Photoisomerization of Linear 1,3-Dienes to Cyclopropane Derivatives

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Abstract: Mercury-photosensitized isomerizations of 2,3-dimethyl-1,3-butadiene, *trans*-2,3-dimethyl-1,3-pentadiene, 4-methyl-1,3-pentadiene, *trans*-2-methyl-1,3-pentadiene, and 2,4-dimethyl-1,3-pentadiene have been investigated. With the exception of the last compound, which yielded no isomeric product, the others gave methyl-substituted cyclopropenes and, in the first two instances, methylenecyclopropanes as well. Quantum yields as a function of diene pressure and of added inert gas at constant diene pressure were obtained for 2,3-dimethyl-1,3-butadiene. Quantum yields as a function of added ethane were obtained for *trans*-2,3-dimethyl-1,3-pentadiene. Mechanisms to explain these transformations are proposed.

Photochemical reactions of linear conjugated dienes include fragmentation,[1-3] stereoisomerization,[4-6] dimerization,[7-10] valence isomerization to cyclobutenes[11,12] and bicyclo[1.1.0]butanes,[13,14] and isomerization to cyclopropane derivatives.[15] Although all of these reactions have been studied extensively, there are only two intensive studies which correlate the structures of a series of dienes with their reactivity (in a particular photochemical transformation). These are the quenching of the singlet fluorescence in certain aromatic hydrocarbons by conjugated dienes[16] and the valence isomerization of dienes to cyclobutenes.[11,12]

In this article, the results of a systematic study of the photosensitized isomerization of several alkyl-substituted 1,3-dienes to cyclopropanes and methylenecyclopropanes is reported. This reaction will be shown to be a very general one for nearly all of the dienes that were studied. It has been suggested before[4b,5,17] that the intermediate in this reaction is probably also involved in the stereoisomerization process as well as in the formation of bicyclo[1.1.0]butanes.

Photoisomerization of olefinic compounds to cyclopropane derivatives is by no means uncommon. However, recent studies show that different mechanisms may be operative in monoolefins,[18-20] in diolefins in which the double bonds are isolated by more than one carbon,[21,22] in 1,4-pentadienes,[23-25] and in extended conjugated systems. The present results show that the formation of cyclopropanes and methylenecyclopropanes from linear 1,3-dienes relate to but differ from most of these systems.

Experimental Section

Materials. The dienes used in this study were obtained from Chemical Samples Co., Columbus, Ohio. All of the samples were found to be of at least 98% purity. Before use, they were distilled from bulb to bulb *in vacuo* and degassed thoroughly.

Apparatus. Quantitative studies were conducted in a cylindrical quartz cell of 500-ml volume. The light source was a Ottawa-style cold cathode mercury resonance lamp operated through a constant-voltage transformer. The absorbed intensity of the mercury resonance radiation at 253.7 nm, as measured by mercury-sensitized isomerization of *cis*-2-butene, was 2.75×10^{16} quanta/sec. All experiments were conducted at room temperature (22°).

Analysis. Fragmentation products were insignificant in all of the systems that were studied here. Isomeric products were analyzed on an F & M gas chromatograph fitted with a 12-ft column of UCON-550X and operated at room temperature. An internal reference was used to measure the yields of the various products. Compounds of greater molecular weights than the starting materials (*e.g.*, dimers) were not investigated.

Identification of Products. With only two exceptions, all of the products found are known compounds. After the molecular weight of each product was established from its mass spectrum, comparisons of the ir and nmr spectra were used as the basis for all identifications.

Results

2,3-Dimethyl-1,3-butadiene. Mercury-photosensitized isomerization of this compound gave rise to 1,3,3-trimethylcyclopropene, TMC (I),[26] and 2,2-dimethylmethylenecyclopropane, DMMC (II). The infrared and nmr spectra of the latter agreed with those reported by Bezaguet and Bertrand,[27] but not with

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(1) J. Collin and F. P. Lossing, *Can. J. Chem.*, **35**, 778 (1957).

(2) (a) R. Srinivasan, *J. Amer. Chem. Soc.*, **82**, 5063 (1960); (b) I. Haller and R. Srinivasan, *J. Chem. Phys.*, **40**, 1992 (1964); (c) I. Haller and R. Srinivasan, *J. Amer. Chem. Soc.*, **88**, 3694 (1966).

(3) R. D. Doepker, *J. Phys. Chem.*, 72, 4037 (1968).

(4) (a) J. Saltiel, L. Metts, and M. Wrighton, *J. Amer. Chem. Soc.*, **91**, 5684 (1969); (b) J. Saltiel, L. Metts, and M. Wrighton, *ibid.*, **92**, 3227 (1970).

(5) S. Boué and R. Srinivasan, *ibid.*, **92**, 3226 (1970).

(6) H. L. Hyndman, B. M. Monroe, and G. S. Hammond, *ibid.*, **91** 2852 (1969).

(7) P. J. Wagner and G. S. Hammond, *Advan. Photochem.*, **5**, 79 (1968), and earlier references therein.

(8) R. Srinivasan and F. I. Sonntag, *J. Amer. Chem. Soc.*, **87**, 3778 (1965).

(9) R. S. H. Liu, N. J. Turro, and G. S. Hammond, *ibid.*, **87**, 3406 (1965).

(10) G. S. Hammond, N. J. Turro, and A. Fischer, *ibid.*, **83**, 4074 (1961); N. J. Turro and G. S. Hammond, *ibid.*, **84**, 2841 (1962); G. S. Hammond and R. S. H. Liu, *ibid.*, **85**, 477 (1963).

(11) R. Srinivasan, *ibid.*, **84**, 4141 (1962); **91**, 7557 (1969).

(12) K. J. Crowley, *Tetrahedron*, **21**, 1001 (1965).

(13) R. Srinivasan, *J. Amer. Chem. Soc.*, **85**, 4045 (1963).

(14) R. E. K. Winter and P. Kalicky, Abstracts, 156th National Meeting of the American Chemical Society, Atlantic City, N. J., 1968, No. ORGN 36.

(15) R. Srinivasan and S. Boué, *Tetrahedron Lett.*, 203 (1970).

(16) (a) L. M. Stephenson, D. G. Whitten, G. F. Vesley, and G. S. Hammond, *J. Amer. Chem. Soc.*, **88**, 3665, 3893 (1966); (b) L. M. Stephenson and G. S. Hammond, *Pure Appl. Chem.*, **16**, 125 (1968).

(17) R. Srinivasan, *ibid.*, **20**, 263 (1969).

(18) R. J. Cvetanović and L. C. Doyle, *J. Chem. Phys.*, **37**, 543 (1962).

(19) M. Avrahami and P. Kebarle, *J. Phys. Chem.*, **67**, 354 (1963).

(20) D. W. Placzek and B. S. Rabinovitch, *Can. J. Chem.*, **43**, 820 (1965).

(21) R. Srinivasan, *J. Phys. Chem.*, **67**, 1367 (1963).

(22) R. Srinivasan and K. A. Hill, *J. Amer. Chem. Soc.*, **87**, 4988 (1965).

(23) R. Srinivasan and K. H. Carlough, *ibid.*, **89**, 4923 (1967).

(24) J. Meinwald and G. W. Smith, *ibid.*, **89**, 4923 (1967).

(25) H. E. Zimmerman and P. S. Mariano, *ibid.*, **91**, 1718 (1969).

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(27) A. Bezaguet and M. Bertrand, *C. R. Acad. Sci.*, **261**, 1695 (1965).

the spectra reported by Rahman and Kuivila[28] or by Schroder [29] In a series of runs, the decomposition of 2,3-dimethyl-1,3-butadiene was measured as a function of time. These results are shown in Figure 1. The measurement of the amount of diene that had been consumed was subject to an uncertainty of ±5 μmol. The uncertainty in the yields of the products was ±0.03 μmol. Although only about 20% of the diene that disappeared is accounted for by the isomeric products, it is evident that secondary reactions do not affect either the disappearance of the starting material or the appearance of these products. The remaining 80% of the diene presumably gives rise to dimeric and polymeric material. A similar situation has been encountered before in the photochemistry of 1,3-butadiene.[2a]

The effects of variations in the pressure of 2,3-dimethyl-1,3-butadiene or of added gases at a constant pressure of the diene on the quantum yields of the two isomers are shown in Table I.

Table I. Mercury($^3P_1$)-Sensitized Isomerization of 2,3-Dimethyl-1,3-butadiene[a]

Diene pressure, Torr	Gas added	Gas pressure, Torr	Conversion, %	Product quantum yields × 10^2  **1**	 **2**	$\frac{\mathbf{2}}{\mathbf{1}}$
10.5	None			3.3	8.5	2.6
15.2				3.8	6.6	1.7
21.0				3.7	4.9	1.3
31.5				3.8	2.9	0.8
45.0				3.8	1.8	0.5
10.5	Oxygen	4.0	12.5	2.4	5.6	2.3
		9.0	8.8	1.3	2.6	2.1
		13.0	8.2	0.8	1.4	1.8
10.5	CO_2	13.0	9.5	3.2	6.3	2.0
		25.5	8.8	2.9	4.6	1.6
		43.5	6.9	2.7	3.3	1.2
		102.5	5.0	1.7	1.2	0.7
10.5	Ethane	12.5	10.8	3.5	5.6	1.6
		24.5	10.8	3.4	3.8	1.1
		41.5	6.2	3.2	2.8	0.9
		84.0	2.0	2.7	1.3	0.5

[a] Temperature 22°, intensity 2.75 × 10^{16} quanta/sec, cell volume 560 ml, time 30 min.

***trans*-2,3-Dimethyl-1,3-pentadiene.** Mercury-photosensitized isomerization of this compound gave rise to a mixture of dienes which were not separated, 1,2,3,3-tetramethylcyclopropane,[26] 2,2,3-trimethylmethylenecyclopropane [C=C stretch at 1745 cm^{-1}; nmr spectrum consisted of δ 1.05 (singlet, 6 H) 1.08 (1 H), 1.13 (3 H), and 5.12 (broad singlet, 2 H)], and 2,2-dimethylethylidenecyclopropane.[28] Quantum yields were measured for only these compounds. At a series of conversions, it was observed that these quantum yields were invariant. The effect of added ethane is recorded in Table II.

Other Dienes. Mercury-photosensitized isomerizations of *trans*-2-methyl-1,3-pentadiene, 2,4-dimethyl-1,3-pentadiene, and 4-methyl-1,3-pentadiene were investigated in order to identify their products and their relative yields. These data are given in Table III.

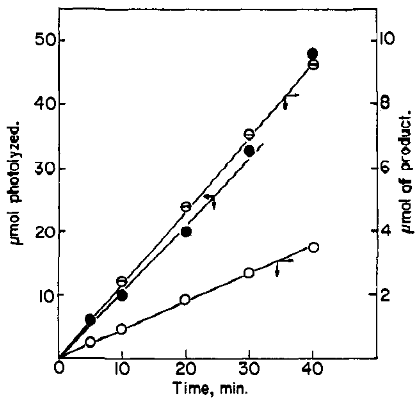
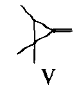
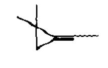


Figure 1. Mercury($^3P_1$)-sensitized decomposition of 2,3-dimethyl-1,3-butadiene; products and diene as functions of time of photolysis (reaction conditions as in Table I): ●, 2,3-dimethyl-1,3-butadiene consumed (left ordinate); ○, 1,3,3-trimethylcyclopropene; ⊖, 2,2-dimethylmethylenecyclopropane (right ordinate).

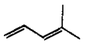
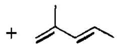
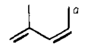
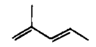
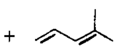
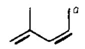
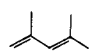
Pyrolysis Studies. In order to establish the thermal pathways that exist between the various dienes which were studied and their photoproducts, the latter were pyrolyzed individually in the vapor phase at low pressure (1–10 Torr) in sealed Pyrex vessels. The products were analyzed by gas chromatography. The following decomposition processes were observed.

Table II. Mercury($^3P_1$)-Sensitized Isomerization of *trans*-2,3-Dimethyl-1,3-pentadiene[a]

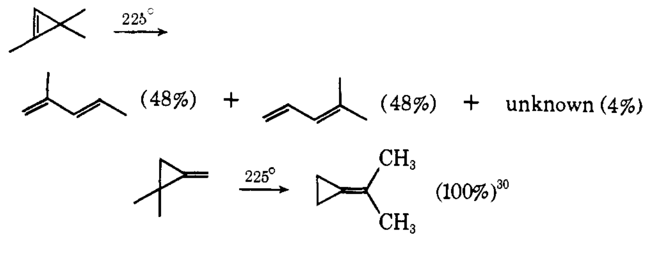
C_2H_6, Torr	Product quantum yields × 10^3  **3**	 V	 VI	$\frac{C^b}{MC}$	$\frac{V}{VI}$
0.0	21.6	11.0	14.0	1.09	0.78
21.5	21.6	5.9	6.6	1.72	0.90
43.0	16.3	4.4	4.4	1.85	0.96
81.5	10.8	2.0	2.0	2.76	1.00
171.0	6.2	1.0	0.9	3.40	1.14
241.0	4.4	0.7	0.6	3.60	1.22

[a] Experimental conditions as in Table I, except diene pressure 9.0 Torr. [b] C = cyclopropenes, MC = methylenecyclopropanes.

Table III. Product Composition in Mercury($^3P_1$)-Sensitized Isomerization of Some 1,3-Dienes

Diene	Diene pressure, Torr	Products, relative yields
	40	1 +  + [a] (1: 16: 4)
	65	1 +  + [a] (1: 16: 3)
	40	None

[a] Infrared and nmr spectra agreed with those reported by J. Wolinsky, B. Chollar, and M. D. Baird, *J. Amer. Chem. Soc.*, **84**, 2775 (1962).



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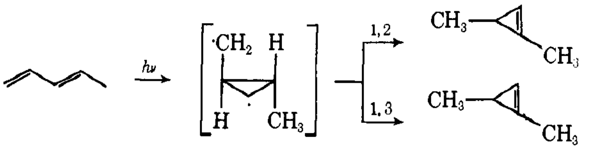
(28) W. Rahman and H. G. Kuivila, *J. Org. Chem.*, **31**, 772 (1966).
(29) G. Schroder, *Chem. Ber.*, **96**, 3178 (1963).

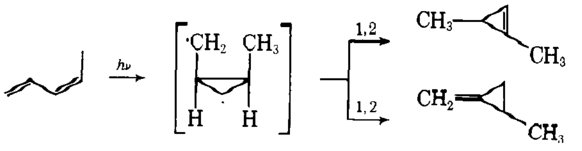
Discussion

In our earlier work[15] on the sensitized photoisomerization of linear conjugated dienes, we had observed that cyclopropenes were obtained from all of the dienes studied, but only in one instance, *viz.*, *cis*-1,3-pentadiene, was a methylenecyclopropane a significant product. This work confirms that from four more dienes cyclopropenes are both common and important products, but methylenecyclopropanes are not formed in every instance.

It has been suggested[5] that each stereoisomer of a diene such as 1,3-pentadiene, on irradiation, cyclizes to a diradical intermediate which can undergo 1,2 or 1,3 hydrogen shifts to give products, as illustrated in eq 1 and 2. Based on earlier work,[15] if it is postulated that the cyclization always occurs by bonding between C_2 and C_4, that methyl migration is not a preferred pathway, and that a 1,3 hydrogen migration will predominate over a 1,2 hydrogen migration, then the present results on the formation of cyclopropene can be satisfactorily explained on the basis of the diradical intermediate.

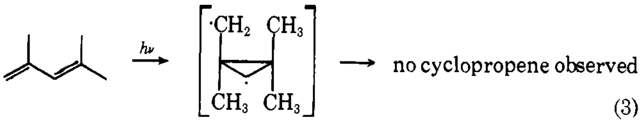


(1a)
(1b)



(2a)
(2b)

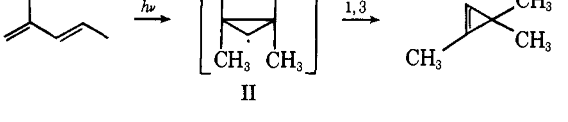
(i) 2,4-Dimethyl-1,3-pentadiene will lead to the diradical I, which can give a cyclopropyl derivative only by the migration of a methyl group. Hence the failure to find a cyclopropene or a methylenecyclopropane as a product is not surprising.



(3)

I

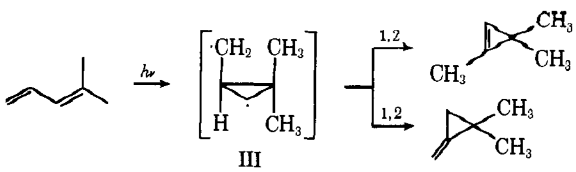
(ii) *trans*-2-Methyl-1,3-penetadiene will give the intermediate II, which, in turn, will lead to 1,3,3-trimethylcyclopropene by a 1,3 hydrogen migration. It can give a methylenecyclopropane only by a methyl migration, but such a product is not observed.



(4)

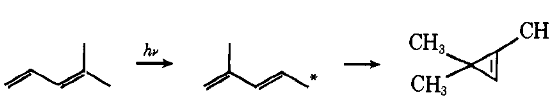
II

(iii) 4-Methyl-1,3-pentadiene will give the diradical III, which could give both a cyclopropene and a methylenecyclopropane by 1,2 hydrogen shifts. The failure to find the latter may be due to a rapid rearrangement according to eq 6. It may be seen that *trans*-2-methyl-1,3-pentadiene is a major product in this system, and the only other product is the cis isomer of this compound. A similar photostationary system has been encountered in the 1,3-hexadienes and 2,4-hexadienes.[15]



(5a)
(5b)

III



(6)

The two dienes from which more extensive data have been obtained also qualitatively fit the simple mechanism that was outlined in eq 1 and 2. But it is of interest to consider first the implications of the quantitative results, especially on the formation of the methylenecyclopropanes.

2,3-Dimethyl-1,3-butadiene. The data in Figure 1 show that both TMC and DMMC are primary products of photosensitization. The data in Table I indicate that both products are formed with comparable efficiencies and that, at best, these two processes account for more than 10% of the photons. The most remarkable results are those that show the effect of variations in pressure on the yields of these products.

In Figures 2 and 3 the reciprocals of the quantum yields for TMC and DMMC are plotted as functions of pressure. The data for TMC show that there is only a slight pressure-quenching effect on this process and that there is probably a shallow minimum in this curve at low pressure. Exceptional behavior is seen when oxygen is the quencher. The quenching process in the three instances (other than oxygen) seems to involve the loss of electronic rather than vibrational energy, as the quenching efficiency is not a function of the number of vibrational degrees of freedom possessed by the quencher. The exceptional efficiency of oxygen will be considered later.

Presumably, the excited species which participates in this quenching reaction and leads to a diminution in the yield of TMC is a triplet state of 2,3-dimethyl-1,3-butadiene. An alternative possibility is that this species is the $^3P_1$ state of the mercury atom. This can be ruled out (at quencher pressures of less than 10 Torr) because CO_2, ethane, and the diene itself are about equally effective or, more appropriately, ineffective, whereas their quenching cross sections for the Hg($^3P_1$) atom are in the ratio of 160:1:320.[31] At CO_2 pressures greater than 100 Torr, the increased slope for the Stern-Volmer plot may indicate some quenching of the Hg($^3P_1$) atoms as well.

The quenching of the formation of DMMC, in contrast, is a highly efficient process, the efficiency increasing in the order CO_2, ethane, and diene. Evidently, the important requirement in this case is the number of vibrational degrees of freedom possessed by the molecule. This indicates that it is the loss of

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(30) *Chem. Abstr.* 7th collective index lists "Isopropylidenecyclopropane–see propane-2-cyclopropylidene"; but there is no entry corresponding to the latter. The product of this reaction had an absorption at 1780 cm^{-1}; nmr δ 1.75 (triplet, 6 H) and 0.93 (quartet, 4 H).

(31) J. G. Calvert and J. N. Pitts, Jr., "Photochemistry," Wiley, New York, N. Y., 1966, pp 74–77.

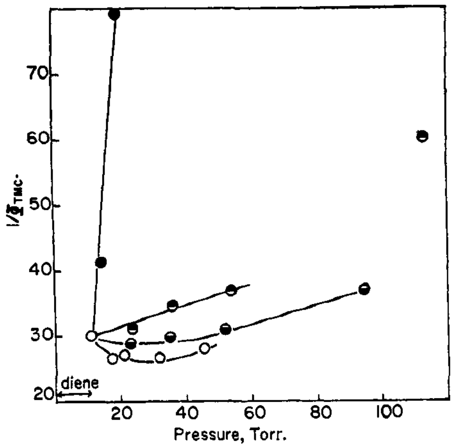


Figure 2. Stern–Volmer plot for the formation of 1,3,3-trimethylcyclopropene; quenchers: ●, oxygen; ◒, CO_2; ◓, ethane; ○, 2,3-dimethyl-1,3-butadiene.

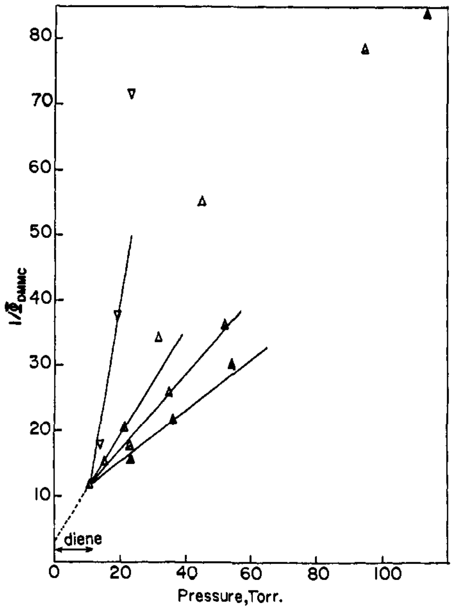


Figure 3. Stern–Volmer plot for the formation of 2,2-dimethylmethylenecyclopropane; quenchers: ▽, oxygen; △, 2,3-dimethyl-1,3-butadiene; ◭, ethane; ▲, CO_2.

vibrational energy from the reactive species that leads to quenching. Once again, the effect of oxygen seems anomalous and will be considered later.

If it is assumed that DMMC and TMC originate from the same intermediate (its reaction path depending on its vibrational energy), the kinetic scheme of eq 7–11

$$D + Hg(^3P) \longrightarrow D_n{}^3 + Hg(^1S) \qquad (7)$$

$$D_n{}^3 \longrightarrow \text{DMMC} \qquad (8)$$

$$D_n{}^3 + M \longrightarrow D_0{}^3 + M \qquad (9)$$

$$D_0{}^3 \longrightarrow \text{TMC} \qquad (10)$$

$$D_0{}^3 + M \longrightarrow D + M \qquad (11)$$

can be set up (D = diene, superscripts refer to multiplicity, subscripts refer to vibrational energy, M = any molecule in the system). Steps which correspond to the quenching of $Hg(^3P)$ by molecules other than the diene and the disappearance of the diene molecules from the excited state by internal conversion and by pathways other than isomerization have been neglected.

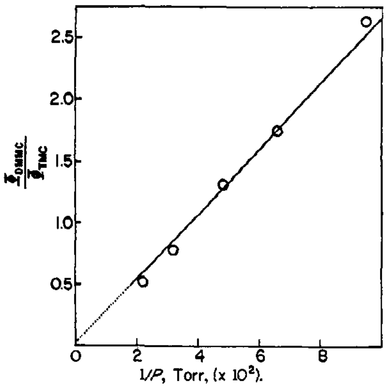


Figure 4. $\Phi_{\text{DMMC}}/\Phi_{\text{TMC}}$ *vs.* $1/P$, Torr.

From eq 7–11, it can be derived that

$$1/\Phi_{\text{DMMC}} = k_9[\text{M}]/k_8 + 1 \qquad (12)$$

which agrees with experiment for a limited pressure range. Similarly

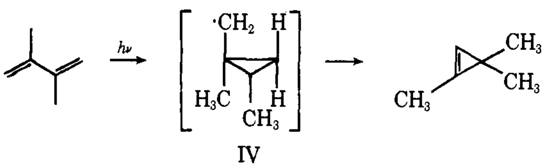
$$1/\Phi_{\text{TMC}} = \frac{k_8}{k_9[\text{M}]} + \frac{k_8k_{11}}{k_9k_{10}} + 1 + \frac{k_{11}[\text{M}]}{k_{10}} \qquad (13)$$

which also agrees with the data for the self-quenching, although the slightness of the curvature in the plot indicates that the coefficients of [M] and 1/[M] in eq 13 are small. The critical test for the assumption made earlier concerning the origin of DMMC and TMC lies in the expression that can be derived for the ratio of DMMC to TMC. Thus

$$\Phi_{\text{DMMC}}/\Phi_{\text{TMC}} = \frac{k_8}{k_9[\text{M}]} + \frac{k_8k_{11}}{k_9k_{10}} \qquad (14)$$

which can be compared to the plot of the experimental values for the ratio of quantum yield *vs.* diene pressure in Figure 4. The linearity of the plot is satisfactory and lends support to the kinetic scheme.

The mechanism by which $D_n{}^3$ and $D_0{}^3$ give rise to DMMC and TMC may be examined at this point. The reasonable structure for the diradical intermediate from 2,3-dimethyl-1,3-butadiene is IV, which can give



IV

(15)

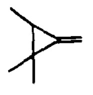
the cyclopropene in a predictable way. The formation of DMMC from this intermediate would require the migration of a methyl group (which it has not been necessary to postulate for the formation of cyclopropenes),[15] successive 1,3 and 1,2 hydrogen shifts, or a 1,4 hydrogen shift. In fact, DMMC may not come from IV, as will be considered later. It should be noted that DMMC as formed does not seem vibrationally "hot" as its pyrolytic rearrangement product, *viz.*, isopropylidenecyclopropane, is not observed in the photolysis mixture.

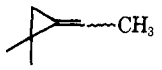
The exceptional efficiency of oxygen in quenching the formation of DMMC suggests that the process cannot be due merely to the loss of vibrational energy from the precursor to DMMC. The efficiency of oxygen as a quencher is 30-fold greater than CO_2, whereas in the removal of vibrational energy from "hot" 1,3,5-cycloheptatriene, oxygen was found to be less efficient than CO_2.[32] If the species undergoing vibrational deactivation is the diradical IV, it is likely that oxygen will tend to react chemically with the intermediate as it quenches. This may explain the high efficiency of oxygen in this reaction. Since the precursor to TMC also would have a similar electronic state, it can also be expected to undergo efficient deactivation.

***trans*-2,3-Dimethyl-1,3-pentadiene.** Although the data that are available in this system are limited to the quenching effect of ethane on the quantum yields of the isomeric products, the kinetic scheme proposed for 2,3-dimethyl-1,3-butadiene seems equally applicable here.

If the quantum yields of the methylenecyclopropanes are considered together, the inverses of these values fit a Stern–Volmer plot up to 100 Torr of ethane. The slope of this plot is three times the slope of the corresponding plot for tetramethylcyclopropene. The ratio of the quantum yields for all of the methylenecyclopropene products to the quantum yield for tetramethylcyclopropane is a linear function of 1/[M] in the system.[33]

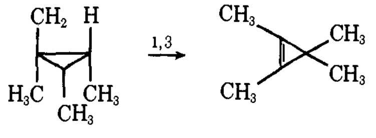
Although it is reasonable to expect that the methylenecyclopropane (V) can rearrange to VI, the data on pressure quenching do not support the idea that VI is formed from a vibrationally "hot" V. Thus the Stern–Volmer plots for the quantum yields for V and VI are linear, whereas a minimum can be expected in the plot for V if it rearranges to VI in this system.


V



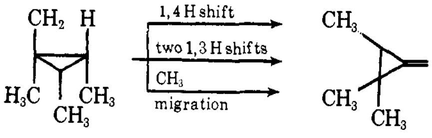
VI

The diradical intermediate which can be expected to take part in this system is VII, which can give tetramethylcyclopropene by a 1,3 H shift. The formation of V can occur in one of three ways.



VII

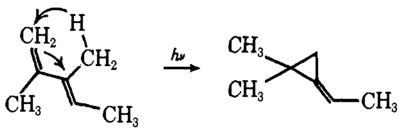
(16)



VII

(17)

However, VII is an awkward intermediate for the formation of VI. The diradical intermediate that can be produced by bridging between C_1 and C_3 is equally cumbersome. VI may conceivably be formed by a H shift as in (18). This mechanism is applicable to 2,3-dimethyl-1,3-butadiene as well, but not to the formation of V from *trans*-2,3-dimethyl-1,3-pentadiene. It should be of considerable interest to study the origin of the methylenecyclopropanes in these two dienes by the use of suitably deuterated precursors.



(18)

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[32] R. Srinivasan, *J. Amer. Chem. Soc.*, 84, 3982 (1962).

[33] Since the diene is capable of quenching itself, the data on the quantum yields at pressures of ethane from 43 to 241 Torr were first plotted and the line was extrapolated to zero pressure. The contribution of the diene (P = 9.0 Torr) was determined by iteration to equal 19.6 Torr of ethane pressure. The function was replotted on this basis.