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THE PHOTOCHEMISTRY OF 1,2-DIHYDRONAPHTHALENE

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Recently Cookson and Coworkers[1] reported their results from the photolysis of 1,2-dihydronapthalene (I). They found that irradiation of a solution of I, with unfiltered light from a medium pressure mercury lamp, resulted in the formation of bicyclohexene (II) and they provided some very convincing evidence for the mechanism involved.

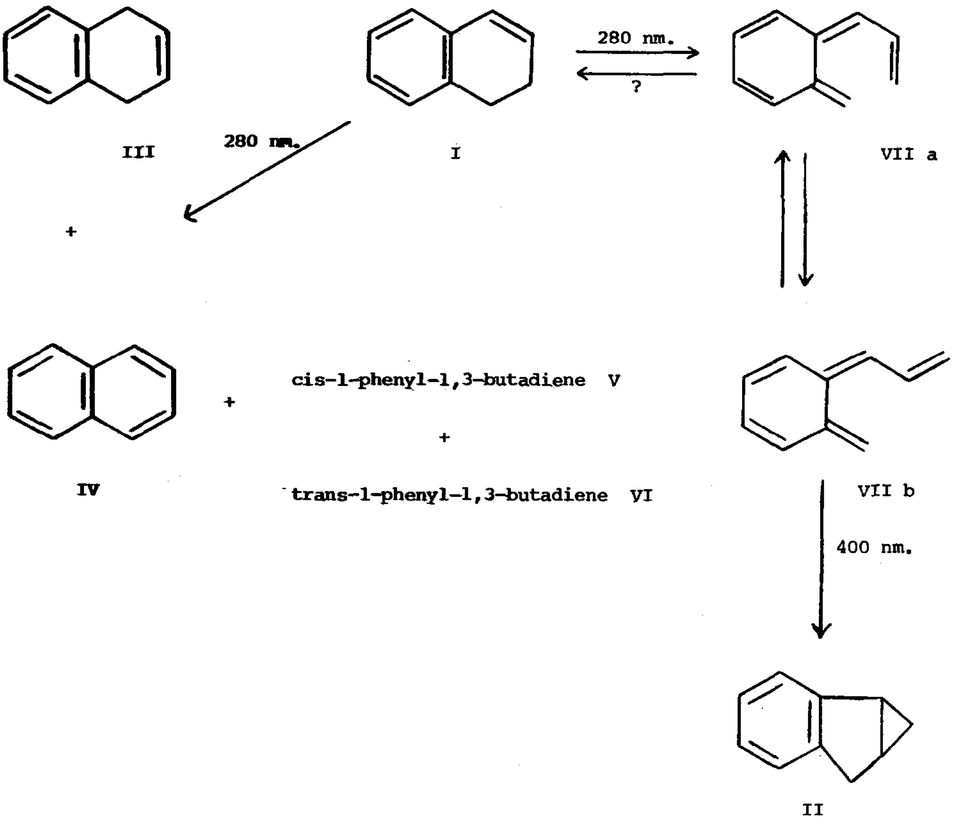
At the time of this publication we were also interested in the photochemistry of the title compound. It was found that irradiation of I in hexane with a range of wavelengths from 238 to 300 nm (the long wavelength limit of absorption) gave none of the bicyclohexene but instead resulted mainly in polymerisation. The monomeric compounds, which were formed, were 1,4-dihydronaphthalene (III), naphthalene (IV) and cis and trans-1-phenyl-1,3-butadiene (V and VI). In addition two unidentified compounds whose quantum yields of formation were always $<5 \times 10^{-3}$ were also detected.

Not surprisingly, the quantum yields were found to be concentration dependent but on irradiation of a 10^{-1} M solution at 280 ± 4 nm they were;

$$\Phi_{-I} = 0.5; \ \Phi_{III}\ 1.0 \times 10^{-2}; \ \Phi_{IV}\ 3.0 \times 10^{-2}; \ \Phi_{V} = 2.5 \times 10^{-2}; \ \Phi_{VI} = 2.0 \times 10^{-2}$$

It was suspected that the formation of II was due to two separate photochemical processes (see scheme). However, attempts to build up measureable amounts of VII, by irradiation of dihydronaphthalene in a variety of glasses at -196°, failed. The following simple experiment provided the necessary proof that two separate processes were involved. Using an all suprasil square cell, a 10^{-1}M solution of I was irradiated simultaneously with light of 280 ± 4 nm. (from a 500 watt Osram high pressure mercury lamp and using a Bausch and Lomb grating monochromator) and at right angles to the first beam with light of 400 nm ± 40 nm. (from a 1000 watt Hanovai mercury xenon compact arc and using a Farrad grating monochromator with enlarged slits). The bicyclohexene was formed in yields dependent on the intensity of both beams, falling to zero when either beam was switched off.

Based on the above results Cookson's mechanism may bs supplemented as follows:



Here it is seen that I, on absorption in its aromatic absorption band, undergoes a photochemical electrocyclic ring opening to the vinyl-0-quinodimethane VIIa. VIIa may isomerise to VIIb and VIIb can then photocyclise to the benzobicyclohexene. The vinyl-0-quinodimethanes are almost certainly very reactive species and it is suggested that much of the polymerisation may be attributed to them.[2] Furthermore VIIa may ring close to give back I photochemically or thermally. There are several precedents for the above type of mechanism, but involving more stable intermediates, e.g. the cyclohexadiene to hexatriene to bicyclohexene rearrangements.[3]

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