Orbital control in the selective photolysis of azido groups of 2,4,6-triazido-3,6-dichloropyridine

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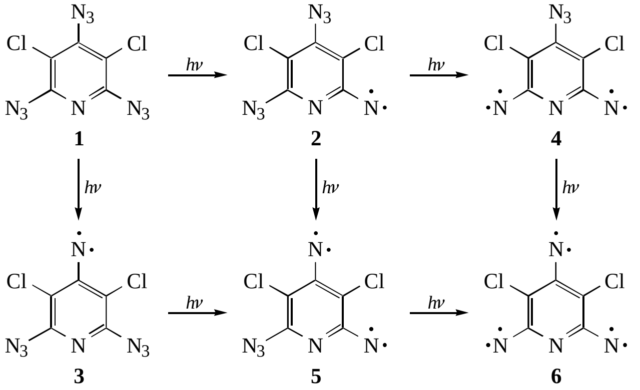
The selective photolysis of α-azido groups in 2,4,6-triazido-3,5-dichloropyridine has been explained by the orbital control of the azido group photodynamic dissociation processes.

The selective cleavage of chemical bonds in organic compounds under exposure to light is of considerable theoretical and practical interest.[1,2] Recently,[3] we found that 2,4-diazidopyridines undergo selective photolysis of the azido groups to form only one of the two possible isomeric triplet nitrenes. These primary photoproducts were tentatively identified as pyridyl-2-nitrenes according to their EPR spectral characteristics. The lack of more solid experimental clarity concerning this selective photolysis of the α-azido groups in the 2,4-diazidopyridines prompted us to reexamine the photochemistry of 2,4,6-triazido-3,5-dichloropyridine **1**, which yields two easily identifiable isomeric quintet dinitrenes **4** and **5** upon irradiation with light at $\lambda > 300$ nm.[4] The predominant formation of one of two possible quintet dinitrene isomers in the selective photolysis of **1** provides information on the sequential decomposition of inequivalent azido groups in the pyridines.

The photolysis of triazide **1** was carried out in degassed frozen solutions of 2-methyltetrahydrofuran (MTHF) at 77 K using monochromatic light at 313 or 335 nm. This allowed us to irradiate **1** at its longest wavelength absorption band extending from 305 to 350 nm (maximum at 333 nm). Furthermore, since many triplet nitrenes also exhibit strong absorption bands at 300–330 nm,[5] the use of light at 313 or 335 nm is favourable for more efficient conversion of mononitrenes **2** and **3** into easily identifiable quintets **4** and **5**. The less selective irradiation of **1** with filtered light at $\lambda > 300$ nm gave rise to a mixture of isomeric triplet nitrenes **2** and **3**, quintet dinitrenes **4** and **5**, and septet trinitrene **6**, displaying characteristic EPR signals at 6821, 7157, 3345, 3009 and 2120 G, respectively.[4]

The EPR spectrum obtained after 10 min irradiation of **1** at 313 nm is shown in Figure 1. The major peak at 3345 G corresponds[†] to quintet dinitrene **4**, while the tiny peak at 3009 G and a signal of moderate intensity at 6821 G belong to quintet dinitrene **5** and triplet nitrene **2**, respectively. A weak signal at 7157 G most likely results from the overlapping signals of triplet nitrene **3** and quintet dinitrene **4**, which both have transitions in this magnetic field.[4] A similar EPR spectrum, but with a more intense signal of **5** at 3009 G, was also obtained after 10 min irradiation of **1** with light at 335 nm. At shorter irradiation times of 3–5 min, only very weak signals at 3345, 6821 and 7157 G were observed, of which the signal at 6821 G was predominant.



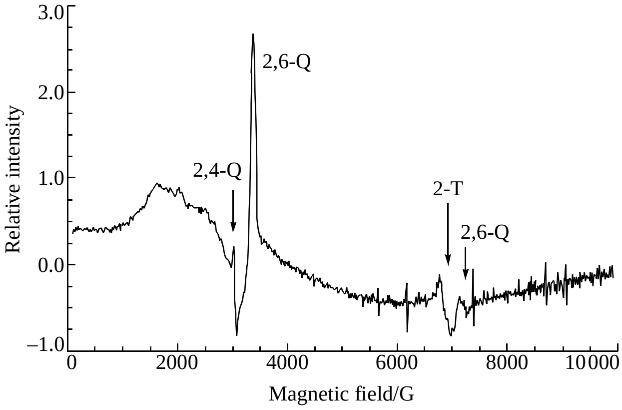


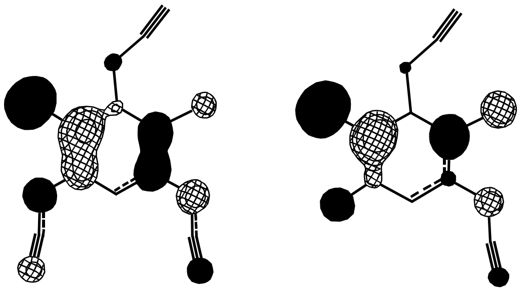
Figure 1 EPR spectrum after photolysis of triazide **1** (ν_0 = 9.606 GHz) with light at λ = 313 nm for 10 min in MTHF at 77 K. The 2-T, 2,6-Q and 2,4-Q peaks correspond to nitrenes **2**, **4** and **5**, respectively. A peak at 7157 G may result from overlapping signals from triplet **3** and quintet **4**.

The results unambiguously show that triazide **1** undergoes selective deazetation of the α-azido groups upon irradiation with light at 313 or 335 nm to form quintet dinitrene **4** as the main photoproduct. The selectivity of the reaction is somewhat lower with the use of light at 335 nm. These effects can be explained in terms of photodynamically controlled dissociation processes. Thus, according to the theory,[6] the higher energy of two excited states is less stable and decomposes more rapidly (fast diabatic dissociation).[7] During continuous irradiation, when the energy of excitation substantially exceeds the energy gaps between the ground and two different excited states of molecules, the photoproducts predominantly arise from the less stable excited state. The shorter the irradiation wavelength, the higher the selectivity of such reactions due to the larger population of high-energy excited states.[2]

The PM3 computations[‡] of two parent excited states corresponding to the local[2,3] excitation of the α- and γ-azido groups in **1** and **2** (*e.g.*, α-T_0 and γ-T_0 triplet excited states for **1** or α-Q_0 and γ-Q_0 quintet excited states for **2**) demonstrated that the α-excited states of **1** and **2** are 2 and 8 kcal mol^{-1} higher in energy than the γ-excited states, respectively. This suggests that the photodissociation of α-azido groups in both azides should be preferred. The smaller energy gap between the α-T_0 and γ-T_0 excited states of **1** also suggests that trace amounts of **5** formed in the reaction can be explained by partial photolysis of triazide **1** to nitrene **3** followed by deazetation of the latter.

[†] No signal of radical impurity from MTHF was detected on irradiation of **1** with light at 313 nm for 10 min. This signal usually appears at about 3400 G and has the characteristic hyperfine splitting.[8]

[‡] The structures of triplet and quintet excited states for **1** and **2** were calculated with the full geometry optimization parameters using the PM3 method (UHF, SCF level).[9] The energies of the α-T_0 and γ-T_0 triplet excited states of **1** and of the α-Q_0 and γ-Q_0 quintet excited states of **2** were calculated as described earlier[3] using the preliminary computational distortion of the N–N–N angle in an appropriate azido group to 135°.



HOMO of **1** HOMO of **2**

Figure 2 The orbital density distribution in the HOMO of **1** and **2**. The higher bonding orbital density at the N$_\alpha$ atom of the α-azido groups in the HOMO of **1** and **2** indicates that α-excited states of **1** and **2** should be less stable and more readily undergo fast diabatic dissociation.

The non-degeneracy of the α- and γ-excited states for **1** and **2** derives from an inequivalent distribution of the bonding orbital density in the α- and γ-azido groups of starting compounds (Figure 2). Because of stronger bonding interactions in the α-azido groups of **1** and **2**, the local excitation of these groups requires more energy. In principle, the non-equivalent distribution of the HOMO orbital density in two azido groups makes possible selective decomposition of either of these groups under appropriate photolysis conditions. Thus, an azido group with the lowest HOMO orbital density should theoretically[6] decompose first on selective excitation of polyazides in their lowest excited states (slow adiabatic photodissociation).[7] The reactions described belong to another type of photochemical transformations, which can occur only on excessive irradiation of the starting polyazides.

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