

# Search for dioxocarbenes in photochemical reactions of 5-diazo-4,6-dioxo-1,3-dioxanes, associated diazirines, and *S*-ylides

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**Abstract**—On direct photolysis of 2,2-dialkyl-5-diazo-4,6-dioxo-1,3-dioxanes in the presence of pyridine, methanol or dimethyl sulfide as carbene traps, the yield of ‘carbene’ products does not exceed 27–28%. At the same time photochemical transformations of the related 3,3-diacyldiazirines and dioxosulfonium ylides of this series, evidently, occur without generation of carbene intermediates. © 2004 Elsevier Ltd. All rights reserved.

Useful information on the intermediacy of carbenes in chemical reactions can be obtained by generating these species from independent precursors. A potential source of carbenes, which complements diazo compounds and diazirines<sup>1,2</sup> are ylides.<sup>3</sup>

This work<sup>4</sup> is concerned with a comparison of the photochemical reactions of potentially independent precursors of dioxocarbenes **1**, namely, diazo compounds **2**, diazirines **3**, and *S*-ylides **4** (Scheme 1).

Previous investigations of the photochemical reactions of diazodioxodioxane **2a**<sup>5,6</sup> using long wavelength irradiation ( $\lambda > 280$  nm) revealed two main photochemical

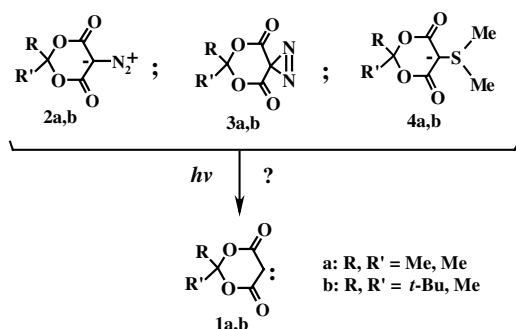
processes: Wolff rearrangement (W.R.) and isomerization of diazo compound **2a** to 3,3-diacyldiazirine **3a**.<sup>5b,c,6</sup> The results of laser flash photolysis (LFP) (XeF, 351 nm) studies of diazodioxane **2a** in the presence of pyridine also gave evidence of W.R. under these conditions.<sup>5d</sup> At the same time, direct photolysis of diazodioxane **2a** in the presence of alkene carbene traps gave very low yields of cyclopropanes (1–2%),<sup>5a</sup> which are typical carbene reaction products.<sup>7</sup>

Photochemical transformations of 3,3-diacyldiazirines **3** and dioxosulfonium ylides **4** have not been previously investigated.<sup>4,6</sup>

We have studied pyridine, methanol, and dimethyl sulfide as carbene traps in the photochemical reactions of **2–4** (Scheme 1). Irradiation of substrates **2–4**<sup>8</sup> was typically performed by conventional photolysis using a medium-pressure Hg-lamp through quartz ( $\lambda > 210$  nm), pyrex ( $\lambda > 280$  nm) or ‘simple glass’ ( $\lambda > 310$  nm) filters without any further monochromatization. Pyridine has been previously used in LFP experiments.<sup>9</sup>

Attempts to detect the generation of ylides of dioxocarbenes **1a,b** using LFP of diazodioxodioxanes **2a,b** in solutions of cyclohexane or 1,1,2-trifluoroethane with pyridine<sup>10</sup> failed. Thus, in succeeding experiments more effective traps of dioxocarbenes, namely methanol and dimethyl sulfide<sup>11</sup> were employed in conditions of conventional photolysis.<sup>12</sup>

Irradiation of diazodioxodioxanes **2a,b** in a solution of pure methanol through a quartz filter ( $\lambda > 210$  nm)



Scheme 1.

**Keywords:** Diazo compounds; Diazirines; Sulfonium ylides; Carbenes; Photochemistry.

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**Table 1.** Photolysis of diazodioxodioxanes **2a,b**

Diazo	Reaction conditions	Yields of the products, (%)			
		3 <sup>a</sup>	5/6	7	4
<b>2a,b</b>	$\lambda > 210$ nm, 1–2 h <sup>b</sup>	5–12	56/64	3–6	—
<b>2a,b</b>	$\lambda > 280$ nm, 6 h <sup>b</sup>	24–25	30/31	7–9	—
<b>2a,b</b>	$\lambda > 310$ nm, 9 h <sup>b</sup>	43–44	13/18	5–13	—
<b>2a</b>	$\lambda > 210$ nm, 1.3 h <sup>c,d</sup>	13 (12)	0/48	—	27
<b>2a,b</b>	Me <sub>2</sub> S; $\lambda > 310$ nm, 28 h	—	—	—	27–28 <sup>e</sup>
<b>2b</b>	$\lambda > 310$ nm, 8 h <sup>c</sup>	43 (19)	0/19	—	2

<sup>a</sup> In brackets are given the percentage of diazo compound **2** in the reaction mixture.

<sup>b</sup> Reaction was carried out in solution of THF/R''OH (molar ratio of R''OH/**2a,b** = 10/1).

<sup>c</sup> Reaction was carried out in solution of Me<sub>2</sub>S/MeOH (molar ratio of MeOH/**2a,b** = 10/1).

<sup>d</sup> The yields of the products were calculated from the data of <sup>1</sup>H NMR spectra of reaction mixture after photolysis.

<sup>e</sup> Quantity of other reaction products were not estimated.

furnished, with high yields, only W.R. products—Meesters **6a,b** (more than 85–90%) (Table 1 and Scheme 2).<sup>13</sup> Photolysis of diazodioxanes **2a,b** in a mixture of THF/H<sub>2</sub>O or MeOH (mole ratio NuH/**1a,b** = 10/1) also gave rise mainly to the W.R. products **5,6** (56–64%), but here small amounts of diazirines **3a,b** (5–12%), and dioxodioxanes **7a,b** (3–6%) were also formed.

Photolysis of diazo compounds **2** through a Pyrex filter ( $\lambda > 280$  nm) yielded the same three reaction products, but the yield of diazirines **3** in these irradiation conditions was considerably increased (24–25%) with a corresponding reduction of the yield of W.R. products (30–31%). Finally, on irradiation of diazodioxanes **2** with long wavelength UV light ( $\lambda > 310$  nm) the efficiency of the two main photoprocesses (isomerization to diazirines and W.R.) in comparison with short wavelength irradiation was reversed (43–44% and 13–18% correspondingly).

The maximum yields of carbene products—sulfonium ylides **4a,b** and dioxodioxanes **7a,b**—produced on photo-

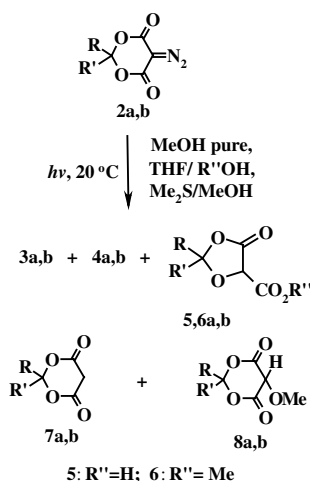
lysis of diazo compounds **2a,b** depends to a certain extent on the wavelength of irradiation and the nature of the solvent/trap, were only 27–28% and 9–13%, respectively. The formation of insertion products **8a,b** into the O–H bond of MeOH was observed only qualitatively by the appearance of the relevant signals of the methine proton of the H–COMe group at 6.30 and 6.34 ppm in <sup>1</sup>H NMR spectra of reaction mixtures.

Thus, one can conclude that the contribution of carbene processes in the photochemical reactions of diazo compounds **2a,b** does not exceed 27–28% (Table 1). Diazirines **3** and *S*-ylides **4**, which are formed on long wavelength irradiation of diazodioxodioxanes **2**, are photochemically rather stable and do not experience significant further transformations under these conditions. As a consequence, photolysis of diazirines **3** and *S*-ylides **4** in subsequent experiments were performed with short wavelength irradiation ( $\lambda > 210$  nm).

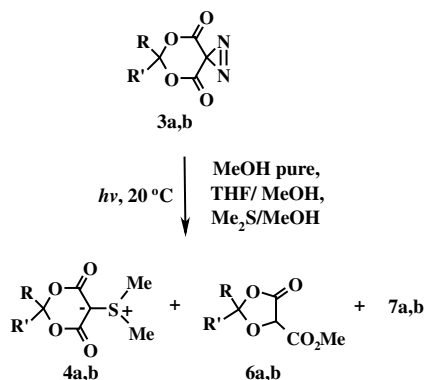
Before proceeding to investigate the photochemistry of the diazirines we established<sup>14</sup> that the lifetimes of dioxodiazirines **3a,b** at 50 °C are 3.5–3.6 h in solution in CDCl<sub>3</sub> and about 4 h—in solution in C<sub>6</sub>D<sub>6</sub>. Since photochemical experiments with diazirines **3** were carried out at lower temperatures (18–20 °C) and for shorter times (1–1.5 h) it was assumed that the thermal transformations of these diaza-substrates could be safely ignored.

Photolysis of diazirines **3a,b**<sup>15</sup> through a quartz filter ( $\lambda > 210$  nm) in solution in MeOH or in a mixture of THF/MeOH (mole ratio MeOH/**3** = 10/1) led solely to W.R. products **6** (more than 85–90%) (Table 2 and Scheme 3). The only 'side' products in the reaction mixtures which we managed to identify by means of <sup>1</sup>H NMR and TLC were traces of 4,6-dioxo-1,3-dioxanes **7**. It is significant that no detectable amount of diazodioxodioxanes **2** were revealed at any stage of the photo-reaction, which was monitored by <sup>1</sup>H NMR spectroscopy at 5–10 min intervals.

At the same time, formation of diazo compounds **2** (6–8%) and sulfonium ylides **4** (14–16%), along with W.R. products **6** (49–52%), was found upon photolysis of diazirines **3a,b** in a solution of Me<sub>2</sub>S/MeOH (mole ratio MeOH/**3a,b** = 10/1) (Table 2). It seems likely that under these conditions isomerization of diazirines **3** into diazo compounds **2** occurs partially with their subsequent carbene decomposition to *S*-ylides **4**.

**Scheme 2.****Table 2.** Photolysis of diazirines **3a,b** ( $\lambda > 210$  nm)

Diazirine	Reaction conditions	Product yield (%)			
		2	4	6	7
<b>2a,b</b>	MeOH; 1.3 h	—	—	95–97	Traces
<b>2a,b</b>	THF/MeOH; 0.8–1.3 h	—	—	89–97	Traces
<b>2a,b</b>	Me <sub>2</sub> S/MeOH; 1.1–1.25 h	6–8	14–16	49–52	—

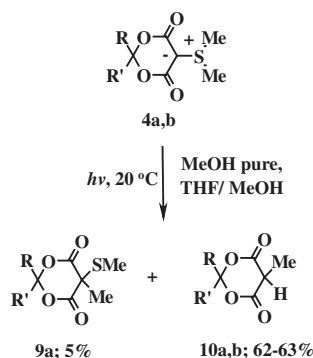


Scheme 3.

Photochemical transformation of *S*-ylides **4** proceeds in a quite different manner than photolysis of diaza-analogs **2** and **3** (Scheme 4). The main photo-process in this case<sup>16</sup> is not elimination of Me<sub>2</sub>S, but intramolecular 1,2-migration of a methyl group (Stevens rearrangement) and apparently subsequent cleavage by a Norrish Type II photoreaction of the initially formed 5-methyl-5-(methylthio)-substituted dioxodioxanes **9a,b** to produce 5-methyldioxanes **10a,b** [ratio of stereoisomers in the case of **10b** was about 4/1].

Thus, chemical analysis of photolysis mixtures indicates that during photolysis of dioxosulfonium ylides **4a,b** under the specified conditions the generation of carbene products [O–H-insertion **8**, dioxodioxanes **7** etc.] is not observed.

In summary, diazo compounds **2** and diazirines **3** of the 4,6-dioxo-1,3-dioxane series on short wavelength irradiation ( $\lambda > 210$  nm) are mainly decomposed with elimination of dinitrogen, whereas in the case of dioxosulfonium ylides **4** an intramolecular 1,2-shift of a methyl group (Stevens rearrangement) prevails followed by photochemical transformations of the original reaction products. The yield of carbene processes realized upon direct photolysis of diazo dioxodioxanes **2** using the most efficient trap (dimethyl sulfide) is only 27–28%, yet photolysis of diacyldiazirines **3** and *S*-ylides **4** of this series, evidently occurs without generation of the corresponding heterocyclic dioxocarbenes **1**.



Scheme 4.

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12. The conventional photolysis of compounds **2–4** was performed in solutions of THF or Me<sub>2</sub>S in the presence of nucleophiles (H<sub>2</sub>O, MeOH) with a mol ratio ~ 1/10 (substrate/nucleophile), or directly in solutions of MeOH, Me<sub>2</sub>S. Isolated compounds were identified with the help of <sup>1</sup>H, <sup>13</sup>C NMR and mass spectra. All new compounds were characterized and gave satisfactory spectral data.
13. *Typical procedure for photolysis of diazodioxanes 2*: a solution of 1.09 g (5 mmol) of diazo compound **2b** in Me<sub>2</sub>S/MeOH (70/1 ml) was irradiated ( $\lambda > 310$  nm) during 8 h. On completion of the photolysis the solvent and nucleophile were removed in vacuo, the crude reaction mixture was analyzed by <sup>1</sup>H NMR spectroscopy and thereafter separated using chromatography on neutral silica gel (30 g; eluents 0–100% Et<sub>2</sub>O/petroleum, then pure EtOH) to give the products: diazirine **3b**, 456 mg (43%); methyl esters **7b**, 200 mg (19%, ratio of stereoisomers ~ 1/1.5); diazodioxodioxane **2b**, 200 mg (19%); sulfonium ylide **4b**, 21 mg (2%).
14. On investigation of the reactions of diazirines **3a,b** and during kinetic experiments, an analytical alternative was applied for the determination of composition of reaction mixture using <sup>1</sup>H NMR spectroscopy (internal standard *p*-C<sub>6</sub>H<sub>4</sub>Br<sub>2</sub>) without isolation of reaction products. In these cases the products in analyzed solutions were identified using <sup>1</sup>H spectra of individual compounds, obtained in the course of preparative photolysis of diazo compounds **2a,b**.
15. *Typical procedure for photolysis of diazirines 3*: a solution of diazirine **3a** (0.22 g, 1.3 mmol) in 20 ml of freshly distilled THF and 1 ml MeOH was irradiated ( $\lambda > 210$  nm) for 60 min, while samples (0.5 ml) of reaction mixture were taken at 5–10 min intervals. Easily volatile material from each sample was evaporated in vacuo (1–2 mmHg, 18–20 °C), internal standard (*p*-C<sub>6</sub>H<sub>4</sub>Br<sub>2</sub>) was added to the residue and quantitative composition of each sample was determined by <sup>1</sup>H NMR spectroscopy. Thus, components of the reaction mixture after photolysis of diazirine **3a** were identified as the methyl ester of 5-oxocarboxylic acid **6a**<sup>5a,c</sup> (> 95%) and traces of dioxane **7**.
16. Photoreactions of *S*-ylides **4** were carried out on a preparative scale. *Typical procedure*: a solution of 0.49 g (2 mmol) of *S*-ylide **4b** in 20 ml of freshly distilled THF and 1 ml of MeOH was irradiated ( $\lambda > 210$  nm) for 3 h, unreacted ylide was separated by filtration, the residue after evaporation of the solvent and MeOH in vacuo was subjected to chromatography on silica gel (30 g, eluents 0–100% Et<sub>2</sub>O/petroleum) to give 5-methyldioxodioxanes **10b** (248 mg, 62%) as a mixture of *cis*- and *trans*-stereoisomers ~ 1/4 (by <sup>1</sup>H NMR spectra in CDCl<sub>3</sub>).