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Photolysis of Matrix-Isolated 4-R-1,2,4-triazoline-3,5-diones: Identification of Aziridine-2,3-dione Transients

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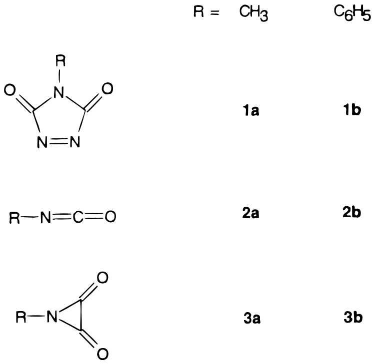
Matrix-isolated 4-methyl-1,2,4-triazolinedione **1a** and 4-phenyl-1,2,4-triazolinedione **1b** were photolyzed at $\lambda \geq 335$ nm and $\lambda \geq 310$ nm, respectively. The reactions induced by photolysis were monitored by FT−IR spectroscopy. The isocyanates **2a** and **2b** are always the more abundant products with carbon monoxide. Methyl- and phenylaziridine-2,3-diones (**3a** and **3b**) were detected as minor, but well-identified reaction products. The IR experimental absorption bands were assigned by comparison with literature data and with simulated infrared spectra obtained by *ab initio* calculation at the 6-31G* level. Stable at the matrix temperature (10 K), **3a** and **3b** photolyzed to isocyanates and CO when irradiated at $\lambda \geq 230$ nm. Irradiation of **2b** at this wavelength induces its decomposition. The kinetic data show that the rate constant process **1a** → 2**a** is faster than the **1a** → 3**a** process (3.29×10^{-3} and 2.35×10^{-4} min^{-1} respectively).

Introduction

The chemical properties of the 4-R-1,2,4-triazoline-3,5-diones have been extensively studied because of their extremely high reactivity as dienophiles in Diels−Alder reactions[1] and as enophiles[2] in ene reactions. Furthermore, these compounds exhibit rather unique photochemical properties. They react photochemically with compounds having easily abstracted protons and undergo self-reaction to form polymers.[3] Reactions with benzene,[4] naphthalene,[5] and phenanthrene[6] give $(4\pi + 2\pi)$ adducts.

Previously, Wamhoff and Wald[7] have shown that photolysis of 4-aryl-1,2,4-triazoline-3,5-diones at $\lambda > 313$ nm produces nitrogen, carbon monoxide, and isocyanates. In the present study, we report the first photolysis experiments on 4-methyl- and 4-phenyl-1,2,4-triazoline-3,5-diones (**1a** and **1b**, respectively) isolated in argon matrices at 10 K. The aim of this work was to obtain experimental results on the photolysis mechanism and to trap the 1-R-aziridine-2,3-dione transients **3**. Aziridine-2,3-diones are three-membered-ring compounds possessing two carbonyl groups. They are unstable and quite reactive because of the large strain energy.[8−10] Aziridine-2,3-diones were obtained for the first time by Aoyama *et al.*[11] in the low-temperature photolysis of diphenylmaleimide ozonides.

Scheme 1



In the present study, the photolysis experiments were monitored by FT−IR spectroscopy. The experimental IR spectra were then compared with calculated ones to achieve assignment of absorption bands and identification of the products. Finally, the quantity of the reaction products was carefully examined and kinetic profiles were obtained.

Results and Discussion

The formulas of the compounds are represented in Scheme 1. Reaction products **2a**, **2b**, **3a**, and **3b** were identified by comparison of the experimental IR spectra with data found in the literature.[11−13] The experimental IR spectra of methyl derivatives **2a** and **3a** were also compared to simulated spectra obtained by *ab initio* calculations using the 6-31 G* basis set.[14,15]

The experimental IR spectra obtained after deposition are composed of the characteristic absorption bands of

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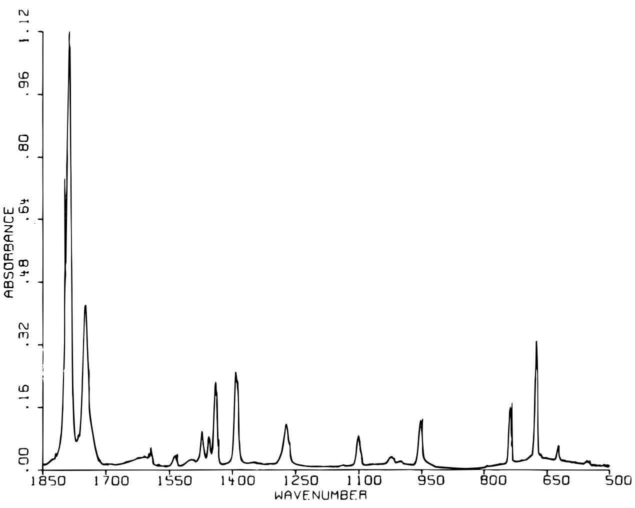

Figure 1. Argon matrix IR spectrum of **1a** (1850 and 500 cm^{-1} range).

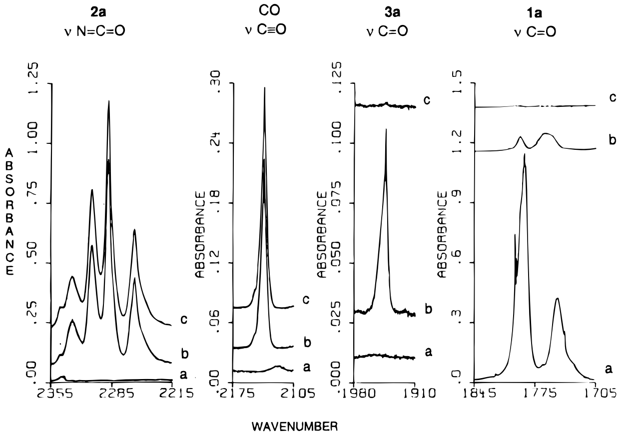

Figure 2. IR spectra of the reaction mixture from the photolysis of **1a**: (a) before irradiation, $t = 0$; (b) irradiation at $\lambda \geq 335$ nm, $t = 1500$ min; (c) irradiation at $\lambda \geq 230$ nm, $t = 225$ min.

1a (or **1b**), together with the multiplet structure of the absorption bands arising from alternative trapping sites. Quantities of the corresponding isocyanates **2a** (or **2b**) and carbon monoxide are also present, which result from limited decomposition of the triazolinedione derivatives during the vaporization process.

The range of irradiation frequencies has been choosen from observation of electronic spectra of **1a** and **1b** (Experimental Section). Irradiation at $\lambda \geq 514$ nm in the $n \rightarrow \pi^*$ absorption band proceeds in a very slow photodecomposition whose final products are quite similar to those obtained from irradiation at $\lambda \geq 335$ nm (**1a**) and 310 nm (**1b**) in the $n \rightarrow \pi^*$ and $\pi \rightarrow \pi^*$ absorptions.

Irradiation of 1a in Argon Matrix. The experimental spectrum (Figure 1) of **1a** is identified by comparison with the theoretical spectrum obtained from *ab initio* calculations using 6-31G* basis. This vibrational spectrum is characterized by two strong carbonyl stretching absorption bands at 1789 and 1749 cm^{-1}.

The photochemical behavior of **1a** and of the reaction products, embedded in an argon matrix at 10 K, is shown in Figure 2, where evolution of the spectra is illustrated for three irradiation times. The lower trace shows the spectrum after deposition and before irradiation (time $t = 0$). The middle trace shows the appearance of the spectrum after 1500 min of irradiation at $\lambda \geq 335$ nm and the upper trace after 225 min of irradiation at $\lambda \geq 230$ nm after the complete disappearance of **1a**.

Under irradiation at $\lambda \geq 335$ nm, the intensity of the **1a** absorption bands decrease whereas new absorption bands appear in different areas of the spectrum. These bands were assigned to three different compounds.

In the range 2360−2200 cm^{-1}, there is observed a multiplet of strong absorption bands centered at 2285 cm^{-1} (Figure 2) characteristic of the $\nu_{N=C=O}$ stretching mode of **2a**[12] in different sites. A broad absorption band characteristic of the $\nu_{C\equiv O}$ stretching mode appears at 2145 cm^{-1}. These absorptions belong to two different products whose concentrations increase at the same rate.

Simultaneously, a weak absorption band at 1944 cm^{-1} and a group of very weak ones at 1760, 1325, and 880 cm^{-1} appear. All these bands increase with the same rate and can be assigned to **3a** by comparison with the literature data[11] and with the simulated infrared spectra (Table 1). The weak intensity of the 1944 and 1760 cm^{-1} carbonyl stretching bands (α-diketone) as well as the small number of the observed experimental bands (4 of the 21 theoretical) agrees with a very low concentration of this compound.

After the complete disappearance of **1a**, the reaction products are irradiated at $\lambda \geq 230$ nm. At this wavelength, the aziridinedione **3a** is further photodecomposed leading to the formation of carbon monoxide and methyl isocyanate (**2a**). The electronic spectrum of **2a** shows a broad $^1A'' \rightarrow {}^1A'$ transition at $\lambda \approx 210$ nm ($\epsilon \approx 60$):[16] **2a** is not decomposed during irradiation at $\lambda \geq 230$ nm.

Irradiation of 1b in Argon Matrix. Irradiation of **1b** isolated in the argon matrix at $\lambda \geq 310$ nm induces a slow decrease of its absorption bands with simultaneous formation of carbon monoxide, phenyl isocyanate (**2b**), and phenylaziridinedione **3b**. All reaction products were characterized by their absorption bands observed in the experimental IR spectra in the ranges 2100−2170 cm^{-1} (CO, $\nu_{C\equiv O}$), 2200−2300 cm^{-1} (**2b**, $\nu_{N=C=O}$), and 1955−1935 cm^{-1} (**3b**, $\nu_{C=O}$).

Irradiation at shorter wavelengths $\lambda \geq 230$ nm induces the decomposition of **3b** and the formation of carbon monoxide and **2b**. The electronic spectrum of **2b** presents two absorption bands at $\lambda = 220$ nm and $\lambda = 260$ nm.[16] Irradiation at $\lambda \geq 230$ nm induces in the infrared spectra the decrease of the phenyl isocyanate absorption bands and an increase of the $\nu_{C\equiv O}$ stretching mode. Concurrently, very weak absorption bands appear and slowly grow in different parts of IR spectra. These new bands could not be assigned but they are probably due to phenylnitrene or one of its rearrangement derivatives.[17]

Kinetic Analysis. In the case of the photolysis of **1a** it is possible to obtain the molar ratio values X_i of the different reaction products at different times (Table 2) from the evolution of the integrated absorbances versus time.

To evaluate these molar ratios we proceed as following for the reaction

$$R \rightarrow P \qquad \text{with } R = \text{reactant, } P = \text{product}$$

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Table 1. Observed and Simulated Infrared Spectra of 3a

	our experiment		literature	calculation (MP2/6−31G*)				
modes	ν_{exp}	I[a]	ν_{exp}[b]	ν[c]	ν[d]	I	$\Delta\nu/\nu$ %	assignment, %
1				3240	3091	0.3		100 $\nu(\mathrm{CH_3})$
2				3222	3073	0.7		100 $\nu(\mathrm{CH_3})$
3				3123	2979	2		100 $\nu(\mathrm{CH_3})$
4	1944	100	1940	2025	1932	45	0.6	98 $\nu(\mathrm{CO})$
5	1760	14	1755	1840	1755	100	0.03	100 $\nu(\mathrm{CO})$
6				1548	1476	1		99 $\delta(\mathrm{HCH})$
7				1536	1465	2		99 $\delta(\mathrm{HCH})$
8				1483	1415	0.1		66 $\delta(\mathrm{NCH})$ + 34 $\delta(\mathrm{HCH})$
9	1325	32		1373	1310	20	0.01	93 $\nu(\mathrm{NC_6})$
10				1222	1166	0.5		98 $\delta(\mathrm{NCH})$
11				1146	1093	0.3		100 $\delta(\mathrm{NCH})$
12	880	weak		909	867	3	0.02	25 $\nu(\mathrm{CC})$ + 52 $\nu(\mathrm{NC_6})$
13				806	769	8		60 $\nu(\mathrm{NC_{2,3}})$ + 32 $\delta(\mathrm{NCH})$
14				733	700	0		90 $\nu(\mathrm{NC_6})$
15				676	645	0		50 $\delta(\mathrm{OCN})$ + 48 $\delta(\mathrm{OCC})$
16				663	632	0		86 $\gamma(\mathrm{O})$
17				480	458	4		95 $\gamma(\mathrm{O})$
18				288	275	0.6		27 $\nu(\mathrm{CC})$ + 26 $\delta(\mathrm{OCN})$ + 38 $\delta(\mathrm{OCC})$
19				167	159	0.1		87 $\delta(\mathrm{CNC})$
20				120	115	0		26 $\gamma(\mathrm{H})$ + 43 $\gamma(\mathrm{O})$ + 30 $\gamma(\mathrm{C_6})$
21				−15	4	0		73 $\gamma(\mathrm{H})$ +11 $\Gamma(\mathrm{NC})$

[a] Relative intensity. [b] Reference 11. [c] Calculated frequencies. [d] Scaled frequencies (scaling factor 0.91).

Table 2. Irradiation of 4-Methyl-1,2,4-triazoline-3,5-dione (1a). Evolution of the Molar Ratios of the Reaction Products

irradiation times (min)	$\lambda \geq 335$ nm											
	0	5	10	20	40	70	115	183	270	440	720	1500
X (**1a**)	1	0.9700	0.9500	0.9100	0.8500	0.7600	0.6200	0.5300	0.4300	0.2900	0.1700	0.0600
X (**2a**)	0	0.0071	0.0131	0.0243	0.0457	0.0728	0.1100	0.1483	0.1832	0.2287	0.2679	0.3030
X (**3a**)	0	0.0008	0.0013	0.0026	0.0045	0.0076	0.0112	0.0149	0.0180	0.0216	0.0249	0.0276
X (CO)	0	0.0071	0.0131	0.0243	0.0457	0.0728	0.1100	0.1483	0.1832	0.2287	0.2679	0.3030
X ($\mathrm{N_2}$)	0	0.0079	0.0144	0.0269	0.0502	0.0804	0.1212	0.1632	0.2012	0.2503	0.2928	0.3306

irradiation times (min)	$\lambda \geq 230$ nm			
	0	35	90	225
X (**2a**)	0	0.2665	0.4266	0.4976
X (**3a**)	1	0.4670	0.1467	0.0048
X (CO)	0	0.2665	0.4266	0.4976

we can write

$$\begin{array}{lccc} & \mathrm{R} & \rightarrow & \mathrm{P} \\ t=0 & C_0(\mathrm{R})X_0(\mathrm{R}) & & 0 \\ t & C_t(\mathrm{R}) = C_0(\mathrm{R})X_t(\mathrm{R}) & & C_t(\mathrm{P}) = C_0(\mathrm{R})X_t(\mathrm{P}) \end{array}$$

$$X_t(\mathrm{R}) + X_t(\mathrm{P}) = 1 \qquad (1)$$

where $X_t(i)$ is the reaction product (i) molar ratio at time t and $C_t(i)$ its concentration at the same time t.

According to Beer−Lambert law we can write

$$A_t(i) = \epsilon(i)C_t(t) = \epsilon(i)X_t(i)C_0(\mathrm{R})$$

where $A_t(i)$ is the reaction product (i) integrated absorbance at time t and $\epsilon(i)$ its molar absorption coefficient.

Also

$$A_t(\mathrm{R}) = \epsilon(\mathrm{P})X_t(\mathrm{P})C_0(\mathrm{R})$$

$$A_t(\mathrm{P}) = \epsilon(\mathrm{P})X_t(\mathrm{P})C_0(\mathrm{R})$$

Between t_0 and t we can write

$$\Delta A_t(\mathrm{R}) = A_0(\mathrm{R}) - A_t(\mathrm{R}) = \epsilon(\mathrm{R})X_0(\mathrm{R})C_0(\mathrm{R}) - \epsilon(\mathrm{R})X_t(\mathrm{R})C_0(\mathrm{R})$$

$$\Delta A_t(\mathrm{R}) = \epsilon(\mathrm{R})C_0(\mathrm{R})(1 - X_t(\mathrm{R}))$$

$$\Delta A_t(\mathrm{P}) = A_0(\mathrm{P}) - A_t(\mathrm{P}) = -\epsilon(\mathrm{P})X_t(\mathrm{P})C_0(\mathrm{R})$$

If $\Delta < 0$, the product decrease during the experiment. If $\Delta > 0$, the product increase during the experiment.

Taking in account the absolute values $|\Delta|$ and from relation 1 we can write

$$1 - X_t(\mathrm{R}) = X_t(\mathrm{P})$$

Also

$$|\Delta A_t(\mathrm{R})| = \epsilon(\mathrm{R})X_t(\mathrm{P})C_0(\mathrm{R})$$

$$|\Delta A_t(\mathrm{P})| = \epsilon(\mathrm{P})X_t(\mathrm{P})C_0(\mathrm{R})$$

$$\left|\frac{\Delta A_t(\mathrm{R})}{\Delta A_t(\mathrm{P})}\right| = \frac{\epsilon(\mathrm{R})}{\epsilon(\mathrm{P})} = \mathrm{Cte}$$

$$X_t(\mathrm{R}) = \frac{A_t(\mathrm{R})}{A_0(\mathrm{R})} \qquad X_t(\mathrm{P}) = \frac{|\Delta A_t(\mathrm{R})|}{A_0(\mathrm{R})}$$

This process has been applied for the photolysis of **1a**. The complete calculation of the molar ratios determination for Scheme 2 is presented in supporting information.

The kinetic behaviour of X_i vs time (Figure 3 and 4) is consistent with the mechanism presented in Scheme 2. In the case of the photolysis of **1b**, the weak nature of the absorption bands due to **3b** and the concomittant decomposition of **2b** and **3b** at $\lambda \geq 230$ nm (Scheme 2) do not permit an analysis similar to that of **1a**.

In the two examples, isocyanates and carbon monoxide are formed immediately in the low-temperature photolysis and are presumed to be produced by cleavage of the 1,3-biradical postulated by Kjell *et al.*[18] (Figure 5) formed

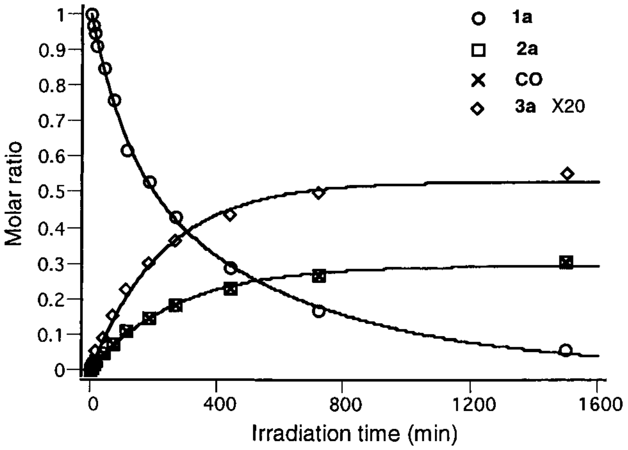

Figure 3. Curve fit of **1a**, **2a**, CO, and **3a** (×20) molar ratios during the irradiation at $\lambda \geq 335$ nm.

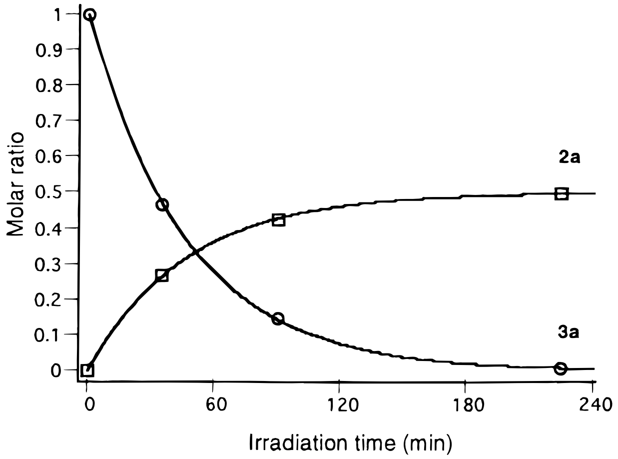

Figure 4. Curve fit of photolysis of **3a** and formation of **2a** during the irradiation at $\lambda \geq 230$ nm.

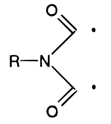

Figure 5. 1,3-Biradical.

Scheme 2

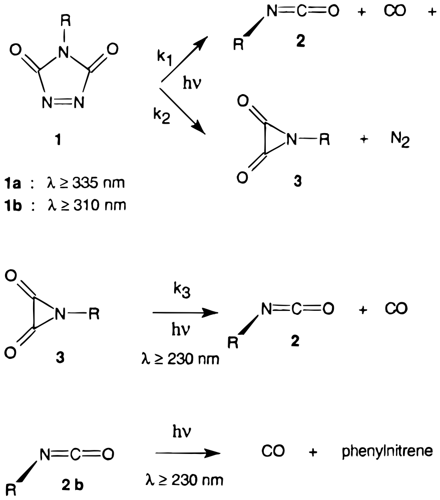

Table 3. Experimental Rate Constant Values (min^{-1}) for the Photolysis of 1a

K_1	K_2	K_3
$(3.29 \pm 0.10) \times 10^{-3}$	$(2.35 \pm 0.09) \times 10^{-4}$	$(2.16 \pm 0.01) \times 10^{-2}$

by the loss of nitrogen and not by decomposition of aziridinediones.

Scheme 2 shows evidence for a unimolecular decomposition process for **1a** (order kinetic first) which leads to formation of CO, **2a**, and **3a** by fission of two or three CN bonds; the N_2 molecule expelled is not observable by IR spectroscopy. This 1,3-biradical is not detected in agreement with the very short lifetime of this species.[19] Even if the 1,3-cyclopentadiyl biradical obtained by UV irradiation of 2,3-diazabicyclo[2.2.1]heptene-2 and observed by ESR has a half-life time of ~30 min.[20] A similar biradical is obtained by irradiation of azo derivatives as pyrazolines.[21]

This transient obtained in the first step of the photolysis evolves by two competitive pathways to give the isocyanate, carbon monoxide, and aziridinedione. The aziridinediones decompose yielding CO and isocyanate, when irradiated at the lower wavelength.

In order to fit the experimental molar ratio at different times to monoexponential rates (decay of **1a** or increase of **2a**, **3a**, and CO), least-squares analyses were performed using a computer program[22] that provides the first-order rate constants and the molar ratios at zero and infinite times and the standard deviations.

The photolysis reaction was studied as a sum of elementary steps:

$$A \underset{k_j}{\overset{k_i}{\rightleftharpoons}} B$$

whose kinetic is governed by the equation $X_\infty + (X_0 - X_\infty)\exp(-kt)$ with $k = k_i + k_j$. If the reaction is not reversible, X_0 or X_∞ equals zero for increasing or decreasing products, respectively. The values of the rate constants k are summarized in Table 3 (**2a**/**3a** = 11.92 and $K_1/K_2 = 13.75$).

Experimental Section

Matrix Isolation Technique. The apparatus and experimental techniques have been described elsewhere.[22] The vaporized triazolinediones **1a** or **1b** were mixed with an excess of argon at room temperature. The relative concentrations of rare gas to **1** (M/S ratio) was unknown because vapor pressures of **1a** and **1b** at room temperature were not sufficient to obtain a suitable matrix. The deposition was achieved of means of moderate heating inducing a broadening of IR absorption bands (Figure 1). The mixture was deposited at 20 K on a CsBr window, cooled down in a cryostat by a closed cycle helium refrigerator (C.T.I Cryodyne, Model 21). Temperature measurement, stabilization, and control were achieved by a single controller (D.R.C. 84C, Lake Shore Cryotronics Inc.). A second independent diode, placed in close vicinity to the window, was used as a permanent probe to check the temperature. The gaseous mixture was slowly sprayed onto the cold window through a long and very narrow stainless steel tube in order to promote matrix-isolated monomers. The deposi-

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Table 4. Geometric Parameters of *N*-Methylaziridine-2,3-dione (3a)

bond lengths[a]	PM2/6-31G*	bond angles[b]	PM2/6−31G*
N(1)−C(2)	141.1	N(1)−C(3)−O(5)	142.1
N(1)−C(3)	141.2	N(1)−C(2)−O(4)	142.0
C(2)−C(3)	147.9	C(2)−N(1)−C(3)	63.2
C(2)−O(4)	120.5	C(2)−C(3)−O(5)	159.5
C(3)−O(5)	120.5	C(2)−N(1)−C(6)	148.2
N(1)−C(6)	145.7	C(3)−C(2)−O(4)	159.6
C(6)−H(7)	109.2	C(3)−N(1)−C(6)	148.6
C(6)−H(8)	109.0	N(1)−C(6)−H(7)	109.2
C(6)−H(9)	109.2	N(1)−C(6)−H(8)	108.1
		N(1)−C(6)−H(9)	109.5
		H(7)−C(6)−H(9)	109.7
		H(8)−C(6)−H(9)	110.1
		H(7)−C(6)−H(8)	110.2

[a] pm. [b] Degrees.

tions were made perpendicular to the window; then, the inlet tube was rotated by 45° for the spectroscopy investigations.[23]

The deposition rate of gas mixtures was controlled with an Air Liquide microleak (V.P/RX) and never exceeded 2 mmol/h. This rate was chosen to minimize splitting of the vibrational absorption bands due to alternative trapping sites.

FT−IR Spectroscopy. The IR spectra were recorded on a 7199 Nicolet spectrometer equipped with a liquid N_2 cooled MCT detector; the resolution was 0.12 cm^{-1} without apodization. The integrated absorbances A (cm^{-1}) were measured as the area under a simulated peak (giving the best fit with the experimental data) by use of the FOCAS program of the Nicolet library.

Photoirradiation Techniques. Irradiations were carried out using an Osram 200 W high-pressure mercury lamp equiped with a quartz envelope. The broad band was filtered at $\lambda \geq 335$ nm, $\lambda \geq 310$ mn, and $\lambda \geq 230$ nm (Oriel filters).

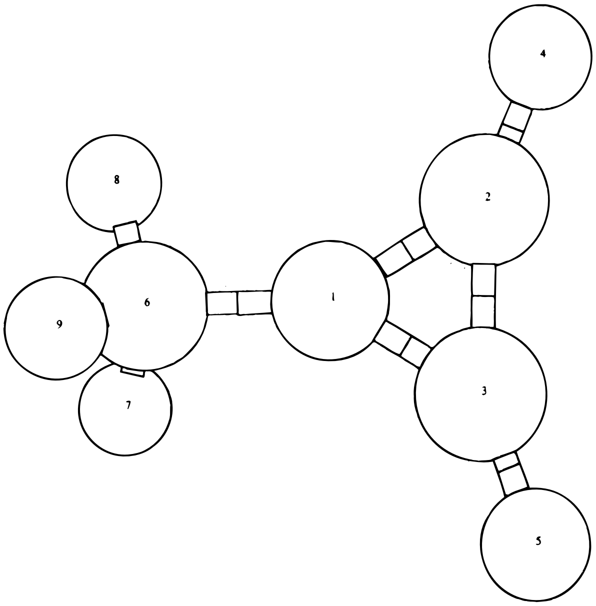
Ab Initio Calculations. The *ab initio* molecular orbital calculations were performed with the GAUSSIAN 92 program package[24] using the Møller−Plesset second-order (MP2) procedure with the standard split valence 6-31G* Gaussian basis set.[14,15] The geometry of **3a** was optimized by means of analytical gradient techniques. The bond lengths and bond angles of molecule **3a** are summarized in Table 4. The labeling of the atoms is given in Scheme 3.

Synthesis of 4-R-1,2,4-triazoline-3,5-diones. 4-Substituted-1,2,4-triazoline-3,5-diones were synthesized by oxidation of the corresponding 4-R-1,2,4-triazolidine-3,5-diones (4-substituted-urazoles) according to previously reported procedures.[3,25,26] These urazoles were dispersed in dichloromethane and oxidized at 0 °C by bubbling dinitrogen tetraoxide to give quantitatively the corresponding 4-substituted-1,2,4-triazoline-3,5-diones (**1a**,**b**). These triazolinediones were purified by sublimation under high vacuum before use.

Spectra of solids were carried out using KBr pellets. Vibrational transition frequencies are reported in wavenumber (cm^{-1}). Band intensities are assigned as very weak (vw), weak (w), medium (m), strong (s), and broad (br).

4-Methyl-1,2,4-triazoline-3,5-dione (1a) (81%): pink solid; mp 112 ± 2 °C (Aldrich 107−109 °C); ^1H NMR ($CDCl_3$,TMS) δ 3.05 (s, 3H); ^{13}C NMR ($CDCl_3$) δ 24 (1C, N−CH_3), 157 (2C, C═O); IR (KBr) 2966 (vw), 1782 (s, br), 1745 (s), 1540 (w), 1445 (m, br), 1392 (m), 1273 (m), 1101 (w), 1025 (vw), 952 (m), 739 (m), 673 (s, br), 626 (w), 554 (w). UV (CH_2Cl_2) $n \rightarrow \pi^*$ λ_{max} 535 nm, ϵ_{max} 184 mol^{-1} L cm^{-1}, $\pi \rightarrow \pi^*$ λ_{max} 290 nm, ϵ_{max} 2000 mol^{-1} L cm^{-1}.

Scheme 3



4-Phenyl-1,2,4-triazoline-3,5-dione (1b) (86%): dark red solid; mp 169 ± 2 °C (Aldrich 170 °C); ^1H NMR ($CDCl_3$, TMS) δ 7.42 (s, 5H); ^{13}C NMR (CD_2Cl_2) δ 158.3 (2C, C═O), 130.3 (2C, C_{meta}), 130.0 (1C, C_{para}), 129.8 (1C, C_{ipso}), 124.6 (2C, C_{ortho}); IR (KBr) 3060 (w), 1768 (s, br), 1620 (w), 1585 (m), 1525 (m), 1503 (s), 1480 (w), 1400 (s), 1315 (w), 1289 (m), 1174 (s), 1070 (m), 1031 (m), 1000 (m), 910 (w), 892 (m), 765 (m), 724 (s), 678 (s, br), 605 (m) cm^{-1}; UV (CH_2Cl_2) $n \rightarrow \pi^*$ λ_{max} 540 nm, ϵ_{max} 118 mol^{-1} L cm^{-1}, $\pi \rightarrow \pi^*$ λ_{max} 310 and 232 nm with respectively ϵ_{max} 359 mol^{-1} L cm^{-1} and 6137 mol^{-1} L cm^{-1}.

Conclusion

In this work, experimental data for the photochemical reaction of 4-methyl- and 4-phenyl-1,2,4-triazoline-3,5-diones trapped at 10 K in argon matrices were obtained. The products of photolysis, CO, isocyanates, and aziridine-2,3-diones, were identified. These results have to be compared to those obtained by Wamhoff *et al.*[7] on the photolysis of 4-phenyl-1,2,4-triazoline-3,5-dione in solution (acetonitrile, benzene) at room temperature. Although our final products are the same (N_2, CO, isocyanate) we show that photolysis of the molecule isolated in a cryogenic rare gas matrix gives in addition a strained compound identified as *N*-R-aziridine-2,3-dione. The latter which has been previously identified at 77 K by Aoyma *et al.*[11] decomposes spontaneously at temperatures >77 K.

In our experiment the decomposition occurs at 10 K under irradiation ($\lambda \geq 230$ nm). This compound is in agreement with the hypothesis of an evolution via a biradical intermediate able to exhibit decarbonylation or cyclization.

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Supporting Information Available: Geometric parameters and observed and simulated IR spectra of **2a**, IR spectra of **1b** photolysis reaction mixtures, and kinetic study (6 pages). This material is contained in libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.

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