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ORGANIC PHOTOCHEMISTRY. VIII. THE PHOTOSENSITIZED AND THERMAL CYCLOADDITION REACTIONS OF BUTADIENE AND ACRYLONITRILE[1]

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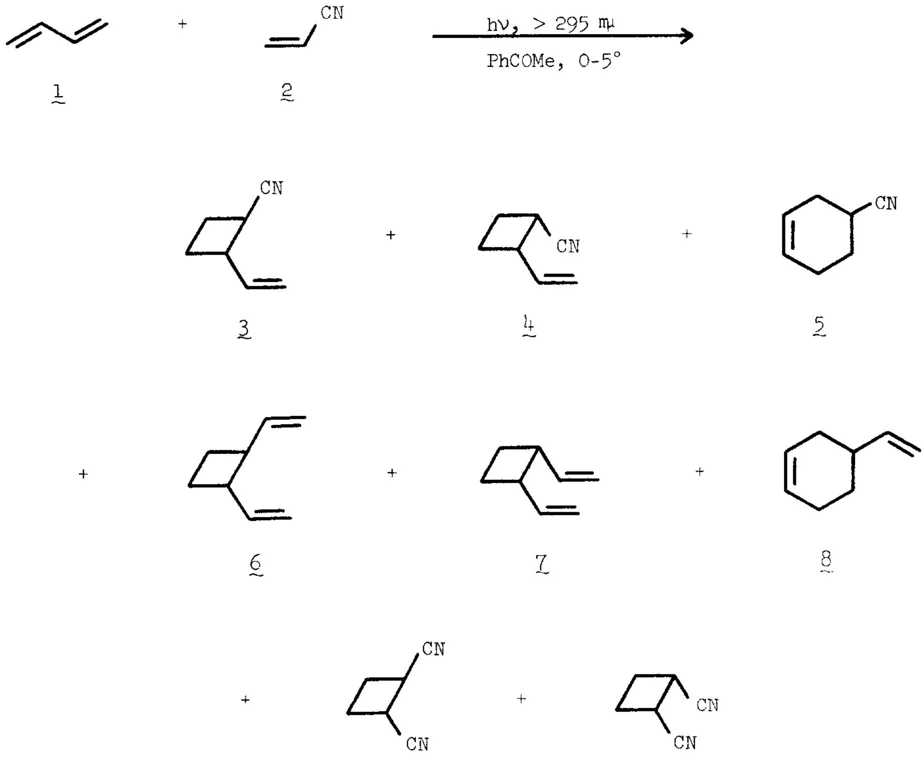
The thermal 4 + 2 cycloaddition of butadiene 1 to acrylonitrile 2 to give the cyanocyclohexene 5 is one of the classic examples of the Diels-Alder reaction.[2] In view of the increasing number of competitive 4 + 2 and 2 + 2 thermal cycloaddition reactions which have been reported,[3] we have reexamined the reaction of 1 and 2 and find that at 150° in the dark 0.5% of the isomeric cyclobutanes 3 and 4 is indeed formed.

In order to obtain larger quantities of the cyclobutanes 3 and 4 we have carried out the photosensitized addition of the diene 1 to the nitrile 2 using acetophenone as the sensitizer.[1b] In addition to the cyclobutyl cross-adducts 3 and 4,[4] the diene dimers 6-8,[5] nitrile dimers 9 and 10,[6] and a small amount of the cyclohexene 5 were formed.[7]

The stereochemical assignments of the cyclobutane derivatives 3 and 4 were made on the basis of the nmr chemical shifts of the vinylic and allylic protons (Table I). Examination of molecular models indicated that the vinylic protons, H^A, H^B, and H^C, of the *cis* isomer 4 should be more deshielded by the cyano group[8] than are the corresponding protons of the *trans* isomer 3. The allylic proton, H^D, should be more shielded in the *trans* isomer 3 than in the *cis* isomer 4.[9]

The product distributions for the photosensitized and thermal cycloadditions are shown in Table II. No reaction occurred at 5° in the absence of light. The small amount of cyclobutyl products 3 and 4 formed in the thermal reaction could arise via either branching of a two-step reaction,[11] giving both 5 and 3, 4 via a common diradical or dipolar intermediate, or via an independent two-step process while the cyclohexene 5 is formed in a concerted manner.[12] The finding of a small amount of the 1,2-addition products in this reaction points out that this phenomenon may be much more general than once thought.

The large amount of cyclobutanes 3 and 4, and 6 in the photosensitized reaction is a consequence of the high *s-trans* diene 1 concentration in equilibrium with the *s-cis* form[5,13]



1 2 3 4 5 6 7 8 9 10

Table I. Proton Chemical Shifts in <u>trans</u>-(3) and <u>cis</u>-1-Cyano-2-vinylcyclobutane (4)

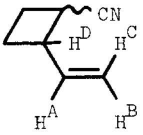
 Proton	Chemical shift, ppm trans- 3	 cis- 4
H^A	-5.92	-6.09
H^B	-5.06	-5.19
H^C	-5.08	-5.14
H^D	-2.87	-3.3

Table II. Product Distributions from Acetophenone Photosensitized and Thermal Cycloadditions of Butadiene (1) and Acrylonitrile (2)

Reaction no.	Reaction type, temp (°C)	Initial molar ratio 1/2	Reaction time (hr)	Conversion, % based on 2	Distribution of products, %[a] Cross-adducts 3-5	Diene dimers 6-8[b]	Nitrile dimers 9-10
1	hν,[c] 5°	0.90	10	13	43	56	1.6
2	hν, 5°	0.86	54	68	49	29	23
3	hν, 0°	0.33	12	11	43	7	50
4	Δ,[d] 150°	0.98	3	74	96	4	0

Reaction no.	Reaction type	Isomer distribution of, %[a]: Cross-adducts 3	4	5	Diene dimers 6	7[b]	8	Nitrile dimers 9	10
1	hν	50	50	0.8	87	11	2	53	47
2	hν	48	51	1.5	84	13	3	50	50
3	hν	49	50	0.8	92	7	2	46	54
4	Δ	0.27	0.21	99.5	5	4[e]	91	—	—

[a] Determined by gas chromatography assuming equal thermal conductivities on a weight basis for all products. [b] The *cis*-divinylcyclobutane 7 was partially isomerized to 1,5-cyclooctadiene under the analytical conditions; the amount of 7 was taken to be the sum of 7 and the octadiene. [c] All photoreactions run with *ca.* 20% (mole, based on diene 1) of acetophenone as the sensitizer using a 450 watt medium pressure mercury arc lamp with a Pyrex filter ($\lambda > 295$ mμ), no solvent. [d] One percent of 2,4-dinitro-*o*-cresol added as a polymerization inhibitor, no solvent. [e] Entirely 1,5-cyclooctadiene.

and the relative vertical triplet energies of the species involved: acetophenone, 73.6 kcal./mole;[14] *s-trans*-1, 59.6 kcal./mole;[15] *s-cis*-1, *ca.* 53 kcal./mole.[5] Although the triplet energy of the nitrile 2 (*ca.* 61 kcal./mole[6b]) is lower than that of acetophenone, the dimerization of the nitrile 2 is rather inefficient (see reaction no. 1, Table II) compared with diene dimerization and cross-addition. Therefore the cross-addition probably occurs mainly by addition of diene 1 triplets to ground state nitrile 2 and not vice versa.

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