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# Light-induced Reactions of Diazotetrahydrofuranone without Elimination of Nitrogen: Experimental and Mechanistic Study

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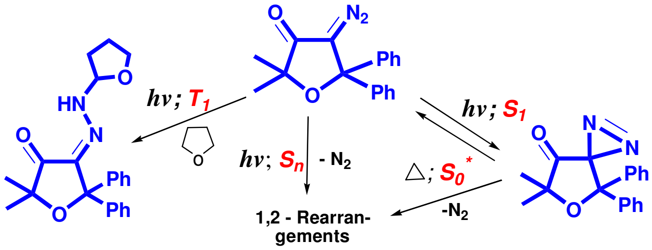


## Abstract

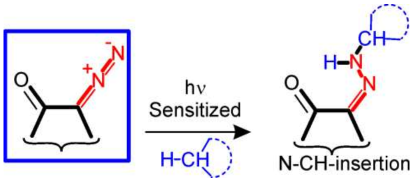
The energies and lifetimes of the excited states ($\boldsymbol{S_1}$, $\boldsymbol{S_2}$, $\boldsymbol{S_5}$, $\boldsymbol{T_1}$) of a diazotetrahydrofuranone were determined using experimental and computational methods. It was shown that direction of the diazoketone photochemical transformations without elimination of nitrogen is determined by multiplicity and energy of the excited state, generated by UV irradiation of diazo compound: isomerization to α-ketodiazirine proceeds from the singlet $\boldsymbol{S_1}$ state, whereas the alternative process of C-H-insertion with hydrazone formation occurs through the triplet $\boldsymbol{T_1}$ state. The most probable excited state that leads to elimination of nitrogen and Wolff rearrangement is one of the highest singlet excited states of diazotetrahydrofuranone.

## Introduction

The development and application of “green chemistry” methods are the priority objectives of modern organic chemistry.[1–3] From this viewpoint one of the most attractive and promising techniques for the initiation of chemical reactions is optical excitation which has unambiguous advantages over the thermal and catalytic activation of chemical processes.[4] That is why the actuality of developing the effective synthetic methods and investigation of the mechanism of light-induced formation of new bonds in organic molecules are of fundamental importance.

The submitted research is devoted to investigation of the novel recently discovered photochemical reaction of diazo compounds which provides a way for the creation of new C-N-bonds in organic molecules.

According to established opinion, irradiation of aliphatic diazo compounds with UV light usually gives rise to elimination of $N_2$, which excludes nitrogen atoms of diazo group from the succeeding chemical transformations.[5-8] The universally known light-induced reactions of diazocarbonyl compounds without elimination of nitrogen are essentially limited to their isomerisation to α-ketodiazirines.[9,10] At the same time, it was found lately that diazoketones of tetrahydrofurane series, under distinct conditions of photochemical reaction, can avoid elimination of nitrogen molecule. Instead, they lead to insertion of the terminal N-atom of diazo group into C-H bonds of organic compounds,[11,12] that is can subject to light-induced processes with conservation of nitrogen atoms of diazo group in the compounds formed (Scheme 1).



**Scheme 1.** Sensitized photochemical reactions of diazotetrahydrofuranones.[11,12]

The main goal of our presented study is elucidation of the pathways of these light-induced reactions without elimination of nitrogen using the example of 4-diazo-2,2-dimethyl-5,5-diphenyltetrahydrofuran-3-one (Figure 1), determination of multiplicity and lifetimes of the generated excited states, as well as their function in photochemical transformations of diazoketone **1**.

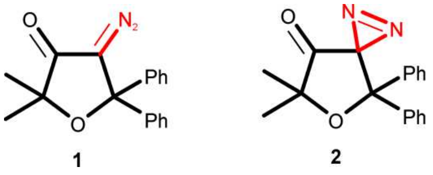


**Figure 1.** Objects of investigation: diazoketone **1** and α-ketodiazirine **2.**

In addition, light-induced and thermal reactions of α-ketodiazirine **2** (the cyclic isomer of diazoketone **1**), were also studied to understand its role in the processes under examination. By analogy with our previous studies,[11,12] tetrahydrofuran was used in photochemical experiments as the main reaction partner with C-H bonds.

## Results and Discussion

**Electronic excited states of diazoketone 1 and α-ketodiazirine 2**. The information on the electronic excited states of diazoketone **1** were obtained using experimental spectra of absorbance (Figure S1a), luminescence (Figure S2) and phosphorescence (Figure S4), observed lifetimes of the excited states (Figure S3, Table S2), computational studies(Figure S1b, Table S1) and some literature data. [13-19]

UV-Vis spectra of diazoketone **1** in various solvents demonstrate three main bonds: the highest observed optical density at 252 nm, lower band at 302 nm and the smallest band around 410 nm, which was observed in concentrated solution of diazoketone **1** only (Figure S1). The computational and literature data allow us to assign the shortwave absorption to **$\pi$-$\pi^*$** transitions of diazoketone **1**, as well as the longwave band at 410 nm can be equally assigned to **$\pi$-$\pi^*$** and ***n*-$\pi^*$** transitions (Table S1). Based on the experimental and computational spectra of absorbance, fluorescence and phosphorescence kinetics curves of diazofuranone **1**, the energy level diagram for diazoketone **1** was created (Figure 2). The lifetimes of electronic excited states were also determined, which were further used for interpretation of the observed transformations of diazoketone **1**.

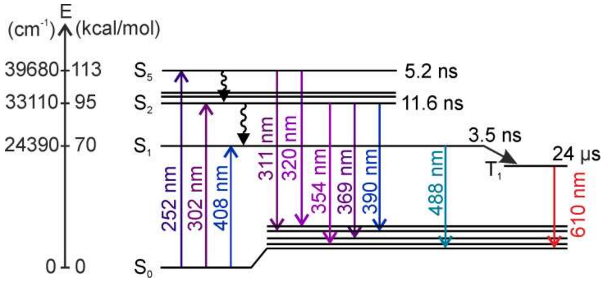


**Figure 2.** Energy level diagram of diazoketone **1** with optical transitions and lifetimes of excited states.

As can be seen from Figure 2, the observed absorption bands corresponds to the electron transitions from the ground state to the singlet excited states $S_1$, $S_2$ and $S_5$ of diazoketone **1**. It should be noted that the lifetime of the singlet state $S_2$ is greater than with the state $S_1$ ($11.6 \bullet 10^{-9}$ s and $3.5 \bullet 10^{-9}$ s respectively), so the probability of photochemical reactions through the state $S_2$ should be higher in comparison to $S_1$.[4,20] The lifetime of state $S_1$ is less than $S_2$, probably because of the intersystem crossing (ISC) into the triplet state $T_1$ (the energy difference between $S_1$ and $T_1$ is only 2-4 kcal/mol). The lifetime of the $T_1$ state is about $24 \bullet 10^{-6}$ s, which provides a good possibility for intermolecular processes.

Similarly to diazoketone **1**, the energy level diagram of diazirine **2** was created (Figure 3) based on the spectral data (Figure S8). Relying on the position of the energy levels in this diagram, one can conclude that diazirine **2** should be rather stable when excited by 405 nm light, but could subject to photochemical reactions when excited by UV radiation with wavelengths less than 370 nm.

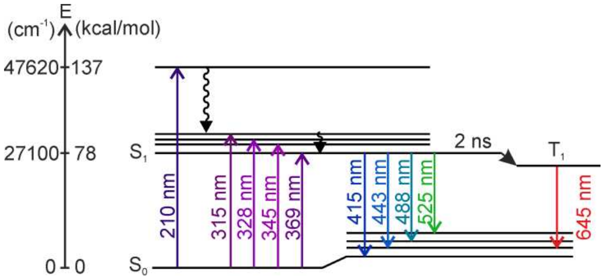
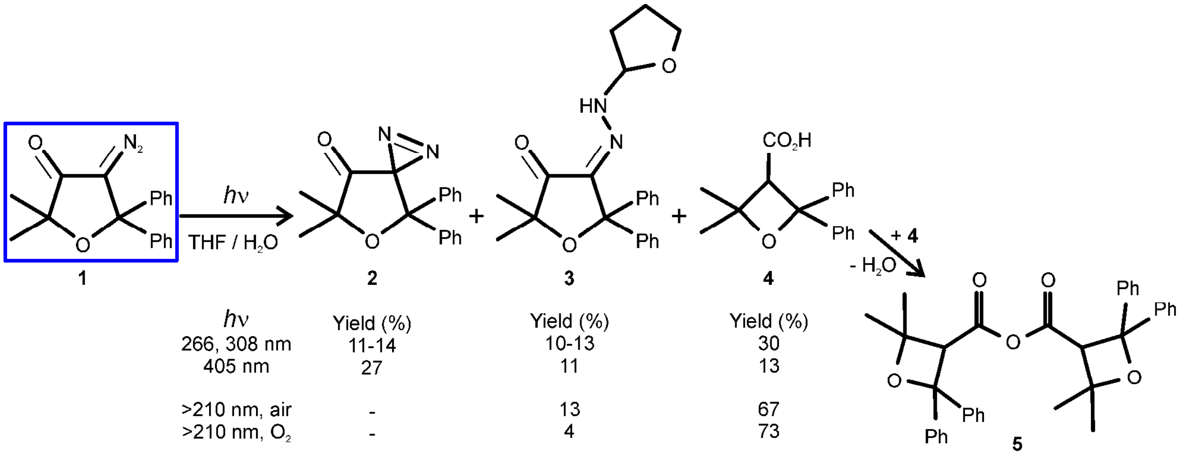


**Figure 3.** Energy level diagram of α-ketodiazirine **2**.

**Photochemical transformations of diazoketone 1**. Excitation of diazoketone **1** for the singlet states ***$S_1$***, ***$S_2$*** and ***$S_5$*** was carried out by monochromatic sources with wavelengths 405 nm, 308 nm and 266 nm respectively. Photolysis occurred at 20-25 °C in solution of tetrahydrofurane with the addition of $H_2O$ (100/1) to trap the assumed ketene formed by Wolff rearrangement of diazoketone **1**.[7,21-25] The reactions were monitored by IR (Figure S5) and $^1$H NMR spectroscopies.

Optical excitation of diazoketone **1** with 266 nm or 308 nm light leads to formation of three main reaction products: α-ketodiazirine **2**, hydrazone **3** and oxetanecarboxylic acid **4** (or its anhydride **5**) in the yields of 10-30 % each (Scheme 2).



**Scheme 2.** Photochemical transformations of diazoketone **1**.

The kinetics of photochemical transformations of diazoketone **1** upon irradiation with 266 nm light is represented in Figure 4a. As is seen from these data, during irradiation of diazoketone **1** the concentration of diazirine **2** at first increases but then begins to decrease with time. Similar behaviour of the kinetic curve is also observed in the case of oxetanecarboxylic acid **4**. These observations most likely point to a partial photochemical decomposition of the initially formed reaction products upon continuous UV irradiation of the reaction mixture.[26-28]

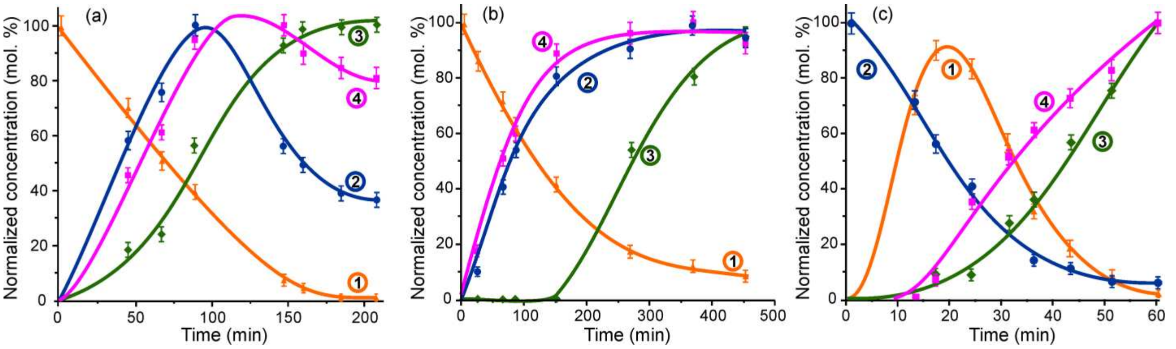


**Figure 4.** Kinetic curves of the reaction mixtures composition upon diazoketone **1** irradiation by light with wavelengths of (a) 266 nm*⁾, (b) 405 nm; diazirine **2** irradiation by (c) 266 nm light.

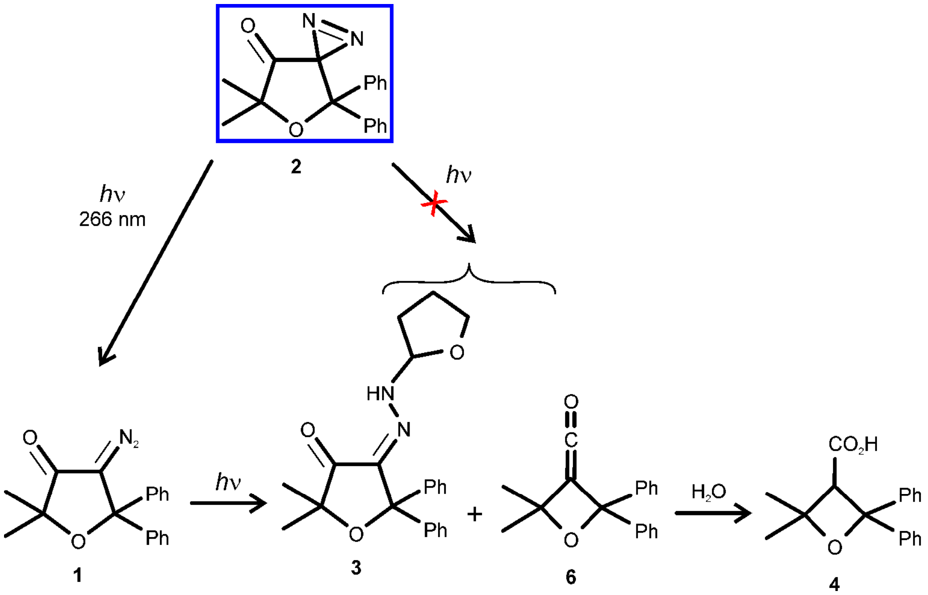
*⁾ Similar kinetic results were obtained upon irradiation of diazoketone **1** with 308 nm UV light.

Irradiation of diazoketone **1** with 405 nm light also leads to formation of three main reaction products **2**–**4** (Scheme 2, Figure 4b). However in this case, contrary to photolysis at a wavelength of 266 nm, the formation of hydrazone **3** in the reaction mixture begins only after a considerable time from the beginning of irradiation (more than 100 min). It is probably that this "induction" period is necessary for the accumulation in the reaction mixture of a sufficient amount of benzophenone which is usually formed by photochemical decomposition of oxetan-carboxylic acid **4** [26,27] and is mediated by the formation of hydrazone **3**. At the same time, after total conversion of diazoketone **1** concentration of diazirine **2** remains practically unchanged, since it does not absorb in the spectral region of about 405 nm.

It should be also noted that irradiation of diazoketone **1** in the oxygen atmosphere leads to an almost threefold decrease of the yield of hydrazone 3 (Scheme 2). This observation can evidently serve as an argument in favor of the participation of the triplet excited states of diazofuranone **1** in the process, since its concentration in the presence of the "quenching" triplets ($O_2$) goes down significantly. [11]

Thus, it was shown that the optical excitation of diazoketone **1** by monochromatic light with wavelengths of 405 nm, 308 nm and 266 nm into singlet states $S_1$, $S_2$, $S_5$ respectively leads to formation of three basic reaction products of photolytic reaction: diazirine **2**, hydrazone **3** and oxetancarboxylic acid **4** (or anhydride **5**). According to the kinetic data, upon irradiation of diazoketone **1** with 405 nm light, a monotonic accumulation of diazirine **2** occurs (Figure 4b), but when irradiation of diazoketone **1** proceeds with 266 nm light, the concentration of diazirine **2** is initially increased, and then decreased in the course of time.

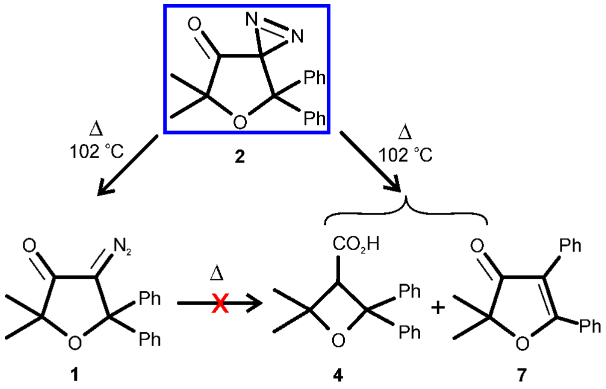
**Photochemical transformations of α-ketodiazirine 2.** The irradiation of α-ketodiazirine **2** was carried out with 266 nm monochromatic light at 30-35 °C in solution of THF and monitored by IR spectroscopy. The main directions, as well as kinetics of photochemical transformations of diazirine **2** and accompanying processes under the indicated conditions are presented in the Scheme 3 and Figure 4c.



**Scheme 3.** Photochemical transformations of α-ketodiazirine **2**.

As evident from the kinetic data on Figure 4c, in the first 10-15 min of the diazirine **2** irradiation the main photochemical process is isomerization to diazoketone **1**. At the same time, the concentrations of hydrazone **3** and oxetanecarboxylic acid **4** at this initial stage of the process (5-10 min) are close to zero and begin to increase only after diazoketone **1** appears in the reaction mixture. It is pertinent to note here that photolysis of diazoketone **1** under similar conditions leads to formation of oxetancarboxylic acid **4** in the reaction mixture immediately after the beginning of irradiation (Figure 4a). Thus, it can be concluded that irradiation of diazirine **2** with 266 nm light gives rise only to isomerization of it to diazoketone **1**, which is further converted upon irradiation to N-substituted hydrazone **3** and oxetanecarboxylic acid **4** (Scheme 3). It is also evident that α-ketodiazirine **2** is not an intermediate on the way from diazoketone **1** to the products of photolytic reaction studied.

**Thermal transformations of α-ketodiazirine 2.** To recognize a possibility of parallel thermal processes during photochemical reactions in hand, the thermolysis of α-ketodiazirine **2** was studied. The reaction was carried out at 102 ± 4 $^{o}$C in DMSO-$d_6$ solution with the addition of $H_2O$ (100/1) to trap the product of Wolff rearrangement – ketene **6**. The conversion of diazirine **2** was controlled by TLC, reaction mixture was analyzed by $^1$H NMR spectroscopy. As a result of thermolysis three basic reaction products were obtained - diazoketone **1**, oxetanecarboxylic acid **4** and vinylketone **7** (Scheme 4).



**Scheme 4.** Thermal reactions of α-ketodiazirine **2**.

In view of the fact that diazoketone **1** is thermally quite stable at these conditions,[29,30] it can be concluded that the products of diazirine **2** thermolysis (diazoketone **1**, oxetanecarboxyic acid **4** and vinyl ketone **7**) are formed solely from diazirine itself. This means that, unlike photochemical transformations, thermolysis of diazirine **2** occurs in two parallel directions: isomerization to diazoketone **1** and elimination of nitrogen to produce Wolf rearrangement product **4** and 1,2-aryl group migration **7**.

**General scheme of diazoketones and diazirines of tetrahydrofuran series transformations.** Based on the obtained experimental data, energy levels of the excited states of diazoketone **1** and diazirine **2**, as well as the calculated energies of the ground states of the reactants and reaction products, the general diagram of the observed photochemical reactions is proposed (Figure 5). Excitation of diazoketone 1 with light at wavelengths of 405 nm, 308 nm and 266 nm into singlet states $S_1$, $S_2$ and $S_5$ leads to formation of three main products of the photolytic reactions studied: α-ketodiazirine **2** and hydrazone **3** (in reactions without nitrogen elimination), as well as the products of 1,2-nucleophilic rearrangements **4**-**7** (in reactions with elimination of $N_2$).

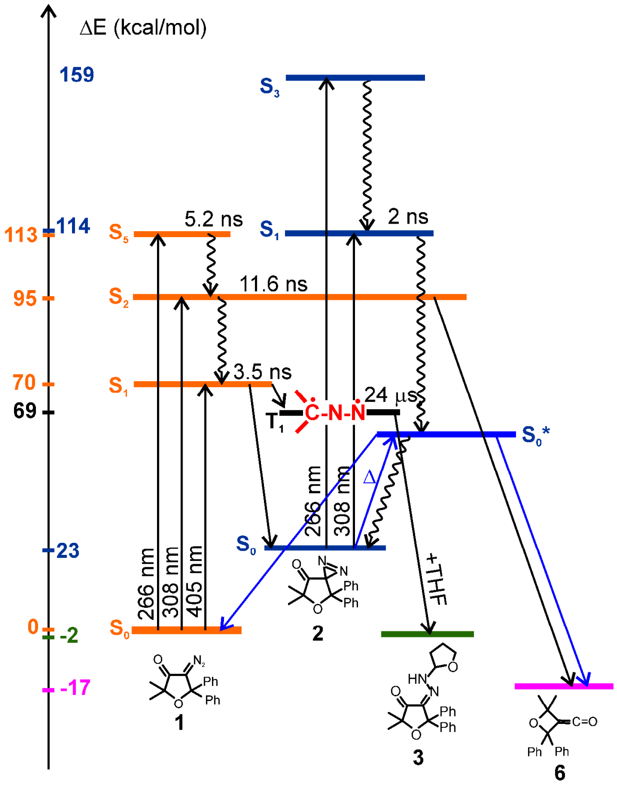
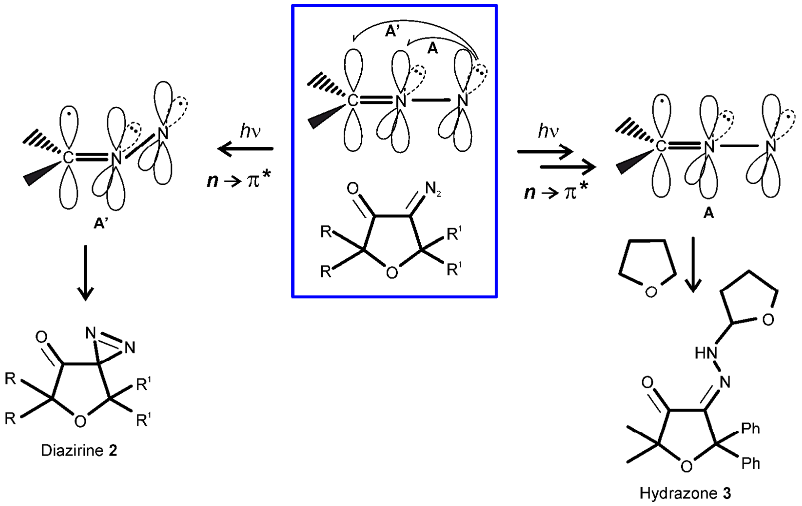


**Figure 5.** General diagram of the photochemical transformations of diazoketone **1** and α-ketodiazirine **2**. The diagram shows the wavelengths of the pump.

Two versions of diazoketone **1** excited state can be represented in the form of mesomeric structures of biradical **A**,**A'** formed upon the transition of one of the *n*-electrons from $p_y$-orbital of the terminal nitrogen atom to disintegrating $\pi_x$*-orbital (Scheme 5). Placed at the neighboring atom ***N*** (mesomeric form **A**) this electron can promote abstraction of H-atom from hydrogen donor to give eventually N-substituted hydrazone **3** (Scheme 5, right pathway).



**Scheme 5.** The assumed alternatives of the diazoketone **1** excited states stabilization without elimination of nitrogen.

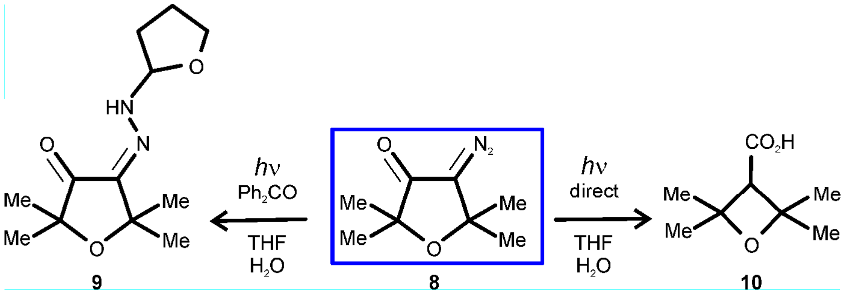
In the alternative case with the location of this electron at the atom ***C*** of diazo group (as is shown in **A'**) the stabilization of such a biradical intermediate may be intramolecular recombination with the formation of diazirinic heterocycle **2** (Scheme 5, left pathway).

The resulting α-ketodiazirine **2** can relax from the excited states to vibrationally excited sublevels of the ground state $S_0$*. The subsequent stabilization of these "hot" states can principally take place in three ways (Figure 5): a) vibrational relaxation to ground state of diazirine **2**; b) a large energy loss and conversion to the initial diazoketone **1**; c) elimination of nitrogen and subsequent rearrangements with the formation of ketene **6** or vinylketone **7**. The possibility of the last direction was confirmed by experimental results on diazirine **2** thermolysis, which in this case gave rise to Wolff rearrangement products (**4** and **5**) and 1,2-migration of the aryl group **7** (Scheme 4).

Most efficiently diazirine **2** is produced by excitation of diazoketone **1** at the wavelength of 405 nm (Scheme 2). As this takes place a monotonic increase in its concentration is observed (Figure 4b) since diazirine **2** does not absorb in this spectral region and, obviously, does not undergo further transformations. At the same time when diazoketone **1** is excited at the wavelengths of 266 nm (and 308 nm), the growth of diazirine **2** concentration is observed at the beginning of irradiation followed by a decrease with time (Figure 4a), which evidently points to the reversibility of diazoketone **1** - diazirine **2** photoisomerization.

The potential energy curves along the reaction coordinate diazirine – diazoketone for ground state $S_0$ and excited singlet $S_1$, $S_2$ and triplet $T_1$ states were calculated to clarify the question which excited energy level of diazoketone **1** is responsible for diazirine **2** formation (Figure S6). It was found that the levels of $S_1$ and $T_1$ were very close and there was a conical intersection of the states $S_0$ and $T_1$. Thus it is reasonable to assume, that the formation of biradical **A**,**A'** can occur both in the singlet $S_1$ and in the triplet $T_1$ states, populated by ISC (Figure S6*)*. Further stabilization of this intermediate can occur as a typical diabatic process, proceeding first on the potential surface of the excited state $S_1$ or $T_1$ and passing (without emission of light) onto the ground state of diazirine **2**. At the same time no effect of oxygen on the yield of diazirine **2** upon irradiation of diazoketone **1** was found. Therefore, one can conclude that α-ketodiazirine **2** is formed from the singlet state $S_1$ of diazoketone **1**.

It is evident that formation of C-H insertion product (hydrazone **3**) occurs with the participation of the triplet excited state (with lifetime in microsecond region) as a result of intermolecular interaction of the diazocarbonyl biradical **A**,**A'** with C-H donor, tetrahydrofurane (Scheme 5). As it was already mentioned, the triplet state can arise from the singlet state $S_1$ of diazoketone **1** *via* ISC, which should be very effective, since the energy difference between the levels ***$S_1$*** and ***$T_1$*** is only about 2-4 kcal/mol (Figure 5). Additional indirect argument in favour of participation of the triplet intermediates in these processes originates from the results of photolysis of tetramethylsubstituted analogue of diazoketone **1**, diazotetrahydrofuranone **8** (Scheme 6).[11]



**9** **8** **10**

**Scheme 6.** Photochemical transformations of diazoketone **8** under various conditions.[11]

In contrast to diazoketone **1**, the direct irradiation of tetramethylsubstituted analogue **8** failed to produce the product of the C-H insertion **9**. Instead, only Wolff rearrangement product **C** was isolated from reaction mixture (more than 90%). At the same time, hydrazone **10** was obtained from diazoketone **8** (in the yields of up to 69 %), but under conditions of sensitized photolysis.[11]

Similar alternative apparently is realized upon irradiation of diazoketone **1** with 266 nm and 308 nm light, which also leads to formation of hydrazone **3** (Scheme 2). As it was established earlier [26,27] during direct photolysis of diazoketone **1** a partial decomposition of the resulting diphenylsubstituted oxetane derivatives occurs to produce benzophenone. The latter promotes the appearance of diazoketone **1** in the triplet state, which thereafter reacts with H-donors to furnish the products of C-H insertion under conditions of direct irradiation.

The participation of triplet states in the formation of C-H-insertion products **3** is also confirmed by photochemical experiments in the atmosphere of oxygen – a "quencher" of triplet states. Under these conditions, the yield of hydrazone **3** notably decreases, while the efficiency of Wolff rearrangement is growing (Scheme 2).[11]

As for the products of 1,2-nucleophilic rearrangements **4**-**7**, they are evidently formed from the singlet excited states of diazoketone **1**.[17,18,20,31-35] The potential energy curves along the reaction coordinate of diazoketone **1** - ketene **6** at Figure S7 shows that in order to obtain ketene **6** from diazoketone **1**, it is necessary to overcome the energy barrier of 60 kcal/mol. Since the energy of the ***$S_0$-$S_1$*** transition is about 70 kcal/mol (Figure S7), this process can be realized through any electronically excited state of diazoketone **1**, starting with ***$S_1$***. This preliminary estimation is confirmed by experimental results, demonstrating the possibility of Wolff rearrangement upon irradiation of diazoketone **1** with 405 nm light (Scheme 2), which corresponds to the energy of the ***$S_0$-$S_1$*** transition.

At the same time, excitation at the higher singlet states of diazoketone **1** leads to a more efficient Wolff rearrangement. Thus, it was shown earlier that the yield of oxetancarboxylic acid **4** at short-wavelength excitation (> 210 nm) increases by almost an order of magnitude in comparison to the longwave irradiation (> 310 nm) (Scheme 2).[11] This experimental data indicates that the Wolff rearrangement of diazoketone **1** does not only occur through the lower level of $S_1$ when irradiated with 405 nm light, but also through the upper singlet excited states populated by the short-wave irradiation of diazoketone **1**.

The conversion of diazirine **2** to ketene **6** upon photoexcitation is not realized since there are no conical intersection of $S_0$ and $T_1$ on the potential energy surfaces of photochemical reactions. Thus, one can conclude that diazirine **2** can not directly participate in photochemical Wolff rearrangement, but only through diazoketone **1**, which is formed via photochemical isomerization of diazirine **2**.

## Conclusion

The effect of multiplicity and energy of the excited states of diazotetrahydrofuranone on the direction and pathways of photochemical transformations was established using optical and theoretical methods of investigation. Photochemical reactions of diazoketone without elimination of nitrogen lead to isomerization into α-ketospirodiazirine or to insertion of the terminal nitrogen atom of diazogroup into C-H bond of the solvent to produce N-substituted hydrazone.

Isomerization of diazoketone to α-ketodiazirine proceeds in the singlet $S_1$ excited state, whereas the alternative reaction giving rise to C-H insertion products occurs in the triplet $T_1$ state. The latter arises during the course of photochemical reaction, either by ISC of the diazoketone $S_1$ into $T_1$ state, or by sensitization of diazoketone with benzophenone, which is formed in reaction media due to decomposition of the primary reaction products. The formation of α-ketodiazirine from diazoketone is a diabatic process occuring on the excited potential surface and terminating without emission of photons on the potential surface of the ground state of diazirine.

Irradiation of α-ketodiazirine with 266 nm UV light does not cause elimination of nitrogen, but gives rise solely to reversible isomerization to diazoketone. By contrast, thermolysis of α-ketodiazirine at 102 °C, mainly leads to elimination of nitrogen and 1,2-nucleophilic rearrangements, as well as to partial isomerization to diazoketone.

In photochemical processes studied the most probable excited state leading to elimination of $N_2$ and rearrangements is one of the highest singlet states of diazotetrahydrofuranone.

## Experimental Section

**General.** $^1$H NMR and $^{13}$C NMR spectra were recorded in $CDCl_3$ or DMSO-$d_6$ solutions on a Bruker Avance 400 MHz spectrometer using tetramethylsilane as an internal standard. HRMS experiments were performed on a Bruker micrOTOF instrument. Melting points were recorded on a Büchi B-540 apparatus. Column chromatography was carried out on the neutral silica gel (70-230 mesh) with hexane and acetone as eluents in gradient regime.

**UV-Vis spectroscopy.** Measurement of the UV-Vis spectra was carried out with a Perkin Elmer Lambda 1050 spectrophotometer. The samples of diazoketone **1** or diazirine **2** were dissolved in THF at the 1 mg/ml concentration and placed in a quartz cuvette with the 1 cm optical path length. A cuvette with pure THF was placed in the comparison channel.

**Calculation** of the absorption spectra was carried out by TD DFT. Using the calculated data, the energies of optical transitions from the ground state of molecules to excited singlet states are determined.

**The luminescence and luminescence excitation spectra** were measured with a Horiba Fluorolog-3 spectrometer. The samples of diazoketone **1** or diazirine **2** were dissolved in THF and brought to solutions concentrations with the optical density of 0.05 cm$^{-1}$ at 252 nm wavelength.

**Triplet states determination.** The energy difference between the basic $\boldsymbol{S_0}$ and the triplet $\boldsymbol{T_1}$ states of the molecules was determined from the phosphorescence spectra. The phosphorescence spectra were measured at a liquid nitrogen temperature with 390 nm excitation.

**The lifetime of the excited states** was measured with a Horiba Fluorolog-3 spectrometer using pulsed LED excitation sources with 1 ns pulse duration. The kinetic curves of the luminescence decay at different wavelengths of the molecules were recorded after pulsed optical excitation to measure the lifetime excited states of the samples. The obtained experimental curves were approximated by the following exponential function: $y=A+B*exp(-x/\tau)$ where $A$ and $B$ are the approximation parameters, $\tau$ is the required lifetime of the excited state.

**FTIR spectroscopy.** Photochemical transformations of diazoketones in THF solutions have been investigated under excitation by various radiation sources: THORLABS Mounted High-Power LED 405 nm, Xe-Cl laser 308 nm and Coherent MBD-266 266 nm. Reaction mixtures were monitored by IR spectra at certain time intervals. The IR spectra were measured by Thermo Scientific Nicolet 8700 FT-IR spectrometer equipped with Attenuated Total Reflectance (ATR) sampling accessory.

Most of the considered in the article compounds were obtained and fully characterized by spectroscopic methods in earlier publications: **1**[28,36], **3**[11,28], **4**[11,28], **6**[27], **7**[11,26], **B**[12], **C**[11,12], **D**[11,12]. Diazoketone **1** was obtained according to the previously described protocols,[28,36] α-ketodiazirine **2** was prepared for the first time by photochemical isomerization of diazoketone **1**. [12]

**Synthesis of α-ketodiazirine 2**. Solution of diazoketone **1** (730 mg, 2.5 mmol) in freshly distilled cyclohexane (5 mL), placed in a small quartz vessel, was irradiated at 30–35°C by long-wave UV light with $\lambda$ 395–405 nm (two lamps *UV LED Spotlight,* 3 watt each) for 250 h under air atmosphere. The solvent from reaction mixture was removed in vacuo and residue was analyzed by $^1$H NMR spectroscopy (internal standard – $Cl_2CHCHCl_2$) followed by silica gel column chromatography to afford α-ketodiazirine **2**.

**6,6-Dimethyl-4,4-diphenyl-5-oxa-1,2-diazaspiro[2.4]hept-1-en-7-on** (**2**), yield 267 mg (46%; based on 80% conversion of diazoketone **1**). Colorless solid, mp 73-75 °C (hexane), *Rf* 0.67 (hexane/acetone 10:1). IR (neat), cm$^{-1}$: 1754 (C=O). UV (THF), nm: 315, 328, 345, 367 (Figure S8). $^1$H NMR (400 MHz, $CDCl_3$), δ, ppm : 7.37 – 7.30 (m, 10H), 1.39 (c, 6H) (Figure S9). $^{13}$C NMR (101 MHz, $CDCl_3$), δ, ppm: 210.0, 140.5, 128.5, 128.4, 127.3, 81.8, 80.8, 38.9, 25.1 (Figure S10). HRMS (ESI-TOF): *m/z* [M + Ag]$^+$, calc for $C_{18}H_{16}N_2O_2Ag^+$: 399.0257, found 399.0270.

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**Supporting Information.** UV-Vis spectra for compound **1**, quantum-chemical calculations for compound **1**, luminescence spectrum for compound **1**, kinetic of luminescence for compound **1**, phosphorescence spectrum for compound **1**, observed lifetime of excited states for compound **1**, FTIR spectra of the reaction mixture, vibrational bands in the IR spectra, DFT calculation coordinates for compound **1**, DFT calculation coordinates for compound **2**, DFT calculation coordinates for compound **6**, DFT computation for reaction pathway **2** → **1**, DFT computation for reaction pathway **1** → **6**, UV-Vis spectrum for compound **2**, $^{1}H$ NMR spectrum for compound **2**, $^{13}C$ NMR spectrum for compound **2**. This material is available free of charge via the Internet at http://pubs.acs.org.

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