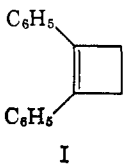
The Multiplicity of the Photochemically Reactive State of 1,2-Diphenylcyclobutene

Sir:

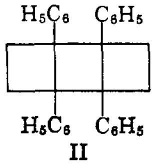
Although the photochemistry of stilbene has been extensively studied, relatively little is known about the photochemistry of the stilbene chromophore in small ring systems. Various 1,2-diphenylcyclopropenes are known to dimerize exclusively in the triplet state, apparently *via* a finite-lived diradical intermediate.[1] White and Anhalt[2] have shown that 1,2-diphenylcyclobutene (I) also gives a cyclobutane dimer upon irradiation. At this time we should like to present evidence that the latter dimerization occurs exclusively by way of the singlet state, and possibly through an eximer intermediate, in sharp contrast to the cases of 1,2,3-triphenylcyclopropene[1a] and 1,2-diphenyl-3-carbomethoxycyclopropene.[1c]

Irradiation of I in the crystal or in hexane solution at 21 ± 1° with light of 313 or 335 mμ produces a bright blue fluorescence ($\tau < 5$ nsec, measured by nanosecond flash spectroscopy). The intensity of the fluorescence decreases with increasing concentration, and there is no change in the emission maximum (385 mμ) or in the shape of the emission curve, thus ruling out the possibility of eximer fluorescence. The quantum yields of fluorescence of I in degassed hexane solution have been measured by the comparison technique described by Bowen[3] as a function of the concentration of I, and the results are given in Figure 1. At infinite dilution the quantum yield of fluorescence is unity, showing that the only pathway from the excited singlet state to the ground state of I is fluorescence.[4] This is further substantiated by the negligible intersystem crossing ratio of I ($<10^{-2}$, as measured by the technique of Hammond and Lamola.)[5]

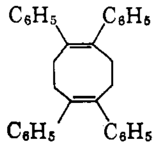
The products of irradiation of I, 1,2,5,6-tetraphenyltricyclo[4.2.0.0^{2,5}]octane (II), and diphenylacetylene + ethylene, first found by White and Anhalt[2] and confirmed by our work, also must be formed from the excited singlet state of I, since irradiation of sensitizers in the presence of I in degassed solution leads to no reaction of quantum yield greater than 10^{-3}, even with sensitizers of triplet energy greater than 60 kcal/mole.



I



II



Measurement of the direct quantum yields of dimer formation at 313 mμ is complicated by secondary side reactions (primarily the formation of 1,2,5,6-tetraphenylcyclooctadiene from II); therefore, 335-mμ radiation was used. This radiation was provided by a 250-w, short-arc medium-pressure mercury lamp, combined with a diffraction-grating monochromator and a glass filter to eliminate short-wavelength scattered light. The light intensity was measured by the Michler's ketone-sensitized isomerization of both *cis*- and *trans*-piperylenes and the sensitized ring closure of myrcene which was calibrated against the sensitized isomerization of *trans*-stilbene at 365 mμ. The results of the quantum yield measurements in degassed hexane solution are given in Figure 2. Although a good linear relationship is found between the inverse of the quantum yield of dimerization and the inverse of concentration of I, the intercept is not unity. Since only bimolecular processes need be considered upon extrapolation to infinitely concentrated solution, this result indicates that there must be a bimolecular energy wasting step in this reaction. The following mechanistic scheme most simply accounts for all of the above results.

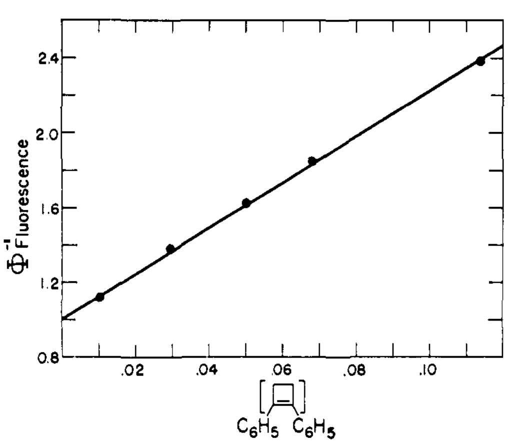


Figure 1. Plot of [quantum yield of fluorescence]$^{-1}$ against concentration of 1,2-diphenylcyclobutene.

$$\mathrm{I} + h\nu \longrightarrow \mathrm{I}^* \tag{1}$$

$$\mathrm{I}^* \longrightarrow \mathrm{I} + h\nu' \tag{2}$$

$$\mathrm{I}^* + \mathrm{I} \longrightarrow \mathrm{II} \tag{3}$$

$$\mathrm{I}^* + \mathrm{I} \longrightarrow 2\mathrm{I} + \text{heat} \tag{4}$$

where I* is the excited singlet state of I.

The unimolecular ring fission reaction is a minor perturbation under the conditions used and can be neglected. Thus, by making the usual steady-state assumption, we can write

$$\varphi_{-1\,\text{fluorescence}} = 1 + (k_3 + k_4)[\mathrm{I}]/k_2$$

$$\varphi_{-1\,\text{dimerization}} = 1 + k_4/k_3 + k_2/k_3[\mathrm{I}]$$

According to this mechanistic scheme, the product of the slope of Figure 1 and the slope of Figure 2 should equal the intercept of Figure 2. We find that the calculated and observed intercepts of Figure 2 agree within 5%, thus substantiating the mechanism.

From the slope of Figure 2 and the fluorescence lifetime it is possible to calculate the rate and thereby to estimate the activation energy for the bond-forming reaction 3 as less than 5 kcal/mole, placing I* near simple free radicals on the reactivity scale.

It is interesting to speculate on the meaning of reaction 4 in our mechanistic scheme. It is at least possible that reactions 3 and 4 proceed by way of a common, finite-lived metastable intermediate, *i.e.*, an eximer of I. If, on the other hand, reaction 4 has considerably less stringent geometric requirements than reaction 3, the two reactions can be viewed as being independent of

---

[1] (a) C. D. DeBoer and R. Breslow, *Tetrahedron Letters*, 1033 (1967); (b) N. Obata and I. Moritani, *ibid.*, 1503 (1966); (c) C. D. DeBoer, unpublished results.

[2] E. H. White and J. P. Anhalt, *Tetrahedron Letters*, 3937 (1965).

[3] E. J. Bowen, *Advan. Photochem.*, 1, 31 (1963).

[4] Although the extrapolated fluorescence quantum yield is 1.0 ± 0.05, the actual quantum yield of fluorescence can be no larger than 0.99, since the formation of diphenylacetylene and ethylene ($\varphi \simeq 0.01$, under the conditions used) must compete with fluorescence.

[5] G. S. Hammond and A. A. Lamola, *J. Chem. Phys.*, **43**, 2129 (1965).

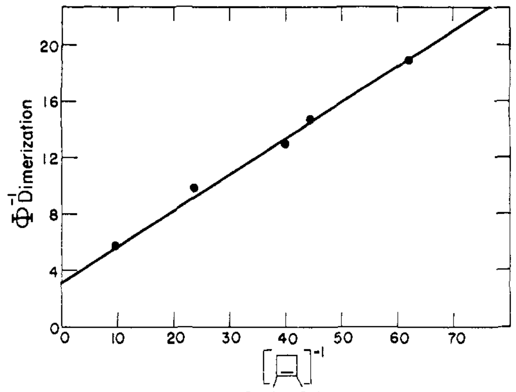


Figure 2. Plot of [quantum yield of dimerization]$^{-1}$ against [1,2-diphenylcyclobutene]$^{-1}$.

each other. We are at present seeking direct experimental evidence for the existence of a metastable eximer of I in solution at room temperature. We are also extending measurements of the kinds described here to several other small-ring unsaturated systems in hopes of determining the importance of various factors influencing the multiplicity of the photochemically active species in any given case.

Acknowledgments. We most gratefully acknowledge the help of Mr. Larry Costa in obtaining the fluorescence quantum yields and spectra and the help of Dr. Paul Gilman in obtaining the fluorescence lifetime limits.

C. D. DeBoer
Research Laboratories, Eastman Kodak
Rochester, New York 14650

R. H. Schlessinger
Department of Chemistry, University of Rochester
Rochester, New York 14627

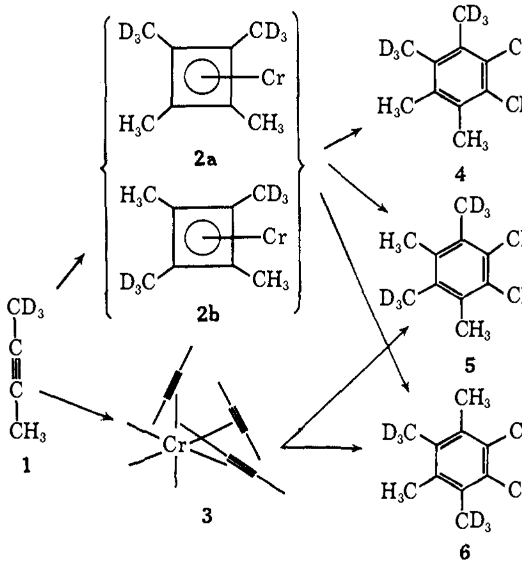
Received November 7, 1967

The Cyclotrimerization of 2-Butyne-1,1,1-d_3 by Triphenyltris(tetrahydrofuran)chromium(III)[1]

Sir:

The cyclotrimerization of substituted acetylenes to benzene derivatives using organometallic catalysts is a transformation of considerable synthetic usefulness.[2,3] A controversial area in mechanistic discussions of this reaction centers around the importance of metal–cyclobutadiene complexes as reaction intermediates. The observation that various isolable transition metal complexes of cyclobutadienes react with acetylenes only in the presence of oxidizing agents or donor ligands has been interpreted as evidence against cyclobutadiene intermediates.[2,4] However, the reactivity of these stable compounds does not bear directly on that of less stable and presumably more reactive complexes which might be formed under the cyclotrimerization conditions. Labeling and product studies have provided no support for cyclobutadiene intermediates in these reactions,[5] but these experiments are amenable to a number of interpretations.[6] We wish to report the results of deuterium-labeling experiments which provide clear evidence *excluding* a chromium-tetramethylcyclobutadiene intermediate in the cyclization of 2-butyne-1,1,1-d_3 (**1**) to hexamethylbenzene-d_9 by triphenyltris(tetrahydrofuran)chromium(III).[3]

If the mechanism of this cyclotrimerization involves dimerization of **1** to a tetramethylcyclobutadiene–chromium complex, the initial stages in the cyclization must produce head-to-head and head-to-tail configurations of the labeled cyclobutadienes **2** with equal probability.[7] Further, ample experimental precedent supports the assumption that a cyclobutadiene moiety complexed with a transition metal will adopt a square geometry in which the carbon–carbon bonds of the ring are chemically equivalent.[8] In consequence, reaction of a tetramethylcyclobutadiene-containing intermediate with another molecule of **1**, either directly or following dissociation of the cyclobutadiene from the metal, will lead to a statistically determined distribution of the labeled hexamethylbenzenes **4**, **5**, and **6** (relative yields 1:5:2). In contrast, cyclotrimerization proceeding in a concerted manner through an intermediate in which three molecules of **1** are simultaneously coordinated with the metal (represented schematically by **3**), or through a metal heterocycle of the type proposed by Blomquist[4] and Collman,[9] should lead only to **5** and **6** in 3:1 relative yield.



We have distinguished experimentally between these two alternative paths by determining the yield of **4** produced in the cyclization, relative to the combined yields of **5** and **6**. Compound **4** is unique among the labeled

---

[1] Supported in part by the U. S. Army Research Office (Durham), Grant ARO-D-31-124-G691, and by Eli Lilly and Co.

[2] P. M. Maitlis, *Advan. Organometal. Chem.*, **4**, 95 (1966).

[3] H. Zeiss in "Organometallic Chemistry," H. Zeiss, Ed., American Chemical Society Monograph No. 147, Reinhold Publishing Corp., New York, N. Y., 1960, p 380.

[4] A. T. Blomquist and P. M. Maitlis, *J. Am. Chem. Soc.*, **84**, 2329 (1962); L. Watts, J. D. Fitzpatrick, and R. Pettit, *ibid.*, **87**, 3253 (1965); **88**, 623 (1966).

[5] J. C. Sauer and T. L. Cairns, *ibid.*, **79**, 2659 (1957); G. N. Schrauzer, *Angew. Chem. Intern. Ed. Engl.*, **3**, 185 (1964).

[6] For example, T. I. Bieber, *Chem. Ind.* (London), 1126 (1957). See also E. M. Arnett and J. M. Bollinger, *J. Am. Chem. Soc.*, **86**, 4729 (1964).

[7] We assume that any kinetic isotope effects in the formation and subsequent degradation (eq 1) of the hexamethylbenzenes can be neglected.

[8] R. P. Dodge and V. Schomaker, *Acta Cryst.*, **18**, 614 (1965); J. D. Dunitz, H. C. Mez, O. S. Mills, and H. M. M. Shearer, *Helv. Chim. Acta*, **45**, 647 (1962); C. S. Yannoni, G. P. Ceasar, and B. P. Dailey, *J. Am. Chem. Soc.*, **89**, 2833 (1967).

[9] J. P. Collman and J. W. Kang, *ibid.*, **89**, 844 (1967).