# Solvent Effects on the Photoaddition of Acenaphthylene and Acrylonitrile

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*Summary* The effect of brominated solvents as compared to acetonitrile and cyclohexane upon the photocycloaddition of acenaphthylene to acrylonitrile suggests that spin–orbit coupling between acenaphthylene solute and heavy-atom solvent increases intersystem crossing efficiency in acenaphthylene.

THE ready photodimerization of acenaphthylene is a well-known process.[1] Conversely, little is known about the cycloaddition of acenaphthylene to other substrates.[2] We have achieved cycloaddition of acenaphthylene to acrylonitrile in a variety of solvents using light of wavelength greater than 290 nm. The time dependence of the reaction is easily followed by observing the disappearance of the yellow colour of acenaphthylene.

Alternative syntheses of the acenaphthene[1,2-*a*]cyclobutane system involved the less viable synthetic precursors, 1,8-divinyl naphthalene moieties.[4,5]

The Table illustrates the time dependence of the reaction in various solvents. The reaction conditions for each run were standardized as follows: 450 w aged Hanovia immersion lamp with Pyrex filter sleeve and water cooling, 1·0 g. of recrystallized acenaphthylene, 120 ml. of freshly-distilled acrylonitrile, 380 ml. of freshly-distilled solvent, and continuous nitrogen purge beginning 15 min. before the irradiation process. The solvents were removed by vacuum rotary evaporation and the solid residues subjected to preparative thick-layer chromatography using Mallinckrodt ChromAr 1000 and 30:70 benzene–hexane as a developer.

TABLE

| Solvent | Reaction time (min.) | Overall[a] yield, % | Isomer[b] ratio (*syn*:*anti*) |
|---|---|---|---|
| Dibromomethane | 36 ± 10 | 43 | 3·8 |
| Bromoethane | 58 ± 10 | 40 | 2·9 |
| 1-Bromopropane | 99 ± 10 | 52 | 3·4 |
| 1-Bromobutane | 95 ± 10 | 40 | 3·0 |
| Acetonitrile[c] | 240 ± 60 | 31 | 2·5 |
| Cyclohexane[c] | 360 ± 60 | 42 | 4·3 |

[a] Yield based upon acenaphthylene after preparative thick-layer chromatography of the cycloadducts from each run.

[b] The lower-melting isomer is presumed to be the *syn*-isomer for this relative ratio.

[c] Extensive polymer formation reduced visual accuracy of the decolorization time.

Isomer (I) whose tentative stereochemistry is assigned *syn, vide infra*, has a m.p. of 80—82°, while compound (II) (tentatively *anti*), has a m.p. of 139—141°. Both isomers† showed i.r. absorption at 2225 cm$^{-1}$ (nitrile) with characteristic doublets at 1600 cm$^{-1}$. The u.v. spectra of both [similar to that of compound (I)] in cyclohexane were:

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† Satisfactory elemental analyses (±0·1%) were obtained for all new compounds.

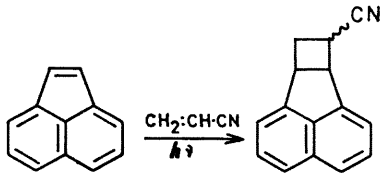
$\lambda_{max}$ nm (log $\epsilon$), 293 (3·89) and 232 (4·51). This shows that the acenaphthene moiety is still intact.[6]

The n.m.r. spectra‡,§ of (I) and (II) are complex. Compound (I) has a 6H multiplet at 450 Hz (aromatics), a 2H multiplet at 262 Hz (benzylic methines), a 2H multiplet at 170 Hz, and a 1H multiplet at 138 Hz. Compound (II) has a 6H multiplet at 450 Hz (aromatics), a 2H multiplet at 255 Hz (benzylic methines), 1H quasiquartet at 225 Hz (cyanomethine), 1H multiplet at 182 Hz, and a 1H multiplet at 130 Hz.

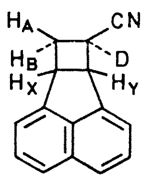
Treatment of (I) with potassium t-butoxide in Bu$^t$OD for 1 hr. at 60° resulted in its isomerization to (III).[7] The absence of appreciable signal at 225 Hz in the n.m.r. and the proper integrated curve of the spectrum suggests that one deuterium atom was incorporated during the isomerization. The fact that (I) is isomerized to (III) by base catalysis suggests that (I) is the *syn*-isomer and (III) the *anti*-isomer.

The n.m.r. of monodeuterio-(III) produced an ABXY spectrum with the AB portion appearing as a slightly perturbed ABX system. Preliminary analysis of the spectrum using double irradiation techniques suggests that the following tentative frequencies and coupling constants fit the spectrum: $\nu_B$ 124 (q), $\nu_A$ 176 (t), $\nu_X$ 244 (m), $\nu_Y$ 260 (m), $|J_{AB}|$ 12·5 ± 0·5, $J_{AX}$ 9·0 ± 0·5, $J_{BX}$ 6·0 ± 0·5, $J_{XY}$ 7·0 ± 0·5, $J_{AY}$ *ca.* 2, $J_{BY}$ >OHz.

We attribute the observed time dependence of solvent effects to a heavy-atom spin–orbit coupling phenomenon causing a more efficient population of the triplet state. Cowan and Drisko[1] observed a similar effect of 1-bromopropane upon the photodimerization of acenaphthylene. While heavy-atom effects are well known photophysical phenomena in spectroscopy,[2] few positive photochemical heavy-atom effects have been reported.[1,8]



(I) = *syn*
(II) = *anti*



(III)

We also note a stereoselective preference for *syn*- over *anti*-adduct. This may be a reflection of charge correlation factors involving highly-oriented collision-complexes between the donor acenaphthylene and the acceptor acrylonitrile.[9]

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‡ A Varian T-60 spectrometer with 10% solutions in solvent $CDCl_3$ and internal $Me_4Si$ was used.

§ A detailed analysis of the n.m.r. spectra of (I) and (II) as well as the spectra of adducts of 1,2-dibromoacenaphthylene and acrylonitrile will be published.

[1] For pertinent references and a suggested mechanism see D. O. Cowan and R. L. Drisko, *Tetrahedron Letters*, 1967, 1255.

[2] N. J. Turro, "Molecular Photochemistry," Benjamin, New York, 1967, p. 197. Maleic anhydride is said to add to acenaphthylene. However, in ref. 3 cited by Turro, only phenanthrene is reported to react with maleic anhydride.

[3] D. Bryce-Smith and B. Vickery, *Chem. and Ind.*, 1961, 429.

[4] The 3,4-diphenylacenaphthene[1,2-*a*]cyclobutane was made by irradiating 1,8-distyrylnaphthalene: P. R. Houlton and W. Kemp, *Tetrahedron Letters*, 1968, 1045.

[5] The parent compound was recently reported to be produced from 1,8-divinylnaphthalene. J. Meinwald, Abstracts of Papers, 21st National Organic Symposium of the American Chemical Society, Salt Lake City, Utah, 1969, p. 67.

[6] The spectrum of acenaphthene has an absorption of $\lambda_{max}$ nm (95% EtOH) (log $\epsilon$) 290 (3·95) and 228 (4·95). H. H. Jaffe and M. Orchin, "Theory and Applications of Ultraviolet Spectroscopy," Wiley, New York, 1962, p. 307.

[7] This reagent was found to isomerize the indene–acrylonitrile adducts in 1 hr. at 25°. J. J. McCullough and C. W. Huang, *Chem. Comm.*, 1967, 815.

[8] A thermochemical heavy-atom effect upon the multiplicity of cyanonitrene has been reported. A. G. Anastassiou, *J. Amer. Chem. Soc.*, 1966, 88, 2322.

[9] D. Bryce-Smith and A. Gilbert, *Chem. Comm.*, 1968, 1701.