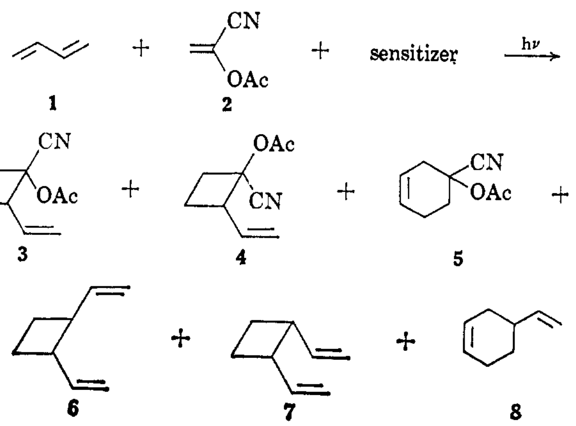

by comparison of their gas chromatographic retention times with those of authentic materials.[7f,11] Also the nmr and infrared spectra of samples isolated by preparative gas chromatography were compared with the spectra of authentic materials.[13]

The product distributions for various sensitizers are reported in the accompanying communication.[10] For the present discussion, let it suffice to say that the cyclohexene **5** constituted 2–31% of the total cross-adducts **3–5**, while the thermal reaction of **1** and **2** at 125–190° gave 77–91% **5**. We interpret the fact that the cyclohexene **5** is formed at all in the sensitized cross-addition to indicate that the cyclohexene can arise *via* a two-step reaction.[11,14]

Experiments on the unsensitized (direct irradiation through quartz[15]) photoreaction of **1** and **2** indicated that of the cross-addition processes only 1,2 addition occurred, probably *via* the excited singlet state of the diene **1**.[16]

Acknowledgment. The authors wish to thank Mr. K. C. Whitman and Mr. F. L. Beman and co-workers for experimental assistance.

employed in this study. The conversions were kept low to avoid complications due to possible further reactions of the products. Another side reaction was observed when camphorquinone was used as the sensitizer. This sensitizer undergoes a photoreaction with butadiene to give a product which we have tentatively identified as a vinyloxetane (possibly several isomers) arising from the addition of one carbonyl group of triplet camphorquinone to one butadiene double bond. We have measured the (**3** + **4**):**5** ratio at different stages of conversion and find no significant change.[10]

(13) The *cis*-divinylcyclobutane (**7**) was isolated as the thermal rearrangement product, 1,5-cyclooctadiene.[7f]

(14) See R. Hoffmann and R. B. Woodward, *J. Am. Chem. Soc.*, **87**, 2046 (1965).

(15) Reference 2c, p 748.

(16) For the results of the unsensitized irradiation of butadiene alone see (a) R. Srinivasan and F. I. Sonntag, *J. Am. Chem. Soc.*, **87**, 3778 (1965); (b) I. Haller and R. Srinivasan, *J. Chem. Phys.*, **40**, 1992 (1964); (c) P. A. Leermakers and G. F. Vesley, *J. Chem. Educ.*, **41**, 535 (1964); (d) ref 2b, p 216.

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Organic Photochemistry. III. 1,2 *vs.* 1,4 Addition as a Function of Sensitizer Triplet Energy in a Cross-Addition Reaction[1]

Sir:

In the preceding communication[1] we described the photosensitized cycloaddition of the diene **1** to the olefin **2**.[2] In this communication we report the effect of the sensitizer triplet energy on the product distribution.

The product distribution between the 1,2-divinylcyclobutanes and the 4-vinylcyclohexenes in the photosensitized dimerization of butadiene or isoprene has been shown to be dependent on the triplet energy of the sensitizer.[3] This dependence was attributed to the difference in the energy levels of the *cis*- and *trans*-diene triplets,[4] the *trans* forms giving mostly cyclobutanes and the *cis* forms giving relatively large amounts of cyclohexenes.

The product distributions for the cross-addition of **1** and **2** with various sensitizers are given in Table I. The relative amount of cyclobutanes **3** and **4** in the total cross-adducts **3–5** as a function of the sensitizer triplet energy is shown in Figure 1 along with the curve obtained by Hammond and co-workers[3c] for the dimerization of butadiene (**1**).

In general, our results on the cross-addition parallel quite closely those for the dimerization except for the depth of the minimum in the amount of cyclobutanes in the 50-kcal/mole region. The breaking point at *ca.* 60 kcal/mole can be explained, as in the case of dimerization,[3c] by the *s-trans*- and *s-cis*-butadienes having their lowest triplet energy levels at 59.6 kcal/mole[3c,5] and *ca.* 53 kcal/mole,[3b,c] respectively.[6] The increase in the relative amount of cyclobutanes with sensitizers having triplet energies lower than 50 kcal/mole could be due to "nonvertical" excitation, as has been proposed for the butadiene and isoprene dimerizations.[3c]

We attribute the difference in the relative amounts of cyclobutanes formed in the cross-addition and the dimerization in the 50-kcal/mole region of Figure 1 to a difference in selectivity of ring closure of the *s-cis*-**1**–**2** triplet adduct, a, and the *s-cis*-**1**–**1** adduct, b (Scheme I). If the reasonable assumptions are made that the same relative amounts of *cis* and *trans* triplets are produced for any one sensitizer whether the olefin **2** is present or not, and that the reactivity of the two isomeric triplets with **2** (and with **1**) are the same, then the difference in product distribution must reflect the difference in selectivity of ring closure of intermediates a and b. Thus the cross-intermediate, a, closed to a four-membered ring, **3** or **4**, to a greater extent than did the dimer intermediate, b. It has been shown from experiments on the termination reaction of free radical copolymerizations that cross-termination between unlike radicals is favored over termination between like radicals, often to a rather large extent.[7] Thus the coupling of unlike radicals such as the ring closure of a (with electron spins paired) is probably faster and therefore less selective than the coupling of like radicals as in b (with spins paired). Since the intermediates a and b can exist in a

(1) Part II: W. L. Dilling and J. C. Little, *J. Am. Chem. Soc.*, **89**, 2741 (1967).

(2) The numbering system in ref 1 is retained in this paper.

(3) (a) G. S. Hammond, N. J. Turro, and A. Fischer, *J. Am. Chem. Soc.*, **83**, 4674 (1961); (b) G. S. Hammond and R. S. H. Liu, *ibid.*, **85**, 477 (1963); (c) R. S. H. Liu, N. J. Turro, Jr., and G. S. Hammond, *ibid.*, **87**, 3406 (1965).

(4) For a theoretical explanation for this energy difference see (a) R. Hoffmann and R. A. Olofson, *ibid.*, **88**, 943 (1966); (b) ref 3c.

(5) (a) R. E. Kellogg and W. T. Simpson, *J. Am. Chem. Soc.*, **87**, 4230 (1965); (b) D. F. Evans, *J. Chem. Soc.*, 1735 (1960).

(6) These explanations are based on the assumption that the reaction proceeded *via* the butadiene triplets rather than the α-acetoxyacrylonitrile triplet.

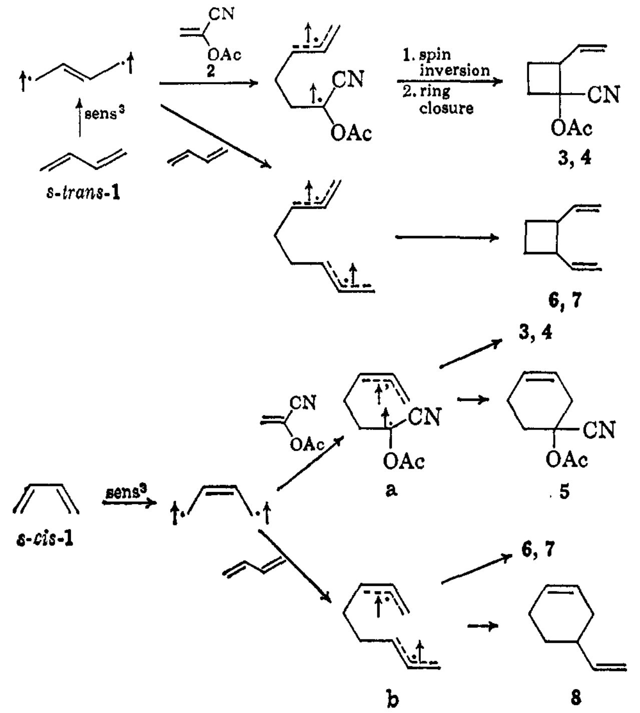
(7) C. Walling, "Free Radicals in Solution," John Wiley and Sons, Inc., New York, N. Y., 1957, p 146.

Table I. Composition of Products from Photosensitized Cross-Addition of Butadiene and α-Acetoxyacrylonitrile

Expt	Sensitizer[a]	E_T[b]	Distribution of cross-adducts and dimers, %[c]				
			3 + 4[d]	5	6	7	8
1	Acetophenone	73.6	34	0.7	56	7	2
2	Benzophenone	68.5	33	0.9	54	10	3
3	Triphenylene[e]	66.6	30	0.9	69	...[f]	...[g]
4	Anthraquinone[e]	62.4	60	3	31	6	...[g]
5	Flavone	62.0	32	1.6	52	12	3
6	β-Naphthyl phenyl ketone	59.6	41	7	47	4	2
7	Biacetyl	54.9	38	12	28	7	14
8	Benzil	53.7	34	12	30	5	18
9	Camphorquinone	50	28	12	23	7	29
10	Pyrene[e]	48.7	38	17	34	11	...[g]
11	Anthracene[e]	42.5	41	6	45	8	...[g]
12	9,10-Dibromoanthracene[e]	40.2	45	1	44	10	...[g]

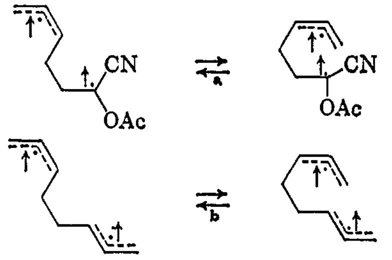
[a] Sensitizer (1.0 mmole) in 5.0 mmoles of 1 and 5.0 mmoles of 2. [b] Lowest triplet energy level in kilocalories per mole: W. G. Herkstroeter, A. A. Lamola, and G. S. Hammond, *J. Am. Chem. Soc.*, **86**, 4537 (1964). See also ref 3c. [c] Determined by gas chromatography with each component corrected for thermal conductivity variation in detector. [d] The *cis* and *trans* isomers were not separated. The nmr spectrum of the product isolated from the benzophenone-sensitized reaction showed two acetyl methyl groups at −2.05 and −2.07 ppm from internal TMS of approximately equal intensity. [e] Saturated solution of sensitizer in equimolar mixture of 1 and 2. [f] Not determined due to low over-all conversion. [g] Not determined due to interference by a large excess of 2 and the presence of a small amount of 8 in the starting diene 1.

Scheme I



large number of conformations ranging from cyclic to extended (Scheme II), at the moment of spin inversion

Scheme II



the diradicals may be at least partially in the extended conformation. If the ring closure of a is more rapid than b, then a larger proportion of the cyclobutanes 3 and 4 would be expected. By virtue of its selectivity, b has a greater chance to reach a conformation which will lead to the more stable product, namely the cyclohexene 8.[8]

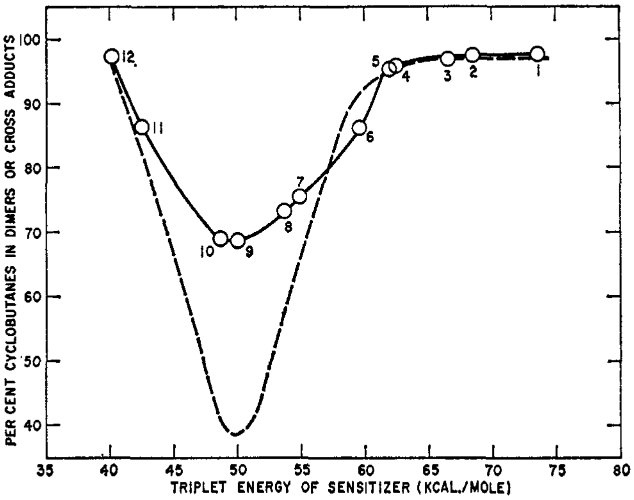


Figure 1. Butadiene-α-acetoxyacrylonitrile cross-adduct composition *vs.* triplet energy of sensitizer (solid line); butadiene dimer composition (dashed line, data of Hammond, *et al.*[3c]).

Acknowledgment. The author wishes to thank Dr. J. C. Little, Dr. T. Alfrey, Jr., and Dr. V. R. Sandel for many helpful discussions during this work, and Mr. K. C. Whitman for experimental assistance.

(8) "Steric Effects in Organic Chemistry," M. S. Newman, Ed., John Wiley and Sons, Inc., New York, N. Y., 1956: (a) W. G. Dauben and K. S. Pitzer, p 38; (b) F. H. Westheimer, p 533.

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A New Peptide Coupling Reagent

Sir:

In recent years the potential utility of activated esters as coupling agents in peptide synthesis has been extended, first by the development of the isoxazolium salts and their derivatives[1] which generate enolic or

(1) (a) R. B. Woodward, R. A. Olofson, and H. Mayer, *J. Am. Chem.*