Stereospecific Photocycloaddition of 1-Naphthonitrile with *cis*- and *trans*-1-Phenoxypropenes

By KAZUHIKO MIZUNO, CHYONGJIN PAC,* and HIROSHI SAKURAI

(*The Institute of Scientific and Industrial Research, Osaka University, Suita-shi, Osaka* 565, *Japan*)

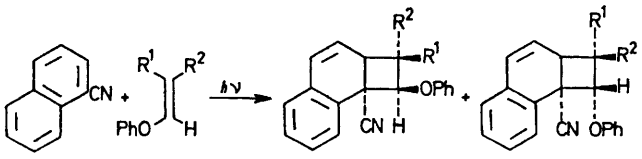
Summary Photocycloaddition of 1-naphthonitrile with *cis*- or *trans*-1-phenoxypropenes occurs stereospecifically to yield dihydrocyclobutanaphthalenes in good yields.

RECENTLY, the stereochemistry of photocycloaddition to aromatic rings has been discussed in terms of exciplexes.[1-3] In a previous paper,[1] we reported the stereoselective 2 + 2 photocycloaddition of 1-naphthonitrile with phenyl vinyl ether which gave exclusively an *endo* adduct, unlike that with alkyl vinyl ethers.[2] This *endo*-selective orientation would imply a stereospecific nature of the photocycloaddition. We report here the stereospecific photocycloaddition of *cis*- and *trans*-1-phenoxypropenes [(**2c**) and (**2t**)] to 1-naphthonitrile (**1**).

Irradiation of a benzene solution containing (**1**) and an excess of (**2c**) through Pyrex by a high-pressure mercury arc gave (**3c**) (80%), m.p. 138·5—139·5 °C and (**4c**) (10%), m.p. 101—102 °C. Similarly, irradiation of (**1**) and (**2t**) gave (**3t**) (85%), m.p. 97·5—98·5 °C and (**4t**) (5%) an oil. Products were isolated by column chromatography on silica gel.

Analytical and spectral data were in accord with the assigned structures, and the assignments were based mainly on n.m.r. spectra; close analyses of chemical shifts of the aliphatic and olefinic protons of the four adducts allowed us

to determine *endo* or *exo* configuration of the phenoxy and methyl groups of each adduct by considering anisotropic effects of the dihydronaphthalene ring and the substituents. These structural assignments were also supported by retrograde thermolyses and photolyses of the adducts. Thermolyses of (**3c**) and (**4c**) to (**2c**) at 300—350 °C took place in



(1) (2c) R^1=Me, R^2=H (3c) (4c)
(2t) R^1=H, R^2=Me (3t) (4t)

90 ± 5% specificity, whereas (**3t**) and (**4t**) were decomposed into (**2t**) in 70 ± 5% specificity. Among these adducts, (**3c**) was least stable. On the other hand, irradiation of acetonitrile solutions of the *cis*- and *trans*-adducts in the presence of ferrocene† resulted in complete stereospecific formation of (**2c**) and (**2t**) respectively.

It is noteworthy that (**3c**) and (**3t**) possessing the *endo*-located phenoxy group are much more favourably formed than (**4c**) and (**4t**) respectively, though this *endo* orientation is sterically unfavourable. The *endo*-selective orientation of the phenoxy group can be interpreted by assuming the intervention of exciplexes possessing fairly rigid configuration between excited (**1**) and the phenoxy ring of the olefins, as previously speculated.[1] The formation of the '*exo* adducts' (**4c**) and (**4t**) apparently arises from the *exo* approach of olefins which can intervene in competition with the *endo* one, even in minor importance, by added steric effects of the methyl group to the exciplex formation and the subsequent process. Thus, the orientational selectivity in the photocycloaddition of (**1**) with vinyl ethers appears to be affected by both electronic and steric factors of the substituents of vinyl ethers, though the former would be important with olefins containing a phenoxy group. In this regard, it is of interest to note that the photocycloaddition of (**1**) with *cis*- and *trans*-1-trimethylsiloxybut-1-enes, having no planar π-electron system conjugated with double bond, occurs stereospecifically but leads to the complete loss of such orientational selectivity, such that two stereospecific cycloadducts are formed in equal amounts with each olefin.[4] The stereospecificity would therefore be maintained independently of the nature of the substituents.

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† In the absence of ferrocene or 1,3-dienes, irradiation of (**3c**) and (**3t**) gave (**2c**) and (**2t**) in 95 ± 1% and 98 ± 1% specificity at zero time irradiation, respectively.

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