Photosensitized Dimerization of Styrene Derivatives by a Cation Radical Transfer Mechanism

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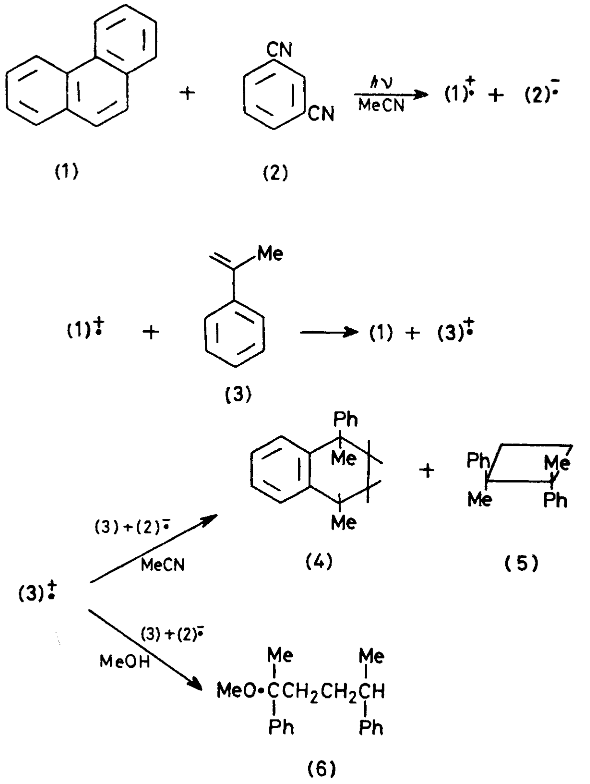
Summary Selective photoexcitation of phenanthrene in a mixture of phenanthrene, α-methylstyrene, and *m*-dicyanobenzene in MeCN and in MeCN–MeOH (1 : 1) gave 1,4-dimethyl-1-phenyl-1,2,3,4-tetrahydronaphthalene and 1,4-dimethyl-1-methoxy-1,4-diphenylbutane, respectively, products which are formed from the α-methylstyrene cation radical which is formed by cation radical transfer from phenanthrene cation radical to α-methylstyrene.

Recently the photodimerization of olefins *via* cation radicals has been extensively studied and a cation radical transfer mechanism has been proposed for the dimerization of olefins in the dark reaction,[1] and in the photochemical reaction.[2] We have previously reported photodimerization of styrene derivatives *via* cation radicals[3] and we now report photochemical dimerization of styrene derivatives *via* a cation radical transfer mechanism.

Irradiation of a degassed solution of phenanthrene (**1**) (20 mmol/l), *m*-dicyanobenzene (**2**) (20 mmol/l), and α-methylstyrene (96 mmol/l) in MeCN through a filter (> 320 nm) with a 300 W high-pressure mercury lamp at room temperature gave the dimeric products (41·1% after 20 h irradiation) (**4**) and (**5**) in the ratio of 95 : 5.† The tetralin (**4**) is a characteristic product of the α-methylstyrene cation radical.[3] In the absence of the sensitizer (**1**) or the electron acceptor (**2**), the system gave no photoproduct under these conditions. Addition of triethylamine (0·5 vol %) to the system quenched the reaction completely. Addition of MeOH (50 vol %) to the system suppressed the yield of dimers (16·0% after 20 h irradiation) and gave mainly the methanolysis product (**6**),† together with (**4**) and an unknown product in a ratio of 71 : 14 : 15, respectively. G.l.c. analysis showed that the sensitizer (**1**) was not consumed. This photodimerization occurred efficiently in MeCN; the overall rate in other solvents decreased in the following order: MeCN > Pr^{n}CN > PhCN > Me$_2$CO > C$_6$H$_6$ (no reaction), the order of which corresponds that of photoionization quantum yield. Naphthalene could replace (**1**) as an efficient sensitizer. Other electron acceptors, *e.g.*, *o*- and *p*-dicyanobenzene and dimethyl terephthalate were also effective.

The reaction of styrene in this system [naphthalene or (**1**), (**2**), and styrene] was similar to that of α-methylstyrene; excitation of naphthalene or (**1**) by irradiation through Pyrex in MeCN or MeCN–MeOH (1 : 1) gave the characteristic cation radical products 1-phenyl-1,2,3,4-tetrahydronaphthalene (97% of the total dimer) or 1-methoxy-1,4-diphenylbutane† (50% of the total dimer).

We suggest the reaction mechanism in the Scheme. Excited singlet (**1**) and the electron acceptor form an exciplex in non-polar solvents; in polar solvents the system produces the cation radical (**1**)$^{+\cdot}$ and the anion radical (**2**)$^{-\cdot}$. Electron transfer from (**3**) to (**1**)$^{+\cdot}$ results in the cation radical‡ (**3**)$^{+\cdot}$ which gives the characteristic products (**4**) or (**6**).[3,4]



Scheme

The cation radical transfer (**1**)$^{+\cdot}$ to (**3**)$^{+\cdot}$ could be shown spectroscopically by irradiation with a ruby laser (347 nm excitation) of the system (**1**)–*p*-dicyanobenzene in MeCN which gave a superposed absorption spectrum of (**1**)$^{+\cdot}$ (400, 430, and 900)[5] and *p*-dicyanobenzene anion radical (430 nm).[6] Addition of (**3**) to this system quenched the absorption spectrum of (**1**)$^{+\cdot}$ and a new absorption peak appeared around 470 nm within 50 ns, which can be ascribed to the α-methylstyrene dimer cation radical.[7]

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† Structures of the products were determined on the basis of i.r. and n.m.r., spectroscopy, mass spectrometry, and elemental analysis.

‡ For cation radical transfer, the electron affinity of (**1**)$^{+\cdot}$ needs to be larger than the ionization potential of (**3**).

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