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Organic Photochemistry in the Far-ultraviolet: Unusual Wavelength Dependence in Solution-phase Irradiations

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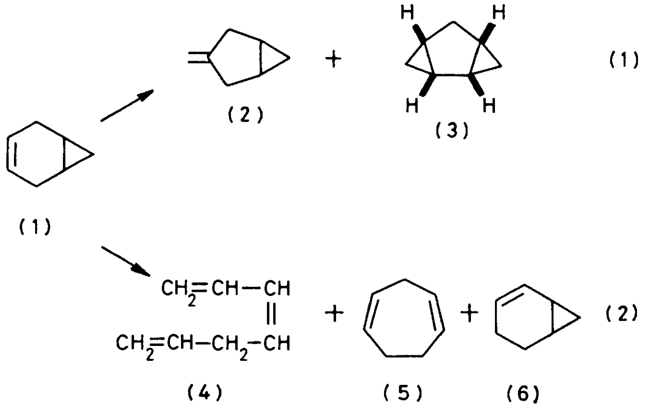
Summary In the region from 185 to 215 nm certain compounds show extreme selectivity in their photodecomposition modes in solution depending on the wavelength even though such compounds possess only one intense absorption in this region.

IT has been amply demonstrated that at wavelengths longer than 220 nm, in solution, compounds with more than one electronic transition can undergo distinctly different photochemical processes depending upon the absorption band in which they are irradiated.[1,2] Wavelength dependence within a single absorption band is not observed in solution at long wavelengths because vibrational relaxation by interaction with the solvent molecules is much faster than photochemical processes. It is therefore of considerable interest that in the far-ultraviolet, even within the narrow wavelength region from 185 to 215 nm, certain compounds undergo wavelength dependent photochemistry. This behaviour is best illustrated in bicyclo[4.1.0]hept-3-ene (**1**). The electronic spectrum of this compound in the far-u.v. is quite similar to that of cyclohexene.[3] It has been reported to yield (**2**), and (**4**)—(**6**) on photolysis at 185 nm.[3] These products may be grouped as those that result from fission of the cyclopropane ring, (**4**) and (**5**), and that which comes from the reaction of the olefinic group, (**2**). As shown in the Table, when the wavelength of the light is increased by 29 nm, there is a strong shift in favour of the latter process. Product (**3**), which had been overlooked in the study at 185 nm[3] because of its insignificance accounted for 20·1% of the products at 214 nm. It is noteworthy that this wavelength dependence is a continuous function of the change in wavelength and persists even at 228 nm although the weak absorption of (**1**) at this wavelength made it difficult to obtain reliable quantitative data.

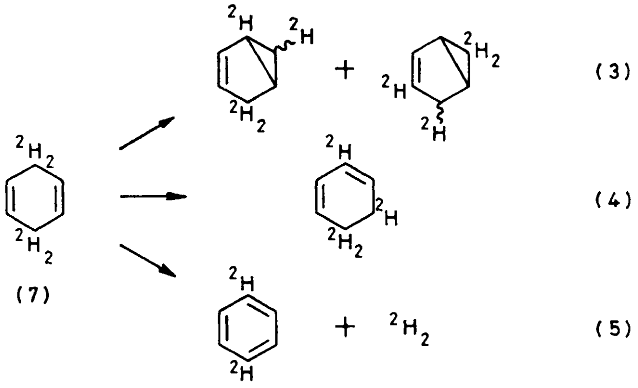
TABLE. Relative yields of products in the photolysis of (**1**)[a]

Wave-length/ nm	(**2**)	(**3**)	(**4**)	(**5**)	(**6**)
185[b]	11·6	3·9	16·7	37·5	17·4
193[c]	13·1	12·9	26·7	31·6	15·7
214[d]	22·9[e]	20·1	6·0	37·3	1·5

[a] All reactions in pentane solution. [b] Mercury resonance lamp with band-pass filter. [c] Argon fluoride laser. [d] Zinc resonance lamp. [e] Includes <5% of *anti*-tricyclo[3.1.0.0^{2,4}]heptane.

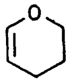


Similar wavelength-dependent photochemistry has been noted in the tetradeuteriocyclohexa-1,4-diene (**7**), in which reactions (3), (4), and (5) amount to 43·0, 25·9, and 31·1%, respectively, of the total at 185 nm while at 214 nm, these reactions account for 13·2, 27·2, and 51·6% of the products. Other compounds in which similar wavelength dependences are observed are (**8**)[4] and (**9**). At the same time cyclohexene[5] or *endo*-tricyclo[3.2.1.0^{2,4}]oct-6-ene (**10**)[6] both of which undergo more than one photochemical process at 185 nm, do not show a significant change in the relative yields of these products at 214 nm.



(7)

In the absence of a detailed analysis of the far-u.v. spectra of (**1**), (**7**), (**8**), or (**9**), an explanation for the effect of the wavelength of the radiation on the photochemistry as described here can only be tentative. The need for two interacting chromophores suggests a requirement that there be two or more allowed singlet electronic transitions in the spectral region under investigation. In (**1**) and (**7**) the excited-state energies of the first two transitions were calculated using the INDO/S program[7] and found to fall between 180 and 220 nm. If each of these transitions leads to characteristic photochemical reactions, a slight shift in the wavelength can cause a drastic change in the product mix. However the failure of (**10**) and norbornadiene[8] to show a dramatic wavelength effect in spite of fulfilling the first condition suggests that a conformational requirement may also exist. Further calculations on the energy levels of the lowest electronic transitions in (**1**) and (**7**) as a function of the dihedral angle show that the spacing between the levels is at a minimum (*ca.* 0·5 eV) when the angle approaches 180° and diverges by 1·9 eV at the limit of the folding motion (dihedral angle 120°). Therefore, small changes in conformation would drastically alter the ratio in which two (or more) electronic transitions are excited by a photon of given energy.



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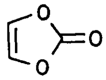

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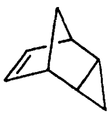

(10)

The present observation broadens the scope of far-u.v. photochemistry in the condensed phase by demonstrating that in certain organic compounds, when tunable light sources in the far-u.v. are used, a variety of photochemical reactions may be discovered.

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