

Wavelength-Dependent Photochemistry of Diazo Meldrum's Acid and Its Spirocyclic Isomer, Diazirino Meldrum's Acid: Wolff Rearrangement versus Isomerization

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Wavelength dependence is a rarely observed phenomenon in organic photochemistry, as most photoreactions occur from the lowest singlet or triplet excited state of the molecule.^{1,2} The composition of product mixtures in photolysis of diazo compounds, however, sometimes depends on the wavelength of irradiation.³ In most cases this dependence is due to the secondary photoreactions of primary products or due to a separate excitation of weakly interacting chromophores. There are only a handful of examples of "real" wavelength dependence, the phenomenon in which excitation to the lowest and higher excited states results in the formation of different products.^{3b,c} In this work we report a remarkable wavelength selectivity of photoreactions of diazo Meldrum's acid (**1**) and its diazirino isomer, 6,6-dimethyl-5,7-dioxo-1,2-diaza-spiro[2,5]oct-1-ene-4,8-dione (**2**).⁴ We also demonstrate the first example of the direct photo-Wolff reaction of α,α' -dicarbonyl diazirine.

The UV spectrum of the diazo Meldrum's acid (**1**) has a strong absorbance at 248 nm and much weaker band at 329 nm (Figure 1). Position of these absorbance bands is virtually independent from the polarity of the solvent. No fluorescence or phosphorescence could be detected at room temperature in solutions of **1** using 254- and 330-nm excitation light. This fact indicates a fast nonradiative depopulation of excited states.

The UV spectrum of isomeric diazirine **2** is very different: it shows only two weak shoulders on the tail of the short-wavelength band at ca. 244 nm and at ca. 284 nm (Figure 1).

UV irradiation of the methanolic solution of diazo Meldrum's acid (**1**) results in the formation of two major products: ketoester **3**, the product of the Wolff rearrangement, and diazirine **2**, the product of isomerization of starting diazo compound (Scheme 1). Small amounts of Meldrum's acid (**4**) were also detected in the reaction mixtures.

The thermal decomposition of **1** in methanol at 80 °C, on the other hand, results only in Wolff rearrangement and in the quantitative formation of ketoester **3**.⁵ This observation agrees well with DFT calculations at the B3PW91/6-311+G(d,p) level that predict an energy barrier for the loss of nitrogen from **1** is 6–9 kcal mol⁻¹ lower than the barrier for isomerization reaction.⁶

The ketoester **3**-to-diazirine **2** ratio was found to be strongly dependent on the wavelength of irradiation in direct photolyses. Product ratios presented in the Table 1 were measured at low conversion (ca. 10%) to ensure that these values were not affected by secondary photochemistry.

The Wolff rearrangement is the main process when diazo Meldrum's acid (**1**) is irradiated with the wavelength close to λ_{max} of the major absorbance band.⁷ At a longer wavelength, isomerization of diazo Meldrum's acid **1** into diazirine **2** becomes more pronounced,⁸ and at 350 nm diazirine becomes the major product. This dramatic change of reactivity becomes even more evident when **1** is irradiated with a 355-nm monochromatic light. In this case

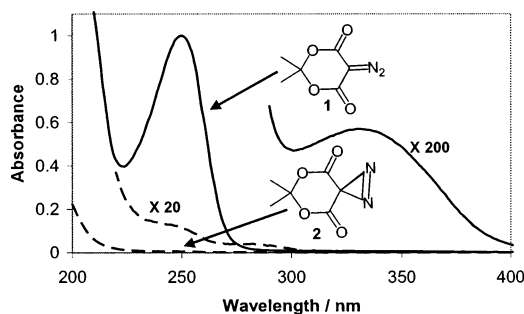


Figure 1. UV spectra of ca. 0.0001 M solutions of diazo Meldrum's acid (**1**, solid line) and diazirine **2** (dotted line) in methanol.

Scheme 1

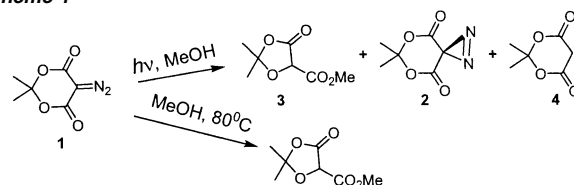


Table 1. Product Ratios Observed in Low-Conversion Photolyses of Diazo Meldrum's Acid (**1**) in Methanol at Different Wavelengths

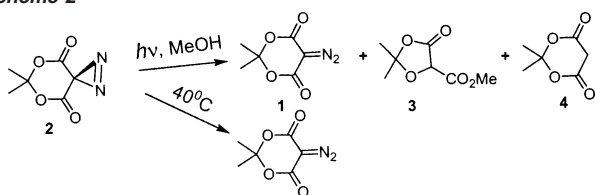
product	wavelength of irradiation λ (nm)					
	254	254/sens.	266 ^a	300	350	355 ^a
Fraction in Product Mixture						
2	0.065	0	0.17	0.17	0.55	0.94
3	0.91	0	0.83	0.81	0.42	< 0.06
4	0.025	1	—	0.02	0.03	—
quantum yield	0.34				0.025	

^a Monochromatic light using frequency up converted output of Nd:YAG laser; 20–30% conversion.

diazirine **2** is produced in a high yield, and only traces of ketoester **3** are observed. The 254- and 350-nm photolyses of diazo Meldrum's acid differs not only in the major photoproduct but also in the quantum yields (Table 1). Irradiation into the major absorbance band of **1** results in a chemical transformation 14 times more efficiently than irradiation into the weaker band.

According to TD-B3PW91/6-311+G(3df,2p) calculations the longer-wavelength absorbance band corresponds to the excitation of **1** to the lowest singlet excited state (S_1) by HOMO \rightarrow LUMO transition.⁶ The HOMO of diazo Meldrum's acid (**1**) is a p-type orbital, which is mainly localized on the carbon of the diazogroup and is orthogonal to the plane of the COC₂N₂CO fragment. The LUMO is a π^* orbital of N \equiv N bond, which lies in the plane. Thus, HOMO-to-LUMO transition is a forbidden process due to poor orbital overlap, which agrees with the low extinction coefficient of the 329-nm band. The thermal deactivation of S_1 to the ground

Scheme 2



state is very rapid, evidenced by the fact that no fluorescence or phosphorescence is observed. A small fraction of S_1 population (ca. 3%) undergoes isomerization into diazirine **2**. We believe that this reaction proceeds from the excited-state S_1 rather than from "hot" ground state as thermal reaction of **1** does not produce diazirine **2** and DFT calculations predict isomerization to be much slower than the Wolff rearrangement.⁶

The short-wavelength irradiation of diazo Meldrum's acid results in the formation of a higher excited state, most probably S_2 . The major component of this excitation is HOMO-1 to LUMO transition. The HOMO-1 is a nonbonding orbital localized on carbonyl oxygens, which lies in the plane of diazocarbonyl fragment and has a good and in-phase overlap with LUMO. This excited state undergoes an extremely rapid loss of nitrogen. For the latter reaction to compete efficiently with an internal conversion ($\phi_{254} = 0.34$), it should proceed at 10^{12} s^{-1} or a faster rate.^{1b} The rest of the excited molecules undergo internal conversion to S_1 , participation of which is evident from the formation of small amounts of diazirine **2**, before falling onto the ground-state surface. The much higher quantum yield of 254 nm photolysis, on the other hand, provides an argument against the formation of a Wolff rearrangement product from a "hot" S_1 . According to MP2 calculations corresponding dicarbonyl carbene lies in a very shallow energy well ($<1 \text{ kcal M}^{-1}$), indicating that Wolff rearrangement of **1** is essentially a concerted process.⁵

The laser flash photolysis of the diazo Meldrum's acid (**1**) conducted at 248 nm using KrF laser demonstrated that the formation of a corresponding ketene was complete during the laser pulse (ca 20 ns).⁹ This allows us to estimate the lower rate limit for the photo-Wolff rearrangement of **1** at 10^8 s^{-1} .

The triplet sensitized photolysis of **1** results in a quantitative formation of Meldrum's acid (**4**). This observation is in line with the accepted mechanism of photochemical reduction of α -diazocarbonyl compounds through triplet carbonylcarbene intermediate.¹⁰ The absence of the ketoester **3** in reaction mixtures of the triplet sensitized photolyses indicate that the spin equilibration of this carbene is much slower than the reaction of the triplet state with methanol. The small amounts of Meldrum's acid found in direct photolyses of **1** is apparently due to the low efficiency intersystem crossing yielding triplet excited state of **1**.

UV irradiation of diazirino Meldrum's acid (**2**) results in the processes similar to that observed in photolysis of its diazo isomer: Wolff rearrangement to produce ketoester **3**, isomerization to **1**, and formal reduction to **4** (Scheme 2).

The composition of product mixtures in the photolysis of diazirine **2** also depends on the wavelength of irradiation. This dependence, however, is less pronounced: the ketoester **3** is always the major product, while the yield of diazo compound **1** increases at longer wavelength (Table 2). The product ratios shown in the Table 2 were obtained at ca. 10% conversion of the starting material.

Analysis of the data summarized in Table 2 allows us to conclude that ketoester **3** can be formed directly in the Wolff rearrangement

Table 2. Results of Low-Conversion Photolyses of Diazirine (**2**) in Methanol at Different Wavelengths

product	wavelength of irradiation λ (nm)		
	254	300	350
	Fraction in Products Mixture		
1	0.04	0.44	0.36
3	0.93	0.56	0.63
4	0.02	0.002	0.01

of α, α' -dicarbonyl diazirine **2**. The results of photolysis at 300 nm are especially indicative. At 300 nm diazirine **2** and diazo Meldrum's acid (**1**) have very similar extinction coefficients (19 and $23 \text{ M}^{-1} \text{ cm}^{-1}$, respectively), and at low conversion of starting diazirine **2** absorbs practically all light. The photodecomposition of **1** becomes noticeable only when the conversion reaches ca. 30%.

The Wolff rearrangement of diazirine **2** apparently proceeds via a dicarbonyl carbene. The absence of O-H insertion products, on the other hand, indicates an extremely short lifetime of this intermediate. The rate of reaction of structurally similar dicarbonyl carbene with methanol is $1.5 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$.¹¹ This value allows us to estimate the lower rate limit for the Wolff rearrangement of the cyclic dicarbonyl carbene at 10^{11} s^{-1} .

The thermal reaction of diazirine **2** results in quantitative reverse isomerization to diazo Meldrum's acid. Theoretical analysis of the ground-state reactivity of the diazirine **2** shows that isomerization to **1** is the only feasible process.

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Supporting Information Available: Preparation, photolysis, quantum yield measurements, and spectral data for compounds **1–3**; Gaussian 98 output files for DFT calculations. (PDF). This material is available free of charge via the Internet at <http://pubs.acs.org>.

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