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ORGANIC PHOTOCHEMISTRY. IV. THE PHOTOSENSITIZED AND THERMAL CYCLOADDITION REACTIONS OF ISOPRENE AND α-ACETOXYACRYLONITRILE (1)

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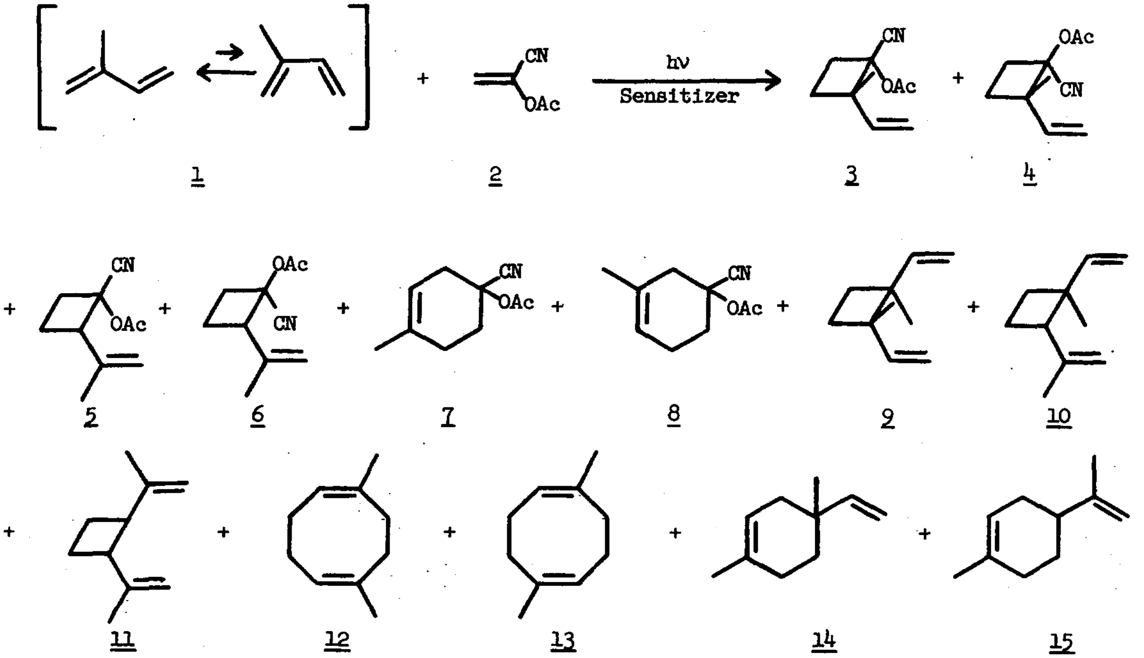
We would like to report the results of a comparative study of the photosensitized and thermal cycloaddition reactions of isoprene 1 and α-acetoxyacrylonitrile 2. The thermal reaction represents another example of the few known competitive 2 + 2 and 2 + 4 cycloadditions (2). Further evidence is presented concerning the mechanism of the photosensitized cycloaddition of conjugated dienes to negatively substituted olefins. Evidence relating to the *s-cis* - *s-trans* conformational equilibrium of isoprene was also obtained.

Irradiation (3) of an equimolar mixture of the two olefins 1 and 2 with 0.2 mole of either acetophenone or benzil as a triplet sensitizer gave six cross-adducts 3-8 in addition to the same seven diene dimers 9-15 reported by Hammond and co-workers (4-6). The products were sepa-



rated by preparative g.c. and identified by their n.m.r., infrared, and mass spectra (8).

The product distributions for the two sensitizers are given in Table I.

Table I. Product Distributions from Photosensitized Addition of Isoprene to α-Acetoxyacrylonitrile

		Distribution, %									
Sensitizer	E_T[a]	3	4	5+6[b]	7+8[b]	9	10	11	12+13[b]	14	15
PhCOMe	73.6	8.1	8.4	10.7	1.5	19.9	22.0	6.4	20.6	2.1	0.5
$(\mathrm{PhCO})_2$	53.7	7.6	5.6	10.0	16.8[c]	7.2	7.2	1.8	12.6	22.8	8.4

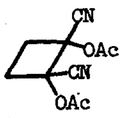
[a] Lowest triplet energy level in kilocalories per mole: W. G. Herkstroeter, A. A. Lamola, and G. S. Hammond, *J. Am. Chem. Soc.*, **86**, 4537 (1964). [b] The two isomers were not separated. The presence of both isomers was established by n.m.r. [c] The ratio of 7:8 was *ca.* 2:1.

The thermal (Diels-Alder) reaction of equimolar amounts of the olefins 1 and 2 at 150° without solvent gave all six cross-adducts (84% yield) in the following proportions: 7 (9), 63%; 8 (9), 32%; 3, 2.1%; 4, 1.7%; 5+6, 1.2% (11). The cross-adducts 3-8 were the same in both the photosensitized and thermal reactions, but the distribution of these adducts was very different.

The photoreaction is believed to proceed primarily via energy transfer from the sensitizer to the diene (see below) (1a), and therefore the cross-adduct distributions are the result of a two-step addition of the *s-cis* and *s-trans* diene triplets (4a,c) to the nitrile 2 in the ground state. The relatively large amount of cyclobutyl derivatives is a result of the predominance of *s-trans* isoprene in the ground state (see below).

The thermal cycloaddition occurs in the ground state, and thus the cyclobutane-forming portion of the reaction must be non-concerted (12). The cyclohexene-forming reaction could be either two step (13) or concerted (14) and must involve the *s-cis* conformation of the diene. It is not clear which isoprene conformer is the precursor of the cyclobutyl cross-adducts. The proportion of the latter (5%) was less than that reported for the analogous reaction of butadiene and the olefin 2 (9-23%) (13). A lower amount of *s-trans* isoprene in equilibrium with the *s-cis* form, compared with butadiene, could be one reason for the lower amount of cyclobutanes obtained from isoprene.

Prolonged irradiation of the cyanoolefin 2 with acetophenone gave small quantities of two isomeric dimers 16 and 17 in approximately equal amounts (7). Gas chromatographic examination



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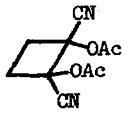

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of the crude photoproduct mixtures from isoprene and the olefin **2** showed that these dimers could not have been formed in amounts exceeding 1% of the total cross-adducts **3**-**8**. Therefore we feel that the mechanism previously proposed (1a) for the cross-addition involving the addition of the triplet diene to the ground state olefin **2** is probably correct; if the cross-addition reaction were proceeding via the attack of triplet olefin **2** on ground state diene we would expect larger amounts of dimers **16** and **17** to be formed and no diene dimers **9**-**15**.

A comparison of the cyclobutane + cyclooctadiene (15):cyclohexene ratios for the photosensitized cross-addition and dimerization of both butadiene and isoprene with the cyanoolefin **2** is presented in Table II. The increased amount of cyclohexene derivatives with benzil sensitization for the isoprene cross-adducts is in agreement with the other three cases, and probably is due to the same phenomenon, namely selective energy transfer to the *s-cis* isoprene conformer which has a lower triplet energy than the *s-trans* conformer (1a,4a,c,6).

Table II. Comparison of Product Distributions from Butadiene and Isoprene with α-Acetoxyacrylonitrile

		Distribution, %	
Products	Sensitizer	Cyclobutanes + Cyclooctadienes	Cyclohexenes
Butadiene Cross-Adducts[a]	PhCOMe	98	2
	$(PhCO)_2$	73	27
Butadiene Dimers[b]	PhCOMe	97	3
	$(PhCO)_2$	55	45
Isoprene Cross-Adducts	PhCOMe	95	5
	$(PhCO)_2$	58	42
Isoprene Dimers[b,c]	PhCOMe	92	8
	$(PhCO)_2$	45	55

[a] Data from ref. 1a. [b] Data from ref. 4c. [c] Our data for the dimerization of **1** were in reasonably good agreement with those reported in ref. 4c.

We recently proposed that the different cyclobutane:cyclohexene ratios obtained from the photosensitized (using sensitizers with E_T 50-60 kcal./mole) cycloaddition of butadiene to the cyanoolefin **2** and to itself (Table II) were due to the ring closure rate of the cross-adduct diradical being faster than that of the dimer diradical (1a). The distributions for the benzil sensitized isoprene reactions (58% cyclobutanes for cross-addition, 45% cyclobutanes for dimerization, Table II) are consistent with this proposal.

The larger amounts of cyclohexene derivatives for all of the isoprene reactions compared with the analogous butadiene reactions indicate a slightly higher concentration of *s-cis* isoprene in equlibrium with the *s-trans* form than of *s-cis* butadiene in equilibrium with its *s-trans* form (16,17). One can estimate a *s-trans*:*s-cis* ratio of 90-95:5-10 for isoprene at *ca*. 0-30° based on the above product distributions.

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1. (a) Part III: W. L. Dilling, *J. Am. Chem. Soc.*, **89**, 2742 (1967); (b) Presented at the 155th ACS National Meeting, San Francisco, April 1968, Abstracts of Papers, No. P 218.

2. W. C. Herndon and J. Feuer, *J. Org. Chem.*, **33**, 417 (1968) and references cited therein.

3. Irradiations were carried out at 0-5° with a 450 watt Hanovia medium pressure mercury arc lamp using a Pyrex filter.

4. (a) G. S. Hammond and R. S. H. Liu, *J. Am. Chem. Soc.*, **85**, 477 (1963); (b) G. S. Hammond, N. J. Turro, and R. S. H. Liu, *J. Org. Chem.*, **28**, 3297 (1963); (c) R. S. H. Liu, N. J. Turro, Jr., and G. S. Hammond, *J. Am. Chem. Soc.*, **87**, 3406 (1965).

5. Compounds **3**-**15** were the major products when the conversion was kept below *ca*. 30-40%. At higher conversions polymeric material was formed. Several minor products were observed in the reactions involving benzil as the sensitizer; these appeared to be adducts of benzil with the diene **1**. The side reactions had little effect on the cross-adduct and dimer distribution as shown by the constancy of the distributions at different conversions.

6. Acetophenone and benzil were chosen as sensitizers because the former has a triplet energy higher than either isoprene conformer while the latter has a triplet energy higher than that of the *s-cis* isoprene conformer but lower than that of the *s-trans* conformer (4c).

7. Details of the spectra will be discussed in the full paper. The head-to-head nature of the cyclobutane adducts has not been established, but is assumed to be such by analogy with similar reactions (8).

8. (a) W. L. Dilling and J. C. Little, *J. Am. Chem. Soc.*, **89**, 2741 (1967); (b) W. L. Dilling and R. D. Kroening, manuscript in preparation.

9. The position of the methyl group was assigned on the basis of analogous Diels-Alder reactions of isoprene (10).

10. A. S. Onishchenko, "Diene Synthesis", L. Mandel, Translator, Daniel Davey and Co., Inc., New York, N. Y., 1964, p. 26.

11. Small amounts of isoprene dimers were also obtained; no detailed analysis of these products was made.

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

13. J. C. Little, *J. Am. Chem. Soc.*, **87**, 4020 (1965).

14. See e.g., P. D. Bartlett, G. E. H. Wallbillich, A. S. Wingrove, J. S. Swenton, L. K. Montgomery, and B. D. Kramer, *J. Am. Chem. Soc.*, **90**, 2049 (1968).

15. The cyclooctadienes **12** and **13** probably arise via rearrangement of *cis*-1,2-dialkenylcyclobutanes (4b).

16. For a summary of recent references on the *s-cis*:*s-trans* equilibrium of isoprene see: A. A. Bothner-By and D. Jung, *J. Am. Chem. Soc.*, **90**, 2342 (1968).

17. The *s-trans*:*s-cis* ratio for the conformational equilibrium of butadiene is estimated to be 96:4 at 25° (18).

18. J. G. Aston, G. Szasz, H. W. Woolley, and F. G. Brickwedde, *J. Chem. Phys.*, **14**, 67 (1946).