Photodimerization of Styrene, *p*-Methylstyrene, and α-Methylstyrene in the Presence of 1,2,4,5,-Tetracyanobenzene

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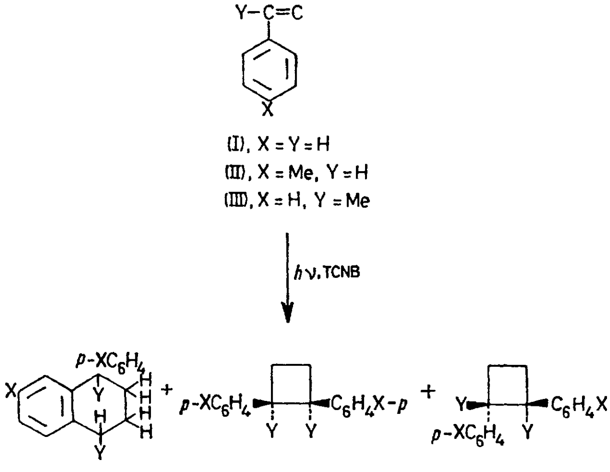
Summary U.v. excitation of styrene, *p*-methylstyrene, and α-methylstyrene in the presence of the electron acceptor tetracyanobenzene produces 1,2,3,4-tetrahydronaphthalene derivatives as the main products in addition to 1,2-*cis*- and 1,2-*trans*-disubstituted cyclobutanes.

THE dimerization of styrene and its derivatives has been reported to occur thermally,[1] by either cationic[2] or anionic[3] mechanisms, by photochemical reactions[4,5] either upon direct photolysis or with triplet sensitizers, and by high energy radiation,[4] with characteristic product patterns. It has been shown previously[6,7] that electron-donating vinyl compounds such as *p*-methoxystyrene produce 1,2-*trans*-bis-(4-methoxyphenyl)cyclobutane photochemically in the presence of 1,4-dicyanobenzene, and that more easily photoionizable vinyl monomer, *p*-*NN*-dimethylaminostyrene, also dimerizes photochemically without electron acceptors to give the 1,2-*cis*-and 1,2-*trans*-isomers of cyclobutane, whose ratio depends on solvent polarity.



(I), X = Y = H
(II), X = Me, Y = H
(III), X = H, Y = Me

(IV), X = Y = H
(VII), X = Me, Y = H
(X), X = H, Y = Me

(V), X = Y = H
(VIII), X = Me, Y = H

(VI), X = Y = H
(IX), X = Me, Y = H

During an investigation on the photodimerization of less electron-donating vinyl compounds such as styrene (I), *p*-methylstyrene (II), and α-methylstyrene (III), we found that photochemical excitation of these compounds in the presence of 1,2,4,5-tetracyanobenzene (TCNB) produces 1-phenyl-1,2,3,4-tetrahydronaphthalene derivatives as main products in addition to 1,2-*cis*- and 1,2-*trans*-diphenylcyclobutanes.

Irradiation of a degassed solution of (I) in acetonitrile (0·9 mol/l) in the presence of TCNB (5×10^{-3} mol/l) through Pyrex with a 300 W high-pressure mercury arc (Toshiba 300H) at room temperature gave the dimers† (12·3% after 20 h irradiation): (IV),‡ (V), and (VI), and some oligomers (20% per 20 h), in the ratio [(IV) : (V) : (VI)] of *ca.* 70 : 22 : 8. It is worth noting that reaction does not take place upon excitation of (I) (0·83 mol/l) in the presence of TCNB (5×10^{-4} mol/l) in n-hexane, but in benzene the reaction rate increases to 40% per 20 h and only the dimers (IV), (V), and (VI) (*ca.* 70 : 20 : 10) were obtained.

Similarly, irradiation of a degassed solution of (II) in the presence of TCNB gave the dimers† (VII),‡ (VIII), and (IX), in the ratio *ca.* 54 : 20 : 26 for benzene solvent and *ca.* 57 : 15 : 28 for acetonitrile or benzonitrile. Benzophenone-sensitized photochemical reaction of (II) in benzene also produced dimeric products, composed of 20% of (VIII) and 80% of (IX). The dimer (VII) was not observed.§

Compound (III) also produces the tetrahydronaphthalene (X)‡ as the main product with minor amounts of dimers or oligomers. U.v. irradiation of a degassed acetonitrile solution of (III) (0·9 mol/l) in the presence of TCNB (5×10^{-3} mol/l) gave dimeric (12% per 20 h) and oligomeric products (8% per 20 h). In benzene solvent, the reaction rate increased to 46% per 20 h and only dimeric products were obtained.

Since extremely dry conditions are known to favour ionic mechanisms,[8] the effect of water was examined; the solvents were dried over baked molecular sieves and the styrene derivatives were dried over barium oxide baked *in vacuo*, but no appreciable effect on the reaction rates and products was observed.

It is known that in the direct photolysis of styrene, 1,2-*cis*-cyclobutane is the main product produced by a singlet excitation mechanism, and that with triplet sensitizers the 1,2-*trans*-dimer is favoured. In contrast to these results, 1-phenyltetralin was the main product in this work. Hence a singlet or triplet excitation mechanism for styrene derivatives may be excluded, and instead an ionic mechanism is involved in these photochemical processes through photoionization of the exciplex of styrene derivatives with TCNB.

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† These products were analysed by g.p.c., g.l.c. (Apiezon grease L), and 60 MHz n.m.r. spectroscopy. The structures were confirmed by n.m.r. spectroscopy.

‡ The structures of the main dimeric products, (IV), (VII), and (X) were established by independent syntheses following the procedures of Zwierzak *et al.*[3] Compound (VII) has not been reported before. The synthetically produced tetralins were identical with (IV), (VII), and (X) according to g.l.c. and n.m.r. spectroscopy.

§ This result is in good agreement with that for styrene by previous workers[4] and indicates a characteristic product pattern for triplet excitation.

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