Photoreaction of 2-Naphthonitrile and Vinyl Ethers; a Novel Photorearrangement of the Primary Cycloadduct

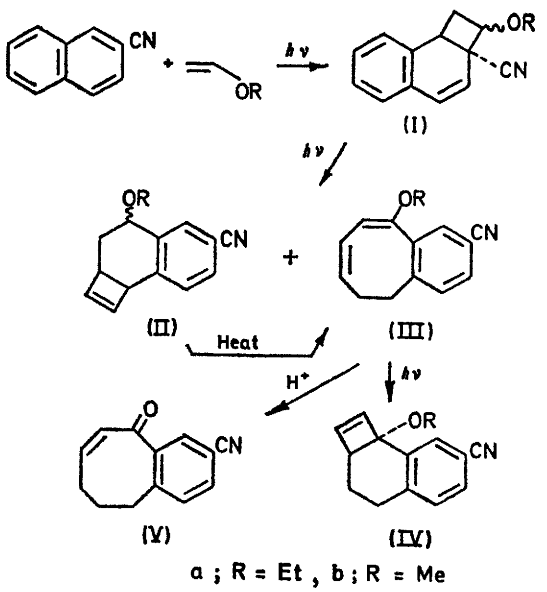
By Kazuhiko Mizuno,* Chyongjin Pac, and Hiroshi Sakurai

(*The Institute of Scientific and Industrial Research, Osaka University, Suita-shi, Osaka, Japan*)

Summary Irradiation of the dihydrocyclobutanaphthalene adduct (I), obtained by photocycloaddition of 2-naphthonitrile to alkyl vinyl ethers, affords the isomeric dihydrocyclobutanaphthalene (II) and the dihydrobenzocyclooctene (III); pyrolysis of (II) gives (III), whereas irradiation of (III) gives the dihydrocyclobutanaphthalene (IV) quantitatively.

Recently, much attention has been paid to the photoreactions of aromatic compounds in connection with exciplexes,[1] and the photoreactions of 2-naphthonitrile with 2,3-dimethylbut-2-ene have been reported.[2] We report here the photocycloaddition of 2-naphthonitrile with alkyl vinyl ethers giving (I) as sole primary product as well as a novel photorearrangement of (I).

Irradiation of a benzene solution of 2-naphthonitrile containing a large excess of ethyl vinyl ether through Pyrex by a high-pressure mercury arc for 30 h gave (IIa) as the main product along with (IIIa) and (IVa) in good yields. However, irradiation for less than 10 h resulted in the exclusive formation of (Ia). Control runs established that (IIa) and (IIIa) were the secondary photoproducts of (Ia),



and that (IVa) was produced by the photoelectrocyclic reaction of (IIIa). Pyrolysis of (IIa) at 230—240 °C gave (IIIa) in good yield. Similar reactions were observed with methyl vinyl ether, giving (I–IVb). Products were isolated by column chromatography on silica gel.

Analytical and spectral (i.r., u.v., and mass) data were in accord with the assigned structures, and assignments were based mainly on n.m.r. spectra; the detailed n.m.r. data (100 MHz; CCl_4 solutions) as well as spin-decoupling results will be reported elsewhere. Acid hydrolysis of (IIIa), m.p. 98—98·5 °C, and (IIIb), m.p. 106·5—108 °C, afforded the ketone (V), m.p. 106·5—107·5 °C.

The photorearrangement of (I) is unusual and cannot be fully interpreted at present. It is noteworthy that similar compounds with the same skeleton are quantitatively photolysed into the starting component.[1a,3]

In contrast to the photoreaction with 2,3-dimethylbut-2-ene,[2] irradiation of methanolic solutions of 2-naphthonitrile and vinyl ethers gave no solvent-incorporated product, but led to results which were identical to those for benzene solutions.

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