N. Pitts Jr.) Vol I, p. 323, Interscience, New York (1963).

[4] 1,3-Dienes can also undergo photochemical valence isomerization to bicyclo[1.1.0]butanes: R. Srinivasan, *J. Amer. Chem. Soc.* **85**, 4045 (1963); W. G. Dauben and F. G. Willey, *Tetrahedron Letters* 893 (1962).

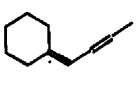
from two ethylenic bonds have been reported, the reaction occurring both inter- and intra-molecularly.[3] We here record an example of the latter type—the photoisomerization of myrcene (I) to β-pinene (II). This type of cyclobutane formation might be expected to give rise to four bicyclic photoisomers of myrcene. In fact, UV irradiation of this terpene in dilute solution in a non-polar solvent until no diene absorption remains yields mainly a cyclobutene (*vide infra*), together with five other photoproducts (3–10%). Of the latter, only the chief product (10%) was identified, after being isolated in 75% purity. This had the physical properties (b.p. and IR spectrum) of β-pinene (II), and was not separated from this compound when the mixture was passed through a high resolution capillary column gas chromatograph.[5]


I


II



XIV


XXI

Cyclobutene formation. Instances of reaction (a) are reported for compounds in which R_1 and R_4 are united to form a single chain of two, three or four carbon atoms, or a link of the type CO—O—CO.[3] The extension of the reaction to acyclic dienes was reported contemporaneously by ourselves[2b] and by Srinivasan.[6] The latter author described the isomerization of three acyclic dienes, isoprene, 1,3-pentadiene and 2,3-dimethylbutadiene, to the corresponding cyclobutenes on irradiation with 2537 Å light, and obtained quantum yields in the range 0·03–0·12 for the cyclobutene formation. The present work is primarily concerned with the preparative aspects[7] of the reaction, as applied to the dienes listed in Table 1. As shown in this Table the yield of isolated cyclobutene varied from 71% to 21% for hydrocarbon dienes, and was 13% in the single case examined in which a hydroxy group was present. No cyclobutene has yet been encountered in the irradiation products of conjugated dienoic acids.[8]

The 1-methylcyclobutene (IV) obtained on irradiation of isoprene (III) was identified by its b.p., refractive index and IR spectrum.[9] A second photoproduct, of somewhat lower volatility, was formed in 4% yield, but not examined.

1,2-Dimethylclobutene (VI) was obtained in 97% purity on irradiation of 2,3-dimethylbutadiene (V); two other slightly less volatile photoproducts, each formed in ca. 1% yield, were detected by gas chromatography, but not examined. The IR spectrum of the cyclobutene showed ethylenic absorption at 1689 cm^{-1} but no =CH— stretching absorption. Pyrolysis resulted in the normal scission of the allylic

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[4] R. S. H. Liu and G. S. Hammond, *J. Amer. Chem. Soc.* **86**, 1892 (1964).

[5] At the IUPAC Symposium on Organic Photochemistry, Strasburg, France, in July, 1964, Prof. W. G. Dauben reported the photoproduction from myrcene of the cyclobutene and β-pinene together with a further minor component which was identified as 5,5-dimethyl-l-vinylbicyclo[2.1.1.]hexane; this compound had previously been obtained[4] as the principal product of the sensitized photoisomerization of myrcene.

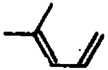
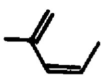
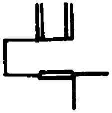
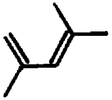
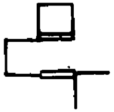
[6] R. Srinivasan, *J. Amer. Chem. Soc.* **84**, 4141 (1962).

[7] Some mechanistic aspects have been examined by Prof. Dauben *et al.* (cf. Ref. 5).

[8] Cf. K. J. Crowley, *J. Amer. Chem. Soc.* **85**, 1210 (1963).

[9] F. F. Cleveland, M. J. Murray and W. S. Gallaway, *J. Chem. Phys.* **15**, 742 (1947): cf. J. Shabtai and E. Gil-Av, *J. Org. Chem.* **28**, 2893 (1963).

TABLE 1. IRRADIATION OF 1,3-DIENES TO FORM CYCLOBUTENES

Starting material	 III	 V	 VII (20)% +  VIII (80)%	 X	 XII	 XV	 I	 XVIII	 XIX	 XX
Cyclobutene	 IV	 VI	 IX	 XI	 XIII	 XVI	 XVII			
Solvent	Hexane	ether	isoöctane	ether	ether	ether	ether	ether	hexane	ether
Temp.	25°	25°	30°	15°	25°[c]	25°	30°	5°	30°	0°
Diene wt. (g)	6·8	8·8	11·3	3·9	6·2	20·3	35·6	4·8	2·2	10·9
Diene conc. (g/l.)	7·3	9·5	23	7·8	12·5	22	35	9·6	11	22
Irradiation time (hr)	114	45	66	19	20	127	113	94	66	37
Cyclobutene yield[a] g	2·42	6·33	2·4	1·69	0·82	7·95	21·1	no cyclobutene identified		
Cyclobutene yield[a] %	36	71	21	43	13	45	68[f]			
Reaction followed by	UV[b]	UV[b]	gas chr.[c]	UV[b]	UV[d]	gas chr.[e]	UV[b]	gas chr.[c]	UV[b]	UV[d]

[a] Yields are calculated by summation of the cyclobutene content (indicated by gas chromatography) of the several fractions obtained on distillation of the irradiation product, and are based on the amount of diene consumed.

[b] UV absorption: the irradiation was stopped when the absorption at 225 mμ was reduced to between 0·5 and 2·5% of its original value.

[c] Gas chromatography: the irradiation was stopped when the starting materials comprised ca. 10% of the volatile components: polymeric products predominated.

[d] The irradiation was stopped when the absorption at 225 mμ had reached half of the original value.

[e] The irradiation was stopped when starting material comprised 26% of the volatile components: a non-volatile residue (44%) remained after distillation of the crude irradiation product.

[f] See also Table 2.

carbon-carbon bond of the cyclobutene to give the starting material, while oxidation of the photoproduct with potassium permanganate gave 2,5-hexanedione. When stirred in isoöctane over Pd—C, the cyclobutene absorbed one equivalent of hydrogen; the product was not isolated, but its low UV absorption showed that it was saturated.

Irradiation of the mixture of 4-methyl-1,3-pentadiene (VII) and 2-methyl-1, *trans*-3-pentadiene (VIII) which results on iodine catalyzed dehydration of 2-methyl-2,4-pentanediol, gave the photoisomer (IX). This product showed IR maxima indicative of a trisubstituted double bond (806, 3020 cm^{-1}), was quantitatively isomerized to VIII when heated at 230° for 0·5 min, and was dihydrogenated to the known 1,3-dimethylcyclobutane.[10]

In 1956 Grummitt and Mandel[11] reported that UV irradiation of 1-cyclohexyl-1,3-butadiene (X) in ethanol or cyclohexane decreased the UV absorption and that only starting material was recovered when the product of a large scale irradiation in the former solvent was distilled. In agreement with these authors, we have found that on irradiation of the diene (a mixture of *cis* and *trans* isomers: *vide infra*) in ethanol, the intensity of the UV maximum was steadily reduced although the position remained unchanged. However, examination of the product ($\varepsilon_{225} = 0{\cdot}5\%$ of original value) by gas chromatography revealed the presence of a new compound (ca. 5%) which was not readily separable by distillation from the polymeric photoproducts owing to its thermal instability. This isomer (XI) was obtained in better yield when the irradiation was carried out in diethyl ether (Table 1), and was isolated in 86% purity. Its IR spectrum shows maxima at 3040 and 697 cm^{-1} indicative of the *cis* —CH=CH— group, and its UV end absorption (ε, 3000 at 195 mμ) is in agreement. On catalytic hydrogenation one equivalent of hydrogen was taken up, and these IR maxima disappeared. As with the other lightly substituted cyclobutenes, brief heating caused reformation of the original diene. The isolation of cyclohexylsuccinnic acid when the photoproduct was treated with either ozone–performic acid or potassium permanganate confirmed the assigned structure (XI).

Sorbic alcohol (XII) gave two photoproducts in similar yield. The more volatile of these appeared to be an aldehyde. It was not obtained pure but appeared to be isomeric with the starting material. The cyclobutene structure (XIII) was assigned to the second photoisomer. This compound was also not obtained pure, being apparently hygroscopic. It has low UV end absorption, and gives IR maxima indicative of a *cis* disubstituted double bond (719, 3040 cm^{-1}), a methyl group (1374 cm^{-1}) and a primary alcohol (1040 cm^{-1}). Its NMR spectrum* shows a doublet centred at τ 8·88 ($J = 8$ c/s) due to the methyl group, a singlet at τ 7·53 due to the hydroxyl proton, a multiplet at ca. τ 6·9 attributable to the two allylic methine groups, the methylene doublet at τ 6·21 ($J = 8$ c/s) and a quartet at τ 3·77 ($J = 3$ c/s) due to the olefinic protons. The proton ratios for the methyl, allylic methine, methylene and vinyl protons were of the expected order (3·2, 2·0, 2·0 and 1·8) but that of the hydroxyl (1·6) was high, probably because of water in the sample.

The cyclobutene was destroyed on being briefly heated, and *trans-trans* sorbic alcohol was the main volatile product; smaller amounts of the other two geometrical

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* Run in $CDCl_3$ on a Varian A-60, through the kindness of Drs. L. Stautzenberger and R. M. Geudin, Celanese Corp., Clarkwood, Texas.

[10] F. F. Caserio, S. H. Parker, R. Piccolini and J. D. Roberts, *J. Amer. Chem. Soc.* **80**, 5507 (1958).

[11] O. Grummitt and Z. Mandel, *J. Amer. Chem. Soc.* **78**, 1054 (1956).

isomers were obtained, together with several minor components. Ozonolysis of the cyclobutene gave a 43% yield of methyl paraconic acid (XIV). The stereochemistry of this acid has not been satisfactorily determined[12] and consequently that of the cyclobutene is uncertain.

Irradiation of 1,1′-bi(cyclohex-1-enyl) (XV) gave three volatile products in the ratio 20:5:1. Only the major photoproduct (XVI), which was also the most volatile, was examined in detail. An isomer of the starting material, it showed IR (1703 cm^{-1}) and UV (λ_{max} 204 mμ, ε, 10,400) maxima indicative of a highly substituted non-conjugated double bond. The product of dihydrogenation of this photoisomer possessed only low end absorption in the UV and no IR maximum indicative of unsaturation. The cyclobutene (XVI) was a re-isomerized thermally to the starting diene. The stereochemistry of (XVI) was not determined.

The second photoproduct was not isolated in the pure state, but showed greater thermal stability than the main product, and appeared from its UV absorption and hydrogen uptake to be a non-conjugated diene.

The cyclobutene (XVII) was obtained as the chief photoproduct of myrcene (I). Isolated as a 90% concentrate, containing 9% of a minor, unidentified, photoproduct, it showed IR maxima indicative of the presence of trisubstituted ethylenic bonds (ν_{max} at 3040, 1647, 1634, 851 and 833 cm^{-1}); its UV absorption (no max; ε, 16,000 at 191 mμ) is in agreement. The tetrahydro-derivative, $C_{10}H_{20}$, showed none of these IR maxima, but gave a new doublet at 1385 and 1368 cm^{-1} due to the isopropyl group formed on hydrogenation. Its low UV end absorption (ε, 225 at 191 mμ) indicated the absence of further unsaturation. The structure (XVII) of the photoproduct was indicated by its thermal isomerization (99%) to myrcene when heated at 215° for 3 min, and was confirmed by the identification of γ-ketopimelic acid as the main (40%) product of oxidation of the cyclobutene by ozone followed by performic acid.

The amounts of cyclobutene (XVII) obtained under a variety of conditions are shown in Table 2. The use of polar solvents reduces the yield, and results in the formation of more non-volatile products. This appears to be a general phenomenon. Thus, the crude product of irradiating 1-cyclohexyl-1,3-butadiene in ethanol contains about 5% of the cyclobutene (XI), but this compound can be isolated in 43% yield if diethyl ether is used as the solvent. When formic acid is present in the solvent, myrcene gives a complex mixture of photoisomers, few of which correspond in gas chromatographic retention time to the minor products formed in the other irradiation experiments. The cyclobutene (XVII) was obtained in higher yield when the irradiation was carried out in warm, rather than cold, solvents. Similar results have been obtained for the photoisomerization of sorbic alcohol to the cyclobutene (XIII) and of α-phellandrene to a bicyclo[2.1.1]hexene.[13] In view of the thermal instability of cyclobutenes these results are surprising, and may help to elicit the nature of the intermediate excited states in these transformations.

When the Vycor filter was not used the proportion of minor photo-isomers

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[12] But see N. A. Preobrazhenskii, M. E. Maurit, G. I. Bazilevskaya, G. V. Smirnova, M. M. El'manovich, A. I. Valakhanovich and E. Persiyanova, *J. Gen. Chem. USSR* **30**, 2233 (1960); M. E. Maurit R. P. Shternberg, A. M. Pakhomov, G. I. Basilevskaya, G. V. Smirnova and N. A. Preobrazhenskii, *Ibid.* 2238 (1960).

[13] K. J. Crowley, *J. Amer. Chem. Soc.* **86**, 5692 (1964).

increased, which suggests that the cyclobutene formation is photochemically reversible. This was shown to be the case by irradiation of the isolated (88%) cyclobutene in isoöctane at 33°, using no filter. This resulted in partial re-isomerization to myrcene which, according to the UV and gas chromatographic data, reached an equilibrium value of ca. 1%; the amount of minor photoproducts, mainly those of myrcene, steadily increased. The cyclobutene was virtually unchanged after a similar irradiation in which a Vycor filter was used.

TABLE 2. IRRADIATION OF MYRCENE (86%; 6·4 g) IN 500 ml SOLVENT FOR 15 HR IN A WATER-COOLED QUARTZ IMMERSION WELL

Filter	Solvent	Temp	Optical density at 224 mμ[b] (% of orig. value)	Irradiation product (b.p. 40–75°/20 mm)		Yield of XVII[c] (%)
				Wt. (g)	% of XVII	
Vycor[a]	Hexane	50°	0·5	4·8	64	56
Vycor	Hexane	25°	0·3	4·27	61	48
Vycor	Hexane	0°	1·3	3·11	48	27
Vycor	Ether	25°	5·3	4·38	60	48
Vycor	Ether (60%) Ethanol (40%)	25°	3·0	0·47	68	6
Vycor	Ether (90%) Formic acid (10%)	25°	7·7	0·33	10	1
None	Ether	25°	30·5	3·75	37	26

[a] This 7910 Vycor glass filter supplied by Corning, N.Y., U.S.A., transmits 75% of 260 mμ wavelength light, 5%/220 mμ, 0%/210 mμ.

[b] Since the amount of light emitted by the (450 watt) lamp slowly decreases with age, these values do not give a reliable estimate of the velocity of the reaction.

[c] Calc. on the basis of 86% myrcene.

Ulery and McClenon recently discussed the IR spectra of cyclobutane derivatives.[14] In agreement with these authors, only one of the cyclobutenes described, 1,2-dimethylcyclobutene, shows strong absorption near 1235 cm^{-1}. On the other hand, all six hydrocarbon cyclobutenes have one of their eight strongest bands in the range 903–885 cm^{-1}, which can be attributed to the 4-ring methylene rocking mode except in the case of (XVI). Only the cyclobutene (XIII) which, like (XVI), contains no four-membered ring methylene, shows no strong absorption in this region.

In the UV, the λ_{1000} values[15] of these cyclobutenes are similar to or a little lower than those of most unstained ethylenic compounds. The di-substituted olefins (XI and XIII) have λ_{1000} 205 mμ and 206 mμ respectively. For the trisubstituted compounds 1-methylcyclobutene (IV), 1,3-dimethylcyclobutene (IX) and 1-isohex-3-enycyclobutene (XVII) the corresponding values are λ_{1000} 199, λ_{1000} 208 and λ_{2000} 210 mμ. The

[14] H. E. Ulery and J. R. McClenon, *Tetrahedron* **19**, 749 (1963): cf. G. Chiurdoglu, Th. Doehaerd and M. Duts, *Bull. Soc. Chim. Belges* **70**, 642 (1961).

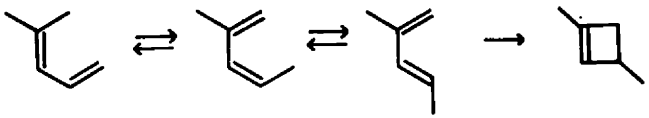
[15] D. W. Turner, *Determination of Organic Structures by Physical Methods* (Edited by Ed. F. C. Nachod and W. D. Phillips) Vol. II, p. 369. Academic Press, N.Y. (1962)

fully substituted cyclobutenes (VI and XVI) have λ_{1000} values of 208·5 and 220 mμ respectively.

No cyclobutene was identified among the irradiation products of XVIII, XIX or XX. 2,4-Dimethyl-1,3-pentadiene (XVIII) gave three volatile photoproducts (ca. 1% each), but none was isolated. No volatile products were detected in the product of irradiation of 2,5-dimethyl-2,4-hexadiene (XIX). Several were present in that of 1,1′-bi(cyclopent-1-enyl): only the most abundant of these (3%) was examined, but it was not obtained pure and its structure was not determined.

Diene migration. Reversible heat-induced migration of certain 1,3-dienes, involving 1,5-hydrogen transfer, has been shown to be a general reaction.[16] Here are reported two instances of this isomerization (Eq. b) being brought about reversibly by UV light, without the thermodynamic limitations of the thermal reaction.

Wolinsky *et al.* reported[16] that 4-methyl-1,3-pentadiene (VII) and 2-methyl-1, *cis*-3-pentadiene (VIII, *cis*) equilibrate when heated and that the latter is simultaneously isomerized irreversibly to the *trans* isomer. As mentioned above, prolonged irradiation of a (1:4) mixture of VII and VIII (*trans*) yields the cyclobutene (IX). During the irradiation the ratio of the two dienes approaches unity, while a fourth component forms in low yield and then disappears. The latter was isolated by distillation and identified as VIII (*cis*). When a small sample of pure[17] VIII (*trans*) was irradiated, and the change followed by gas chromatography, the formation of the two other dienes, VIII (*cis*) and VII, and of the cyclobutene (IX) was observed; while the proportion of 2-methyl-1,*cis*-3-pentadiene remained almost constant at 1–2% throughout the irradiation, the amount of cyclobutene steadily increased. Irradiation of pure VII gave similar results but the rate of cyclobutene formation was 4–5 times slower. This is explicable if, in the latter case, three steps are involved in cyclobutene formation, while in the former, the 2-methyl-1,*trans*-3-pentadiene gives the cyclic compound directly. We can thus formulate the photochemical changes as:



VII VIII *cis* VIII *trans* IX

Grummitt and Mandel reported[11] the preparation of the conjugated dienes (X and XXI), and suggested that both were the *trans* isomers. We have prepared these dienes by the same procedure and obtained the two compounds, apparently homogeneous by gas chromatography using the normal packed column, and having the published IR spectra. However, gas chromatography using the high resolving power of a capillary column showed both to be mixtures, each of two components.

The cyclohexyl-1,3-butadiene (X) contained two components in the ratio 3:1. That this mixture is mainly cyclohexyl-1,3-butadiene is shown by its oxidation,[11] in 65% yield, to cyclohexane carboxylic acid. The 972 cm^{-1} maximum suggests that the main component is the *trans* isomer. In our hands the mixture showed two UV maxima (in isoöctane) at 224 mμ (log ε, 4·36) and 221 mμ (log ε, 4·34), attributable

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[16] J. Wolinsky, B. Chollar and M. D. Baird, *J. Amer. Chem. Soc.* **84**, 2775 (1962); cf. J. Zirner and S. Winstein, *Proc. Chem. Soc.* 235 (1964); W. R. Roth and B. Peltzer, *Angew. Chem.* **76**, 378 (1964).

[17] G. B. Bachman and C. G. Goebel, *J. Amer. Chem. Soc.* **64**, 787 (1942).

to the *trans* and the *cis* compounds respectively. The quantitative addition of maleic anhydride at room temperature[11] shows that both components are conjugated dienes. Grummitt and Mandel interpreted this addition and the formation (54%) of a cyclic sulfone to indicate that the pyrolysis product was the *trans* isomer, but examination of molecular models suggests that the *cis* isomer would also form an adduct with maleic anhydride without difficulty.

The cyclohexylidene-2-butene (XXI) was separated into two components in the ratio 52:48. The published evidence[11] would suggest that these are the *cis* and *trans* isomers, and the UV spectrum (Experimental) is in agreement. These conclusions were confirmed by thermal and photochemical isomerizations.

In the light of the results of Wolinsky *et al.*[16] we would expect these four compounds to equilibrate on heating. Thermal isomerizations of X (*cis* and *trans*) and of XXI (*cis* and *trans*) showed that these interconversions do occur, and suggest that at the same time both *trans* isomers rapidly polymerize (Table 3).

TABLE 3. THERMAL ISOMERIZATION OF X AND XXI AT 370°

Starting material	Heating time (sec)	Product composition[a] (%) X		XXI		Polymer[b] (%)
		trans	*cis*	*cis*	*trans*	
X	0	77	23	0	0	0
	5	65	26	8	1	15
	7	58	20	14	8	45
	10	38	20	21	21	60
XXI	0	1	1	47	51	0
	20	1	18	38	43	5
	60	1	17	41	41	10

[a] Determined by gas chromatography using the capillary column; minor components, which never totaled more than 10% of the whole, were discounted.

[b] A rough value obtained by comparison of total gas chromatographic peak area arising from injection of equal volumes before and after heating.

It appears from these results that X (*trans*) is both more slowly formed, and more rapidly polymerized, than XXI (*trans*), but other reactions are also involved in these equilibria. When the isomerizations were carried out at higher temperatures a higher proportion of minor products was obtained.

The photochemical isomerizations of this system are more complex. The principal changes occurring on irradiation of the mixture of *cis* and *trans* isomers of cyclohexyl-1,3-butadiene are shown on Fig. 1. The proportion of cyclobutene (XI) increases at a steady rate, and both *cis* and *trans* cyclohexylidene-2-butene (XXI) are rapidly formed and then slowly destroyed. The other main intermediate product, formed in a maximum proportion of ca. 13%, was not identified.

Irradiation of *cis* and *trans* XXI, on the other hand, gave a complex mixture of unidentified products (none > 3%), and no product was identified. Polymerization was slightly more rapid than in the case of X.

We can thus write the principal photochemical changes (full arrows) as

$$\mathrm{XI} \leftarrow \mathrm{X}\ \textit{trans} \rightleftharpoons \mathrm{X}\ \textit{cis} \rightleftharpoons \mathrm{XXI}\ \textit{cis} \rightleftharpoons \mathrm{XXI}\ \textit{trans} \rightarrow \begin{array}{l}\text{unidentified}\\ \text{photoproduct}\end{array}$$

and by analogy with the above hexadiene photoisomerization, postulate others (broken arrows) as occurring more slowly.

It thus appears from the available data that, as in the thermal reaction, the photochemical diene shift to form a terminal methylene group occurs to only a slight extent unless the concomitant hydrogen migration results in the formation of another methyl group.

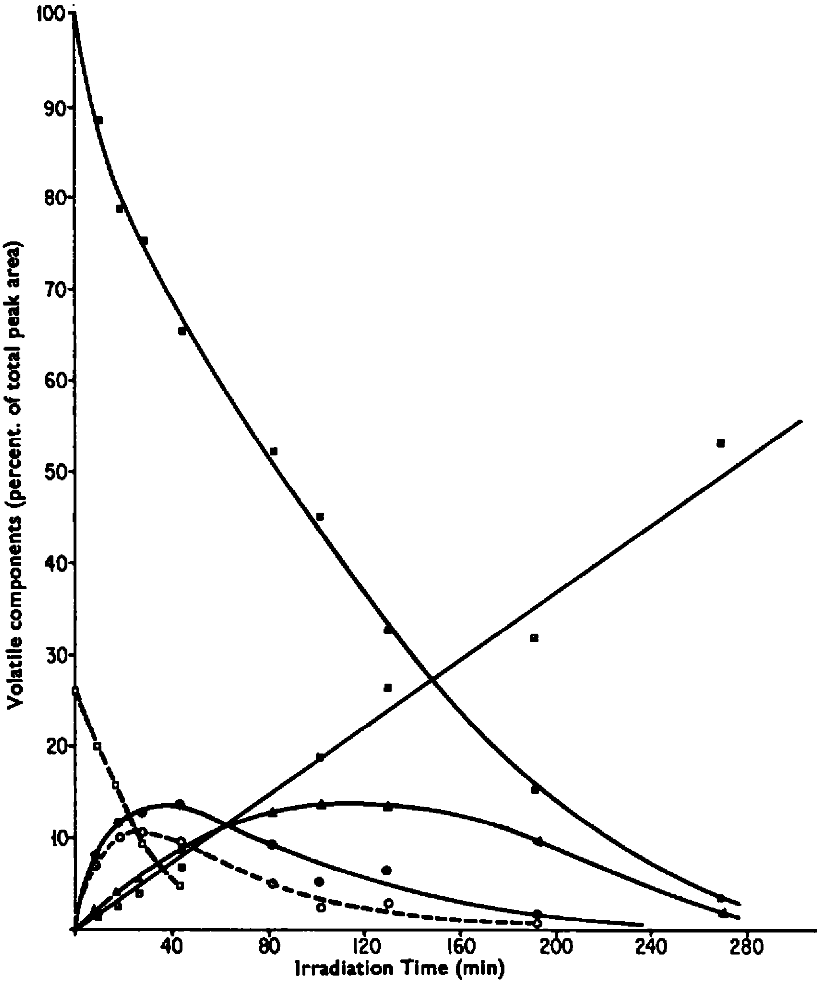

FIG. 1 Irradiation of 1-cyclohexyl-1,3-butadiene (X) in ether: ■—X (*cis* + *trans*); □—X (*cis*); ●—XXI (*cis* + *trans*); ○—XXI (*cis*); ▲—unidentified product, eluted between X and XXI; ⊡—cyclobutene (XI).

EXPERIMENTAL

Except where otherwise stated m.ps were determined on a Kofler Block; IR spectra (solids in KCl discs and liquids as films without solvent) on a Perkin-Elmer model 237 instrument; and UV spectra on a Unicam S.P. 500 spectrophotometer, using isoöctane as solvent. B.ps refer to atm. press. (620–625 mm) unless otherwise specified.

Gas chromatographic analyses were performed on a Perkin-Elmer model 154-D Vapour Fractometer. In all unspecified cases a 200 cm packed column of polyethylene glycol adipate was used. A 150′ × 0·01″ capillary column containing polypropylene glycol as the stationary phase was used when convenient, in conjunction with a flame ionization detector. This gave separations of 25,000–60,000 theoretical plate (T.P.) equivs.

Except where otherwise indicated, the light source was a 450 watt Hanovia lamp, No. 679A-36, in a standard Hanovia water-cooled well of Vycor glass, suspended in the solution being irradiated. The temp of this solution was altered by varying the water flow and/or by passing a cold (−40°) liquid through an auxiliary cooling coil.

As an irradiation solvent, ether (Absolute, Anhydrous, A.C.S. analysed reagent, Matheson, Coleman and Bell) was used without purification; isoöctane (Eastman Spectro grade) was redistilled; hexane was treated with conc H_2SO_4 and with $KMnO_4$, dried ($CaCl_2$) and distilled. Details of individual irradiations are given in Table 1.

Isoprene (Eastman) was redistilled through a 36″ spinning band column and appeared to be 99·8% pure (capillary column analysis). The mixture of 2-methyl-1,*trans*-3-pentadiene (80%) and 4-methyl-1,3-pentadiene (20%) was obtained by iodine catalyzed dehydration[18] of 2-methylpenta-2,4-diol. It had b.p. 62·8–62·9°, and was 99·8% pure (capillary column analysis). Sorbic alcohol (L. Light and Co.) was redistilled through a 36″ spinning band column; the fraction, b.p. 86°/20 mm, m.p. ca. 26°, was used. Capillary column analysis showed the presence of one major component (60%) and two minor (20% each). Its IR spectrum showed a very strong maximum at 980 cm^{-1} of the *trans* disubstituted double bond, but only weak absorptions corresponding to other olefin types. 2,4-Dimethyl-1,3-pentadiene (Aldrich; 99·8% by capillary column analysis) was used without purification. 2,5-Dimethyl-2,4-hexadiene (Eastman) was redistilled through the 36″ spinning band column, and had b.p. 127–127·5°. 1,1′-Bi(cyclopent-1-enyl), prepared from cyclopentanone,[19a] had b.p. 76–77°/5 mm, m.p. 8°, n_D^{25} 1·5255. 1,1′Bi(cyclohex-1-enyl), prepared from cyclohexanone,[19] was obtained as prisms, m.p. 21–22°, b.p. 79°/1·2 mm, after fractionation through the 36″ spinning band column.

Myrcene (L. Light and Co.) was fractionated through the 36″ spinning band column. The best fraction (91%) contained, as the main impurity (5%), a component separated from myrcene only by means of the capillary column.

1-*Methylcyclobutene* (IV). The solution of isoprene (10 ml; 6·77 g) was irradiated as indicated in Table 1, and then distilled through a 36″ spinning band column. The first fraction (10 ml, b.p.up to 55°) was redistilled through an 18″ spinning band column. Examination of the resulting fractions by gas chromatography (capillary column, 25°) indicated a total yield of 2·42 g (36%) of the main irradiation product. This, as a 92% concentrate (b.p. 31°), had n_D^{21} 1·4024 (literature value[20] n_D^{25} 1·4034) UV end absorption ε_{205} 420, ε_{200} 900, ε_{196} 1250, ε_{192} 1600. It has an IR spectrum identical with that of 1-methylcyclobutene except for the absence of the band at 1670 cm^{-1}; this band in the published spectrum[9] is probably due to the presence of methylenecyclobutane.

1,2-*Dimethylcyclobutene* (VI). 2,3,-Dimethylbutadiene (8·85 g) in dry ether (930 ml) was irradiated, and the ether carefully removed through a 36″ spinning band column. The residue was distilled through an 18″ spinning band column and the resulting fractions were found to contain a total of 6·33 g (71%) cyclobutene. The best fraction (97%), b.p. 61·5°, n_D^{23} 1·4194, had no UV maximum but showed end absorption (ε_{220} 480, ε_{210} 910, ε_{200} 3370, ε_{194} 6800, ε_{191} 8100); it gave IR maxima at 2940–2810, 2717, 2074, 1686, 1428, 1373, 1285, 1215, 1174, 1107, 893, 763, 694 and 637 cm^{-1}. (Found. C, 87·43; H, 12·22. C_6H_{10} requires: C, 87·73; H, 12·27%).

The dimethylcyclobutene (97%; 25 mg) was sealed in glass under red. press. and heated in an oil bath at 210° for 10 min. The product appeared, on capillary column analysis, to consist of 90% 2,3-dimethylbutadiene with 10% unchanged cyclobutene; its IR spectrum is identical with that of 2,3-dimethylbutadiene except for the presence of additional weak bands due to the minor component.

The dimethylcyclobutene (97%; 148 mg) was stirred in H_2 with a prereduced mixture of Pd—C (100 mg) and isoöctane (5 ml). After 20 min the H_2 uptake ceased, 51·6 ml (1·01 equivs) having been absorbed. No attempt was made to isolate the dihydro product, which showed no UV maxima, but had ε_{190} 44.

The dimethylcyclobutene (1·0 g; 80%, the main contaminant being ether) was added to a mixture of acetone (20 ml), water (10 ml) and $KMnO_4$ (2·0 g). After 0·5 min 10% NaOH aq (3 ml) was

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[18] S. A. Ballard, R. T. Holm and P. H. Williams, *J. Amer. Chem. Soc.* **72**, 5734 (1950).

[19a] E. de B. Barnett and C. A. Lawrence, *J. Chem. Soc.* 1104 (1935); [b] E. E. Gruber and R. Adams, *J. Amer. Chem. Soc.* **57**, 2555 (1935).

[20] S. W. Ferris, *Handbook of Hydrocarbons.* Academic Press, N.Y. (1958).

added. The mixture was rapidly filtered through kieselguhr, acidified and extracted with ether, which was then washed with water. The aqueous solutions were combined, heated to volatilize the acetone, and split into 3 parts. These gave 3 derivatives of 2,5-hexanedione, the semicarbazone, m.p. 222° (lit.[21] m.p. 220°), the 2,4-dinitrophenylhydrazone, m.p. 258·5° (lit.[22] m.p. 260°), and the *bis* oxime, m.p. 135·5° (lit.[23] m.p. 134·5°). The yields of semicarbazone and of 2,4-dinitrophenylhydrazone both correspond to a 23% yield of the diketone in the oxidation.

1,3-*Dimethylcyclobutene* (IX). A mixture (11·3 g) containing 20% VII and 80% VIII in isoöctane (500 ml) was irradiated as indicated in Table 1. The solution was distilled through a 36″ spinning band column until only solvent remained in the residue. The distillate (12·9 g), which contained 19% of IX (21% yield based on the mixed dienes), was fractionated through an 18″ spinning band column. The fraction, b.p. 50·3–50·5°, n_D^{23} 1·4041, was shown by gas chromatography to be 99% pure. This product showed UV end absorption at 190 mμ (ε, 6800) and in the IR had ν_{max} 3076, 3000–2840, 2717, 2624, 2252, 1721, 1633, 1453–1428, 1370, 1317, 1272, 1212, 1189, 1176, 1061, 1023, 980, 925, 900, 869, 806 and 757 cm^{-1}. (Found: C, 87·63; H, 12·12; C_6H_{10} requires: C, 87·73; H, 12·27%).

The product from the last reaction (71·3 mg) in isoöctane (14 ml) over 5% Pd—C absorbed 1·02 equivs H_2 during 20 min, after which absorption stopped. The dihydro product was isolated from a larger scale hydrogenation and identified as 1,3-dimethylcyclobutane by its IR spectrum.[10]

The cyclobutene (99%; 20 μl) was heated in a sealed evacuated tube at 230° for 0·5 min. Gas chromatography showed the product to be 99% 2-methyl-1,*trans*-3-pentadiene; this identification was confirmed by the IR spectrum.

3-*Cyclohexyl-cyclobutene* (XI). 1-Cyclohexyl-1,3-butadiene (3·9 g; 94%, containing 4% cyclohexylidene-2-butene: *vide infra*) was irradiated in diethyl ether (500 ml). The crude product, after removal of the ether, contained about 60% volatile material, of which 80% was a single new compound. Fractional distillation through an 18″ spinning band column gave the cyclobutene (XI; 43%). The best fraction (86% by capillary column analysis) had b.p. 71°/20 mm, n_D^{22} 1·4702, showed no UV maximum (end absorption ε, 700 at 210 mμ, 1000/205, 1700/200 and 3000/195), and gave IR maxima at 3125, 3039, 2924, 2840, 1745, 1570, 1450, 1290, 1265, 1243, 1219, 1206, 1152, 1064, 978, 932, 916, 885, 869, 800, 769, 730, 719, 699 and 678 cm^{-1}. (Found: C, 88·22; H, 11·42; $C_{10}H_{16}$ requires: C, 88·16; H, 11·84%).

Irradiation of X (5·53 g) in 95% ethanol (200 ml) at 31–33° until the UV absorption at 225 mμ had decreased to 0·5% of its original value gave a viscous product which was found, by gas chromatography, to contain ca. 5% of XI. This could not be separated from the accompanying polymer by distillation owing to its thermal instability.

A portion (30 μl) of the cyclobutene (86%) was sealed in an evacuated glass tube and heated at 200° during 4 min. The product was shown by gas chromatographic and IR measurements to be 1-cyclohexyl-1,3-butadiene (ca. 90%). The same isomerization to the conjugated diene occurred during gas chromatographic analysis at 110° if the injection block was maintained at about 280°. The cyclobutene is, however, stable on storage; thus after standing for 2 weeks at room temp it gave an IR spectrum indistinguishable from that of the freshly prepared sample.

Hydrogenation of the cyclobutene (116 mg) in acetic acid (5 ml) over PtO_2 (30 mg) resulted in the uptake of 0·97 equivs H_2. The dihydro product (n_D^{28} 1·4610) was 90% homogeneous and, according to its IR spectrum, contained no unsaturated bonds.

The cyclobutene (XI; 187 mg), dissolved in a mixture of MeOH (20 ml) and $CHCl_3$ (20 ml), was cooled to −80° and treated with a stream of O_3 until the solution was faintly blue. The solvents were evaporated under red. press., and the residue, in 30% H_2O_2 (5 ml) and formic acid (5 ml), was heated until reaction began, and again for 30 min after it had ceased. The mixture was evaporated under red. press., and the residual oil, in ether, washed with Na_2CO_3 aq. The latter was acidified, and extracted with ether to yield an acidic oil (128 mg) which crystallized during 2 weeks. After being washed with ether–pentane (1:1) and recrystallized from ethyl acetate–hexane, this yielded rhombic crystals (59 mg; 24%), m.p. 148–149°. These, after recrystallization from hot water, had m.p. 145–146°; reported[24] for cyclohexylsuccinic acid, m.p. 146–147°, (Found: C, 59·90; H, 8·09;

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[21] W. H. T. Davison and P. E. Christie, *J. Chem. Soc.* 3389 (1955).

[22] L. A. Jones, C. K. Hancock and R. B. Seligman, *J. Org. Chem.* **26**, 228 (1961).

[23] W. Reppe, *Liebigs Ann.* **596**, 180 (1955).

[24] G. Swain, A. R. Todd and W. S. Waring, *J. Chem. Soc.* 548 (1944).

Equiv. 108. Calc. for $C_8H_{14}(COOH)_2$: C, 59·98; H, 8·06%; Equiv. 100). The same acid (m.p. and mixed m.p.) was obtained in 28% yield when the oxidation was carried out with $KMnO_4$ as described above for 1,2-dimethylcyclobutene.

3-*Methyl-4-hydroxymethylcyclobutene* (XII). Sorbic alcohol (XII; 6·26 g) in ether (500 ml) was irradiated for 20 hr. Gas chromatographic analysis (capillary column) showed the presence of 2 main new products (20% each) as well as the 3 isomers of the starting material (15%, 15% and 20%). The noxious mixture was fractionated through an 18″ spinning band column. The fraction, b.p.$_{21}$ 40–46°, appeared on the capillary column to consist of ca. 97% of the more volatile photoproduct; it had n_D^{25} 1·4331, λ_{max} 272 mμ (ε, 52) end absorption at 205 mμ (ε, 660) in EtOH, and showed strong maximum at 2725 and 1727 cm^{-1} indicative of the aldehydic grouping. (Found: C, 71·40; H, 10·28%). The second main photoproduct (ca. 94%: capillary column) had b.p. 65°/21 mm, n_D^{25} 1·4603, end absorption at 200 mμ (ε, 1900 in EtOH) and IR maxima at 3333, 3040, 2970–2880, 1458, 1375, 1330, 1075, 1040, 988, 757, 736 and 720 cm^{-1}. (Found. C, 72·46; H, 10·30. $C_6H_{10}O$ requires: C, 73·43; H, 10·27%). Two other samples of this cyclobutene, prepared subsequently, gave similar analytical results. Both photoproducts were apparently wet, although this could not be verified as the flame ionization detector which is used in conjunction with the capillary column is insensitive to water: satisfactory separations were not achieved with normal packed columns.

On hydrogenation in MeOH over Pt, the cyclobutene absorbed 0·98 equivs H_2. The dihydro product had ε_{200} 147 and showed no alkene absorption in the IR. Thermal isomerization of the cyclobutene for 2 min at 230° yielded (capillary column analysis and IR spectrum) *trans*, *trans* sorbic alcohol (50%), the two other isomers of the same diene (10% each) and 4 other compounds.

Ozonolysis of the cyclobutene (XIII). The photoproduct (239 mg) in MeOH (15 ml) at −80° was treated with O_3 and performic acid as described for XI. The Na_2CO_3 aq was acidified and extracted first with ethyl acetate and then continuously with ether during 4 hr. After recrystallization the product (152 mg; 43%) had m.p. 100–101·5° (Fisher Johns) (lit.[25] 104°), ν_{max} 1780 (γ-lactone) and 1723 cm^{-1} (carboxyl) in $CHCl_3$. (Found: C, 50·17; H, 5·50; equiv. 138. Calc. for $C_5H_7O_2(CO_2H)$: C, 50·00; H, 5·59%; equiv. 144).

1,4:2,3-*Dibutanocyclobutene* (XVI). 1,1′-Bi(cyclohex-1-enyl) (20·3 g) in ether (950 ml) was irradiated as indicated in Table 1. Removal of the ether and fractionation of the residue through a 36″ spinning band column yielded fractions containing the 3 photoproducts, 45%, 10% and 2%, in order of decreasing volatility. The best fraction (92%) (b.p. 65°/5 mm) of the main product (XVI) had n_D^{23} 1·5115, λ_{max} 204 mμ (ε, 10,400), ε_{230} 34, ε_{220} 1000, ε_{214} 5200, ε_{190} 8600, and gave IR maxima at 1706, 1458, 1447, 1340, 1318, 1307, 1269, 1230, 1165, 1124, 1085, 1043, 976, 965, 927, 917, 833, 825 and 766 cm^{-1}. (Found: C, 88·83; H, 11·00. $C_{12}H_{18}$ requires: C, 88·82; H, 11·18%). A higher-boiling fraction, b.p. 69–75°/5·5 mm, contained the main (45%) and the second (42%) photoproducts, and starting material (5%); this fraction showed UV absorption corresponding to ε ca. 500 at 215 mμ for the second photoproduct, while its H_2 uptake (over 5% Pt–C in isoöctane) corresponded to 2·1 double bond equivs in the same compound.

Part of the 92% fraction from the last experiment (309 mg; 1·91 mmoles) was added to a pre-reduced mixture of acetic acid (10·0 g) and PtO_2 (42 mg). After 30 min H_2 absorption ceased, the total uptake being 61·2 ml (2·06 mmoles). The mixture was filtered, poured into excess NaOHaq, extracted with ether, dried and the ether evaporated. The residue showed no UV maxima but had ε_{200} 160, ε_{190} 650. It gave a new IR maximum at 1754 cm^{-1}, and was found by gas chromatography to consist of 2 new components present in the same ratio (15:1) as the 2 in the starting material.

When the cyclobutene (25 μl) was sealed in glass under red. press., and heated at 280° for 2·5 hr, gas chromatographic analysis indicated 85% of the diene (XV); the minor component being largely unchanged. The product had m.p. 19°, and gave an IR spectrum closely resembling that of the diene.

1-(*Isohex*-3-*enyl*)*cyclobutene* (XVII). Myrcene (35·6 g; 87%) was irradiated in ether (1000 ml). The ether was evaporated and the residue rapidly distilled through a 36″ spinning band column. Gas chromatographic analysis (capillary column) of the distillate (31·3 g, b.p. 70–105°/40 mm) indicated yields of β-pinene, of the most volatile photoproduct, and of cyclobutene, of 10·5%, 3% and 68% respectively (based on 87% myrcene in the starting material).

On careful redistillation through the same column the β-pinene was obtained in 75% purity

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[25] C. K. Ingold, *J. Chem. Soc.* 397 (1925); F. Fichter and E. Rudin. *Ber. Dtsch. Chem. Ges.* 37, 1610 (1904).

(b.p. 62·3–62·4°/21 mm). This product was not separated from an admixed authentic sample on the capillary column operated at 50,000 T.P. efficiency, and gave an IR spectrum identical with that of β-pinene in respect of the 30 major maxima.

The most volatile photoproduct, b.p. 49–50·5°/19 mm, n_D^{24} 1·4539 was isolated in 3% yield and 83% purity. This compound had UV (λ_{1000} 206) and IR (3077, 1825, 1634, 993 and 910 cm^{-1}) absorption consistent with the presence of a monosubstituted double bond, and absorbed 1·1 equivs H_2 (over Pt, in acetic acid).

After redistillation the purest fraction of cyclobutene (90%) had b.p. 70·0°/20 mm, n_D^{25} 1·4618, ε_{210} 2000, ε_{200} 10,400, ε_{191} 16,000, and showed IR maxima at 1675, 1647, 1634, 1449, 1379, 1282 1234, 1213, 1176, 1106, 1070, 985, 892, 851 and 833 cm^{-1}. (Found: C, 88·23; H, 11·80. $C_{10}H_{16}$ requires: C, 88·16; H, 11·84%).

The cyclobutene (XVII; 83%; 375 mg; 2·76 mmoles) was dissolved in glacial acetic acid (5 ml) and hydrogenated over prereduced PtO_2 (40 mg) at 23°. Reaction stopped after 30 min, when 164 ml (5·52 mmoles) H_2 had been absorbed. The solution was filtered, poured into water, neutralized with NaOH and extracted with ether. The product, purified by gas chromatography, had an IR spectrum closely resembling that of another specimen, obtained in a later non-quantitative experiment, and purified by distillation through an 18" spinning band column. This *tetrahydro product* had b.p. 65·4°/20 mm, n_D^{23} 1·4275, ε_{191} 225, IR maxima at 1387, 1370, 1250 and 917 cm^{-1}. (Found: C. 85·48; H, 14·42. $C_{10}H_{20}$ requires: C, 85·63; H, 14·37%).

The cyclobutene (1·095 g; 79%, containing 8% mycrene) in MeOH (20 g) was cooled to −80° and treated with ozonized O_2 until the solution was faintly blue. The excess O_3 was removed with a stream of O_2 and the solution evaporated at room temp. To the resulting syrup, formic acid (10·5 g) and 30% H_2O_2 (5·5 g) were added, and the mixture was warmed until the reaction commenced. After 90 min refluxing the solution was evaporated under red. press. The resulting solid was recrystallized from water and then from MeOH–$CHCl_3$–pet. ether (b.p. 40–60°) to give γ-keto-pimelic acid (443 mg: 40% based on 79% starting material) m.p. 141·5°, mixed m.p. 140° with an authentic sample (synthesized according to Gardner *et al.*[16]). (Found: C, 48·36, H, 5·84. Calc. for $C_7H_{10}O_5$: C, 48·28; H, 5·79%). The two acid samples had identical IR spectra.

A further portion of the same cyclobutene fraction (24 mg) was heated *in vacuo* at 215° for 3 min. Gas chromatographic examination of the product showed 95% conversion of the cyclobutene to myrcene, the other components remaining unchanged. The product had an IR spectrum differing from that of myrcene only in the presence of a few additional weak maxima.

Photochemical interconversion of 4-methyl-1,3-pentadiene (VII) *and 2-methyl-1,* trans*-3-pentadiene* (VIII). 4-Methyl-1,3-pentadiene was isolated from the above mixture by treatment with maleic anhydride.[17] Pure 2-methyl-1,*trans*-3-pentadiene was obtained by thermal isomerization of IX. A 2% ethereal solution (1 ml) of each of the two dienes (both > 99%) in a small Vycor glass tube, which contained a water-cooled cold-finger condenser, was irradiated for 22 hr with 2537 Å light by suspending the tube between two 15 watt Germicidial lamps (General Electric, No. G15T8). The reactions were followed by gas chromatography using a squalane column. In each case the proportion of 2-methyl-1,*cis*-3-pentadiene rapidly reached a constant value (ca. 1%). At the end of the irradiation the isomeric products from the *trans*-2-methyl diene (VIII, *trans*) were starting material (48·6%); VIII, *cis* (1·0%); VII (8·2%); and cyclobutene (42·2%). The corresponding figures for VII were starting material, 77·5%; VIII, *trans*, 12·0%; VIII, *cis*, 1·6%; and cyclobutene, 8·9%.

The intermediate photoproduct was identified as 2-methyl-1,*cis* 3-pentadiene by partial irradiation of the diene mixture (14·74 g) in isoöctane (500 ml). The *cis* diene was isolated in 6% yield after distillation; the best fraction (78%, containing 16% of the *trans* isomer) had b.p. 61–63° and showed all the reported[16] IR maxima of the *cis* diene.

Preparation of cis *and* trans-1-*cyclohexyl*-1,3-*butadiene* (X) *and* cis *and* trans-*cyclohexylidene-2-butene* (XXI). 1-Cyclohexyl-1-acetoxy-2-butene, prepared as reported[11] had b.p. 90–92°/2 mm, n_D^{22} 1·4618 after fractional distillation through a 36" spinning band column. Pyrolysis of this acetate (90% homogeneous by gas chromatography) at about 500° followed by working up as indicated,[11] and fractionation through a 36" spinning band column, gave overall yields (determined by gas chromatographic examination of the distillate fractions) of cyclohexyl-1,3-butadiene and 1-cyclohexylidene-2-butene of 30% and 8% respectively. The former had b.p. 58°/5 mm, n_D^{22} 1·4906, (reported[11] b.p. 64°/8 mm, n_D^{20} 1·4925), appeared by gas chromatography to be 98% homogeneous,

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[16] P. D. Gardner, L. Rand and G. R. Haynes, *J. Amer. Chem. Soc.* **78**, 3425 (1956).

and showed UV maxima at 221 mμ (log ε, 4·34), 224 mμ (log ε, 4·36), shoulder at 231 mμ (log ε, 4·22). Its IR spectrum differed from that published only in the diminution of a medium intensity maximum at 838 cm^{-1} probably due to the reduction in the amount of a minor product of the pyrolysis.

The 1-cyclohexylidene-2-butene had b.p. 66·5°/6 mm, n_D^{23} 1·5117 (reported[11] b.p. 59°/4 mm, n_D^{20} 1·5105) and appeared by gas chromatography to consist of 96% of XXI and 4% of X. Its IR spectrum was virtually indistinguishable from that reported for XXI; it showed UV maxima at 230·5 mμ (log ε, 4·34), 237 mμ (log ε, 4·39), shoulder at 245 mμ (log ε, 4·23).

Subsequent examination of these two products by means of the capillary column showed both to be mixtures of two components (see discussion), although in neither case was the separation complete.

Thermal isomerizations of 1-*cyclohexyl*-1,3-*butadiene* (X) *and cyclohexylidene*-2-*butene* (XIX). These were carried out on 10 μl samples sealed in glass at 20 mm. The ampoules (total interior volume 20–30 μl) were heated in a liquid metal bath at 370°, and the products examined by gas chromatography (Table 3).

Photoisomerizations of 1-*cyclohexyl*-1,3-*butadiene* (X) *and cyclohexylidene*-2-*butene* (XXI). Cyclohexyl-1,3-butadiene (1·317 g; 75% *trans*, 23% *cis*) in ether (200 ml) at 28° was irradiated as usual for a total of 270 min, and the reaction was followed on the capillary column operated at 35,000 T.P. efficiency. The proportions of the volatile photoproducts, calculated from relative peak areas, are given in Fig. 1. Besides the cyclobutene (XI), the final product contained about 20 minor components (0·2–8%).

Cyclohexylidene-2-butene (1·2 g; 47% *cis*, 51% *trans*) was irradiated in a similar fashion for 152 min; the ratio of the two starting materials remained virtually unchanged, and no other single volatile compound comprised more than 3% of the total at the end of the irradiation. About half of the 16 minor products detected corresponded in retention time with minor products formed on irradiation of cyclohexyl-1,3-butadiene. The UV absorption curve of the mixture did not change markedly in shape during the irradiation but diminished steadily to 45% of the original intensity.

Note added in Proof. Since methyl paraconic acid (XIV) is probably[12] *trans* the cyclobutene (XIII) is probably *cis*. If XIII is formed *via* the first excited state of the 1,3-diene (XII) this would be in agreement with the predictions of R. B. Woodward and R. Hoffmann (*J. Amer. Chem. Soc.* in press), to whom thanks are due for sending a copy of the manuscript.