

Organic photochemistry with 6.7 eV photons: internal photocycloaddition in non-conjugated olefins

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Internal photocycloaddition of two double bonds to give a cyclobutane derivative is a well-known reaction in 1,4-, 1,5- and 1,6-diolefins at wavelengths longer than 250 nm. At 185 nm this reaction is only observed infrequently in diolefins on irradiation in solution. The geometric and electronic constraints on this reaction in the far UV were investigated for norbornadiene, 1,5-cyclo-octadiene, *endo*-dicyclopentadiene and bicyclo[3.2.0.]hepta-2,6-diene.

Wavelength-dependent photochemistry of trienes

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The strong influence of the irradiation wavelength λ_{irr} on the primary photoproduct composition of the simple (*Z*)-2,5-dimethyl-1,3,5-hexatriene in solution establishes the validity of the non-equilibration of excited rotamers (NEER) principle proposed as a working hypothesis in the early stages of previtamin D photochemistry. With the very flexible (larger) molecules of previtamin D itself (smaller) differences in quantum yields of photoproduct formation have also been found recently. Vitamin D in solution consists of a mixture of conformers; the predominant conformers have the *tZc* form of the chromophore and identical UV absorption spectra. Even so there appears to be a difference in photoproduct formation with 313 nm light and 254 nm light.

We conclude that (1) on the basis of the validity of the NEER principle a dependence of the primary product formation on λ_{irr} must be expected whenever conformers show different absorption spectra, and (2) a rotamer (in solution) may show different photochemistry, depending on the vibrational level reached on absorption of a light quantum.