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PROPERTIES OF TRIPLET TETRACHLORO-4-PYRIDYLNITRENE ISOLATED IN INERT MATRICES

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Photolysis of 4-azidotetrachloropyridine isolated in inert matrices at low temperatures leads to formation of triplet tetrachloro-4-pyridylnitrene as the sole product of the photochemical reaction. In the EPR spectrum, this nitrene gives an intense signal and is characterized by zero-field splitting parameters. The UV spectrum of nitrene in solid argon contains a series of high-intensity and medium-intensity absorption bands. The IR spectrum in solid argon agrees well with nonempirical and semiempirical calculations. On exposure to light, nitrene easily reacts with molecular carbon(II) oxide, forming the corresponding isocyanate. Irradiation with light does not result in formation of bicyclic azirine, but initiates the reverse reaction of fixation by nitrene of the molecular nitrogen contained in the solid argon, leading to the starting azide.

Keywords: azides, nitrenes, pyridines, IR spectroscopy, matrix isolation, photolysis, EPR.

The photochemistry of aromatic azides has attracted attention in connection with their widespread use as photoresists in microelectronics and photoaffinity labels in molecular biology and biochemistry [1-3]. Using EPR spectroscopy, it has been demonstrated that the mechanism of photolytic decomposition of arylazides **1** includes intermediate formation of nitrenes **2**, generally having a triplet ground spin state [4, 5]. The subsequent fate of arylnitrenes is mainly determined by the structure of their aromatic ring, the photolysis conditions, and the nature of the environment. Thus in the absence of *ortho* substituents at the nitrene center, even at 8 K arylnitrenes undergo fast ring expansion to form azaheptatetraenes **3** [6-9]. The latter are found in equilibrium both with the starting nitrenes **2** and with the structurally isomeric pyridylcarbenes **4**. Both equilibria are so strongly shifted toward formation of azaheptatetraenes **3** that for a long time, the presence of compounds **2** and **4** in the equilibrium mixture could be detected only by EPR spectroscopy [10-12]; the interconversion of **2** and **3** has been studied only recently by IR spectroscopy [8].

One of the most hotly debated questions in discussion of the mechanism of the interconversions between nitrenes **2** and azaheptatetraenes **3** and between the azaheptatetraenes and pyridylcarbenes **4** is still the hypothesis that bicyclic azirines **5** participate as intermediates in these reactions. Although there have been reports in the literature about IR spectra being recorded for azirines **6-9**, formed during photolysis of the corresponding azides [13, 14], in our opinion the evidence presented in the papers for the structure of such compounds does not seem completely convincing.

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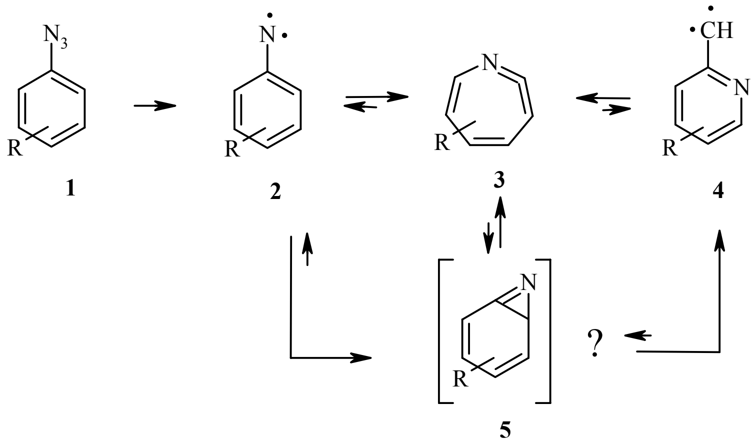

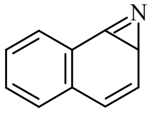

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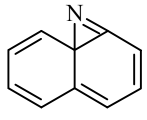

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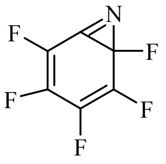

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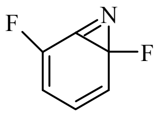

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From a practical standpoint, the most interesting studies are of arylnitrenes having *ortho* substituents at the nitrene center in the aromatic ring. Such nitrenes do not undergo undesirable intramolecular rearrangements and react with organic compounds exclusively at the nitrene center [15, 16]. Owing to the high stability of the *ortho*-disubstituted arylnitrenes in inert matrices at low temperatures, the UV [14, 17], IR [8, 14-16], and EPR [4, 5] characteristics have been studied for a number of representatives of compounds in this class. However, the properties of heterocyclic analogs of phenylnitrene stabilized in inert matrices have not be able to be obtained and studied.

In this work, for the first time we have studied the UV, IR, and EPR characteristics of triplet tetrachloro-4-pyridylnitrene that has been isolated in inert matrices, and we have also studied its photochemical conversions under various photolysis conditions and in the presence of CO.

Irradiation of 4-azidotetrachloropyridine (**10**) in 2-methyltetrahydrofuran at 77 K by exciting light with wavelength $\lambda > 300$ nm for 5 min caused the sample to acquire a blue color and the appearance in the EPR spectrum of an intense signal for triplet nitrene **11** with center at 7045 G. The zero-field splitting parameters of nitrene **11** ($S = 1$, $g = 2.003$) were: $|D/hc| = 1.040$, $|E/hc| = 0.000$ cm^{-1}. Comparing the values of the parameters $|D/hc|$ for compound **11** and the previously investigated 2-pyridylnitrenes (1.108-1.051 cm^{-1} [5, 9]) and 3-pyridylnitrenes (1.005 cm^{-1} [4,5]), we may arrive at the conclusion that nitrene **11** occupies an intermediate position between 2-pyridylnitrene and 3-pyridylnitrenes with respect to the degree of delocalization of the π-unpaired electron in the aromatic system. The absence of any signals of the photolysis products of azide **10** in the 4500-6000 G regions in the EPR spectrum suggested that the nitrene **11** formed does not undergo intramolecular rearrangement to form hetarylcarbenes of type **4** [9].

In contrast to EPR spectroscopy, the IR spectroscopy method makes it possible to follow photochemical conversions of compounds which do not have paramagnetic properties. The IR spectrum of azide **10**, isolated in solid argon, is presented in Fig. 1*a*; the absorption band frequencies are presented in Table 1.

Along with the characteristic signals of the azide group in the 2143-2082 cm^{-1} region and at 1332 cm^{-1}, the azide spectrum contains intense absorption bands for the pyridine ring at 1528, 1513, and 1412 cm^{-1}, and also weak bands at 750, 732, and 727 cm^{-1} assigned to stretching vibrations of the C–Cl bonds. Irradiation of the matrix with exciting light ($\lambda > 290$ nm) caused it to rapidly acquire an intense blue color. In this case, in the IR spectrum we observed a gradual decrease in the intensity of the absorption bands for the starting azide and the

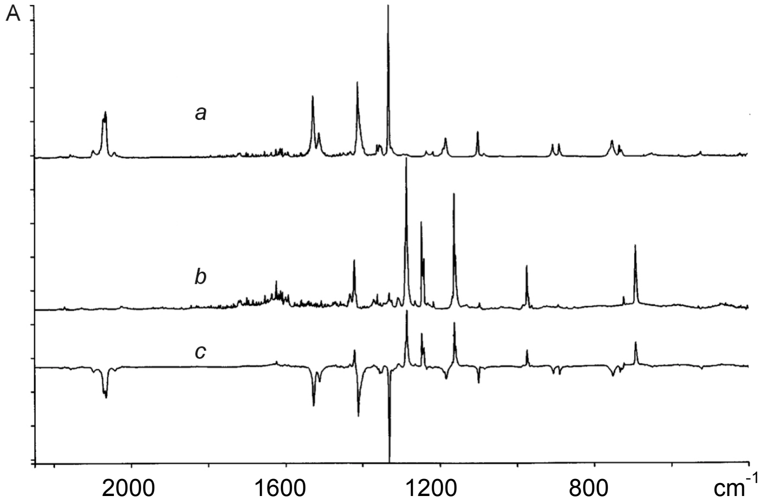

Fig. 1. IR spectra in solid argon at 7 K for azide **10** (*a*), nitrene **11** (*b*); difference IR spectrum obtained by subtracting the spectrum of azide **10** from the spectrum of nitrene **11** (*c*).

appearance of a group of new bands. Complete decomposition of the azide was achieved after 2 h of continuous irradiation. During this entire time period, in the spectrum we did not observe the appearance of any new bands in the 2000-1600 cm^{-1} region which could be assigned to intermediates **12** and **14**. The IR spectrum of the end products of photolysis for azide **10** is presented in Fig. 1*b* and in the form of a difference spectrum in Fig. 1*c*. Comparing these spectra, it is easy to notice that each of them contains the same new absorption bands at 1433, 1421, 1285, 1246, 1240, 1162, 1158, 974, 721, and 691 cm^{-1}.

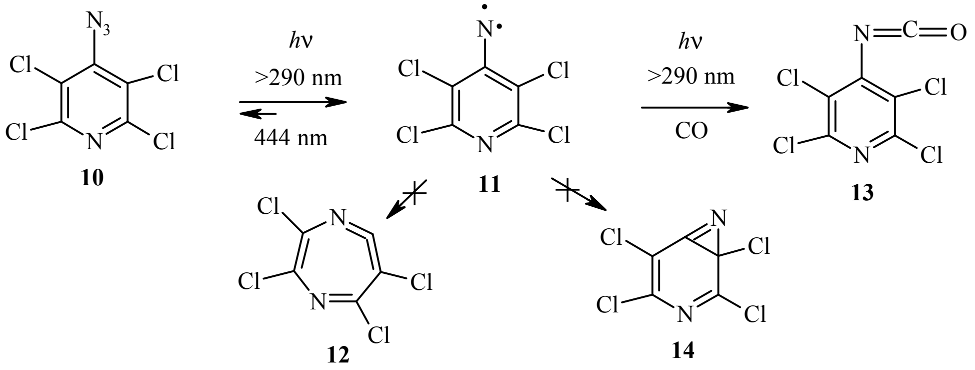

TABLE 1. IR Spectrum of Azide **10**

Frequency, ν (cm^{-1})	Intensity, I (%)	Frequency, ν (cm^{-1})*	Intensity, I (%)	Frequency, ν (cm^{-1})^{*2}	Intensity, I (%)
2139	0.26	1351	0.06	1084	0.02
2130	0.31	1332	1.00	905	0.08
2082	0.03	1233	0.03	888	0.09
1528	0.41	1216	0.03	750	0.11
1513	0.16	1190	0.05	732	0.07
1412	0.50	1183	0.13	727	0.04
1356	0.06	1100	0.17	648	0.01

The authors of the only paper [18] on simulation of IR spectra for triplet and singlet phenylnitrene using nonempirical methods noted that the calculated values for the absorption frequency of triplet nitrene that are about 10% higher than the experimental ones. Calculations using higher basis sets made it possible to achieve better agreement between the theoretically calculated and experimentally measured differences in the energies of the triplet and singlet phenylnitrenes, which also served as a criterion for the accuracy of the calculations [18-20]. With higher basis sets for the calculations, the geometry of the triplet phenylnitrene molecule was increasingly more accurate, especially the C–N bond length (Table 2).

With the objective of developing a simpler method for identification of triplet arylnitrenes based on quantum-chemical methods, we calculated the geometry of the same molecule using the UHF/PM3-SCF semi-empirical method. From the data in Table 2, we see that the geometric parameters calculated by this method for the triplet phenylnitrene molecule practically coincide with the results of *ab initio* calculations of the IR spectrum of triplet nitrene **11** in the CASSCF(8,8)/6-31G* basis set. Based on this, we may conclude that the UHF/PM3-SCF method quite adequetely describes the properties of arylnitrenes, and as needed may successfully replace more laborious nonempirical calculations for large organic molecules.

In Table 3, we present the frequencies of the absorption bands for the photolysis product of azide **10** and the spectrum of triplet nitrene **11** calculated theoretically by UHF/PM3-SCF and *ab initio* in the UB3LYP/6-31G* basis set. The closeness of all three spectra provides a basis for saying that the new compound obtained during photolysis of azide **10** is triplet pyridylnitrene **11**.

Since the calculations yielded values of the nitrene absorption frequencies that were too high, we introduced correction factors: 0.977 for the UB3LYP/6-31G* method and 0.94 for the UHF/PM3-SCF method. The values of the correction factors were found by dividing the frequency of the most intense absorption band in the experimentally obtained spectrum at 1285 cm^{-1} by the frequency of the most intense absorption in the theoretically calculated spectrum. The presence in the experimental spectrum of two pairs of intense bands at 1247, 1240 cm^{-1} and 1162, 1158 cm^{-1} and only one band each at the same frequencies in the simulation spectra makes it possible to suggest that the doubling of the bands at 1240 cm^{-1} and 1162 cm^{-1} in the experimental spectrum is probably due to effects of the packing of the nitrene molecules in the solid argon rather than to intrinsic features of the structure of nitrene itself. Heating the matrix up to 35 K did not lead to any appreciable changes in the IR spectrum of nitrene **11**, except for some change in the intensity ratio of the bands at 1247, 1240 cm^{-1} and 1162, 1158 cm^{-1}. It is important to note that with subsequent lowering of the matrix temperature down to 7 K, the previous intensity ratio of the indicated bands is no longer restored, thus supporting the conclusion that their doubling in the IR spectrum is connected with matrix effects. Irradiation of nitrene **11** with exciting light ($\lambda > 290$ nm, 10 h) did not cause any changes in the IR spectrum, which suggested rather high photostability of this nitrene relative to exposure to such light. In the IR spectra of azide **10** and nitrene **11**, note the significant shift toward lower frequencies of the absorption bands for the pyridine ring, due to replacement of the azide group by a nitrene center (from 1528 and 1513 cm^{-1} for azide **10** to 1433 and 1421 cm^{-1} for nitrene **11**). This effect indicates that with the appearance of a nitrene substituent, the pyridine ring becomes less

TABLE 2. Geometric Parameters of Triplet Phenylnitrene from *ab initio* Calculations in DZ SCF, MCSCF(8,8)/3-21G*, DZ+d CISD, CASSCF(8,8)/6-31G* Basis Sets and UHF/PM3-SCF Semiempirical Method Calculations

Parameter	DZ SCF [18]	3-21G* [19]	DZ+d CISD [18]	6-31G* [20]	PM3 SCF
$C_{(1)}$–N	1.431	1.402	1.388	1.338	1.326
$C_{(1)}$–$C_{(2)}$	1.398	1.404	1.403	1.425	1.434
$C_{(2)}$–$C_{(3)}$	1.393	1.391	1.390	1.386	1.387
$C_{(3)}$–$C_{(4)}$	1.396	1.396	1.396	1.404	1.402

TABLE 3. Experimental and Calculated (UB3LYP/6-31G* and UHF/PM3-SCF) IR Spectrum of Nitrene **11**

Experiment		UB3LYP/6-31G*		UHF/PM3-SCF	
frequency, ν ($\mathrm{cm^{-1}}$)	intensity, *I* (%)	frequency, ν ($\mathrm{cm^{-1}}$)*	intensity, *I* (%)	frequency, ν ($\mathrm{cm^{-1}}$)*[2]	intensity, *I* (%)
1433	0.09	1464	0.03	1468	0.03
1421	0.32	1435	0.32	1442	0.16
1361	0.09	—	—	1377	0.01
1285	1.00	1278	1.00	1281	1.00
1247	0.58	1238	0.42	1260	0.22
1240	0.33	—	—	—	—
1162	0.76	1206	0.42	1198	0.43
1158	0.36	—	—	—	—
—	—	1082	0.04	1080	0.08
974	0.29	949	0.28	929	0.53
892	0.01	870	0.01	886	0.00
721	0.05	708	0.01	694	0.03
691	0.39	670	0.31	610	0.51

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* Correction factor 0.977.

*[2] Correction factor 0.94.

aromatic due to its strong conjugation with the nitrene center. We can arrive at the same conclusion as a result of analysis of other absorption bands in the IR spectra of pyridines **10** and **11**. It was shown earlier that the vibrational frequencies of the C–N bond in the IR spectra of anilines and substituted phenylazides lie in the 1100-1200 $\mathrm{cm^{-1}}$ region, while for triplet phenylnitrene they are seen at 1287 $\mathrm{cm^{-1}}$ [18]. In analogy with these data, the bands at 1183 and 1285 $\mathrm{cm^{-1}}$ in the IR spectrum of respectively azide **10** and nitrene **11** may be assigned to vibrations of the C–N bond. The 102 $\mathrm{cm^{-1}}$ shift toward higher frequencies of the vibrations of the C–N bond of nitrene supports a predominantly double-bond character for this bond. PM3 calculations show that the length of the C–N bond in molecules **10** and **11** is respectively 1.420 and 1.322 Å.

In Fig. 2, we show the UV spectrum of the starting azide **10** isolated in solid argon and the triplet nitrene **11** formed during its photolysis.

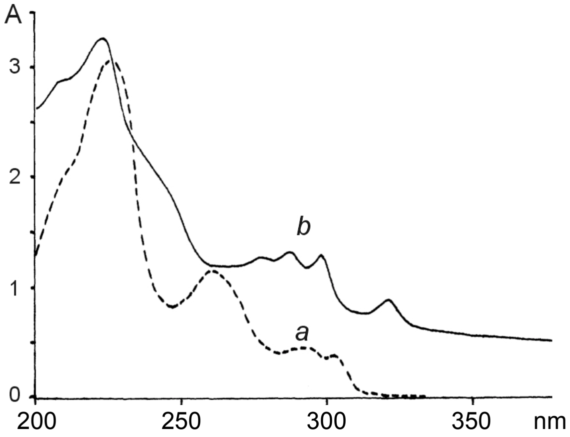


Fig. 2. UV spectra in solid argon at 12 K for azide **10** (*a*) and nitrene **11** (*b*).

In addition to the easily distinguished absorption bands with maxima at 223, 278, 287, 298, 320, and 322 nm, the UV spectrum of nitrene contains two bands of very low intensity with maxima at 383 and 400 nm. The most intense band at 223 nm has a shoulder in the 240-250 nm region. Comparing the UV spectra of the starting azide and nitrene **11**, it is easy to notice that the major difference between the spectral characteristics of these compounds is associated with the absence in the nitrene spectrum of an absorption band with maximum at 261 nm, characteristic of arylazides [2], and the appearance of a new band of medium intensity with maximum at 320 nm, typical for most arylnitrenes [17]. On the whole, the UV spectrum of nitrene **11** is very close to the spectrum of 2,6-difluorophenylnitrene, which also has three absorption regions with maxima at 236, 284, and 312 nm [14].

With the objective of studying the chemical properties of nitrene **11**, we investigated the reaction of this compound with carbon(II) oxide. Irradiation of pentafluorophenylazide in an argon matrix containing 12% CO by exciting light with wavelength > 300 nm leads to formation of pentafluorophenylnitrene, which when exposed to light with wavelength > 330 nm reacts with the CO, forming the corresponding isocyanate [15]. In this case, due to the reversibility of the photochemical reaction, the final IR spectrum of the photolysis products simultaneously contained characteristic signals of both the isocyanate obtained and the starting nitrene.

The IR spectra of azide **10** in solid argon containing 13% CO and also the products of its photochemical decomposition after 1.5 h and 3 h of continuous exposure to exciting light with wavelength > 290 nm are presented in Fig. 3*a*-*c*.

The intense absorption at 2196, 2143, 2140, 2092, and 2050 cm^{-1} in all three spectra belongs to vibrations of the CO triple bond [21], which is superimposed on the absorption of the azide group of pyridine **10** in the 2143-2130 cm^{-1} region. The IR spectrum obtained after 1.5 h of continuous irradiation (Fig. 3*b*) contains easily distinguished signals from the starting azide **10** and the nitrene **11** formed during its photolysis. Furthermore, in the spectrum we see a new and rather intense band at 2263 cm^{-1}, which indicates the presence of isocyanate **13** among the photolysis products. Thus the N=C=O group of the closest analog of **13**, tetrachloro-2-pyridylisocyanate, gives an absorption at 2250 cm^{-1} [22], while biphenyl derivatives in solid argon give an absorption at 2264 cm^{-1} [21]. Subtraction of the characteristic signals for pyridines **10** and **11** from the spectrum allowed us to identify a number of other absorption frequencies for isocyanate **13**, specifically at 1558, 1523, 1420, 1371, 1364, 1334, 1321, 1235, 1167, 1113, 1097, 921, 890, 739, and 718 cm^{-1}, which were rather close to

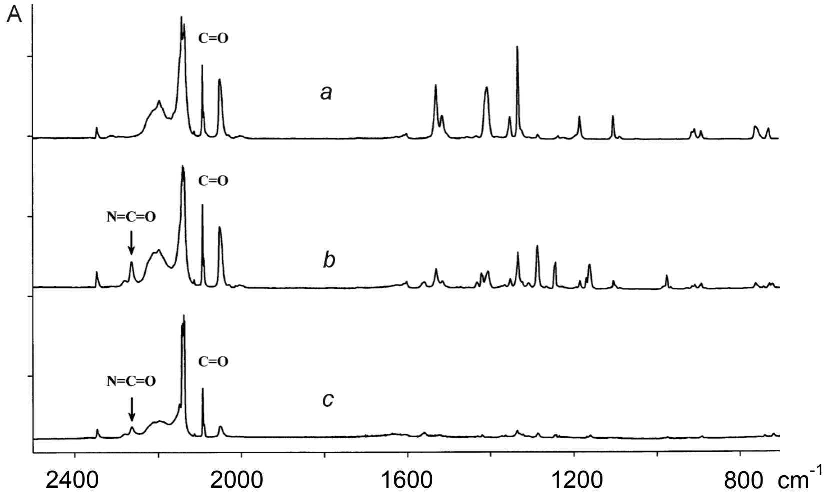


Fig. 3. IR spectra in solid argon containing 13% CO, azide **10** (a), photolysis products of azide **10** in solid argon containing 13% CO, after 1.5 h of continuous exposure to exciting light with λ > 290 nm (*b*) and the IR spectrum of the photolysis products of azide **10** in solid argon containing 13% CO, after 3 h of continuous exposure to exciting light with λ > 290 nm (*c*).

the vibrational frequencies of azide **10** (Table 1). Considering the presence in the UV spectrum of nitrene **11** of a whole series of absorption bands in the region above 290 nm (see Fig. 2), the reaction of this nitrene with CO on exposure to light with wavelength > 290 nm is represented by a quite characteristic process. New features compared with the result of the previously studied photochemical reaction of CO with pentafluorophenylnitrene include the rather high photostability of isocyanate **13** relative to comparatively hard radiation and consequently formation of this compound even in the early stage of photolysis of azide **10**. Longer exposure of azide **10** (3 h, Fig. 3*c*) led to its complete decomposition and formation of pyridines **13** and **11** as the major and minor products respectively. In this case, the simultaneous presence among the photolysis products of isocyanate **13** and nitrene **11** was evidence for the equilibrium character of this reaction.

One of the most hotly debated questions in discussion of the mechanism of photolytic decomposition of arylazides is still the hypothesis that bicyclic azirines **5** participate as intermediates in these reactions. It has been shown that prolonged exposure of 2,6-difluoro- and pentafluorophenylnitrene in solid argon to exciting light with wavelength of 444 nm leads to formation of new compounds that in the author's opinion are azirines **8** and **9** [14]. On exposure to short-wavelength light (λ = 336 nm), these compounds undergo the reverse reaction, forming the starting nitrenes. The authors discussed the hypothesis that all prior attempts to record the IR spectra of bicyclic azirines were unsuccessful due to irradiation of nitrenes by light with λ < 444 nm.

With the objective of determining the possibility of formation of azirine **14**, we studied the action of light with λ = 444 nm on nitrene **11**. The close correspondence between the UV spectra of this nitrene and the previously studied 2,6-difluorophenylnitrene [14] provided a basis for assuming that the photochemical conversions of these compounds should be similar. In Fig. 4, we present the IR spectrum of the photolysis products of nitrene **11** obtained after 12 h of continuous exposure.

Careful study of this spectrum and also the difference spectrum obtained from the spectra of the nitrene before and after photolysis did not reveal the presence of absorption bands for any new compound. However, after irradiation, the intensity of the characteristic signals for the nitrene was reduced somewhat (negative absorption in the difference spectrum at 1285, 1246, 1241, 1165, and 1153 cm^{-1}), and very weak absorption bands from the azide **10** appeared in the spectrum at 2143, 1412, 1332, and 1100 cm^{-1}. The same conversions were observed earlier on exposure of phenylnitrene to light with λ > 450 nm, but the authors did not ascribe any

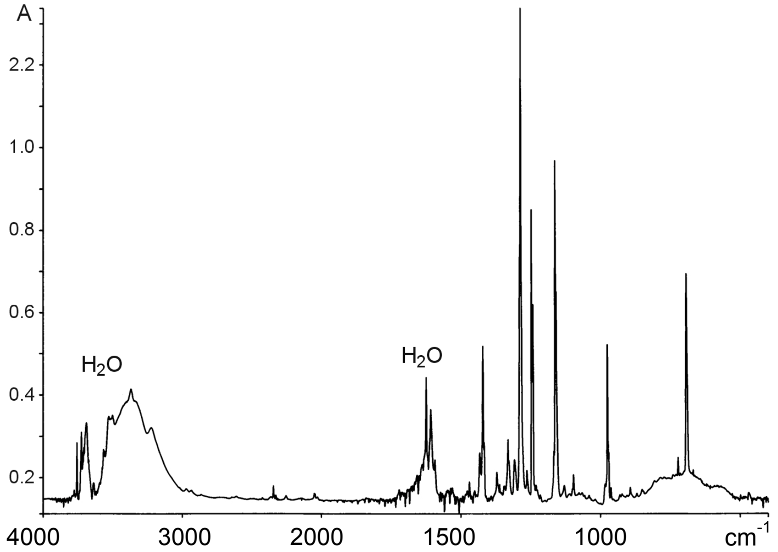


Fig. 4. IR spectrum of photolysis products of nitrene **11** in solid argon at 7 K after 12 h of continuous exposure to light with λ = 444 nm.

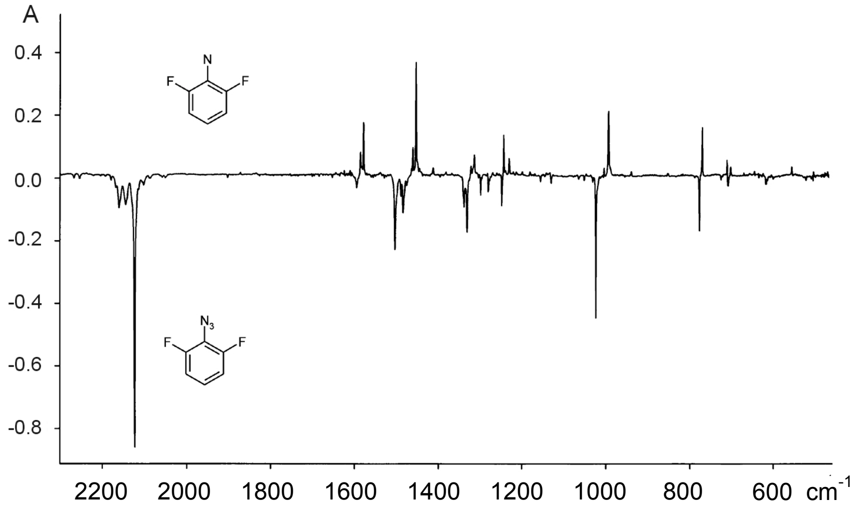


Fig. 5 Difference IR spectrum, obtained by subtracting the spectrum of azide **15** from the spectrum of nitrene **16** (Ar, 7 K).

special importance to this [8]. Moreover, considering the known ability of methylcarbene to photochemically react with molecular nitrogen to form diazomethane [23], it is reasonable to hypothesize that regeneration of azide **10** on exposure of nitrene **11** to light with λ = 444 nm is caused by the reverse photochemical reaction of nitrene with molecular nitrogen present in the argon matrix after decomposition of azide by light with λ > 290 nm. On the whole, the photochemical reaction of nitrene **11** with molecular nitrogen may be considered as a close analogy to the reaction of the same nitrene with CO. Recording the UV spectra of arylnitrenes in solid argon on a BaF_2 or sapphire surface [14] does not make it possible to observe the longer wavelength absorption band of such compounds that is responsible for their violet color and is found in the 500-550 nm region [17, 18]. However, it is specifically this absorption band that corresponds to the energy for excitation of triplet nitrene to singlet nitrene [18] and obviously corresponds to photochemical fixation of molecular nitrogen and CO by nitrenes.

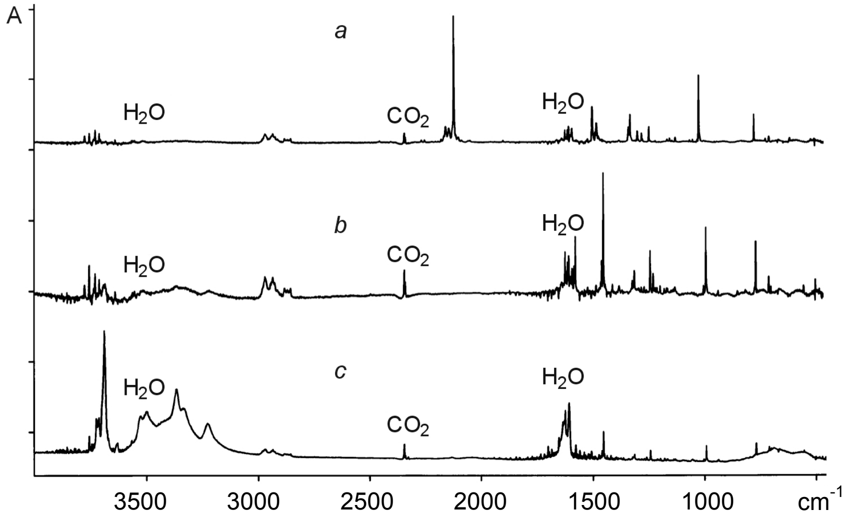


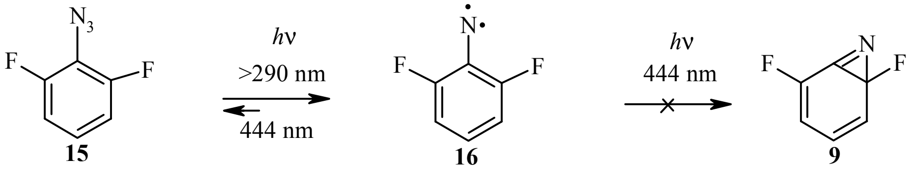
Fig. 6. IR spectra in solid argon at 7 K for azide **15** (*a*), nitrene **16** (*b*), and the photolysis products of nitrene **16** in solid argon at 7 K after 54 h of continuous exposure to light with λ = 444 nm (*c*).

The absence of any new products on exposure of nitrene **11** to light with λ = 444 nm encouraged us to again study the photochemical conversion of 2,6-difluorophenylnitrene to azirine **9**. In Fig. 5, we show the difference spectrum, the lower part of which corresponds to the IR spectrum of the starting azide **15** and the upper part of which corresponds to the IR spectrum of nitrene **16** obtained on exposure of azide **15** to light with λ > 290 nm for 3 h.

The IR spectrum we recorded for nitrene **16** completely corresponds to the literature data [14].

In Fig. 6*c*, we show the IR spectrum for the same nitrene, recorded after 54 h of continuous exposure to light with λ = 444 nm. Study of this spectrum and also the difference IR spectrum obtained from the spectra of nitrene **16** before and after photolysis did not reveal any changes indicating formation of azirine **9** upon photolysis of this nitrene.

The main feature of the IR spectrum of the photolysis products of nitrene **16** (Fig. 6*c*) compared with the spectra of the starting azide **15** (Fig. 6*a*) and nitrene **16** (Fig. 6*b*) is the high intensity of the signals for molecular water in the 3800-3000 cm^{-1} and 1700-1600 cm^{-1} regions, caused by the increase of the water content in the matrix as a result of the prolonged experiment. A similar increase in the intensity of the signals for molecular water was also observed in the IR spectrum of the photolysis products of nitrene **11** (Fig. 4). In analysis of the spectrum of the photolysis products of nitrene **16** (Fig. 6*c*), especially note the very intense absorption band for water at 1608 cm^{-1}. It is specifically the band at 1609.8 cm^{-1} that was previously indicated as the most intense in the IR spectrum of azirine **9** [14]. In our opinion, assignment of this band to the signal for any new compound formed upon photolysis of nitrene **16** is rather doubtful. We note that a whole series of other signals, especially at 1412, 1318, 1259, and 1180 cm^{-1}, that were previously ascribed to azirine **9**, were already present as very weak absorption bands in the IR spectrum of the starting nitrene **16** (Fig. 5), and subsequent photolysis of this nitrene by light with λ = 444 nm results in practically no change in their intensity. Obviously these signals likewise cannot be assigned to any photochemical conversion product of this nitrene. Based on all these data, we propose that nitrene **16**, like its heterocyclic analog **11**, when exposed to light with λ = 444 nm does not tend to undergo intramolecular cyclization with formation of bicyclic azirines; but as in the case of photolysis of nitrene **11**, prolonged exposure of nitrene **16** to light with λ = 444 nm caused some decrease in the intensity of characteristic signals for nitrene and the appearance of very weak absorption bands for the starting azide **15** at 2123, 1503, 1483, 1331, 1023, and 775 cm^{-1}.



Our study revealed that the only direction of photochemical decomposition of 4-azidotetrachloropyridine in inert matrices at low temperatures is formation of triplet tetrachloropyridyl-4-nitrene, whose UV, IR, and EPR characteristics are close to the analogous characteristics of various derivatives of triplet phenylnitrene. On exposure to light with λ > 290 nm, this nitrene easily reacts with CO, forming the corresponding isocyanate. Although the nitrene obtained is stable relative to exposure to short-wavelength radiation, light with λ = 444 nm initiates its photochemical reaction with molecular nitrogen, leading to regeneration of the starting azide.

EXPERIMENTAL

4-Azidotetrachloropyridine and 2,6-difluorophenylazide were synthesized by the known methods [24, 25].

The EPR spectrum was recorded on a Bruker ESP-300 with working range from 100 G to 9900 G. The microwave frequency was determined using a Hewlett-Packard 5350B counter. The zero-field splitting parameters were calculated by the known method [26].

A weighed sample containing azide (2 mg) was dissolved in 2-methyltetrahydrofuran (0.5 ml) that was freshly distilled over $LiAlH_4$, and placed into a standard quartz ampule designed for taking EPR spectra. The solution was degassed and then the cycle of freezing at 77 K, pumping out the air under high vacuum ($5 \cdot 10^{-6}$ atm), and thawing was repeated three times. The ampule with the degassed solution was frozen at 77 K, sealed, and placed in a liquid-nitrogen filled Suprasil II that was part of the spectroscopic cell. The light source was a 1000 W high-pressure xenon lamp equipped with a 150 mm water filter. The sample was placed at a distance of 30 cm from the radiation source, and exposed for 5 min to light with $\lambda > 300$ nm, using a Pyrex filter.

The IR spectra were recorded on a Perkin-Elmer FTIR 2000 with resolution 1 cm^{-1}. To prepare the matrices, we used argon (99.999% pure), carbon(II) oxide (99.999% pure), and a Leybold-Heraus ROK 10-300 cryostat with circulating liquid He. The matrices were made by deposition of argon (or an 87:13 Ar/CO, %) and azide vapors (mole ratio azide/Ar, 1:1000, deposition rate 0.1 mmol/min) onto the surface of a CsI spectroscopic window, cooled down to 25 K and placed in a vacuum chamber ($5 \cdot 10^{-6}$ atm). The IR spectra were recorded for a matrix temperature of 7 K. In irradiation of the matrices, we used a 1000 W Hanovia high-pressure mercury-xenon lamp equipped with a 150 mm water filter, and also a monochromator or a set of filters. The spectra were processed using the program Spectrum for Windows, Version 1.30, 1996 (Perkin-Elmer Corporation).

The UV spectra were recorded on a Varian Cary 1. The matrices were made similarly to the procedure described above except that the content of starting azide in them was about 10 times less. As the spectroscopic window, we used a disk made from BaF_2, which allowed us to record the UV spectra in the region from 200 nm to 450 nm. For recording the spectra, the temperature of the matrices was lowered down to 12 K.

The vibrational frequencies in the IR spectrum of nitrene were calculated using the UHF/PM3-SCF semiempirical method, included in the MORAC 7.0 software package [27], and the UB3LYP/6-31G* nonempirical method, included in the GAUSSIAN 94 software package [28]. The vibrational frequencies were calculated after full optimization of the geometry of the triplet ($S = 1$) nitrene molecule.

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