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Thermal and Photochemical Isomerization of *cis*-3,4-Dimethylcyclobutene

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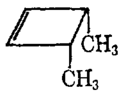
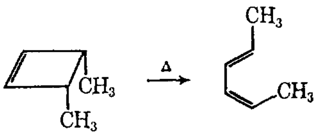
Abstract: The thermal isomerization of *cis*-3,4-dimethylcyclobutene in the vapor phase in the temperature range from 420 to 450°K was found to be a homogenous, unimolecular process. From the temperature dependence of the reaction, the first-order rate constant was observed to fit the equation $k = 10^{13.88} \exp(-34{,}000 \pm 500/RT)$ sec^{-1}. The single product that was obtained was *cis,trans*-2,4-hexadiene in agreement with the observations of Winter. The photosensitized decomposition of *cis*-3,4-dimethylcyclobutene using the $Hg(^3P_1)$ atom as the sensitizer gave a mixture of isomers which consisted of 1,3-hexadiene, *trans,trans*-2,4-hexadiene, *cis,trans*-2,4-hexadiene, and a minor quantity of *cis,cis*-2,4-hexadiene. From quenching studies in which ether was used as the inert gas, it was inferred that three different excited states of *cis*-3,4-dimethylcyclobutene were involved in the photoreactions. The probable identities of these states are discussed in terms of the conservation of energy, orbital symmetry, and spin angular momentum.

A study of the reactions of *cis*-3,4-dimethylcyclobutene (I) is of interest since the results are expected to provide insight into both the reactivity of strained, small-ring compounds and the stereochemistry of concerted reactions. The thermal decomposition of the molecule was studied qualitatively by Winter[1] who reported that the reaction proceeded stereospecifically to give *cis,trans*-2,4-hexadiene.



I



(1)

In the generalized viewpoint based on the conservation of orbital symmetry which was later developed by Woodward and Hoffmann,[2] this is a typical example of a conrotatory electrocyclic reaction.

In this work, the thermal and photosensitized decompositions of I have been quantitatively investigated. The reaction conditions in both cases were such that only isomerization processes were important.

Experimental Section

Materials. I was prepared by the photoisomerization of *trans,trans*-2,4-hexadiene.[3] A solution (8%) of *trans,trans*-2,4-hexadiene in ether (300 ml) was irradiated in a Rayonet Type RS reactor with 2537-Å radiation for 260 hr. At the end of the irradiation, the solvent was removed by distillation and the residue was separated by gas chromatography on a 12-ft UCON-550X column. The yield of I was 15%. Although the conversion of *trans,trans*-2,4-hexadiene to I can be as high as 30%, the practical yield was smaller because the irradiation was terminated when the photostationary state for the 2,4-hexadienes had been reached. It was time consuming to carry the reaction to completion in order to achieve the best possible yield. The sample of I was dried over Drierite, admitted to a vacuum line, and degassed at −78° before use.

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[1] R. E. K. Winter, *Tetrahedron Letters*, 1207 (1965).

[2] R. Hoffmann and R. B. Woodward, *Accounts Chem. Res.*, **1**, 17 (1968), and earlier references mentioned therein.

[3] R. Srinivasan, *J. Am. Chem. Soc.*, **90**, 4498 (1968).

Table I. $Hg(^3P_1)$-Sensitized Decomposition of *cis*-3,4-Dimethylcyclobutene[a]

			% products			
				2,4-Hexadiene		
P_I, Torr	P_{ether}, Torr	Total C_6/min (rel basis)	1,3-Hexadiene	*trans,trans*-	*trans,cis*-	*cis,cis*-
5.6	0	0.57	65.1	17.4	7.4	10.1
10.1	0	1.26	49.2	22.0	19.4	9.5
21.4	0	1.95	36.9	26.0	30.4	6.7
40.6	0	1.96	33.6	33.1	25.7	7.6
20.6	141.8	0.75	26.7	33.5	39.8	0
21.0[b]	162.9	nd[c]	22.0	36.4	40.6	1.0
19.7	202.7	nd[c]	12.5	31.4	54.5	1.6
20.9	269.8	0.56	10.1	27.5	56.8	5.6 (?)
20.2	360.9	0.39	8.6	25.5	65.9	0
20.8	477.4	0.39	3.9	22.7	73.5	0

[a] Room temperature except where noted; one 8-W resonance lamp; t = 0.5 to 6.0 min. [b] 100°. [c] nd = not determined.

Experimental samples of I always contained a trace of *cis,trans*-2,4-hexadiene as an impurity. It was presumably formed by the decomposition of I in the injector block of the gas chromatograph. A correction was applied to all of the thermal and photochemical data for the presence of the impurity.

Authentic samples of 1,3-hexadiene and *cis,cis*-, *cis,trans*-, and *trans,-trans*-1,4-hexadienes were obtained from Chemical Samples Co. (Columbus, Ohio). Ether (Mallinckrodt) was used without purification.

Apparatus and Procedure. The furnace and associated equipment as well as the procedure used in the thermal decomposition studies have been described.[4]

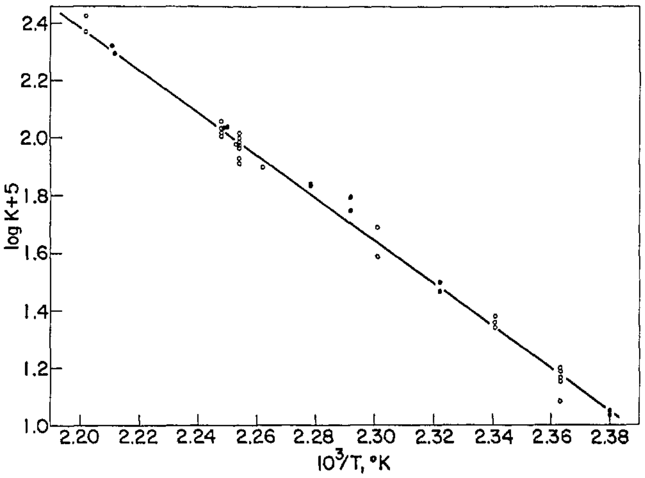

Figure 1. Logarithm of the first-order rate constant for *cis*-3,4-dimethylcyclobutene *vs.* reciprocal of the absolute temperature: open circles, unpacked cell; filled circles, packed cell.

Photochemical experiments were conducted in a cylindrical cell of 2.2-cm diameter and of 106-ml volume. The reactants and products were handled in a conventional high-vacuum system from which stopcock grease was not excluded. The cell was flamed in air at the end of every second or third run to remove any polymer film that may have been formed on the wall.

The light source was a General Electric G8T5 lamp. It was allowed to warm up for at least 15 min before each run in order to reach a stable operating condition.

Analyses of the products from both the thermal and the photochemical experiments were conducted by gas chromatography on a 12-ft UCON-550X column at room temperature. The stereoisomers of 2,4-hexadiene were cleanly separated from one another under these conditions, while both the starting material and 1,3-hexadiene (the other product) were also well separated. The identities of the products were confirmed by infrared spectroscopy.

Results

Thermal Decomposition. Over the whole temperature range from 420 to 450°K, there was no measurable change in the total pressure in the system after various fractions of the material had been decomposed. The pyrolyzed sample could be condensed completely at 77°K. Analysis by vapor phase chromatography indicated only one new peak due to a product. This was identified as *cis,trans*-2,4-hexadiene in agreement with the earlier report.[1]

The disappearance of I fitted a first-order rate equation. The values of the rate constants were unchanged, within experimental uncertainty, at conversions which ranged from 12 to 86%.

In ten runs which were carried out at five different temperatures, the reaction cell was packed with glass tubes which increased its surface-to-volume ratio by 17. The rate at any given temperature was not different from the rate in the unpacked cell by more than the experimental error. The temperature coefficient of the rate in the packed cell was the same as in the unpacked cell. Evidently the surface reaction in the packed cell was insignificant, the reaction being truly homogeneous.

The effect of a change in pressure on the rate constant in the range from 0.21 to 21.35 Torr was studied at 443.7°K. There was no detectable decrease in the rate constant with decreasing pressure within this pressure range.

A plot of the logarithm of the first-order rate constants *vs.* $1/T$ for all of the runs is given in Figure 1. The best straight line through all of the points, as determined by the method of least squares, gave an activation energy of 34.3 ± 0.5 kcal/mole and an A factor of $10^{13.88}$ sec^{-1}.

Photodecomposition. Data on the decomposition of I sensitized by $Hg(^3P_1)$ atoms are given in Table I.

The major products from the $Hg(^3P_1)$-sensitized decomposition of I at pressures greater than 10 Torr were 1,3-hexadiene, *trans,trans*-2,4-hexadiene, *cis,trans*-2,4-hexadiene, and a polymer. A comparison with authentic 1,3-hexadiene suggested that it was mostly only one stereoisomer of this compound that was formed, but the assignment of a structure to this product was not successful since it lacked any clearly identifiable absorptions in the infrared or nmr spectra. There was a small (<10%) amount of *cis,cis*-2,4-hexadiene formed whenever pure I was used in these experiments. Gaseous products containing less than six carbon atoms were negligible except during photosensitization at pressures less than 10 Torr.

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(4) R. Srinivasan and A. A. Levi, *J. Am. Chem. Soc.*, **85**, 3363 (1963).

Data from one run which was carried out at 373°K instead of at room temperature are included in Table I.

In other experiments it was observed that (i) sensitized decomposition of I in the *gas phase* with acetone vapor at 3130 Å as the sensitizer did not give detectable amounts of any of the 1,3- or 2,4-hexadienes; (ii) irradiation at 2537 Å of I *in solution* in acetone gave no 1,3- or 2,4-hexadiene products; (iii) irradiation at 1849 Å of I *in solution* in hexane gave no detectable yield of 1,3- or 2,4-hexadienes. The only detectable products appeared to be adducts of I to the solvent.

The three experiments described above were carried to conversions at which it was made sure that (i) hexadiene products, if formed, were not being removed by secondary processes, and (ii) the number of quanta absorbed by the system was sufficient to give rise to a detectable amount of any product whose quantum yield was greater than 0.001.

A few experiments were also conducted on the mercury-photosensitized isomerization of 2,4-hexadienes at a pressure of 20 Torr. The products that were observed were the stereoisomeric 2,4-hexadienes, other than the starting material, and 1,3-hexadiene.

From *trans,trans*-2,4-hexadiene the relative rates of formation of the isomers were: 1,3-hexadiene, 0.26; *cis,trans*-2,4-hexadiene, 0.61; *cis,cis*-2,4-hexadiene, 0.12.

From *cis,trans*-2,4-hexadiene the relative rates of formation of the isomers were: 1,3-hexadiene, 0.37; *trans,trans*-2,4-hexadiene, 0.43; *cis,cis*-2,4-hexadiene, 0.20.

From *cis,cis*-2,4-hexadiene the relative rates of formation of the isomers were: 1,3-hexadiene, 0.32; *trans,trans*-2,4-hexadiene, 0.32; *cis,trans*-2,4-hexadiene, 0.36.

The individual rates of disappearance of each of the 2,4-hexadienes in sensitized isomerization experiments mentioned above were the same within ±5%.

Discussion

The thermal isomerization of I according to (1) is observed to be a homogenous, unimolecular process. The stereochemistry of the transformation has been discussed in detail by others.[2,5] It is sufficient to consider here the quantitative results obtained in this study.

Branton, Frey, and Skinner,[6] and later Frey, Pope, and Skinner,[7] have pointed out that an empirical correlation exists between the degree of alkyl substitution that is present in a cyclobutene and its rate parameters for homogenous, thermal isomerization. Their estimate of the activation energy for I, which is based entirely on known values for other alkylcyclobutenes, is 34.2 kcal/mole which is in striking agreement with the experimental value. It follows that the unimolecular isomerization of this molecule is "normal." There is no noticeable fall-off in the first-order rate constants in the pressure range from 21.0 to 0.2 Torr. It is reasonable to expect this in a molecule which contains 16 atoms, and it fully conforms to the known kinetics of other molecules of similar complexity.

The $Hg(^3P_1)$-photosensitized decomposition of I appears to be quite a complex process. From earlier work on the $Hg(^3P_1)$-sensitized decompositions of other olefins, and particularly the pressure dependence in such systems,[8,9] it is reasonable to expect that the initial process will be the transfer of energy from the triplet mercury atom to the olefin to give an excited molecule. Since the collisional deactivation of this excited molecule is seen to be important, we propose that this initially formed state is a vibrationally excited triplet ($C^3{}_m$) of I. The data on the subsequent reactions of this triplet seem to be obscured by secondary reactions between the products and triplet mercury atoms. This is not surprising as the major products are conjugated dienes which have a considerably larger cross section for the quenching of $Hg(^3P_1)$ atoms than monoolefins.[10] The rates of formation of the various products in runs in which a constant pressure of I and various pressures of ether (which does not undergo any detectable reaction in this system) have been used appear to be less subject to, if not entirely free from, secondary photosensitized reactions. Hence, these data were used as the basis of the interpretation that will be given here.

With an increase in pressure, the formation of *cis,-trans*-2,4-hexadiene was favored relative to *trans,trans*-2,4-hexadiene while the formation of *trans,trans*-2,4-hexadiene was, in turn, favored relative to 1,3-hexadiene. It follows that there are three reactive states of I to deal with in this system. We invoke the rules proposed by Woodward and Hoffmann[2] and identify:

(i) The precursor for *cis,trans*-2,4-hexadiene to be the vibrationally excited ground state of I. This reaction is conrotatory and can take place only in the ground electronic state as a concerted process. The thermal decomposition study detailed earlier and the work of Winter[1] have already demonstrated this.

(ii) The precursor for *trans,trans*-2,4-hexadiene to be the triplet excited state of I. This reaction is disrotatory and can take place only in the electronic excited state as a concerted process.[11] The alternative state from which it can conceivably occur is a highly vibrationally excited molecule in the ground electronic level, in which case the reaction would be an orbital symmetry-forbidden process. We shall advance arguments against this proposal at the end of this section.

A complication that should be considered is that *trans,trans*-2,4-hexadiene, when it is formed from a triplet state of I, may retain its excess energy long enough to isomerize to *cis,trans*- and *cis,cis*-2,4-hexadienes. The sensitization experiments on *trans,trans*-2,4-hexadiene itself indicated that the rate of formation of the *cis,trans* and *cis,cis* isomers was 5:1. Since the relative yield of *cis,cis*-2,4-hexadiene in the sensitized isomerization of I was of the order of 1% at significant pressures of ether, no more than 5% of the *cis,trans*-2,4-hexadiene could have been formed by this route.

1,3-Hexadiene is formed only under conditions which do not favor the formation of the 2,4-hexadienes. Therefore, it must be formed on the initial state, *i.e.*, $C^3{}_m$, the vibrationally excited triplet.

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(5) H. C. Longuet-Higgins and E. W. Abrahamson, *J. Am. Chem. Soc.*, **87**, 2045 (1965).

(6) G. R. Branton, H. M. Frey, and R. F. Skinner, *Trans. Faraday Soc.*, **62**, 1540 (1966).

(7) H. M. Frey, B. M. Pope, and R. F. Skinner, *ibid.*, **63**, 1166 (1967).

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

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

(10) J. G. Calvert and J. N. Pitts, Jr., "Photochemistry," John Wiley and Sons, Inc., New York, N. Y., 1966, pp 75, 76.

(11) The conservation of orbital symmetry appears to be independent of the multiplicity of electronic state that is involved.

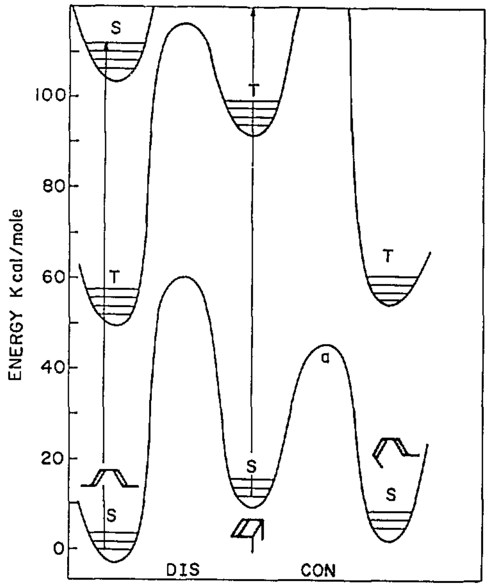

Figure 2. Energy diagram for the system *cis*-3,4-dimethylcyclobutene-*trans,trans*-2,4-hexadiene-*cis,trans*-2,4-hexadiene. Vertical lines correspond to photons of 2537 Å; energies based on $\Delta H_f{}^\circ$ of *trans,trans*-2,4-hexadiene as reference. [Upper singlet and triplet levels of 2,4-hexadienes are based on ref 16 and G. S. Hammond and R. S. H. Liu, *J. Am. Chem. Soc.*, **85**, 477 (1963). The ground state of *cis*-3,4-dimethylcyclobutene is based on K. B. Wiberg and R. A. Fenoglio, *ibid.*, **90**, 3395 (1968); triplet level based on estimate in ref 15. This may be low by 12.5 kcal/mole since the strain energy difference between cyclobutene and cyclobutane was taken to be 15 kcal/mole; see previous reference for experimental value. The activation energy for disrotatory opening in the ground state is from the estimate in ref 13. Activation energies in electronic excited state are hypothetical.]

The following reaction scheme can be constructed in which the subscripts *m* and *n* represent vibrational levels above the zeroth level, and Q is any quencher molecule.

$$\mathrm{Hg(^1S_0)} + h\nu \longrightarrow \mathrm{Hg(^3P_1)} \qquad (2)$$

$$\mathrm{Hg(^3P_1)} + \mathrm{C} \longrightarrow \mathrm{Hg(^1S_0)} + \mathrm{C}^3{}_m \qquad (3)$$

$$\mathrm{Hg(^3P_1)} + \mathrm{Q} \longrightarrow \mathrm{Hg(^1S_0)} + \mathrm{Q} \qquad (4)$$

$$\mathrm{C}^3{}_m \longrightarrow \text{1,3-hexadiene} \qquad (5)$$

$$\mathrm{C}^3{}_m + \mathrm{Q\ or\ C} \longrightarrow \mathrm{C}^3{}_0 + \mathrm{Q\ or\ C} \qquad (6)$$

$$\mathrm{C}^3{}_0 \longrightarrow \textit{trans,trans}\text{-2,4-hexadiene} \qquad (7)$$

$$\mathrm{C}^3{}_0 + \mathrm{Q\ or\ C} \longrightarrow \mathrm{C}_n + \mathrm{Q\ or\ C} \qquad (8)$$

$$\mathrm{C}_n \longrightarrow \textit{cis,trans}\text{-2,4-hexadiene} \qquad (9)$$

$$\mathrm{C}_n + \mathrm{Q\ or\ C} \longrightarrow \mathrm{C} + \mathrm{Q\ or\ C} \qquad (10)$$

The products in (5), (7), and (9) may be vibrationally excited and perhaps electronically excited as well in the first two instances. Such complexities are not indicated here. It is assumed that these products end up as thermally equilibrated ground-state molecules in every instance.

Qualitatively this sequence of reactions requires that $\Phi_{\text{1,3-hexadiene}}$ decrease steadily with an increase in pressure, $\Phi_{\textit{trans,trans}\text{-2,4-hexadiene}}$ go through a maximum with an increase in pressure, and $\Phi_{\textit{cis,trans}\text{-2,4-hexadiene}}$ increase with an increase in pressure. The data in Table I show that this was actually observed. With the usual stationary-state assumptions, it can be derived that

$$\Phi_{\text{1,3-hexadiene}}/\Phi_{\textit{trans,trans}\text{-2,4-hexadiene}} = k_5/k_6[\mathrm{M}] + k_5k_8/k_6k_7 \qquad (11)$$

$$\Phi_{\textit{trans,trans}\text{-2,4-hexadiene}}/\Phi_{\textit{cis,trans}\text{-2,4-hexadiene}} = k_7/k_8[\mathrm{M}] + k_7k_{10}/k_8k_9 \qquad (12)$$

where [M] represents the pressure of quenching molecules in the system.[12]

The plot of $\Phi_{\textit{trans,trans}\text{-2,4-hexadiene}}/\Phi_{\textit{cis,trans}\text{-2,4-hexadiene}}$ *vs.* 1/[M] was a satisfactory straight line whose slope and intercept were 5.9×10^{-3} mole l.$^{-1}$ and 0.08, respectively. The plot of $\Phi_{\text{1,3-hexadiene}}/\Phi_{\textit{trans,trans}\text{-2,4-hexadiene}}$ *vs.* 1/[M] was a reasonably good straight line, but there was considerable scatter in the points as $1/[\mathrm{M}] \rightarrow 0$ principally because the yield of both these products tended to be small (and therefore subject to large error in measurement) at high pressures. The extrapolation of this plot to 1/[M] = 0 was not attempted.

From the plot of (12), $k_9/k_{10} = 13k_7/k_5$. This result requires that $k_{10} < k_8$ or $k_9 > k_7$. If (8) is a collision-induced internal conversion, a process for which there is precedent, it is difficult to believe that its rate can be greater than (10) which represents a bimolecular transfer of vibrational energy between polyatomic molecules. It seems reasonable to assume that the maximum value of k_8 can be no greater than k_{10}. It follows that k_9 is an order of magnitude greater than k_7. This result is intriguing since both reactions are essentially similar orbital symmetry-allowed reactions, but in the absence of more information to define the reactants and the products, nothing more can be said about the disparity.

In principle, the pressures at which the quantum yields of any two of the products are identical (three such pressures) and the yield of *trans,trans*-2,4-hexadiene goes through an inflection may be used (with some additional assumptions) to evaluate almost all of the rate constants k_3 through k_{10}. Actually, the dominance of *cis,trans*-2,4-hexadiene in the product mixture largely obscured the amount of information that could be extracted from the data.

It is possible to construct an approximate energy diagram (Figure 2) for the system made up of *trans,trans*-2,4-hexadiene, *cis,trans*-2,4-hexadiene, and I. The diagram is of use in analyzing the course of the six possible reactions in this system, *viz.*

$$\mathrm{I} \xrightarrow{\Delta} \textit{cis, trans}\text{-2,4-hexadiene} \qquad (1)$$

$$\mathrm{I} \xrightarrow{\Delta} \textit{trans,trans}\text{-2,4-hexadiene} \qquad (13)$$

$$\mathrm{I} \xrightarrow{h\nu} \textit{trans,trans}\text{-2,4-hexadiene} \qquad (14a)$$

$$\mathrm{I} \xleftarrow{h\nu} \textit{trans,trans}\text{-2,4-hexadiene} \qquad (14b)$$

$$\mathrm{I} \xrightarrow{h\nu} \textit{cis,trans}\text{-2,4-hexadiene} \qquad (15a)$$

$$\mathrm{I} \xleftarrow{h\nu} \textit{cis,trans}\text{-2,4-hexadiene} \qquad (15b)$$

The analysis will be based on three considerations, which are: (i) conservation of energy, (ii) conservation of orbital symmetry, and (iii) conservation of spin angular momentum.

Reaction 1 is an allowed process from all three considerations and its activation energy (the saddle-point a) was discussed before. Reaction 13 is an allowed process from considerations i and iii but not ii. Its activation energy can be placed about 15 kcal/mole above that

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[12] In the present study, since the pressure of I that was used was 5- to 20-fold smaller than the pressures of the quencher, [M] can be taken to be proportional to the total pressure in the system.

of (1) in accordance with the estimate of Brauman and Golden[13] for the energy difference between symmetry-allowed and symmetry-disallowed processes.

In this connection, it is of interest to explore the possibility that was suggested before, namely, that (13) may become important relative to (1) when I is formed in a high vibrational level of the ground electronic state, as in reaction 8. The rate $k^*(E)$ of a unimolecular reaction with an activation energy E^* (where $E > E^*$ is given by

$$k^*(E) = A(1 - E^*/E)^{S-1}$$

where S is the number of degrees of freedom in the molecule and A is a frequency. If we consider the relative rates of (1) and (13) at some energy E, then

$$k_1(E) = A_1(1 - E^*{}_1/E)^{S_1-1} \qquad (16)$$

$$k_{13}(E) = A_{13}(1 - E^*{}_{13}/E)^{S_{13}-1} \qquad (17)$$

If we set E_1 = 34 kcal/mole, E_{13} = 49 kcal/mole, E = 112 kcal/mole, $S_1 = S_{13} \simeq 21$,[14] and $A_1 \approx A_{13}$

$$k_{11}(E)/k_1(E) = 10^{-2}$$

This estimate is admittedly quite approximate, but it seems safe to infer that for photon energies of the magnitude used here, no more than 1% of the *trans,-trans*-2,4-hexadiene can be formed *via* (13).

Of the four photochemical reactions, only (14a) and (14b) are allowed by a consideration of orbital symmetry. The singlet state of I is almost certainly greater in energy than photons of 2537-Å wavelength and would not be involved in the experiments discussed here. If the triplet of I lies at about 85 kcal/mole[15] and the singlet of *trans,trans*-2,4-hexadiene at *ca.* 107 kcal/mole,[16] then

trans,trans-2,4-hexadiene (singlet) ⟶ I (triplet) (14b)

will conserve orbital symmetry and energy, but not spin, while

I (triplet) ⟶ *trans,trans*-2,4-hexadiene (triplet) (14a)

will be an allowed process from all three considerations.

The question of the exact initial and final states of the molecules involved in a reaction such as (14b) is a fascinating one. A reaction such as *trans,trans*-2,4-hexadiene (excited singlet) → I (excited singlet) would not conserve energy. In discussing such reactions, Hoffmann[17] has suggested that the reaction may be initiated in the electronically excited state of the diene in a manner indicated by the conservation of orbital symmetry, but that the product may be formed in its ground electronic state, *i.e.*

trans,trans-2,4-hexadiene (excited singlet) ⟶
I (ground singlet) (14b′)

Essentially, the same explanation has been advanced by Dauben, *et al.*,[18] for the closure of the 1,1′-bicyclohexenyl system, although, in their approach reaction 14b′ is not viewed as an elementary step. If (14b′) is looked upon as an elementary process, it seems as if the forward reaction is orbital symmetry allowed but the reverse process is not.

There is a third possibility which is that spin angular momentum is not conserved in these reactions (as in (14b)). It should be noted that only the excited singlet state of 1,3-butadiene (and not its triplet) isomerizes to cyclobutene.[19] If the product of this unimolecular reaction is a vibrationally excited cyclobutene in its ground state (as in (14b′)), this difference becomes difficult to explain, but if the reaction is constrained to proceed from an electronically excited state of the reactant to an electronically excited state of the product, the singlet can isomerize in the same fashion as in (14b), but the triplet would not have access (from an energy consideration) to any of the excited electronic states of cyclobutene.

Acknowledgment. The author acknowledges with pleasure the assistance provided by Mr. A. R. Taranko in obtaining the data on the thermal isomerization, and by Mrs. J. M. Picone in carrying out the photochemical studies. He is deeply grateful to Dr. H. E. Hunziker for many helpful discussions.

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[13] J. I. Brauman and D. M. Golden, *J. Am. Chem. Soc.*, **90**, 1920 (1968).

[14] Only about half the total number of oscillators in a molecule are usually found to be active in a unimolecular reaction.

[15] For a discussion of the energy of the triplet state of cyclobutene, see R. Srinivasan and K. A. Hill, *J. Am. Chem. Soc.*, **88**, 3768 (1966).

[16] This is the best estimate of the upper singlet level in 1,3-butadiene itself: R. Srinivasan, *Advan. Photochem.*, **4**, 117 (1966).

[17] R. Hoffmann, private communication.

[18] W. G. Dauben, R. L. Cargill, R. M. Coates, and J. Saltiel, *J. Am. Chem. Soc.*, **88**, 2742 (1966).

[19] Reference 16, p 116.