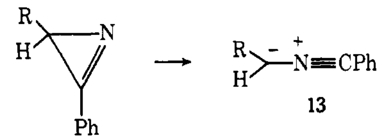

13

1, R = H
7, R = Ph

mesoionic oxazolium 5-oxide which then combines with the dipolarophile.[12] Formation of the less thermodynamically stable *cis*-Δ^1-pyrroline **11** may be the result of preferred geometrical or electronic factors operative in the transition state for cycloaddition. The orientation of the groups in the Δ^1-pyrrolines is similar to that observed by Huisgen in related 1,3-dipolar additions.[14] It is interesting to note that Huisgen has reported that diarylazirenes do not undergo thermal cycloaddition with dipolarophiles.[9]

Irradiation of a mixture of **7**, a dipolarophile, and xanthone, under conditions where xanthone absorbs >95% of the light (3660 Å), gave no photoadduct. This result tentatively suggests that the cycloaddition proceeds *via* the excited singlet state of **7**. Additional studies are currently in progress to further elucidate the nature of the excited state and the mechanistic implications of the above observations.

Acknowledgment. We gratefully acknowledge support of this work by the National Institutes of Health (Grant No. CA 12195-04).

(14) R. Huisgen, *J. Org. Chem.*, **33**, 2291 (1968).
(15) Alfred P. Sloan Fellow, 1968–1970.
(16) NDEA trainee, 1969–1970.

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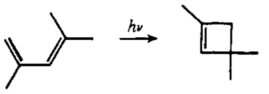
Absolute Rate of the Photochemical Valence Isomerization of a Conjugated Diene

Sir:

It has been demonstrated that the rates at which stereoisomers of a linear, 1,3-diene photoisomerize to cyclobutenes are distinctly different.[1,2] However, the absolute rate of each of these reactions was slower than the rate at which the diene isomerized stereochemically. These studies[1] also indicated that (i) stereoisomerization in these compounds cannot be a simple, elementary reaction which occurs in the same electronically excited state as cyclobutene formation, and (ii) very little can be inferred about the absolute rate of the valence isomerization from these results.

It was considered desirable to obtain the rate of cyclobutene formation from a diene relative to some other process whose rate can be estimated, *e.g.*, a collisional quenching process. Such a measurement would give a fundamental rate in the singlet photochemistry of conjugated dienes and would help to calibrate the rates of the other reactions in these systems. Hitherto, this was not possible because the linear 1,3-dienes which were known to isomerize to cyclobutenes did so with maximum efficiency in solution.

We now wish to report that we have discovered an example of a linear 1,3-diene which photoisomerizes to the corresponding cyclobutene in the gas phase but not in solution. 2,4-Dimethyl-1,3-pentadiene when irradiated at 253.7 nm in the gas phase isomerizes cleanly to 1,3,3-trimethylcyclobutene. The latter was identified from its molecular weight (mass spectrum,



(1)

parent peak at *m/e* 96), infrared spectrum (C=C at 1640 cm^{-1}), and nmr spectrum [(CCl$_4$ solution, TMS as internal reference) δ 1.13 (6 H, singlet), 1.65 (3 H, multiplet), 2.08 (2 H, multiplet), 5.68 (1 H, multiplet)] and from its ready isomerization to 2,4-dimethyl-1,3-pentadiene on pyrolysis to 190° in the vapor phase.[3] It is noteworthy that earlier attempts[1a,5] to bring about reaction 1 in solution in solvents such as isooctane, diethyl ether, and cyclohexane yielded negative results.

In order to establish the activation process that allows (1) to occur in the gas phase only, inert gases such as argon, carbon dioxide, or ethane were added to the system. Typical results which were obtained with ethane are given in Table I. The increase in the quantum yields for the cyclobutene on the addition of small amounts of ethane parallels the effect that has been observed in other systems[6] in which a thermally labile product is formed in a photochemical reaction in the vapor phase. It can be attributed to the stabilization of the product by the removal of its excess vibrational energy in quenching collisions. At an ethane pressure of 1 atm this process is overtaken by the deactivation of the excited state of the diene. The latter effect can be only due to the removal of vibrational energy from the excited molecule, as it seems unlikely that electronic energy transfer can occur to molecules as diverse as the three quenchers used here. A reaction scheme which takes into account these effects is as follows (D = diene, C = cyclobutene, M = any molecule; superscript = excited electronic level, subscript = excited vibrational level)

Table I. Relative Quantum Yields for Reaction 1 in Vapor Phase[a]

Ethane pressure, Torr					
0	54.50	192.5	382.5	718.5	1440
Cyclobutene,[b] µmol/min × 10					
0.95	1.15	1.60	1.90	2.16	1.56

[a] Medium-pressure mercury arc; DDDP = nickel sulfate filter; room temperature; $I = 2.75 \times 10^{16}$ quanta/sec; volume = 560 ml; diene pressure = 13.5 Torr. [b] These rates are estimated to be precise to ±3%.

$$D + h\nu \longrightarrow D_m{}^1 \tag{2}$$

$$D_m{}^1 + M \longrightarrow D_0{}^1 + M \tag{3}$$

$$D_m{}^1 \longrightarrow C_n \tag{4}$$

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(1) (a) R. Srinivasan, *J. Amer. Chem. Soc.*, **84**, 4141 (1962); (b) *ibid.*, **91**, 7557 (1968); (c) S. Boué and R. Srinivasan, *ibid.*, **92**, 3226 (1970).
(2) J. Saltiel, L. Metts, and M. Wrighton, *ibid.*, **92**, 3227 (1970).
(3) This pyrolysis reaction has been reported before,[4] but none of the spectral properties of 1,3,3-trimethylcyclobutene has been published.
(4) H. M. Frey, B. M. Pope, and R. F. Skinner, *Trans. Faraday Soc.*, **63**, 1166 (1967).
(5) K. J. Crowley, *Tetrahedron Lett.*, 1001 (1965).
(6) For one instance, see R. Srinivasan and S. Boué, *ibid.*, 203 (1970).

$$C_n + M \longrightarrow C + M \qquad (5)$$

$$C_n \longrightarrow D \qquad (6)$$

$$D_m{}^1 \longrightarrow D \qquad (7)$$

With the usual steady-state assumptions, it can be derived that

$$1/\Phi_C = \frac{k_3k_6 + (k_4 + k_7)k_5}{k_4k_5} + \frac{k_6(k_4 + k_7)}{k_4k_5}[M^{-1}] + \frac{k_3}{k_4}[M] \qquad (8)$$

The Stern–Volmer plot would hence have a minimum, as the data in Table I actually display. At the minimum $k_4 = (k_3k_5[M]^2/k_6) - k_7$, which makes it possible to calculate k_4, the rate constant for the valence isomerization process, if k_3, k_5, k_6, and k_7 are known. The first two were calculated from simple kinetic theory on the assumption that every collision between $D_m{}^1$ or C_n and M will lead to deactivation.[7] k_6 was calculated from the known[4] parameters for the thermal decomposition of 1,3,3-trimethylcyclobutene. This led to a value for k_6 of $10^{8.92}$ sec^{-1}.[8] k_7 was taken to be $19k_4$ since the quantum yield for reaction 1 had a maximum value of 0.05. By inserting these values, it was calculated that

$$k_4 = 2 \times 10^9 \text{ sec}^{-1}$$

The effects that the various assumptions that were made in this calculation had on the accuracy of k_4 will be as follows. (i) In setting $k_7 = 19k_4$, there was an implicit assumption that $k_7 >> k_3[M]$. Errors created by this simplification will tend to underestimate the value for k_4. However, since the maximum for Φ_C is only a factor of 2 smaller than the maximum quantum yield realized for the valence isomerization of a linear 1,3-diene, *i.e.*, 2,3-dimethyl-1,3-butadiene in solution,[1a] it is reasonable to assume that the deactivation step 3 is an insignificant route for the loss of $D_m{}^1$ at that pressure. (ii) In the calculation of k_6, the principal uncertainty is in the magnitude of the vibrational energy possessed by the activated molecule C_n. The value of 101 kcal/mol that was used must represent the maximum possible. If this value is less, the net result will be to increase the magnitude of k_4. For example, if the activation energy possessed by C_n is only 96 kcal/mol, k_4 will be increased by a factor of 2.2. (iii) The assumed rate of k_5 will lead to an overestimate in the value of k_4[7] and partially compensate for the error from ii. The value of k_4 is probably a minimum, accurate to wihin a factor of 5.

The rate of radiative decay for the diene that can be calculated from its absorption spectrum is of the order of, and smaller than, 10^9 sec^{-1}. The value of k_4 given above is hence a reasonable one as linear conjugated dienes have not been observed to fluoresce[9] and reactions from the excited state would be expected to be faster than the rate of radiative decay.

A remarkable implication of this result is that dienes such as the one in this study, although sterically hindered by methyl groups at the C_4 position, can cyclize with a quantum yield comparable to that of 2,3-dimethyl-1,3-butadiene, *provided activation energy is available to overcome some internal energy barrier.* This barrier may be the rotation of the *cis*-methyl group on C_4, but this does not seem likely in view of other data.[1,2] A more attractive possibility is that some rotation around the C_2–C_3 bond does occur in the excited singlet state of this diene. A comparison of the quantum yields for ring closure as a function of pressure in other 1,3-dienes may be of considerable interest.

We intend to use the photochemical closure of linear 1,3-dienes as a reference and measure rates of the reactions such as cyclopropene formation and dimerization relative to it.

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[7] This assumption is probably wholly valid in estimating k_3, as the vibrational energy possessed by $D_m{}^1$ is less than 15 kcal/mol. Since C_n may have considerably more vibrational energy (see ref 8), the estimate of k_5 may be high by a factor of 2–4. An average collision diameter of 4 Å was used in both calculations.

[8] The photon used in the reaction corresponded to 112 kcal/mol. The conversion of a linear 1,3-diene to a cyclobutene can be taken to be endothermic by 11 kcal/mol [K. B. Wiberg and R. A. Fenoglio, *J. Amer. Chem. Soc.*, **90**, 3305 (1968)], so that C_n may possess 101 kcal/mol of vibrational energy. k_6 was calculated from the expression $k_6 = A(1 - E/E^*)^{s-1}$, where log $A = 13.9$, $E = 37.0$,[4] and S was set equal to 26.

[9] R. Srinivasan, *Advan. Photochem.*, **4**, 115 (1966).

Electronic Effects on the Ring Opening of Cyclopropylidenes

Sir:

Some years ago[1] we reported that the ring opening of diphenylcyclopropylidene gave rise to optically active 1,3-diphenylallene.[2] It was further pointed out that the cause for the retention of dissymmetry is dominated (and probably limited to) a steric effect.[3]

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(1) *Cf.* J. M. Walbrick, J. W. Wilson, Jr., and W. M. Jones, *J. Amer. Chem. Soc.*, **90**, 2895 (1968); and W. M. Jones and J. W. Wilson, Jr., *Tetrahedron Lett.*, 1587 (1965).

(2) Ring opening of a cyclopropylidene (or its carbenoid) to give an allene was first reported by W. von E. Doering and P. M. Laflamme (*Tetrahedron*, **2**, 75 (1958)). For more recent examples of this ring opening—a number of which occur from free carbenes as well as carbenoids—see: W. M. Jones and J. M. Walbrick, *J. Org. Chem.*, **34**, 2217 (1969); L. Skattebol, *Tetrahedron Lett.*, 2175 (1965); P. S. Skell and R. R. Engel, *J. Amer. Chem. Soc.*, **89**, 2912 (1967); K. D. Bayes, *ibid.*, **85**, 1730 (1963); M. Marshall, R. Wolfgang, and C. McKay, *Tetrahedron Lett.*, 2033 (1963); L. Friedman and H. Shechter, *J. Amer. Chem. Soc.*, **83**, 3159 (1961); E. T. Marquis and P. D. Gardner, *Tetrahedron Lett.*, 2793 (1966); J. Maier, *ibid.*, 3603 (1965); H. Ward, R. G. Lawler, and H. Y. Loken, *J. Amer. Chem. Soc.*, **90**, 7359 (1968), and references cited in the above.

(3) In fact, it is difficult to visualize an electronic effect in any way influencing the retention of dissymmetry in the opening of a *trans*-disubstituted cyclopropylidene. Thus, placing a substituent on a phenyl ring that has no effect on its steric bulk may be expected to promote or retard its rotation (due to electronic effects) relative to the other ring (for example, path "a" over path "b"), but this would leave the optical purity of the product allene unaffected. Only if the substituent changed the amount of product arising from path "c" plus path "d" would any effect on optical purity be observed, and there is no obvious way an electronic effect would cause this.