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Chemistry of Diazocarbonyl Compounds: XXV.* Comparative Photochemistry of Diazo Compounds and Sulfur Ylides of the 1,3-Dioxane-4,6-dione Series

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Abstract—Photochemical decomposition of 2,2-dialkyl-5-diazo-1,3-dioxane-4,6-diones in the presence of pyridine, methanol, or dimethyl sulfide as carbene traps involves mainly the Wolff rearrangement which is likely to follow a concerted pattern, while the yield of the "carbene" products does not exceed 27–28%. No carbene intermediates are formed in the photolysis of the corresponding dioxo sulfonium ylides under analogous conditions, and the main photochemical process is 1,2-methyl shift (Stevens rearrangement), followed by photochemical transformations of the primary products according to the Norrish type II pattern.

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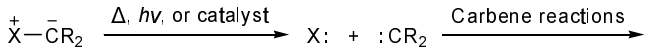
Apart from diazo compounds and diazirines [2], ylides are believed to be a promising source of carbenes; their photochemical decomposition could provide a convenient method for generation of carbenes [3–8]. However, studies in the field of "carbene" transformations of ylides were concerned mainly with thermocatalytic reactions of ylide-like substrates [9, 10]. These studies revealed some analogy between reactions of ylides and diazo compounds under similar conditions, and intermediate formation of carbene-like species was postulated in a number of thermocatalytic processes involving ylides [10] (Scheme 1).

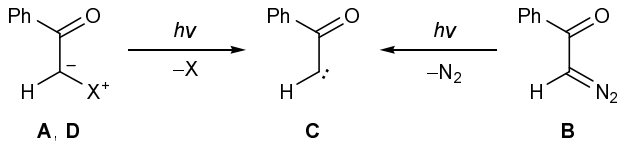
Scheme 1.



X = Hlg, S, P, N, or other heteroelement.

Unlike thermocatalytic reactions, photochemical transformations of ylides were studied to a considerably lesser extent, and the results are often contradictory. As was shown by Trost in his pioneering and the most fundamental study in this field [3], direct photolysis of dimethyl(phenacyl)sulfurane (**A**) with long-wave UV light (λ > 280 nm) in the presence of alcohols or cyclohexene leads mainly to cleavage of the ylide C–S bond with formation of almost the same products as in the photolysis of diazoacetophenone (**B**) under analogous conditions [11]. According to the author, these data suggest formation of the same intermediate, benzoylcarbene (**C**) from both precursors (Scheme 2).

Scheme 2.



A, X = SMe_2; **D**, X = PPh_3.

The results of both direct and Ph_2CO-sensitized photolysis of a phosphonium analog of sulfurane **A**, ylide **D**, indicated intermediate formation of singlet (S) and triplet (T) benzoylcarbenes **C** [6, 8]. On the one hand, these data are consistent with the results of photochemical decomposition of diazoacetophenone (**B**) in the presence of alkenes as carbene trap [11] (both direct and sensitized photolysis of diazo compound **B** also gave a mixture of singlet and triplet carbenes **C**). However, more recent studies showed that direct photolysis of **B** in the presence of, e.g.,

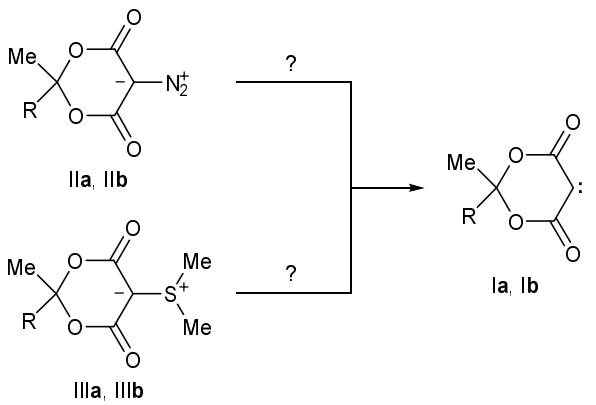
* For communication XXIV, see [1].

methanol, yields mainly the corresponding Wolff rearrangement products while carbene insertion products (as an evidence in favor of intermediate formation of benzoylcarbenes **C**) were not detected in the reaction mixture [8]. Furthermore, Nagao et al. [7] found that photolysis of another phosphonium ylide, triphenylphosphonio(ethoxycarbonyl)methanide $Ph_3P^+–C^-HCO_2Et$, involves mainly cleavage of the P–Ph bond rather than ylide P–C bond.

The formation of products typical of carbene reactions (insertion into the C–H bond of cyclohexane and cyclopropanation of olefins) was detected in the thermolysis and photolysis of phenyliodonium ylide $PhI^+–C^-(CO_2Et)_2$ in the presence of cyclohexane and alkenes [5, 8], but the contribution of the carbene path to the photochemical decomposition of that ylide was very small (<2%). According to Streith et al. [4], photochemical decomposition of pyridinium ylide $C_5H_5N^+–C^-(CN)_2$ in benzene gave 13% of dicyanonorcaradiene, presumably via reaction of dicyanocarbene with benzene. Thus the available published data indicate some similarity in the photochemical behavior of diazo compounds and structurally related ylides containing sulfur, phosphorus, nitrogen, and other heteroelements. However, these data do not allow us to conclude with certainty whether effective generation of carbenes by photochemical decomposition of ylide substrates is possible or not.

In the present work we performed a comparative study of photochemical reactions of diazo compounds and sulfonium ylides of the 1,3-dioxane-4,6-dione series with the goal of determining main pathways of their photochemical transformations and elucidating the possibility of using them as precursors of heterocyclic dioxo carbenes **I** [12] (Scheme 3). We also planned to estimate the relative efficiency of pyridine, methanol, and dimethyl sulfide as traps for dioxo carbenes which were assumed to mediate the photochemical processes under study. It should be noted that photochemical transformations of sulfonium ylides like **III** were not studied previously.

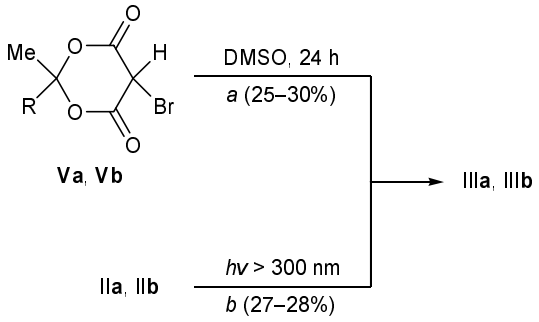
Scheme 3.



R = Me (**a**), *t*-Bu (**b**).

As substrates we used 2,2-dialkyl-5-diazo-1,3-dioxane-4,6-diones **IIa** and **IIb** and the corresponding sulfonium ylides **IIIa** and **IIIb**. We selected cyclic structures **II** and **III** with fixed *Z*,*Z* orientation of the substituents at the carbonyl groups in order to avoid effect of conformational factors on the direction of photochemical processes; such effect is known to be typical of acyclic diazocarbonyl compounds [13]. In addition, compounds **II** and **III** contained methyl and *tert*-butyl groups as substituents on C^2 for reasons of simplifying spectral identification of the products, taking into account that these groups give singlet signals in ^1H NMR spectra. Diazo compounds **IIa** and **IIb** were synthesized from the corresponding 1,3-dioxane-4,6-diones **IVa** and **IVb** [14] by the diazo transfer reaction [15] using KF as a base [16]. Sulfur ylides **IIIa** and **IIIb** were obtained in two ways: (*a*) by reaction of 5-bromo-1,3-dioxane-4,6-diones **Va** and **Vb** with dimethyl sulfoxide [17] and (*b*) by photolysis of diazo compounds **IIa** and **IIb** in dimethyl sulfide [18] (Scheme 4). Both procedures afforded relatively low yields of ylides **III** (27–30%); therefore, they cannot be regarded as optimal. From the preparative viewpoint, the condensation of bromo-substituted dioxanediones **V** with DMSO is preferred, for it ensures enlarged syntheses and requires a shorter time.

Scheme 4.



R = Me (**a**), *t*-Bu (**b**).

The yields and physical constants of compounds **II** and **III** are given in Experimental, and the structure of newly synthesized compounds was confirmed by spectral data. Before use in photochemical reactions, compounds **II** and sulfur ylides **III** were thoroughly

purified by recrystallization; diazo compounds **II** were additionally sublimed under reduced pressure. Compounds **III**, as well as diazodioxanediones **II**, are stable nonhygroscopic crystalline substances which can be stored for many months without appreciable decomposition.

The electronic spectra of diazo compounds **IIa** and **IIb** and sulfur ylides **IIIa** and **IIIb** are characterized by strong absorption in the region λ 232–252 nm and a weaker absorption at 306–337 nm (Table 1). These maxima correspond to π–π* and *n*–π* transitions, respectively [17, 19]. In photochemical experiments, the substrates were irradiated with a Hanau S-81 medium-pressure mercury lamp (100–130 W) through a quartz (λ > 210 nm), Pyrex (λ > 280 nm), or glass light filter (λ > 310 nm) without additional monochromatization. As a rule, the reaction mixtures were separated by column chromatography on silica gel to isolate individual products. In kinetic experiments, the qualitative and quantitative compositions of the reaction mixtures were determined by ^{1}H NMR spectroscopy without preparative separation.

Photochemical transformations of 5-diazo-1,3-dioxane-4,6-diones IIa and IIb. Photochemical reactions of diazodioxanedione **IIa** were studied previously; it was found that the main photolysis pathways are the Wolff rearrangement [12, 20–24] and isomerization of initial diazo compound **IIa** into diazirine **VIa** [12, 20, 21, 24]. The results of laser flash photolysis (XeF, λ 351 nm) of compound **IIa** in the presence of pyridine indicated that the Wolff rearrangement predominates under the conditions of direct photolysis [23]. On the other hand, photochemical decomposition of **IIa** in the presence of olefins as carbene trap was shown to give cyclopropanes; however, the yields of such typical carbene reaction products** in unsensitized photolysis did not exceed 1–2% [25].

This part of our study was aimed mainly at elucidating the efficiency of carbene-mediated processes in the photolysis of diazo compounds **IIa** and **IIb** in the presence of dimethyl sulfide and methanol as carbene traps, i.e., at determininng the yields of sulfur ylides **III** [26], dioxanediones **IV**, and/or OH-insertion products **IX** [27]. Pyridine is known as the most widely used and convenient trap of carbenes which are invisible in UV light [28]; however, it turned out to be inapplicable under the conditions of stationary photolysis used in our study. We previously examined laser flash photolysis of diazodioxanedione **IIa** in cyclohexane and 1,1,2-trifluorotrichloroethane [23] and found that pyridine gives rise to an intensely colored pyridinium ylide via reaction with the major product, 2-oxoketene, formed as a result of Wolff rearrangement. Therefore, carrying out prolonged stationary photolysis in the presence of strongly absorbing species could involve considerable experimental difficulties. Moreover, by preliminary experiments with bis(methoxycarbonyl)carbene as an acyclic analog of carbene **I** we showed that the efficiency of dimethyl sulfide and methanol as carbene traps exceeds the efficiency of pyridine by a factor of 6 and 3, respectively.

Table 1. UV spectra of diazo compounds **IIa** and **IIb** and sulfonium ylides **IIIa** and **IIIb**

Compound no.	UV spectrum, λ_{max}, nm (log ε)		
	heptane	THF	methanol
IIa	249 (3.86),[a] 336 (1.08)	252 (4.10), 336 (1.30)	251 (4.14), 334 (1.30)
IIb	249 (3.95), 337 (1.30)	251 (4.02), 335 (1.48)	250 (4.08), 334 (1.48)
IIIa	232 (4.00)	237 (4.13),[b] 312 (1.90)	232(4.23), 308 (2.23)
IIIb	233 (4.01)	236 (4.00)[b]	232 (4.09), 306 (1.00)

[a] In octane.
[b] Inflection.

Diazo compounds **IIa** and **IIb** were irradiated (Table 2) either directly in a solution in nucleophilic reagent (MeOH, Me_2S) or in a mixture of THF (Me_2S) and nucleophile (H_2O, MeOH), the diazo compound–nucleophile molar ratio being 1:10. When the reaction was complete, the solvent and excess nucleophile were removed under reduced pressure, and the product mixture was analyzed by ^{1}H NMR spectroscopy and separated by chromatography on silica gel. The isolated products were identified by ^{1}H and ^{13}C NMR and mass spectra.

The results showed that photolysis of diazo compounds **II** with short-wave UV light (λ > 210 nm) occurs most selectively in pure methanol. In this case, the corresponding Wolff rearrangement products were formed in almost quantitative yield (Fig. 1). Irradiation of **IIa** and **IIb** in THF–H_2O or THF–MeOH also led mainly to the Wolff rearrangement products (56–64%), but small amounts of diazirines **VIa** and **VIb** (5–12%)

** Apart from cyclopropanes, by "typical carbene reaction products" we mean pyridinium, oxonium, and sulfonium ylides, as well as OH-insertion and hydrogen abstraction products.

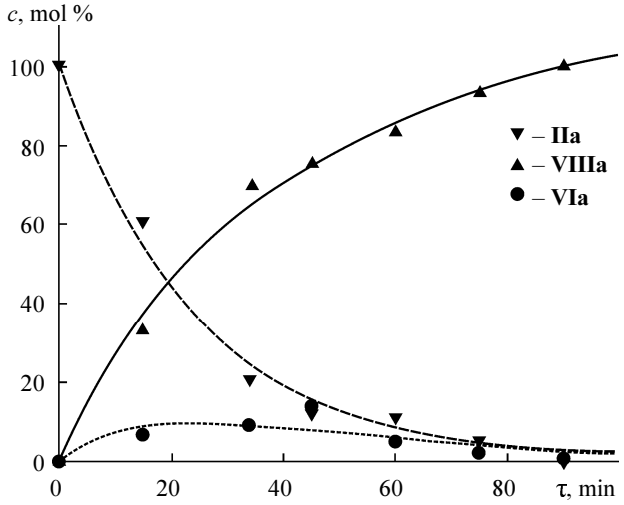


Fig. 1. Kinetics of the photolysis of 5-diazo-2,2-dimethyl-1,3-dioxane-4,6-dione (**IIa**) in MeOH ($\lambda \geq 210$ nm).

and dioxanediones **IVa** and **IVb** (3–6%) were also isolated (Scheme 5). Photolysis of compound **IIa** at $\lambda >$ 280 nm (Pyrex light filter) gave the same compounds, but the fraction of diazirine **VIa** was considerably greater; correspondingly, the fractions of Wolff rearrangement products **VIIa** and **VIIIa** decreased.

When diazo compounds **IIa** and **IIb** were irradiated with long-wave UV light ($\lambda > 310$ nm), the contributions of the main processes, isomerization to diazirine **VI** and Wolff rearrangement leading to compounds **VII** and **VIII**, changed to almost the opposite: 39–43 and 13–19%, respectively. Apart from compounds **VI**–**VIII**, we detected by ^{1}H NMR spectroscopy products of dioxocarbene insertion into the O–H bond of methanol (compounds **IXa** and **IXb**). Compounds **IX** were

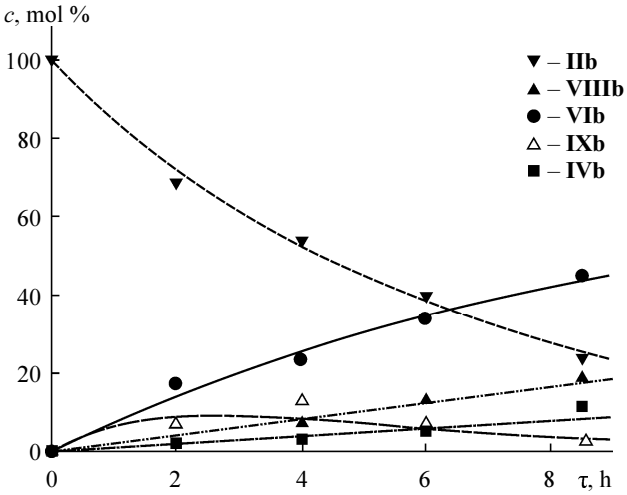
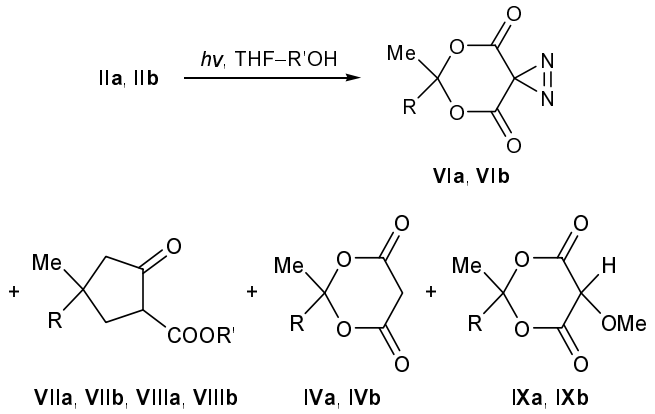


Fig. 2. Kinetics of the photolysis of 2-*tert*-butyl-5-diazo-2-methyl-1,3-dioxane-4,6-dione (**IIb**) in a THF–MeOH mixture ($\lambda \geq 310$ nm).

identified by the presence of characteristic signals from the 5-H and 5-OCH_3 protons at δ 6.30/6.34 and 3.75/3.76 ppm (**a**/**b**), respectively, in the ^{1}H NMR spectrum of the reaction mixture (Fig. 2). We failed to isolate 5-methoxydioxanediones **IX** as individual substances; presumably, they decompose under UV irradiation or during the isolation procedure. Analogous instability was observed in [5] for a carbocyclic analog of **IX**, an alkoxy-substituted dimedone.

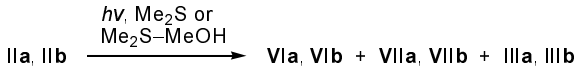
Scheme 5.



R = Me (**a**), *t*-Bu (**b**); **VII**, R' = H; **VIII**, R' = Me.

The photolysis of diazodioxanediones **II** in dimethyl sulfide as solvent was characterized by the same general relations as those observed in tetrahydrofuran: short-wave UV irradiation induces mainly the Wolff rearrangement, while long-wave UV irradiation gives diazirines **VI** as the major products (Scheme 6, Table 3). However, the yields of sulfonium ylides **IIIa** and **IIIb**, regardless of the reaction medium (Me_2S or Me_2S–MeOH) and irradiation wavelength, did not exceed 22–28%.

Scheme 6.



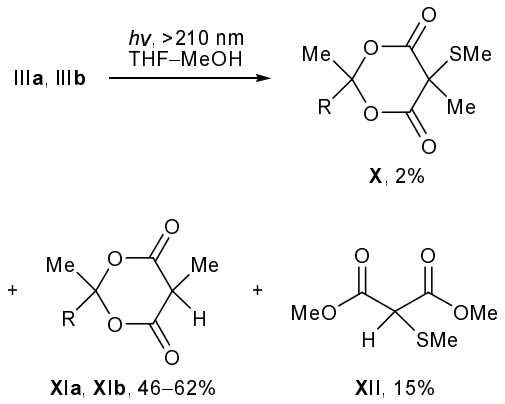
Chromatographic separation of the product mixture obtained by photolysis of diazodioxanedione **IIa** in aqueous medium (THF–H_2O) also gave 6% of malonic acid and 12% of tartronic acid. Obviously, these compounds were formed from **IVa** and **VIIa** during chromatography on silica gel. This is consistent with published data [21, 29] according to which 2,2-disubstituted 1,3-dioxanes and 1,3-dioxolanes readily undergo hydrolysis in the presence of acid catalysts or on silica gel.

The structure of photolysis products **IVa**, **IVb**, **VIIa**, **VIIb**, **VIIIa**, and **VIIIb** was confirmed by spectral methods (see Experimental). Unlike the data of [22], 5-oxo acid **VIIa** turned out to be quite stable under normal conditions; it melted at 105–106°C without decomposition and underwent decarboxylation to 2,2-dimethyl-1,3-dioxolan-4-one only on heating above 160°C [21]. The ^{1}H and ^{13}C NMR spectra of acid **VIIb** and its methyl ester **VIIIb** in $CDCl_3$ contained two sets of signals at a ratio of ~1:1. Obviously, these compounds are mixtures of *cis* and *trans* isomers; however, we failed to separate these stereoisomers by preparative chromatography, for they were characterized by almost similar R_f values.

Photochemical transformations of sulfonium ylides IIIa and IIIb. As noted above, photochemical reactions of compounds **III** were not studied previously. Taking into account that ylides **IIIa** and **IIIb** are fairly stable under long-wave UV irradiation, their photolysis was performed at $\lambda > 210$ nm. The reactions were carried out on a preparative scale, and irradiation for 7–8 h was necessary to complete the photolysis of ylides **III** (unlike their diazo analogs **II**). The product mixtures were separated by column chromatography on silica gel, and the structure of the isolated products was determined by spectral methods (^{1}H and ^{13}C NMR and mass spectrometry).

The major products of photolytic decomposition of dioxo sulfonium ylides **IIIa** and **IIIb** were 5-methyl-1,3-dioxane-4,6-diones **XIa** and **XIb** (Scheme 7; the stereoisomer ratio for compound **XIb** was ~ 4:1). The photolysis of ylide **IIIa** also gave small amounts of 5-methyl-5-methylsulfanyl-1,3-dioxane-4,6-dione (**X**) and acyclic dimethyl 2-methylsulfanylmalonate (**XII**); the later was identified by comparing its spectral parameters with those reported in [30]. No data indicating photochemical cleavage of the ylide C–S bond and formation of carbene reaction products (as in the photolysis of sulfur and phosphorus ylides **A** and **D** [3, 8]) was obtained in the reactions of sulfur ylides **IIIa** and **IIIb**.

Scheme 7.



R = Me (**a**), *t*-Bu (**b**).

Table 2. Photolysis of diazodioxanediones **IIa** and **IIb** in methanol and THF–R'OH mixtures

Comp. no.	Conditions	Yield, %			
		VI	**VII, VIII**	**IV**	**IX**
IIa	>210 nm, 1 h, MeOH	–	>90[a]	–	–
IIa, **IIb**	>210 nm, 1–2 h, THF–R'OH	5–12	56–66	3–6	–
IIa	>280 nm, 6 h, THF–R'OH	23–31	24–25	8–9	14[a]
IIa, **IIb**	>310 nm, 8–12 h, THF–R'OH	39–43[a]	13–19[a]	5–12[a]	14–16[a]

[a] According to the ^{1}H NMR data; the maximal yields of compounds **IX** during the photolysis are given: after 6 h for **IXa** and after 4 h for **IXb**.

The results of our comparative study on the efficiency of carbene processes in the photolysis of diazo dicarbonyl compounds **II** and dioxo sulfonium ylides **III** led us to the following conclusions.

The yield of carbene reaction products in the direct photolysis of diazodioxanediones **II** in the presence of dimethyl sulfide, methanol, and pyridine does not exceed 27–28%. Among these traps for carbene **I**, the

Table 3. Photolysis of diazodioxanediones **IIa** and **IIb** in dimethyl sulfide

Comp. no.	Conditions	Yield, %		
		VI	**VII**	**III**
IIa[a]	>210 nm, 2 h, Me_2S			18
IIa, **IIb**[a]	>310 nm, 28 h, Me_2S			27–28
IIa[b, c]	>210 nm, Me_2S–MeOH	7–13	48–50	22–27
IIb[d]	>310 nm, 8 h, Me_2S–MeOH	43	19	2

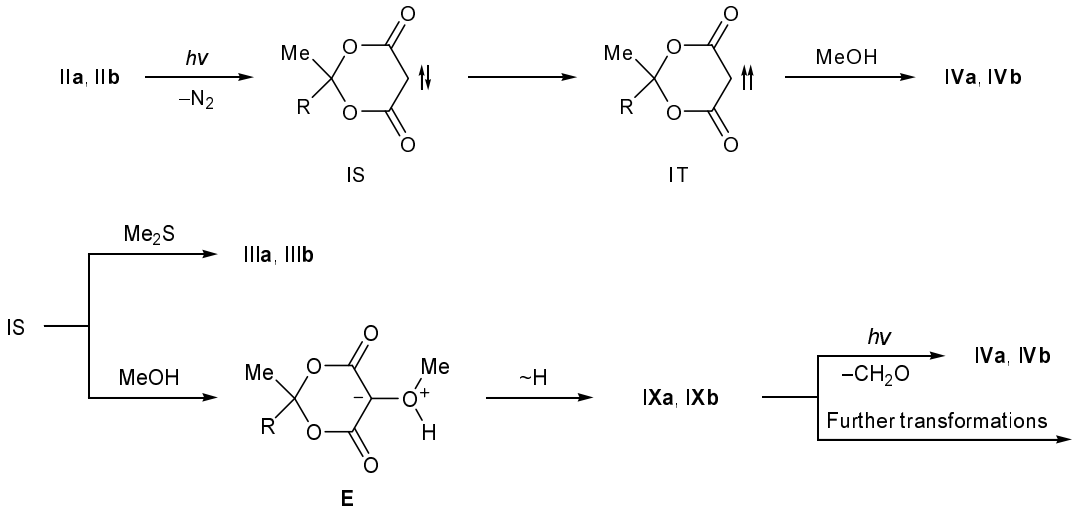
[a] The concentration of photolysis products other than **IIIa** or **IIIb** was not determined.

[b] According to the ^{1}H NMR data for two experiments (reaction time 80 and 140 min).

[c] The reaction mixture also contained 22% (in 80 min) and 12% (in 140 min) of initial diazo compound **IIa**.

[d] The reaction mixture also contained 19% of initial diazo compound **IIb**.

Scheme 8.



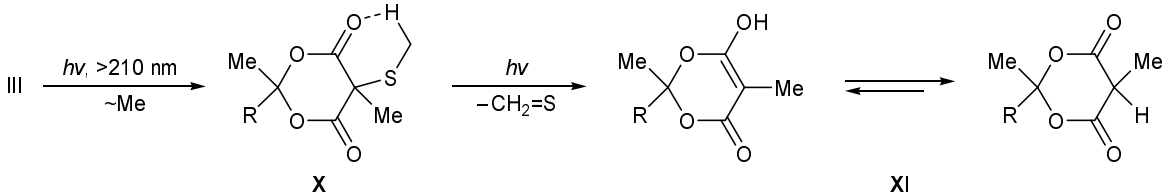
most efficient is dimethyl sulfide which ensures the highest yield of dioxo sulfonium ylides **III** in the reaction with singlet carbene **I**S. Ylides **III** are fairly stable under short-wave UV irradiation ($\lambda > 210$ nm); therefore, dimethyl sulfide can be used as an efficient carbene trap and convenient tool for studying reactions of dioxo carbenes.

The reaction of dioxo carbenes **I** with methanol is less selective than with dimethyl sulfide. According to published data, oxo carbenes usually react with alcohols along two pathways, resulting in insertion products into the O–H bond of the alcohol and/or hydrogen abstraction products (photodehydrogenation) [27]. It is assumed that singlet carbenes are responsible for the formation of OH-insertion products and that triplet carbenes give rise to hydrogen abstraction [27]. Taking into account the results of our study and those obtained by other authors, the photolysis of diazodioxanedione **IIa** may be represented by Scheme 8. Direct photolysis of compound **IIa** gives electrophilic singlet dioxo carbene **I**S which reacts with the oxygen atom of methanol. Oxonium ylide **E** thus formed undergoes 1,2-hydride shift, leading to compound **IX** which can be regarded as a formal product of insertion of carbene **I** into the O–H bond. Partial transformation of singlet carbene **I**S into triplet carbene **I**T via intersystem crossing and the subsequent reaction of **I**T with the solvent (MeOH) yields hydrogen abstraction products, dioxanediones **IV**. Judging by the yield of dioxanedione **IV** in the presence of benzophenone, the latter path becomes the only one in the triplet-sensitized photolysis of diazo compound **IIa**.

However, a different path may be proposed on the basis of published data [31] for the formation of dioxanediones **IV** in the direct photolysis of diazo compounds **II**. It does not imply participation of triplet carbene species but involves the Norrish type II phototransformation of OH-insertion product **IX**, which directly leads to dioxanediones **IV**. We failed to obtain experimental proofs for this path because of instability of cyclic 5-methoxy-substituted dioxanediones **IX**. On the other hand, we were the first to reveal that irradiation with short-wave UV light of an acyclic analog of 5-methoxydioxanedione **IXa**, dimethyl 2-methoxymalonate leads to the formation of just dimethyl malonate; this fact may be considered to be an experimental proof for the formation of compounds **IV** according to the Norrish type II scheme.

Thus, both our results and published data indicate the carbene origin of OH-insertion products **IX** and

Scheme 9.



dioxanediones **IV** in the photolysis of diazo compounds **II**. The lower yields of **IX** and **IV** (3–16%), as compared to ylides **III** (22–28%), may be rationalized by their ready subsequent transformations under UV irradiation.

The photolysis of dioxo sulfonium ylides **IIIa** and **IIIb** was found to involve quite different transformations than those typical of their diazo analogs **II** and ylides **A** and **D** studied previously [3, 6, 8]. The main photochemical process is intramolecular 1,2-migration of the S-methyl group (Stevens rearrangement), followed by decomposition of the primary product to give 5-methyldioxanediones **XI**. An analogous rearrangement was observed previously in thermal decomposition of acyclic sulfonium and ammonium ylides [30, 32]; according to the CIDNP data, the key intermediates in this process are radical pairs. Presumably, photochemical decomposition of the primary products, 5-methyl-5-methylsulfanyl-1,3-dioxane-4,6-diones **Xa** and **Xb** follows the intramolecular Norrish type II pattern (Scheme 9) leading to 5-methyl-1,3-dioxane-4,6-diones **XIa** and **XIb**.

It still remains difficult to rationalize paths of formation of dimethyl 2-methylsulfanylmalonate (**XIIa**), which should include transesterification of cyclic malonic acid ester. Most probably, these paths (like those leading to compounds **X** and **XI**) do not involve carbene decomposition of ylides **III**.

We can conclude that no intermediate carbene species is formed in the photolysis of dioxo sulfonium ylides **III** of the 1,3-dioxane series; therefore, photochemical decomposition of such sulfur ylides cannot be used for generation of heterocyclic dioxo carbenes like **I**.

EXPERIMENTAL

The ^{1}H and ^{13}C NMR spectra were recorded on a Bruker AM-300 spectrometer at 300 and 75.5 MHz, respectively, from solutions in $CDCl_3$ using tetramethylsilane as internal reference. The IR spectra were obtained on a Specord 75IR instrument from solutions in $CHCl_3$ with a concentration of 0.02–0.03 M. The UV spectra were measured in the λ range from 200 to 500 nm on a Specord M-40 spectrophotometer from solutions in methanol ($c = 3\times10^{-4}$–6×10^{-3} M) using 0.05–1.0-cm cells.

The reactions were carried out in anhydrous solvents which were purified by standard procedures. The reaction mixtures were separated by column and flash chromatography on Silicagel L (40/100 μm) using gradient elution; analytical TLC was performed on Silufol UV-254 plates (Czechia) using as eluent mixtures of petroleum ether and diethyl ether at various ratios, chloroform, acetone, ethanol, or their mixtures.

1,3-Dioxane-4,6-diones **IVa** and **IVb** were synthesized from malonic acid and the corresponding ketones according to the procedure described in [14].

2,2-Dimethyl-1,3-dioxane-4,6-dione (IVa). Yield 70%, mp 91–93°C (from $CHCl_3$) [14]. ^{1}H NMR spectrum, δ, ppm: 1.72 s (6H, $2CH_3$), 3.64 s (2H, CH_2).

2-*tert*-Butyl-2-methyl-1,3-dioxane-4,6-dione (IVb). Yield 50%, mp 78–80°C (from $CHCl_3$). ^{1}H NMR spectrum, δ, ppm: 1.09 s (9H, $3CH_3$), 1.69 s (3H, CH_3), 3.58 d (1H, CH, J = 21 Hz), 3.69 d (1H, CH, J = 21 Hz). ^{13}C NMR spectrum, δ_C, ppm: 22.3 (CH_3), 24.5 ($3CH_3$), 36.4 (C^5), 39.8 (**C**Me_3), 111.7 (C^2), 163.7 (C^6).

5-Diazo-1,3-dioxane-4,6-diones IIa and IIb (*general procedure*). A solution of 25 mmol of dicarbonyl compound **IVa** or **IVb** and 5 g (25 mmol) of *p*-toluenesulfonyl azide in 100 ml of chloroform was placed in a 250-ml Erlenmeyer flask equipped with a magnetic stirrer and protected from light. The solution was cooled to 0°C, a required amount of anhydrous potassium fluoride (catalyst) was added, and the mixture was stirred for 30 min at 0°C and then at room temperature until the reaction was complete (according to the TLC data). The catalyst and *p*-toluenesulfonamide were separated on a Schott filter, the filtrate was washed in a separatory funnel with a 2% aqueous solution of potassium hydroxide (3×20 ml) to remove residual *p*-toluenesulfonamide and with water (3×10 ml), the aqueous washings were extracted with chloroform (3×15 ml), the extracts were combined with the organic phase and dried over anhydrous magnesium sulfate, the solvent was distilled off at 25–35°C under reduced pressure (10–20 mm), and the residue was purified by recrystallization.

5-Diazo-2,2-dimethyl-1,3-dioxane-4,6-dione (IIa) was obtained from 3.6 g (25 mmol) of dioxanedione **IVa** using 7.2 g (125 mmol) of potassium fluoride (reaction time 24 h). After treatment of the reaction mixture according to the general procedure, the residue was recrystallized from carbon tetrachloride (15 ml) and sublimed at 40°C under reduced pressure (0.1–0.3 mm). Yield 2.1 g (49%), mp 96–97°C (sublimes) [21]. UV spectrum, λ_{max}, nm (logε): 251 (9.53), 334 (2.99). IR spectrum, ν, cm^{-1}: 1732 (C=O), 2179

(C=N_2). ^{1}H NMR spectrum, δ, ppm: 1.80 s (6H, 2CH_3). ^{13}C NMR spectrum, δ_C, ppm: 26.6 (CH_3), 65.4 (C^5), 107.0 (C^2), 158.5 (C^4). Mass spectrum, *m*/*z* (I_{rel}, %): 170 (18) $[M]^+$, 155 (40), 69 (12), 58 (17), 43 (100). Found, %: C 42.38; H 3.54; N 16.48. $C_6H_6N_2O_4$. Calculated, %: C 42.40; H 3.60; N 16.50.

2-*tert*-Butyl-5-diazo-2-methyl-1,3-dioxane-4,6-dione (IIb) was obtained from 4.65 g (25 mmol) of dioxanedione **IVb** using 1.9 g (33 mmol) of potassium fluoride (reaction time 29 h). Yield 2.8 g (53%), mp 76–78°C (from petroleum ether–diethyl ether, 3:1). UV spectrum, λ_{max}, nm (logε): 250 (9.39), 334 (3.40). IR spectrum, ν, cm^{-1}: 1732 (C=O), 2164 (C=N_2). ^{1}H NMR spectrum, δ, ppm: 1.12 s (9H, 3CH_3), 1.71 s (3H, CH_3). ^{13}C NMR spectrum, δ_C, ppm: 21.0 (3CH_3), 24.6 (CH_3), 39.6 (**C**Me_3), 65.1 (C^5), 112.8 (C^2), 158.9 (C^4). Mass spectrum, *m*/*z* (I_{rel}, %): 197 (1) $[M - 15]^+$, 155 (40), 100 (5), 85 (9), 57 (100), 43 (60). Found, %: C 51.25; H 5.68; N 13.27. $C_9H_{12}N_2O_4$. Calculated, %: C 50.94; H 5.66; N 13.21.

5-Bromo-1,3-dioxane-4,6-diones Va and Vb (*general procedure*). A solution of 1.45 g (36 mmol) of sodium hydroxide in 5.5 ml of water was placed in a 100-ml Erlenmeyer flask and cooled to 0°C with an ice–water mixture, and 35 mmol of dioxanedione **IVa** or **IVb** was added. When the mixture became homogeneous, 2.8 g (17.5 mmol) of bromine was added over a period of 20 min under vigorous stirring using a magnetic stirrer, the mixture was diluted with 5.5 ml of water, the second portion of bromine, 2.8 g (17.5 mmol), was added over a period of 20 min, and the precipitate was filtered off, washed with 15 ml of water, and dried in air over a period of 2 h. 5-Bromodioxanediones **Va** and **Vb** thus obtained were immediately used in further syntheses.

5-Bromo-2,2-dimethyl-1,3-dioxane-4,6-dione (Va). Yield 5.1 g (65%), mp 90–91°C. ^{1}H NMR spectrum, δ, ppm: 1.85 (3H, CH_3), 1.93 (3H, CH_3), 5.16 s (1H, CH). ^{13}C NMR spectrum, δ_C, ppm: 28.2 (CH_3), 28.3 (CH_3), 34.4 (C^5), 107.7 (C^2), 161.3 (C^4).

5-Bromo-2-*tert*-butyl-2-methyl-1,3-dioxane-4,6-dione (Vb) (a mixture of two stereoisomers at a ratio of 2:3**).** Yield 7.04 g (76%), mp 120–122°C (decomp.). ^{1}H NMR spectrum, δ, ppm: stereoisomer **1**: 1.13 s (9H, 3CH_3), 1.77 s (3H, CH_3), 4.87 s (1H, CH); stereoisomer **2**: 1.15 s (9H, 3CH_3), 1.92 s (3H, CH_3), 5.40 s (1H, CH).

Sulfonium ylides IIIa and IIIb (*general procedure*). A 100-ml Erlenmeyer flask equipped with a magnetic stirrer and drying tube was charged with 20 mmol of 5-bromo derivative **Va** or **Vb**, and 15 ml of dimethyl sulfoxide was added in one portion under stirring at room temperature. The mixture was stirred for 24 h, diluted with 15 ml of water, and extracted with chloroform (4×15 ml), and volatile substances were removed from the extract at 25–30°C under reduced pressure (first at 15–20 mm and then at 1–2 mm). The residue was dissolved in 5 ml of methanol, and ylide **IIIa** or **IIIb** was precipitated by adding 15 ml of diethyl ether. The precipitate was filtered off and dried in air.

5-Dimethylsulfonio-2,2-dimethyl-4,6-dioxo-1,3-dioxan-5-ide (IIIa) was obtained from 4.46 g (21 mmol) of 5-bromodioxanedione **Va**. Yield 1.22 g (30%), mp 199–201°C (decomp.; from MeOH–Et_2O, 1:4) [18]. UV spectrum, λ_{max}, nm (logε): 232 (9.74), 308 (5.14). IR spectrum: ν(C=O) 1650 cm^{-1}. ^{1}H NMR spectrum, δ, ppm: 1.64 s (6H, 2CH_3), 2.98 s (6H, 2CH_3). ^{13}C NMR spectrum, δ_C, ppm: 26.5 (CH_3), 27.2 (SCH_3), 58.3 (C^5), 104.1 (C^2), 163.7 (C^4). Mass spectrum, *m*/*z* (I_{rel}, %): 204 (40) $[M]^+$, 189 (4), 147 (40), 102 (100), 87 (67). Found, %: C 47.11; H 5.84. $C_8H_{12}O_4S$. Calculated, %: C 47.05; H 5.92.

2-*tert*-Butyl-5-dimethylsulfonio-2-methyl-4,6-dioxo-1,3-dioxan-5-ide (IIIb) was obtained from 5.3 g (21 mmol) of 5-bromodioxanedione **Vb**. Yield 1.23 g (25%), mp 166–168°C (decomp.; from MeOH–Et_2O, 1:4). UV spectrum, λ_{max}, nm (logε): 232 (9.42), 306 (2.30). IR spectrum: ν(C=O) 1640 cm^{-1}. ^{1}H NMR spectrum, δ, ppm: 1.08 s (9H, 3CH_3), 1.62 s (3H, CH_3), 3.00 s (6H, SMe_2). ^{13}C NMR spectrum, δ_C, ppm: 18.9 (CH_3), 24.9 (CH_3), 27.4 (SCH_3), 39.4 (**C**Me_3), 57.9 (C^5), 109.2 (C^2), 164.0 (C^4). Mass spectrum, *m*/*z* (I_{rel}, %): 246 (3) $[M]^+$, 231 (2), 205 (2), 189 (23), 147 (100), 103 (14), 89 (21). Found, %: C 53.58; H 7.32. $C_{11}H_{18}O_4S$. Calculated, %: C 53.64; H 7.37.

General procedure for carrying out photochemical reactions. Diazodioxanediones **II** and sulfonium ylides **III** were irradiated at 18–20°C with full spectrum of a Hanau S-81 medium-pressure mercury lamp (100–130 W) in a 80- or 25-ml reactor equipped with a quartz or Pyrex jacket or a glass filter (λ > 210, 280, and 310 nm, respectively). The progress of reactions was monitored by TLC or (in the transformations of diazo compounds **II** and diazirines **III**) by the volume of liberated nitrogen. The reactor was charged with a solution of 1–10 mmol of compound **II** or **III** in 20–80 ml of freshly distilled THF or Me_2S containing (if

necessary) 1–2 ml of a nucleophilic reagent (H_2O or MeOH), and the solution was irradiated until the initial compound (**II** or **III**) disappeared according to the TLC data. The solvent and excess nucleophile were distilled off at 18–20°C under reduced pressure (first at 15–20 mm and then at 1–2 mm), the residue was dissolved in 25–30 ml of methylene chloride, the solution was dried for 2 h over anhydrous magnesium sulfate, the solvent was distilled off, and the residue was subjected to chromatography on neutral silica gel (20–35 g) using petroleum ether–diethyl ether mixtures as eluent (gradient elution). Particular fractions were dried over magnesium sulfate and evaporated, and the products were purified by recrystallization or sublimation and analyzed by spectral methods. The yields of compounds **III**, **IV**, and **VI**–**XII** are given for the isolated and purified substances.

Photolysis of diazodioxanediones IIa and IIb with short-wave UV light (λ > 210 nm, quartz filter). Irradiation of 1.7 g (10 mmol) of diazo compound **IIa** in THF–H_2O (70 : 1) over a period of 75 min, followed by treatment of the reaction mixture according to the general procedure, gave (in the order of elution) 0.2 g (12%) of diazirine **VIa**, 0.034 g (2%) of diazodioxanedione **IIa**, 0.95 g (56%) of 5-oxo acid **VIIa**, and 0.085 g (6%) of dioxanedione **IVa**.

Irradiation of 1.7 g (10 mmol) of diazo compound **IIa** in THF–MeOH (80 : 1) over a period of 75 min, followed by treatment of the reaction mixture according to the general procedure, gave 0.07 g (5%) of diazirine **VIa**, 1.1 g (64%) of methyl ester **VIIIa**, 0.015 g (1%) of initial compound **IIa**, and 0.045 g (3%) of dioxanedione **IVa**.

A solution of 0.17 g (1 mmol) of diazo compound **IIa** in 25 ml of freshly distilled dimethyl sulfide was irradiated until the initial diazo compound disappeared (120 min; TLC and IR monitoring). According to the ^{1}H NMR data, the mixture contained 0.037 g (18%, determined with the use of internal standard) of sulfonium ylide **IIIa**.

Irradiation of 1 g (4.7 mmol) of diazo compound **IIb** in THF–H_2O (70 : 1) over a period of 75 min, followed by treatment of the reaction mixture according to the general procedure, gave (in the order of elution) 0.044 g (5%) of diazirine **VIb**, 0.014 g (~2%) of initial compound **IIb**, 0.592 g (62%) of stereoisomeric 5-oxo acids **VIIb** (ratio ~1 : 1), and 0.026 g (3%) of dioxanedione **IVb**.

Irradiation of 0.318 g (1.5 mmol) of diazo compound **IIb** in THF–MeOH (24 : 0.6) over a period of 100 min, followed by treatment of the reaction mixture according to the general procedure, gave 0.214 g (66%) of methyl ester **VIIIb** (stereoisomer ratio 1 : 1.05). Diazirine **VIb** and dioxanedione **IVb** were detected in the reaction mixture during the photochemical process by ^{1}H NMR spectroscopy.

Photolysis of diazodioxanediones IIa and IIb at λ > 280 nm (Pyrex filter). Irradiation of 0.85 g (5 mmol) of diazo compound **IIa** in THF–H_2O (70 : 2) over a period of 6 h, followed by treatment of the reaction mixture according to the general procedure, gave 0.263 g (31%) of diazirine **VIa**, 0.192 g (24%) of acid **VIIa**, and 0.064 g (9%) of dioxanedione **IVa**.

Irradiation of 0.91 g (5.3 mmol) of diazo compound **IIa** in THF–MeOH (60 : 2) over a period of 9 h, followed by treatment of the reaction mixture according to the general procedure, gave 0.207 g (23%) of diazirine **VIa**, 0.23 g (25%) of methyl ester **VIIIa**, and 0.061 g (8%) of dioxanedione **IVa**. During the photolysis, 0.13 g (14% in 8 h) of ether **IXa** was identified in the reaction mixture, but we failed to isolate this product when the photolysis was complete.

Photolysis of diazodioxanediones IIa and IIb with long-wave UV light. Irradiation of 1.7 g (10 mmol) of diazo compound **IIa** in THF–H_2O (70 : 0.5) over a period of 8 h, followed by treatment of the reaction mixture according to the general procedure, gave 0.731 g (43%) of diazirine **VIa**, 0.51 g (30%) of initial compound **IIa**, 0.208 g (13%) of 5-oxo acid **VIIa**, and 0.029 g (5%) of dioxanedione **IVa**.

Irradiation of 0.85 g (5 mmol) of diazo compound **IIa** in THF–MeOH (20 : 1) over a period of 9 h in a 25-ml reactor, followed by treatment of the reaction mixture according to the general procedure, gave 0.332 g (39%) of diazirine **VIa**, 0.15 g (17%) of methyl ester **VIIIa**, 0.217 g (26%) of initial compound **IIa**, and 0.058 g (8%) of dioxanedione **IVa**. During the photolysis, 0.122 g (14% in 6 h) of ether **IXa** was identified in the reaction mixture, but we failed to isolate this product when the photolysis was complete.

Irradiation of 1.02 g (4.8 mmol) of diazo compound **IIb** in THF–H_2O (70 : 1) over a period of 12 h gave 0.407 g (40%) of diazirine **VIb**, 0.132 g (13%) of initial compound **IIb**, 0.174 g (18%) of 5-oxo acid **VIIb**, and 0.054 g (5%) of dioxanedione **IVb**.

Irradiation of 1.61 g (7.6 mmol) of diazo compound **IIb** in THF–MeOH (70 : 3) over a period of 9 h, followed by treatment of the reaction mixture according to the general procedure, gave 0.692 g (43%) of

diazirine **VIb**, 0.311 g (19%) of methyl ester **VIIIb**, and 0.370 g (23%) of initial compound **IIb**; dioxanedione **IVb** was detected among the products by TLC. During the photolysis, 0.17 g (16% in 4 h) of compound **IXb** was identified in the reaction mixture, but we failed to isolate this product when the photolysis was complete.

Irradiation of 1.07 g (6.3 mmol) of diazo compound **IIa** in 80 ml of dimethyl sulfide over a period of 28 h, followed by treatment of the reaction mixture according to the general procedure, gave 0.36 g (28%) of sulfonium ylide **IIIa** (by chromatography on 12 g of silica gel using 150 ml of ethanol as eluent).

Irradiation of 1.06 g (5 mmol) of diazo compound **IIb** in 80 ml of Me_2S over a period of 28 h, followed by treatment of the reaction mixture as in the preceding experiment, gave 0.332 g (27%) of ylide **IIIb**.

Diazo compound **IIb**, 1.06 g (5 mmol), in Me_2S–MeOH (70:2) was irradiated over a period of 8 h, volatile substances were removed at 25–30°C under reduced pressure (1–2 mm), the dry residue was applied to a column charged with neutral silica gel (30 g), and the column was eluted first with petroleum ether–diethyl ether (gradient elution) and then with ethanol (150 ml) to isolate (in the order of elution) 0.456 g (43%) of diazirine **VIb**, 0.205 g (19%) of methyl ester **VIIIb**, 0.201 g (19%) of initial compound **IIb**, and 0.025 g (2%) of sulfonium ylide **IIIb**.

Irradiation of diazo compound IIa in the presence of benzophenone as sensitizer. A solution of 0.51 g (3 mmol) of diazo compound **IIa** in 60 ml of methanol containing 2.93 g (16 mmol) of benzophenone was irradiated over a period of 25 min. In the reaction mixture we identified 2,2-dimethyl-1,3-dioxane-4,6-dione (**IVa**) as the only product. The yield of **IVa** was determined by the internal standard technique: 0.404 g (93.6%).

6,6-Dimethyl-5,7-dioxa-1,2-diazaspiro[2.5]oct-1-ene-4,8-dione (VIa). Yield 0.73 g (43%), mp 82–83°C (from petroleum ether–diethyl ether, 3:1) [20, 21]. UV spectrum, λ_{max}, nm (logε): 251 (2.00), 289 (1.48). IR spectrum: ν(C=O) 1799 cm^{-1}. ^1H NMR spectrum, δ, ppm: 2.00 s (6H, $2CH_3$). ^{13}C NMR spectrum, δ_C, ppm: 25.3 (C^5), 28.4 ($2CH_3$), 108.1 (C^2), 162.0 (C^4). Mass spectrum, *m*/*z* (I_{rel}, %): 170 (18) $[M]^+$, 155 (40), 69 (12), 58 (17), 43 (100). Found, %: C 42.90; H 3.60; N 16.50. $C_6H_6N_2O_4$. Calculated, %: 42.40; H 3.61; N 16.50.

6-*tert*-Butyl-6-methyl-5,7-dioxa-1,2-diazaspiro-[2,5]oct-1-ene-4,8-dione (VIb). Yield 0.85 g (40%), mp 71–73°C (from petroleum ether–diethyl ether, 3:1). UV spectrum, λ_{max}, nm (logε): 250 (2.18), 289 (1.48). IR spectrum: ν(C=O) 1770 cm^{-1}. ^1H NMR spectrum, δ, ppm: 1.21 s (9H, $3CH_3$), 1.98 s (3H, CH_3). ^{13}C NMR spectrum, δ_C, ppm: 23.8 ($3CH_3$), 24.7 (CH_3), 25.3 (C^5), 39.8 (**C**Me_3), 113.4 (C^2), 162.3 (C^4). Mass spectrum, *m*/*z* (I_{rel}, %): 197 (1) $[M - 15]^+$, 155 (40), 100 (5), 85 (9), 57 (100), 43 (60). Found, %: C 50.89; H 5.60; N 13.20. $C_9H_{12}N_2O_4$. Calculated, %: C 50.92; H 5.66; N 13.18.

2,2-Dimethyl-5-oxo-1,3-dioxolane-4-carboxylic acid (VIIa). mp 105–107°C (from diethyl ether) [21]. IR spectrum, ν, cm^{-1}: 1743, 1779 (C=O). ^1H NMR spectrum, δ, ppm: 1.66 s (3H, CH_3), 1.72 s (3H, CH_3), 5.03 s (1H, CH), 8.00 br.s (1H, COOH). ^{13}C NMR spectrum, δ_C, ppm: 27.3 (CH_3), 27.4 (CH_3), 73.9 (C^4), 114.1 (C^2), 166.4 (C^5), 169.3 (CO_2H). Found, %: C 45.05; H 5.10. $C_6H_8O_5$. Calculated, %: C 45.00; H 5.04.

2-*tert*-Butyl-2-methyl-5-oxo-1,3-dioxolane-4-carboxylic acid (VIIb) (a mixture of stereoisomers**).** mp 94–95°C (from $CHCl_3$). IR spectrum, ν, cm^{-1}: 1730, 1780 (C=O). ^1H NMR spectrum, δ, ppm: stereoisomer **1**: 1.10 s (9H, $3CH_3$), 1.55 s (3H, CH_3), 4.95 s (1H, CH), 9.28 br.s (1H, OH); stereoisomer **2**: 1.04 s (9H, $3CH_3$), 1.67 s (3H, CH_3), 4.97 s (1H, CH), 9.35 br.s (1H, OH). ^{13}C NMR spectrum, δ_C, ppm: stereoisomer **1**: 20.7 ($3CH_3$), 24.7 (CH_3), 38.9 (**C**Me_3), 73.5 (C^4), 118.4 (C^2), 166.7 (C^5), 168.8 (CO_2H); stereoisomer **2**: 21.9 ($3CH_3$), 24.7 (CH_3), 40.1 (**C**Me_3), 75.1 (C^4), 119.8 (C^2), 166.7 (C^5), 170.1 (CO_2H). Found, %: C 53.50; H 7.00. $C_9H_{14}O_5$. Calculated, %: C 53.46; H 6.98.

Methyl 2,2-dimethyl-5-oxo-1,3-dioxolane-4-carboxylate (VIIIa). bp 55–60°C (1–2 mm) [21]. IR spectrum, ν, cm^{-1}: 1772, 1805 (C=O). ^1H NMR spectrum, δ, ppm: 1.63 s (3H, CH_3), 1.71 s (3H, CH_3), 3.86 s (3H, OCH_3), 4.95 s (1H, CH). ^{13}C NMR spectrum, δ_C, ppm: 21.3 (CH_3), 53.8 (OCH_3), 74.3 (C^4), 113.7 (S^2), 166.0 (C^5), 166.6 (**C**O_2Me). Mass spectrum, *m*/*z* (I_{rel}, %): 159 (50) $[M - 15]^+$, 131 (17), 115 (4), 90 (6), 73 (82), 59 (76), 43 (100). Found, %: C 48.22; H 5.66. $C_7H_{10}O_5$. Calculated, %: C 48.28; H 5.79.

Methyl 2-*tert*-butyl-2-methyl-5-oxo-1,3-dioxolane-4-carboxylate (VIIIb) (a mixture of stereoisomers**).** bp 65–70°C (1–2 mm). IR spectrum, ν, cm^{-1}:

1747, 1795 (C=O). ^{1}H NMR spectrum, δ, ppm: stereoisomer **1**: 1.04 s (9H, $3CH_3$), 1.68 s (3H, CH_3), 3.88 s (3H, OCH_3), 4.93 s (1H, CH); stereoisomer **2**: 1.10 s (9H, $3CH_3$), 1.54 s (3H, CH_3), 3.88 s (3H, OCH_3), 4.95 s (1H, CH). ^{13}C NMR spectrum, δ_C, ppm: stereoisomer **1**: 21.9 ($3CH_3$), 24.6 (CH_3), 40.0 (**C**Me_3), 53.7 (OCH_3), 75.3 (C^4), 119.2 (C^2), 165.0 (C^5), 166.8 (CO_2Me); stereoisomer **2**: 20.6 ($3CH_3$), 24.7 (CH_3), 38.8 (**C**Me_3), 53.5 (OCH_3), 73.6 (C^4), 117.8 (C^2), 165.0 (C^5), 166.4 (CO_2Me). Mass spectrum, *m*/*z* (I_{rel}, %): 201 (1) $[M - 15]^+$, 159 (100), 131 (55), 115 (9), 101 (10), 85 (20), 69 (9), 57 (38), 43 (97). Found, %: C 55.51; H 7.43. $C_{10}H_{16}O_5$. Calculated, %: C 55.55; H 7.46.

Photochemical reactions of sulfonium ylides IIIa and IIIb. The photolysis of sulfonium ylides **IIIa** and **IIIb** was performed in THF–MeOH (10:0.5 or 10:1) at 18–20°C under irradiation with short-wave UV light (λ > 210 nm) in a 25-ml quartz reactor.

A solution of 1.02 g (5 mmol) of ylide **IIIa** in a mixture of 20 ml of THF and 1 ml of MeOH was irradiated over a period of 1.8 h. The solvent was distilled off at 20–25°C under reduced pressure (first at 15–20 mm and then at 1–2 mm), the residue was dissolved in 25–30 ml of diethyl ether, the undissolved material, 0.525 g (51%) of unreacted ylide **IIIa**, was filtered off, the filtrate was evaporated, and the residue was subjected to column chromatography on 30 g of silica gel (gradient elution with petroleum ether–diethyl ether mixtures). The obtained fractions were dried over anhydrous magnesium sulfate and evaporated. We isolated (in the order of elution) 0.064 g (15%) of dimethyl 2-methylsulfanylmalonate (**XII**), 0.01 g (2%) of 5-methylsulfanyldioxanedione **X**, and 0.176 g (46%) of 5-methyldioxanedione **XIa**.

A solution of 0.49 g (2 mmol) of sulfonium ylide **IIIb** in a mixture of 20 ml of THF and 1 ml of MeOH was irradiated over a period of 3 h, and the mixture was then treated as described above to isolate 0.248 g (62%) of 5-methyldioxanedione **XIb** as a mixture of two stereoisomers at a ratio of ~4:1 (according to the ^{1}H NMR spectrum of the crude reaction mixture).

2,2,5-Trimethyl-5-methylsulfanyl-1,3-dioxane-4,6-dione (X). Oily substance. ^{1}H NMR spectrum, δ, ppm: 1.75 s (3H, CH_3), 1.87 s (3H, CH_3), 1.98 s (3H, CH_3), 2.33 s (3H, SCH_3). Mass spectrum, *m*/*z* (I_{rel}, %): 204 (100) $[M]^+$, 158 (57), 149 (29), 147 (71). Found, %: C 46.95; H 5.94. $C_8H_{12}O_4S$. Calculated, %: C 47.05; H 5.92.

2,2,5-Trimethyl-1,3-dioxane-4,6-dione (XIa). mp 114–115°C (from $CHCl_3$) [33]. IR spectrum: ν(C=O) 1779 cm^{-1}. ^{1}H NMR spectrum, δ, ppm: 1.58 d (3H, CH_3, J = 6.5 Hz), 1.77 s (3H, CH_3), 1.82 s (3H, CH_3), 3.60 q (1H, J = 6.5 Hz). ^{13}C NMR spectrum, δ_C, ppm: 11.2 (CH_3), 26.8 (CH_3), 29.0 (CH_3), 41.8 (C^5), 105.3 (C^2), 166.4 (C^4). Mass spectrum, *m*/*z* (I_{rel}, %): 158 (8) $[M]^+$, 143 (12), 114 (6), 83 (5), 59 (13), 56 (73), 43 (100). Found, %: C 52.96; H 6.30. $C_7H_{10}O_4$. Calculated, %: C 53.16; H 6.37.

2-*tert*-Butyl-2,5-dimethyl-1,3-dioxane-4,6-dione (XIb) (a mixture of stereoisomers at a ratio of ~1:4**).** ^{1}H NMR spectrum, δ, ppm: stereoisomer **1**: 1.12 s (9H, $3CH_3$), 1.59 d (3H, CH_3, J = 6.9 Hz), 1.75 s (3H, CH_3), 3.62 q (1H, CH, J = 6.9 Hz); stereoisomer **2**: 1.12 s (9H, $3CH_3$), 1.47 d (3H, CH_3, J = 7.2 Hz), 1.72 s (3H, CH_3), 3.62 q (1H, CH, J = 7.2 Hz). ^{13}C NMR spectrum, δ_C, ppm: stereoisomer **1**: 11.2 (CH_3), 21.2 (CH_3), 24.4 ($3CH_3$), 40.1 (C^5), 41.7 (**C**Me_3), 109.9 (C^2), 166.7 (C^4). Mass spectrum, *m*/*z* (I_{rel}, %): 201 (2) $[M + H]^+$, 185 (4), 156 (13), 143 (100).

Dimethyl 2-methylsulfanylmalonate (XII). ^{1}H NMR spectrum, δ, ppm: 2.21 s (3H, SCH_3), 3.74 s (6H, $2OCH_3$), 3.91 s (1H, CH) [30]. ^{13}C NMR spectrum, δ_C, ppm: 28.2 (SCH_3), 54.4 (OCH_3), 107.67 (SCH), 161.27 (C=O). Mass spectrum, *m*/*z* (I_{rel}, %): 178 (31) $[M]^+$, 132 (100), 119 (56), 102 (50). Found, %: C 40.44; H 5.66. $C_6H_{10}O_4S$. Calculated, %: C 40.54; H 5.68.

Kinetic study of the photolysis of diazodioxanedione IIa. A reactor equipped with a quartz or glass jacket was charged with a solution of 1.3–3.7 mmol of diazo compound **IIa** in 20 ml of freshly distilled THF or Me_2S containing 1 ml of MeOH, and the solution was irradiated at 16–18°C until the initial diazo compound disappeared (according to the TLC data). During the process, 0.5- or 1-ml samples of the reaction mixture were withdrawn at definite time intervals, volatile components were removed from these samples under reduced pressure (1–2 mm) at 16–18°C, and the composition of the residue was determined by ^{1}H NMR spectroscopy. The components were quantitated using the internal normalization technique.

A solution of 0.255 g (1.5 mmol) of diazo compound **IIa** in 24 ml of anhydrous methanol was irradiated at λ ≥ 210 nm over a period of 1.5 h. Samples were withdrawn in 15, 34, 45, 60, 75, and 90 min; the results are shown in Fig. 1.

A solution of 1.61 g (7.6 mmol) of diazo compound **IIb** in 70 ml of THF containing 3 ml of methanol was irradiated over a period of 9 h in a glass-jacketed reactor ($\lambda > 310$ nm); samples of the reaction mixture were withdrawn in 2, 4, 6, and 8.5 h; the results are shown in Fig. 2. When the photolysis was complete, the products were separated by chromatography on silica gel.

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