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	$h\nu$ (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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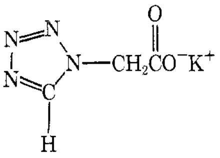
During routine laboratory work, it became necessary to isolate sizable quantities of the potassium salt of tetrazoleacetic acid (1). As this compound has been reported in the literature[1] without precautions, no extraordinary safety measures were employed. Routine Differential Thermal Analysis and Thermal 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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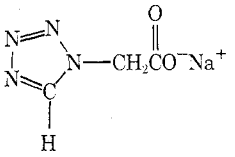

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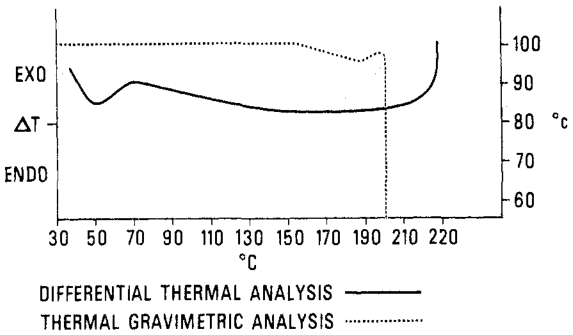


Figure 1. Differential Thermal and Thermal Gravimetric Analyses of tetrazoleacetic acid, potassium salt.

Thermal Gravimetric Analysis. These data resembled data obtained from several other heterocyclic ring systems.[3]

However, during a routine drying operation involving a hot forced air tray dryer, kilogram quantities of the potassium salt of tetrazoleacetic acid violently exploded, resulting in damage to the dryer. Fortunately, no injury to personnel occurred.

Subsequent investigations into the accident suggested that the decomposition was initiated by a solvent fire caused by a spark of unknown origin. Additional studies showed that any source of heat (>200°) could initiate the decomposition [*e.g.*, hot flint spark, continued (10 sec) static spark, or flame]. Since this extremely rapid decomposition is self-propagating, a sample of any size held at room temperature will completely explode when any part of the entire sample is subjected to flame or hot spark. The decomposition is characterized by instantaneous evolution of gas without significant flame resulting in a water-soluble black residue. Even if 1 is placed on filter paper at room temperature and exploded by a hot flint spark, little or no charring of the filter paper results. A test of the sodium salt of tetrazoleacetic acid (2) shows a similar violent decomposition that only could be initiated by flame. In both cases, the more pure the sample, the more violent the decomposition.

Further studies showed the parent tetrazoleacetic acid to have similar TGA and DTA data but to be much less sensitive to flame or hot spark. Similar other heterocycles[3] and their corresponding potassium or sodium salts showed much less sensitivity to flame or hot spark.

Therefore, the potassium and sodium salts of tetrazoleacetic acid should be isolated with due caution and should be protected from any contact with high heat, flame, or hot spark. Additionally, any compound that is to be prepared in large quantities should be spark and flame tested to check sensitivity along these parameters.

Registry No.—1, 51286-83-0; 2, 51286-84-1.

References and Notes

(1) R. Raap and J. Howard, *Can. J. Chem.*, **47**, 813 (1969).

(2) These analyses were performed by the Analytical Department of Eli Lilly and Co., Indianapolis, Ind.

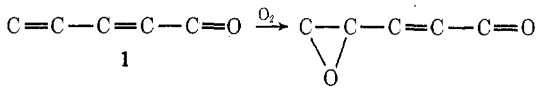
(3) Some of the heterocyclic systems analyzed were tetrazole, sodium tetrazole, 5-aminotetrazoleacetic acid and its potassium salt, and sydnoneacetic acid and its sodium salt. All of these compounds show similar thermal gravimetric data and differential thermal analyses but did show radically different combustion characteristics compared to the salts of tetrazoleacetic acid.

Communications

Synthetically Useful Epoxidations with Molecular Oxygen

Summary: Conjugated dienones and diene esters are epoxidized at the γ,δ double bond by molecular oxygen when heated in solvents which have readily abstractable hydrogen atoms.

Sir: We have found that the conversion 1 → 2 occurs readily when compounds containing the moiety represented by

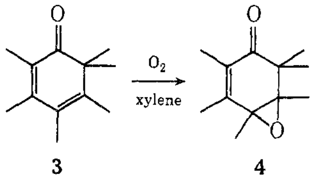


$$\underset{\mathbf{1}}{\mathrm{C{=}C{-}C{=}C{-}C{=}O}} \xrightarrow{O_2} \mathrm{\underbrace{C{-}C}_{O}{-}C{=}C{-}C{=}O}$$

1

2

1 are heated in the presence of air or oxygen, in a solvent which has readily abstractable hydrogen atoms.[1] For example, when a xylene solution of dienone 3 was heated at 120–130° for 21 hr in the presence of air, epoxide 4[2] was formed in 65–75% yield. The reaction occurred at the same temperature in cyclooctane (13 hr, 70–75%), mesitylene (14 hr, 80%), and cumene (8 hr, 90–95%), but in chlorobenzene no 4 was formed even after 48 hr. There is very little advantage in reaction time, yield, or reproducibility by bubbling air or oxygen through the reaction mixture; indeed, our experience thus far is that the yield of undesired side-products increases if the reaction is hurried in this way or by use of initiators. Experiments along these lines are, however, continuing.



3 4

Table I lists several other epoxides which have been prepared by autoxidation of the corresponding unsaturated precursors. The reaction may be highly stereoselective. Thus with 3,5-cholestadien-7-one the product is the