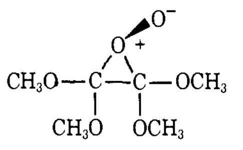
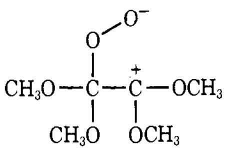
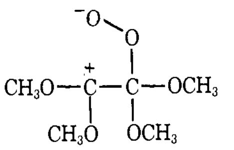


3

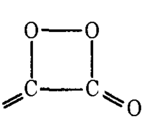


4a

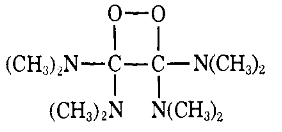


4b

diate (6) in the chemiluminescent oxidation of tetrakis(dimethylamino)ethylene.[11]



5



6

When **2** was heated to 80° in dilute benzene solution with several different fluorescent hydrocarbons, distinct luminescence was observed; the color corresponded to the hydrocarbon fluorescence.

This represents the first preparation of a 1,2-dioxetane by photooxygenation[12] but by no means requires that 1,2 cycloaddition of singlet oxygen be concerted;[3b] in particular, dipolar ions such as **4** may well be intermediate.[4] Furthermore, these experiments do not provide evidence either for or against the assertion[3c] that dioxetanes may be intermediate in the formation of allylic hydroperoxides in the ene-type photooxygenation.

Acknowledgment. Miss Heather King carried out microanalyses; Dr. Gwendolyn Chmurny recorded the 100-MHz nmr spectra.

---

(11) J. P. Paris, *Photochem. Photobiol.*, **4**, 1059 (1965).

(12) See P. D. Bartlett and A. P. Schaap, *J. Amer. Chem. Soc.*, **92**, 3223 (1970), for similar results. We thank Professor Bartlett for communicating these results, reported in part at the International Conference on Singlet Oxygen, New York, N. Y., Oct 1969 (*Ann. N. Y. Acad. Sci.*, in press).

Stephen Mazur, Christopher S. Foote
Department of Chemistry, University of California
Los Angeles, California 90024

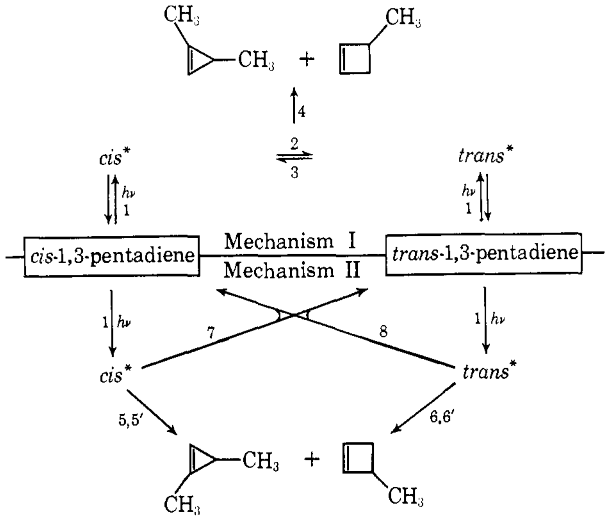
Received February 23, 1970

Differences in Reactivity between Excited States of *cis*- and *trans*-1,3-Pentadiene

Sir:

We have observed that 1,3-pentadiene can photoisomerize to 1,3-dimethylcyclopropene in solution, on direct irradiation, in a reaction similar to that previously observed[1] in the gas phase on sensitization by Hg($^3P_1$) atoms. The reaction offers a unique probe into the nature of the electronically excited states that are formed from the *cis* and trans isomers. The photoisomerization of 1,3-pentadiene to 3-methylcyclobutene[2] is observed only on direct irradiation in solution and thus can serve the same purpose in a more limited way.[3]

Two mechanisms may be visualized to explain the possible reactions when one of the stereoisomers of 1,3-pentadiene is irradiated. In the first one (steps 1–4) the electronically excited states of *cis* and *trans* are assumed to come into rapid equilibrium while the cyclization reactions (4) are relatively slow. In the second scheme (steps 1, 5, and 6) there is little or no equilibration between the *excited* states of *cis*- and *trans*-1,3-pentadiene; as a result, the rates of cyclization of each of these stereoisomers to products should be distinctly different. Steps 7 and 8 are internal conversion processes which are postulated to result in partial stereoisomerization; these steps are necessary to explain the experimental observation that stereoisomerization is considerably faster than any of the cyclizations under all irradiation conditions.



We have obtained quantum yields for the cyclization and stereoisomerization reactions of pure *cis*- and *trans*-1,3-pentadienes in solution (solvent cyclohexane; ambient room temperature) at a series of concentrations when irradiated at 253.7 nm. Corrections were applied for the progressive increase in the concentration of the stereoisomer that is formed as a product in any given instance. The actual quantum yields are given in Table I, the values extrapolated to infinite dilution being indicated in dark print. In discussing these results, the contribution of bimolecular (*e.g.*, dimerization) processes to the overall reaction of the excited states can be disregarded if the quantum yield values at zero concentration are considered.

The data in Table I show that the excited states of *cis*- and *trans*-1,3-pentadiene yield 3-methylcyclobutene as well as 1,3-dimethylcyclopropene at distinctly different rates, which is compatible only with the second mechanism. Further, the quantum yield for *cis* → *trans* or *trans* → *cis* isomerization is no more than 10%. These data suggest that the singlet excited states of *cis*- and *trans*-1,3-pentadiene are (i) chemically distinct species[4] and (ii) undergo interconversion with none of

---

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

(2) R. Srinivasan, *J. Amer. Chem. Soc.*, **84**, 4141 (1962).

(3) In the vapor phase, direct irradiation of 1,3-pentadiene yields 1,4-pentadiene as the major product along with many other minor products, including 1,3-dimethylcyclopropene.

(4) On sensitization to the triplet state by Hg($^3P_1$) atoms, we found no detectable difference between *cis* and *trans* isomers in the rate of forma-

Table I. Quantum Yields for Products from 1,3-Pentadienes[a]

M	Quantum yields × 10^3		
cis	3-Methylcyclobutene	*trans*-1,3-Pentadiene	1,3-Dimethylcyclopropene
2.85	3.4	110	0.67
2.42	3.4	100	0.70
1.75	3.4	100	0.75
1.34	3.3	100	0.78
0.89	3.4	100	0.80
0.60	3.3	100	0.82
0.00	**3.4**	**100**	**0.88**
trans	3-Methylcyclobutene	*cis*-1,3-Pentadiene	1,3-Dimethylcyclopropene
2.02	30	84	1.2
1.57	30	83	1.3
1.29	31	84	1.4
0.99	31	84	1.5
0.70	30	83	1.6
0.41	30	81	1.6
0.00	**30**	**83**	**1.9**

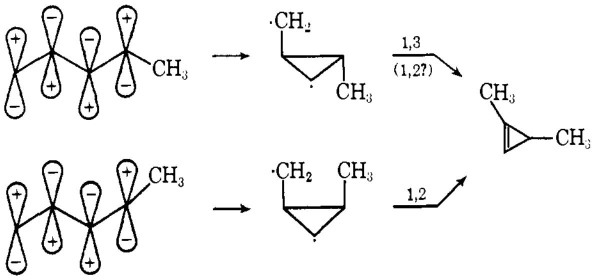
[a] Wavelength 253.7 nm; intensity 8.03 × 10^{-7} einstein sec^{-1}; solvent cyclohexane; ambient room temperature.

the ease that has been reported for the triplet excited states.

The effect that the structures of the stereoisomers have on the course of the cyclizations can be explained in the following way. In the formation of 3-methylcyclobutene, which is presumably a concerted process,[5] the methyl group may constitute a steric hindrance to the closure when the molecule has a *cis* configuration.

The tenfold difference in rate between the excited states of *cis*- and *trans*-1,3-pentadiene may mean that both are well removed from the configuration at the energy minimum in which a 90° rotation about the C_3–C_4 bond has occurred.

The photoisomerization to cyclopropenes is best explained in terms of the diradical intermediate that was previously proposed.[1] The excited states of the *cis*- and *trans*-1,3-pentadienes can be visualized as giving rise to different diradicals (the sense of the closure seems unimportant). The diradical derived from the *cis* can give the cyclopropene only by a 1,2 shift of an H atom, but a similar process can also give 2-methylmethylenecyclopropane, a product which actually is formed, in a yield comparable to that of 1,3-dimethylcyclopropene, in the irradiation of *cis*-1,3-pentadiene.[6] That derived from *trans* can give a cyclopropene not only by a similar 1,2-hydrogen shift but also by a 1,3-hydrogen shift which seems to be the uniquely preferred pathway for cyclopropene formation in 1,3-butadiene and isoprene.[1] It may also be noted that the diradicals do not have any simple pathway for interconversion which is consistent with the low quantum yield for stereoisomerization.



Since the energy profile (as a function of angle of rotation) between the perpendicular state and the *cis* or *trans* isomers of any olefin in their excited singlet state does not contain any barrier,[7] the difference in photochemical reactivity between the *cis* and *trans* forms that is observed here becomes understandable only if the lifetimes of these excited states[8] are quite small—possibly of the order of the time for a rotation about the C_3–C_4 bond in 1,3-pentadiene. The short radiative lifetimes of the excited singlet states of linear 1,3-dienes, coupled to their failure to fluoresce,[9] make this a very real possibility.

---

tion of 1,3-dimethylcyclopropene. No 3-methylcyclobutene was formed from either isomer.

[5] R. Hoffmann and R. B. Woodward, *Accounts Chem. Res.*, **1**, 17 (1968).

[6] The total absence (within experimental uncertainty) of 2-methylmethylenecyclopropane as a product from *trans*-1,3-pentadiene is significant since it underscores the possibility of two distinct diradical intermediates being formed from *trans*- and *cis*-1,3-pentadienes, *i.e.*, a two-step rather than a concerted mechanism for the formation of 1,3-dimethylcyclopropene.

[7] A. J. Merer and R. S. Mulliken, *Chem. Rev.*, **69**, 639 (1969).

[8] In this study, we have compared the quantum yields for two cyclization reactions from the *cis* and *trans* isomers and tacitly equated them to the ratio of the rate constants for these processes (*i.e.*, k_5/k_6). This equality is true only if the ratio of the rate constants for all processes (or just the unimolecular processes at infinite dilution) from the *cis* and the *trans* isomers is unity; in turn it means that the ratio of the lifetimes of their singlet excited states is unity under identical experimental conditions. Since 90% of the time both species return unchanged to the ground state, these assumptions seem warranted.

[9] R. Srinivasan, *Advan. Photochem.*, **4**, 119 (1966).

[10] Postdoctoral Fellow, 1968–present.

S. Boué,[10] R. Srinivasan
IBM T. J. Watson Research Center
Yorktown Heights, New York 10598

Received February 20, 1970

The Direct *cis–trans* Photoisomerization of 1,3-Dienes in Solution

Sir:

Evidence has been presented which shows that the benzophenone-sensitized photoisomerization of the 2,4-hexadienes in solution proceeds *via* common triplet-state diene intermediates, with transfer of triplet excitation to any of the three diene isomers leading to isomerization at both double bonds.[1] The results could be explained by assuming either a 1,4-biradical geometry for the common triplet state or the intermediacy of two rapidly equilibrating triplets of the allylmethylene type.[1–3] Direct excitation of the 2,4-hexadienes in diethyl ether solution has been reported to yield *cis–trans* interconversion as well as valence isomerization.[4] Of particular interest is the suggestion that intermediates of the cyclopropylmethylene type, **1**, are produced reversibly and are precursors of bicyclobutane, cyclopropene, and dimeric products.[4] Clearly, intermediates of type **1** provide a mechanism for *cis–*

1

---

[1] J. Saltiel, L. Metts, and M. Wrighton, *J. Amer. Chem. Soc.*, **91**, 5684 (1969).

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

[3] E. M. Evleth, *Chem. Phys. Lett.*, **3**, 122 (1969).

[4] R. Srinivasan, *J. Amer. Chem. Soc.*, **91**, 4498 (1969).