for the early work on the 2-methylbutenes, which was done on a Perkin-Elmer instrument. The solid support was Chromosorb, and columns were 0.25 in. in diameter (0.125 in. for those on the Hy-Fi). The 2-methylbutenes were separated at room temperature on a 15-ft. didecyl phthalate column or on two 1-m. columns in series packed with didecyl and dinonyl phthalate, respectively. Originally, 1- and 2-pentene were separated on a 25-ft. didecyl phthalate column at 15°. This column failed to separate cis- and trans-2-pentene, but a 15-ft. column of ethylene glycol saturated with silver nitrate accomplished the job at room temperature with slight overlap of the 1-pentene and cis-2-pentene peaks. In addition, product mixtures from 2-pentyl chloride had to be redistilled to remove unreacted chloride, since it would react with the silver nitrate. In later work the 1-pentene and cis- and trans-2-pentene were determined simultaneously on a 20-ft. adiponitrile column at room temperature. None of the column materials had any effect on unreacted alkyl halide under the analytical conditions except for the ethylene glycol–silver nitrate mixture noted above.

The 2- and 3-chloropentanes were separated on a 15-ft. Apiezon-L column at 67°. The same column at 103° separated the 2- and 3-iodopentanes, and at 110° the 2- and 3-bromopentanes. Separation of the 2- and 3-fluoropentanes could not be accomplished under any conditions tried.

Base-Promoted Elimination vs. Solvolysis. Rough kinetics on the second-order reaction with ethoxide ion and the first-order reaction with ethanol were run on most of the halides used in this investigation. Runs were in the refluxing solvent and no particular effort to attain precision was made. Concentrations similar to those of the preparative runs were used, and three to five points were determined per run by titration of chilled aliquots with sodium hydroxide (in the solvolyses) or hydrochloric acid (in the second-order reactions). The rate constants are useful only as orders of magnitude, and will not be tabulated.

The qualitative conclusions are as follows. 2-Pentyl iodide and bromide had $k_2 > 500k_1$. 2-Pentyl chloride underwent less than 0.25% solvolysis in 22 hr., which is longer than the time of the preparative run. 2-Methyl-2-butyl fluoride when heated in ethanol at 120° for 85 hr. with a slight excess of sodium acetate (to prevent acid-catalyzed solvolysis) produced less than 1.7% olefin. From this result it was assumed that solvolysis would also be negligible with 2-pentyl fluoride. 2-Methyl-2-butyl chloride had $k_2 \sim 3k_1$, and the bromide had $k_2 \sim 5k_1$ (no correction applied for solvolysis accompanying the second-order reaction). These figures indicate that as much as 10–20% solvolysis may accompany the preparative elimination reactions of these two compounds under the conditions used.

Mechanisms of Photochemical Reactions in Solution. XXXI. Activation and Deactivation of Conjugated Dienes by Energy Transfer

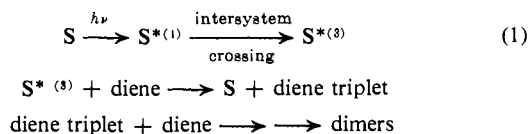Robert S. H. Liu, Nicholas J. Turro, Jr.,[1] and George S. Hammond[2]

Contribution No. 3213 from the Gates and Crellin Laboratories of Chemistry, California Institute of Technology, Pasadena, California.
Received February 17, 1965

The photosensitized dimerizations of isoprene and butadiene have been studied in detail. Similar variations in the composition of the product mixtures are observed as the excitation energies of the triplet states of the sensitizers are varied. The results suggest that excitation of s-cis-dienes to triplet states requires less excitation energy than is needed to excite s-trans forms. cis triplets added to dienes give much larger yields of cyclohexene derivatives than are obtained from trans triplets. Other quantitative studies of the reaction of isoprene included: (1) measurement of quantum yields, (2) dependence of quantum yields on isoprene concentration, and (3) the influence of an added quencher (azulene). The results are all consistent with a mechanism in which the diene is activated by transfer of triplet excitation from a sensitizer to a diene molecule.

Earlier reports[3-6] have shown that irradiation of solutions containing conjugated dienes and various photosensitizers, with light absorbed only by the latter, leads to formation of dimers of the dienes. The following mechanism has been suggested.

$$S \xrightarrow{h\nu} S^{*(1)} \xrightarrow[\text{crossing}]{\text{intersystem}} S^{*(3)} \qquad (1)$$

$$S^{*(3)} + \text{diene} \longrightarrow S + \text{diene triplet}$$

$$\text{diene triplet} + \text{diene} \longrightarrow \longrightarrow \text{dimers}$$

It has further been inferred that stereoisomeric triplets of the dienes are formed in varying amounts in the presence of different sensitizers.[5] This paper will

(3) G. S. Hammond, N. J. Turro, Jr., and A. Fischer, *J. Am. Chem. Soc.*, 83, 4674 (1961).
(4) N. J. Turro, Jr., and G. S. Hammond, *ibid.*, 84, 2841 (1962).
(5) G. S. Hammond and R. S. H. Liu, *ibid.*, 85, 477 (1963).
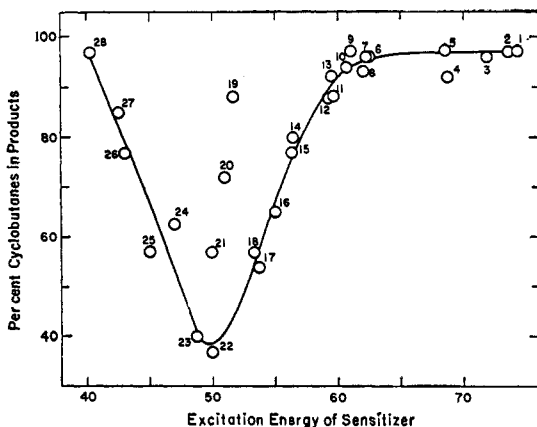(6) G. S. Hammond, N. J. Turro, Jr., and R. S. H. Liu, *J. Org. Chem.*, 28, 3297 (1963).

Figure 1. Butadiene dimer composition vs. triplet energy of sensitizers.

Figure 2. Isoprene dimer composition vs. triplet energy of sensitizers.

report quantitative studies that tend to confirm the mechanism.

Results and Discussion

Variation of the Sensitizers. Sensitized dimerization of butadiene gives three products, cis- and trans-1,2-divinylcyclobutane and 4-vinylcyclohexene.[3,6] Isoprene gives seven products, three 1,2-dialkenylcyclobutanes, two derivatives of cyclohexene, and 1,6-dimethyl- and 1,5-dimethylcyclooctadiene-1,5.[5,6] In both cases the distribution of products is a function of the nature of the sensitizers used to implement the reactions. Table I presents data obtained with butadiene and Table II shows representative data from the study of isoprene. Inspection of the results shows in each case that variations really represent only one degree of freedom in each case. The ratio of the 1,2-divinylcyclobutanes formed from butadiene is constant within experimental error, and formation of the two compounds is competitive with production of 4-vinylcyclohexene. In dimerization of isoprene five compounds, the cyclobutanes and cyclooctadienes, behave as a unit and compete with production of the two derivatives of cyclohexene. The significant trends can, therefore, be summarized, as is done in Figures 1 and 2 in which the relative yields of cyclobutanes (plus cyclooctadienes in the case of isoprene) are plotted as a function of the excitation energies of the lowest triplet states of the sensitizers.[7-9]

The first significant fact in each case is that high-energy sensitizers all give essentially the same results, producing mixtures that are relatively rich in cyclobutanes with both substrates. In both cases a regular change is initiated when the excitation energy of the sensitizer is decreased below 60 kcal./mole and increasingly large amounts of cyclohexenes are produced as the sensitizer energy is lowered from 60 to about 50 kcal./mole. Sensitizers having very low excitation energies again give product mixtures containing relatively large amounts of cyclobutanes. However, there is a marked change in the behavior of the reactions with sensitizers having excitation energies less than ~50

(7) Plots of chemical response against excitation energies of sensitizers are known as "Saltiel plots"[3] in our laboratory.

(8) G. S. Hammond, *et al., J. Am. Chem. Soc.*, **86**, 3197 (1964).

(9) Determination of excitation energies of the sensitizers is described by W. G. Herkstroeter, A. A. Lamola, and G. S. Hammond, *ibid.*, **86**, 4537 (1964).
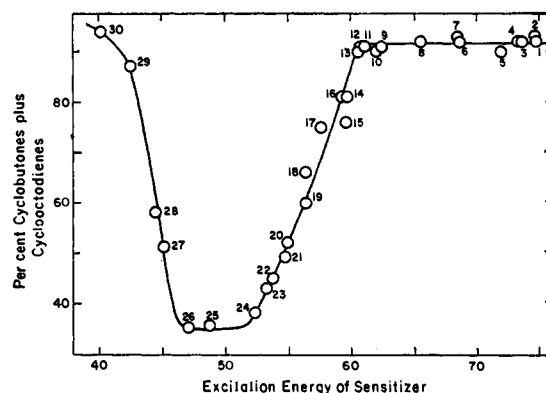
kcal./mole. The reaction rates become very slow and, although careful measurements have not been made, it is obvious that the quantum yields become very small. In contrast, there is no significant change in

Table I. Composition of Products from Photosensitized Dimerization of Butadiene

| | | —Percentage distribution of dimers— | | | |
		trans-1,2- Divinyl-cyclo-butane	cis-1,2- Divinyl-cyclo-butane	4-Vinyl-cyclo-hexene	E_T, kcal./ mole
1.	Xanthone[b]	78	19	3	74.2
2.	Acetophenone[b]	78	19	3	73.6
3.	Benzaldehyde	80	16	4	71.9
4.	o-Dibenzoylbenzene	76	16	7	68.7
5.	Benzophenone[b]	80	18	2	68.5
6.	2-Acetylfluorenone	78	18	4	62.5
7.	Anthraquinone	77	19	4	62.4
8.	Flavone	75	18	7	62.0
9.	Michler's ketone	80	17	3	61.0
10.	4-Acetylbiphenyl	77	17	6	60.6
11.	β-Naphthyl phenyl ketone	71	17	12	59.6
12.	β-Naphthaldehyde	71	17	12	59.5
13.	β-Acetonaphthone[b]	76	16	8	59.3
14.	α-Acetonaphthone	63	17	20	56.4
15.	α-Naphthaldehyde	62	15	23	56.3
16.	Biacetyl	52	13	35	54.9
17.	Benzil	44	10	45	53.7
18.	Fluorenone	44	13	43	53.3
19.	Duroquinone[c]	72	16	12	(51.0)[d]
20.	β-Naphthil	57	15	28	51.0
21.	Benzoquinone[c]	~51	~6	~43	50
22.	Camphorquinone	30	7	63	50
23.	Pyrene	~30	~10	~60	48.7
24.	Benzanthrone	55	10	35	47
25.	3-Acetylpyrene	43	12	45	45
26.	Eosin	60	17	23	43.0
27.	Anthracene	75	10	15	42.5
28.	9,10-Dibromoanthracene	78	19	3	40.2

[a] Sensitizer was 0.1 M in ether unless otherwise specified. [b] Sensitizer 0.1 M in benzene. [c] By-products formed may have influenced the course of the reaction. [d] Approximation to lowest energy emission observed. The compound probably gives two triplets: W. G. Herkstroeter, J. Saltiel, and G. S. Hammond, *J. Am. Chem. Soc.*, **85**, 482 (1963).

reaction efficiencies on passing from "high-energy" sensitizers to those lying in the 53–60-kcal. range. By way of contrast, the composition of product mixtures

Table II. Composition of Products from Photosensitized Dimerization of Isoprene

Sensitizer[a]	$E_T{}^c$	Σ^d	Distribution of dimers, %[b]					
			1	2	3	4	5	6 and 7
1. Propiophenone	74.6	93	29.7	30.7	9.7	4.4	2.2	23.3
2. Cyclopropyl phenyl ketone	74.4	92	28.0	30.5	8.0	5.4	2.9	25.2
3. Acetophenone	73.6	92	29.0	29.7	8.2	4.8	3.0	25.4
4. 1,3,5-Triacetylbenzene	73.3	92	29.5	29.6	6.7	4.6	3.7	25.8
5. Benzaldehyde	71.9	90	28.4	26.1	7.5	6.3	3.4	28.2
6. o-Dibenzoylbenzene	68.7	92	29.6	31.2	7.7	4.9	2.8	23.9
7. Benzophenone	68.5	93	29.0	30.1	9.0	4.7	2.1	25.2
8. Thioxanthone[e]	65.5	92	28.6	26.0	8.0	5.2	3.2	28.9
9. 2-Acetylfluorene[e]	67.5	91	29.2	30.0	8.0	6.1	3.0	23.8
10. Anthraquinone[e]	62.4	91	28.6	29.5	7.5	6.2	3.2	25.1
11. Flavone[e]	62.0	90	26.2	28.3	5.8	7.8	3.9	28.1
12. Michler's ketone[e]	61.0	91	27.8	29.5	7.7	5.8	3.3	25.8
13. Acetylbiphenyl	60.6	90	28.6	29.1	8.3	6.8	3.1	24.2
14. β-Naphthyl phenyl ketone	59.6	81	24.4	26.9	8.7	13.7	5.9	21.1
15. β-Acetonaphthone	59.3	81	26.3	27.2	9.3	14.5	4.5	18.2
16. β-Naphthaldehyde	59.5	76	22.1	21.7	6.3	15.9	7.5	26.5
17. α-Naphthyl phenyl ketone	57.5	75	23.2	25.0	5.4	18.7	6.9	20.9
18. α-Acetonaphthone	56.4	66	19.6	19.5	8.7	27.0	7.7	17.4
19. α-Naphthaldehyde	56.3	60	18.3	19.3	5.2	29.2	11.0	16.8
20. Biacetyl	54.9	53	18.8	19.8	4.1	34.6	12.7	10.0
21. 2,3-Pentanedione	54.7	49	14.5	14.6	4.9	38.6	12.4	15.0
22. Benzil	53.7	45	13.5	12.4	3.5	38.5	16.9	15.3
23. Fluorenone	53.3	43	12.7	11.7	4.6	42.5	14.6	14.1
24. 1,2,5,6-Dibenzanthracene[e]	52.3	38	11.9	10.0	2.6	43.3	18.6	13.6
25. Pyrene[e]	48.7	36	12.1	12.4	2.1	45.4	18.4	9.5
26. Benzanthrone[e]	47	35	11.9	11.8	2.2	46.6	18.7	8.7
27. 3-Acetylpyrene	45	51	13.5	15.5	6.4	36.6	12.3	15.7
28. 9,10-Dimethyl-1,2-dibenz-anthracene[e]	44.4	58	17.5	19.0	5.0	30.3	12.1	16.1
29. Anthracene[e]	42.5	87	27.3	29.8	8.2	8.5	4.9	21.4
30. 9,10-Dibromoanthracene[e]	40.2	94	30.8	33.8	7.9	3.6	2.1	21.8

[a] Sensitizer was 0.1 M in neat isoprene unless otherwise stated. [b] **1**, trans-1,2-dimethyl-1,2-divinylcyclobutane; **2**, trans-1-methyl-1-vinyl-2-isopropenylcyclobutane; **3**, trans-1,2-diisopropenylcyclobutane; **4**, 1-methyl-4-isopropenylcyclohexene; **5**, limonene; **6**, and **7**, 1,5- and 1,6-dimethylcyclooctadiene-1,5. [c] In kcal./mole. [d] Sum of percentages of **1**, **2**, **3**, **6**, and **7**. [e] Saturated solution of sensitizer in isoprene.

formed in the sensitized dimerization of cyclic dienes is independent of the nature of the sensitizer.[6,10]

Results with all except the sensitizers having less than 50-kcal./mole excitation energy are reasonably explained on the presumption that energy transfer from sensitizer triplets having higher energies effect excitation of s-cis- and s-trans-diene molecules in accordance with the Franck–Condon principle.

s-trans-diene ⇌ s-cis-diene

trans-triplet   cis-triplet
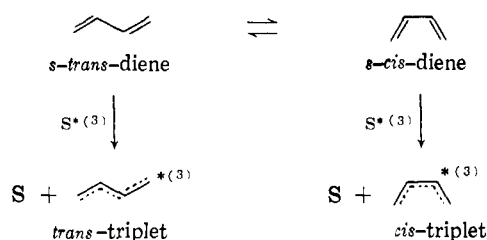
The equilibrium constants for s-cis ⇌ s-trans equilibria in dienes are not precisely known, although it is certain that at room temperature the s-trans forms predominate. The difference in enthalpy content has been estimated at about 2 kcal./mole for butadiene.[11,12] If the entropy contents are similar butadiene should contain more than 95% of the s-trans form at room temperature. The study of isoprene merely indicates that the s-trans form is also the predominant species in that system.[13] High-energy sensitizers should transfer

energy to either isomer at diffusion-controlled rates.[8,14,15] This is consistent with the constancy of results obtained with such sensitizers. Under these conditions most diene triplets should be formed with the trans configuration. The change in results with sensitizers having less than 60 kcal./mole to donate indicates that these species have insufficient energy to promote trans dienes by Franck–Condon processes. Excitation of cis forms must require less energy, so sensitizers having 50–60 kcal./mole seek them out with consequent preferential formation of cis triplets. Spectroscopic data are consistent with the theory. Evans[16] reported the long wave length limits for singlet–triplet absorption spectra of butadiene and isoprene at 20,830 (59.6 kcal.) and 21,000 cm.$^{-1}$ (60.0 kcal.), respectively. The transitions are almost certainly due to the predominant trans forms. He also reported the corresponding limit for 1,3-cyclohexadiene, a model cis diene, at 18,700 cm.$^{-1}$ (53.5 kcal.). Kellogg[17] has redetermined the value as 18,350 cm.$^{-1}$ (52.5 kcal.). The spectroscopic limits are remarkably close to the turning points in Figures 1 and 2.

There should be a large barrier to rotation about the central bonds in the lowest excited states of conjugated dienes since excitation promotes an electron from an

(10) D. H. Valentine and G. S. Hammond, J. Am. Chem. Soc., **86**, 5202 (1964).

(11) E. B. Reznikova, V. I. Tyulin, and V. M. Tatevsky, Opt. Spectry. (USSR) (Engl. Transl.), **13**, 201 (1962).

(12) J. G. Aston and G. Szasc, J. Chem. Phys., **14**, 67 (1946).

(13) M. I. Batuev, A. S. Onishchenko, A. D. Matveeva, and N. I. Aronova, Proc. Acad. Sci. USSR, **132**, 543 (1960).

(14) K. Sandros and H. L. J. Bäckström, Acta Chem Scand., **16**, 958 (1962).

(15) G. Porter and F. Wilkinson, Proc. Roy. Soc. (London), **A264**, 1 (1961).

(16) D. F. Evans, J. Chem. Soc., 1735 (1960).

(17) R. E. Kellogg, private communication.

orbital that is antibonding to one that is bonding in that region.[18] The rate of interconversion of *cis* and *trans* triplets should be enormously slow in comparison with triplet decay times. Consequently, the stereoisomeric triplets should each undergo characteristic chemical reactions. Our results indicate that *trans* triplets give mostly cyclobutanes and cyclooctadienes whereas *cis* triplets give relatively large amounts of cyclohexenes. Consideration of the stereochemistry of biradicals expected from addition of *cis* and *trans* triplets to *cis* and *trans* diene molecules shows that the results are entirely reasonable.[19]

With sensitizers having very low triplet excitation energies, a striking reversal in behavior is found. Products believed to be characteristic of *trans* triplets again become predominant with both dienes. Figure 3 summarizes the known relationships among the spectroscopic states of butadiene.

It is evident that no "crossover" transition, such as *trans* ground state to *cis* triplet, has a lower energy requirement than the spectroscopic $cis \rightarrow cis^{*(3)}$ transition. Since low-energy sensitizers effect excitation of the dienes, we are apparently observing another case of "nonvertical" excitation[8,20] of energy acceptors. If this is correct, low-energy sensitizers must produce directly nonplanar diene triplets from one or both of the stereoisomeric ground-state molecules. The data indicate strongly that such relaxed triplets have rigid stereochemistry in the centers of the molecules, so nonplanar distortions must be introduced at the ends. Whether or not twist is introduced at both ends or only at one is a matter of speculation at the moment. If distortion occurs at one end only, the triplet would consist of two nonconjugated parts, an allylic unit, and a localized radical center.
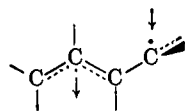
Similar relaxation of spectroscopic, *cis* triplets should occur, and the data imply that about the same proportions of *cis* and *trans* triplets are formed with high energy sensitizers and those having *very low* excitation energies. Our results convey a couple of additional intriguing implications. Apparently the *cis* triplet is the more stable of the two spectroscopic states of both dienes since the apparent differences in transition energies are larger than the estimated differences in the ground-state energies. However, when nonvertical excitation becomes necessary, *trans* triplets are again formed preferentially. This may merely reflect again the fact that the triplets are formed predominantly by excitation of the more abundant *trans* ground-state molecules. However, it is also interesting to speculate that preferential stabilization of the *cis* triplet may disappear after nonplanar distortions occur. This view would be consistent with the prediction of simple molecular orbital theory that there should be some bonding interaction between carbon atoms 1 and 4 in the lowest (planar) excited states.

(18) See, for example, J. D. Roberts, "Notes on Molecular Orbital Calculations," W. A. Benjamin, Inc., New York N. Y., 1961, p. 51.
(19) G. S. Hammond and N. J. Turro, Jr., *Science*, 142, 1541 (1963).
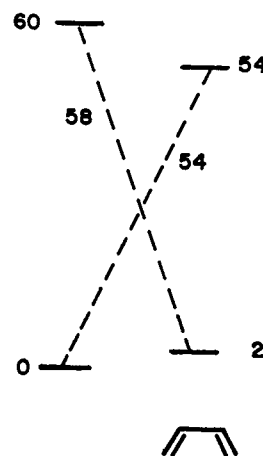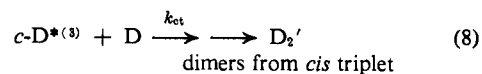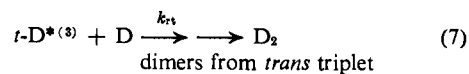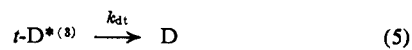(20) G. S. Hammond, P. Wyatt, C. D. DeBoer, and N. J. Turro, Jr., *J. Am. Chem. Soc.*, 86, 2532 (1964).
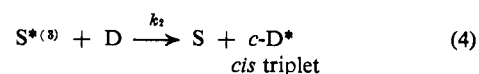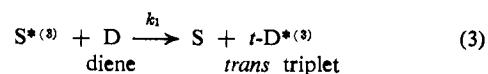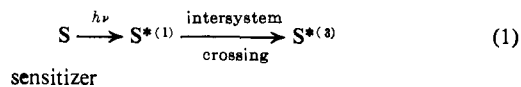
Figure 3. Energy relationships among spectroscopic states of butadiene.

Quantum Yields in the Dimerization of Isoprene. The following abbreviated mechanism is adequate for treatment of the data for quantum yields in the dimerization of isoprene.

$$S \xrightarrow{h\nu} S^{*(1)} \xrightarrow[\text{crossing}]{\text{intersystem}} S^{*(3)} \tag{1}$$
sensitizer

$$S^{*(3)} \xrightarrow{k_{ds}} S \tag{2}$$

$$S^{*(3)} + D \xrightarrow{k_1} S + t\text{-}D^{*(3)} \tag{3}$$
$\qquad\qquad$ diene $\qquad\qquad$ *trans* triplet

$$S^{*(3)} + D \xrightarrow{k_2} S + c\text{-}D^* \tag{4}$$
$\qquad\qquad\qquad\qquad$ *cis* triplet

$$t\text{-}D^{*(3)} \xrightarrow{k_{dt}} D \tag{5}$$

$$c\text{-}D^{*(3)} \xrightarrow{k_{dc}} D \tag{6}$$

$$t\text{-}D^{*(3)} + D \xrightarrow{k_{rt}} \longrightarrow D_2 \tag{7}$$
$\qquad\qquad\qquad$ dimers from *trans* triplet

$$c\text{-}D^{*(3)} + D \xrightarrow{k_{ct}} \longrightarrow D_2' \tag{8}$$
$\qquad\qquad\qquad$ dimers from *cis* triplet

The rate constants k_1 and k_2 are actually complex since they are sums of the rate constants for energy transfer with nonvertical excitation as well as vertical excitation. Moreover, as formulated, k_1 and k_2 will not be equal even for high-energy sensitizers that transfer energy at every collision since no account is taken of the difference in the numbers of *cis* and *trans* ground-state molecules. The quantum yields for the two sets of dimeric products may be expressed as follows

$$\frac{1}{\Phi_{D_2}} = \frac{1}{a\alpha\beta} + \frac{k_{dt}}{a\alpha\beta k_{rt}[D]} \tag{9}$$

$$\frac{1}{\Phi_{D_2'}} = \frac{1}{a\beta(1-\alpha)} + \frac{k_{dc}}{a\beta(1-\alpha)k_{rc}[D]} \tag{10}$$

where a = the fraction of sensitizer molecules undergoing intersystem crossing, α = the fraction of energy transfers that give *trans* triplets = $k_1/(k_1 + k_2)$, and β = the fraction of sensitizer triplets that transfer excitation to diene molecules = $(k_1 + k_2)[D]/\{k_d + (k_1 + k_2)[D]\}$.
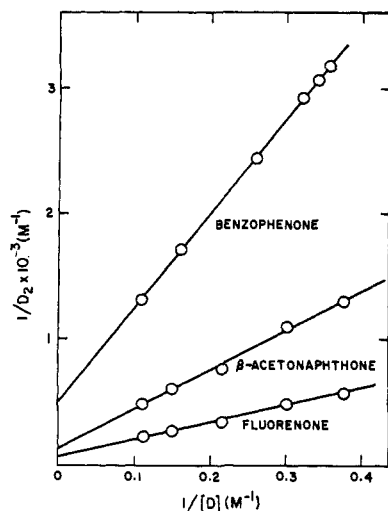
Figure 4. Yield of dimers (D_2) with varying concentrations of isoprene.

The values of a for many sensitizers have been accurately measured independently,[21] and for many high-energy sensitizers β becomes equal to unity at concentrations of diene far below those involved in studies of quantum yields. Furthermore, the mechanism suggests that with high-energy sensitizers α should be greater than 0.95. For these sensitizers the function $1/(\Phi_{D_2} + \Phi_{D_2'})$ should approximate a linear function of $1/[D]$ with a slope equal to $k_{dt}/a\alpha k_{rt}$. As a matter of convenience, the yield of dimers was measured with solutions containing sensitizers and varying concentrations of isoprene. All solutions in a set were irradiated for equal time intervals under conditions ensuring equivalent irradiation. Equation 9 can be transformed to eq. 11 to treat yield data directly

$$\frac{1}{\text{yield of } D_2} = \frac{1}{a\alpha\beta It} + \frac{k_{dt}}{a\alpha\beta It k_{rt}[D]} \qquad (11)$$

where I = intensity of light absorbed and t = time of irradiation. An analogous equation can be written for the yields of D_2'. If a, α, and β are known, the intercept of a plot of 1/yield against $1/[D]$ can be used to obtain the value of I, and conventional quantum yields can be calculated. The method avoids direct dependence on conventional actinometry with consequent improvement of the precision of the work. Improvement stems from the fact that the incident light was only filtered through Pyrex glass; consequently, conventional actinometry would require approximate double integration of the light from the arc and the absorption spectra of the sensitizers over a wide range of wave lengths.[22] Direct comparison of the light intensities estimated by this method and by independent actinometry was made with benzophenone and the agreement was good (2.02 × 10⁻³ einstein estimated from eq. 11 and 2.39 × 10⁻³ einstein calculated from actinometric measurements).

Figure 4 shows plots of the yields of dimers against $1/[D]$ for three sensitizers, benzophenone, β-aceto-

(21) A. A. Lamola, unpublished studies.
(22) Reference to other standards is implicit in the use of values of a determined in experiments with narrow bands produced by suitable filter systems.[20]

naphthone, and fluorenone. As anticipated, the fit to linearity is excellent with benzophenone, a high-energy sensitizer. One might have anticipated that the slopes of the lines would be quite different with the other two sensitizers since they give markedly different product distributions (cf. Figure 2), indicating involvement of both cis and trans triplets in the reactions. Furthermore, the values of the ratios of the slopes to the intercepts are similar (benzophenone-β-acetonaphthone-fluorenone, 16:26:22 mole/l.).[23] Apparently all the data can be fitted to an equation of the form of (11). This is only consistent with the general picture if k_{dt}/k_{rt} and k_{dc}/k_{rc} have very close to the same values. The variations observed probably are within the cumulative experimental errors in the present measurements. In addition to establishing the similarity in the dynamic behavior of the two triplets, the data eliminate a number of conceivable reaction mechanisms such as those involving formation of products by reaction of triplets with triplets.

The quantum yields in 10 M isoprene are as shown in Table III.

Table III

Sensitizer	Φ	a^a
Benzophenone	0.40	1.00
β-Acetonaphthone	0.25	0.85
Fluorenone	0.29	0.92

ᵃ See ref. 20.

Quenching by Azulene. The absorption spectrum of azulene has a virtual "window" in the interval 3550–4200 Å. ($\epsilon < 50$). Using fairly high concentrations of sensitizers and a filter system designed to isolate the group of lines near 3660 Å., it is possible to do experiments with added azulene in which virtually all of the light is absorbed by the sensitizer. Quantum-yield measurements were carried out with such solutions to see whether isoprene triplets can be quenched by azulene. Using benzophenone as the sensitizer, two series of experiments were carried out, one in which the isoprene concentration was varied and another in which the azulene concentration was changed. Reciprocal plots of the data are shown in Figures 5 and 6. The data apparently fit eq. 12 in which no distinction is made between cis and trans triplets.

$$\frac{1}{\Phi_{D_2} + \Phi_{D_2'}} = \frac{1}{a\beta}\left(1 + \frac{k_d}{k_r[D]} + \frac{k_q[Q]}{k_r[D]}\right) \qquad (12)$$

$$k_d/k_r \cong k_{dt}/k_{rt} \cong k_{dc}/k_{rc}$$

Since the experiments were carried out with relatively high concentrations of isoprene (β = unity), the value of k_q/k_r can be estimated from the slopes of the plots. Values of 7.4 × 10² and 1.2 × 10³ are obtained from the data of Figures 5 and 6, respectively, with the latter figure undoubtedly being the more accurate of the two.

The fact that the data of Figure 5 approximate a straight line is an indication that k_q/k_r is about the same for cis and trans triplets. However, the test is

(23) Note that the largest value is obtained with β-acetonaphthone which has an excitation energy intermediate between those of the other two sensitizers.
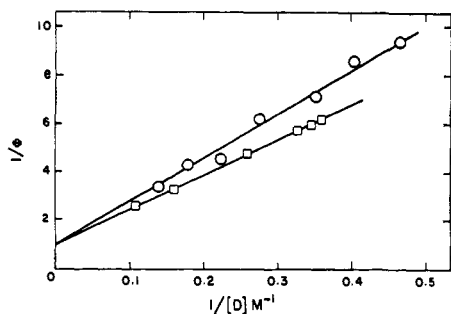
Figure 5. Quantum yield (Φ) of dimerization by varying concentrations of isoprene (D): O, run with 5×10^{-3} M azulene; □, run without quencher.

Figure 6. Quantum yield of dimerization by varying concentrations of azulene.

not very significant since benzophenone produces mostly *trans* triplets and so in any case the measured slopes should approximate k_{qt}/k_{rt}. A more sensitive test is found in the variation of the dimer composition in the presence of azulene. The data in Table IV show that, with both benzophenone and biacetyl as sensitizers, addition of azulene decreases the relative yields of cyclohexene derivatives.[24] The quenching effect must be more important with the *cis* triplet than with its *trans* isomer. The effect is most easily accounted for by the assumption that k_{qc} is significantly larger than k_{qt} although it is possible that there is considerable variation in all of the rate constants, with the equality of the k_d/k_r ratios being fortuitous.

Table IV. Effect of Azulene on Dimer Composition

Sensitizer	Azulene concentration, M	Cyclohexene derivatives in products, %
Benzophenone	0	7.4 ± 0.4
Benzophenone	5×10^{-3}	4.4 ± 0.7
Biacetyl	0	51.3 ± 1.6
Biacetyl	5×10^{-3}	45.5 ± 1.0

That diene triplets can be quenched by azulene at all is a matter of considerable significance. First of all, quenching was significant in experiments in which the azulene concentration was only 1.1×10^{-3} M. Obviously, the diene triplets must live at least 5×10^{-6} sec.[25] and probably survive much longer. The guess that lifetimes are longer than the lower limit derives from the fact that quenching by energy transfer *must*

$$D^{*(3)} + Az \longrightarrow D + Az^{*(3)}$$
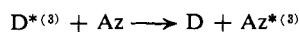
involve nonvertical deexcitation of the diene triplets. The presumption that diene triplets relax to nonplanar forms was necessary to explain the behavior of low-energy sensitizers (Figures 1 and 2) and is also strongly suggested by theory.[26] Such an assumption is necessary to account for the fact that triplets can be quenched by azulene, which has an excitation energy between 31 and 38 kcal./mole,[27,28] but not by the ground states

(24) Quantum yields of individual products were not measured explicitly. In order to maximize the precision of measurement of the total quantum yields, v.p.c. analysis was carried out using a Carbowax column that does not separate the dimers completely. Product distributions were measured using Apiezon J.
(25) This estimate would be predicated upon diffusion-controlled quenching with a rate constant of about 6×10^9 l./mole sec.
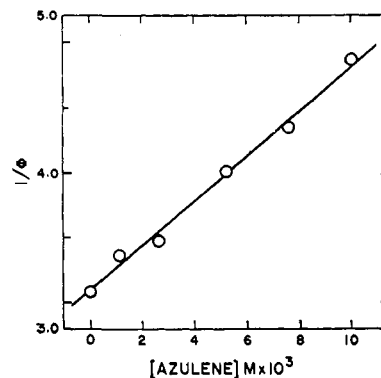(26) Private communication from Dr. Roald Hoffman of Harvard University.

of sensitizers used in this study (*vide infra*). Energy transfer with nonvertical deactivation of a triplet is no more surprising than the reverse process, nonvertical excitation,[8] but this is the first experimental evidence to demand it.

Variation of the Concentrations of Sensitizers. Quenching by azulene led to speculation that low-energy sensitizers might undergo reversible energy transfer with dienes.[13] A series of experiments were done in which the concentrations of sensitizers (β-acetonaphthone, biacetyl, fluorenone, pyrene, benzanthrone, and 9,10-dibromoanthracene) were varied. In no case was there any significant change in the composition of mixtures of dimers. Since azulene does have a quenching effect, the failure to undergo reversible energy exchange with sensitizers cannot be attributed to very high rates of decay of diene triplets. The result is a further indication that diene triplets at thermal equilibrium with their surroundings have lower excitation energies and different geometric configurations than the spectroscopic triplets.

Solvent Viscosity. Solutions of isoprene (2 M) and benzophenone in hexadecane ($\eta = 3.34$ cp.) were irradiated with and without azulene (5×10^{-3} M). Quantum yields for dimerization were 0.121 and 0.098, respectively. Corresponding values with isopentane ($\eta = 0.223$ cp.) as the solvent are 0.122 and 0.101 (extrapolation of Figure 3). Since a large increase in viscosity of the medium has no significant effect on the quantum yields, neither the addition of triplets to diene molecules nor quenching by azulene can be diffusion controlled.

The Addition–Elimination Mechanism. Professor G. O. Schenck[29] has been the principal proponent of a generalized mechanism for sensitized photoreactions that involves bonding of the sensitizer and substrate rather than physical excitation transfer. Application of the mechanism to dimerization of dienes gives the following scheme

$$S \xrightarrow{h\nu} S^* \xrightarrow{D} \cdot S\text{-}D\cdot \xrightarrow{D} \cdot S\text{-}D\text{-}D\cdot \longrightarrow S + D_2$$
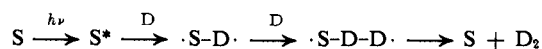
Our principal reasons for favoring the energy transfer mechanism presented earlier in the paper are the following.

(27) R. Pariser, *J. Chem. Phys.*, 25, 1112 (1956).
(28) A. A. Lamola, W. G. Herkstroeter, J. C. Dalton, and G. S. Hammond, *ibid.*, in press.
(29) G. O. Schenck and R. Steinmetz, *Bull. soc. chim. Belges*, 71, 781 (1962).

1. The rates of the addition and elimination would have to be more rapid than is expected by comparison with seemingly analogous steps in vinyl polymerization.

2. The response to changes in the structure of the sensitizers requires postulation of only two kinds of intermediates. The Schenck mechanism would require a different intermediate from each sensitizer.

3. The apparent relationship between the efficiencies of activation and the excitation energies of sensitizers and substrates would appear to be semifortuitous if the reaction involved addition and elimination.

Flash spectroscopic studies[30] indicate that conjugated dienes quench high-energy sensitizers with rates that are at, or close to, the diffusion-controlled limits. Some such postulate also seems necessary to account for the constancy of results obtained in our studies with high-energy sensitizers. Addition of free radicals to vinyl monomers including butadiene and isoprene are six to eight orders of magnitude smaller than this limit.[31] Furthermore, we know of no precedent that would lead to the expectation that fragmentation of the species $\cdot$S–D–D$\cdot$ would compete with high efficiency with cyclization[32] and subsequent addition reactions.

The addition–elimination mechanism could be used to explain the results with different sensitizers on a basis similar to that discussed above. The allylic units in the biradicals $\cdot$S–D$\cdot$ should exist in two stereochemical modifications. The mechanism would require an *ad hoc* correlation between the rates of addition of S* to diene molecules and the triplet excitation energies of the reactants. We should also expect that factors such as the steric requirements of various sensitizers would exert some control over the subsequent reactions of $\cdot$S–D$\cdot$ and $\cdot$S–D–D$\cdot$

The arguments presented are not as compelling when applied to the relatively inefficient reactions caused by sensitizers having excitation energies below 50 kcal./mole. A change from excitation transfer to the Schenck mechanism is a conceivable alternate to our preferred explanation of these reactions. Further work with such systems is in progress.

Experimental

Isolation and characterization of the photodimers has been reported elsewhere.[6]

Butadiene (Matheson Coleman and Bell, instrument grade) was used without further purification. *Isoprene* (Phillips, pure grade) was distilled before use, b.p. 33.0°. *Isopentane* (Phillips, pure grade) was used without further purification.

Commercially available samples of *sensitizers* were in most instances purified by distillation, recrystallization, or chromatography. *Anthracene* (Matheson Cole-

man and Bell, reagent grade), *9,10-dimethylbenzanthracene* (Eastman Kodak), and *flavone* (Aldrich, research grade) were used as supplied.

Product Distribution. The following general procedure was used. Solutions of sensitizers (0.1 M) in liquid diene (with appropriate solvent in the case of butadiene) were introduced into previously constricted Pyrex tubes (13 $\times$ 100 mm.) and sealed *in vacuo* after degassing by at least two freeze–pump–thaw cycles. The sealed samples were irradiated in parallel in an apparatus known as a "merry-go-round." In this apparatus the samples are held in slots in a turntable that is placed in a constant temperature (27–29°) water bath. A 450-w. medium pressure Hanovia lamp is situated at the center of the turntable. Conversions were carried to 5–10% and without preliminary separation the samples were analyzed by vapor phase chromatography. Carbowax 20M (butadiene dimers) or Apiezon J (isoprene dimers) column was used.

Quantum Yields. Stock solutions containing 1.00 M sensitizer in benzene were prepared and mixed with varying amounts of isoprene. The resulting solutions were then diluted with isopentane. The concentration of sensitizer was 0.1 M in all experiments in the series. The samples were degassed and irradiated in parallel in the merry-go-round (*vide supra*). The samples were analyzed by vapor chromatography using a Carbowax column (6 ft., 15% liquid phase, 70°). The benzene served as an internal standard. Although the dimers are not entirely separated from each other on Carbowax, precision of measurement of the total yields is better than in analyses with Apiezon columns because the peaks are more compressed and closer to that of the standard. Calibration experiments showed that the integrated area of the dimer peaks and the area of the benzene peak did not stand in the same ratio as the actual concentrations. It was found that reproducible results were obtained if the benzene peak area was multiplied by the factor 1.41. In the run with benzophenone as a sensitizer, tubes containing benzophenone and benzhydrol in benzene were irradiated in parallel with the isoprene samples. Samples were analyzed as described previously,[33] thus providing independent actinometry. In runs with added azulene, samples were prepared in the same manner as described above except that some of the isopentane was replaced with an appropriate volume of a stock solution of azulene in benzene. For this part, a combination of filters (Corning 0-52 and 7-37) was used which allowed transmission of light of wave length centered at 3650 Å. with the width of the transmission peak at its half-height being 50 Å.

(30) R. S. H. Liu and A. Fry, unpublished results.
(31) C. Walling, "Free Radicals in Solution," John Wiley and Sons, Inc., New York N. Y., 1957, p. 95.
(32) B. H. Zimm and J. K. Bragg, *J. Polymer Sci.*, 9, 476 (1952).
(33) R. P. Foss and G. S. Hammond, *J. Phys. Chem.*, 68, 3739 (1964).