Photodimerization of 1-Substituted Acenaphthylenes in Solution and in the Solid State

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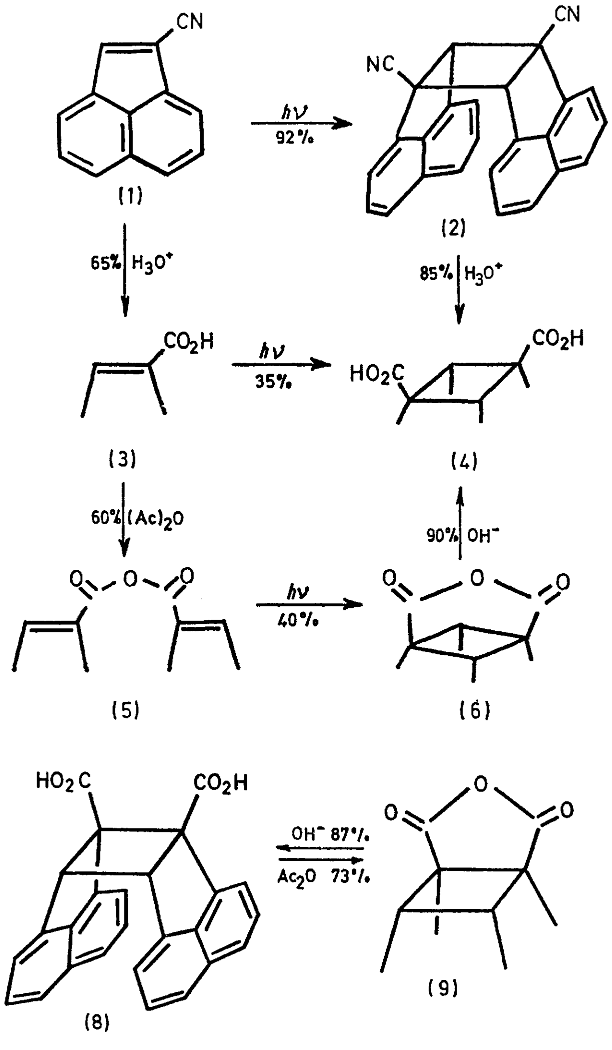
Summary U.v. irradiation of solutions of 1-substituted (CN, CO_2H, CO–O–CO) acenaphthylenes gives mainly head-to-tail *cis* photocyclisation, whereas the heavy atom effect favours the head-to-head *trans* photodimer of 1-cyanoacenaphthylene; topochemical photodimerization of acenaphthylene-1-carboxylic acid in the solid state results in the head-to-head *cis* dimer.

The photochemistry of acenaphthylene is well documented.[1,2] In particular, it has been shown that the singlet state S_1 leads to the *cis* photodimer whereas the triplet state T_1 generates the *trans* photodimer as the major product.[1] As the CN substituent is known to stabilise carbanionic as well as radical intermediates we might expect a strong orientating influence of this group in the photochemistry of 1-cyanoacenaphthylene (**1**). We report our preliminary results on the u.v. irradiation of (**1**) as well as that of acenaphthylene-1-carboxylic acid (**3**) and its anhydride (**5**) which proved useful in structural determinations.

Solution: (i) U.v. ($\lambda > 300$ nm) irradiation with a 500 W high-pressure mercury lamp of (**1**) in ether (conc. *ca.*10^{-1}M) for 4 h produced a product in high yield (92%) and a minor compound (2%). In the same solvent (25°, conc. 5×10^{-2} M, λ 365 nm) the initial quantum yield of disappearance of 1-cyanoacenaphthylene is *ca.* 0·1. The major product was shown by u.v., i.r., n.m.r., dipole moment (5·90 D§), and m.s. analysis to be the *cis* dimer (**2**). Chemical evidence for the head-to-tail orientation of the CN groups was provided by the following: (**2**) was hydrolysed to (**4**). Compound (**4**) was also obtained by hydrolysis of (**1**) to (**3**) and subsequent photodimerization (in degassed ether) as shown in the Scheme. The anhydride (**5**) photoisomerized to (**6**) in which the position of the anhydride bridge is given by the ν(C=O) frequencies typical of a six-membered ring.[3] Alkaline hydrolysis of (**6**) produced (**4**). Final confirmation of the structures of (**2**) came from *X*-ray structure analysis.[4]

(ii) U.v. irradiation of (**1**) in the same conditions as above but in degassed ether containing a heavy atom solvent (Me I; 50% mole) led to two photodimers: (**2**) 4·5% and (**7**) 80·5%. Compound (**7**) was the minor product of the irradiation in pure ether. It was shown by u.v., i.r., n.m.r., m.s. analysis, and dipole moment (3·65 D§) to be the head-to-head *trans* photodimer. The dipole moment of *trans*-1,2-dicyanocyclobutane has been shown to be 4·0 D.[5]

Solid state: Whereas photochemical reactions of both crystalline and molten acenaphthylene have been studied,[7,8] the photochemistry of acenaphthylene derivatives has not so far been investigated. U.v. irradiation of microsublimed crystals of acenaphthylene-1-carboxylic acid (39 mg) in a sealed Pyrex tube gave 25 mg (64%) of a single (t.l.c.) photoproduct (unchanged monomer was recovered) which was shown by u.v., i.r., n.m.r., and m.s. analysis to be the head-to-head *cis* photodimer (**8**); the spectroscopic evidence was confirmed by chemical transformation of (**8**) to its anhydride (**9**) and alkaline hydrolysis of (**9**) back to (**8**); ν(C=O) frequencies of (**9**) are typical of a five-membered ring.[3] *X*-Ray structure analysis of (**3**) shows that the molecules are stacked along one of the crystal axes and that the distance between the neighbouring molecules is favourable for a topochemical reaction.[9] Further evidence is



Scheme

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§ Dipole moments were measured in benzene at 25°, using the method of approximation.[6]

found in the striking contrast of reactivity of (**3**) in the solid and liquid phase. This strongly suggests that the reaction is controlled by the crystal lattice.

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