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THE PHOTOLYSIS OF 1-AZIDO-4-METHYLBICYCLO[2.2.2]OCTANE AND 1-AZIDOADAMANTANE IN LOW-TEMPERATURE MATRICES

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Summary· Photolysis of the bridgehead azides (1) and (5) in N_2 and Ar matrices at 12K produces the strained bridgehead imines (2) and (6)

In earlier studies[1-3] of the photolysis of the bridgehead azides (1) and (3)-(5), the isolated products suggested the intermediacy of strained, anti-Bredt, bridgehead imines, such as (2) and (6). The imines, however, were not observed directly We now report our findings on the photolysis of 1-azido-4-methylbicyclo[2 2 2]octane (1) and 1-azidoadamantane (5) in N_2 and Ar matrices at 12K, under which conditions, the imines (2) and (6) have been detected and characterized by means of their IR spectra

1-Azido-4-methylbicyclo[2 2 2]octane[1] (1) was isolated in N_2 and Ar matrices by vaporization from a side-arm and deposition on a CsI window at 12K, with simultaneous deposition of the matrix host gas [4] The matrix-isolated azide was photolysed using a 200W high-pressure Hg-arc fitted with a water filter, and its decomposition was monitored by IR spectroscopy [5] As the IR bands of (1) disappeared ($\nu(N_3)_{as}$ 2118, 2096 cm^{-1} in N_2, 2117, 2094 cm^{-1} in Ar), new bands arose (Fig 1) Amongst the strongest of the new bands were absorptions at 1601 cm^{-1} (N_2 matrices) or 1603 cm^{-1} (Ar matrices), which we assign to ν(C=N) of the strained imine (2) Annealing the matrices containing (2) to 30-35K produced no further changes in the IR spectra, and once the matrix host gas was boiled off and the CsI window allowed to warm to room-temperature, no involatile residue remained

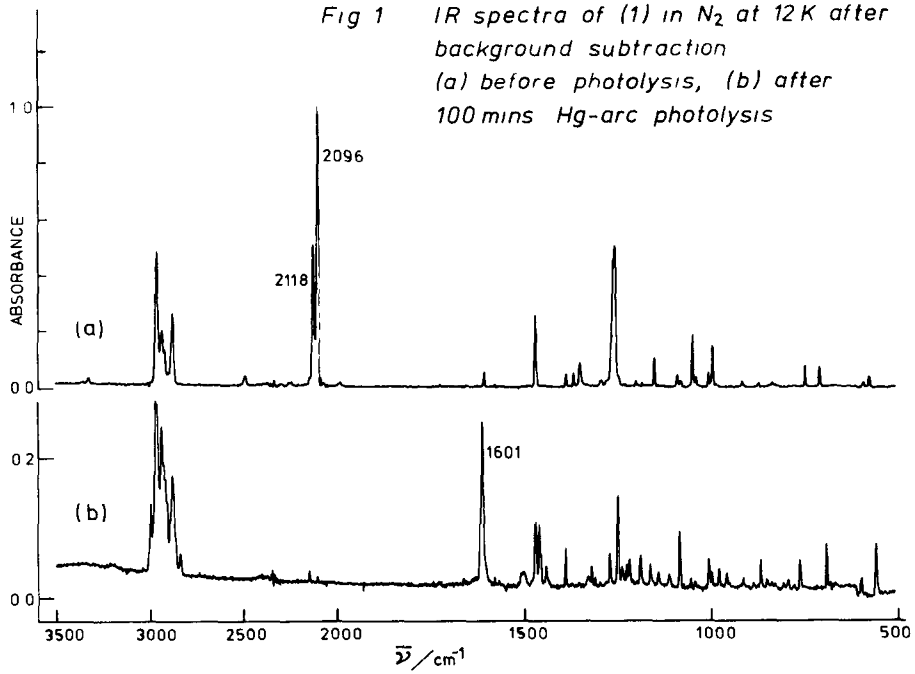


Fig 1 IR spectra of (1) in N_2 at 12 K after background subtraction (a) before photolysis, (b) after 100 mins Hg-arc photolysis

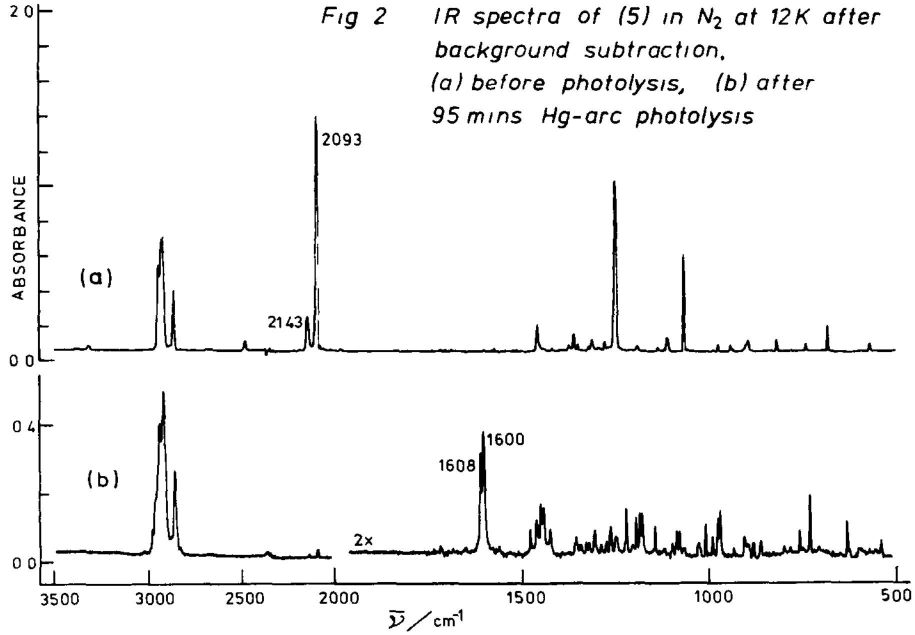
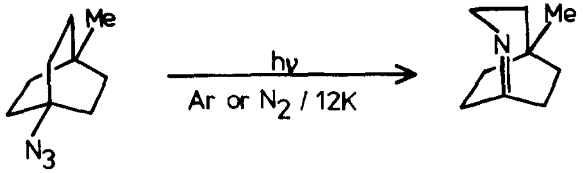
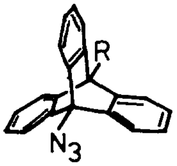


Fig 2 IR spectra of (5) in N_2 at 12 K after background subtraction, (a) before photolysis, (b) after 95 mins Hg-arc photolysis

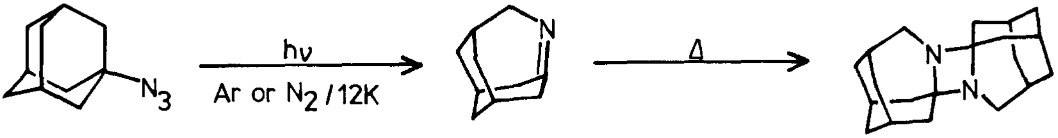


(1) (2)



(3) R = H

(4) R = Me



(5) (6) (7)

1-Azidoadamantane[2] (5) was similarly isolated in N_2 and Ar matrices by sublimation from a side-arm Photolysis of matrix-isolated (5) also resulted in the formation of an imine with ν(C=N), showing some splitting, at 1608 and 1600 cm^{-1} (in both N_2 and Ar matrices) (Fig 2). We assign the resulting spectra to the azahomoadamantene (6) Annealing the matrices containing (6) to 30-35K produced no further changes in the IR spectra, but after boiling off the host gas and allowing the CsI window to warm to room temperature, a colourless solid remained A small amount (<0 1 mg) of this residue was scraped off the window holder The mass-spectrum of this material was essentially the same as that of an authentic sample of the dimer (7) isolated previously (M^+298, an accurate mass gave $C_{20}H_{30}N_2$) [2] Attempts to obtain enough of this material for a 250 MHz ^{1}H-NMR spectrum have so far proved unsuccessful

For both the imines (2) and (6) the ν(C=N) frequency is lower than that of unstrained alkyl imines[6] by about 40-60 cm^{-1}, revealing the expected weakening of the C=N bond We found no indication of a long-lived nitrene intermediate in either reaction

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4 Cooling was achieved by means of an Air Products Displex, model CSA-202 Matrix gases were from BOC Ltd , research grade Owing to the vaporization or sublimation technique used for matrix deposition, matrix ratios could not be estimated

5 IR spectra were recorded on a Perkin-Elmer 684 spectrometer interfaced with a Perkin-Elmer 3600 Data Station The spectrometer was calibrated regularly with a polystyrene film, and quoted frequencies are accurate ± 2 cm^{-1}

6 See, for example, L J Bellamy, "Advances in Infrared Group Frequncies", Chapman and Hall, London (1968)

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