

Figure 1. Oscilloscope traces at 610 (a and c) and 341 nm (b and d) after flashing a 2×10^{-4} M solution of *N*-methyldiphenylamine (A) in methylcyclohexane: a and b, degassed; c and d, aerated. Time scale: a and b, 20 msec/div; c and d, 0.2 msec/div. Vertical scale, per cent transmission (T). The flash intensity in c and d was twice as high as that in a and b.

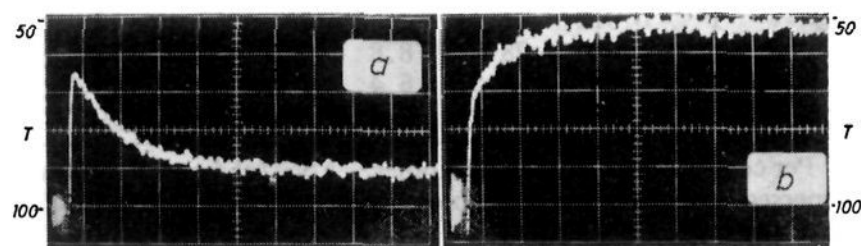


Figure 2. Oscilloscope traces at 520 (a) and 610 nm (b) after flashing a 2×10^{-4} M degassed solution of A in 3-methylpentane at -111° : time scale, 0.1 msec/div; vertical scale, per cent transmission (T)

of the 610 transient from the amine triplet state is measurable only at low temperatures. Between -100 and -160° the decay of the amine triplet is slow in comparison with the flash lifetime and we observed the triplet decay at 520 nm and at 610 nm the growing in of the 610 transient (Figure 2).

Both processes are first order and occur with the same rate, which clearly shows that the amine triplet is, at least in this temperature range, the precursor of 610. That this mechanism is also operative at room temperature can be shown as follows. The activation energy for the triplet decay is 5.5 kcal/mol in ethanol. The triplet lifetime at room temperature, $\tau_0 = 2 \times 10^{-8}$ sec, as obtained by extrapolation from the Arrhenius plot (Figure 3) agrees quite well with the value derived from the 610 quantum yields in flash experiments on degassed (ϕ_0^{610}) and aerated (ϕ^{610}) solutions using the Stern-Volmer equation, $\phi_0^{610}/\phi^{610} = 1 + k_3[\text{O}_2]\tau_0$, where (neglecting phosphorescence) $\tau_0 = 1/(k_1 + k_2[\text{M}])$. Since 610 decays by a first-order reaction both in the presence of oxygen ($\tau_{610} = 3 \times 10^{-4}$ sec) and in degassed solutions ($\tau_{610} = 3.5 \times 10^{-2}$ sec), the ratio of the 610 quantum yields is easily determined by extrapolating the decay curves back to zero time. In ethanol and methylcyclohexane $\phi_0^{610}/\phi^{610} = 2$; $k_3[\text{O}_2]$ is assumed to be $6 \times 10^7 \text{ sec}^{-1}$ (based on Ware's measurements⁹) so that $\tau_0 = 1.7 \times 10^{-8}$ sec. Tris-*p*-tolylamine has an absorption spectrum which makes this compound suitable for nitrogen-laser excitation at 337 nm.¹⁰ The decay of the triplet state can therefore be measured directly at room temperature; we found $\tau_0 = 5 \times 10^{-8}$ sec. The agree-

(9) W. Ware, *J. Phys. Chem.*, **66**, 455 (1962).

(10) The authors are indebted to Dr. H. Staerk of this institute who performed the experiment.

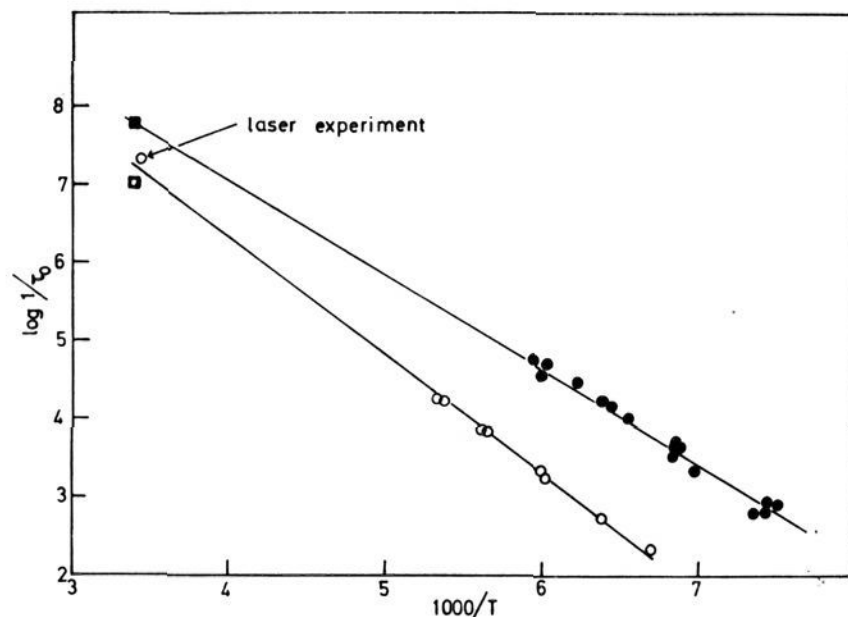


Figure 3. Arrhenius plot of the triplet decay of *N*-methyldiphenylamine (●) and tris-*p*-tolylamine (○). Points calculated from quenching experiments: ■; □.

ment between the values of τ_0 determined from the laser experiment, from the extrapolated Arrhenius plot, and from the 610 quantum yield ratio ($\phi_0^{610}/\phi^{610} = 7$) is good (cf. Figure 3).

The quantum yield for carbazole formation from A is, according to our measurements in aerated solutions, 0.42,¹¹ and therefore $\phi^{610} = k_1/(k_1 + k_2[\text{M}] + k_3[\text{O}_2]) \geq 0.42$. Since $\phi_0^{610}/\phi^{610} = 2$, it follows that $\phi_0^{610} = k_1/(k_1 + k_2[\text{M}]) \geq 0.84$. These amazingly high yields imply that the chemical relaxation process 1 competes at room temperature very effectively with the normal triplet deactivation reactions (2 and 3). Process 1 is not suppressed in highly viscous media. Even solutions of A in polymethylmethacrylate matrices show the 610 absorption on flashing at room temperature. Presumably, $k_2[\text{M}] \ll k_1$, because in photochemically stable amines, such as tris-*p*-carbomethoxyphenylamine (I) or *N*-methylbis-*p*-carbomethoxyphenylamine, where there is no detectable 610 and carbazole formation, the triplet lifetime is 3 orders of magnitude longer and liquid solutions of I phosphoresce even at room temperature.¹²

(11) The carbazole concentration was determined spectrophotometrically, using an extinction coefficient $\epsilon_{343} = 5400 \text{ l.}/(\text{mol cm})$. The value 3900 used by Tanaka, *et al.*,⁵ is too low and consequently their quantum yield of 0.62 too high.

(12) K. H. Grellmann, *Ber. Bunsenges. Phys. Chem.*, **73**, 827 (1969).

(13) Part of Ph.D. Thesis, Göttingen, 1971.

E. W. Förster,¹³ K. H. Grellmann*

Max-Planck-Institut für Biophysikalische Chemie
Abteilung Spektroskopie, 34 Göttingen, Germany

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Competing Diradical and Electrocyclic Reactions. Difference in Activation Volumes

Sir:

Numerous examples are now known in which thermal reaction of a diene with a dienophile reagent produces mixtures of cyclohexenes and vinylcyclobutanes.¹ It is generally accepted that the cyclohexenes result from concerted, electrocyclic reaction allowed by orbital

(1) (a) P. D. Bartlett, *Quart. Rev., Chem. Soc.*, **24**, 473 (1970); (b) C. A. Stewart, Jr., *J. Amer. Chem. Soc.*, **84**, 117 (1962); (c) J. C. Little, *ibid.*, **87**, 4020 (1965).

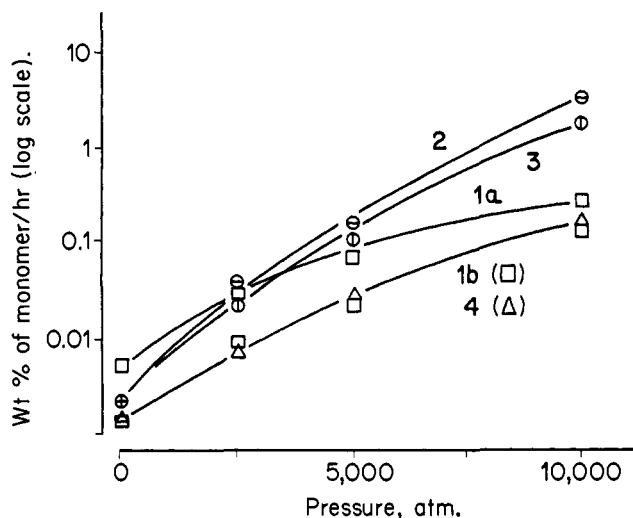
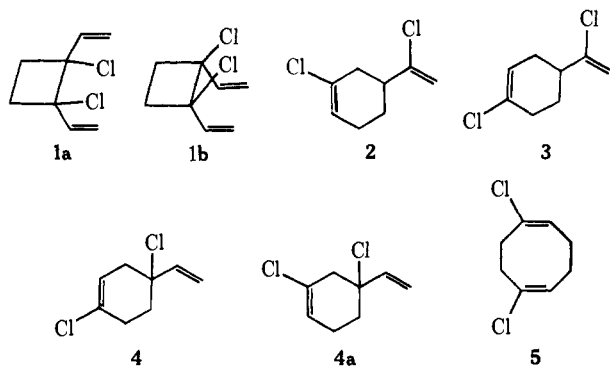


Figure 1.

symmetry, and that the vinylcyclobutanes result from a two-step, or at least two-stage reaction with an intermediate or intermediate stage which is usually diradical in character.² Mixtures of such products are also produced in photochemical reactions of similar materials³ in which both types of product are believed to result from diradical intermediates, although the energy levels and conformations leading to ring closure are not necessarily the same as for the thermal process. In a previous paper⁴ it was proposed that in thermal dimerization of 2-chloro-1,3-butadiene, one of the cyclohexene isomers, **4**, as well as cyclobutanes **1a** and **1b** and cyclooctadiene **5**⁵ resulted from diradical reaction, while the other two observed cyclohexenes, **2** and **3**, resulted from electrocyclic reaction. The primary basis for this proposal was the absence of the remaining



cyclohexene isomer, **4a**, and alternatively substituted cyclobutanes in the products: diradical reaction of chloroprene is favorable only with head-to-head orientation of the reacting molecules, while electrocyclic reaction is favorable only with the unsubstituted vinyl group serving as the dienophile. The other evidence given to support this proposal is largely circumstantial in nature: energetics and substituent effects are com-

(2) Apparent dipolar stepwise reactions are also known; see ref 1a and 1b.

(3) W. L. Dilling, *Chem. Rev.*, **69**, 845 (1969), and references cited.

(4) C. A. Stewart, Jr., *J. Amer. Chem. Soc.*, **93**, 4815 (1971).

(5) Isomer **5** results from rearrangement of **1b** during the course of the dimerization. This rearrangement is accelerated by pressure with an estimated $\Delta\bar{V}^\ddagger$ of -7 cm³/mol, but data are too limited to assess the accuracy of this value.

patible with variations in amounts of cyclobutane isomers produced from a variety of dienes, and the reaction of cyclopentadiene with chloroprene takes place almost entirely with the vinyl group serving as dienophile. A more direct test that the proposed diradical and electrocyclic products are actually formed by different mechanisms was indicated.

We have now shown, from dimerization of chloroprene as a function of pressure, that the mechanism leading to **1a**, **1b**, and **4** is indeed significantly different from that leading to the electrocyclic products **2** and **3**. Overall rates of dimerization and isomer distributions^{4,5} are given in Table I. Calculated rate constants for the

Table I. Overall Rate and Isomer Distribution (Per Cent) for Dimerization of Chloroprene at $23 \pm 4^\circ$

Pressure, atm	k^a	1a	1b + 5	4	2	3
1 ^b	0.012	42	12	13	17	16
2,500 ^c	0.10	28	8.8	7.0	33	23
5,000 ^d	0.36	18.5	6.4	7.0	41.5	26.5
10,000 ^d	5.4	4.6	2.8	3.0	59	30

^a Per cent per hour of bulk monomer. ^b See ref 4 and 5. ^c Water immersed, collapsible tube in pressure bomb. ^d Teflon poly-TFE capsule in piston apparatus.

separate isomers are shown as a function of pressure in Figure 1. It is apparent that the transition state or states leading to the diradical products is considerably less compact, about 6–9 cm³/mol, than the corresponding states for the electrocyclic products, as expected if the former involve incipient bonding at only one end of each reactant and the latter involve incipient formation of two bonds.

From the curvature in Figure 1, it is apparent that the volumes of activation ($\Delta V^\ddagger = -RT \ln k/dP$) are not independent of pressure. Several of the difficulties in assessing accurate values for volumes of activation have recently been reviewed.⁶ The average activation volume over the range of measurements, $\Delta\bar{V}^\ddagger$, can be assessed with reasonable accuracy but is of dubious theoretical significance. The desired activation volume at zero pressure, ΔV^\ddagger_0 , cannot be estimated with reasonable accuracy unless very precise data free of systematic errors are available over a range of moderate pressures to permit extrapolation of $d \ln k/dP$. Values of $\Delta\bar{V}^\ddagger$ and ΔV^\ddagger_0 which are given in Table II com-

Table II. Volumes of Activation (Cubic Centimeters per Mole)

Isomer ^a	$-\Delta V_R^b$	$-\Delta\bar{V}^\ddagger$	$-\Delta V^\ddagger_0$	$\Delta\Delta V^\ddagger_0$
1a	27	10	22	8.4
1b + 5 ^c	(27)	12	22	9.4
4	32	12	22	9.4
2	32	18	31	(0)
3	32	16	29	2.2

^a See text for definition of symbols. ^b Density of **1b** is assumed from **1a**. Densities of **2**, **3**, and **4** are known only from mixtures. ^c See ref 5 in text.

pared to the volume change for reaction, ΔV_R , are questionable for these reasons. Differences in volume

(6) R. A. Grieger and C. A. Eckert, *J. Amer. Chem. Soc.*, **92**, 7149 (1970).

of activation for the various isomers can be estimated with much greater precision, however. Values of $\Delta\Delta V^\ddagger_0$, calculated by extrapolating the slopes of relatively linear plots of $\ln k_2/k_1$ against pressure, are independent of any errors in absolute rate measurements and are apparently accurate to within approximately 1 cm³/mol. These agree as well as can be expected with differences in ΔV^\ddagger or ΔV^\ddagger_0 . There has been considerable controversy⁷ previously over attempts to compare an *absolute* value for *one* observed process to absolute values predicted for the two processes from theory. This difficulty is not relevant in the present case where the *difference* between the *two* processes is observable.

If, as proposed, diradical and electrocyclic reactions are usually comparable in energy in diene dimerizations, similar pressure effects should be observable in other systems. At least one trend in the appropriate direction can be seen in the data of Walling and Peisach⁸ on the dimerization of isoprene, where the proportion of cyclooctadiene dimers was found to decrease with increasing pressure. Because the cyclooctadienes are presumably secondary products resulting from decomposition of initially formed cyclobutanes (comparable to formation of **5** from **1a** and **1b**), and because additional amounts of cyclohexenes can be formed similarly as well as by the electrocyclic process, quantitative interpretation is hazardous, but the apparent activation volume is about 3 cm³/mol less negative for these "diradical" products than for the predominant methylisopropenylcyclohexenes.

- (7) See, for example, S. W. Benson and J. A. Berson, *J. Amer. Chem. Soc.*, **86**, 259 (1964); C. Walling and D. D. Tanner, *ibid.*, **85**, 612 (1963).
 (8) C. Walling and J. Peisach, *ibid.*, **80**, 5819 (1958).

Clare A. Stewart, Jr.
 Elastomer Chemicals Department
 E. I. du Pont de Nemours and Company
 Wilmington, Delaware 19898
 Received September 7, 1971

Mechanisms of Photochemical Reactions in Solution. LXXI.¹ Photochemistry of 1,3-Cyclohexadiene at Long Wavelength

Sir:

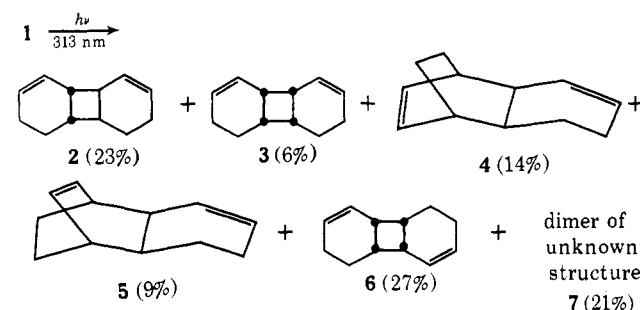
The long wavelength absorption of conjugated dienes is of interest in view of uncertainty regarding the position of the 0-0 level of the first excited singlet state.^{2,3} In addition, the nature of the absorbing species at wavelengths too low in energy to be reasonably assigned to excitation to S₁ has not been determined. The characterization of photochemical processes at these wavelengths, as distinct from those at energies in the region of the first absorption maximum, might be a useful approach to the resolution of these questions. We wish to report the occurrence of such unique photochemical processes in 1,3-cyclohexadiene (**1**), an *s-cis*-diene, during direct 313-nm (91 kcal mol⁻¹) irradiation.

- (1) Part LXX: J. W. Meyer and G. S. Hammond, *J. Amer. Chem. Soc.*, in press.
 (2) R. Srinivasan, *Advan. Photochem.*, **4**, 113 (1966).
 (3) R. Srinivasan and F. I. Sonntag, *J. Amer. Chem. Soc.*, **87**, 3778 (1965).

Schenck and coworkers⁴ first studied the photo-reactivity of neat **1** at long wavelengths, which they designated as >330 nm. They reported that the same three dimers **2-4** formed by triplet sensitization^{4,5} were produced, although in different proportion. Based on this result the suggestion was made that the long wavelength dimerization was due to direct singlet-triplet absorption by ground-state collision aggregates, followed by formation of the triplet dimers.

Our own studies, conducted at 313 nm, show that irradiation of neat **1** or its pentane or cyclohexane solutions at >1 M leads to the formation of three further dimers **5-7** in amounts comparable to those of the triplet dimers, together with trace amounts of several other presumably dimeric constituents. The composition of the dimer fraction obtained on irradiation of neat **1** is given in Scheme I. Dimers **2**, **4**, and **6** and a mixture

Scheme I



of dimers **3**, **5**, and **7** were isolated by chromatography on a 10% silver nitrate-alumina column;⁶ dimer **7** was isolated, although not in analytical purity,⁷ by preparative gas-solid partition chromatography on Porasil D.

Dimer **5** (*endo*-dicyclohexadiene) is the major dimer produced thermally;^{4,5} it is also formed by γ irradiation^{4,8,9} and, in trace amounts, by the sensitized irradiation of **1**.⁵

Dimer **6**¹⁰ (*cis,syn,cis*-tricyclo[6.4.0.0^{2,7}]dodeca-3,9-diene) is cleanly converted by catalytic hydrogenation to a tricyclic hydrocarbon¹⁰ (*cis,syn,cis*-tricyclo[6.4.0.0^{2,7}]dodecane), which is identical with the compound produced by catalytic hydrogenation of **3** but differs from that produced⁵ on hydrogenation of dimer **2**. The structure and stereochemistry of dimers **2** and **3** have been assigned previously.^{4,5}

Compounds **2**, **6**, and **7**, collectively, constitute *ca.* 70% of the mixture of dimers produced on irradiation of neat (10.4 M) **1** at 313 nm. On dilution with pentane or cyclohexane, the relative contribution of dimers **5-7** decreases uniformly until, at 1.0 M, they comprise only *ca.* 25% of the mixture; the relative distribution of dimers **2-4** successively approaches the 3:1:1 ratio obtained on sensitized irradiation of **1** as the solutions are diluted. This change in product distribution on

- (4) G. O. Schenck, S.-P. Mannsfeld, G. Schomburg, and C. H. Krauch, *Z. Naturforsch.*, **B**, **19**, 18 (1964).
 (5) D. Valentine, N. J. Turro, Jr., and G. S. Hammond, *J. Amer. Chem. Soc.*, **86**, 5202 (1964).
 (6) L. R. Chapman and D. F. Kuemmel, *Anal. Chem.*, **37**, 1598 (1965).
 (7) The mass spectrum of dimer **7** shows contamination by tri- and tetrameric materials which presumably form on standing.
 (8) R. Schutte and G. R. Freeman, *J. Amer. Chem. Soc.*, **91**, 3715 (1969).
 (9) T. L. Penner, D. G. Whitten, and G. S. Hammond, *ibid.*, **92**, 2861 (1970).
 (10) Satisfactory microanalytical and spectral data were obtained for this compound.