Chemistry of Diazocarbonyl Compounds: XXVII.*
Thermolysis and Photolysis of Diazirines, Derivatives of 1,3-Dioxane-4,6-dione

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Abstract—Photolysis of diazirines, 1,3-dioxane-4,6-dione derivatives, occurs in the presence of methanol or dimethyl sulfide as carbene traps without a formation of carbene intermediates. It was established for the first time that the thermolysis and photolysis of diazirines from the 1,3-dioxane-4,6-dione series led mainly to Wolff rearrangement with a subsequent formation of 5-oxo-1,3-dioxolane-4-carboxylic acids or their derivatives. The data obtained show that the α-oxodiazirines are the key intermediates in the photolysis and Wolff rearrangement of α-diazocarbonyl compounds.

Diazirines with alkyl and aryl substituents attached to the carbon atom of the three-membered heterocycle are as a rule far more stable and less hazardous for application that their linear isomers, aliphatic diazo compounds. The diazirines are widely used in the carbene chemistry, and their transformations are well documented [2]. However the α-oxodiazirines containing in their structure 3-acil or 3-alkoxycarbonyl groups are virtually unstudied and are seldom used in the "carbene " reactions presumably because of their unavailability and instability already mentioned by Schmitz et al. [3] who have first synthesized the cyclic analogs of the aliphatic diazo compounds.

In the course of studies of the photochemical transformations of 5-diazo-2,2-dialkyl-1,3-dioxa-4,6-diones **I** we [1, 4] and other researchers [5, 6] identified in the reaction mixture relatively stable cyclic isomers of the initial diazo compounds, α,α-dioxodiazirines **II**, and an efficient photochemical method for preparation of these compounds was developed [4]. We report here on the results of studies of the chemical properties of α,α-dioxodiazirines **II** from the 1,3-dioxane series, on establishing the main routes of their thermolysis and photolysis, and on the prospects to apply diazirines **II** as a source of cyclic α,α-dioxocarbenes **III**.

We chose as the objects of investigation 2,2-dimethyl- and 2-methyl-2-*tert*-butyl-substituted dioxodiazirines **IIa**

* For communication XXVI, see [1].

and **IIb** having singlet signals in the ^{1}H NMR spectra which facilitated the identification of the reaction products.
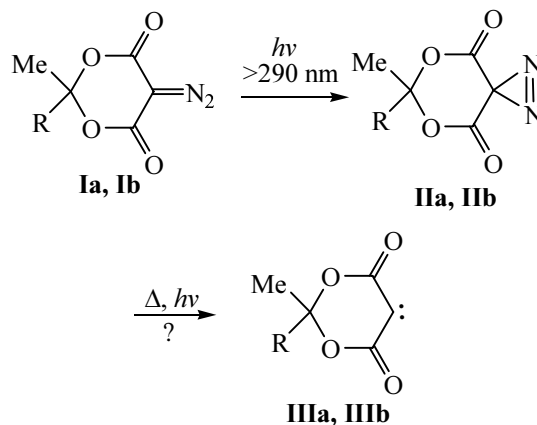
R = Me (**a**), *t*-Bu (**b**).

Dioxodiazirines **IIa** and **IIb** were prepared by the photochemical isomerization of the corresponding diazodioxanediones **Ia** and **Ib** in a solution THF–NuH (NuH = H_2O, MeOH), 20:1, using irradiation with long-wave UV light ($\lambda > 310$ nm). The highest yield (40–43%) was obtained by irradiation of diazo compounds **I** in the mixture THF–MeOH [1, 4] (see EXPERIMENTAL). The procedure we developed for of the photolysis and the subsequent separation of the reaction products enabled us within several hours to obtain from diazo compounds **I** 1–2 g of diazirines **II**. Before use in the photochemical reactions diazirines **II** were subjected to thorough

Table 1. Thermolysis of diazirines **IIa** and **IIb** in CDCl$_3$ and C$_6$D$_6$ solutions

Diazirine **II**, solvent	$k \times 10^5$, s^{-1}	$\tau_{1/2}$, h (50°C)	Thermolysis products, %	
			I	**IV, V**
IIa, CDCl$_3$–MeOH	4.7	4.1	47[a]	40
IIb, CDCl$_3$–H$_2$O	5.6	3.5	34[a]	48
IIa, C$_6$D$_6$–MeOH	4.8	4.0	22[b]	78[b]
IIb, C$_6$D$_6$–MeOH	15.3	1.3	34	66

[a] Initial diazirine is also present in the reaction mixture (**IIa** 13%, **IIb** 18%).

[b] According to the ^{1}H NMR data, at diazirine **IIa** conversion ~15%.

purification by recrystallization and an additional sublimation in a vacuum. Inasmuch as the diazirines are relatively prone to isomerization into the corresponding diazo compounds [7], α,α-dioxodiazirines **II** were used in subsequent reactions either just after preparation and purifying or after short storage at –10...–15°C.

UV spectra of diazirines **IIa** and **IIb** considerably differ from spectral characteristics of diazo compounds **I** [1, 4, 6]. Two weak absorption bands appear in the spectra in the regions 245–250 and 285–290 nm as shoulders on the tail of a more short-wave strong absorption band ($\lambda < 230$–240 nm). The long-wave absorption of diazirines was previously assigned to the σ–π*, π–π*, or π–π* transition [3], and the latter was believed to be the most probable [8]. The weak long-wave absorption band was later shown by quantum-chemical calculations to correspond more likely to the transition of an electron from the unshared pair of the nitrogen to the π* antibonding orbital of the three-membered ring (π–π*
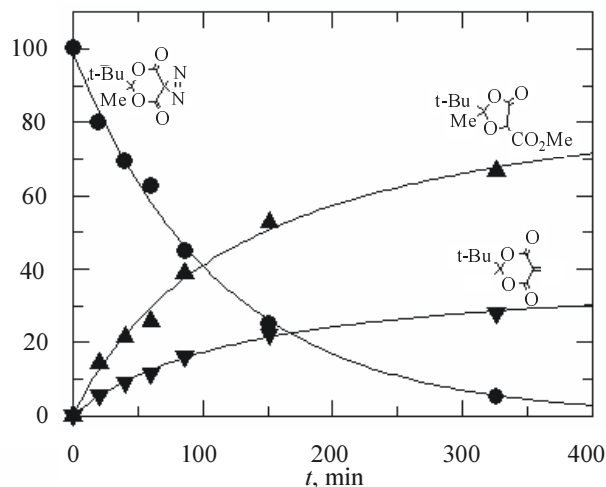

Fig. 1. Thermolysis of diazirine **IIb** in C$_6$D$_6$–MeOH solution at 50°C.

transition), whereas the short-wave band corresponded to the π–π* transition [9].

The irradiation of diazirines **IIa** and **IIb** was performed with the use of a mercury lamp of a medium pressure passing its total light thorough a quartz filter ($\lambda > 210$ nm) with no additional monochromatization. The reaction products were identified in the solution analyzed by ^{1}H NMR spectra of individual compounds which had been prepared and completely characterized in the course of the photolysis studies on diazo compounds **I** [1, 4]. In the kinetic experiments we performed a qualitative and quantitative analysis of the reaction mixture by means of ^{1}H NMR spectroscopy without the preparative separation of the mixture.

Thermolysis of diazirine IIa and IIb. Pure crystalline dioxodiazirines **IIa** and **IIb** can be stored without notable decomposition or isomerization for many days. However in solutions the isomerization proceeds much faster, and therefore prior to studying the photochemical reactions of dioxodiazirines **IIa** and **IIb** we tested their thermal stability and measured the lifetime of these diazo substrates. The thermolysis of diazirines was carried out directly in the probe of the NMR spectrometer at 50 ± 1°C charging into the NMR tube solutions in CDCl$_3$ or C$_6$D$_6$ with nucleophile added [MeOH–(**IIa** and **IIb**), 10:1] and registering the changes in the amounts of the components of the reaction mixture at regular time intervals. From the results of the kinetic experiments we calculated the half-life of diazirines **IIa** and **IIb** ($\tau_{1/2}$, 50°C) [10].

The data presented in Table 1 show that the half-life of diazirines **IIa** and **IIb** in solution of CDCl$_3$ and C$_6$D$_6$ at 50°C amounts to 3.5–4.0 h.

$$\textbf{IIa, IIb} \xrightarrow[\text{CDCl}_3 \text{ or C}_6\text{D}_6]{\Delta,\ 50°\text{C}} \textbf{Ia, Ib} +$$

IV, Va, Vb
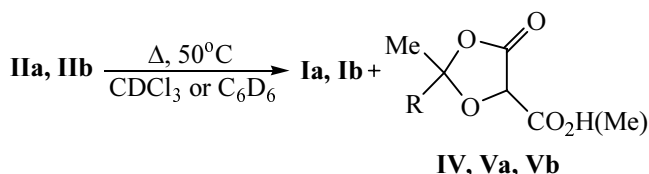
Inasmush as the photolysis experiments were carried out at lower temperature (18–20°C) and for a shorter time (1–1.5 h) we assumed that the probable thermal transformations of diazirines **IIa** and **IIb** in the course of the photochemical experiments were negligible.

By these experiments we also established that the thermolysis of diazirines **II** in CDCl$_3$ at 50°C led to the formation of dioxolanonecarboxylic acid derivatives **IV** and **V** and diazo compounds **I** in approximately equal amounts. At the same time in C$_6$D$_6$ solution at the similar

temperature Wolff rearrangement into **V** dominated (66–78%), whereas the isomerization of diazirines **II** into the corresponding diazodioxanes **I** occurred under these conditions to a lesser extent (22–34%) (Fig. 1).

Photolysis of diazirines IIa and IIb was carried out in methanol solution or in a mixture of THF (Me$_2$S) with methanol at the molar ratio diazirine **II** : methanol 1:10. In the preparative runs the reaction mixture after the photolysis was subjected to chromatography on silica gel, the isolated substances were characterized by spectral methods under the same conditions as described for the study of diazo compounds reactions [1, 4].

$$\text{II} \xrightarrow{\lambda > 210 \text{ nm}} \text{Ia + Va, Vb}$$
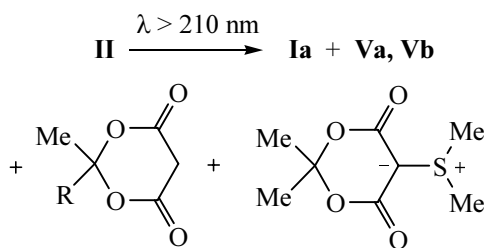
The kinetic experiments were carried out by sampling from the photochemical reaction at regular intervals, evaporating the solvent from the sample in a vacuum (1–2 mm Hg), the residue was mixed with a required quantity of an internal reference, the mixture was dissolved in CDCl$_3$ and immediately analyzed by ^{1}H NMR spectroscopy. The principle findings of this part of the research are given on the scheme and in Table 2.

As seen from the data, the photolysis of diazirines **II** under the short-wave light ($\lambda > 210$ nm) in pure MeOH (**IIa**) or in a mixture THF–MeOH (**IIa** and **IIb**) led to the almost exclusive formation of Wolff rearrngement products **Va** and **Vb** (Fig. 2). In the reaction products obtained in the THF–MeOH mixture we succeeded only to detect traces of diazodioxanediones **I** and dioxanediones **VI** as impurities. According to the IR spectroscopy used as analytical tool during the irradiation of diazirine **IIa** in the mixture THF–MeOH, the maximum amount of diazo compound **Ia** in the photolysate did not exceed 1–2%. The formation of 1,3-dioxane-4,6-dione **VIa** was qualitatively established by means of ^{1}H NMR spectroscopy and TLC on completion of the photolysis of diazirine **IIa** under the same conditions.

Photolysis of diazirine **IIa** in a mixture Me$_2$S–MeOH gave rise to the same set of the reaction products (Table 2) that had been found at the photochemical decomposition of diazo compound **Ia** [1, 4], and the efficiency of the carbene processes is here somewhat

Table 2. Photolysis of diazirines **IIa** and **IIb**

Compd. no.	Reaction conditions	Photolysis products, %			
		I	V	VI	VIIa
IIa	80 min, MeOH	–	96	–	–
IIa, IIb	50–80 min, THF–MeOH	1–2[a]	89–97	traces[a]	–
IIa	70–75 min, Me$_2$S–MeOH	6–8	49–52	–	14–16
IIa, IIb	2–4 h, ROH[b]–Ph$_2$CO	–	–	93–97	–

[a] According to IR, ^{1}H NMR spectroscopy and TLC.
[b] R = Me for **IIa**, *i*-Pr for **IIb**.

worse as shown by the yield of sulfonium ylide **VIIa** at the completion of the photolysis (14–16%).

Triplet-sensitized photolysis of diazirines **IIa** and **IIb** in methanol or 2-propanol in the presence of benzophenone resulted in an exclusive formation of dioxanediones **VIa** and **VIb** (93–97%) (Table 2).

The investigation of diazirine **II** transformations on heating showed that the main thermolysis path at 50°C in CDCl$_3$ and C$_6$D$_6$ solution consisted in nitrogen elimination and Wolff rearrangement with the formation of 5-oxoacids **IV** or their methyl esters **V**, and also in the isomerization into diazo compound **I** (the ratio of these processes was ~1:1 in CDCl$_3$ solution and ~2.5:1 in C$_6$D$_6$). Taking into consideration that diazodioxanediones **I** under similar conditions (50°C, solution in CDCl$_3$ or C$_6$D$_6$) are quite stable and even at heating for 10 h at 80°C remain virtually intact, we can unambiguously conclude that they are not intermediates on the route from diazirines **II** to Wolff rearrangement products **IV** and **V**, and therefore the latter form in the course of the thermolysis directly
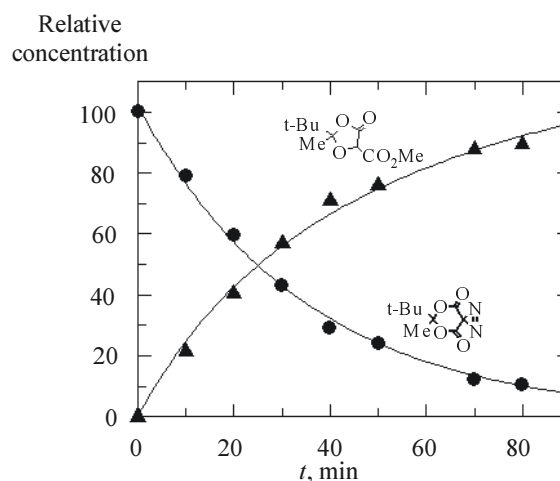

Fig. 2. Irradiation of diazirine **IIb** in THF–MeOH solution ($\lambda \geq$ 210 nm).

from diazirines **II** omitting a preliminary isomerization stage into diazo compounds **I**. Besides the lack in the reaction products after thermolysis of diazirines **II** of substances originating from dioxocarbenes **III** insertion into the O–H bond of methanol and of dioxanediones **VI** which is characteristic of carbenes **III** [1, 4] indicates that the latter also are not intermediates in this process.

Thus we for the first time experimentally have established the direct thermal transformation of α,α-dioxodiazirines **II** into Wolff rearrangement products, 2-oxoacids **IV** or their esters **V**, and these data are not consistent with the current concepts of this well studied reaction. The common scheme of Wolff rearrangement implies that the α-diazocarbonyl compounds convert into ketenes by a ketocarbene (*a*) or concerted (*b*) route [11]. The present study demonstrated that in the thermolysis of dioxodiazirines **II** Wolff rearrangement products formed directly from diazirines **II**, namely, not involving diazodioxanediones **I** and intermediate carbenes **III**. Therefore we are able to conclude, that here we are dealing with a new, "diazirine" Wolff rearrangement represented below.
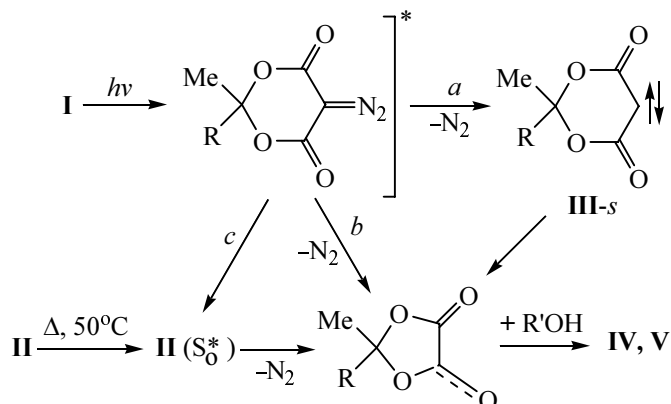
Moreover, since the thermal rearrangement proceeds through the vibrational levels of the ground state (S_0^*) of diazirines **II** it is reasonable to suggest that it may easily occur also in the photochemical reactions of the diazocarbonyl compounds **I** (by the route *c*), for the isomerization of the latter into the corresponding oxodiazirines also goes through a "hot" ground state of diazirines. Thus in all likelihood just the α-oxodiazirines are the key intermediate stage in the photochemical Wolff rearrangement of the α-diazocarbonyl compounds.

The photolysis of diazirines **II** under short-wave UV irradiation in a straight methanol resulted exclusively in Wolff rearrangement that also here occurred apparently not through diazo compound **I**. This conclusion is based on the kinetics of diazirines **II** decomposition and on the

absence of diazodioxanediones **I** or their characterisic phototransformation products, dioxanediones **VI**, which appear in small amount in the reaction products only when the photolysis of diazirines **II** is carried out in the presence of THF or dimethyl sulfide.

The formation of photoreduction products **VI** and *S*-ylides **VII** detected when the photolysis of diazirines **II** was carried out in THF–MeOH or Me$_2$S–MeOH solutions may be formally ascribed either to the photochemical decomposition of diazirines **II** proper or to the same process occurring with their isomerization products, diazo compounds **I**. It is not possible to make an unambiguous choice among these opportunities basing on the experimental data obtained. However we presume that during the photolysis of diazirines **II** ylides **VII** and dioxanediones **VI** are generated by carbene decomposition of diazo compounds **I** that arise by partial isomerization of initial diazirines **II** in the course of the photochemical reaction [7].

The main products of the triplet-sensitized photolysis of diazirines **II** are dioxanediones **VI** apparently originating from the photolysis of the primary products of insertion into OH of singlet carbenes (**I**-*s*), 5-methoxy-dioxanediones [1, 12], or from the appearance in the reaction mixture of triplet carbenes [13]. The latter, as in the reactions of the corresponding α-diazocarbonyl compounds (**IIIa** and **IIIb**) attack the solvent (alcohol) giving dioxanediones **VI**.

Thus the direct photolysis of α,α-dioxodiazirines **II** from the 1,3-dioxane series occurred without an intermediate formation of the corresponding carbenes, and these compounds cannot serve as precursors of heterocyclic α,α-dioxocarbenes **III**. Thermolysis and photolysis of diazirines from the 1,3-dioxane-4,6-dione series resulted predominantly in Wolff rearrangement leading to the formation of dioxolanonecarboxylic acids or their derivatives. The finding obtained evidence that the diazirines take part in the photolysis and Wolff rearrangement of the α-diazocarbonyl compounds.

EXPERIMENTAL

thickness 0.05–1.0 cm, concentration of solutions 3×10^{-4}–6×10^{-3} mol l^{-1}.

The reactions were carried out in anhydrous solvents purified by standard procedures. The preparative separation of the reaction mixtures was performed by column and flash-chromatography on Silicagel L 40/100 μm in a gradient mode, analytical TLC was done on Silufol UV-254 plates (Czechia), eluents petroleum ether and Et$_2$O in various ratios, and also chloroform, acetone, ethanol, and their mixtures.

Diazirines IIa and IIb. General procedure. Into a reactor for photolysis equipped with a filter of ordinary glass ($\lambda > 310$ nm) was charged a solution of 10 mmol diazo compound **Ia** or **Ib** in 80 ml of a freshly distilled THF containing 3 ml of H$_2$O, the solution was irradiated for 7–9 h at 16–18°C, the solvent was distilled off in a vacuum (15–20, then 1–2 mm Hg) at 18–20°C, the reaction mixture was dissolved in 25–30 ml of CH$_2$Cl$_2$, dried with anhydrous magnesium sulfate for 2 h, the solvent was distilled off, the residue was subjected to chromatography on neutral silica gel (20 g) eluting diazirines **II** with a mixture petroleum ether–ether, 50:1, the residue on removing the solvents was crystallized from a mixture petroleum ether–ether, 3:1.

Diazirines **II**, invisible at common vizualization of the spot on a TLC plate (Silufol UV-254) with UV irradiation, are easily detected as a strongly absorbing spot of the corresponding diazodioxanedione **I** after heating the plate for 1–2 min at 80–100°C [4].

6,6-Dimethyl-4,8-dioxa-5,7-dioxo-1,2-diaza-spiro[2,5]oct-1-ene (IIa). Yield 0.73 g (43%), mp 82–83°C (petroleum ether–ether, 3:1), R_f 0.8 (petroleum ether–ether, 1:1) [4, 5]. UV spectrum, λ_{max} (log ε): 251 (2.00), 289 (1.48). IR spectrum, ν, cm^{-1}: 1799 (C=O). Mass spectrum, m/z (I_{rel}, %): 170 (18) [M]$^+$, 155 (40), 69 (12), 58 (17), 43 (100). ^{1}H NMR spectrum (CDCl$_3$), δ, ppm: 2.00 s (6H, 2CH$_3$). ^{13}C NMR spectrum (CDCl$_3$), δ, ppm 25.3 (C^5), 28.4 (2CH$_3$), 108.1 (C^2), 162.0 (C^4). Found, %: C 42.09; H 3.60; N 16.50. C$_6$H$_6$N$_2$O$_4$. Calculated, %: 42.40; H 3.61; N 16.50.

6-Methyl-6-*tert*-butyl-4,8-dioxa-5,7-dioxo-1,2-diazaspiro[2,5]oct-1-ene (IIb). Yield 0.85 g (40%), mp 71–73°C (petroleum ether–ether, 3:1), R_f 0.75 (petroleum ether–ether, 3:1). UV spectrum, λ_{max} (log ε): 250 (2.18), 289 (1.48). IR spectrum, ν, cm^{-1}: 1770 (C=O). Mass spectrum, m/z (I_{rel}, %): 197 (1) [M–15]$^+$, 155 (40), 100 (5), 85 (9), 57 (100), 43 (60). ^{1}H NMR spectrum (CDCl$_3$), δ, ppm: 1.21 s (9H, 3CH$_3$), 1.98 c (3H, CH$_3$). ^{13}C NMR spectrum (CDCl$_3$), δ, ppm: 23.8 (3CH$_3$), 24.7 (CH$_3$), 25.3 (C^5), 39.8 (CMe$_3$), 113.4 (C^2), 162.3 (C^4). Found, %: C 50.89; H 5.60; N 13.20. C$_9$H$_{12}$N$_2$O$_4$. Calculated, %: C 50.92; H 5.66; N 13.18.

General procedure of photolysis experiments. The irradiation of diazirines **II** was performed at 18–20°C in a reactor of 25 ml capacity equipped with a quartz filter ($\lambda > 210$ nm). The monitoring of the reaction progress was done by TLC or by measuring the volume of nitrogen liberated.

In a reactor for photolysis was charged a solution of 3 mmol diazirine **II** in 20 ml of MeOH or in 20 ml of a freshly distilled THF containing 1.2 ml of MeOH, and the solution was irradiated till disappearance from the mixture of initial diazirines **IIa** and **IIb** (TLC monitoring). The solvent and excess nucleophilic reagent was distilled off at 18–20°C in a vacuum (15–20, then 1–2 mm Hg), the reaction mixture was dissolved in 25–30 ml of CH$_2$Cl$_2$, dried with anhydrous magnesium sulfate for 2 h, the solvent was distilled off, the residue was subjected to column chromatography on the neutral silica gel (20–35 g) at gradient elution with a mixture petroleum ether– ether. The main fraction containing methyl esters **Va** and **Vb** was dried with magnesium sulfate and distilled in a vacuum (1–2 mm Hg) on a micro distillation apparatus.

Methyl 2,2-dimethyl-5-oxo-1,3-dioxolane-4-carboxylate (Va). Yield 0.506 g (97%), bp 55–60°C (1– 2 mm Hg). ^{1}H NMR spectrum (CDCl$_3$), δ, ppm: 1.65 s (3H, CH$_3$), 1.73 s (3H, CH$_3$), 3.87 s (3H, OCH$_3$), 4.97 s (1H, CH) [1, 4].

Methyl 2-methyl-2-*tert*-butyl-5-oxo-1,3-dioxo-lane-4-carboxylate (Vb) (stereoisomers mixture). Yield 0.576 g (89%), bp 65–70°C (1–2 mm Hg). ^{1}H NMR spectrum (CDCl$_3$), δ, ppm: 1.05 s, 1.10 s (9H, 3CH$_3$), 1.55 s, 1.68 s (3H, CH$_3$), 3.88 s (3H, OCH$_3$), 4.93 s, 4.96 s (1H, CH) [1].

Irradiation of diazirines II in the presence of a sensitizer (Ph$_2$C=O). **General procedure.** Into a quartz cell of 15 ml capacity was charged a solution of 1 mmol of diazirine **II** in 7–13 ml of a freshly distilled MeOH (*i*-PrOH) containing 0.5 (2.0) mmol of sensitizer (at this concentration the extinction of benzophenone at the wavelength 254 nm exceeds 80 times that of compound **II**). The solution was irradiated with a short-wave UV light ($\lambda > 210$ nm) till disappearance from the mixture of initial diazirines **IIa** and **IIb** (TLC monitoring). On completion of the photolysis the reaction mixture was analyzed by means of ^{1}H NMR spectroscopy. The quantitative analysis was performed using an internal reference, *p*-dibromobenzene.

Table 3. Results of thermolysis of diazirine **IIb** in C_6D_6–MeOH solution at 50°C

Thermolysis time, min	Content of components in reaction mixture at thermolysis, %		
	IIb	**Ib**	**Vb**
0	100.0	0.0	0.0
20	80.0	5.7	14.3
40	69.5	8.9	21.6
60	62.4	11.7	25.9
86	45.0	16.3	38.7
151	25.0	22.2	52.8
326	5.0	28.2	66.8

Table 4. Results of irradiation of diazirine **IIb** in THF–MeOH ($\lambda \geq 210$ nm)

Photolysis time, min	Content of components in reaction mixture at photolysis, %	
	IIb	**Vb**
0	100	0
10	78.8	21.2
20	59.5	40.5
30	43.2	56.8
40	29.1	70.9
50	23.9	76.1
70	12.4	87.6
80	10.7	89.3

Photochemical decomposition of diazirine IIa in methanol solution. On irradiation of 0.170 g (1 mmol) of diazirine **IIa** for 120 min in a methanol solution (7 ml) containing 0.091 g (0.5 mmol) of benzophenone we identified in the reaction mixture by means of ^{1}H NMR spectroscopy only 2,2-dimethyl-1,3-dioxane-4,6-dione (**VIa**). Yield 0.134 g (93%).

Photochemical decomposition of diazirine IIb in 2-propanol. On irradiation of 0.212 g (1 mmol) of diazirine **IIb** for 240 min in a 2-propanol solution (13 ml) containing 0.364 g (2 mmol) of benzophenone we identified in the reaction mixture by means of ^{1}H NMR spectroscopy only 2-methyl-2-*tert*-butyl-1,3-dioxane-4,6-dione (**VIb**). Yield 0.180 g (97%).

Kinetics of the thermolysis of diazirine IIa and IIb. The thermolysis of diazirines **II** was carried out in an NMR tube placed in a temperature-controlled device or directly in the probe of the NMR spectrometer at 50 ± 1°C in CDCl$_3$ or C$_6$D$_6$ solution. The content of the reaction mixture components was registered at regular time intervals. The concentration of diazirines **IIa** and **IIb** in solution was 0.09–0.1 mol l^{-1}, the ratio diazirine **II**–

nucleophile, 1:10. The content of components in the reaction mixture was estimated by the internal normalization method. From the results of kinetic runs we calculated the half-life of diazirines **II** ($\tau_{1/2}$, 50°C) [10].

Thermolysis of diazirine **IIb** in C$_6$D$_6$–MeOH was performed for 60 min directly in the probe of the spectrometer; the content of components **Ib, IIb**, and **Vb** in the reaction mixture was estimated from the integral intensity of proton signals of the following groups: diazo compound **Ib**, CH$_3$ (1.11 ppm); diazirine **IIb**, CH$_3$ (1.8 ppm); methyl ester of 5-oxocarboxylic acid **Vb**, CH$_3$ (1.07 and 1.57 ppm). The results of the analysis are presented in Fig. 1 and Table 3. To estimate the yield of reaction products at higher conversion the thermolysis of diazirine **IIb** was continued at 80°C for 9 h. On completion of the reaction the components of the reaction mixture were present in the following amounts: diazo compound **Ib**, 34%; methyl ester of 5-oxocarboxylic acid **Vb**, 66%.

Kinetics of photolysis of diazirines IIa and IIb. Into a reactor for photolysis equipped with a jacket of quartz was charged a solution of 1.4–1.6 mmol of diazirine **II** in 20 ml of a freshly distilled THF or Me$_2$S containing 0.6 ml of MeOH, and the mixture was subjected to irradiation at 16–18°C till disappearance from the mixture of initial diazirine **II** (TLC monitoring). In the course of the photolysis the sampling (0.5 or 1 ml) was performed at regular intervals, the volatile components from the samples of the reaction mixture were removed in a vacuum (1–2 mm Hg) at 16–18°C. The content of components in the reaction mixture was estimated by the internal normalization method or with the help of an internal reference (*p*-dibromobenzene, 3–5 mg/ml CDCl$_3$).

Photolysis of diazirine IIb in THF–MeOH. A solution of 0.34 g (1.6 mmol) of diazirine **IIb** in 22 ml of THF and 0.6 ml of MeOH was irradiated for 80 min with sampling of the reaction mixture (0.5 ml) after 10, 20, 30, 40, 50, 60, 70, and 80 min from the start of the reaction, the quantitative analysis of the reaction mixture was performed with the help of the internal reference. The results of analyses are presented in Fig. 2 and Table 4. On completion of the photolysis according to ^{1}H NMR spectroscopy the only product was methyl ester of 5-oxocarboxylic acid **Vb**, yield 0.308 g (89%).

The study of the heat resistance of diazo compounds Ia and Ib. The thermolysis of diazo compounds **I** was carried out in an NMR tube at 50 ± 1°C in CDCl$_3$ solution and at 80 ± 1°C in C$_6$D$_6$ solution with methanol

added (content of diazo compounds **I** in solution 0.01–0.02 g, molar ratio **I**–MeOH 1:10), after 10 h the reaction mixture was cooled to room temperature and analyzed by means of ^{1}H NMR spectroscopy. In all runs (**Ia**–CDCl$_3$–MeOH, **Ia**–C$_6$D$_6$–MeOH, **Ib**–CDCl$_3$–MeOH, **Ib**–C$_6$D$_6$–MeOH) at the end of heating in the reaction mixtures were identified only initial diazo compounds **Ia** and **Ib**.

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