Solvent Participation in the Photoreaction of 2-Naphthonitrile and 2,3-Dimethylbut-2-ene in Methanol

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Summary Irradiation of 2-naphthonitrile and 2,3-dimethylbut-2-ene in methanol gives products containing a molecule of methanol; it is suggested that they are formed by reaction of an ion pair with methanol.

There has been considerable interest recently in photophysical and photochemical processes in solution, involving charge- or electron-transfer. The physicochemical work of Weller,[1a] Evans,[1b] and Schulte-Frohlinde[1c] on fluorescence quenching are of particular note. Recently, Hammond, Taylor, and Labianca[1d] have studied the quenching of naphthalene fluorescence by dienes.

Product studies indicate that certain photoadditions involve highly polar intermediates or ion pairs.[2] This is suggested by proton catalysis in certain cases[2c—e] and the isolation of products of reduction.[2b,c]

We now report our study of the photochemistry of 2-naphthonitrile and 2,3-dimethylbut-2-ene in methanol, in which solvent incorporation in the photoproducts is observed. This process is strongly suggestive of ion pair formation.

Irradiation of 2-naphthonitrile (3·0 g) and 2,3-dimethylbut-2-ene (6·0 g) in methanol (400 ml) with a Hanovia 450 W lamp and a Pyrex filter for 36 h, resulted in the formation of products (I)—(III) (see Scheme).

Products (I) (m.p. 97—99°) and (II) (m.p. 89—92°) were isolated by column chromatography over silica gel. Their structures† are assigned mainly from their n.m.r. spectra.‡ The details will be reported elsewhere, but the significant point is that the resonance of the vinyl proton in (I) appeared as a doublet of doublets, J 7·0 and 3·0 Hz, at δ 6·75, while this resonance in (II) was a doublet, J 7·0 Hz at δ 7·10. This points to the structures in the Scheme. Dehydrogenation of (II) by heating under reflux in xylene with palladium–charcoal gave the naphthalene derivative (IV), which showed the resonance of one proton of the aromatic system at δ 8·91, and this is assigned to the proton *peri* to the bulky substituent. A similar downfield shift is attributed to steric compression in t-butylnaphthalenes.[3] The structure of (III) follows from the n.m.r. spectrum, and the dehydrogenation to afford 2-naphthonitrile.

There is good evidence that the solvent is acting as a proton donor in this reaction. Use of CH_3OD led to incorporation of one deuteron in the methylene groups of (I) and (II). Also, irradiation in 2·6 M-acetic acid–methanol gave an increase in reaction rate of 70% and changed the

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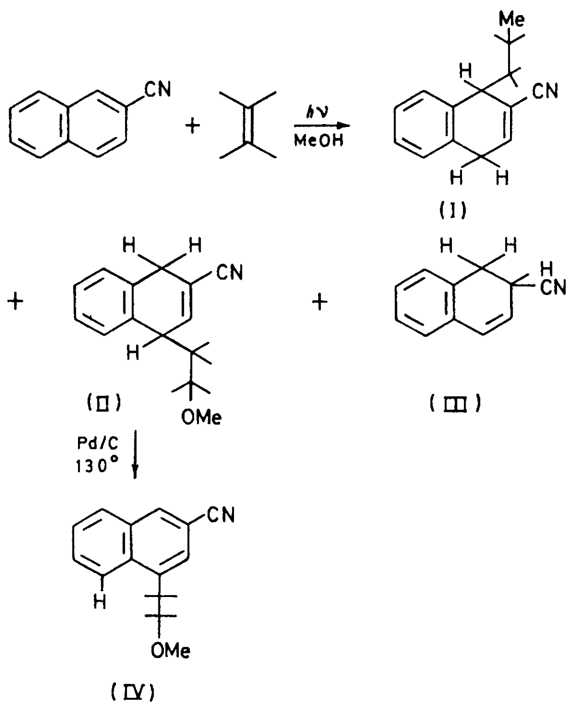
† All products gave satisfactory analytical figures, and the i.r. spectra were in accord with the assigned structures.

‡ Spectra were measured at 100 MHz on a Varian HA-100 instrument; the solvent was $CDCl_3$.

fraction (II)/(I) from 60 to 80%. No deuterium incorporation was observed when 2-naphthonitrile was irradiated in CH_3OD.

Significant to the primary photochemical process was the observation that 2,3-dimethylbut-2-ene quenched the fluorescence of 2-naphthonitrile, both in methanol and acetonitrile, giving linear Stern–Volmer plots. The slopes were $1{\cdot}48 \times 10^2$ and $1{\cdot}67 \times 10^2$ M^{-1}, respectively, and using the lifetime of 2-naphthonitrile fluorescence in methanol (11·3 nsec),[4] the Stern–Volmer quenching constant is calculated as $1{\cdot}31 \times 10^{10}$ M^{-1} s^{-1}, for methanol. In hexane no quenching of the fluorescence was observed, even at 2·0 M-olefin.

We suggest the following mechanism for the formation of (I) and (II): (i) electron-transfer from the olefin to S_1 of 2-naphthonitrile. This results in formation of an ion pair, and does not occur in hexane; (ii) protonation, bond formation, and solvent capture to afford (I) and (II). The timing of the latter processes is not known, but protonation probably occurs first, since the reaction is affected by added acid. In the absence of a high nucleophile concentration, proton loss from the olefin moiety could occur, a process which we did not observe, but was described by Bryce-Smith and his co-workers in the acid-catalysed photolysis of benzene and 2,3-dimethylbut-2-ene.[2d]



Scheme.

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