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Synthesis and Characterization of *N*-Nitroso-4-aza-1,2-dioxolanes, and Their Thermolysis and Photolysis

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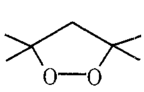
The introduction of the peroxide bond into a five-membered ring, *e.g.*, the 1,2-dioxolane **1**, promotes ring fragmentation by homolysis of the peroxide bond either by thermal[1] or photochemical[2] activation. Alternatively, scission of the five-membered ring **2** can be induced either by thermal or photochemical extrusion of a small stable fragment, *e.g.*, sulfur dioxide,[3] nitrogen,[4] phosphonites,[5] and nitrous oxide.[3] Usually a double bond is essential to effect such ring fragmentations. Since the thermal stability of the peroxide linkage in **1** is dramatically enhanced as compared to that of *tert*-butyl peroxide (*ca.* 10^4 factor),[6] we decided to investigate the thermal and photochemical behavior of bifunctional peroxides such as **3**. The extrusion reaction could aid peroxide bond homolysis, or vice versa, by providing for more selective conditions of ring fragmentation through such potential symbiosis. Therefore, the hitherto unknown *N*-nitroso-4-aza-1,2-dioxolanes **3a–c** have been prepared and characterized and their thermolysis and photolysis investigated.



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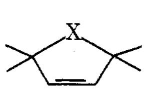
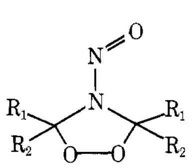


2

	X
a	SO_2
b	N_2
c	$RP(OR)_2$
d	N_2O



3

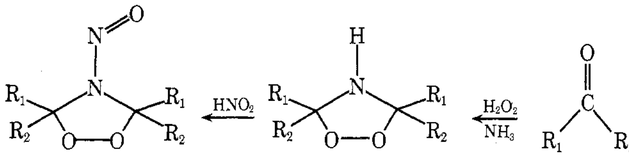
	R_1	R_2
a	Me	Me
b	Me	Et
c	$-(CH_2)_5-$	

The derivatives **3a–c** of these novel bifunctional peroxides are readily prepared in good yields (50–80%) by nitrosation of the respective 4-aza-1,2-dioxolanes **4a–c**. The latter are available from the ketones **5a–c** (eq 1).[7] The peroxides **3a–c** gave a positive Liebermann test for the nitroso group, which was also identified by infrared analysis in terms of its 6.8-, 7.0-, and 7.8-μ bands, characteristic of dialkyl *N*-nitrosamines.[8] The assigned structures were further substantiated by elemental analysis and mass spectra. Molecular ions at m/e 160, 174, and 240 for **3a–c**, respectively, were obtained in addition to NO, NO_2, O_2, and the corresponding ketone fragments.

Table I
Nmr Spectra of 4-Aza-1,2-dioxolanes and *N*-Nitroso-4-aza-1,2-dioxolanes[a,b]

	R_1	R_2	3		$\Delta\delta$	4	Multiplicity
			syn	anti			
a	Me	Me	1.58	1.82	0.24	1.17	Singlet
b	Me		1.50	1.74	0.24	1.20	Singlet
		Et	0.92	1.03	0.11	0.83	Triplet
			2.10	2.10	0.00	1.50	Quartet
c	$-(CH_2)_5-$		1.62	1.70	0.08	1.49	Multiplet
			2.06	2.10	0.04		Multiplet

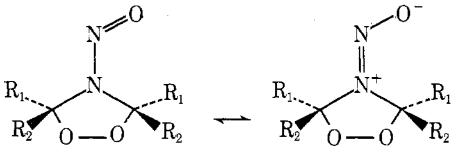
[a] Values given in δ (parts per million). [b] Syn is the isomer having R_2 and R_1 cis to the oxygen.



3a—c **4a—c** **5a—c**

(1)

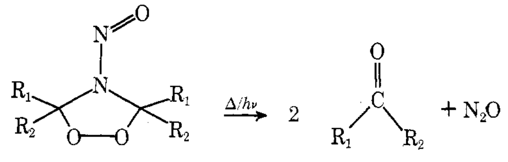
Most reassuring were the nuclear magnetic resonance data for **3a–c** (Table I). The spectrum of compound **3a**, for example, indicated two different types of methyl groups present in equal proportion. These results are best explained in terms of the respective syn and anti isomers **3′** (eq 2), since such isomerism is well documented for *N*-nitrosamines,[9] and attributed to significant dipolar contributions to the *N*-nitroso group, the barrier for syn–anti interconversion being 23 kcal/mol.[9c] In the case of **3b**, the present data do not distinguish between the cis and trans arrangement of the ethyl and methyl groups with respect to the ring. A nuclear magnetic resonance spectrum of **3a** taken at 100° was exactly equal to that taken at 35°.



3 **3′**

(2)

The products of the thermolysis of **3a–c** at 110–120° (25–30 hr) in carbon tetrachloride were characterized as the respective ketones **5** and nitrous oxide by means of infrared and gas–liquid partition chromatography. Comparison of infrared and glpc data with those of authentic materials afforded identical spectra (eq 3). The quantitative results established by infrared analysis are summarized in Table II. Thus for **3a** and **3b** the formation of ketone was essentially quantitative, while for **3c** a fraction of the product was an unidentified high molecular weight residue. Similarly, the photolysis of **3** at 300 nm (2–6 hr) in



3a—c **5a—c**

(3)

Table II
Absolute Yield of Thermo- and Photoproducts of *N*-Nitroso-4-aza-1,2-dioxolanes 3a–c

	3			Mole ratios[a–c]			
	R_1	R_2	Ketone	hν (300 nm)	Time,[c] hr	Δ (110°)	Time,[c] hr
a	Me	Me	**5a**	1.91 ± 0.05	2	1.93 ± 0.03	25
b	Me	Et	**5b**	1.60 ± 0.08[d,e]	6	1.86 ± 0.05[e]	30
c	$-(CH_2)_5-$		**5c**	1.50 ± 0.01[d,e]	4	1.70 ± 0.03[e]	30

[a] Moles of ketone **5** per mole of **3** decomposed. [b] Analyzed by infrared using the C═O band at 1715, 1720, and 1712 cm^{-1} of **5a–c**, respectively. [c] Time for complete decomposition of **3**. [d] Partial photodegradation of ketone **5b,c**.[11] [e] The remainder was an unidentified high molecular weight residue.

hexane gave the respective ketone **5** and nitrous oxide (eq 3). As expected under the photolytic conditions employed, acetone (**5a**) was photostable, while 2-butanone (**5b**) and cyclohexanone (**5c**) were photoconsumed,[11] as indicated in the quantitative results in Table II. A detailed kinetic study is planned to elucidate the mechanisms of the thermolysis and photolysis reactions of **3**.

Experimental Section

Nuclear magnetic resonance spectra were obtained on a Varian T-60. Infrared spectra were measured on Perkin-Elmer Model 137 and 237 B spectrometers. Mass spectra were obtained on a Hitachi Perkin-Elmer RMS-4 mass spectrometer at 70 eV. All irradiations were conducted in a Rayonet RPR-100 photochemical reactor supplied with 300-nm lamps. Uncorrected melting points were obtained with a Thomas-Hoover capillary melting point apparatus. A general procedure for the synthesis of 4-aza-1,2-dioxolanes 4 was followed.[7]

General Method for the Synthesis of *N*-Nitroso-4-aza-1,2 dioxolanes 3. The azadioxolane 4, ice, and 10% aqueous hydrochloric acid were mixed in an erlenmeyer flask. A cold aqueous sodium nitrite solution was gradually added with stirring and the mixture was left at room temperature for 2 hr. Extraction with ether was followed by washings with sodium bicarbonate and water and drying over anhydrous sodium sulfate. The solvent was then removed to afford the respective dioxolanes. Elemental analyses and mass spectra of all new compounds gave satisfactory results.

3,5-Di(1,5-pentylene)-*N*-nitroso-4-aza-1,2-dioxolane (3c) was prepared in 81% yield by the above-mentioned method, mp 52–53°, starting with 1.0 g (4.7 mmol) of **4c**, 0.2 g (5.6 mmol/1 ml of water) of hydrochloric acid, and 0.4 g (5.8 mmol) of sodium nitrite in 1 ml of water. The spectral data are ir (CCl_4) 1472, 1270 (N–N═O), and 1320 cm^{-1}; nmr (60 MHz, CCl_4, TMS) δ 1.62 and 1.70 [m, 16, $(CH_2)_8$], 2.06 and 2.10 ppm [m, 4, $(CH_2)_2$]; mass spectrum (70 eV) *m/e* 30 (NO), 32 (O_2), 44 (N_2O), 98 ($C_6H_{10}O$), and 240 (M^+).

Anal. Calcd for $C_{12}H_{20}N_2O_3$: C, 59.98; H, 8.39; N, 11.66. Found: C, 59.58; H, 8.36; N, 11.94.

3,5-Diethyl-3,5-dimethyl-*N*-nitroso-4-aza-1,2-dioxolane (3b) was prepared in 70% yield by the above-mentioned method, bp 120° (20 mm, molecular distillation), $n^{20}D$ 1.4520, starting with 1.0 g (6.2 mmol) of **4b**, 0.3 g (8.4 mmol/1 ml of water) of hydrochloric acid, and 0.5 g (7.1 mmol) of sodium nitrite in 1 ml of water. The spectral data are ir (CCl_4) 1470, 1425, and 1270 (N–N═O) and 1300 cm^{-1}; nmr (60 MHz, CCl_4, TMS) δ 0.92 (t, 3, CH_3CH_2), 1.03 (t, 3, CH_3CH_2), 1.50 (s, 3, CH_3), 1.74 (s, 3, CH_3), 2.10 ppm (m, 4, CH_3CH_2).

3,3,5,5-Tetramethyl-*N*-nitroso-4-aza-1,2-dioxolane (3a) was prepared in 50% yield by the above-mentioned method, mp 49–50° (sublimated), starting with 1.0 g (7.7 mmol) of **4a**, 0.3 g (8.4 mmol/l. of water) of hydrochloric acid, and 0.6 g (8.4 mmol) of sodium nitrite in 1 ml of water. The spectral data are ir (CCl_4) 1470, 1425, and 1270 (N–N═O), 1380 cm^{-1} (*gem*-dimethyl); nmr (60 MHz, (CCl_4, TMS) δ 1.58 (s, 6, CH_3) and 1.82 ppm (s, 6, CH_3).

Photolysis and Thermolysis of 3a–c. A solution of the *N*-nitroso-4-aza-1,2-dioxolane **3** in the appropriate solvent was transferred by means of a syringe into constricted Pyrex tubes and sealed at Dry Ice–acetone temperature under reduced pressure.

One set of ampoules was heated in an oil bath at 110°. The other set was irradiated in the Rayonet photoreactor at 300 nm. The product mixture was measured quantitatively using standard infrared techniques. The results are summarized in Table II.

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Registry No.—**3a**, 51271-04-6; **3b**, 51211-99-5; **3c**, 51212-00-1; **4a**, 24075-03-4; **4b**, 24075-04-5; **4c**, 21842-28-4; **5a**, 67-64-1; **5b**, 78-93-3; **5c**, 108-94-1.

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A Cautionary Note Concerning the Isolation of Some Metal Salts of 1-Tetrazoleacetic Acid

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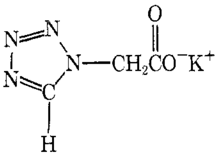
During routine laboratory work, it became necessary to isolate sizable quantities of the potassium salt of tetrazoleacetic acid (**1**). As this compound has been reported in the literature[1] without precautions, no extraordinary safety measures were employed. Routine Differential Thermal Analysis and Thermal Gravimetric Analysis[2] were performed on **1**. The data generated by these tests indicate that **1** is stable at temperatures below 175° and only above 200° did the compound exhibit a sharp exotherm in Differential Thermal Analysis with a weight loss as shown by



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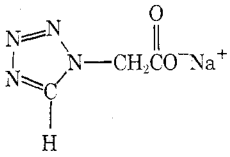

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