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Study of photochemical transformations of organic azides by matrix isolation techniques and quantum chemistry

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Contents

I.	Introduction	1139
II.	Detection and properties of the simplest nitrene NH	1140
III.	Photochemical transformations of alkyl azides	1141
IV.	Photochemical transformations of acyl azides	1143
V.	Photochemical transformations of aryl azides	1146
VI.	Reactions of triplet nitrenes with oxygen	1153
VII.	Conclusion	1157

Abstract. Results of investigations of organic azide photochemistry in inert gas matrices and the most important spectroscopic studies of the last decade, which formed the basis for the modern views on the photochemistry of azides, are analysed. The unique potential of the matrix isolation technique for the reliable identification of reaction intermediates is demonstrated. The bibliography includes 226 references.

I. Introduction

The term 'matrix isolation' was introduced by Pimentel [1,2] and Porter [3] in 1954 to describe the technique in which the substrate in a mixture with an inert gas is deposited onto a rather cold surface providing rapid freezing of the mixture. This gives rise to solid samples in which (in the ideal case) each substrate molecule is surrounded by one or several layers of the inert gas and is thus isolated from other substrate molecules. Argon, neon, nitrogen, their mixtures and xenon are most commonly used as inert gases. The technical details of the method and its numerous applications have been considered in a series of monographs and reviews.[4–10]

In the course of time, the term 'matrix isolation' came to be applied in a more general sense, encompassing a range of techniques where substrate (guest) molecules are trapped in a solid inert material (host). Crystals, zeolites, polymers, *etc*. can serve as such materials. Numerous studies of reaction intermediates were carried out in frozen glassy organic solvents. This method of investigation is also sometimes referred to as the matrix isolation. However, in the present review the term matrix isolation will be used only in its original sense.

Two presently available methods for the detection and investigation of reaction intermediates are based on either time-resolved spectroscopic techniques or the stabilisation of intermediates in different matrices at low temperatures and their studies by conventional spectroscopic methods. In the former case, not only spectroscopic but also kinetic data can be obtained. In the latter case, the structures of possible intermediates can be more reliably predicted due to more detailed spectroscopic information. The use of the matrix isolation techniques is particularly promising in combination with IR spectroscopy of intermediates, because well-resolved IR spectra with a linewidth of $\sim 1-3$ cm^{-1} can be recorded in inert gas matrices at very low temperatures even for rather complex species in a very wide spectral range.

In early studies on the matrix isolation, the assignment of bands in IR spectra of intermediates was based primarily on the record of the characteristic absorption bands with a wide use of the isotopic substitution, reactions of primary intermediates, *etc*. The interpretation of experimental IR and electronic absorption spectra was greatly simplified due to the development of accurate theoretical methods for their calculation. For example, good agreement between calculated and experimental IR spectra can be achieved with the use of the density functional theory (DFT). The hybrid B3LYP method [11,12] with the 6-31G* basis set is most widely used for this purpose. In these calculations, the vibrational frequencies are somewhat overestimated, which is accounted for by introducing the correction coefficient of 0.9614.[13]

The positions of maxima in electronic absorption spectra and the oscillator strengths for transitions can also be calculated by quantum chemical methods with good accuracy. The CASSCF/CASPT2 approach,[14,15] which is implemented, for example, in the MOLCAS programme package,[16] provides the most accurate results. The time-dependent DFT method [17,18] also gives reliable results, particularly, for systems with closed-shell electronic configurations.

The aim of the present review is to analyse the role of the matrix isolation technique in revealing the mechanisms of photolysis of certain classes of organic azides. Organic azides have found use as photoresists in lithography,[19] in the design of conducting polymers,[20] organic synthesis,[21] photoaffinity labelling of biopolymers [22] and covalent labelling of the polymer surface.[23–25] Numerous spectroscopic studies of the intermediates of the organic azides photolysis were performed in the gas phase, in low-temperature glasses and inert gas matrices, and in solutions using time-resolved methods. The results of early studies were summarised in reviews (see, for

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example, Refs 26–31). The data obtained by the matrix isolation technique were considered in reviews.[32, 33]

In the last decade, there has been dramatic progress in the understanding of the mechanisms of photochemical transformations of alkyl, acyl and aryl azides. The successful use of time-resolved spectroscopic methods for the detection of singlet arylnitrenes (primary photolysis products of aryl azides) and high-level quantum chemical calculations for the analysis of the spectra and reactivity of these compounds provided a detailed understanding of the complex mechanism of the phototransformations of aryl azides.[34–37] A considerable progress in the elucidation of the unusual nature of singlet acylnitrenes was achieved due to the use of the matrix isolation technique combined with high-level quantum chemical calculations.[38–40]

In the present review, the results of studies on photochemistry of alkyl, aryl and acyl azides in inert gas matrices are analysed. The most interesting recent data obtained with the use of time-resolved methods and the most important spectroscopic and theoretical results underlying the modern views on the photochemistry of azides are considered.

II. Detection and properties of the simplest nitrene NH

Singlet nitrenes are the primary photolysis products of most of azides.[36, 37] Almost all nitrenes exist in the triplet ground state.[29–31, 35–37] (Acylnitrenes considered in Section IV are exceptions.)

The imino radical NH generated in the photolysis,[41–46] thermolysis[47] or the multiphoton dissociation[48, 49] of hydrazoic acid is the simplest nitrene.

Pimentel and co-workers[50] were the first to study the photolysis of HN_3 by the matrix isolation technique. The IR spectrum of the photolysis products was recorded in an argon and nitrogen matrices, and a series of lines in the spectrum were assigned to nitrene NH and the radical NH_2. This publication was followed by a number of investigations of matrix-isolated nitrene NH and its deuterium-substituted analogue (ND) both in the triplet ground state $^3\Sigma^-$ and the excited metastable state $^1\Delta$ by UV and luminescence spectroscopy.[51–55] The spectroscopic characteristics and the relaxation of the lowest excited singlet state of nitrene NH (or ND) ($^1\Delta$) in Ne, Ar, Kr and Xe matrices were studied in detail.[54, 55] The diagram of the lowest energy levels of the NH radical (Fig. 1) can be constructed based on the results of spectroscopic investigations in matrices[54, 55] and in the gas phase.[41–46]

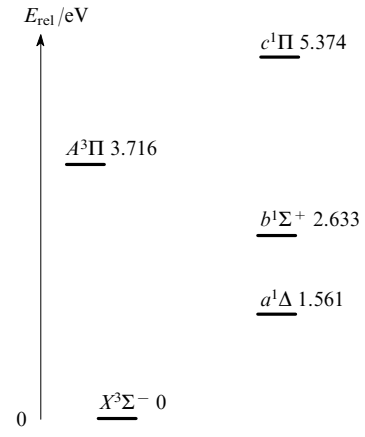


Figure 1. Energy level diagram for nitrene NH based on experimental data.[41–46, 54, 55]

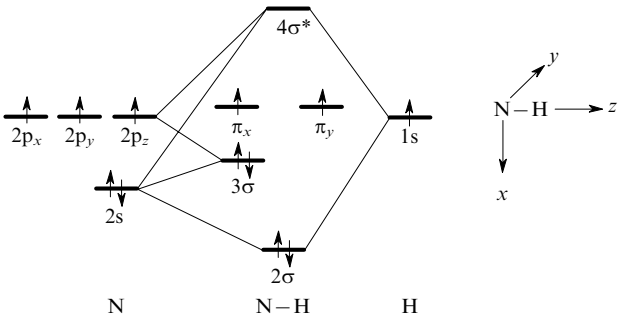


Figure 2. Molecular orbitals of nitrene NH.
(The 1σ orbital, the 1s atomic orbital of the nitrogen atom, is omitted.)

A knowledge of the electronic structure and the spectra of the simplest nitrene is very useful in the analysis of more complex nitrenes formed by the photolysis of alkyl, acyl and aryl azides. In the NH species, the molecular orbital (MO) corresponding to the N–H bond (2σ) and the MO of the nitrogen lone pair (3σ) are occupied by electron pairs (Fig. 2). Two valence electrons should be distributed between two degenerate antibonding MO, π_x and π_y. This electronic configuration gives rise to three lowest electronic states (terms) of NH, $^3\Sigma^-$, $^1\Delta$ and $^1\Sigma^+$; the triplet state $^3\Sigma^-$ is the ground state (Fig. 3). This figure gives also components of the doubly degenerate lowest singlet state $^1\Delta$ with the closed- and open-shell electronic configurations and the electronic state $^1\Sigma^+$. Two configurations, which are mixed in the lowest singlet state $^1\Delta$ with a minus sign, are mixed with a plus sign in the state $^1\Sigma^+$. It can easily be demonstrated that in this state the probability of finding two non-bonding electrons at a single point in the space is much higher compared to the state $^1\Delta$ and consequently the energy of the state $^1\Sigma^+$ is substantially higher.

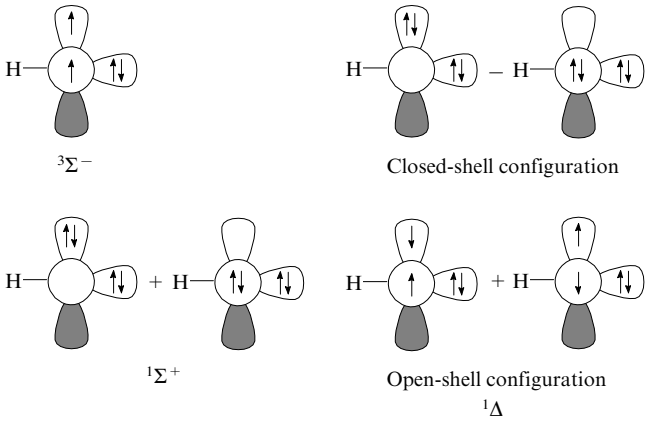


Figure 3. Schematic representation of the electronic states of nitrene NH: one of three spin components of the lowest triplet state $^3\Sigma^-$, two components of the lowest singlet state $^1\Delta$ (having the closed- and open-shell electronic configurations) and the second singlet state $^1\Sigma^+$.

The electronic absorption spectra of NH both in the triplet ground state ($^3\Sigma^-$) and the lowest singlet state ($^1\Delta$) show intense lines in the near-UV region with maxima at 336 and 324 nm, respectively.[41, 46] Both transitions are associated with the electron excitation from the lone pair (3σ) to the π orbital occupied by one electron (π_x or π_y in Fig. 2). This transition is

observed also in the electronic absorption spectra of other organic nitrenes (see Sections III and V).

III. Photochemical transformations of alkyl azides

Photolysis of alkyl azides, including those in which the azido group is bound to the tertinary carbon atom, in solution at room temperature affords the corresponding imines or their further transformations products in quantitative yields.[56, 57] No reaction products of alkylnitrenes with solvents or active additives could be detected.[57]

The photochemistry of the simplest alkyl azide, *viz*., methyl azide, was studied in sufficient detail,[57–60] including the use of the matrix isolation technique.[61, 62] According to the IR spectroscopic data, the photolysis of methyl azide and its different isotopically substituted analogues in Ar, N_2 and CO_2 matrices at 4 and 14 K gives methyleneimine as the only product.[61, 62] It cannot be ruled out that singlet methylnitrene is the primary species formed in the photolysis of methyl azide; however, this species readily undergoes isomerisation to methanimine even at cryogenic temperatures and has no time to relax to the triplet ground state.

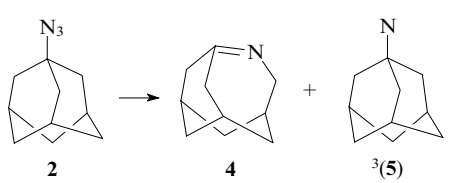
$$CH_3N_3 \xrightarrow[4\,K]{h\nu} {}^1[CH_3N] \longrightarrow H_2C{=}NH$$

In subsequent studies, emphasis was given to the matrix photochemistry of alkyl azides in which the azide group is bound to the tertiary carbon atom. The absence of the α-H atom gave promise that the rate of isomerisation of singlet alkylnitrene to imine would be lower, thus making possible the relaxation of singlet alkylnitrene to the triplet ground state. The photolysis of *tert*-butyl azide in a nitrogen matrix was performed at 12 K.[63] Imine **1** was detected by IR spectroscopy as the only reaction product.

$$Me_3CN_3 \xrightarrow[-N_2]{h\nu} \underset{\mathbf{1}}{Me_2C{=}NMe}$$

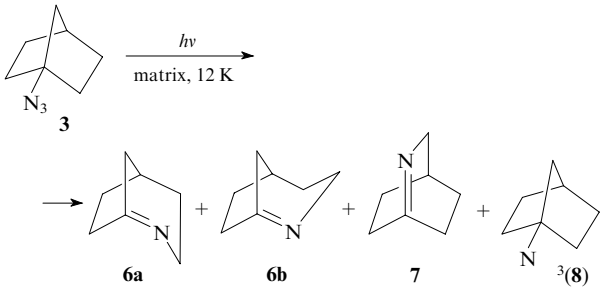
The formation of strained bridgehead imines was observed in the photolysis of matrix-isolated bridgehead azides, for example, of adamantyl, bicyclo[2.2.2]octyl, bicyclo[3.2.1]heptyl and norbornyl azides.[64–68] The matrix photochemistry of 1-azidoadamantane (**2**)[67] and 1-azidonorbornane (**3**)[68] was studied in most detail.

The low-temperature photolysis of azide **2** in argon and nitrogen matrices, 3-methylpentane glasses, a polyethylene matrix and the solid state afforded strained imine **4**, which was characterised by IR, electronic absorption, Raman and circular dichroism spectra, along with trace amounts of triplet 1-adamantylnitrene ^{3}(**5**), which was identified from the ESR spectrum at 8210 G ($E = 0$, $|D/hc| = 1.69$ cm^{-1}) and based on the reaction with CO.[67] Heating of the matrices (for example, to 36 K in the case of an argon matrix) led to dimerisation of imine **4**.



2 **4** ^{3}(**5**)

1-Azidonorbornane (**3**) was irradiated in an argon or polyethylene matrix at 12 K using monochromatic radiation with different wavelengths, and the reaction products were identified by IR, UV and ESR spectroscopy method, as well as based on the reaction with methanol or CO.[68] The photolysis of azide **3** is a more complex process compared to the photolysis of azide **2**. Three types of imines (**6a**,**b** and **7**) and trace amounts of triplet nitrene **8** were detected.[68] Imines **6** and **7** are light-sensitive, undergo interconversions and are decomposed to unidentified products.

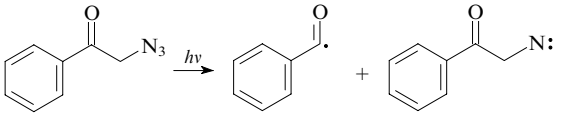


3 **6a** **6b** **7** ^{3}(**8**)

Triplet nitrene **8** was identified based on the ESR signal at 8124 G ($E = 0$, $|D/hc| = 1.65$ cm^{-1}), the narrow band in the electronic absorption spectrum at 298 nm and its reaction with CO in an argon matrix at 36 K.[68]

Since the photolysis of alkyl azides in solution, low-temperature glasses and inert gas matrices affords the corresponding imines as the major primary products, it was hypothesised[57] that the elimination of molecular nitrogen from alkyl azides in the excited singlet state and the formation of imine are concerted processes and occur without the involvement of singlet alkylnitrene as an intermediate. This hypothesis has been neither confirmed nor denied experimentally.

Since the irradiation of alkyl azides in inert gas matrices and low-temperature glasses affords triplet alkylnitrenes only in trace amounts, the sensitised photolysis was proposed as a method for the detection of these species.[58, 69, 70] More recently, a series of alkylnitrenes have been generated by intramolecular sensitisation,[71–73] including that in an argon matrix.[73] For example, the irradiation of α-azidoacetophenone (**9**) and its derivatives gives benzoyl radical (**10**) (through the α-C–C bond cleavage) and triplet nitrene **11**. In solution at room temperature, the main reaction involves the C–C bond cleavage.[73] In an argon matrix, only nitrene **11** was detected at 12 K based on the absorption band in the near-UV region with a maximum at 280 nm.[73]



9 **10** ^{3}(**11**)

As mentioned above, the photochemistry of methyl azide was studied in most detail. Triplet methylnitrene was detected in numerous studies both in the condensed phase by the triplet sensitisation[58, 60] and in the gas phase in the corona discharge.[74–77] The zero-field splitting parameters ($|D/hc| = 1.595$ cm^{-1}), which have been initially determined[58, 60] based on the results of experiments in low-temperature glasses, were doubted.[75] The commonly accepted value $|D/hc| = 1.720$ cm^{-1} was determined by gas-phase spectroscopy.[78]

The electronic absorption spectrum[79–82] and the luminescence spectrum[74–77, 78–82] of triplet methylnitrene were recorded many times. The 0–0 transition in its electronic absorption spectrum is observed at 316.9 nm in a nitrogen matrix[80] and at 314.3 nm in the gas phase,[81] which is close to the maximum observed in the electronic absorption spectrum of the NH radical (336 nm).[41, 42] The singlet–triplet splitting in methylnitrene ($\Delta E_{ST} = 1.352 \pm 0.011$ eV or 130.7 ± 1.3 kJ mol^{-1}) was determined from the photoelectron spectrum of the CH_3N^- anion.[83] This parameter appeared to

be somewhat smaller than that for the NH radical (1.561 eV, see Fig. 1).

Therefore, it is impossible to decide between two probable mechanisms of photolysis of methyl azide based on the published data. According to one mechanism, singlet methylnitrene is formed as the primary intermediate, but its lifetime, even in cryogenic matrices, is too short (due to the isomerisation to methyleneimine) for the relaxation of this species to the triplet ground state. According to another mechanism, the elimination of molecular nitrogen from methyl azide in the excited singlet state and the formation of imine are concerted and proceed without the involvement of singlet nitrene as an intermediate. To understand whether $^1[CH_3N]$ is the real intermediate, *i.e.*, whether it is characterised by a minimum on the potential energy surface (PES), the properties of this species were calculated by quantum chemical methods.[84–93]

Based on the results of earlier studies,[84–88] it was concluded that no minima on the PES correspond to singlet methylnitrene. However, these calculations were carried out at a low level of theory with the use of small basis sets. Because of this, quantum chemical calculations were repeated in 1990s.[89–93]

As in the case of the NH radical, the components of the lowest singlet state with the closed- and open-shell electronic configurations in singlet methylnitrene having the C_{3v} symmetry form the doubly degenerate state ^1E. The latter undergoes a Jahn–Teller distortion to give the states $^1A'$ and $^1A''$ (C_s symmetry) with the energy difference smaller than 0.04 kJ mol^{-1}.[86,93] The isomerisation of $^1[CH_3N]$ in the state $^1A'$ was studied[89] at the TC-CISD+Q level of theory (the configuration interaction with single and double excitations based on two-configuration wavefunctions) with a rather large basis set (TZ2P+f), The maximum with a barrier height of $\sim$4 kJ mol^{-1} was found on the PES. Nevertheless, the authors of this study suggested that lowering of the symmetry of the system and a more accurate account of the electronic correlation would lead to the disappearance of the barrier in accordance with the results of earlier calculations.[85,86]

In 2000, a new attempt was made[93] to establish the presence of a barrier between the positions $^1[CH_3N]$ and $H_2C{=}NH$ on the PES. The calculations were carried out by the CASSCF(12/11) and CASPT2 methods with the cc-pVDZ and cc-pVTZ basis sets. As in the earlier study,[89] the maximum on the PES was found, and its energy appeared to be higher than that of the reagent by $\sim$2 kJ mol^{-1} (CASSCF calculations) and 16 kJ mol^{-1} (CASPT2 calculations). An analysis of vibrations calculated by the CASSCF(12/11) method showed that the maximum with the C_s symmetry corresponds to the true transitions state. Since the electronic correlation is generally overestimated by the CASPT2 method, it was suggested that the barrier height for the isomerisation of $^1[CH_3N]$ to $H_2C{=}NH$ is in the range of 11 ± 4 kJ mol^{-1}.[93] Since the reaction is highly exothermic ($\Delta H = -348$ kJ mol^{-1}, the CASPT2 method), the transition state is early, the C–H bond in this state is elongated by only 0.01 Å, and the C–N bond is shortened by 0.016 Å.[93] Therefore, according to the results of calculations at the highest levels of theory, singlet methylnitrene does correspond to a minimum on the PES, but its formation was not detected even by femtosecond spectroscopy.[59]

Recently, the photolysis of trifluoromethyl azide (**12**) has been studied[94] by IR and UV spectroscopy in an argon matrix at 12 K and by the ESR method in polycrystalline pentane. After irradiation of a solution of azide **12** in polycrystalline pentane at 6–10 K with light with a wavelength of 254 nm, the ESR signal centered at 8620 G was observed. This signal was assigned to triplet trifluoromethylnitrene (**13**). The parameters

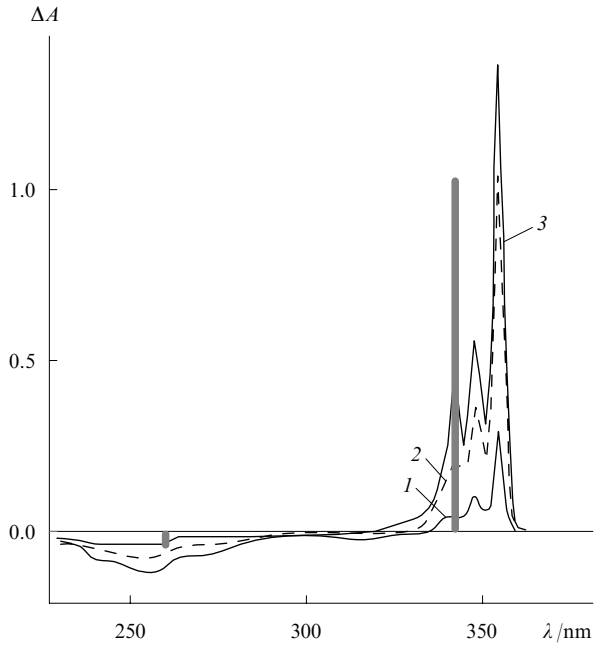
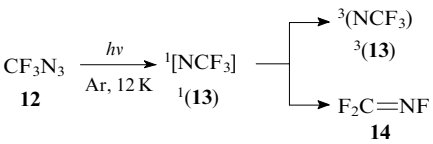


Figure 4. Difference electronic absorption spectra recorded after irradiation of trifluoromethyl azide in an argon matrix at 12 K for 5 (*1*), 25 (*2*) and 45 min (*3*).[94]
The positions and relative intensities of the absorption bands in the spectra of triplet nitrene **13** (positive peak) and azide **12** (negative peak) calculated at the TD-B3LYP/6-31G* level of theory are indicated by vertical bars.

of this spectrum ($|D/hc| = 1.736$ cm^{-1}) are similar to those for nitrenes ^{3}(NH) ($|D/hc| = 1.863$ cm^{-1})[95] and $^3(CH_3N)$ ($|D/hc| = 1.720$ cm^{-1}).[78]

Upon irradiation of azide **12** in an argon matrix at 12 K with a wavelength of 254 nm, its absorption ($\lambda_{max} = 257$ nm) decreased and an intense absorption band with a pronounced vibrational structure ($\lambda_{max} = 342$, 347.5 and 354 nm) appeared (Fig. 4).[94] The latter band was assigned to triplet nitrene **13** based on the similarity to the spectrum of $^3(CH_3N)$ and agreement with the results of calculations. The IR spectrum showed new bands, one of which (1185 cm^{-1}) was assigned to nitrene ^{3}(**13**); a series of bands (929, 1015, 1379 and 1735 cm^{-1}) were assigned to perfluoromethyleneimine (**14**) (Fig. 5). A comparison of the experimental and calculated IR spectra shows that nitrene ^{3}(**13**) and imine **14** are produced in comparable amounts. The formation of $^3(NCF_3)$ upon irradiation of azide **12** is indicative of the formation of singlet nitrene ^{1}(**13**) as an intermediate, and a minimum on the PES corresponds to this species.



According to the results of CASSCF (8,8)/6-31G* calculations, the isomerisation of $^1[NCF_3]$ to imine **14** is exothermic ($\Delta H = -193$ kJ mol^{-1}).[94] However, it is substantially less exothermic than the presumed isomerisation of singlet methylnitrene ($\Delta H = -348$ kJ mol^{-1}),[93] which is indicative of the presence of a much higher barrier to the isomerisation of nitrene ^{1}(**13**) compared to methylnitrene.

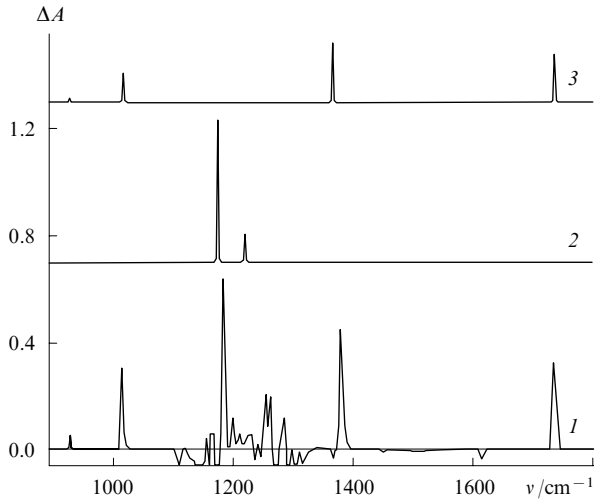
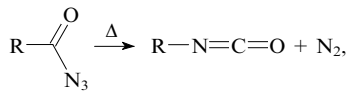


Figure 5. IR difference spectrum recorded after irradiation of azide **12** in an argon matrix at 12 K for 25 min (*1*). The IR spectra of triplet nitrene **13** (*2*) and imine **14** (*3*) calculated at the B3LYP/6-31G* level of theory (the calibration factor is 0.97) (data of the author of the present review).

IV. Photochemical transformations of acyl azides

The thermal rearrangement of acyl azides $RC(O)N_3$ (the Curtius rearrangement) giving isocyanates in quantitative yields at 60–80 °C has been known over the years and has been studied in detail.[39, 96–99]

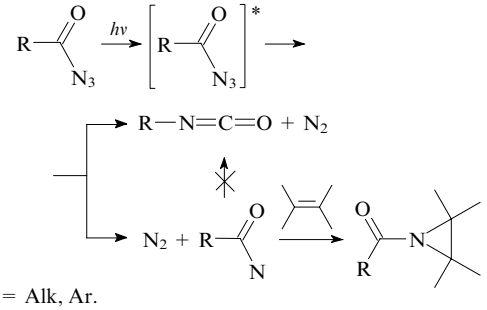


$$R{-}C(=O){-}N_3 \xrightarrow{\Delta} R{-}N{=}C{=}O + N_2,$$

R = Alk, Ar.

The photolysis of acyl azides in solution affords two types of products, *viz*., isocyanates (the photo-Curtius rearrangement) and products derived from capture of the carbonyl nitrenes [RC(O)N] by solvent molecules.[98] For example, the thermolysis of pivaloyl azide [$Bu^tC(O)N_3$] in cyclohexane produces the corresponding isocyanate in 99.4% yield.[100, 101] The photolysis of $Bu^tC(O)N_3$ gives isocyanate in a yield of only 40% both in inert solvents and alkenes, which react with acylnitrenes to form the corresponding aziridines.[100, 101] The photolysis of benzoyl azide and a series of its derivatives in both inert solvents and solvents giving adducts with acylnitrenes affords isocyanates in similar yields (40% – 50%).[102, 103]

Based on these facts, it was concluded that isocyanates and acylnitrenes are independently formed in the photolysis of acyl azides and that acylnitrenes do not undergo isomerisation to isocyanates.[98, 100–103]



$$R{-}C(=O){-}N_3 \xrightarrow{h\nu} \left[R{-}C(=O){-}N_3\right]^* \longrightarrow$$

$$\rightarrow R{-}N{=}C{=}O + N_2$$

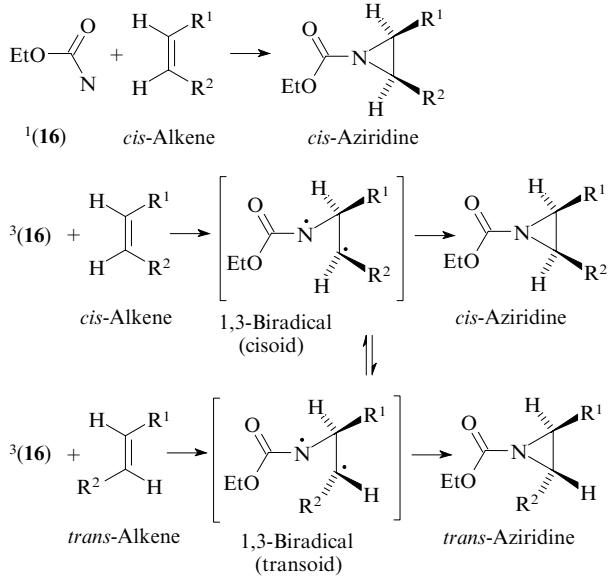
$$\rightarrow N_2 + R{-}C(=O){-}N \longrightarrow$$

R = Alk, Ar.

The photolysis and thermolysis of alkoxycarbonyl and aryloxycarbonyl azides [$ROC(O)N_3$] afford mainly products derived from the corresponding nitrenes [ROC(O)N] as precursors.[98] The yields of isocyanates and their transformation products are generally low.

Ethoxycarbonyl azide **15** has received the most attention in the literature. The analysis of the reaction products led to the conclusion that the thermolysis of azide **15** affords ethoxycarbonylnitrene (**16**) in the singlet state, which stereospecifically reacts with alkenes to give the corresponding aziridines (Scheme 1) and undergoes the relaxation to the triplet ground state ^{3}(**16**).[98, 104, 105] Triplet nitrene ^{3}(**16**) also reacts with alkenes, but this reaction is not stereospecific (apparently, the reaction proceeds *via* the intermediate biradical) (see Scheme 1).[98]

Scheme 1

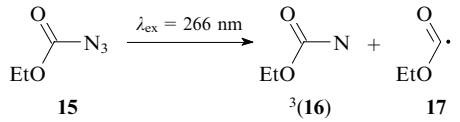


R = Alk, Ar.

In the photolysis of azide **15**, the yield of the products generated in the reaction of nitrenes was ~70%.[104, 105] The analysis of aziridines showed that singlet ^{1}(**16**) and triplet ^{3}(**16**) nitrenes are simultaneously formed in the primary process in a ratio of 2 : 1.[98, 105] Singlet nitrene ^{1}(**16**) is also inserted into the C–H bonds of alkanes and O–H bonds of alcohols and is captured by alkynes and benzene to form azepine.[98]

The triplet nature of the ground state of nitrene **16** was confirmed by the observation of the ESR spectrum in low-temperature glasses ($|D/hc| = 1.603\ cm^{-1}$, $|E/hc| = 0.0215\ cm^{-1}$).[60] A similar spectrum ($|D/hc| = 1.65\ cm^{-1}$, $|E/hc| = 0.024\ cm^{-1}$) was recorded for triplet (4-acetylphenoxy)carbonylnitrene.[106, 107]

Recently, the photochemistry of azide **15** has been studied[108] by laser flash photolysis ($\lambda_{ex} = 266$ nm) in Freon ($CF_2ClCFCl_2$) at room temperature. The formation of at least two intermediates, *viz*., triplet nitrene **16** ($\lambda_{max} = 400$ nm, the lifetime was $\tau = 1.5$ μs) and ethoxycarbonyl radical **17** ($\lambda_{max} = 333$ nm, $\tau = 0.4$ μs), was observed. Triplet nitrene **16** reacted with tetramethylethylene ($k = 3 \times 10^8$ litre mol^{-1} s^{-1}) and triethylsilane ($k = 1 \times 10^6$ litre mol^{-1} s^{-1}).[108]



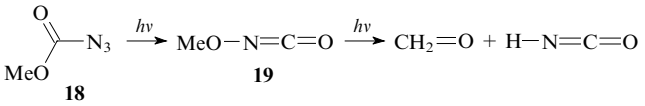
$$EtO{-}C(=O){-}N_3 \xrightarrow{\lambda_{ex} = 266\ nm} EtO{-}C(=O){-}N + EtO{-}C(=O){\cdot}$$

15 ^{3}(**16**) **17**

The photolysis of (4-acetylphenoxy)carbonyl azide was also studied.[106, 107] Only the reaction products of the corre-

sponding nitrene were found, whereas isocyanate and its transformation products were not detected.[107]

The photochemistry of methoxycarbonyl azide (**18**) and its deuterium derivative was studied in inert gas matrices at 4 and 10 K.[109, 110] The IR spectrum of the reaction products shows characteristic lines assigned to methoxy isocyanate (**19**) and its further transformations products, *viz*., formaldehyde and isocyanic acid.



18 **19**

Triplet methoxycarbonylnitrene was not detected.[110] This is apparently due to the photochemical transformation of the latter into isocyanate.

Thus, the photochemical reactions of azides $ROC(O)N_3$ (R = Alk or Ar) have not been adequately studied, and it is necessary to study these reactions in more detail by the matrix isolation technique. However, the analysis of the reaction products showed that the photolysis and thermolysis of these azides produce the corresponding nitrenes having the triplet ground state [60, 106–108] in high yields.[98, 101, 102, 104–108]

As was mentioned in the beginning of this Section, the photolysis of acyl azides $RC(O)N_3$ (R = Alk or Ar) affords isocyanates in rather high yields.[98] The ESR spectra of acylnitrenes in the triplet state were not observed after the photolysis of azides $RC(O)N_3$, as opposed to the photolysis of azides $ROC(O)N_3$. The characteristic features of the photolysis of carbonyl azides were revealed and the unusual properties of the corresponding nitrenes were explained with the use of the matrix isolation techniques [38, 40] combined with the results of quantum chemical calculations.[38–40, 99, 111, 112]

Among acyl azides, benzoyl azide (**20**) has received most attention.[38–40, 102, 103, 113–116] In early studies,[102, 103, 113–116] the photolysis of this compound was demonstrated to give the photo-Curtius rearrangement product (phenyl isocyanate **21**, ~40% yield) along with the reaction products of singlet benzoylnitrene (**22**) with alkenes, sulfides, *etc*. The direct and triplet-sensitised photolysis of benzoyl azide in alkenes affords the same products characteristic of the reactions of nitrene ^{1}(**22**).[115, 116] No ESR spectra of triplet benzoylnitrene were observed upon the photolysis of benzoyl azide in glassy solvents.[60, 70]

To reveal the multiplicity of the ground state of aroylnitrenes, the photochemistry of 2-naphthoyl azide (**23**) and a series of acetyl and nitro derivatives of benzoyl azide was studied in detail,[106, 107, 117, 118] including investigations by the laser flash photolysis technique. As in the case of benzoyl azide, the corresponding isocyanate (~50%) and the reaction products of singlet 2-naphthoylnitrene (**24**) with alkenes and cyclohexane (~45%) were detected upon irradiation of azide **23**. The triplet sensitisation also affords products typical of the reactions of nitrene ^{1}(**24**).[106] The ESR spectrum of triplet nitrene **24** was not observed. Analogous results were obtained in studies of the photolysis of acetyl and nitro derivatives of benzoyl azide. Although the authors failed to detect singlet aroylnitrenes by spectroscopic methods, their data leave little doubt that the ground state of aroylnitrenes is singlet.[106, 107, 117, 118] However, this unusual fact remained unexplained.

To understand why aroylnitrenes can have the singlet ground state, we calculated the singlet–triplet splitting (ΔE_{ST}) for nitrenes **22** and **24** by the B3LYP method.[111] The calculated ΔE_{ST} is small (~21 kJ mol^{-1}); however, according to the calculations, the triplet state is the ground state. Recall that ΔE_{ST} = 150.6 kJ mol^{-1} for the simplest nitrene NH and 130.7 kJ mol^{-1} for CH_3N. The significant stabilisation of the singlet state compared to the triplet state in aroylnitrenes is attributed to the special bonding between the nitrogen and oxygen atoms, due to which the structure of the singlet nitrenoid species is intermediate between the nitrene and oxazirine structures.[111]

Having understood the nature of the singlet nitrenoid species, we studied the photolysis of benzoyl azide by the matrix isolation technique with the aim of detecting this species by spectroscopic methods.[38] After irradiation for 2 min in an argon matrix with light with the wavelength of 254 nm, the electronic absorption spectrum of azide **20** disappeared and a new band with a maximum at 300 nm appeared (Fig. 6, spectrum *1*). Simultaneously, absorption bands of azide **20** virtually completely disappeared in the IR spectrum, and new bands appeared, among which the intense absorption at ~2270 cm^{-1} was assigned to phenyl isocyanate.[38] The subsequent irradiation with light with the wavelength of 313 nm led to the disappearance of the absorption band in the UV spectrum (see Fig. 6, spectrum *2*). At the same time, the intensity of some bands in the IR spectrum substantially decreased, whereas the intensity of other bands increased (Fig. 7, spectrum *1*).

Thus, the photolysis of benzoyl azide affords at least two products. One of these products is characterised by absorption with a maximum at ~300 nm and it is transformed into another product upon irradiation with light with the wavelength of 313 nm. Most of the lines in the experimental IR spectrum recorded 8 min after irradiation are in good agreement with the calculated spectrum of isocyanate (see Fig. 7, spectrum *2*), except for one rather intense band at 1193 cm^{-1}, which is absent in the calculated spectrum.[38] The results of our investigations [38, 40] were reproduced in the study,[119] and the previously unidentified band was assigned to phenyl cyanate (**25**) produced in a small amount. Therefore, isocyanate **21** and trace amounts of cyanate **25** are the final products.[40, 119]

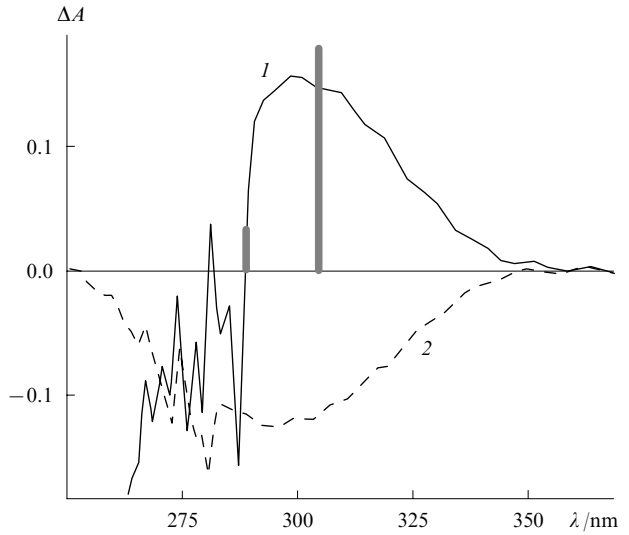


Figure 6. Diffrence electronic absorption spectra recorded upon irradiation of compound **20** at 254 nm for 2 min in an argon matrix at 12 K (*1*) and of the same sample irradiated at 313 nm for 8 min (*2*).[38]
The positions and relative intensities of the absorption bands of nitrene ^{1}(**22**) calculated at the CASSCF/CASPT2 level of theory are indicated by vertical bars.

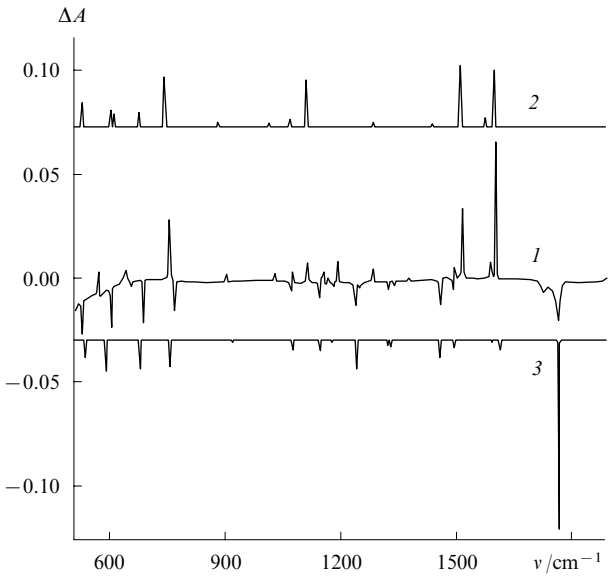
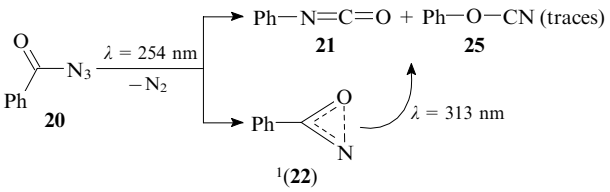


Figure 7. IR difference spectrum of the photolysis products of benzoyl azide upon irradiation with light with $\lambda = 254$ nm for 2 min followed by irradiation for 8 min with light with $\lambda = 313$ nm in an argon matrix at 12 K (*1*).
Positions and relative intensities of the bands in the IR absorption spectrum of isocyanate **21** (*2*) and nitrene ^{1}(**22**) (*3*) calculated at the B3LYP/6-31G(d) level (the correction factor is 0.97).[38, 40]



The band in the electronic absorption spectrum at 300 nm (see Fig. 6, spectrum *1*) belongs to the singlet nitrenoid species ^{1}(**22**), which has the structure intermediate between the nitrene and oxazirine structures. According to CASSCF/CASPT2 calculations, two most intense transitions in the optical absorption spectrum of the species ^{1}(**22**) have maxima at 306 and 290 nm (see Fig. 6). In addition, the calculated spectrum shows a band corresponding to the transition to the first excited state with a maximum at 513 nm and a very low intensity. This band is associated with the electron excitation from the allyl-type π orbital to the σ* orbital of a very weak N—O bond.

The calculated IR spectrum of the species ^{1}(**22**) is also in excellent agreement with the experimental IR spectrum of an intermediate species having an absorption maximum at 300 nm (see Fig. 7, spectrum *1*, negative peaks).

The ratio of the yields of **21** and ^{1}(**22**) in the primary process is estimated as 64 : 36 from the initial slope of the kinetic curves of the formation of these products upon irradiation ($\lambda = 254$ nm).[38]

Thus, the use of the matrix isolation techniques combined with quantum chemical calculations provided an insight into the unusual nature of singlet aroylnitrenes.

It should be noted that the calculations of the properties of the simplest acylnitrenes HC(O)N and HOC(O)N were carried out in numerous studies.[38–40, 99, 111, 112, 120–127] In early studies,[120–124] quantum chemical calculations were performed at a rather low level of theory, and, as a consequence, the results of these calculations are inconsistent with the modern views of the electronic and geometric structures of acylnitrenes. In 1999, the potential energy surfaces for the model systems CHNO [125] and CH_2NO [126] were studied in detail by the high-level G2, CASSCF, CASPT2 and QCISD(T) methods. Numerous local minima and transition states between these minima were found, and structures of triplet formylnitrene and singlet cyclic oxazirine with a very long N—O bond (1.73 Å) were located. According to calculations by the G2 method, the energy of the singlet species is lower than that of the triplet species by 12 kJ mol^{-1}.[126] In turn, according to CASPT2/cc-pVTZ and QCISD(T)/cc-pVTZ calculations (with the CASSCF/cc-pVTZ geometry), the energy of the triplet state is lower than that of the singlet state by 16 and 3 kJ mol^{-1}, respectively.[126] It is known [127–129] that the CASPT2 method underestimates the energy of systems with open-shell electronic configurations (in the case under consideration, of the triplet state) compared to those with closed-shell electronic configurations (the singlet species) by 13–17 kJ mol^{-1}. Our calculations by the CCSD(T) method with an extrapolation to the infinite basis-set limit [38] predicted that the singlet state lies 3 kJ mol^{-1} lower in energy than the triplet state. For acetylnitrene [MeC(O)N], according to the recent calculations by the high-level CBS-QB3 method, the singlet state is lower in energy than the triplet state by ~17 kJ mol^{-1} (Ref. 39).

In addition, the energy of the singlet species calculated by the B3LYP method was demonstrated [38–40] to be substantially overestimated (by ~38 kJ mol^{-1}) compared to the energy of the triplet nitrene. Hence, the energy of the singlet nitrenoid species ^{1}(**22**) should be ~17 kJ mol^{-1} lower than that of the triplet species ^{3}(**22**), which is consistent with its detection in an argon matrix.

The CCSD(T) calculations with an extrapolation to the infinite basis-set limit for the simplest nitrene HOC(O)N [40] showed that the triplet state for both the *syn* and *anti* rotamers is the ground state, and the singlet nitrenoid species lies higher in energy by 26 and 16 kJ mol^{-1}, respectively. For methoxycarbonylnitrene, the ground state is also the triplet. According to CBS-QB3 calculations, the singlet state is higher in energy by 23.8 kJ mol^{-1} (Ref. 39).

The singlet–triplet splittings for nitrenes ROC(O)N and RC(O)N are different due to the weaker bonding between the nitrogen and oxygen atoms in the ^{1}A′ state of the former, which manifests itself in lengthening of the N—O bond. It is unlikely that the oxygen atom of the alkoxy or aryloxy group can hinder the σ bonding between the nitrogen and oxygen atoms in the CON fragment. Presumably, the π bonding between these atoms is weaker due to an extension of the π system in the presence of the OR group.

The commonly accepted view (presented in many handbooks and reviews [21, 22, 26–33]) is that the addition at double bonds and the insertion into the C—H, O—H and N—H bonds are typical of singlet nitrenes. However, these reaction products were detected only for acylnitrenes and, as will be demonstrated in the next section, for perfluoro-substituted phenylnitrenes. However, these singlet nitrenes do not belong to 'usual' nitrenes. The electronic and geometric structures of these nitrenoid species are characteristic of oxazirines, although the N—O bond in these species (1.7–1.8 Å) is substantially longer than the typical single bond (~1.5 Å).

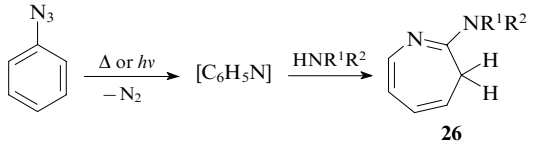
The calculations demonstrated [39, 40] that the above-considered reactions (the addition at double bonds and the insertion into the bonds) of nitrenoid species with an unusual structure proceed with a low or even zero activation energy. Recently, the temperature dependence of the rate constant for the reaction of nitrene ^{1}(**22**) with hex-1-ene in Freon has been experimentally studied.[39] It appeared that the rate of this reaction is virtually temperature independent, and even a small negative activation energy ($E_a = -0.25$ kJ mol^{-1}) was measured.

V. Photochemical transformations of aryl azides

As mentioned in the Introduction, considerable progress in understanding the photochemical transformations of aryl azides was achieved in the last decade. This is mainly due to the fact that the primary products of their photolysis, *viz*., singlet arylnitrenes, were detected and their reactivity was studied.[34–37] The spectroscopic and kinetic data were analysed using high-level quantum chemical calculations (CASSCF/CASPT2).[34–37] Combined theoretical and experimental studies of the properties of phenylnitrene and its simple derivatives were covered in reviews.[34,36] The kinetic and spectroscopic properties of short-lived ($\sim$100 ps–100 ns) singlet arylnitrenes were examined in detail.[35,37] However, investigations by the matrix isolation techniques have received little attention. In addition, a series of very recent studies [130–133] dealt with the photolysis of aryl and heteroaryl azides by the matrix isolation techniques, which provided deeper insight into the characteristic features of these processes.

1. Photochemistry of phenyl azide

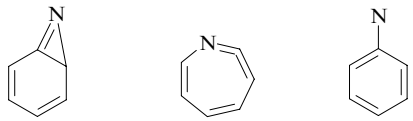
The photochemistry of the simplest aryl azide, *viz*., phenyl azide, has attracted most attention. For many years, only polymeric tars have been detected upon the photolysis and thermolysis of this compound.[21,27] However, the thermolysis [134] and photolysis [135] of phenyl azide in the presence of aniline or diethylamine (DEA) afforded the corresponding azepines **26** in high yield (no lower than 70%). It was postulated that the thermolysis and photolysis of phenyl azide lead to the elimination of molecular nitrogen and the formation of the [C_6H_5N] intermediate.[134,135]



26

$R^1 = R^2 = Et$; $R^1 = H$, $R^2 = Ph$.

It was hypothesised that either benzoazirine (**27**) or cyclic ketene imine (1-azacyclohepta-1,2,4,6-tetraene or 1,2-didehydroazepine, **28**) is a species reacting with amines.[134,135] It was not ruled out that singlet phenylnitrene (**29**) can be the precursor of these compounds.



27 **28** **29**

An analysis of the photolysis products of phenyl azide under different conditions is indicative of the formation of all the above-mentioned intermediates. At lower concentrations of solutions of phenyl azide, tarring decreases and the reaction produces azobenzene.[136,137] This indicates that singlet intermediates [compounds **27** and(or) **28**] serve as a reservoir for triplet nitrenes ^{3}(**29**), which either undergo dimerisation or react with the starting azide to give azobenzene as the final product. Unfortunately, the formation of azobenzene was not studied by direct methods, for example, by the laser flash photolysis.

In 1962, the ESR spectrum of triplet nitrene ^{3}(**29**) was recorded in a glassy matrix at 77 K ($|D/hc| = 0.998$ cm^{-1}), and the triplet state of this nitrene was demonstrated to be the ground state.[69] Shortly thereafter, the low-temperature electronic absorption spectrum of nitrene ^{3}(**29**) was recorded in a glassy matrix.[138] More recent studies [139] showed that this nitrene readily undergoes isomerisation to ketene imine **28** upon irradiation.

It was hypothesised that the nucleophilic addition of amines to benzoazirine **27** affords substituted 3*H*-azepines **26** as the major products.[134,140–142] The transient absorption spectrum observed in experiments on the laser flash photolysis was also assigned to compound **27**.[140–142]

The situation changed when ketene imine **28** was detected upon the photolysis of phenyl azide in an argon matrix.[143] The irradiation of phenyl azide in an argon matrix at 8 K with light at $\lambda > 360$ nm (or $\lambda > 216$ nm) led to the formation of a product giving an intense band in the IR spectrum at 1895 cm^{-1} characteristic of heterocumulene structures (–N=C=C–).

It appeared that ketene imine **28** is unstable upon further irradiation ($\lambda > 360$ nm); however, the formation of benzoazirine **27** was not observed.[143] In a more thorough investigation [144] of the photolysis of phenyl azide and its ^{15}N-labelled analogue in argon and neon matrices at 12 K, at least 40 new bands were found in the IR spectrum, and 11 bands were assigned to compound **28**.[144] The assignment of the other bands was not made; however, the authors hypothesised that these bands belong to photolysis products of ketene imine. In addition, the ESR spectrum characteristic of nitrene ^{3}(**29**) ($|D/hc| = 1.027$ cm^{-1}, $E = 0$ cm^{-1}) was observed upon irradiation ($\lambda > 216$ nm) of phenyl azide in an argon matrix at 12 K.[145]

Detailed study of the photolysis products of phenyl azide in organic solvents in a wide temperature range (77–293 K) combined with the measurements of their electronic absorption and luminescence spectra led to the conclusion [139] that triplet nitrene **29** is the major product at 77 K.

Studies by time-resolved IR spectroscopy and the laser flash photolysis convincingly demonstrated [146,147] that ketene imine **28** ($\lambda_{max} \approx 350$ nm, $\nu_{max} = 1889$ cm^{-1}) is the intermediate detected in time-resolved experiments at room temperature. This ketene imine reacts with DEA to give intermediate 1*H*-azepine, which is transformed into 3*H*-azepine (**26**) as the final product.[146,147]

Thus, the results obtained in solutions and inert gas matrices differ substantially from those obtained in low-temperature glasses. In glasses, triplet nitrene **29** is formed as the major product, whereas ketene imine **28** is the major reaction product in solution at room temperature and in inert gas matrices at $\sim$10 K. Two hypotheses were put forward to explain this contradiction.[139] According to one hypothesis, the secondary photolysis of nitrene ^{3}(**29**) proceeds in inert gas matrices to give ketene imine **28**. According to another hypothesis, the primary intermediate, *viz*., vibrationally excited singlet nitrene ^{1}(**29**), has no time to relax to the ground vibrational state and undergoes rapid isomerisation to ketene imine.

To find an explanation for this contradiction, new investigations of the photolysis of phenyl azide in the inert gas matrices and low-temperature glasses were carried out.[148,149] The irradiation in nitrogen or argon matrices at 12 K with light with the wavelength of 334 nm afforded compound **28** in a small amount, whereas another species was generated as the major product. The IR spectrum of the latter was assigned to nitrene ^{3}(**29**).[148] The irradiation of nitrene ^{3}(**29**) with long-wavelength light (485 nm or >450 nm) caused its transformation into ketene imine **28**, which, in turn, could be transformed into nitrene ^{3}(**29**) under irradiation with light with $\lambda = 334$ nm. The ratio between the concentrations of the nitrene and the ketene imine in the initial steps of irradiation ($\lambda = 334$ nm) was found [148] to be $\sim$4:1 in all matrices (nitrogen, argon and glassy 2-methylbutane). It was hypothesised [148] that ketene imine **28** is generated from the vibrationally or electronically excited state of singlet nitrene ^{1}(**29**).

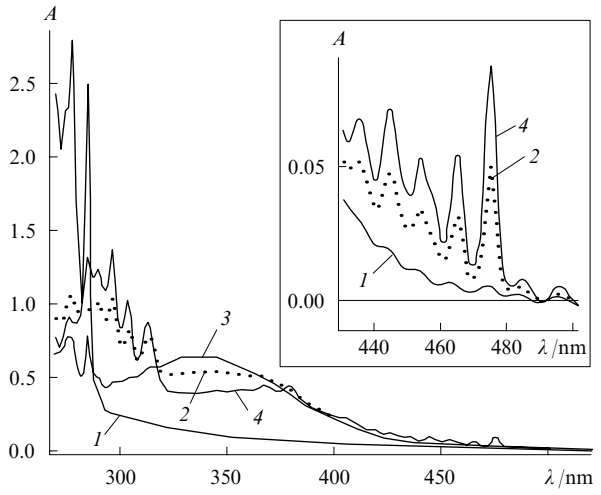


Figure 8. Electronic absorption spectra of the starting phenyl azide in an argon matrix (with an addition of 10% nitrogen for the improvement of the optical properties) at 12 K (*1*) and of a sample after irradiation: $\lambda = 254$ nm, 10 min (*2*); visible light ($\lambda > 455$ nm), 15 min (*3*); UV irradiation ($\lambda = 334$ nm), 130 min (*4*).

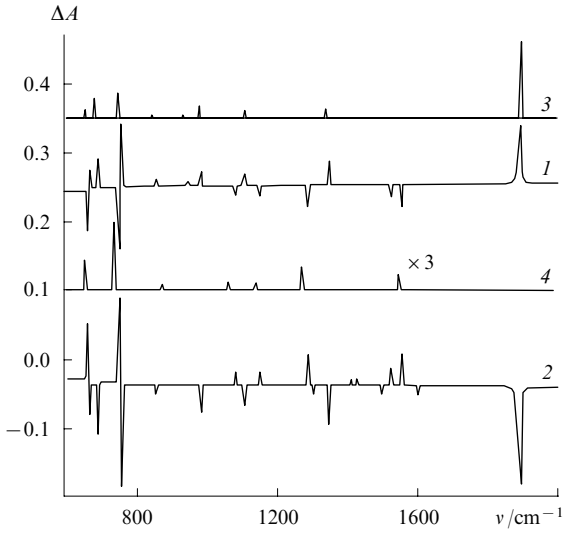


Figure 9. IR difference spectra of preirradiated ($\lambda = 254$ nm, 10 min) matrix-isolated phenyl azide (an argon matrix with 10% nitrogen, 12 K) after irradiation with visible light ($\lambda > 455$ nm) for 15 min (*1*) and after UV irradiation ($\lambda = 334$ nm) for 130 min (*2*).
The IR spectra of ketene imine **28** (*3*) and triplet nitrene **29** (*4*) calculated at the B3LYP/6-31G* level of theory (the correction factor is 0.9614).

The influence of the nature of the matrix (Ar, CH_4 or 3-methylpentane) on the photolysis of phenyl azide was studied [149] but the irradiation was performed with shorter-wavelength light ($\lambda = 280 \pm 5$ nm). A conclusion was reached that the formation of nitrene ^{3}(**29**) is more preferable in CH_4 and 3-methylpentane matrices than in an argon matrix. This effect was attributed to the faster relaxation of vibrationally excited singlet nitrene ^{1}(**29**) in polyatomic solvents compared to that in a one-atom argon matrix.

The spectra, which we recorded upon irradiation of phenyl azide in an argon matrix, are given as examples in Figs 8 and 9. The short-wavelength irradiation ($\lambda = 254$ nm) affords a mixture of nitrene ^{3}(**29**), which gives a well-resolved spectrum at 290–320 and 430–480 nm, and ketene imine **28** with a characteristic broad band at $\lambda_{max} = 340$ nm (Fig. 8, spectrum *2*). The further irradiation with visible light ($\lambda >$ 455 nm, 15 min) leads to the virtually complete disappearance of the absorption of nitrene ^{3}(**29**) and an increase in the intensity of the absorption of ketene imine **28** (Fig. 8, spectrum *3*). The subsequent irradiation with light with $\lambda = 334$ nm leads to an increase in the intensity of the absorption of nitrene ^{3}(**29**) (Fig. 8, spectrum *4*).

As can be seen from Fig. 9, all lines in the experimental IR spectra of the photolysis products can be assigned to nitrene ^{3}(**29**) and ketene imine **28**, and there is a good agreement between the calculated and experimental IR spectra of both intermediates. It can also be seen from this Figure that nitrene ^{3}(**29**) is transformed into ketene imine upon irradiation with visible light (spectrum *1*), whereas the irradiation with UV light causes the transformation of ketene imine **28** into nitrene ^{3}(**29**).

Assuming that the photolysis affords only products **27** and ^{3}(**29**), which is consistent with the observed IR spectrum, the individual electronic absorption spectra of these compounds can be obtained (Fig. 10). The calculated electronic absorption spectra of these intermediates are in good agreement with experimental data. It should be noted that transitions of an electron of the lone pair to the π-type singly occupied molecular orbital (SOMO) ($\lambda_{calc} = 289$ nm) and the p_x-type SOMO lying in the plane of the ring ($\lambda_{calc} = 287$ nm) make a considerable contribution to the absorption band of triplet phenylnitrene at 270–320 nm. The spectra of the simplest nitrenes ^{3}(NH) ($\lambda_{max} = 336$ nm) [41, 42] and ^{3}(CH_3N) (316.9 nm) are also associated with analogous transitions.[80]

As opposed to the results of the study,[148] according to which irradiation of phenyl azide at 334 nm affords compounds ^{3}(**29**) and **28** as the primary products in a ratio of 4 : 1, our investigation showed that the irradiation with shorter-wavelength light ($\lambda = 254$ nm) gives primary products in a yield of ~0.5 : 1, *i.e.*, the formation of ketene imine **28** is more preferable. This fact indicates that the latter is actually formed in the course of isomerisation of vibrationally excited singlet nitrene **29** and is consistent with the results of the recent studies

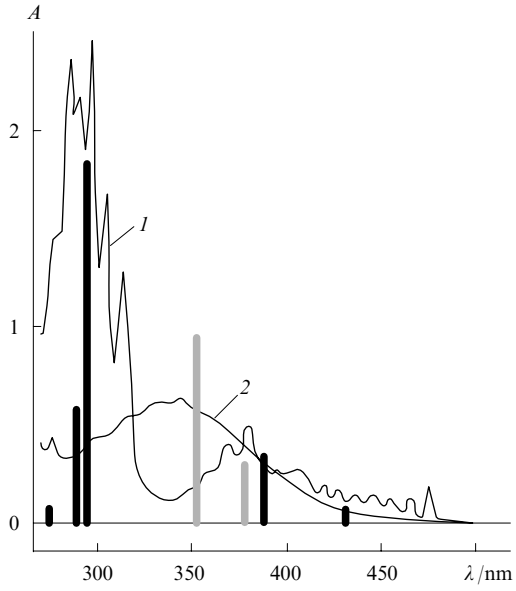


Figure 10. Electronic absorption spectra of triplet nitrene **29** (*1*) and ketene imine **28** (*2*). The calculated positions and relative intensities of the absorption bands of nitrene ^{3}(**29**) [solid bars, CASSCF(12,12)/CASPT2//CASSCF(8,8)/6-31G* calculations] [150] and ketene imine **28** (dotted bars, B3LYP/6-31+G* calculations) are indicated by vertical bars.

on the photolysis of phenyl azide and a series of its derivatives in solution at room temperature by femtosecond electronic absorption spectroscopy [151–154] and femtosecond IR spectroscopy.[155] It was found that the N–N bond dissociation in aryl azides under study proceeds on the femtosecond time scale (*ca.* 100–500 fs).[151–154] For example, the time of formation of singlet biphenyl-4-ylnitrene in the photodissociation of biphenyl-4-yl azide (λ_{ex} = 266 nm) in acetonitrile is ~100 fs, and the time of formation of the corresponding nitrene from biphenyl-2-yl azide is 280 ± 150 fs.[152, 153] The resulting singlet arylnitrenes [including nitrene ^{1}(**29**)] are vibrationally excited, and the shorter the wavelength of the photoexcitation the larger the excess of vibrational energy. The vibrational relaxation in acetonitrile proceeds within 10 ps (for singlet biphenyl-4-ylnitrene [152, 153] and 3,5-dichlorobiphenyl-2-ylnitrene in cyclohexane,[151] the relaxation time is 11 ps).

The theoretical analysis [153] of the PES section along the reaction coordinate corresponding to the elimination of molecular nitrogen for the ground (S_0) and two excited singlet states (S_1 and S_2) of aryl azides suggests that the first excited state (S_1) is apparently dissociative. The second excited state (S_2) is the bound state, and its geometry is similar to that of the state S_0. Upon absorption of UV irradiation, the excitation to the state S_2 takes place. The time of formation of vibrationally excited singlet arylnitrene (< 500 fs) corresponds to the time of internal conversion into the dissociative state S_1. It was also found [153] that the surfaces for S_1 and S_0 intersect each other. Consequently, the S_1 state of arylnitrenes can be deactivated to the ground state. This explains why, in spite of a high rate of formation of arylnitrenes, the quantum yield of photodissociation can be substantially smaller than unity; for example, the quantum yield for phenylnitrene is close to 0.5 and is temperature independent (300 and 77 K).[31]

Singlet arylnitrene [for example, ^{1}(**29**)], which is formed upon dissociation of aryl azide, has a considerable exess of vibrational energy and can easily overcome the potential barrier. Actually, studies by femtosecond time-resolved IR spectroscopy showed that a part of ketene imine **28** is very rapidly formed in acetonitrile at room temperature (also in the vibrationally excited state).[155] The formation of ketene imine and its vibrational relaxation proceed on the time scale of 10–50 ps. Unfortunately, attempts to separate these two processes and determine the time of formation of ketene imine failed.[155]

Although the hypothesis about the possible involvement of vibrationally excited singlet phenylnitrene ^{1}(**29**)$^{\#}$ in the isomerisation was made [139, 148] many years ago, it was confirmed only very recently.[155] However, the isomerisation of nitrene ^{1}(**29**)$^{\#}$ to ketene imine **28** competes with its vibrational relaxation to the ground vibrational state ^{1}(**29**), in which this species also undergoes the thermally activated isomerisation to form ketene imine **28**.[34–37]

In 1997, the spectrum of singlet nitrene ^{1}(**29**) (λ_{max} = 350 nm, Fig. 11) with a lifetime of ~1 ns at room temperature was recorded for the first time.[156, 157] The kinetics of transformations of this species was studied in detail in a wide temperature range (170–270 K), which allowed the simultaneous determination of the rate constant of its intersystem crossing to the triplet ground state and the activation parameters of the isomerisation (A and E_a).[150] The observed rate constant (k_{obs}) decreases as the temperature is lowered to ~170 K, and then reaches the constant value of $\sim 3.2 \times 10^6$ s^{-1}, which was assigned [150] to the rate constant of the intersystem crossing (k_{isc}) of singlet nitrene **29** to the triplet ground state. The temperature dependence of the rate constant of isomerisation $k_R = k_{obs} - k_{isc}$ obeys the Arrhenius law (Fig. 12). The activation energies (E_a = 23.4 ± 1.3 kJ mol^{-1}) and the preexponential factors ($A = 10^{13.1 \pm 0.3}$ s^{-1}) were determined.[150]

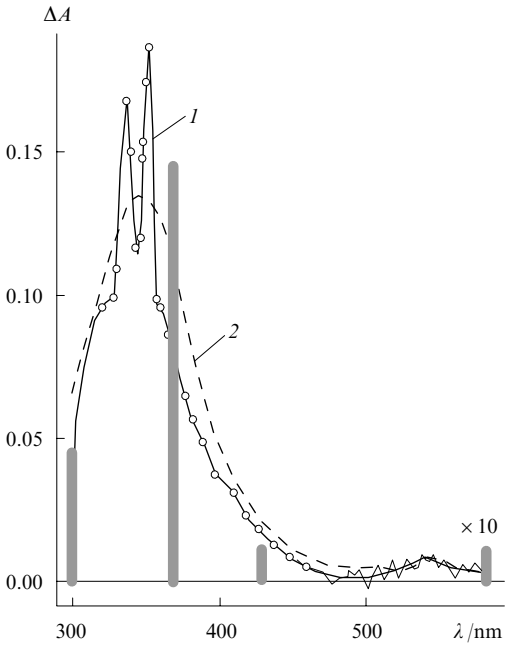


Figure 11. Electronic absorption spectra recorded after the laser excitation (266 nm, 35 ps) of phenyl azide in pentane: after 2 ns at 233 K (*1*) and after 10 ns at 295 K (*2*).[150, 156]
The calculated positions and relative intensities of transitions in nitrene ^{1}(**29**) [at the CASSCF(12,12)/CASPT2 level of theory with the geometry calculated at the CASSCF(8,8)/6-31G* level] [150] are indicated by vertical bars.

The rate constants of the intersystem crossing estimated from the data obtained in solution [$(3.2 \pm 0.3) \times 10^6$ s^{-1}] [150] and in glassy methylcyclohexane at 77 K [$(3.8 \pm 0.3) \times 10^6$ s^{-1}] [158] have similar values, thus confirming the hypothesis that the constant k_{isc} is temperature independent.[150]

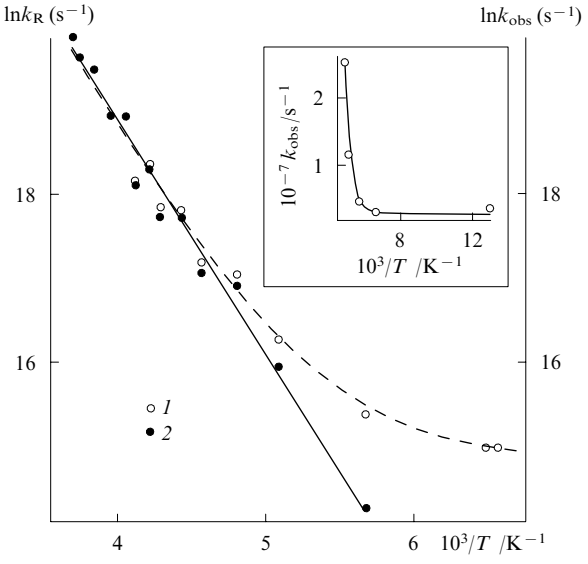


Figure 12. Temperature dependences of the observed rate constant for the decay of singlet nitrene ^{1}(**29**) (k_{obs}) (*1*) and the rate constant for the isomerisation k_R ($k_R = k_{obs} - k_{ics}$) (*2*) in the Arrhenius coordinates.[150]
The inset shows the temperature dependence of the rate constant k_{obs}.

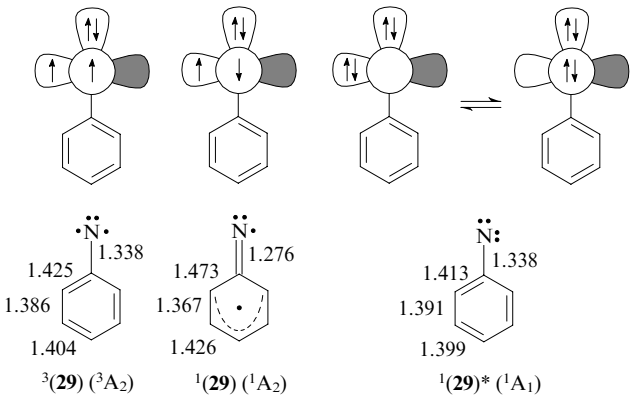


Figure 13. Occupation of the orbitals in nitrene **29** by non-bonding electrons and the bond lengths (in Å) for the lowest states calculated at the CASSCF/6-31G* level.[129]

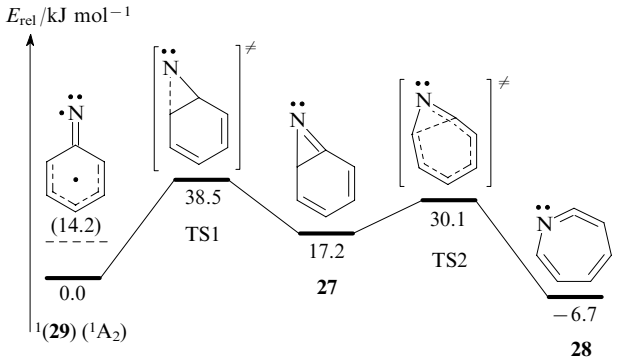
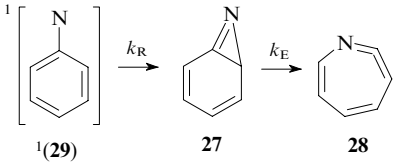


Figure 14. Energetics of the isomerisation of singlet phenylnitrene ^{1}(**29**) calculated at the CASPT2(8,8)/6-311G(2d,p)//CASSCF/6-31G(d) level.[129]
TS is the transition state.

It has long been commonly accepted that singlet phenylnitrene, like other singlet arylnitrenes, has a closed-shell electronic configuration (^{1}A$_1$).[21,26–30] However, relatively recently it has been shown that the lowest singlet state of nitrene **29** (^{1}A$_2$) has an open-shell electronic configuration, *i.e.*, two electrons with opposite spins occupy two different orbitals, *viz.*, the π-type orbital and the p_x orbital located on the nitrogen atom and lying in the ring plane.[159–161] The excited singlet state ^{1}A$_1$ lies higher in energy by ~60 kJ mol^{-1} (Ref. 162). The orbital populations and the bond lengths for three lowest spin states of nitrene **29** are shown in Fig. 13.

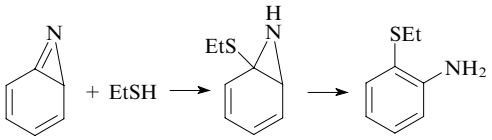
The singlet–triplet splittings (ΔE_{ST} = 73–76 kJ mol^{-1}) calculated at high levels of theory[129,160,161,163] are in good agreement with the experimental values estimated by photoelectron spectroscopy (75 ± 8 kJ mol^{-1})[162] and photoionisation spectroscopy (77 ± 3 kJ mol^{-1}).[164]

In 1997, quantum chemical calculations at the CASSCF/CASPT2 level of theory showed that the isomerisation of nitrene ^{1}(**29**) to ketene imine **28** proceeds in two steps.[129] In the first rate-limiting step, the nitrene undergoes isomerisation to azirine **27**. The second step involves the three-membered ring opening to form compound **28**.



The barrier for the cyclisation reaction evaluated at the CASPT2 level is 39 kJ mol^{-1} (Ref. 129). However, this method generally overestimates the stabilisation of systems having an open-shell electronic configuration compared to species containing paired electrons[127] [for an analogous system, the error was 14 kJ mol^{-1} (Ref. 129)]. Taking into account this error, the barrier for the cyclisation of nitrene ^{1}(**29**) is 25 kJ mol^{-1}, which is in excellent agreement with the measured activation energy of isomerisation (23.4 ± 1.4 kJ mol^{-1}).[150]

According to calculations,[129] the barrier for the second step (**27** → **28**) is as low as 13 kJ mol^{-1} (Fig. 14). This result is consistent with the fact that azirine **27** was not detected in time-resolved experiments.[139,146,147,150,156,157] Although the lifetime of this intermediate is very short, the formation of the reaction product of this species with ethanethiol, *viz.*, the corresponding *ortho*-substituted aniline (in 39% yield), in the photolysis of phenyl azide in ethanethiol was documented.[165]



The mechanism of photolysis of phenyl azide taking into account the results of the very recent studies[150,155–158] is presented in Scheme 2.

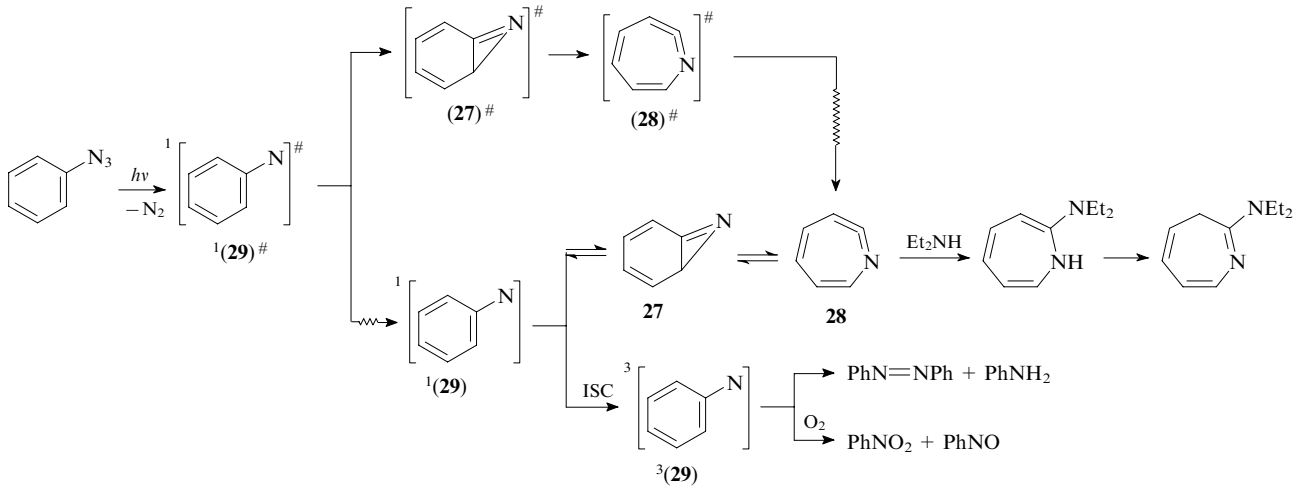
The above-considered data can be briefly summarised as follows. The photodissociation of phenyl azide proceeds on the femtosecond time scale (< 500 fs) to form singlet phenylnitrene in the vibrationally excited state ^{1}(**29**)$^{\#}$. The vibrational relaxation of the latter competes with the isomerisation to azepine, which is also formed in the vibrationally excited state. Singlet phenylnitrene in the ground vibrational state ^{1}(**29**) can undergo relaxation to the triplet ground state ^{3}(**29**) (the intersystem crossing, ISC) or, by overcoming the barrier, transformed into benzoazirine **27**, which, in turn, is transformed into azepine **28**. At room temperature, the isomerisation is the major process. The contribution of the intersystem crossing increases as the temperature is lowered; it becomes the major process at temperatures below 170 K.

2. Photochemistry of phenyl azide derivatives

The photochemistry of simple derivatives of phenyl azide has been studied in sufficient detail, including investigations by the matrix isolation technique.[144,166–170] The spectroscopy and kinetics of the reactions of substituted singlet phenylnitrenes in solution in a wide temperature range (150–300 K) have been investigated recently.[151,158,171–178] The influence of substituents was considered in detail in the reviews.[35,37] It should be noted that the influence of substituents on the rate constant for the cyclisation of phenylnitrene to azirine is not very significant. For example, the presence of two methyl substituents in the *ortho* position with respect to the nitrogen atom leads to an increase in the reaction barrier due to the steric effect and an increase in the lifetime of nitrene at room temperature by approximately an order of magnitude.[173] Such substituents as the cyano and phenyl groups in the *para* position also increase the lifetime by approximately an order of magnitude.[176,178]

The introduction of two fluorine atoms at the *ortho* position with respect to the nitrogen atom has the maximum effect on the rate constant for the cyclisation.[175,177] For

Scheme 2



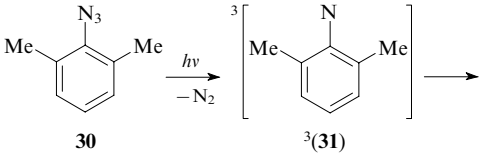
ISC is the intersystem crossing; ⇝ is the vibrational relaxation.

example, the lifetime of singlet 2,6-difluorophenylnitrene at room temperature increases by two orders of magnitude. This is due to the high electronegativity of the fluorine atom.[37, 177] Due to rather long lifetimes, polyfluorinated singlet arylnitrenes can be involved in bimolecular reactions, including the insertion into C–H bonds and the addition at double bonds.[179–185] Hence, polyfluorinated aryl azides are the most promising reagents for photoaffinity labelling of biopolymers[186–192] and covalent modification of the surface of polymer coatings.[23–25]

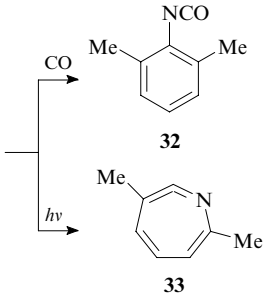
The introduction of substituents can lead also to changes in the relative reaction rates of the two-step isomerisation of singlet nitrene to the corresponding ketene imine. For example, the second step (the ring opening) is the rate-limiting step for biphenyl-2-ylnitrene and 2,4,6-tri-(*tert*-butyl)phenylnitrene, and it is possible to detect the derivative of azirine **27**.[158, 178] All these effects have been analysed in detail earlier[37] and are beyond the scope of the present review.

In the study,[144] the photolysis of phenyl azide was investigated (along with the photolysis of ten its *para* and *meta* derivatives containing F, Cl, CN, Me or MeO substituents) in nitrogen and argon matrices. In all cases, the IR spectra of the photolysis products in the matrices at 12 K show the most intense band (or a series of bands) at 1890–1906 cm^{-1}. Consequently, it was concluded that the corresponding ketene imine derivatives **28** are the major products in all reactions.

Unlike the photolysis of *para*- and *meta*-methyl derivatives of phenyl azide,[144] the photolysis of 2,6-dimethylphenyl azide (**30**) in a nitrogen matrix at 12 K affords the corresponding triplet nitrene ^{3}(**31**) as the major product. In the presence of CO, the latter gives 2,6-dimethylphenyl isocyanate (**32**).[167] Insignificant amounts of the corresponding ketene imine **33** were found upon UV irradiation of triplet nitrene.

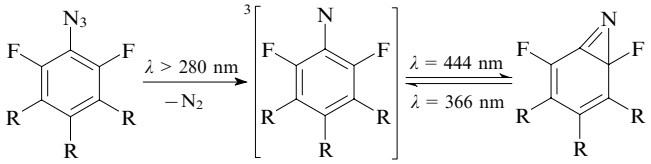


30 ^{3}(**31**)



Analogous results were obtained[166] in the study of the photolysis of perfluorophenyl azide (**34a**) in a nitrogen matrix. The major primary product, *viz*., perfluorophenylnitrene (**35a**) in the triplet state, was involved in the photochemical reaction with CO to give the corresponding isocyanate. Azirine and ketene imine were not found.[166]

More recently, it was confirmed[168] that the photolysis of perfluorophenyl azide (**34a**) and 2,6-difluorophenyl azide (**34b**) in an argon matrix affords the corresponding triplet nitrenes **35a**,**b** as the major products. However, as opposed to the previous study,[166] the irradiation of nitrenes ^{3}(**35a**,**b**) with visible light (λ = 444 nm) was found to give the corresponding azirines **36a**,**b**. This process is reversible, and the irradiation of azirines **36** with light with λ = 366 nm leads to their transformation into the corresponding triplet nitrenes **35**.[168]

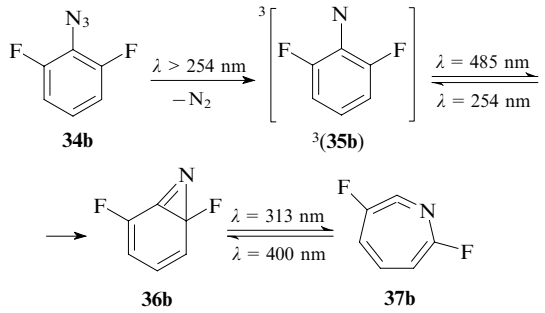


34a,**b** ^{3}(**35a**,**b**) **36a**,**b**

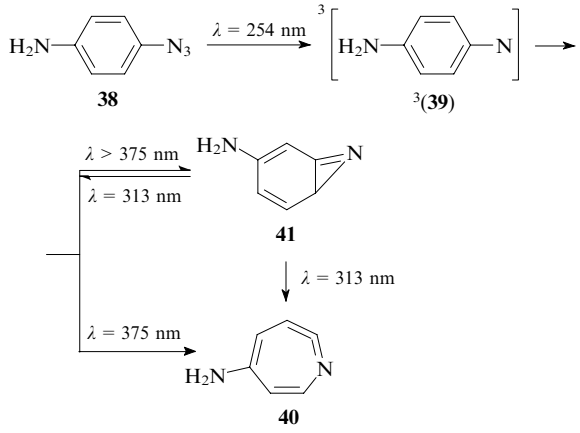
R = F (**a**), H (**b**).

In the very recent past, the photolysis of azide **34b** in an argon matrix at 12 K has been more thoroughly studied by IR and electronic absorption spectroscopy combined with quantum chemical calculations.[169] As opposed to the earlier studies,[166, 168] the interconversions of benzazirine **36b** and ketene imine **37b** were also observed. The complete scheme of the

phototransformations of azide **34b** can be represented as follows.



The formation not only of the corresponding triplet nitrene and ketene imine but also of azirine was observed [170] in the photolysis of *p*-azidoaniline (**38**) in an argon matrix at 12 K. The irradiation of triplet nitrene **39** was found to give not only ketene imine **40** but also azirine **41**, which, in turn, disappears upon irradiation at 313 nm.



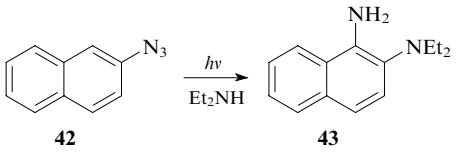
Therefore, the photolysis of phenyl azide and a series of its *meta* and *para* derivatives in nitrogen and argon matrices at ~10 K affords the corresponding ketene imines in high yield. The latter are, most likely, generated from vibrationally excited singlet nitrene, as well as in the course of the secondary photolysis of the corresponding triplet nitrenes.

The photolysis of phenyl azide derivatives containing two substituents in the *ortho* position (azides **30** and **34a**,**b**) or a strong electron-donating substituent in the *para* position (azide **38**) gives the corresponding triplet nitrene, ^{3}(**31**), ^{3}(**35**) or ^{3}(**39**), as the only primary photolysis product.[166–170, 193] This result correlates with a substantial increase in the barrier for the cyclisation of the corresponding singlet nitrenes [^{1}(**31**), ^{1}(**35**) or ^{1}(**39**)] to azirines.[37, 194] In some cases, azirines (**36a**,**b** and **41**) were detected. According to calculations,[37, 177, 194] the barriers for the isomerisation of the latter azirines to the corresponding ketene imines (**37a**,**b** and **40**) are rather high.

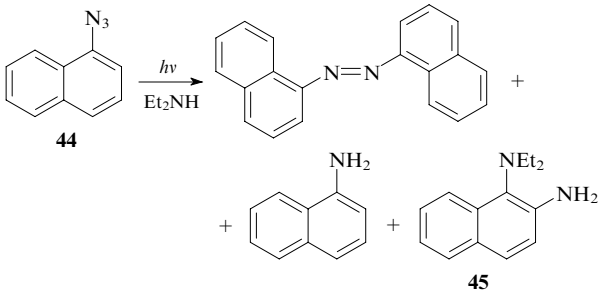
3. Photochemistry of polycyclic aryl azides

As in the case of phenyl azide and its derivatives, the formation of polycyclic arylnitrenes in the triplet ground state giving characteristic ESR spectra was observed upon irradiation of polycyclic aryl azides in glassy matrices at 77 K.[60, 195–198] The photochemistry of 1- and 2-naphthyl azides was studied in most detail, including investigations by the matrix isolation technique.[131, 198, 199]

The photolysis of 2-naphthyl azide (**42**) in solution in the presence of diethylamine affords the corresponding diamino derivative **43** in high yield.[200]

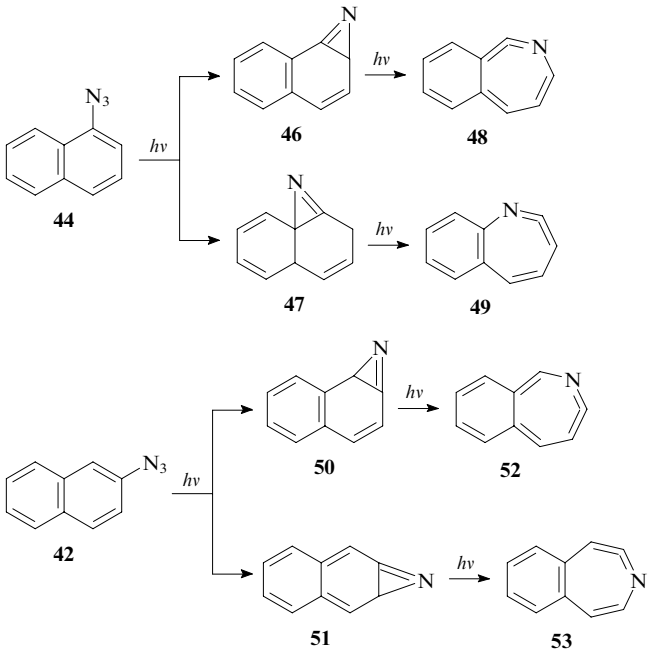


However, the photolysis of 1-naphthyl azide (**44**) in the presence of DEA gives mainly azanaphthalene [200] along with small amounts of 1-aminonaphthalene [200] and diamino derivative **45**.[201] The yield of compound **45** increases as the temperature decreases.[201]

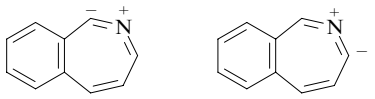


The formation of products **43** and **45** suggests that the corresponding tricyclic azirines are involved as intermediates of the photolysis of azides **42** and **44**. The spectrum of the products recorded in the photolysis (λ > 330 nm) of these azides in nitrogen and argon matrices at 12 K showed characteristic bands, which can be assigned to the corresponding azirines and ketene imines.[199] In the case of azide **44**, the band that appeared at 1730 cm^{-1} was assigned to tricyclic azirines **46** and(or) **47**. Upon prolonged photolysis, the spectrum showed bands at 1926 and 1912 cm^{-1} assigned to the corresponding didehydroazepines **48** and(or) **49**. Analogously, bands with maxima at 1708, 1723 and 1736 cm^{-1} were initially observed in the IR spectrum recorded in the photolysis of azide **42**; these bands can be assigned to azirines **50** and(or) **51**. The secondary photolysis was accompanied by the appearance of bands at 1911 and 1923 cm^{-1} assigned to didehydroazepines **52** and(or) **53** (Scheme 3). Unfortunately, it was impossible to make a more precise assignment at that time.

Scheme 3



As mentioned above, the development of more precise methods for calculations of IR and electronic absorption spectra of possible products allowed a more reliable and comprehensive analysis of the results obtained by the matrix isolation technique. Recently, the photolysis of azides **42** and **44** in an argon matrix has been reinvestigated,[132] and the new assignment of the bands in experimental electronic absorption and IR spectra was carried out based on detailed theoretical calculations. In the experimental IR and electronic absorption spectra, bands of triplet nitrenes **54** and **55**, azirines **46** and **50**, ketene imines **49** and **53** (Figs 15 and 16) and cyclic ylides **56** and **57** were identified.



56 **57**

Detailed calculations of PES, on which interconversions of the species under consideration proceed (see Figs 15 and 16), were performed in the study.[132] According to the calculations, singlet nitrene ^{1}(**55**) undergoes cyclisation to form exclusively azirine **46**, whereas nitrene ^{1}(**54**) gives azirine **50**. Azirines **47** and **51**, being highly energetic, are not formed.

The photolysis of 1- and 2-naphthyl azides with light with $\lambda = 313$ nm initially affords singlet nitrenes ^{1}(**55**) and ^{1}(**54**), whose relaxation to the triplet ground state competes with the cyclisation to azirines **46** and **50**. The latter are generated also in the secondary photolysis of triplet nitrenes ^{3}(**55**) and ^{3}(**54**).[134] The prolonged irradiation of the triplet nitrenes can lead to their transformations into cyclic ketene imines **49** and **53**, respectively, which have been observed earlier.[199]

The photolysis of azirines **46** and **50** affords new previously unknown isomers **56** and **57** instead of the expected ketene imines **48** and **52**. These compounds can formally be assigned to cyclic nitrile ylides the existence of which has been predicted.[202]

Recently, the photolysis of naphthyl azides has been studied in solution at room temperature by IR spectroscopy with a time resolution of $\sim$200 ns and by the laser flash photolysis technique in glassy 3-methylpentane at 77 K.[203] Upon the lader excitation of azide **44** at 77 K, singlet nitrene ^{1}(**55**) was found, and this compound relaxed to the triplet ground state ^{3}(**55**) with a rate constant of $k_{isc} = (1.1 \pm 0.1) \times 10^7$ s^{-1}. In turn, azirine **46** having a lifetime of 3.2 ± 0.6 μs in acetonitrile at room temperature was detected by time-resolved IR spectroscopy.[203] The rate constant of the reaction of **46** with DEA was estimated at $\sim 1.4 \times 10^5$ litre mol^{-1} s^{-1}. The low rate constant is consistent with low yields of diamine **45** in steady-state experiments.

As opposed to the photolysis of azide **44**, no intermediates having absorption at >320 nm were observed upon the laser excitation of azide **42** in glasses at 77 K. Under steady-state conditions, the formation of triplet nitrene **54** was also not observed. These data are in contradiction with the fact that triplet nitrene **54** was obtained as the major primary photolysis product of azide **42** in an argon matrix.[132] Two explanations were given for this contradiction.[203] First, nitrene ^{3}(**54**) could be the product of the secondary photolysis of azirine **50** in an argon matrix. According to an alternative hypothesis, $k_R \gg k_{isc}$ for singlet nitrene ^{1}(**54**) at 77 K, but $k_{isc} \gg k_R$ at 12 K (k_R is the rate constant for the cyclisation of singlet nitrene, and k_{isc} is the rate constant for the intersystem crossing to the triplet ground state). For the fulfillment of these conditions, the barrier for the cyclisation of nitrene ^{1}(**54**) (E_a)

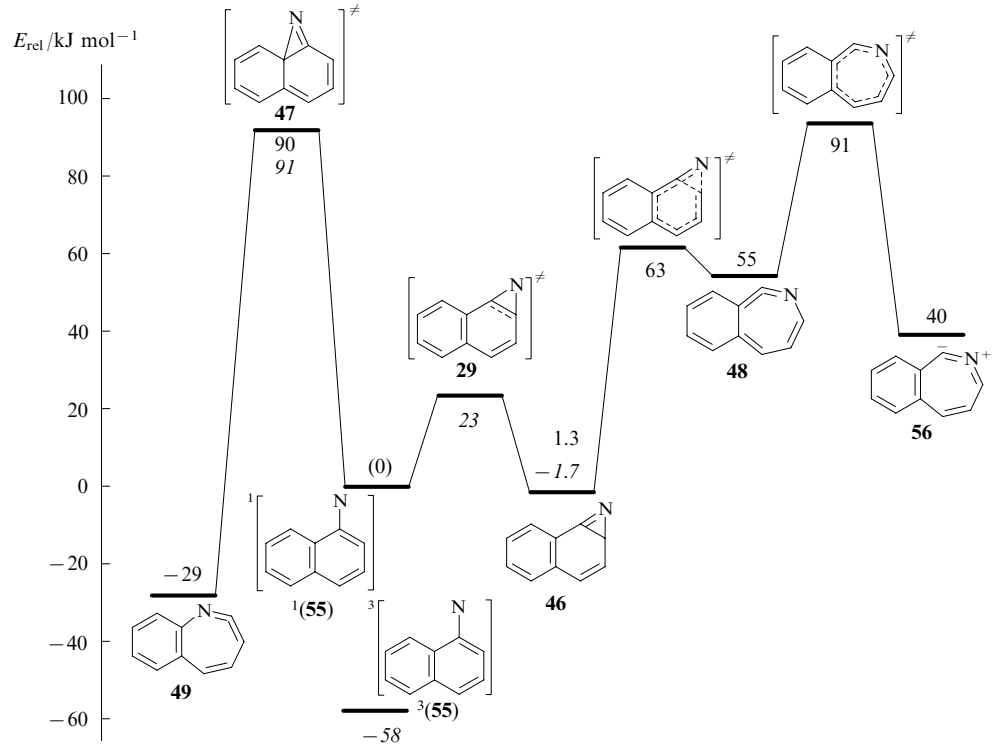


Figure 15. Relative energies of isomers of 1-naphthylnitrene and the transition states of their transformations.[132]
The CASPT2//CASSCF(12,12)/6-31G* calculations relative to the energy of ^{1}(**55**) (italic) and the B3LYP/6-311 + G(2d,p)//B3LYP/6-31G* calculations relative to the energy of ^{3}(**55**) and taking into account the singlet – triplet splitting for nitrene **55** calculated at the CASPT2 level (normal font). In all cases, the zero-point energy was taken into account. Structure **47** corresponds to the transition state in the DFT calculations and a shallow minimum in the CASSCF calculations.

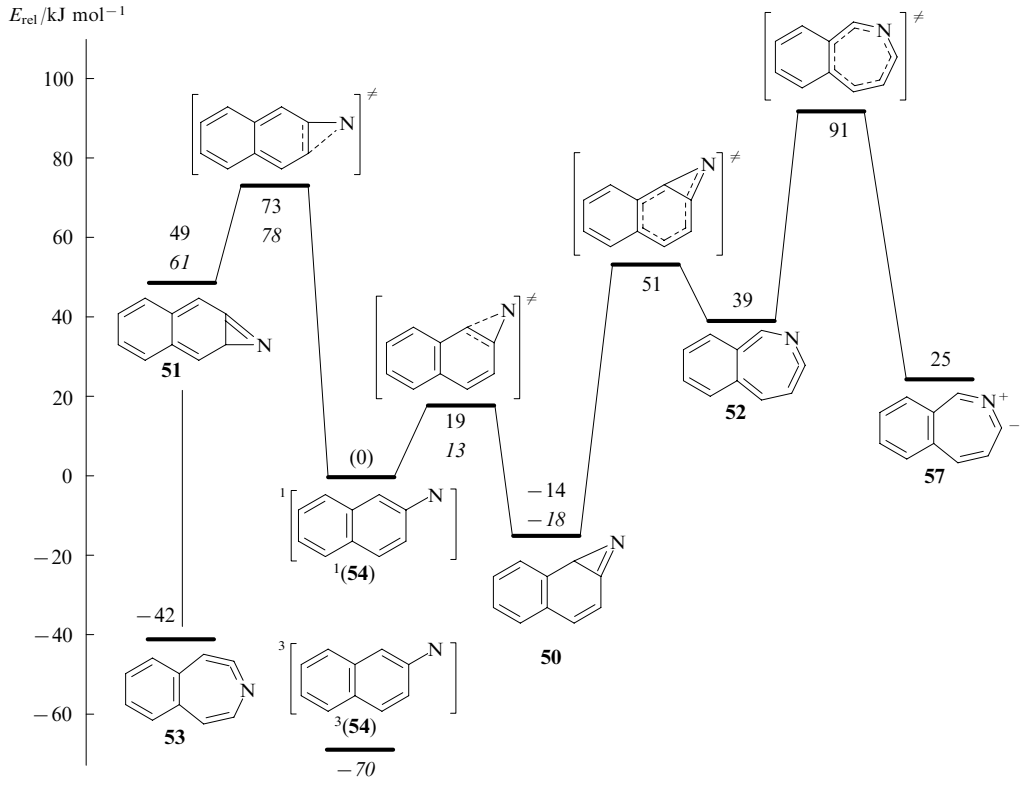
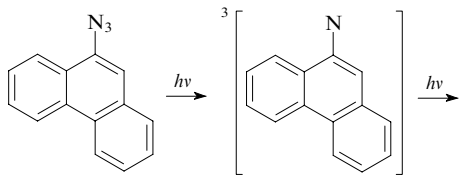


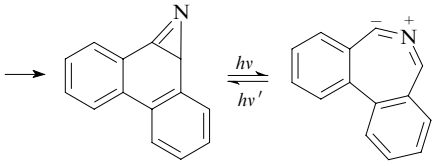
Figure 16. Relative energies of isomers of 2-naphthylnitrene and the transition states of their transformations.[132]
The CASPT2//CASSCF(12,12)/6-31G* calculations relative to the energy of ^{1}(**54**) (italic) and the B3LYP/6-311 + G(2d,p)//B3LYP/6-31G* calculations relative to the energy of ^{3}(**54**) and taking into account the singlet – triplet splitting for nitrene **54** calculated at the CASPT2 level (normal font). In all cases, the zero-point energy was taken into account.

should be in the range of $1.26 < E_a < 8.80$ kJ mol^{-1}, which is consistent with the calculated data (see Fig. 16).[132]

Azirine **50** was also detected as the photolysis product of 2-naphthyl azide in acetonitrile at room temperature by time-resolved IR spectroscopy. The lifetime of this compound appeared to be substantially longer (150 ± 10 μs) than that of azirine **46**, which is consistent with the theoretical calculations (see Figs 15 and 16).[203] The rate constant of the reaction of azirine **50** with DEA ($\sim 2.5 \times 10^5$ litre mol^{-1} s^{-1}) is almost twice as high as that for azirine **46** ($\sim 1.4 \times 10^5$ litre mol^{-1} s^{-1}). The substantially higher yield of diamine **43** is attributed to the longer lifetime of azirine **50** compared to azirine **46**.

The photolysis (λ = 308 and 313 nm) of phenanthren-9-yl azide in an argon matrix has been studied recently,[198] and the corresponding azirine was detected. Under irradiation, the latter (like 1- and 2-naphthyl azides, see Figs 15 and 16) was transformed into the corresponding cyclic ylide. The ESR spectrum of triplet phenanthren-9-ylnitrene was also observed. The following scheme of the phototransformations of this azide was proposed.





Therefore, the difference in the photochemistry of phenyl azide (and its simple derivatives) and polycyclic aryl azides (1- and 2-naphthyl azides, phenanthren-9-yl azide, *etc.*) is associated mainly with the differences in the thermodynamics of the isomerisation of the corresponding singlet arylnitrenes. As can be seen from the PES for the transformations of singlet phenylnitrene ^{1}(**29**) (and a series of its derivatives),[35, 37] ketene imine is thermodynamically more favourable than azirine (see Fig. 14, $\Delta H = -10.5$ kJ mol^{-1}). This is why ketene imine is involved in the reactions with nucleophiles. The introduction of one more phenyl ring into the molecule substantially stabilises one of isomeric azirines and destabilises another isomer (see Figs 15 and 16). For energy reasons, only one azirine can be formed, the isomerisation of which to the corresponding ketene imine is thermodynamically impossible. As a result, the photolysis of naphthyl azides and some other polycyclic azides in the presence of amines affords the corresponding diamines.[200, 201]

VI. Reactions of triplet nitrenes with oxygen

As mentioned in Section V.2, triplet arylnitrenes can react with a CO molecule either upon slight heating of a matrix or under the photochemical conditions.[166, 167] The present Section deals with reactions of nitrenes in the triplet ground state with

molecular oxygen. For arylnitrenes, this reaction was studied primarily in glasses at 77 K (Refs 159 and 204–207) and in solutions at room temperature by the flash photolysis technique.[159,206–212] The reactions of triplet *p*-aminophenylnitrene ^{3}(**39**) with oxygen was studied by the matrix isolation technique.[170] This reaction was studied also for the simplest triplet nitrene ^{3}(NH) in the gas phase[213,214] and in xenon and argon matrices.[215]

The NO$^\bullet$ and HO$^\bullet$ radicals are generated as the major reaction products of the ^{3}(NH) species with molecular oxygen in the gas phase.[213,214] Based on the results of quantum chemical calculations,[214,216] it was hypothesised that the primary event affords imine peroxide HNOO; the isomerisation of the latter (the 1,3-hydrogen shift) gives rise to hydroperoxynitrene HOON, which is rapidly decomposes to radicals.

$$^3(NH) + {}^3(O_2) \longrightarrow HNOO \longrightarrow [HOON] \longrightarrow NO^\bullet + HO^\bullet$$

The IR spectrum of imine peroxide and its ^{18}O-isotopically substituted analogue was recorded in the course of the photolysis of HN_3 followed by heating of an oxygen-containing xenon matrix.[215] After irradiation of an HN_3-O_2-Xe mixture (in a ratio of 1 : 5 : 550), *cis*- and *trans*-HONO, NH_2OH, N_2H_2 and ^{3}(NH) were obtained. After heating of the preirradiated sample to 50 K followed by cooling to 12 K, a group of lines in the IR spectrum (3132.2, 3120.5 and 3109.8 cm^{-1}) assigned to nitrene ^{3}(NH) completely disappeared and five new intense lines assigned to imine peroxide HNOO appeared.

Analogous results were obtained upon irradiation of HN_3 in an O_2-containing argon matrix. However, in this case, HNOO is formed without heating upon storage of a sample at 12 K for several hours. Based on a comparison of the calculated and experimental IR spectra, it was concluded that only one isomer (most likely, *trans*-HNOO) is formed.[215] Unfortunately, the electronic absorption spectra were not measured in the study.[215] However, it is evident that HNOO has absorption in the visible spectral region, because the irradiation with light with 400–600 nm led to the disappearance of peroxide and the appearance of an additional amount of nitrous acid (HONO).

The reaction of triplet arylnitrenes with oxygen has received much more attention. It has long been believed that the corresponding nitro compounds ($ArNO_2$) are the major oxygen-containing photolysis products of aryl azides (ArN_3) in the presence of oxygen.[193,204,217–219] Later, the formation of small amounts of nitroso compounds (ArNO)[220,221] and azoxy compounds that are formed apparently, by the reaction of triplet arylnitrenes with ArNO has been documented.[137,218]

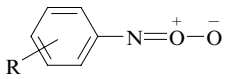
$$^3(ArN) + ArNO \longrightarrow Ar{-}N{=}\overset{+}{N}{-}Ar \quad (O^-)$$

It was stated[222] that PhNO is the primary photolysis product of phenyl azide in acetonitrile in the presence of oxygen, and only this compound is formed at a low concentration (10^{-4} mol litre^{-1}) of the irradiated solution. Nitrobenzene becomes the major reaction product upon irradiation of a concentrated ($\sim 10^{-2}$ mol litre^{-1}) solution of phenyl azide.[222]

More recently, it has been shown[159,206,207] that the corresponding nitro and nitroso compounds are the primary photolysis products of *p*-amino-, *p*-nitro- and *p*-methylphenyl azides. It should be noted that in these studies, small volumes of solutions containing azides at low concentrations ($\sim 10^{-4}$ mol litre^{-1}) were irradiated, thus excluding the secondary phototransformations of the initially formed products. The photolysis of all azides under study in alkanes affords nitro compounds in higher yields.

In the case of *p*-azidoaniline, the influence of the medium on the ratio of the yields of *p*-nitro- to *p*-nitrosoanilines was investigated, and this ratio was demonstrated to decrease on going from hexane (2.4) to acetonitrile (0.53).[205,206] Recently, the kinetics of the consumption of phenyl azide and the accumulation of the photolysis products in acetonitrile (2.5×10^{-4} mol litre^{-1}) has been studied.[210] It was demonstrated that during irradiation of phenyl azide, the concentration of $PhNO_2$ monotonically increased, and the concentration of PhNO first increased and then decreased virtually to zero, the yield of PhNO being substantially higher than that of $PhNO_2$ in the initial step of irradiation, as in the irradiation of *p*-azidoaniline.[206,207]

Heating of glassy matrices containing triplet arylnitrenes and dissolved O_2 to temperatures, at which the mobility of the latter substantially increases (90–110 K), affords diamagnetic adducts giving an intense absorption band in the near-UV or visible spectral region.[159,204–207] The structures of arylnitroso oxides were assigned to these adducts.

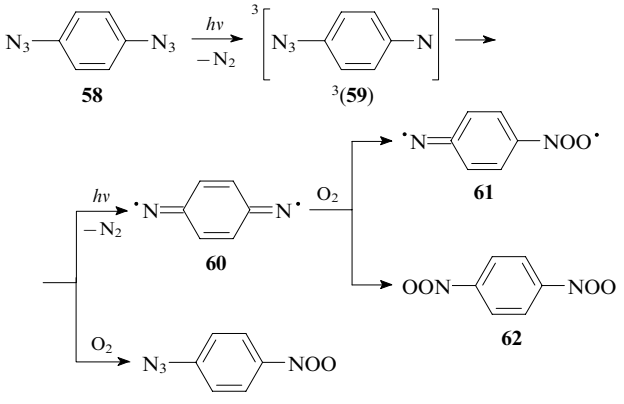


In the pioneering study,[204] emphasis was given to diazide **58**, photolysis of which can afford triplet nitrene ^{3}(**59**) and dinitrene ^{3}(**60**). Upon prolonged storage of the irradiated sample, both diamagnetic and paramagnetic products were obtained, and both these products were assigned to adducts of mononitrene ^{3}(**59**) with oxygen. In the study,[204] based on the fact that the intensity of the ESR spectrum assigned to dinitrene **60** remains unchanged, it was stated that dinitrene does not react with O_2. However, the accuracy of the ESR method is low. Hence, these results cannot completely exclude the formation of adducts **61** and **62**, among which paramagnetic compounds can be present (Scheme 4).

Although the assignment of the paramagnetic species to the adduct of mononitrene **59** with oxygen was erroneous,[204] it has long been commonly accepted that the reaction of triplet arylnitrenes produces both diamagnetic arylnitroso oxides and paramagnetic aryliminodioxy biradicals.

Recently, the reaction of triplet *p*-aminophenylnitrene ^{3}(**39**) with oxygen in a matrix consisting of 86% argon, 10% N_2 and 4% O_2 has been studied.[170] The irradiation of azide **38** in this matrix with light with $\lambda = 254$ nm, as well as in the absence of O_2, gave triplet nitrene **39** (Fig. 17, spectrum *1*). After slow heating of the matrix to 30 K followed by the storage at this temperature for 5 min and the subsequent cooling to 12 K, the intensity of the bands of nitrene ^{3}(**39**) in the electronic absorption spectrum slightly decreased, a band characteristic of arylnitroso oxides appeaeds in the visible spectral region at $\lambda_{max} = 445$ nm (Fig. 17, spectrum *2*), and

Scheme 4



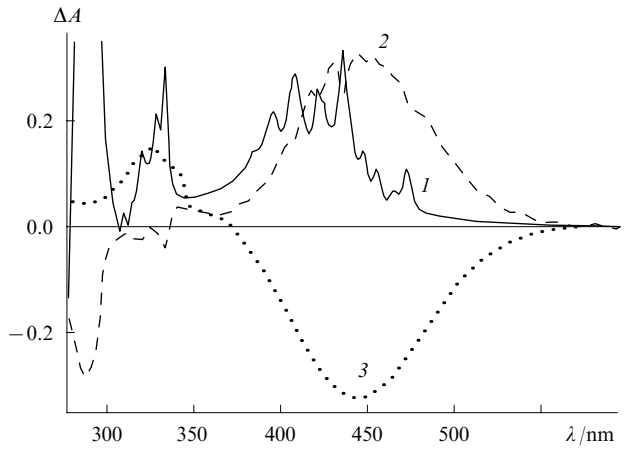


Figure 17. Difference electronic absorption spectra recorded in an argon matrix containing 4% O_2 at 12 K after irradiation of azide **38** with light at $\lambda = 254$ nm (*1*), after annealing of a sample at 30 K (*2*) and after irradiation with light at $\lambda > 515$ nm for 5 min (*3*).[170]

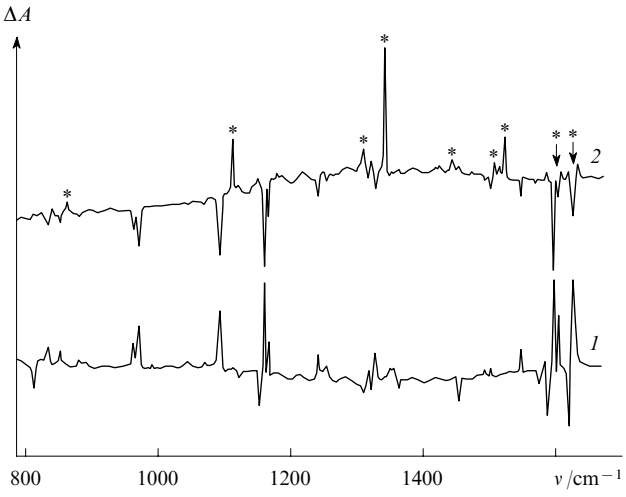


Figure 18. IR difference spectra recorded after annealing of a preirradiated sample of azide **38** at 30 K (*1*) and after irradiation with light at $\lambda > 515$ nm for 5 min (*2*).[170]
The signals of *p*-nitroaniline are marked with asterisks.

the IR spectrum showed a series of new bands (Fig. 18, spectrum *1*). It should be noted that the reaction of nitrene ^{3}(**39**) with oxygen has been studied earlier in a glassy mixture of tetrahydrofuran and toluene (1 : 1) at 95 K; the formation of the adduct giving a band at $\lambda_{max} = 495$ nm was observed.[207, 208]

The irradiation of a sample with visible light ($\lambda > 515$ nm) leads to the disappearance of the absorption band of nitroso oxide **63** and the appearance of a new band in the near-UV region at $\lambda_{max} = 326$ nm (Fig. 17, spectrum *3*) and a series of bands in the IR spectrum (Fig. 18, spectrum *2*), which are identical to the bands in the IR spectrum of *p*-nitroaniline (**64**) (marked with asterisks in Fig. 18).

It appeared [170] that two isomers of nitroso oxide (*cis*- and *trans*-**63**) are formed. One of them disappears after irradiation for 30 s ($\lambda > 515$ nm) being transformed into *p*-nitroaniline. This isomer is characterised by a long-wavelength band at $\lambda_{max} = 460$ nm (Fig. 19, spectrum *1*) and a series of bands in the IR spectrum (Fig. 20, spectrum *1*, the negative differential

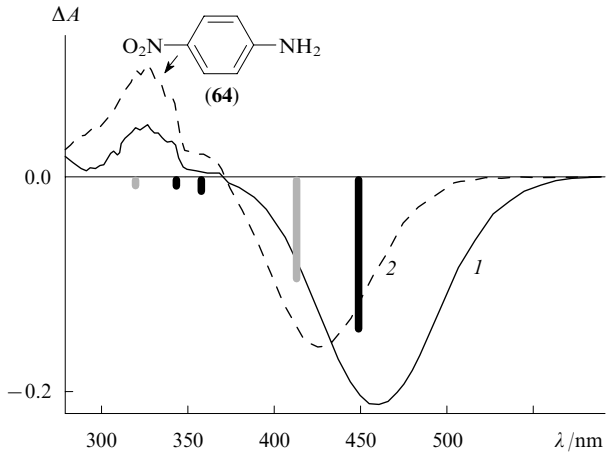


Figure 19. Difference electronic absorption spectra recorded in an argon matrix at 12 K after irradiation of the adduct of triplet nitrene **39** with O_2 with light at $\lambda > 515$ nm for 30 s (*1*) and after additional irradiation for 5 min (*2*).
The positions and relative intensities of electron transitions in the spectrum of the *trans* isomer of nitroso oxide **63** (black bars) and its *cis* isomer (gray bars) calculated at the CASSCF/CASPT2 level with the geometry optimised at the CASSCF level [170] are indicated by vertical bars.

absorption). Another isomer, the absorption spectrum of which is shifted to shorter wavelengths ($\lambda_{max} = 425$ nm), is also transformed into *p*-nitroaniline upon further irradiation (see Figs 19 and 20, difference spectra *2*).[170]

The validity of the assignment of the adducts of nitrene ^{3}(**39**) with oxygen to the *cis* and *trans* isomers of nitroso oxide **63** was confirmed by a good agreement between the experimental and calculated electronic absorption spectra (see Fig. 19) and IR spectra (see Fig. 20). The agreement between the calculated and experimental electronic absorption spectra is much poorer when the geometry calculated by the density functional theory is used.[170] The agreement between the IR spectra calculated by the DFT method and the experimental spectra of the *cis* and *trans* isomers of nitroso oxide **63** is

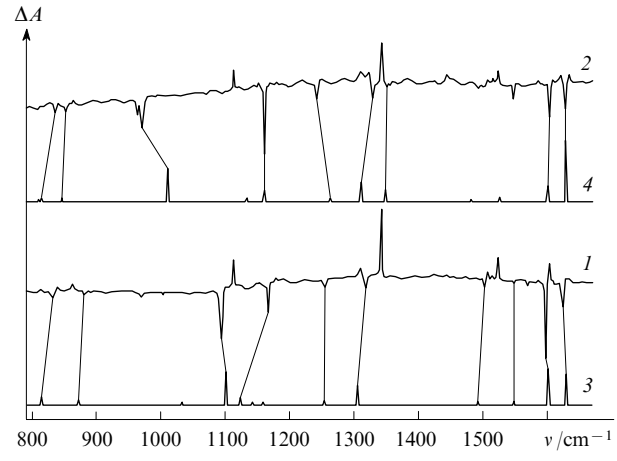


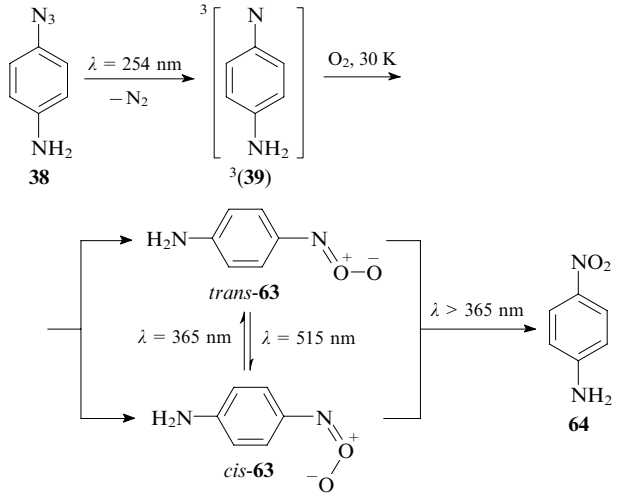
Figure 20. IR difference spectra recorded in an argon matrix at 12 K after irradiation of the adduct of triplet nitrene **39** with O_2 with light at $\lambda > 515$ nm for 30 s (*1*) and after additional irradiation for 5 min (*2*). IR spectra of the *cis* isomer of nitroso oxide **63** (*3*) and its *trans* isomer (*4*) calculated at the B3LYP/6-31G* level (the correction factor is 0.9614).[170]

satisfactory (see Fig. 20) but it is noticeably poorer than that for triplet nitrene **39**. Hence, it is incorrect to describe nitroso oxides by single-determinant wavefunctions. For example, the contribution of the ground state configuration to the wave function of the *cis* and *trans* isomers of nitroso oxide **63** estimated at the CASSCF level of theory is ~82%, and the contribution of the doubly excited configurations is ~18%.[170]

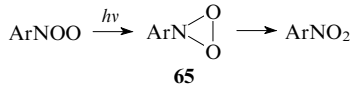
However, the population numbers of the CASSCF natural orbitals only slightly differ from 0 and 2 (the largest deviation is 0.13 for HOMO and LUMO), and this fact contradicts the statement [220, 221, 223] that arylnitroso oxides are essentially biradical in character.

The use of low-intensity monochromatic radiation allows the observation of interconversions of the *cis* and *trans* isomers of compound **63** along with their transformation into *p*-nitroaniline (Scheme 5).

Scheme 5



It is commonly accepted [2204, 210, 212, 220, 221, 224, 225] that the photolysis of arylnitroso oxides (ArNOO) affords cyclic dioxaziridines **65**, which are transformed into nitro compounds through the ring opening. Actually, intermediate species were observed [224] in the photolysis of a series of nitroso oxides of stilbene and *p*-biphenyl in glassy tetrahydrofuran at 77 K. These species were transformed into the corresponding nitro derivatives in the dark at a rate constant of 3×10^{-3} s^{-1}. It was hypothesised that these species can be assigned to the corresponding dioxaziridines **65**. Unfortunately, we failed to detect intermediate species in the photolysis of nitroso oxide **63**.[170]



The formation of nitroso oxides in cryogenic matrices is evidence for a low activation energy of the reaction of triplet nitrenes with molecular oxygen. The rate constants for this reaction were measured for triplet phenylnitrene,[210] a series of its derivatives [159, 206, 207] and pyren-1-ylnitrene.[193] It appeared that the rate constant is substantially lower than the diffusion limit and is in a range of $(0.8-8) \times 10^6$ litre mol^{-1} s^{-1} for all arylnitrenes under study. For phenylnitrene, the temperature dependence of the rate constant was studied and the activation parameters were estimated ($A = 10^{9.6 \pm 0.4}$ litre mol^{-1} s^{-1} and $E_a = 18 \pm 2$ kJ mol^{-1}).[210]

Numerous attempts were made to calculate the thermodynamics of the reaction of triplet nitrenes with oxygen.[170, 207, 216, 224–226] The results obtained [170, 226] with the use of the CBS-QB3 approach, which is one of the most accurate multi-level techniques, are presented in Fig. 21. According to

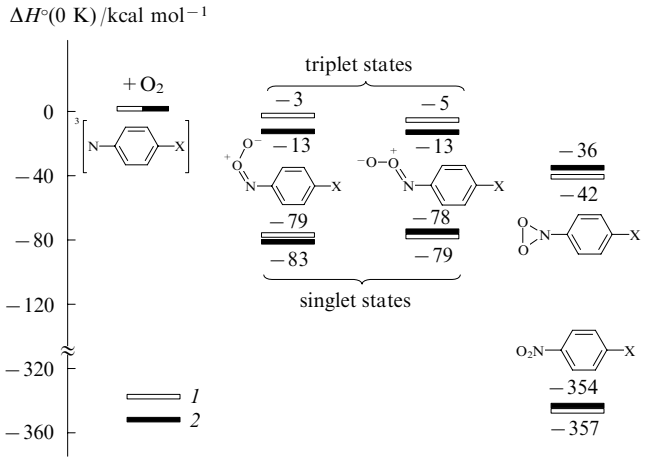
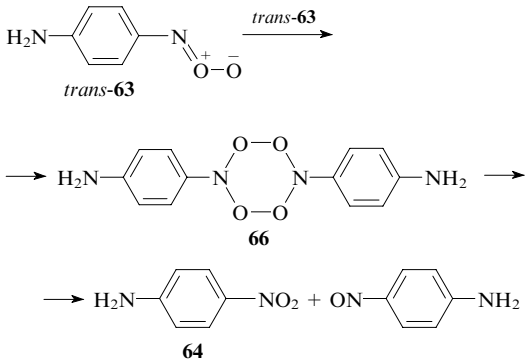


Figure 21. Relative enthalpies (at 0 K) of species involved in the formation and transformations of phenyl- (*1*, X = H) and *p*-aminophenylnitroso oxides (*2*, X = NH_2) calculated by the CBS-QB3 method.[170, 226]

the Wigner rule, the reaction of triplet nitrene with a triplet oxygen molecule can, in principle, produce nitroso oxide both in the singlet and triplet states. The reaction giving nitroso oxides in the triplet state is virtually thermoneutral and, according to calculations,[226] its activation energy is rather high (45–55 kJ mol^{-1}). The reaction producing arylnitroso oxides in the singlet ground state is exothermic ($\Delta H \approx -80$ kJ mol^{-1}). However, the transition state on the singlet PES was not located.[226]

The mechanism of the transformation of arylnitroso oxides into the final nitroso and nitro compounds remains obscure. Only in the case of arylnitroso oxide **63**, the flash photolysis study showed that the decay kinetics of this compound is described by the second-order reaction with a rate constant close to the diffusion limit.[206, 208] The electronic absorption spectrum of the intermediate, the precursor of the final products (ArNO and $ArNO_2$), was recorded, and the structure of dimeric peroxide **66** was assigned to this intermediate. The formation of the final nitro and nitroso compounds from this intermediate can easily be conceived.



The decay kinetics of all other nitroso oxides under study (PhNOO and its *p*-Me, *p*-NO_2, *p*-Br, *p*-OMe and *p*-NMe_2 derivatives) is not described by the second-order reaction and is either exponential or biexponential.[159, 207, 209–212] The biexponential character of the decay kinetic curves is associated with the formation of the *cis* and *trans* isomers of arylnitroso oxides having different reactivities.[211, 212]

It was hypothesised that thermal transformations of arylnitroso oxides (like photochemical transformations) proceed through the formation of intermediate dioxaziridine **65**.[209–214, 225] However, this reaction cannot explain the for-

mation of ArNO. The assumption of the possible formation of ArNO in the reaction of aryl azide in the triplet excited state $^3(ArN_3)$* with oxygen is invalid because the dissociation of the azido group in the singlet excited state of aryl azides proceeds on a hundred femtosecond time scale.[152–155] The intersystem crossing to the triplet state cannot proceed on such a short time scale.

The possibility of the formation of ArNO in the reaction with solvents cannot be ruled out. For example, the irradiation of phenyl azide in the presence of O_2 in acetonitrile with 10% benzene additive was found [220, 221] to give phenol in 15% yield. The irradiation of phenyl azide in acetonitrile in the presence of 10% toluene afforded kresol (in 12% yield) and benzaldehyde (in 5% yield). The addition of cyclohexane to the solution resulted in the isolation of cyclohexanone (5%) and cyclohexanol (17%).

Thus, both the simplest triplet nitrene ^{3}(NH) and triplet arylnitrenes react with molecular oxygen in cryogenic matrices to form the corresponding nitroso oxides. In the case of imino peroxide HNOO, only the *trans* isomer was detected, whereas the formation of both the *cis* and *trans* isomers was observed for arylnitroso oxides. Nitrous acid (HONO) is formed in the course of photolysis of imino peroxide HNOO. Upon irradiation of arylnitroso oxides (ArNOO), the reversible *cis–trans* isomerisation and the irreversible transformation into the nitro compounds ($ArNO_2$) were observed. The formation of intermediates, *viz*., dioxaziridines, in the course of photolysis was not reliably confirmed. The mechanism of dark transformations of arylnitroso oxides into the final nitro and nitroso compounds was not ultimately established as well.

VII. Conclusion

Before the modern physicochemical methods were developed, knowledge about intermediate species could be obtained solely based on the analysis of the reaction products. Only in the mid-20th century, when two powerful tools of investigation (the flash photolysis and matrix isolation techniques) were devised, the direct observation and studies of the properties of the reaction intermediates became possible. Considerable progress has been achieved in the development of the flash photolysis techniques allowing experiments to be performed with femtosecond and even attosecond time resolution. Although the progress in the matrix isolation techniques is less impressive, it remains one of the main methods of obtaining the most complete spectroscopic information on the reaction intermediates, which allows their reliable identification. The matrix isolation technique is particularly promising in combination with IR spectroscopy of intermediates, because well-resolved IR spectra with a linewidth of ~ 1 cm^{-1} can be recorded in a very wide spectral range in inert gas matrices at very low temperatures (~ 10 K). In the last decade, the procedure of the assignment of bands in the experimental electronic absorption and IR spectra of intermediates has been substantially simplified and it has become more reliable due to the development of rather precise theoretical calculation methods.

Investigations of the photolysis of azides by the matrix isolation technique made a considerable contribution to the elucidation of the rather complex mechanism of this important photochemical reaction. For example, the detection of ketene imine in the course of photolysis of phenyl azide in an argon matrix had a considerable effect on the interpretation of the results obtained by alternative methods, including the flash photolysis technique. The hypothesis about the possibility of the formation and isomerisation of singlet arylnitrenes in the vibrationally excited state, which has been made for the first time to interpret the results obtained in cryogenic matrices, has been confirmed very recently in femtosecond studies.[151–155] In very recent years, the use of the matrix isolation technique combined with high-level quantum chemical calculations allowed the elucidation of the unusual nature of singlet acylnitrenes,[38–40] which are promising for the photoaffinity labelling of biopolymers, and provided an insight into the detailed mechanism of photolysis of polycyclic aryl azides.[132]

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References

1. E Whittle, D A Dows, G C Pimentel *J. Chem. Phys.* **22** 1943 (1954)
2. E D Becker, G C Pimentel *J. Chem. Phys.* **25** 224 (1956)
3. I Norman, G Porter *Nature (London)* **174** 58 (1954)
4. M Moskovits, G A Ozin *Cryochemistry* (New York: Wiley-Interscience, 1976)
5. *Matrix Isolation Spectroscopy (NATO Advanced Study Institute, Ser. C* Vol. 76) (Eds J Barnes, W J Orville-Thomas, A Muller, R Gaufres) (Dordrecht: Reidel, 1981)
6. *Chemistry and Physics of Matrix Isolated Species* (Eds L Andrews, M Moskovits) (Amsterdam: North-Holand, 1988)
7. M J Almond, A J Downs *Spectroscopy of Matrix Isolated Species* (Chichester: Wiley, 1989)
8. R Dunkin *Matrix Isolation Techniques: a Practical Approach* (Oxford: Oxford University Press, 1998)
9. V E Bondybey, A M Smith, J Agreiter *Chem. Rev.* **96** 2113 (1996)
10. T Bally *Reactive Intermediate Chemistry* (Eds R A Moss, M S Platz M.Jones) (Hoboken, NJ: Wiley, 2004) p. 797
11. A D Becke *J. Chem. Phys.* **98** 5648 (1993)
12. C Lee, W Yang, R G Parr *Phys. Rev. B* **37** 785 (1988)
13. C Cramer *Essentials of Computational Chemistry* (Chichester: Wiley, 2002) p. 305
14. B O Roos *Adv. Chem. Phys.* **69** 399 (1987)
15. K Andersson, B O Roos *Modern Electronic Structure Theory* (Singapore: World Scientific, 1995) Pt 2 P. 55
16. K Andersson, M R A Blomberg, M P Fülscher, V Kelll, R Lindh, P Å Malmqvist, J Noga, J Olson, B O Roos, A Sadlej, P E M Siegbahn, M Urban, P-O Widmark *MOLCAS, Version 5* (Lund: University of Lund, 2002)
17. E K U Gross, W Kohn *Adv. Quantum Chem.* **21** 255 (1990)
18. K B Wiberg, R E Stratmann, M J Frisch *Chem. Phys. Lett.* **297** 60 (1998)
19. D S Breslow *Azides and Nitrenes; Reactivity and Utility* (Ed. E F V Scriven) (New York: Academic Press, 1984) p. 491
20. E W Meijer, S Nijhuis, F C B M Von Vroonhoven *J. Am. Chem. Soc.* **110** 7209 (1988)
21. P A S Smith *Nitrenes* (Ed. W Lwowski) (New York: Wiley-Interscience, 1970)
22. H Bayley *Photogenerated Reagents in Biochemistry and Molecular Biology* (New York: Elsevier, 1983)
23. S X Cai, D J Glenn, J F W Keana *J. Org. Chem.* **57** 1299 (1992)
24. H Niino, Y Koga, A Yabe *J. Photochem. Photobiol. A: Chem.* **106** 9 (1997)
25. H Niino, T Sato, A Yabe *Appl. Phys. A* **69** 605 (1999)
26. E F V Scriven *Reactive Intermediates* Vol. 2 (Ed. R A Abramovitch) (New York: Plenum, 1982)
27. P A S Smith *Azides and Nitrenes; Reactivity and Utility* (Ed. E F V Scriven) (New York: Academic Press, 1984) p. 95
28. M S Platz, V M Maloney *Kinetics and Spectroscopy of Carbenes and Biradicals* (Ed. M S Platz) (New York: Plenum, 1990)
29. G B Schuster, M S Platz *Adv. Photochem.* **17** 69 (1992)

30. M F Budyka, M M Kantor, M V Alfimov *Usp. Khim.* **61** 48 (1992) [*Russ. Chem. Rev.* **61** 25 (1992)]
31. N P Gritsan, E A Pritchina *Usp. Khim.* **61** 910 (1992) [*Russ. Chem. Rev.* **61** 500 (1992)]
32. C Wentrup *Reactive Molecules. The Neutral Reactive Intermediates in Organic Chemistry* (New York: Wiley-Interscience, 1984)
33. C Wentrup *Azides and Nitrenes; Reactivity and Utility* (Ed. E F V Scriven) (New York: Academic Press, 1984) p. 395
34. W T Borden, N P Gritsan, C M Hadad, W L Karney, C R Kemnitz, M S Platz *Acc. Chem. Res.* **33** 765 (2000)
35. N P Gritsan, M S Platz *Adv. Phys. Org. Chem.* **36** 255 (2001)
36. N P Gritsan, M S Platz, W T Borden *Computational Methods in Photochemistry*. (Ed. A G Kutateladze) (Boca Raton, FL: CRC, 2005) p. 235
37. N P Gritsan, M S Platz *Chem. Rev.* **106** 3844 (2006)
38. E A Pritchina, N P Gritsan, A Maltsev, T Bally, T Autrey, Y Liu, Y H Wang, J P Toscano *Phys. Chem. Chem. Phys.* **5** 1010 (2003)
39. J Liu, S Mandel, C M Hadad, M S Platz *J. Org. Chem.* **69** 8583 (2004)
40. E A Pritchina, N P Gritsan, T Balli *Izv. Akad. Nauk, Ser. Khim.* 519 (2005) [a]
41. H Okabe *J. Chem. Phys.* **49** 2726 (1968)
42. H Okabe *Photochemistry of Small Molecules* (New York: Wiley, 1978)
43. J R McDonald, R G Miller, A P Baronavski *Chem. Phys. Lett.* **51** 57 (1977)
44. A P Baronavski, R G Miller, J R McDonald *Chem. Phys.* **30** 119 (1978)
45. F Rohrer, F Stuhl *J. Chem. Phys.* **88** 4788 (1988)
46. J Masanet, A Gilles, C Vermeil *J. Photochem.* **3** 417 (1974/75)
47. O Kajimoto, T Yamamoto, T Fueno *J. Phys. Chem.* **83** 429 (1979)
48. J C Stephenson, M P Casassa, D S King *J. Phys. Chem.* **89** 1378 (1988)
49. M H Alexander, H-J Werner, P J Dagdigian *J. Chem. Phys.* **89** 1388 (1988)
50. E D Becker, G C Pimentel, M Van Thiel *J. Chem. Phys.* **26** 145 (1957)
51. M McCarty, G W Robinson *J. Am. Chem. Soc.* **81** 4472 (1959)
52. V E Bondybey, L E Brus *J. Chem. Phys.* **63** 794 (1975)
53. H Esser, J Langen, U Schurath *Ber. Bunsen-Ges. Phys. Chem.* **87** 636 (1983)
54. A Ramsthaler-Sommer, K E Eberhardt, U Schurath *J. Chem. Phys.* **85** 3760 (1986)
55. C Blindauer, N van Riesenbeck, K Seranski, M Winter, A C Backer, U Schurath *Chem. Phys.* **150** 93 (1991)
56. E P Kyba, R A Abramovitch *J. Am. Chem. Soc.* **102** 735 (1980)
57. E P Kyba *Azides and Nitrenes; Reactivity and Utility* (Ed. E F V Scriven) (New York: Academic Press, 1984) p. 2
58. L Barash, E Wasserman, W A Jager *J. Am. Chem. Soc.* **89** 3931 (1967)
59. J H Glowina, J Misewich, P P Sorokin *Supercontinuum Laser Sources* (Ed. R R Alfano) (New York: Springer, 1989)
60. E Wasserman *Prog. Phys. Org. Chem.* **8** 319 (1971)
61. D E Milligan *J. Chem. Phys.* **35** 1491 (1961)
62. M E Jacox, D E Milligan *J. Mol. Spectrosc.* **56** 333 (1975)
63. I R Dunkin, P C P Thomson *Tetrahedron Lett.* **21** 3813 (1980)
64. J Michl, J G Radziszewski, J W Downing, K B Wiberg, F H Walker, R D Miller, P Kovacic, M Jawdosiuk, V Bonacic-Koutecky *Pure Appl. Chem.* **55** 315 (1983)
65. I R Dunkin, C J Shields, H Quasi, B Seiferling *Tetrahedron Lett.* **24** 3887 (1983)
66. R S Sheridan, G A Ganzer *J. Am. Chem. Soc.* **105** 6158 (1983)
67. J G Radziszewski, J W Downing, M Jawdosiuk, P Kovacic, J Michl *J. Am. Chem. Soc.* **107** 594 (1985)
68. J G Radziszewski, J W Downing, C Wentrup, P Kaszynski, M Jawdosiuk, P Kovacic, J Michl *J. Am. Chem. Soc.* **107** 2799 (1985)
69. G Smolinsky, E Wasserman, W A Yager *J. Am. Chem. Soc.* **84** 3220 (1962)
70. E Wasserman, E Smolinsky, W A Yager *J. Am. Chem. Soc.* **86** 3166 (1964)
71. P J Wagner, B J Scheve *J. Am. Chem. Soc.* **101** 378 (1979)
72. S M Mandel, J A K Bauer, A D Gudmundsdóttir *Org. Lett.* **3** 523 (2001)
73. P N D Singh, S M Mandel, R M Robinson, Z Zhu, R Franz, B S Ault, A D Gudmundsdóttir *J. Org. Chem.* **68** 7951 (2003)
74. P G Carrick, P C Engelking *J. Chem. Phys.* **81** 1661 (1984)
75. P G Carrick, C R Brazier, P F Bernath, P C Engelking *J. Am. Chem. Soc.* **109** 5100 (1987)
76. E L Chappell, P C Engelking *J. Chem. Phys.* **89** 6007 (1988)
77. C R Brazier, P G Carrick, P F Bernath *J. Chem. Phys.* **96** 919 (1992)
78. R F Ferrante *J. Chem. Phys.* **86** 25 (1987)
79. T Franken, D Perner, M W Bosnali *Z. Naturforsch., A* **25** 151 (1970)
80. R F Ferrante *J. Chem. Phys.* **94** 4678 (1991)
81. H Shang, C Yu, L Ying, X Zhao *J. Chem. Phys.* **103** 4418 (1995)
82. L Ying, Y Xia, H Shang, X Zhao, Y Tang *J. Chem. Phys.* **105** 5798 (1996)
83. M J Travers, D C Cowles, E P Clifford, G B Ellison, P C Engelking *J. Phys. Chem.* **111** 5349 (1999)
84. D R Yarkony, H F Schaefer, S Rothenberg *J. Am. Chem. Soc.* **96** 5974 (1974)
85. J Demuynck, D J Fox, Y Yamaguchi, H F Schaefer III *J. Am. Chem. Soc.* **102** 6204 (1980)
86. J A Pople, K Raghavachari, M J Frisch, J S Binckley, P v R Schleyer *J. Am. Chem. Soc.* **105** 6389 (1983)
87. M T Nguyen *Chem. Phys. Lett.* **117** 290 (1985)
88. Y Xie, G E Scuseria, B F Yates, Y Yamaguchi, H F Schaefer III *J. Am. Chem. Soc.* **111** 5181 (1989)
89. C Richards Jr, C Meredith, S-J Kim, G E Quelch, H F Schaefer III *J. Chem. Phys.* **100** 481 (1994)
90. M T Nguyen, D Sengupta, T-K Ha *J. Phys. Chem.* **100** 6499 (1996)
91. J F Arenas, J C Otero, A Sánchez-Gálvez, J Soto, P Viruela *J. Phys. Chem.* **102** 1146 (1998)
92. J F Arenas, J I Marcos, J C Otero, A Sánchez-Gálvez, J Soto *J. Chem. Phys.* **111** 551 (1999)
93. C R Kemnitz, G B Ellison, W L Karney, W T Borden *J. Am. Chem. Soc.* **122** 1098 (2000)
94. N P Gritsan, I Likhotvorik, Z D Zhu, M S Platz *J. Phys. Chem. A* **105** 3039 (2001)
95. F D Wayne, H E Radford *Mol. Phys.* **32** 1407 (1976)
96. W Lwowski, G T Tisue *J. Am. Chem. Soc.* **87** 4022 (1965)
97. G M Nazin *Usp. Khim.* **41** 1537 (1972) [*Russ. Chem. Rev.* **41** 711 (1972)
98. W Lwowski *Azides and Nitrenes; Reactivity and Utility* (Ed. E F V Scriven) (New York: Academic Press, 1984) p. 205
99. M V Zabalov, R P Tiger *Izv. Akad. Nauk, Ser. Khim.* 2200 (2005) [a]
100. G T Tisue, S Linke, W Lwowski *J. Am. Chem. Soc.* **89** 6303 (1967)
101. S Linke, G T Tisue, W Lwowski *J. Am. Chem. Soc.* **89** 6308 (1967)
102. E Eibler, J Sauer *Tetrahedron Lett.* 2569 (1974)
103. V P Semenov, A N Studenikov, A D Bespalov, K A Ogloblin *Zh. Org. Khim.* **13** 2202 (1977) [b]
104. W Lwowski, F P Woerner *J. Am. Chem. Soc.* **87** 5491 (1965)
105. J S McConaghy, W Lwowski *J. Am. Chem. Soc.* **89** 4450 (1967)
106. T Autrey, G B Schuster *J. Am. Chem. Soc.* **109** 5814 (1987)
107. M E Sigman, T Autrey, G B Schuster *J. Am. Chem. Soc.* **110** 4297 (1988)
108. C Buron, M S Platz *Org. Lett.* **5** 3383 (2003)
109. R E Wilde, T K K Srinivasan, W Lwowski *J. Am. Chem. Soc.* **93** 860 (1971)
110. J H Teles, G Maier *Chem. Ber.* **122** 745 (1989)
111. N P Gritsan, E A Pritchina *Mendeleev Commun.* 94 (2001)
112. V I Faustov, E G Baskir, A A Biryukov *Izv. Akad. Nauk, Ser. Khim.* 2203 (2003) [a]
113. R Puttner, K Hafner *Tetrahedron Lett.* 3119 (1964)
114. Y Hayashi, D Swern *J. Am. Chem. Soc.* **95** 5205 (1973)
115. M Inagaki, T Shingaki, T Nagai *Chem. Lett.* **10** 1419 (1981)
116. M Inagaki, T Shingaki, T Nagai *Chem. Lett.* **11** 9 (1982)
117. I Woelfle, B Sauerwein, T Autrey, G B Schuster *Photochem. Photobiol.* **47** 497 (1988)

118. T Melvin, G B Schuster *Photochem. Photobiol.* **51** 155 (1990)
119. C Wentrup, H Bornemann *Eur. J. Org. Chem.* 4521 (2005)
120. P F Alewood, P M Kazmaier, A Rauk *J. Am. Chem. Soc.* **95** 5466 (1973)
121. J F Harrison, G Shalhoub *J. Am. Chem. Soc.* **97** 4172 (1975)
122. A Rauk, P F Alewood *Can. J. Chem.* **55** 1498 (1977)
123. D Poppinger, L Radom *J. Am. Chem. Soc.* **100** 3674 (1978)
124. A Mavridis, J F Harrison *J. Am. Chem. Soc.* **99** 7651 (1980)
125. W A Shapley, G B Bacskay *J. Phys. Chem. A* **103** 4514 (1999)
126. W A Shapley, G B Bacskay *J. Phys. Chem. A* **103** 6624 (1999)
127. K Anderson *Theor. Chim. Acta* **91** 31 (1995)
128. V Parasuk, C J Cramer *Chem. Phys. Lett.* **260** 7 (1996)
129. W L Karney, W T Borden *J. Am. Chem. Soc.* **119** 1378 (1997)
130. C Addicott, M W Wong, C Wentrup *J. Org. Chem.* **67** 8538 (2002)
131. B T Hill, M S Platz *Phys. Chem. Chem. Phys.* **5** 1051 (2003)
132. A Maltsev, T Bally, M-L Tsao, M S Platz, A Kuhn, M Vosswinkel, C Wentrup *J. Am. Chem. Soc.* **126** 237 (2004)
133. C Carra, R Nussbaum, T Bally *ChemPhysChem* **7** 1268 (2006)
134. R Huisgen *Angew. Chem.* **67** 756 (1955)
135. W E Doering, R A Odum *Tetrahedron* **22** 93 (1966)
136. A K Schrock, G B Schuster *J. Am. Chem. Soc.* **106** 5228 (1984)
137. T Y Liang, G B Schuster *J. Am. Chem. Soc.* **109** 7803 (1987)
138. A Reiser, G Bowes, R Horne *Trans. Faraday Soc.* **62** 3162 (1966)
139. E Leyva, M S Platz, G Persy, J Wirz *J. Am. Chem. Soc.* **108** 3783 (1986)
140. B A DeGraff, D W Gillespie, R J Sundberg *J. Am. Chem. Soc.* **96** 7491 (1974)
141. R J Sundberg, M Brenner, S R Suter, B P Das *Tetrahedron Lett.* 2715 (1970)
142. R J Sundberg, S R Suter, M Brenner *J. Am. Chem. Soc.* **94** 513 (1972)
143. O L Chapman, J P Le Roux *J. Am. Chem. Soc.* **100** 282 (1978)
144. T Donnelly, I R Dunkin, D S D Norwood, A Prentice, C J Shields, P C P Thomson *J. Chem. Soc., Perkin Trans. 2* 305 (1985)
145. O L Chapman, R S Sheridan, J P Le Roux *J. Am. Chem. Soc.* **100** 6245 (1978)
146. C J Shields, D R Chrisope, G B Schuster, A J Dixon, M Popiakoff, J J Turner *J. Am. Chem. Soc.* **109** 4723 (1987)
147. Y Z Li, J P Kirby, M W George, M Poliakoff, G B Schuster *J. Am. Chem. Soc.* **110** 8092 (1988)
148. J C Hayes, R S Sheridan *J. Am. Chem. Soc.* **112** 5879 (1990)
149. I R Dunkin, M A Lynch, F McAlpine, D Sweeney *J. Photochem. Photobiol. A: Chem.* **102** 207 (1997)
150. N P Gritsan, Z Zhu, C M Hadad, M S Platz *J. Am. Chem. Soc.* **121** 1202 (1999)
151. N P Gritsan, D Polshakov, M-L Tsao, M S Platz *Photochem. Photobiol. Sci.* **4** 23 (2005)
152. G T Burdzinski, T L Gustafson, J C Hackett, C M Hadad, M S Platz *J. Am. Chem. Soc.* **127** 13764 (2005)
153. G T Burdzinski, J C Hackett, J Wang, T L Gustafson, M C Hadad, M S Platz *J. Am. Chem. Soc.* **128** 13402 (2006)
154. R D McCulla, G T Burdzinski, M S Platz *Org. Lett.* **8** 1637 (2006)
155. G T Burdzinski, C T Middleton, T L Gustafson, M S Platz *J. Am. Chem. Soc.* **128** 14804 (2006)
156. N P Gritsan, T Yuzawa, M S Platz *J. Am. Chem. Soc.* **119** 5059 (1997)
157. R Born, C Burda, P Senn, J Wirz *J. Am. Chem. Soc.* **119** 5061 (1997)
158. M-L Tsao, M S Platz *J. Am. Chem. Soc.* **125** 12014 (2003)
159. N P Gritsan, E A, Pritchina *J. Inform. Rec. Mater.* **17** 391 (1989)
160. S J I Kim, T P Hamilton, H F Schaefer III *J. Am. Chem. Soc.* **114** 5349 (1992)
161. D A Hrovat, E E Waali, W T Borden *J. Am. Chem. Soc.* **114** 8698 (1992)
162. M J Travers, D C Cowles, E P Clifford, G B Ellison *J. Am. Chem. Soc.* **114** 8699 (1992)
163. O Castell, V M Carefa, C Bo, R Caballol *J. Comput. Chem.* **17** 42 (1996)
164. R N McDonald, S J Davidson *J. Am. Chem. Soc.* **115** 10857 (1993)
165. S E Carroll, B Nay, E F V Scriven, H Suschitzky, D R Thomas *Tetrahedron Lett.* 3175 (1977)
166. I R Dunkin, P C P Thomson *J. Chem. Soc., Chem. Commun.* 1192 (1982)
167. I R Dunkin, T Donnelly, T S Lockhart *Tetrahedron Lett.* **26** 359 (1985)
168. J Morawietz, W Sander *J. Org. Chem.* **61** 4351 (1996)
169. C Carra, R Nussbaum, T Bally *ChemPhysChem.* **7** 1268 (2006)
170. E A Pritchina, N P Gritsan, T Bally *Phys. Chem. Chem. Phys.* **8** 719 (2006)
171. N P Gritsan, H B Zhai, T Yuzawa, D Karweik, J Brooke, M S Platz *J. Phys. Chem. A.* **101** 2833 (1997)
172. N P Gritsan, D Tigelaar, M S Platz *J. Phys. Chem. A* **103** 4465 (1999).
173. N P Gritsan, A D Gudmundsduttir, D Tigelaar, M S Platz *J. Phys. Chem. A* **103** 3458 (1999)
174. M Cerro-Lopez, N P Gritsan, Z Zhu, M S Platz *J. Phys. Chem. A* **104** 9681 (2000)
175. D A Pol'shakov, Yu P Tsentalovich, N P Gritsan *Kinet. Katal.* **42** 664 (2001) [c]
176. N P Gritsan, I Likhotvorik, M-L Tsao, N Telebi, M S Platz, W L Karney, C R Kemnitz, W T Borden *J. Am. Chem. Soc.* **123** 1425 (2001)
177. N P Gritsan, A D Gudmundsdóttir, D Tigelaar, Z Zhu, W L Karney, C M Hadad, M S Platz *J. Am. Chem. Soc.* **123** 1951 (2001)
178. M-L Tsao, N P Gritsan, T R James, M S Platz, D A Hrovat, W T Borden *J. Am. Chem. Soc.* **125** 9343 (2003)
179. R A Abramovitch, S R Challand, E F V Scriven *J. Am. Chem. Soc.* **94** 1374 (1972)
180. R A Abramovitch, S R Challand, Y Yamada *J. Org. Chem.* **40** 1541 (1975)
181. R E Banks, G R Sparkes *J. Chem. Soc., Perkin Trans. 1* 1964 (1972)
182. R E Banks, A Prakash *Tetrahedron Lett.* 99 (1973)
183. R E Banks, A Prakash *J. Chem. Soc., Perkin Trans. 1* 1365 (1974)
184. R E Banks, N D Venayak *J. Chem. Soc., Chem. Commun.* 900 (1980)
185. R E Banks, I M Madany *J. Fluorine Chem.* **30** 211 (1985)
186. P J Crocker, N Imai, K Rajagopalan, M A Boggess, S Kwiatkowski, L D Dwyer, T C Vanaman, D C Watt *Bioconjugate Chem.* **1** 419 (1990)
187. R R Drake, J T Slama, K A Wall, M Abramova, C D'Souza, A D Elbein, P J Crocker, D S Watt *Bioconjugate Chem.* **3** 69 (1992)
188. K C Pinney, J A Katzenellenbogen *J. Org. Chem.* **56** 3125 (1991)
189. K C Pinney, K E Carlson, S B Katzenellenbogen, J A Katzenellenbogen *Biochemistry* **30** 2421 (1991)
190. M W Reed, D Fraga, D E Schwartz, J Scholler, R D Hinrichsen *Bioconjugate Chem.* **6** 101 (1995)
191. I Kapfer, J E Hawkinson, J E Casida, M P Goeldner *J. Med. Chem.* **37** 133 (1994)
192. I Kapfer, P Jacques, H Toubal, M P Goeldner *Bioconjugate Chem.* **6** 109 (1995)
193. T Yamaoka, H Kashiwagi, S Nagakura *Bull. Chem. Soc. Jpn.* **45** 361 (1972)
194. W T G Johnson, M B Sullivan, C J Cramer *Int. J. Quantum Chem.* **85** 492 (2001)
195. J A R Coope, J B Farmer, C L Gardner, C A McDowell *J. Chem. Phys.* **42** 54 (1965).
196. M Kazaj, H Luerssen, C Wentrup *Angew. Chem., Int. Ed. Engl.* **25** 480 (1986)
197. R Alvarado, J-P Grivet, C Igier, J Barcelo, J Rigaudy *J. Chem. Soc., Faraday Trans. 2* 844 (1977)
198. D Kvaskoff, P Bednarek, L George, S Pankajakshan, C Wentrup *J. Org. Chem.* **70** 7947 (2005)
199. I R Dunkin, P C P Thomson *J. Chem. Soc., Chem. Commun.* 499 (1980)
200. S E Hilton, E F V Scriven, H Suschitzky *J. Chem. Soc., Chem. Commun.* 853 (1974)
201. E Leyva, M S Platz *Tetrahedron Lett.* **28** 11 (1987)

202. A Kuhn, M Vosswinkel, C Wentrup *J. Org. Chem.* **67** 9023 (2002)
203. M-L Tsao, M S Platz *J. Phys. Chem. A* **108** 1169 (2004)
204. J C Brinen, B Singh *J. Am. Chem. Soc.* **93** 6623 (1971)
205. E A Pritchina, N P Gritsan, N M Bazhin *Izv. AN. Ser. khim.* 1749 (1986)
206. E A Pritchina, N P Gritsan *J. Photochem. Photobiol. A: Chem.* **43** 165 (1988)
207. E A Kuklina (E A Pritchina) Candidate Thesis in Chemical Sciences, Institute of Chemical Kinetics and Combustion, Siberian Branch of the Russian Academy of Sciences, Novosibirsk, 1989
208. E A Pritchina, N P Gritsan *Kinet. Katal.* **28** 1044 (1987) [c]
209. E M Chainikova, S L Khursan, R L Safiullin *Dokl. Akad. Nauk* **396** 793 (2004) [d]
210. R L Safiullin, S L Khursan, E M Chainikova *Kinet. Katal.* **45** 680 (2004) [c]
211. E M Chainikova, S L Khursan, R L Safiullin *Dokl. Akad. Nauk* **403** 358 (2005) [d]
212. E M Chainikova, S L Khursan, R L Safiullin *Kinet. Katal.* **47** 566 (2006) [c]
213. C Zetzsch, I Hansen *Ber. Bunsen-Ges. Phys. Chem.* **82** 830 (1978)
214. W Hack, H Kurzke, H G Wagner *J. Chem. Soc., Faraday Trans. 2* 949 (1985)
215. S L Laursen, J E Grace Jr, R L DeKock, S A Spronk *J. Am. Chem. Soc.* **120** 12583 (1998)
216. T Fueno, K Yokoyama, S Takane *Theor. Chim. Acta* **82** 299 (1992)
217. R A Abramovitch, C J Azogu *J. Chem. Soc., Chem. Commun.* 134 (1971)
218. R A Abramovitch, S R Challand *J. Chem. Soc., Chem. Commun.* 964 (1972)
219. P E Nielsen, O Buchardt *Photochem. Photobiol.* **35** 317 (1982)
220. Y Sawaki, S Ishikawa *J. Am. Chem. Soc.* **109** 584 (1987)
221. S Ishikawa, S Tsuji, Y Sawaki *J. Am. Chem. Soc.* **113** 4282 (1991)
222. C L Go, W H Waddell *J. Org. Chem.* **48** 2897 (1983)
223. M P Talipov, A B Ryzhkov, L S Khursan, R L Safiullin *Zh. Strukt. Khim.* **47** 1054 (2006) [e]
224. T Harder, P Wessig, J Bendig, R Stösser *J. Am. Chem. Soc.* **121** 6580 (1999)
225. A A Shchepalov, S V Zelentsov, A G Razuvaev *Izv. Akad. Nauk, Ser. Khim.* 2239 (2001) [a]
226. J Liu, C M Hadad, M S Platz *Org. Lett.* **7** 549 (2005)

[a] — *Russ. Chem. Bull., Int. Ed. (Engl. Transl.)*
[b] — *Russ. J. Org. Chem. (Engl. Transl.)*
[c] — *Kinet. Catal. (Engl. Transl.)*
[d] — *Dokl. Phys. Chem. (Engl. Transl.)*
[e] — *J. Struct. Chem. (Engl. Transl.)*