

# Photochemistry of 2-azido-4,6-dichloro-*s*-triazine: matrix isolation of a strained cyclic carbodiimide containing four nitrogen atoms in a seven-membered ring

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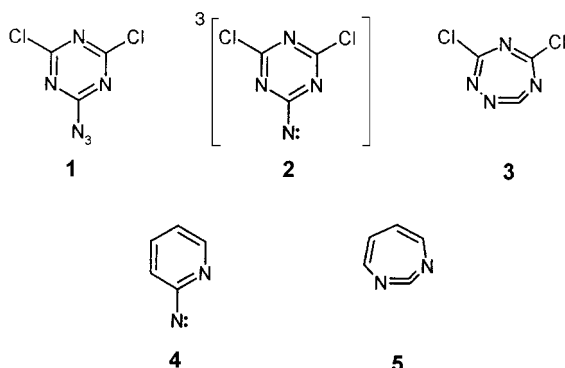
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2-Azido-4,6-dichloro-*s*-triazine **1**, matrix-isolated in Ar at 10 K, yields triplet nitrene **2** and the strained cyclic carbodiimide **3** upon photolysis.

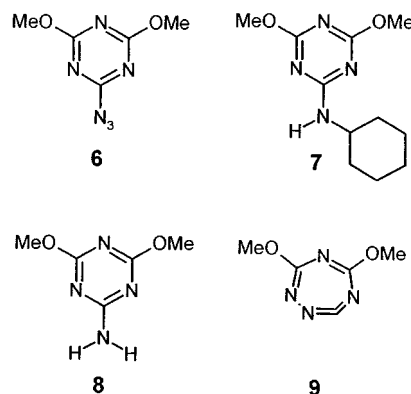
The photochemistry of phenyl azides has been a controversial topic for a long time.<sup>1,2</sup> The generally accepted pathway includes primary formation of an open-shell singlet nitrene<sup>3,4</sup> followed by intersystem crossing (ISC) to the ground-state triplet nitrene and/or cycloaddition to a neighbouring C=C double bond in the arene system. The efficiency of the latter reaction depends on factors such as temperature and substitution. It yields dihydroazepines *via* intermediary azirines.<sup>5</sup> Heteroaromatic aryl azides have also been studied in some detail.<sup>6</sup> For instance, 2-pyridyl nitrene **4**, generated from 2-azidopyridine or the isomeric tetrazolopyridine, yields dihydro-1,3-diazepine **5** (a cyclic carbodiimide) upon photolysis



in an Ar matrix.<sup>7</sup> A variety of heteroaromatic aryl nitrenes could be characterized by EPR,<sup>8</sup> and in some instances also by IR spectroscopy.<sup>6</sup>

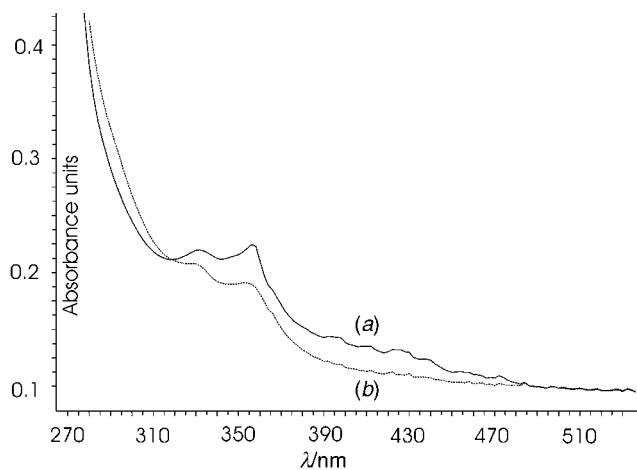
The products isolated following thermolysis<sup>9</sup> or photolysis<sup>10</sup> of azido-*s*-triazines in solution exclusively arise from reactions of the triplet or singlet nitrenes. Thus, thermolysis of 2-azido-4,6-dimethoxy-1,3,5-triazine **6** in cyclohexane yielded the C–H insertion product **7** and the aminotriazine **8**.<sup>9</sup> The formation of **8** is likely due to a reaction of the ground-state triplet nitrene, while **7** is probably formed through the  $S_1$  state of the nitrene. Surprisingly, no products ascribable to reactions of a didehydrotetraazepine (*e.g.* **9**) have been reported. Their absence could be due to a lack of stability, or it could reflect an increased barrier for cycloaddition towards a nitrogen atom. Here we present our recent results on the photolysis of matrix-isolated 2-azido-4,6-dichloro-*s*-triazine **1** which are different from the ones described for **6**.

The matrix isolation set-up used in these experiments has been described elsewhere.<sup>11</sup> Argon was chosen as the matrix material. During deposition, the cold window (KBr or sapphire) was kept at 30 K, otherwise the temperature of the matrix was held at 10 K. Azide **1**<sup>12</sup> was sublimed at 10 °C/10<sup>−6</sup> mbar. In experiments using UV–VIS detection, it was photolysed by the

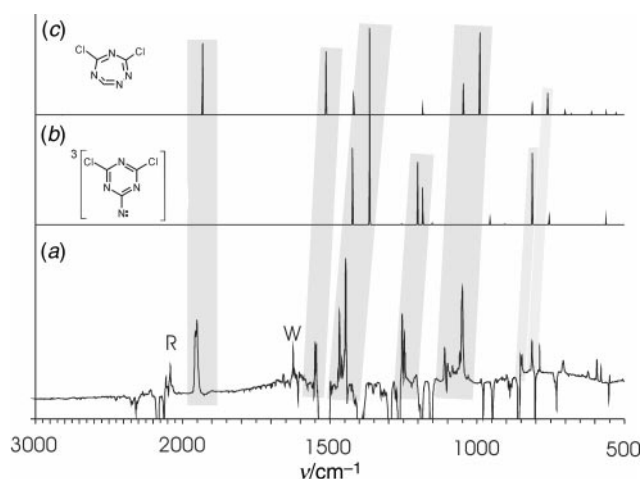


output of a 75 W Xe arc lamp coupled to a monochromator. The irradiation wavelength selected was 320 nm. In the case of IR detection, the output of a mercury low-pressure lamp ( $\lambda = 254$  nm) was used. Brief irradiation (8 min) under these conditions led to the disappearance of the IR bands of **1** and to the formation of new bands at  $\tilde{\nu} = 1951.2, 1550.0, 1467.6, 1446.4, 1254.5, 1246.8, 1110.2$  and  $1050.0$  cm<sup>−1</sup> along with some weaker bands below 900 cm<sup>−1</sup> and around 2100 cm<sup>−1</sup>. Upon extended irradiation with  $\lambda = 254$  nm, these bands disappeared again, while the new absorptions at  $\tilde{\nu} = 2271.2, 2214.2, 2112.9$  and  $2094.4$  cm<sup>−1</sup> were indicative of nitrile and possibly isonitrile and/or cumulene functionalities in the final product mixture.<sup>13</sup> Long-wavelength irradiation ( $\lambda > 420$  nm) of the primary photoproducts led to a decrease in intensity of some bands ( $\tilde{\nu} = 1467.6, 1446.4, 1254.5, 1246.8, 848.7, 787.9$  and  $580.0$  cm<sup>−1</sup>), while the intensity of other bands ( $\tilde{\nu} = 1951.2, 1550.0, 1110.2, 1050.0$  and  $814.4$  cm<sup>−1</sup>) increased. Thus, the experimental findings are consistent with two compounds (these can be interconverted by long-wavelength photolysis) being predominantly formed during the initial stages of photolysis, which yield other, presumably ring-opened products, upon extension of 254 nm photolysis. In the UV–VIS, the product primarily formed showed absorption maxima at  $\lambda = 330$  and 356 nm and a broad band between 380 and 490 nm with vibrational fine structure. Irradiation into this band ( $\lambda > 420$  nm, Hg high pressure lamp with cut-off filter) led to the disappearance of the primary photoproduct and to the formation of a secondary photoproduct with  $\lambda_{\text{max}} = 328$  and 352 nm (Fig. 1). Consistent with the results obtained using IR spectroscopy, this secondary photochemistry proved to be at least partially reversible. Photolysis of the product mixture thus obtained using  $\lambda = 320$  nm again led to the formation of the spectrum with  $\lambda_{\text{max}} = 330, 356$  and 380–490 nm, albeit with slightly reduced intensity. A likely explanation for this behaviour is formation of secondary (ring-opened) photoproducts, which do not show pronounced long-wavelength absorptions.

The vibrational spectra of triplet nitrene **2** and dehydrotetraazepine **3** were calculated using density functional theory (B3LYP with a 6-31G\* basis, unscaled).<sup>14</sup> The comparison with



**Fig. 1** (a) UV-VIS spectrum obtained after photolysis (3 h,  $\lambda = 320$  nm) of **1** in Ar, 10 K. (b) UV-VIS spectrum obtained by photolyzing the same sample subsequently with  $\lambda = 475$ –620 nm, 2 h.



**Fig. 2** (a) Difference IR spectrum obtained by subtracting the spectrum of **1** (Ar, 10 K) from the spectrum obtained after 8 min photolysis ( $\lambda = 254$  nm). The bands pointing downward belong to **1**. Bands pointing upward are assigned to **2** and **3**, with the exception of the bands labelled W (water) and R (ring-opened secondary photoproduct). (b) Calculated IR spectrum (UB3LYP 6-31G\*) of triplet nitrene **2**. (c) Calculated IR spectrum of **3** (B3LYP 6-31G\*). The correlation with the experimental spectrum is highlighted by grey shading. The intensity of the band at  $\tilde{\nu} = 1446.4$   $\text{cm}^{-1}$  is ca. 0.2 absorbance units.

the experimental data shows **2** and **3** to be indeed formed as primary products (Fig. 2).<sup>15</sup> This assignment is also consistent with the UV-VIS data, as the characteristics of the product initially formed upon photolysis at 320 nm ( $\lambda_{\text{max}} = 330$  and 356 nm, broad band between 380 and 490 nm) are in line with the expected behavior of a triplet nitrene.<sup>2</sup>

The UV-VIS-spectrum attributed to **3** ( $\lambda_{\text{max}} = 328$  and 352 nm) is very similar to a spectrum obtained by Yamada *et al.*<sup>16</sup> in a glassy EPA matrix at 77 K that was assigned to arise from triplet 4,6-dimethoxy-*s*-triazinyl nitrene. It thus appears likely that the product observed by them has to be reassigned to didehydrotetrazepine **9** or to its trapping products.<sup>17</sup>

The observation of didehydrotetrazepine **3** upon photolysis of azide **1** in an argon matrix could indicate that tetrazepines may

actually be formed in the solution photochemistry of triazinyl azides. Experiments directed towards the isolation of derivatives of these heterocycles therefore may prove useful and are in progress.

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## Notes and references

- M. S. Platz, *Acc. Chem. Res.*, 1995, **28**, 487.
- G. B. Schuster and M. S. Platz, *Advances in Photochemistry*, Wiley, New York, 1992, vol. 17, p. 69.
- N. P. Gritsan, T. Yuzawa and M. S. Platz, *J. Am. Chem. Soc.*, 1997, **119**, 5059.
- R. Born, C. Burda, P. Senn and J. Wirz, *J. Am. Chem. Soc.*, 1997, **119**, 5061.
- W. L. Karney and W. T. Borden, *J. Am. Chem. Soc.*, 1997, **119**, 1378.
- R. A. Evans, M. W. Wong and C. Wenstrup, *J. Am. Chem. Soc.*, 1996, **118**, 4009.
- C. Wenstrup, C. Thétaz, E. Tagliaferri, H. J. Lindner, B. Klitschke, H.-W. Winter and H. P. Reisenauer, *Angew. Chem., Int. Ed. Engl.*, 1980, **19**, 566.
- M. Kuzaj, H. Lüerssen and C. Wenstrup, *Angew. Chem., Int. Ed. Engl.*, 1986, **25**, 480.
- R. Kayama, S. Hasunuma, S. Sekiguchi and K. Matsui, *Bull. Chem. Soc. Jpn.*, 1974, **47**, 2825.
- R. Kayama, H. Shizuka, S. Sekiguchi and K. Matsui, *Bull. Chem. Soc. Jpn.*, 1975, **48**, 3309.
- W. Sander, *J. Org. Chem.*, 1989, **54**, 333.
- Synthesis of 1**: The preparation given before (C. V. Hart, *J. Am. Chem. Soc.*, 1928, **50**, 1928) gave only mixtures of products that could not be separated by crystallization, and the melting point stated to be 85 °C is most likely incorrect. The following method was successful: To a solution of cyanuric chloride (3.000 g, 16.27 mmol) in acetone (20 ml) in a small separation funnel, a solution of  $\text{NaN}_3$  (1.000 g, 15.38 mmol) in water (10 ml) was added and the mixture shaken for 5 min. The organic phase was then separated and allowed to evaporate at room temperature. The crystals were chromatographed (silica gel,  $\text{CH}_2\text{Cl}_2$ –light petroleum = 1:1) to give pure **1** (1.13 g, 5.92 mmol, 36%) as a colorless powder, mp 59.5–61 °C;  $\delta_{\text{H}}$ (300 MHz,  $\text{CDCl}_3$ ) no signal;  $\delta_{\text{C}}$ (75.5 MHz,  $\text{CDCl}_3$ ) 171.39, 172.60;  $m/z$  (FAB) 190.99 (100, M + H<sup>+</sup>);  $\tilde{\nu}_{\text{max}}/\text{cm}^{-1}$  (Ar, 10 K) 2168.9 (s), 1531.0 (vs), 1512.0 (vs), 1396.8 (s), 1295.8 (s), 1268.0 (s), 1187.6 (m), 1159.9 (m), 947.9 (w), 857.2 (m), 803.8 (w), 730.5 (vw).
- The characterization of these final products is in progress; results will be published at a later time.
- GAUSSIAN 98 software was used in the calculations.
- Selected data for 2**:  $\tilde{\nu}_{\text{max}}/\text{cm}^{-1}$  (Ar, 10 K) 1467.6 (s), 1446.4 (vs), 1254.5 (s), 1246.8 (m), 852.9 (w), 848.7 (w), 787.9 (m), 580.0 (w). For **3**:  $\tilde{\nu}_{\text{max}}/\text{cm}^{-1}$  (Ar, 10 K) 1957.0 (vs), 1951.2 (vs), 1550.0 (m), 1546.2 (m), 1110.2 (m), 1050.0 (vs), 814.4. An N=C=N stretching band at  $\tilde{\nu} = 1957.0$   $\text{cm}^{-1}$  for **3** is in the range expected for such a compound. For comparison, simple open-chain *N*-dialkylamino substituted carbodiimides absorb at  $\tilde{\nu} = 2090$   $\text{cm}^{-1}$  (ref. 18). The decrease in frequency in **3** reflects the decrease in bond energy induced by strain. A similar trend has been observed in the case of other cyclic carbodiimides (ref. 6).
- H. Yamada, H. Shizuka and K. Matsui, *J. Org. Chem.*, 1975, **40**, 1351.
- There is a complete lack of absorption beyond  $\lambda = 420$  nm in the spectra given by Yamada *et al.* However, a broad band would be expected for a triplet nitrene. In an EPA matrix, trapping of the didehydrotetrazepine by EtOH has to be considered.
- W. S. Wadsworth, Jr. and W. D. Emmons, *J. Org. Chem.*, 1964, **29**, 2816.

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