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Chemical, Kinetic, and Spectroscopic Evidence for the Reaction of 1-Naphthylcarbene with Acetonitrile to form a Nitrile Ylid.[1]

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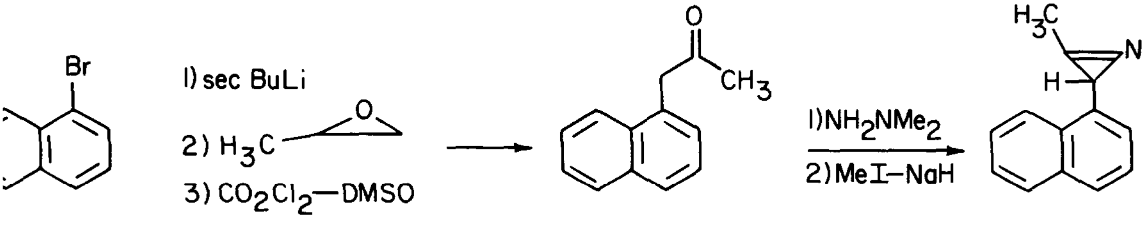
Summary: Laser photolysis of 1-naphthyldiazomethane or azirine 7 in acetonitrile gave the same transient absorption spectrum. The transient from each precursor reacted with acrylonitrile with identical rate constants. Photolysis of 1-naphthyldiazirine 6 in acetonitrile containing acrylonitrile gave products derived from carbenes and nitrile ylids.

The laser flash photolysis of 9-diazofluorene in acetonitrile has been reported.[4] Work in this laboratory has shown that one of the absorption bands originally attributed to fluorenylidene is really that of a nitrile ylid derived from carbenic reaction with solvent.[5] We have also discovered that laser flash photolysis of 1-naphthyldiazomethane in acetonitrile gives a transient absorption at 390 nm.[6] This band was assigned to ylid 2, which was derived from reaction of 1-naphthyl carbene (1) with solvent. This assignment was based upon kinetic and spectroscopic evidence. We report herein chemical evidence for the formation of ylids from carbenic precursors. The reaction of a heterocyclic carbene with benzonitrile to form an ylid was first proposed by Magee and Shechter.[7] Two other examples of this reaction class have been reported by Sheppard[8] and Kende.[9]

The chemistry of nitrile ylids has been developed by Huisgen,[10] Padwa,[11] and Schmid.[12] Nitrile ylids are known to add readily to electron deficient olefins and dimerize. Azirines have been shown to be convenient photochemical precursors of nitrile ylids. This fact has been used to obtain low temperature matrix electronic spectra and solution absolute rate constants for a limited number of nitrile ylids. We therefore synthesized azirine 7 as an alternate precursor to ylid 2.[13]



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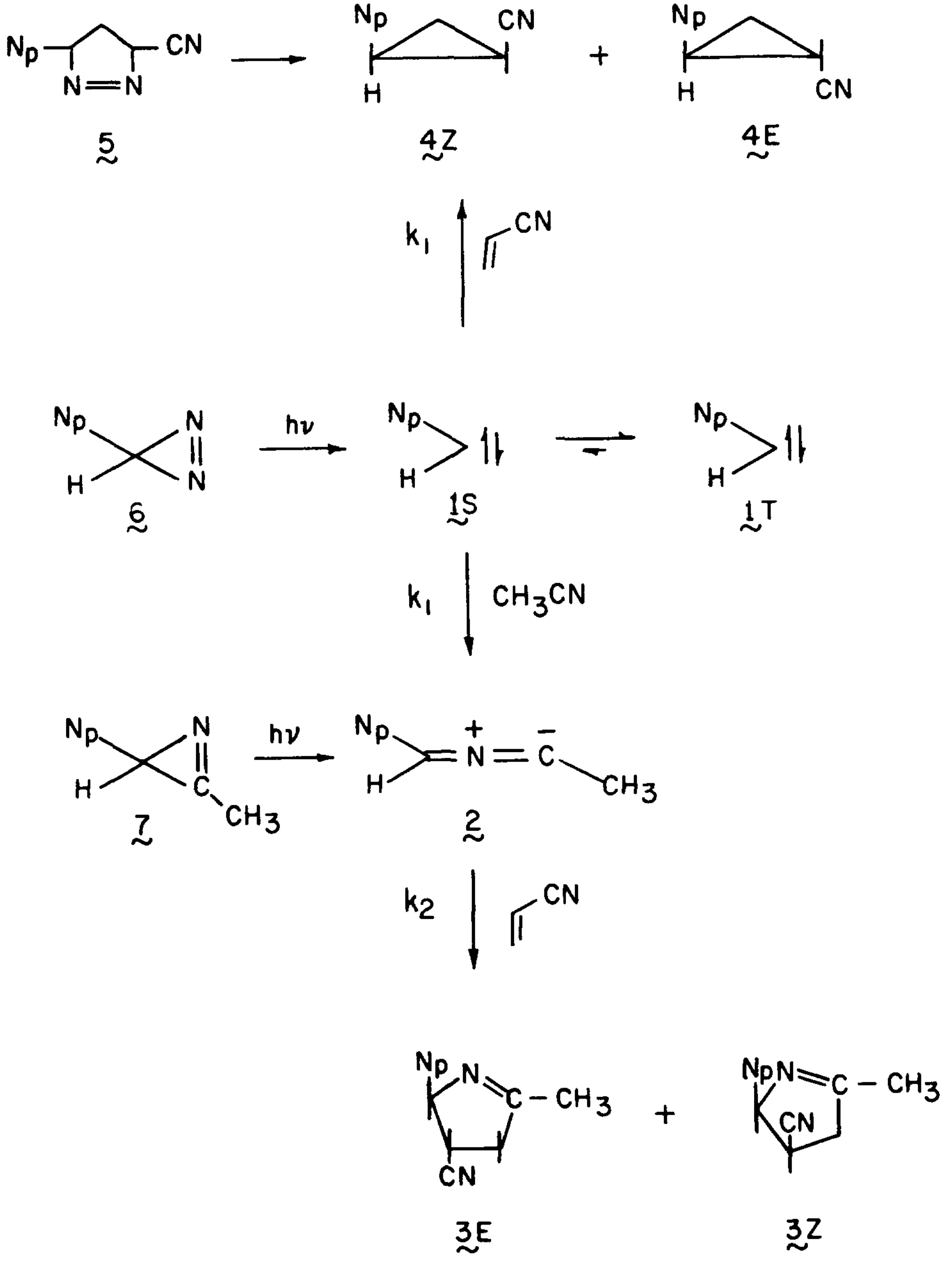
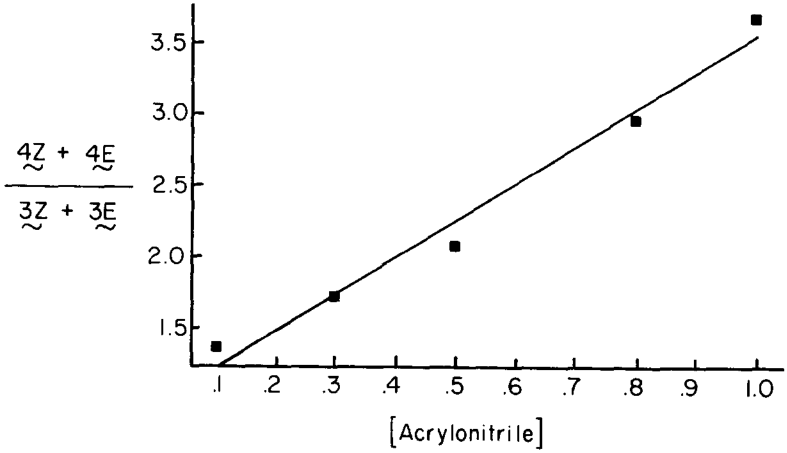
Based on these previous studies we expected that photolysis of azirine 7 would also give ylid 2 as a trappable intermediate. Indeed photolysis of 7 (0.18g 7, 20 ml acrylonitrile, 150 ml benzene; 450 watt Hanovia-vycorr filter; 30 min.) gave 3Z and 3E which were separated by MPLC.[14]

Scheme 1 (N_p = 1-Naphthyl)



1-Naphthyldiazomethane reacts rapidly with acrylonitrile at 0° to give pyrazoline 5Z which was converted to cyclopropane 4Z upon photolysis.[15] Thus, for product studies a different carbene precursor was desired which would be inert towards acrylonitrile. Diazirine 6 was prepared by the method of Schmitz[16] and was stable in solutions of acrylonitrile in acetonitrile. Laser flash photolysis of diazirine 6 in acetonitrile gives the same transient spectrum as laser photolysis of 1-naphthyldiazomethane. Photolysis of 6 (λ=350 nm, Rayonet) in acetonitrile containing acrylonitrile gave cyclopropanes 4Z and 4E as well as heterocycles 3Z and 3E. The latter compounds were identical to those obtained by photolysis of azirine 7. The ratio of cyclopropanes/pyrroline was sensitive to the concentration of acrylonitrile (see figure), high concentrations favoring carbene chemistry. Dilution increases the yield of ylid, as evidenced by increased yields of 3Z and 3E.



Flash photolysis of 7 in acetonitrile (XeCl excimer laser, 308 nm) gave a transient with λmax = 386 nm, virtually identical with that obtained by flash photolysis of 1-naphthyldiazomethane in acetonitrile.[6] The transient derived from azirine 7 reacted with acrylonitrile with $k = 4.77 \pm .34 \times 10^6\ M^{-1}\ s^{-1}$. The transient derived from 1-naphthyldiazomethane reacted with acrylonitrile with $k = 5.44 \pm 0.21 \times 10^6\ M^{-1}\ s^{-1}$. The two values are identical within experimental error, in support of assignment of the transient as nitrile ylid 2.

In conclusion, we have obtained chemical, kinetic, and spectroscopic evidence for the formation of a nitrile ylid from reaction of 1-naphthyl carbene with acetonitrile. These results strongly support our interpretation of previous laser photolysis studies of 1-naphthyldiazomethane.[6] The present work provides indirect support of our reassignment of the laser photolysis data on 9-diazofluorene, in terms of nitrile ylid intermediates.[4]

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13. Compound 7 IR (CCl_4) 3.50, 5.67, 7.15μ NMR (CCl_4, 90 MHz) δ 2.43 (3H,S), 3.30 (1H,S), 7.2-8.3 (7H, m).
14. Compound 3E IR (CCl_4) 3.28, 3.35, 4.48, 6.05, 7.00, 7.25 and 7.60μ; NMR ($CDCl_3$, 300 MHz)δ 2.29 (3H,S), 3.04 (3H, m), 6.25 (1H, br s), 7.19-8.15 (7H, m), m/e 234, 207, 181, 166 (base), 139.

    Compound 3Z , IR (CCl_4) 3.35, 4.45, 6.05, 7.00, 7.25 and 7.60μ NMR ($CDCl_3$, 300 MHz)δ 2.33 (3H,S), 3.13 (2H, m) 3.92 (1H, br s), 6.17 (1H, br s), 7.50-7.88 (7H,m), m/e 234, 207, 181, 166 (base), 139.
15. Compound 4Z NMR ($CDCl_3$, 200 MHz)δ 1.56 (2H, m), 1.78 (1H, m), 3.08 (1H, m). 7.20-8.26 (7H, m); IR(CCl_4) 3.26, 3.37, 6.62, 12.00, 12.15μ, m/e 193, 178 165 (base), 139.
16. Schmitz, E.; Chem. Ber. (1962), 95, 795; Compound 6, m.p. = 65d; NMR ($CDCl_3$, (200 MHz)δ 2.58 (1H, S), 6.42 (1H, d J=8.0 Hz), 7.41 (1H, d, J=8.0 Hz), 7.59 - 7.67 (3H, m), 8.26-8.36 (2H, m); UV λmax (methanol) 360 nm, IR 1620 cm^{-1} (diazirine N=N stretch); MS base peak 139 corresponds to $C_{11}H_7^+$; Irradiation at 77K in ethanol gave the ESR spectrum of 1-naphthylcarbene.

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