Mechanistic Investigations in the Photochemistry of Acyclic Conjugated Dienes. Significance of the [1,5] Sigmatropic Shifts of Hydrogen

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The determination of initial quantum yields for product formation in the direct photolysis of the three interconvertible dienes, 4-methylpenta-1,3-diene and *cis*- and *trans*-2-methylpenta-1,3-diene, leads to revision of the mechanism formerly proposed by Crowley and brings more insight into the properties of the excited dienes in solution. Thus it is shown that *cis*-2-methylpenta-1,3-diene largely assumes an s-*cis* ground state conformation and that its S_1 state makes efficient use of both the [1,5] hydrogen shift and the 1,4-cyclomerization co-ordinates for decaying to the ground state; the two other dienes undergo unambiguously, though with a low quantum yield, an abnormal [1,5] shift of hydrogen which can only originate from a *trans* configuration and hence supports the doubly twisted (bicyclobutane-like) structure which we have previously assigned to at least one of the possible vibrationally relaxed S_1 states of acyclic 1,3-dienes.

A NUMBER of studies [1-5] dealing with the photochemistry of acyclic 1,3-dienes has led to the idea that the singlet excited state initially populated by absorption of light in solution either isomerizes to a cyclobutene derivative [2-4] *via* an unquenchable route [5] or relaxes vibrationally in acquiring a geometrical configuration corresponding to an energy well on the S_1 hypersurface and to an energy maximum in the ground state; [3] the relaxed state would thereafter flow down into one of the several accessible valleys of the S_0 hypersurface thus giving rise either to internal conversion or to photoproducts which are geometrical and structural isomers, the significance of the latter having apparently been underestimated. At this time two major questions remain unanswered, namely: (i) what is the actual structure of the vibrationally relaxed excited state? This point is the subject of much controversy [1,5,6] especially on account of theoretical predictions [7] and more experimental information is needed before a definite conclusion can be reached. It even seems plausible [3] that more than one such relaxed entity should be taken into consideration for explaining the photochemical behaviour of a molecule. (ii) What are the distinct properties of s-*cis*- and s-*trans*-excited dienes? It has widely been assumed that the ground state s-*cis* $\rightleftharpoons$ s-*trans* equilibrium favours the *trans*-form which would thus be essentially the one excited and yet cyclobutenes can only arise (with an unknown real quantum yield) from the s-*cis*-fraction of the molecules. In particular no attention has been paid to the relative contribution of an antarafacial [1,5]hydrogen shift to the decay of the s-*cis* excited singlet dienes although this process has been recognized.[8] A further complication of the problem arises when substituents on the diene produce non-planar conformers and only cisoid or transoid character can then be assumed, the extreme case (*e.g.* 2,3-di-t-butylbuta-1,3-diene) corresponding to two orthogonal ethylenes.[9]

We report here an extensive quantitative study of

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[1] For a recent review, see J. Saltiel, J. D'Agostino, E. D. Megarity, L. Metts, K. R. Neuberger, M. Wrighton, and O. C. Zafiriou, *Org. Photochem.*, 1973, **3**, 1.

[2] W. Th. A. M. van der Lugt and L. J. Osterhoff, *J. Amer. Chem. Soc.*, 1969, **91**, 6042.

[3] J. Michl, 'Chemical Reactivity and Reaction Paths,' ed. G. Klopman, Wiley, New York, 1974, ch. 8.

[4] A. Devaquet, Plenary Lecture presented at the Vth IUPAC Symposium on Photochemistry, Enschede, The Netherlands, 1974; *J. Amer. Chem. Soc.*, 1975, **97**, 6629.

[5] M. Bigwood and S. Boué, *J.C.S. Chem. Comm.*, 1974, 529.

[6] W. G. Dauben and J. S. Ritschers, *J. Amer. Chem. Soc.*, 1970, **92**, 3227.

[7] E. M. Evleth, *Chem. Phys. Letters*, 1969, **3**, 122; N. C. Baird and R. M. West, *J. Amer. Chem. Soc.*, 1971, **93**, 4427; K. Inuzuka and R. S. Becker, *Bull. Chem. Soc. Japan*, 1971, **44**, 3323.

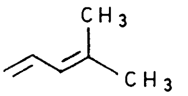
[8] (*a*) K. J. Crowley, *Tetrahedron*, 1965, **21**, 1001; (*b*) E. F. Kiefer and J. Y. Fukunaga, *Tetrahedron Letters*, 1969, 993; E. F. Kiefer and C. H. Tanna, *J. Amer. Chem. Soc.*, 1969, **91**, 4478; (*c*) W. G. Dauben, C. D. Poulter, and C. Suter, *ibid.*, 1970, **92**, 7408.

[9] N. L. Allinger and M. A. Miller, *J. Amer. Chem. Soc.*, 1964, **86**, 2811.

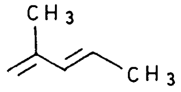
4-methylpenta-1,3-diene (I), *trans*-2-methylpenta-1,3-diene (II), and *cis*-2-methylpenta-1,3-diene (III) excited in their singlet state in solution. The reason for choosing this system of isomeric dienes which were shown to interconvert photochemically[8a] lies in the two-fold observation that [1,5] hydrogen migrations are taking place competitively with other processes and that the u.v. spectra suggest[9] that (III) displays considerable cisoid character, $\lambda_{max.}$ 229 nm ($\varepsilon_{max.}$ 11 000 l mol^{-1} cm^{-1}), whereas the s-*trans*-conformer would be dominant in (II), $\lambda_{max.}$ 227.5 nm ($\varepsilon_{max.}$ 27 200 l mol^{-1} cm^{-1}), and in (I), $\lambda_{max.}$ 234 nm ($\varepsilon_{max.}$ 29 300 l mol^{-1} cm^{-1}).

EXPERIMENTAL AND RESULTS

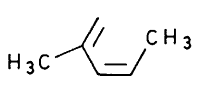
Reagents and Methods.—Pure dienes (I) and (II) obtained from Aldrich were used as such (>99% by g.l.c.); n-pentane (*pro analysi*; UCB) proved transparent in the u.v. down to 210 nm and g.l.c. analysis showed a trace impurity (<1%) at a retention time shorter than that of pentane. The diene (III) was prepared in pyrolysing a vapour sample of (I) at 250° during 15 min in a sealed flask; the resulting mixture was fractionated by g.l.c. and the pure diene was recovered in 20% yield by trapping at 77 K. All qualitative and quantitative analyses were carried out by g.l.c. (Intersmat IGC 16) and satisfactory separation of all components was readily achieved on a Silicone Nitrile XE-60, 20% on Chromosorb P, 5 m column programmed from 30 to 60°. U.v. spectra were recorded on a Cary 14 spectrophotometer, i.r. spectra on a Perkin-Elmer 357 machine, and n.m.r. on a Varian T60 instrument.



(I)



(II)



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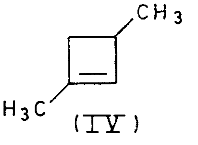

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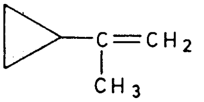
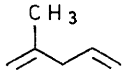
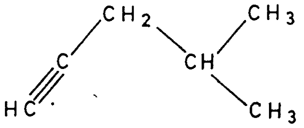


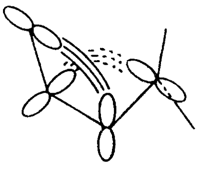
(V)



(VI)



(VII)


(VIII)

Photolyses.—All photolyses were performed on calibrated n-pentane solutions of dienes at 20° in optical quartz cells (1 cm pathlength) set on an optical bench and using the 253.7 nm output of a low pressure Rayonet RPR mercury lamp as the light source. At the concentrations used all the light which entered the cell was absorbed within less than 1 cm and local depletion of substrate was prevented by using a micro-magnetic stirrer; the light intensity was 3.66 × 10^{-9} E s^{-1} cm^{-3} as measured by the *cis* ⟶ *trans* isomerization of penta-1,3-diene ($\phi_{cis \rightarrow trans}$ 0.10).[10]

The irradiation of a 4.13 × 10^{-2}M solution of (III) in pentane ($\varepsilon_{253.7}$ 280 l mol^{-1} cm^{-1}) * resulted in the formation of three products † which accumulated linearly with time and with a zero-intercept (up to 10% conversion) and which thus originate from monophotonic processes; they were trapped at 77 K as they streamed from the gas fractometer and their i.r. spectrum (CCl$_4$) was superimposable respectively on that of (I), of (II), and of 1,3-dimethylcyclobutene (IV).[8a]

The photolysis of a 1.66 × 10^{-1}M solution of (II) in pentane ($\varepsilon_{253.7}$ 82 l mol^{-1} cm^{-1}) * produced four primary compounds,† three of which appeared at a constant rate (conversion <10%) while the fourth proved photochemically (but not thermally) labile and progressively reached a stationary concentration; the first three products analysed for (I), (III), and (IV) (i.r. and g.l.c. retention time) but the labile compound, although corresponding to a major primary process did not accumulate in sufficient amount to be identified.

The diene (I) responded to electronic excitation quite differently from the other two isomers; indeed a 1.78 × 10^{-1}M solution ($\varepsilon_{253.7}$ 461 l mol^{-1} cm^{-1}) * irradiated as described above yielded dimers as by far the most important photoproducts. There were also however five isomeric monomers whose kinetic of formation indicated unambiguously that they arise directly from (I). Structures (II) and (III) were suggested by the g.l.c. retention times and confirmed by i.r. spectroscopy. A new product (V) had δ 4.6 (2 H, s), 1.61 (3 H, s), 1.35 (1 H, m), and 0.50br (4 H), which would accommodate a cyclopropane ring and an olefin; the i.r. absorptions at 1 635 and 876 cm^{-1} indicate a 1,1-disubstituted olefin and the spectra were identical with those reported for isopropenylcyclopropane.[11] The second new product (VI) had characteristic i.r. absorptions at 892 (CH$_2$=C$<$), 917 and 993 (CH$_2$=C$<$), 1 374 (CH$_3$), 1 636 and 1 648 (C=C), and 3 080 cm^{-1} (H–C=C) and δ 5.7br (1 H), 5.2—4.7 (4 H, complex), 2.73 (2 H, d, J 6 Hz), and 1.73 (3 H, s); the structure of 2-methylpenta-1,4-diene clearly fits these data. The last product (VII) was recognized as a monosubstituted acetylene by i.r. absorptions at 3 315 (HC≡C), 2 103 (C≡C), and 640 cm^{-1} (HC≡C); the n.m.r. resonances at δ 2.77br (1 H, s), 1.65br (2 H, d, J 8 Hz), 0.9br (1 H), and 0.9sh (6 H, d, J 3 Hz) lend support to the proposal of 4-methylpent-1-yne.

The kinetics and quantum yields for the measurable transformations are presented in the Table.

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* Determined by measuring log I_0/I for the resonance line of a low pressure mercury lamp.

† Dimers were also formed but not analysed; the total quantum yield for them can be estimated from a consideration of the mas balance expressed by ϕ (disappearance) − $\Sigma\phi$ (isomers) (see Table).

[10] S. Boué and R. Srinivasan, *J. Amer. Chem. Soc.*, 1970, **92**, 3226.

[11] (a) 'Documentation of Molecular Spectroscopy,' Butterworths, London, 1967, DMS spectrum no. 4704; (b) T. Teraji, I. Moritani, and E. Tsuda, *J. Chem. Soc (C)*, 1971, **19**, 3255.

Quantitative determination of the products formed in the direct photolysis of dienes (I)—(III) in n-pentane solution at 20°; light intensity 3.66×10^{-9} E s^{-1} cm^{-3} at 253.7 nm. The figures are calculated in the range of conversion (<10%) where the products appear linearly with time and with a zero-intercept

Diene	Products μmol h^{-1} cm^{-3} (quantum yield)							
(Concentration)	(I)	(II)	(III)	(IV)	(V)	(VI)	(VII)	Unknown
(I) (1.78×10^{-1}M)	1.28 [a] (9.7×10^{-2})	0.053 (4×10^{-3})	0.078 (5.9×10^{-3})	0.000	0.061 (4.6×10^{-3})	0.022 (1.7×10^{-3})	0.037 (2.8×10^{-3})	
(II) (1.66×10^{-1}M)	0.016 (0.12×10^{-2})	1.925 [a] (14.6×10^{-2})	0.16 (1.2×10^{-2})	0.58 (4.4×10^{-2})				~0.8 (6×10^{-2})
(III) (4.13×10^{-2}M)	2.24 (0.17)	2.11 (0.16)	5.94 [a] (0.45)	0.79 (0.06)				

[a] Quantum yield of disappearance.

DISCUSSION

The first point to be stressed is the discrepancy between our results and the mechanism proposed by Crowley,[8a] according to which the equilibrium (1) accounts for the formation of a cyclobutene. Our

$$\text{(I)} \underset{h\nu}{\overset{h\nu}{\rightleftharpoons}} \text{(III)} \underset{h\nu}{\overset{h\nu}{\rightleftharpoons}} \text{(II)} \xrightarrow{h\nu} \text{(IV)} \qquad (1)$$

results clearly indicate that the *cis*-diene (III) directly yields the cyclobutene (IV) even more efficiently than does the *trans*-isomer (II) and this contrasts with the behaviour of other dienes such as penta-1,3-dienes,[10] hexa-2,4-dienes,[12] or diene (I) discussed in this paper. Both [1,4] cyclization and a major contribution from a [1,5] hydrogen shift (which presumably takes place *via* an antarafacial six-membered ring transition state) call for a S_0 configuration of (III) being largely s-*cis*, probably due to the steric repulsion between methyl groups encountered in the s-*trans* form; this confirms the prediction made on the basis of the u.v. spectrum of (III) which corresponds to that calculated by Allinger [9] for a quasi s-*cis*-butadiene, the correction for two methyl substituents [13] being included.

The occurrence of the hydrogen sigmatropic shift in (III) is of more than passing interest upon considering that its quantum yield exceeds that for cyclobutene formation although this process was shown to be so rapid that it proved unquenchable in solution;[5] this means that hydrogen migration is very rapid too and does not encounter a significant energy barrier. Likewise vibrational relaxation by distortion should be very fast and devoid of activation energy. Thus the complete picture which allows for the observed 55% of internal conversion and 16% of geometrical isomerization is as follows: Franck–Condon excitation populates the S_1 hypersurface at a point of energy maximum from where the molecules may dive into different valleys (or wells) of S_1 which are connected with particular points (geometries) of the ground-state hypersurface and which thus eventually lead to particular photoproducts. The quantitative distribution of the excited molecules among these valleys depends on at least two parameters, (i) the amplitude of the corresponding wavefunction which is itself related to the depth of the well potential and (ii) the molecular dynamics, *i.e.* the intramolecular motions (vibrational modes) which predominate at the time of excitation.[3] In the case of diene (III) it seems safe to assume that a minimum of two such valleys * are involved in S_1, one available only to the s-*cis*-conformers and from which the cyclobutene (IV) and the [1,5] shift of hydrogen originate and one in which the excited state acquires a twisted structure before decaying to the starting diene or to its geometrical *trans*-isomer (II).

The second relevant conclusion to be drawn from the present work relates to a more precise description of the vibrationally relaxed S_1 state (or at least one of them) of s-*trans*-dienes. Based on their u.v. spectrum and a reasonable analogy with the penta-1,3-dienes it seems clear that (I) (which does not yield a cyclobutene) and (II) are in their ground state mainly s-*trans*-conformers; neither conformer of (II) has a methyl group available for a classical [1,5] shift to take place. And yet, in contradistinction to previous assertions [8a,c] these two dienes did undergo an abnormal migration of hydrogen $[\text{(I)} \xrightarrow{h\nu} \text{(II)}$ and $\text{(II)} \xrightarrow{h\nu} \text{(I)}]$ as a primary photoprocess though with a low quantum yield, the most favoured path being that of internal conversion; whether the two types of decay proceed *via* the same relaxed state remains an open question but it is obvious that the sigmatropic shift can only arise from a state which is sufficiently distorted to bring the methyl group and the terminal sp^2 carbon close together. One such would be the doubly twisted, bicyclobutane-like conformation (VIII) which we have already suggested on entirely different grounds.[5]

The final point is that whenever none of the usual co-ordinates except that of internal conversion is readily accessible to an acyclic 1,3-diene, any kind of hydrogen(s) shift(s) can become operative as is exemplified by the formation of (V)—(VII) from (I). It seems that the mechanistic significance of hydrogen shifts may have been overlooked and we are currently investigating this problem further by using specifically deuteriated dienes.

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* One cannot discard the possibility that each of the four processes follows a specific co-ordinate in the excited state but there are at present no experimental facts to bear this out.

[12] R. Srinivasan, *J. Amer. Chem. Soc.*, 1968, **90**, 4498.

[13] R. B. Woodward, *J. Amer. Chem. Soc.*, 1942, **64**, 72.