and *N*-norcodeine were obtained in overall yields of 84 and 89%, respectively.

Care should be exercised in the preparation of the carbamate to ensure continuous, efficient stirring, especially in larger scale preparations. Inefficient mixing could be responsible for localized acid formation which might promote the formation of acid-catalyzed by-products from the *N*-normorphine and codeine carbamates to give, possibly, the epimeric 6-hydroxyl (6-iso) or 8-hydroxyl (from allylic rearrangement) *N*-normorphine (or codeine). Efficient stirring and an increased (over the former procedure[3]) amount of base tended to eliminate by-products.

A further precaution involved the use of 64% hydrazine in the hydrazine mixture which ensured the presence of hydrazine hydrate in the vapor of the refluxed mixture, rather than the air-sensitive (explosive) anhydrous hydrazine; safety shields should also be employed.

Experimental Section

Melting points were determined in open capillary tubes using a Thomas-Hoover apparatus and are corrected. Microanalyses were performed by the Laboratory's Section on Microanalytical Services and Instrumentation. Ir (Perkin-Elmer 21), NMR (Varian A-60 or HR-220), and mass (Hitachi Perkin-Elmer RMU 6E) spectra were consistent with the assigned structures.

(±)-5-Methyl-2′-hydroxy-9α-propyl-6,7-benzomorphan (1a). In a modification of the usual procedure,[3] phenyl chloroformate (26.0 g, 166 mmol) was added to a slurry of (±)-2,5-dimethyl-2′-hydroxy-9α-propyl-6,7-benzomorphan (**1b**, 5.0 g, 19.3 mmol) in $CHCl_3$ (500 ml). After stirring for several minutes the reaction mixture became homogenous and $KHCO_3$ (34.0 g, 340 mmol) was added. The mixture was refluxed for 48 hr and cooled and water (200 ml) was added. When the inorganic material had dissolved, the $CHCl_3$ was separated and washed with 1 *N* HCl (50 ml) and water (100 ml). The $CHCl_3$ was evaporated in vacuo and to the residue was added MeOH (310 ml) and a solution of KOH (14.5 g, 220 mmol) and $KHCO_3$ (22 g, 220 mmol) in H_2O (220 ml). After stirring at 25° overnight, the solution was acidified with 37% HCl and concentrated in vacuo until KCl separated. The aqueous suspension was washed with Et_2O and the combined extracts were dried ($MgSO_4$) and solvent was removed. The major portion of the residual phenol by-product was removed by distillation under high vacuum (bath 100–120°), to give a gum which was dissolved in Et_2O and filtered through a layer of silica gel (70–230 mesh). The silica gel was washed with Et_2O and the combined filtrate and washings were evaporated to yield the crude *N*-carbophenoxy derivative of **1a** (9.6 g) as a yellow foam that resisted crystallization from a variety of solvents and which still contained some phenol. To this material was added 64% hydrazine (35 ml) and 95% hydrazine (35 ml). The mixture was stirred (under N_2), and refluxed (behind a safety shield) for 1.5 hr. Crystalline **1a** separated from the reaction mixture. After an additional 18 hr of refluxing, the reaction mixture was cooled. The white solid was filtered and washed well with H_2O and then Et_2O (20 ml). The resulting white solid was dried in vacuo at 65° to yield 4.52 g (95.5%) of analytically pure **1a** directly, as small, irregular prisms, mp 248.5–250.5°.

Anal. Calcd for $C_{16}H_{23}NO$: C, 78.32; H, 9.45; N, 5.71. Found: C, 78.07; H, 9.25; N, 5.73.

Normorphine (2a). To a suspension of anhydrous morphine (**2b**, 2.50 g, 8.76 mmol) and finely divided $KHCO_3$ (15.0 g, 150 mmol) in $CHCl_3$ (250 ml) was added phenyl chloroformate (11.5 g, 73.4 mmol). The reaction mixture was vigorously stirred, refluxed for 60 hr, and cooled, most of the $CHCl_3$ was decanted, and the remaining inorganic material was dissolved in H_2O (100 ml). This solution was added to the decanted $CHCl_3$ and after shaking well the $CHCl_3$ was separated and washed with H_2O (50 ml) and then with 1 *N* HCl (50 ml). The $CHCl_3$ was dried ($MgSO_4$) and evaporated in vacuo, and most of the phenol was evaporated from the residue under high vacuum (bath 100–110°). To the residue was added 64% hydrazine (20 ml) and 95% hydrazine (20 ml) and the solution was refluxed (safety shield) under N_2 for 60 hr. The mixture was cooled, H_2O (100 ml) was added, and the solvent was removed in vacuo. The phenol remaining was evaporated under high vacuum (bath 100–120°), H_2O (20 ml) was added, and 37% HCl was added to pH 2.0 (Hydrion paper). The solutions was filtered, and the filtrate was made alkaline with NH_4OH. When crystallization (at 5°) was complete, the solid was filtered, washed with cold H_2O, and dried to give **2a**·$2H_2O$ (2.24 g, 84%), mp 275–277° dec (lit.[8] mp 276–277°).

Anal. Calcd for $C_{16}H_{17}NO_3 \cdot 2H_2O$: C, 62.52; H, 6.89; N, 4.56. Found: C, 62.45; H, 6.77; N, 4.60.

Norcodeine (2c). To a solution of codeine (**2d**, 2.99 g, 10 mmol) in $CHCl_3$ (250 ml) was added $NaHCO_3$ (21.0 g, 250 mmol) and phenyl chloroformate (11.5 g, 73.4 mmol). The reaction mixture was refluxed with efficient stirring for 18 hr, cooled, filtered, and evaporated. To the resulting syrup (14.1 g) was slowly added 95% hydrazine (5 ml). When the strongly exothermic reaction was over, additional 95% hydrazine (10 ml) and 64% hydrazine (10 ml) were added. The solution, under N_2, was refluxed (safety shield) for 24 hr and cooled, and H_2O was added and then removed (twice, 100 ml each) in vacuo. Most of the remaining phenol was removed (high vacuum, bath 100–120°) to give a semisolid which was dissolved in a mixture of $CHCl_3$ (150 ml) and H_2O (75 ml). The aqueous phase was made alkaline with NH_4OH, and the $CHCl_3$ was separated and extracted with sufficient 10% KOH to remove the remaining phenol. The $CHCl_3$ solution was washed with H_2O (50 ml), dried (Na_2SO_4), and evaporated to give 2.54 g (89%) of norcodeine (**2c**), mp 183.5–185° (lit.[9] mp 185°).

Registry No.—**1a**, 55058-87-2; **1b**, 55058-88-3; **2a**, 466-97-7; **2b**, 57-27-2; **2c**, 467-15-2; **2d**, 76-57-3; phenyl chloroformate, 1885-14-9.

References and Notes

(1) H. A. Hageman, *Org. React.*, **7**, 198 (1953).
(2) J. D. Hobson and J. G. McCluskey, *J. Chem. Soc.*, 2015 (1967).
(3) M. M. Abdel-Monem and P. S. Portoghese, *J. Med. Chem.*, **15**, 208 (1972).
(4) A. Pohland and H. R. Sullivan, Jr., U.S. Patent 3,342,824 (Sept 19, 1967).
(5) K. Kanematsu, M. Takeda, A. E. Jacobson, and E. L. May, *J. Med. Chem.*, **12**, 405 (1969).
(6) T. A. Montzka, J. D. Matiskella, and R. A. Partyka, *Tetrahedron Lett.*, **No. 14**, 1325 (1974).
(7) L. F. Fieser and M. Fieser, "Reagents for Organic Synthesis", Vol. I, Wiley-Interscience, New York, N.Y., 1967, pp 442–444.
(8) D. G. Stecher, Ed., "Merck Index", 8th ed, Merck and Co., Inc., Rahway, N.J., 1968, p 749.
(9) Reference 8, p 747.

Formation of *gem*-Dinitrates from Acetaldehyde and Trifluoroacetaldehyde[1]

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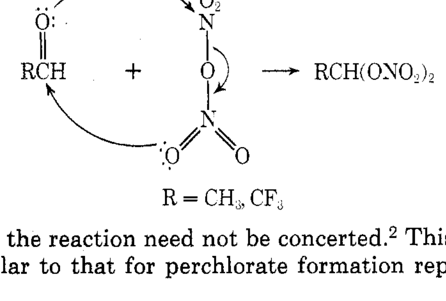
The new *gem*-dinitrates 1,1-dinitratoethane, $CH_3CH(ONO_2)_2$, and 1,1,1-trifluoro-2,2-dinitratoethane, $CF_3CH(ONO_2)_2$, have been synthesized by the reaction between dinitrogen pentoxide and acetaldehyde and trifluoroacetaldehyde. The combination of the aldehydes and N_2O_5 in a 1:1 mole ratio can be explained by the heterolytic cleavage of the latter involving a nucleophilic oxygen atom attack, i.e.



$R = CH_3, CF_3$

although the reaction need not be concerted.[2] This route is also similar to that for perchlorate formation reported by

Table I
Vibrational Spectra of $CF_3CH(ONO_2)_2$

Raman		Infrared		
Frequency, cm^{-1}	Intensity	Frequency, cm^{-1}	Intensity	Tentative assignments
		2996	wm	ν_{C-H} and
		2975	sh	combination 1280 + 1718
		1786	w	
1712 dp	2	1718 doublet		ν_{NO_2} (antisym)
1700 dp	2	1705 doublet	vs	
1458	1			
1375 dp	3	1365	m	ν_{C-F}
1350 dp	3	1348	sh	
1312	26	1302	m	ν_{NO_2} (sym)
1281	2	1280	vs	ν_{C-F} region
		1210	vs	
1181	2	1178	vs	
1086	3	1081	m	
1026	1	1029	ms	
912	17	906	m	ν_{C-O}
837	29	829	vs	ν_{N-O}
781	4	780	s	π_{NO_2}
762	5			
743	2	730	w	
700	6	690	wm	δ_{NO_2} (sym)
650 dp	9			
612 sh				combination 262 + 343
594	19	595	ms	δ_{NO_2} (antisym)
536 dp	13	566		CF_3 group bending and rocking deformations
525 dp	14			
381 sh	17			
356	32			
343 sh				
262	100			δ_{CON}

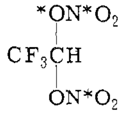
Baum[3] and to that for acylal formation by reaction of an aldehyde with an acid anhydride.[4]

The chemical and physical properties, as well as the synthetic stoichiometry, match the proposed structure for both compounds and appear to favor it over other possibilities. On standing at room temperature or above, $CF_3CH(ONO_2)_2$ appears to decompose to the initial reactants, dinitrogen pentoxide or the elements thereof and trifluoroacetaldehyde. The former is inferred via its decomposition product, NO_2. Nitrogen dioxide is also a thermal decomposition product of alkyl nitrates.[5] The mass spectrum, too, substantiates this result because, upon excitation from electron impact, the compound shows many fragmentation ions common to nitrogen oxides and trifluoroacetaldehyde. The compound hydrolyzes in alkali by a similar path, i.e., by loss of N_2O_5, present in the form of nitrate ion, to give trifluoroacetaldehyde, witnessed by its hydrolysis product, fluoroform.[6] A small amount of nitrite is formed and its

$$CF_3CH(ONO_2)_2 + 2OH^- \longrightarrow CF_3C(O)H\cdot aq + 2NO_3^- + H_2O$$
$$CF_3C(O)H\cdot aq \longrightarrow \text{fluoroform}$$

presence is puzzling; however, it is known that covalent nitrates can produce both nitrate and nitrite ions upon hydrolysis, although nitrate ion is commonly the major product.[5] The thermal disintegration of $CH_3CH(ONO_2)_2$ is strikingly different than that of the trifluoro derivative not only because it disappears at a much faster rate but also because acetaldehyde is not a main product while both HNO_3 and NO_2 are major products. The small amount of CH_3COOH monomer is present owing to oxidation of CH_3CHO by HNO_3. This reaction also explains the presence of N_2O. Analogous to $CF_3CH(ONO_2)_2$, however, 1,1-dinitratoethane yields acetaldehyde and nitrate from base hydrolysis. Refer to the Experimental Section.

The infrared spectrum of $CF_3CH(ONO_2)_2$ is interpreted in terms of the tentative assignments in Table I that are the best choices for the more diagnostic absorption bands.[5,7,8] Also, to further substantiate the nitrogen–oxygen and carbon–oxygen vibrational assignments, tagged ^{17}O dinitrogen pentoxide was prepared by the glow discharge of nitrogen and isotopically enriched oxygen. If the mechanism is correctly described above, then the tagging should appear in the following way.



$$CF_3CH(O^*N^*O_2)_2$$

That is, only one oxygen, from the original carbonyl group, should not be labeled. Consequently, all the X–^{16}O frequencies should become diminished in intensity and bands due to the heavier oxygen atom should appear at lower frequencies. This indeed has been found to be the case. The frequencies ascribed to the NO_2 group stretching and bending motions as well as the N–O and C–O stretching frequencies all show the predicted changes.[9] Furthermore, the splitting of the C–O stretching band at 912 cm^{-1} agrees with the labeled structure and justifies the assignment. Also, all six of the $-ONO_2$ group fundamental frequencies have been assigned.

The infrared spectrum of $CH_3CH(ONO_2)_2$ in the 2.7–15-μ region shows nitrate absorptions at 1722, 1300, 859, 810, and 680 cm^{-1}. The intensities and frequencies are close to those measured for the $CF_3CH(ONO_2)_2$ congener. A band at 910 cm^{-1} near the 906-cm^{-1} absorption in $CF_3CH(ONO_2)_2$, assigned to the C–O stretching vibration, is also present. Bands in the C–H stretching[10] and bending[11] regions are also present.

The NMR spectra of these compounds are also consistent with their formulation (Table II). For $CF_3CH(ONO_2)_2$, the ^{17}O spectrum is of particular interest. It shows two absorptions, at 340 and 430 ppm in a 1:4 area ratio and assigned to the **O**NO$_2$ and ON**O$_2$** oxygen nuclei, respectively. These chemical shifts compare favorably with those obtained from our measurements on other nitrates, e.g., $CH_3C(O)ONO_2$ at 360 (**O**NO$_2$) and 485 ppm (ON**O$_2$**) and N_2O_5 at 331 (N**O**N) and 469 ppm (ON**O$_2$**). Furthermore, the area ratio is expected from the structural formula, above, that shows the positions of the tagged oxygen atoms. The ^1H spectrum of the hydrocarbon derivative shows the predicted two resonances, one for the methyl and the other for the CH group, having proper area ratio and coupling constant.

Table II
NMR Spectra

Compd	$^{19}F^a$	$^{17}O^b$	$^1H^c$	Area ratios
$CH_3CH(ONO_2)_2$	81.3	340, 430	6.2	1:4.0 (^{17}O)
$CF_3CH(ONO_2)_2$			0.37, 6.0^d	2.99:1.0 (^1H)

[a] ϕ^* relative to CCl_3F. [b] Relative to $H_2{}^{17}O$. [c] Relative to Me_4Si. [d] The resonance at 0.37 is a doublet and the one at 6.0 is a quartet, $J = 6$ Hz.

The mass spectra of the dinitratoethanes are similar to a large degree since there are many analogous fragment ions predicted from their assumed structure. In both cases the most abundant ions are NO_2^+, CHO^+ and NO^+. Also, both show the molecule ion less a NO_3 group. Only $CF_3CH(ONO_2)_2$ exhibits a molecule ion.

Experimental Section

General Procedures. Trifluoroacetaldehyde was prepared by the slow addition of trifluoroacetaldehyde ethyl hemiacetal to a large excess of a 50% by weight mixture of 85% orthophosphoric acid and phosphorus pentoxide, polyphosphoric acid, at 170°. The volatile products were passed through traps set at −80 and −126°. The latter contained the trifluoroacetaldehyde and the former unreacted hemiacetal. The dinitrogen pentoxide was made by combining excess ozone with dinitrogen tetroxide within the reactor for the dinitrate synthesis. Enriched ^{17}O (14%) oxygen was purchased from Yeda R & D Co., Ltd., Divison of Miles Laboratories, Inc.

A standard Pyrex-glass vacuum apparatus with an attached preparative gas chromatograph was used to manipulate and purify volatile chemicals. The ozone was generally prepared using a Welsbach Corp. ozonator and collected in a flow-through Pyrex bulb and then separated from the unconverted oxygen by passage through a trap maintained at −196°. Vapor pressures were determined using a diaphragm pointer gauge described for Foord.[12] A cathetometer was employed to observe the null on the pointer, and pressures were monitored with a Wallace and Tiernan Series 1500 gauge. A water bath with an immersion heater was used for temperature control.

Infrared spectra were recorded with a Perkin-Elmer 21 infrared spectrometer. Gas samples were placed in 10-cm path length cells, either Pyrex or Monel, with sodium chloride or silver chloride windows. The spectrum of $CH_3CH(ONO_2)_2$ was recorded at pressures up to 15 Torr and that of $CH_3CH(ONO_2)_2$ at about 2–3 Torr. Raman spectra of liquid samples were obtained with a Spectra-Physics Model 125 helium–neon laser and a Spex Model 1401 double monochrometer. Samples were sealed in Pyrex tubes and excited by the 6328-Å laser line. Table I shows the infrared and Raman spectra of $CF_3CH(ONO_2)_2$. The ^1H NMR spectra were taken with a Varian Model A-60D NMR spectrometer at 56.4 and 8.13 MHz, respectively. Samples were placed in 5-mm o.d. tubes and all spectra were measured between 0 and −30°. External standards were used. See Table II. A Hitachi Perkin-Elmer RMU-6D mass spectrometer operating at 10–70 eV was used to obtain the mass spectra, and the inlet system was at room temperature.

Synthesis and Properties of $CF_3CH(ONO_2)_2$. Dinitrogen tetroxide (1.2 mmol, corrected for monomer) and an excess of ozone, but added in increments, were distilled at −196° into a 100-ml Pyrex reactor. The reactor was allowed to warm very slowly to about −80° and then recooled to −196°. This process was repeated several times until the blue color of liquid ozone no longer appeared on recooling. More ozone was added and the procedure was repeated until the blue color permanently remained. The N_2O_4 was thus completely converted to N_2O_5. The excess ozone was pumped out and then CF_3CHO (1.2 mmol) was distilled into the reactor at −196°. The reactor was brought to −80° and then allowed to warm slowly to −30° over a 4-hr period. The reaction had terminated within this period and the products were slowly distilled through cold traps at −64 and −196°.

The $CF_3CH(ONO_2)_2$ (1.1 mmol, 92% recovery) was retained at −64°, and a trace of the dinitrate as well as small quantities of NO_2 and HNO_3 were collected in the latter. The contents of the −64° trap were then passed through the preparative GC consisting of a 5-ft Pyrex column containing KEL-F grease on Fluoropak 80 at a 60 ml/min helium flow rate; retention time of $CF_3CH(ONO_2)_2$ 9.5 min; gas density molecular weight 208 g/GMV (theory 206); glasses, flow point at −116°; vapor pressures, reported as $P_{(\mathrm{Torr})}$ (temp, °C) 18.2 (0.0), 25.7 (6.2), 32.0 (11.2), 41.5 (15.9), 52.4 (20.9), 80.7 (30.4), 100.7 (33.4), 113.2 (35.4), 145.4 (42.1), 153.3 (44.1), 187.0 (49.9). Decomposition at higher temperatures was too rapid for meaningful measurements. The boiling point (extrapolated) was 85.7°; latent heat and entropy of vaporization 8.392 kcal/mol and 23.3 eu, respectively; vapor pressure equation in the above indicated temperature range $\log P_{(\mathrm{torr})} = -1834/T + 7.966$; mass spectrum NO_2^+, CHO^+, NO^+, CF_3^+, CO_2^+, CO^+, O_2^+, CHF_2^+, CF_2^+, CF_3CHO^+, CF^+, CF_3CH^+, CF_2CH^+, $CF_3CH(ONO_2)^+$, CF_3CO^+, and molecular ion (very low intensity) in the order of decreasing intensity.

Anal. Calcd for $C_2HF_3N_2O_6$: C, 11.65; H, 0.485; N, 13.59. Found: C, 11.66; H, 0.57; N, 13.50.

Synthesis and Properties of $CH_3CH(ONO_2)_2$. A similar procedure (vide ante) was used to prepare this compound. Dinitrogen tetroxide (1.18 mmol) was introduced into the same reactor and was converted to N_2O_5. Acetaldehyde (0.75 mmol) in a 1:10 mole ratio with dry nitrogen was added into the reactor at −45° in very small aliquots over a several-hour period. When all the aldehyde was placed into the reactor, it was cooled to −196° and the nitrogen was pumped out, and then the mixture was allowed to warm very slowly to approximately 0°. The product was purified by distillation through traps kept at −18 and −196°.

The $CH_3CH(ONO_2)_2$ (0.62 mmol, 83% recovery) remained in the former while the excess N_2O_5, along with traces of NO_2 and HNO_3 (0.45 mmol total), was held in the latter. The $CH_3CH(ONO_2)_2$ is a colorless liquid, mp −45.7 ± 0.7°, and has several Torr vapor pressure at 24°: ir spectrum 3040 (w), 2990 (w), 1722 (vs), 1455 (w), 1395 (w), 1350 (w), 1300 (ms), 1098 (m, br), 1076 (sh), 928 (sh), 910 (m), 859 (ms), 810 (s), 743 (w) (possibly due to N_2O_5 trace impurity) and 680 cm^{-1} (m, br); mass spectrum, given in the order of decreasing ion intensity, NO_2^+, NO^+, CHO^+, CO_2^+ and CH_3CHO^+, CH_3CO^+, CH_3^+, CO^+ and CH_3CH^+, CH_2^+ and N^+, $CH_3CH(ONO_2)^+$, CH_2CO^+, $C_2H_2^+$, CH^+, $CHCO^+$, C^+, $C_2H_3^+$, O_2^+, and HNO_3^+.

Anal. Calcd for $C_2H_4N_2O_6$: C, 15.79; N, 18.42; H, 2.63. Found: C, 16.32; N, 18.32; H, 2.82.

Caution: The direct combination of CH_3CHO and N_2O_5 (neat) at −196° leads to a violent explosion. In one elementary analysis trial a sample exploded upon being placed in the hot zone of the C, H, N analyzer.

Synthesis of ^{17}O-Enriched N_2O_5. Oxygen-17 enriched N_2O_5 in each oxygen position was prepared in a Pyrex-glass glow-discharge apparatus in the following way. Equal amounts of nitrogen and labeled oxygen were placed in the discharge at −80° to form $N^{17}O$, which was then allowed to react with excess enriched oxygen to form $N_2{}^{17}O_4$. Ozone was prepared by subjecting $^{17}O_2$ to a discharge at −196°. The $N_2{}^{17}O_5$ was finally obtained from the reaction of $N_2{}^{17}O_4$ with ozone in the manner illustrated previously.

Aging and Hydrolysis. The ir cell described above was loaded with $CF_3CH(ONO_2)_2$ to 10 Torr pressure and allowed to stand at ambient temperature while the ir spectrum was recorded periodically. After 1.5 hr a small amount of decomposition took place and CF_3CHO and NO_2 were the observed products. Upon more prolonged standing, much smaller amounts of CF_3COOH and HNO_3 were found. The decomposition was only partial after 24 hr. A sample of $CF_3CH(ONO_2)_2$ (0.75 mmol) was dissolved in 10% NaOH solution and after standing for several hours at ambient temperature an ir spectrum of the volatile substances over the aqueous solution revealed that fluoroform was produced. Spectrophotometric analysis[13] for nitrate and nitrite, mutually present, indicated NO_3^- (0.93 mmol) and NO_2^- (0.33 mmol).

The $CH_3CH(ONO_2)_2$ is less thermally stable. At ambient temperature the liquid immediately evolved HNO_3 and NO_2 and a viscous liquid residue remained. The decomposition of a gaseous sample of this compound at room temperature produced NO_2, HNO_3, N_2O, CH_3CHO, and probably CH_3COOH monomer, a minor product, according to ir analysis. Initially, NO_2 and HNO_3 were apparent, and CH_3CHO grew in slowly but reached a maximum after a few hours. The HNO_3 also attained its maximum concentration within this period but decreased as time progressed and a new species believed to be CH_3COOH was observed, and N_2O also appeared. Acetaldehyde was a minor product, and within 18 hr no $CH_3CH(ONO_2)_2$ remained. Hydrolysis was accomplished by adding excess base, described above, to a 0.23-mmol sample. An emulsion formed which slowly dissipated within 1 hr of gentle warming and stirring. The odor of acetaldehyde was apparent and the solution turned yellow. Because of the acetaldehyde carbonyl group absorption, λ_{max} 283 nm, that interferes with the spectrophotometric measurements of NO_3^- and NO_2^-, an alternate procedure[14] was used: NO_3^- (0.38 mmol), NO_2^- (ca. 0.05 mmol).

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Registry No.—$CF_3CH(ONO_2)_2$, 55044-05-8; $CH_3CH(ONO_2)_2$, 55044-04-7; trifluoroacetaldehyde, 75-90-1; trifluoroacetaldehyde ethyl hemiacetal, 433-27-2; dinitrogen tetroxide, 10544-72-6; dinitrogen pentoxide, 10102-03-1; acetaldehyde, 75-07-0.

References and Notes

(1) This study was prompted because of the relevance of nitrogen oxides (NO_x) and hydrocarbons to atmospheric chemistry in the urban environment. Unusual nitrate structures have been reported to be formed, acylperoxy nitrates, and it was intented to isolate and more completely characterize some of these substances which have short lifetimes. Our results were unexpected since *gem*-dinitrates were formed. A synthesis involving a fluorinated aldehyde was selected because it would yield a product of greater stability which would lead to a more thorough structural characterization that could be used to compare with $CH_3CH(ONO_2)_2$.

(2) A. L. Ternay, Jr., D. Deavenport, and G. Bledsoe, *J. Org. Chem.*, **39**, 3268 (1974).

(3) K. Baum and C. D. Beard, *J. Am. Chem. Soc.*, **96**, 3223 (1974).

(4) D. R. Husted and A. H. Ahlbrecht, *J. Am. Chem. Soc.*, **74**, 5422 (1952).

(5) C. C. Addison and N. Logan, *Adv. Inorg. Chem. Radiochem.*, **6**, 71 (1964).

(6) H. Shechter and F. Conrad, *J. Am. Chem. Soc.*, **72**, 3371 (1950).

(7) A. H. Arvia, L. F. R. Cafferata, and H. J. Schumacher, *Chem. Ber.*, **96**, 1187 (1963).

(8) E. L. Eduardo and G. C. Pimentel, *Spectrochim. Acta, Part A*, **30**, 1096 (1974).

(9) Examples of the more prominent frequency and band shape changes in the Raman influenced by isotopic substitution are as follows: the two lines near 1700 cm^{-1} are shifted to one centered at 1681 cm^{-1}, the 1312-cm^{-1} line is broadened and reduced in intensity, the line at 912 cm^{-1} shows splitting and a new one appears at 881 cm^{-1}, 837 shifts to 831 cm^{-1} and 594 to 587 cm^{-1}.

(10) J. C. D. Brand and T. M. Cawthon, *J. Am. Chem. Soc.*, **77**, 319 (1955).

(11) N. B. Colthrup. L. H. Daly, and S. E. Wiberly, "Introduction to Infrared and Raman Spectroscopy", Academic Press, New York, N.Y., 1964, pp 193–199.

(12) S. G. Foord, *J. Sci. Instrum.*, **11**, 126 (1934).

(13) J. H. Wetters and K. L. Uglum, *Anal. Chem.*, **42**, 335 (1970).

(14) I. M. Kolthoff and R. Bolcher, "Volumetric Analysis", Vol. III, Interscience, New York, N.Y., 1957, p 184.

Thermolysis of *N,N'*-Dimethyldiazenedicarboxamide

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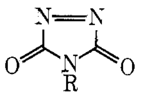
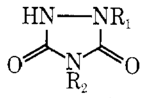
Investigation of the thermal decomposition of carbamoyl-substituted azo compounds has been limited to *N,N'*-diphenyldiazenedicarboxamide,[2] 2-cyano-2-propylazoformamide,[3] and, most recently, diazenedicarboxamide (**1a**) and *N,N'*-diethyldiazenedicarboxamide (**1b**).[4] In the latter study, Fantazier and Herweh convincingly demonstrated that the thermal decomposition of **1a** involves two competitive processes: cyclization of *cis*-**1a** to the unstable triazoline (**2a**) and thermal decomposition of **1a** to produce nitrogen and formamoyl radicals. These authors reported that the thermolysis of **1b** in dimethyl sulfoxide (DMSO) affords 4-ethylurazole (**3a**) and a product that was tentatively identified as tris(*N*-ethylcarbamoyl)hydrazine (**4a**).

RNHCON=NCONHR
1a, R = H
b, R = Et
c, R = Me



2a, R = H
b, R = Me
c, R = Ph



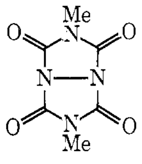
3a, R_1 = H; R_2 = Et
b, R_1 = H; R_2 = Me
c, R_1 = CONHMe; R_2 = Me

This note reports the results of our study of the thermolysis of *N,N'*-dimethyldiazenedicarboxamide (**1c**). Neat thermolysis of **1c** at 176° resulted in rapid, exothermic decomposition yielding 1,3-dimethylurea (47%), 4-methylurazole (**3b**, 37%), and small amounts of 1-methylcarbamoyl-4-methylurazole (**3c**). The volatile components of the reaction were identified as nitrogen (28%), carbon monoxide (8%), and an undetermined quantity of methyl isocyanate. Thermolysis of **1c** in DMSO (120°) gave 36% of 4-methylurazole and unidentified dark oils.

When the thermolysis of **1c** was conducted in refluxing *o*-dichlorobenzene, a very small quantity of 1,3-dimethylurea was formed and no 4-methylurazole could be isolated. Under these conditions, the major product is *N,N'*-dimethyl-1,2-hydrazinedicarboxamide (**5a**, 41%). Small quantities (6% each) of **3c** and 3,7-dimethyl-2,4,6,8-tetraoxo-1,3,5,7-tetraazabicyclo[3.3.0]octane (**6**) were isolated.

$(RNHCO)_2NNHCONHR$
4a, R = Et
b, R = Me

RNHCONHNHCONHR
5a, R = Me
b, R = Et



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Under these conditions, 31% of water-insoluble gases (assumed to be nitrogen and carbon monoxide) were obtained.

Thermolysis of *N,N'*-diethyldiazenedicarboxamide (**1b**)