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# Nitrene—carbene rearrangement during photolysis of 2-azido-1,3,5-triazines in argon matrices*

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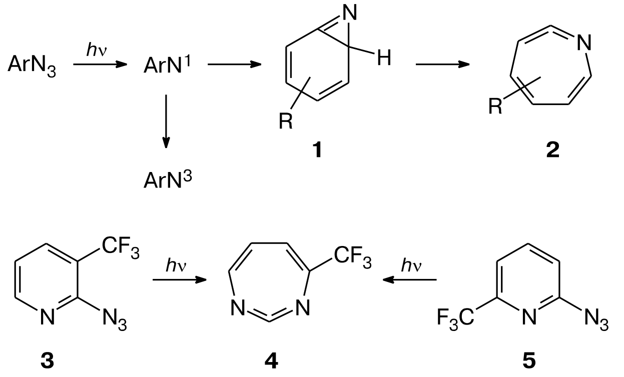
It was shown using IR spectroscopy and ESR spectroscopy that UV irradiation of 2-azido-4,6-dichloro-1,3,5-triazine isolated in solid argon resulted in triplet 4,6-dichloro-1,3,5-triazinyl-2-nitrene ($D = 1.384\ \mathrm{cm}^{-1}$, $E = 0.004\ \mathrm{cm}^{-1}$), whose further photochemical transformation included the consecutive formation of 3-didehydro-1,2,4,6-tetraazepine, 2-chloro-1-diazochloromethyl-2-isocyanocarboimide, and presumably triplet 2-chloro-1-chloromethylidene-2-isocyanocarboimide and isocyanodichloroacetonitrile. The photolysis of 2-azido-4,6-dimethoxy-1,3,5-triazine and 2-azido-4,6-di(dimethylamino)-1,3,5-triazine affords photochemically stable triplet 4,6-dimethoxy-1,3,5-triazinyl-2-nitrene ($D = 1.436\ \mathrm{cm}^{-1}$, $E = 0.0044\ \mathrm{cm}^{-1}$) and 4,6-bis(dimethylamino)-1,3,5-triazinyl-2-nitrene ($D = 1.468\ \mathrm{cm}^{-1}$, $E = 0.0042\ \mathrm{cm}^{-1}$) as the final products.

**Key words:** azidotriazines, nitrenes, carbenes, photolysis, matrix isolation, electron paramagnetic resonance, IR spectroscopy.

Photochemistry of aryl azides attracts attention of researchers due to a wide use of these azides as photoresists in microelectronics, photoactive cross-linking additives in polymer chemistry, and photoaffinic reagents in molecular biology.[1—5] According to a commonly accepted point of view, the mechanism of photolysis of aryl azides includes the photodissociation of the $N—N_2$ bond with the generation of singlet nitrene $ArN^1$, which further either relaxes to more stable triplet nitrene $ArN^3$, or undergoes intramolecular rearrangements to bicyclic azirines **1** and didehydroazepines **2** (Scheme 1).[5] In the case of photolysis of 2-azidopyridines, the insertion of nitrene into the pyridine ring always proceeds at the β-bond. For instance, photolysis of azides **3** and **5** in argon at 7 K gives exclusively 2-didehydro-1,3-diazepine **4**. It is almost impossible to detect intermediate pyridylnitrenes by IR spectroscopy because of their very high reactivity (see Scheme 1).[6] The IR spectra of triplet pyridylnitrenes have been recorded for the first time during the photolysis of 4-azidotetrafluoro- and 4-azidotetrachloropyridines in which the halogen atoms spatially protected the pyridine ring from the reaction with nitrene.[7]

**Scheme 1**



Taking into account the available data on photochemistry of phenyl- and pyridylazides, it was especially interesting to study the photolysis of azido-*sym*-triazines **6a—c**, during which intermediate nitreno-*sym*-triazines **7a—c** have to intramolecularly attack the nitrogen atom of the triazine ring to form a weak N—N bond (Scheme 2). Didehydrotetraazepines **8a—c**, representing a new type of heterocyclic systems, could be possible products of these reactions. It was also interesting to study further photochemical transformations of compounds **8a—c** and a possibility to detect nitrenes **7a—c** using IR spectroscopy.

In the present work we report the detection of a new rearrangement of arylnitrenes by matrix IR spectroscopy. This rearrangement includes the two-step photochemical transformation of nitrene **7a** into diazo compound **9**, whose subsequent photolysis presumably affords carbene **10** and acetonitrile **11** (see Scheme 2). These photochemical

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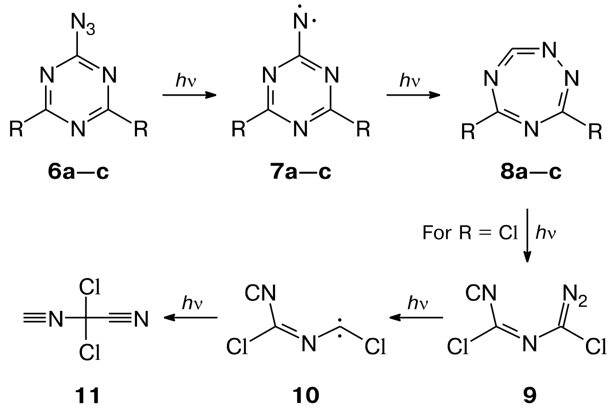
**Scheme 2**



R = Cl (**a**), OMe (**b**), NMe$_2$ (**c**)

transformations were shown to be characteristic only of nitreno-*sym*-triazines bearing the electron-withdrawing substituents in the triazine ring. The preliminary results of this study have been published earlier.[8]

## Experimental

Azides **6a—c** were synthesized by known procedures.[9,10]

ESR spectra were recorded on a Bruker ESP-300 instrument with the working region from 0 to 1000 mT in solutions of 2-methyltetrahydrofuran (MTHF) frozen at 77 K. The microwave frequency during ESR spectra recording of the paramagnetic photolysis products of azides **6a—c** was 9.520 GHz.

**Experimental procedure.** A weighed sample containing 1 mg of azide was dissolved in 10 mL of MTHF freshly distilled over LiAlH$_4$, and the solution was placed in a standard 4-mm quartz cell designed for ESR spectra recording. The solution was deaerated by three cycles of freezing at 77 K, evacuating of air in high vacuum ($5 \cdot 10^{-6}$ atm), and thawing out. The ampule with the degassed solution was filled with argon, sealed off, and placed in a spectroscopic cell cooled to 77 K. The light source was a low-pressure mercury lamp with a power of 1000 W, the wavelength of the emitted light being 254 nm. The sample was placed at a distance of 30 cm from the light source and irradiated recording ESR spectra at an interval of 1, 5, 10, 20, and 30 min. Computer simulation of the ESR spectra and the calculation of the fine structure parameters *D* and *E* were performed using the EasySpin program package based on the exact numerical solution of the spin-Hamiltonian.[11]

Argon (purity 99.999%) and a Leybold—Heraus ROK 10-300 cryostat with circulating liquid helium were used to prepare argon matrices alloyed with azides. The matrices were prepared by a method similar to that described earlier.[12] IR spectra were recorded on a Perkin—Elmer FTIR 2000 instrument.

The IR spectra, geometric parameters, and spin density distribution for nitrene molecules were calculated using the UB3LYP/6-31G* method from the GAUSSIAN-94 program package.[13] All calculations were performed with the full optimization of molecular geometry. Theoretical IR spectra were used without additional scaling.

## Results and Discussion

Photolysis of azide **6a** in a solution of MTHF frozen at 77 K with light at $\lambda = 254$ nm resulted in the appearance of two characteristic ESR signals of triplet nitrene **7a** at 774 and 795 mT corresponding to the lines $X_2$ and $Y_2$ of transitions of triplet molecules with the high parameters *D* and *E* (Fig. 1, *a*). Similar ESR spectra were observed for photolysis of azides **6b**,**c** (see Fig. 1, *b* and *c*). The lines of the $X_2/Y_2$ transitions of triplet nitrenes **7b**,**c** appeared at 785/809 and 793/816 mT, respectively. Computer simulation of the experimental ESR spectra showed the magnetic parameters of triplet nitrenes **7a—c** given below.

| **7** | $D$/cm$^{-1}$ | $E$/cm$^{-1}$ |
|---|---|---|
| **a** | 1.384 | 0.0040 |
| **b** | 1.436 | 0.0044 |
| **c** | 1.468 | 0.0042 |

The results obtained demonstrate that the enhancement of the electron-donating properties of the substituents in the triazine ring favors spin density localization on the nitrene centers of compounds **7a—c**. This means that the ability of the aromatic system to withdraw the spin density from the nitrene center decreased with an increase in the electron density on the atoms of the aromatic ring. The decrease in the degree of conjugation of the nitrene center with the aromatic ring also appears as an elongation of the C—N nitrene bond, which is indicated by the quantum chemical calculation data for triplet molecules **7a—c** (Table 1).

The previous studies showed[14—18] that the magnetic parameters *D* of triplet phenylnitrenes, pyridylnitrenes, and pyrimidylnitrenes were 0.88—1.10, 0.96—1.12, and 1.13—1.25 cm$^{-1}$, respectively. The highest value of parameter *D* equal to 1.480 cm$^{-1}$ was observed for triplet 4-azido-6-dimethylamino-2-nitreno-*sym*-triazine.[8] The data presented clearly demonstrate that the introduction of nitrogen atoms into the aromatic ring favors spin density localization on the nitrene centers of arylnitrenes. Triplet nitrene **7c** obtained in this work has one of the highest magnetic parameters *D* for arylnitrenes. The higher pa-

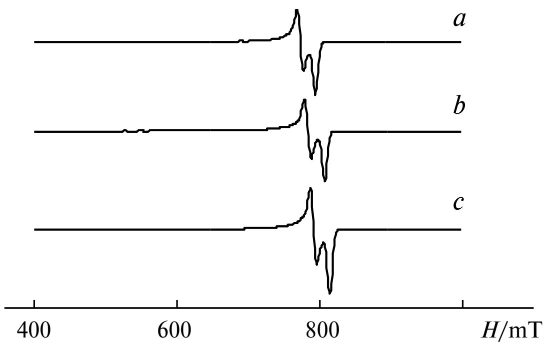


**Fig. 1.** ESR spectra of triplet nitrenes **7a** (*a*), **7b** (*b*), and **7c** (*c*).

**Table 1.** Parameters $D$ and the data of calculations of the spin density on the nitrene centers ($\rho_N$), nitrene bond lengths ($d_{C-N}$), and charges on the nitrogen atoms of the nitrene center ($q_N$) and triazine ring ($q_{N1}$) in molecules of compounds **7a—c**, PhN$^3$, and **13**

| Nitrene | $D$/cm$^{-1}$ | $\rho_N$ | $d_{C-N}$/Å | $q_N$ | $q_{N1}$ |
|---|---|---|---|---|---|
| **7a** | 1.384 | 1.7549 | 1.366 | −0.1951 | −0.3560 |
| **7b** | 1.436 | 1.7791 | 1.371 | −0.2302 | −0.4873 |
| **7c** | 1.468 | 1.7930 | 1.378 | −0.2528 | −0.5222 |
| PhN$^3$ | 0.999[a] | 1.6001 | 1.328 | −0.3641 | +0.0241[b] |
| **13** | 1.402[c] | 1.7700 | 1.371 | −0.2160 | −0.4398, −0.4643[d] |

[a] See Ref. 15.

[b] The C atom in the *ortho*-position to nitrene.

[c] See Ref. 19.

[d] The charges on the nitrogen atoms in positions 3 and 5 of the triazine ring towards which the azido groups of nitrene **13** occupy the *anti*- and *syn*-conformations, respectively.

rameter $D$, the stronger magnetic properties of the molecule. According to the general theory, the higher parameter $D$ and spin state S, the higher the ability of molecular systems to magnetization

$$\Delta E_a = DS^2. \quad (1)$$

According to Eq. (1), the energy barrier between the magnetic states $W_1$ and $W_{-1}$ in nitrene **7c** is 1.468 cm$^{-1}$ (4.2 cal mol$^{-1}$). Interestingly, the energy barrier between magnetic states $W_3$ and $W_{-3}$ in recently[19] obtained septet 2,4,6-trinitreno-*sym*-triazine (S = 3, $D$ = 0.123 cm$^{-1}$, $E$ = 0) turned out to be 25% lower ($\Delta E_a$ = 1.107 cm$^{-1}$).

Prolonged (30 min) irradiation of frozen solutions of azides **6a—c** did not result in any new ESR signals along with the signals from triplet nitrenes **7a—c**, which remained the single paramagnetic products stable in MTHF at 77 K. In order to obtain complete information on all possible photolysis products of azides **6a—c**, we studied photolysis of these azides in argon at 16 K using IR spectroscopy capable of detecting both paramagnetic and diamagnetic reaction products.

Photolysis of azides **6b,c** in argon at 16 K resulted in the gradual disappearance of the IR bands of the initial azides and the appearance of new absorption bands at 1525, 1518, 1452, 1403, 1352, 1284, 1242, 1182, 1110, 1093, 941, 808, 708, and 597 cm$^{-1}$ (in the reaction with **6b**) and at 1483, 1416, 1185, 1149, 930, and 787 cm$^{-1}$ (in the reaction with **6c**). New absorption bands well coincided with the IR spectral bands of triplet nitrenes **7b,c** calculated by the UB3LYP/6-31G* method (Fig. 2). No formation of any other paramagnetic and diamagnetic products, for example, cyclic carbodiimides **8b,c**, whose IR spectra should contain a strong absorption band at 1950 cm$^{-1}$ (see Ref. 20), was observed. After the complete decomposition of azides **6b,c** and the appearance of bands of nitrenes **7b,c**, the IR spectra further remained unchanged during prolonged (>10 h) irradiation of the matrices with light at λ = 254, 308, and >420 nm. The results showed that the only products of photolysis of azides **6b,c** were photochemically very stable triplet nitrenes **7b,c**.

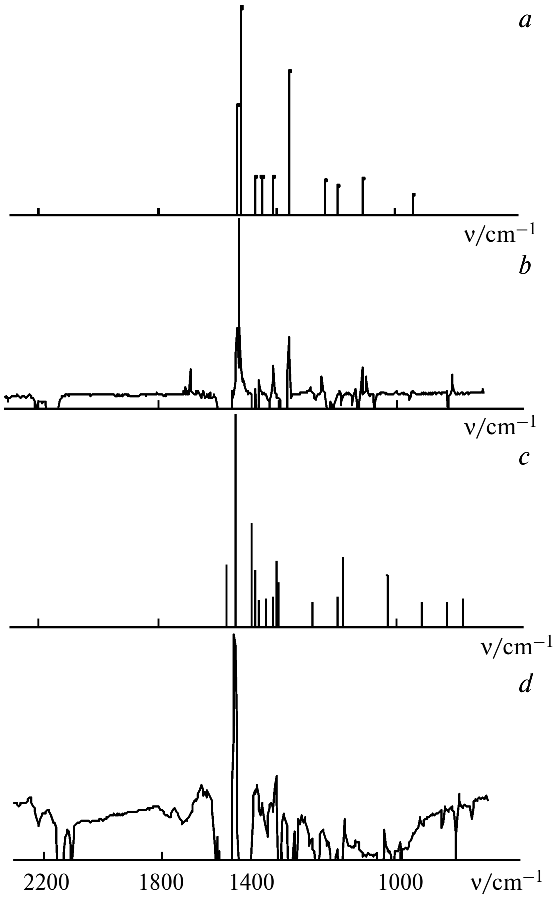


**Fig. 2.** IR spectra of triplet nitrenes **7b** (*a*, *b*) and **7c** (*c*, *d*): calculated (*a*, *c*) and differential (*b*, *d*).

Under similar conditions, photolysis of azide **6a** proceeded quite differently. Three products were formed already at the early stages of photolysis (10 min): triplet nitrene **7a** (bands at 1467, 1446, 1254, 1245, 988, 852, 788, and 588 cm$^{-1}$), cyclic carbodiimide **8a** (bands at 1951, 1546, 1110, 1049, 813, 668, and 624 cm$^{-1}$), and diazo compound **9** (bands at 2092, 2088, 1088, and 708 cm$^{-1}$). The observed bands of these compounds coincided well with the IR spectral bands calculated by the UB3LYP/6-31G* method (Fig. 3). It is likely that the fourth product of this reaction is triplet carbene **10**, which should inevitably formed upon photolysis of diazo compound **9**. According to the calculated data, carbene **10** has the ground triplet state, whose energy is 32.2 kcal mol$^{-1}$ lower than the energy of the excited singlet spin state. The IR spectrum of this carbene should contain four medium-intensity absorption bands at 2085 (185 km mol$^{-1}$), 1620 (205 km mol$^{-1}$), 1113 (219 km mol$^{-1}$), and 701 cm$^{-1}$ (240 km mol$^{-1}$). The cal-

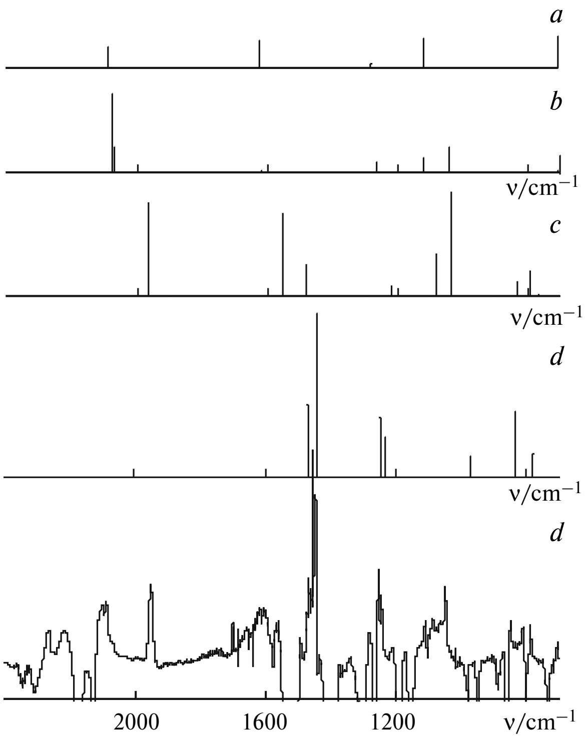


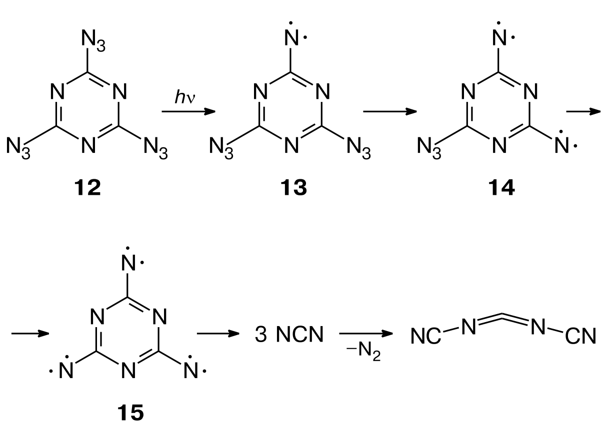
**Fig. 3.** Calculated IR spectra of triplet carbene **10** (*a*), diazo compound **9** (*b*), didehydrotetraazepine **8** (*c*), and triplet nitrene **7a** (*d*) and the differential IR spectrum of the mixture after photolysis (10 min) of azide **6a** (*e*).

culated absorption bands of carbene **10** correspond to the experimentally observed IR bands at 2088 and 708 cm$^{-1}$ and, most likely, they are overlapped with the absorption bands of the starting diazo compound **9** at 2078 (566 km mol$^{-1}$) and 704 cm$^{-1}$ (130 km mol$^{-1}$). Two other absorption bands of carbene **10** (at 1620 and 1113 cm$^{-1}$) are disguised by the absorption of molecular water at 1630—1600 cm$^{-1}$ and the negative-intensity absorption band of azide **6a** in the differential IR spectrum (see Fig. 3). Longer (>1 h) irradiation of the matrix resulted in the gradual disappearance of the IR absorption bands of compounds **7a**, **8a**, and **9** and an increase in the intensity of the absorption bands at 2263 and 2210 cm$^{-1}$ presumably attributed to isocyanodichloroacetonitrile **11** (see Scheme 2). Theoretically assumed triplet carbene **10** should be detected by ESR spectroscopy. However, extensive studies showed[21,22] that the most part of aliphatic carbenes have very low kinetic stability in frozen solutions and readily react with MTHF at $T > 15$ K. Therefore, the absence of signals from triplet carbene **10** in the ESR spectra of the photolysis products of azide **6a** in MTHF solutions frozen at 77 K seems quite regular.

The low photochemical stability of triplet nitrene **7a** and surprisingly high photochemical stability of triplet nitrenes **7b**,**c** can be explained by analyzing the charge distribution in molecules of these nitrenes (see Table 1). It is considered that didehydroazepines **2** are formed predominantly as a result of rearrangements of singlet arylnitrenes; however, there are convincing experimental data[18,23–25] that indicate the equilibrium character of photochemical mutual transformations of triplet arylnitrenes and didehydroazepines. In particular, it has previously[7] been shown that photolysis of 4-azidotetrafluoropyridine in argon at 7 K at the initial reaction stages gave a mixture of the corresponding triplet pyridyl-4-nitrene and didehydrodiazepine. The latter rearranged completely at the deeper photolysis stages to form triplet pyridyl-4-nitrene. Similar transformations of triplet phenylnitrene and didehydroazepine were observed[24] during photolysis of phenyl azide. Based on these data, we may conclude that compound **8a** can be formed as the product of photochemical rearrangement of triplet nitrene **7a**. In the course of this rearrangement the negatively charged nitrene nitrogen atom ($q_N = -0.1951$) should attack the negatively charged nitrogen atom of the triazine ring ($q_{N1} = -0.3560$). Evidently, the higher the negative charges on the interacting atoms, the lower the probability of the rearrangement of nitrenes **7a**—**c** to compounds **8a**—**c**. This is observed for triplet nitrenes **7a**—**c** in which the negative charges on the nitrogen atoms of the nitrene center and the triazine ring increase appreciably with the enhancement of the electron-releasing properties of the substituents in the triazine ring (see Table 1). Very high negative charges on these atoms of triplet nitrenes **7b**,**c** prevent the interaction of these atoms and rearrangement of the nitrenes to form didehydrotetraazepines **8b**,**c**. Triplet phenylnitrene is especially easily rearranged.[24] The calculations show that this nitrene has a positive charge on the carbon atom in the *ortho*-position to the nitrene center (see Table 1).

It has recently been found[19,26] that photolysis of triazide **12** in solid nitrogen at 15 K proceeded without rearrangements of nitrenes to products of cycle expansion, giving consecutively triplet nitrene **13**, quintet dinitrene **14**, and septet trinitrene **15** (Scheme 3). The latter turned out

**Scheme 3**



to be photochemically labile and decomposed to three triplet molecules of NCN, which then interacted with each other to form dicyanocarbodiimide NC—N=C=N—CN. The studied process of photolysis of triazide **12** made it possible to explain the formation of carbide—nitride nanomaterials $C_3N_4$ upon the decomposition of this triazide under detonation conditions.[26]

The absence of cycle expansion products during photolysis of triazide **12** is consistent with our conclusions. For instance, the calculations show that triplet nitrene **13** has $q_N = -0.2160$ and $q_{N1} = -0.4398$ and $-0.4643$* and, hence, should not rearrange to the corresponding didehydrotetraazepine (see Table 1). It can be assumed that the photochemical rearrangement of triplet 1,3,5-triazinylnitrenes to didehydrotetraazepines becomes difficult if $(q_N + q_{N1}) < -0.6$.

Thus, it is shown in the present work that photolysis of 2-azido-1,3,5-triazines can result in the formation of both photochemically stable and photochemically labile triplet nitrenes. The first group includes triazinylnitrenes with strong electron-releasing substituents in the ring. These nitrenes have the high spin density on the nitrene nitrogen atoms ($\rho_N \geq 1.77$) and the high magnetic parameter ($D > 1.4$ cm$^{-1}$) and can be interesting for the production of magnetic materials. The second group consists of triazinylnitrenes with electron-withdrawing substituents in the ring. Their striking representative is nitrene **7a**. It can easily be rearranged under irradiation to form the corresponding didehydrotetraazepine **8a**, which then undergoes ring opening and photolysis with the consecutive formation of diazo compound **9** and presumably carbene **10** and acetonitrile **11**.

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* Non-equivalence of charges on the nitrogen atoms of the triazine ring is caused by different spatial orientation of the azide groups in a molecule of nitrene **13**.