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).

Acknowledgments.—This work was sponsored by the Environmental Protection Agency, Grant R802966-01. The authors are grateful to Ms. Anne O'Donnell for her analytical chemistry support and to Drs. James Keith and Alan Snelson for their advice.

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 $CH_3CH(ONO_2)_2$.

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Thermolysis of *N,N′*-Dimethyldiazenedicarboxamide

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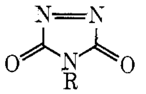
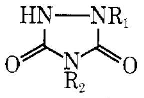
Investigation of the thermal decomposition of carbamoyl-substituted azo compounds has been limited to *N,N′*-diphenyldiazenedicarboxamide,[2] 2-cyano-2-propylazoformamide,[3] and, most recently, diazenedicarboxamide (**1a**) and *N,N′*-diethyldiazenedicarboxamide (**1b**).[4] In the latter study, Fantazier 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



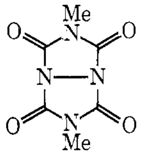
3a, R_1 = H; R_2 = Et
b, R_1 = H; R_2 = Me
c, R_1 = CONHMe; R_2 = Me

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



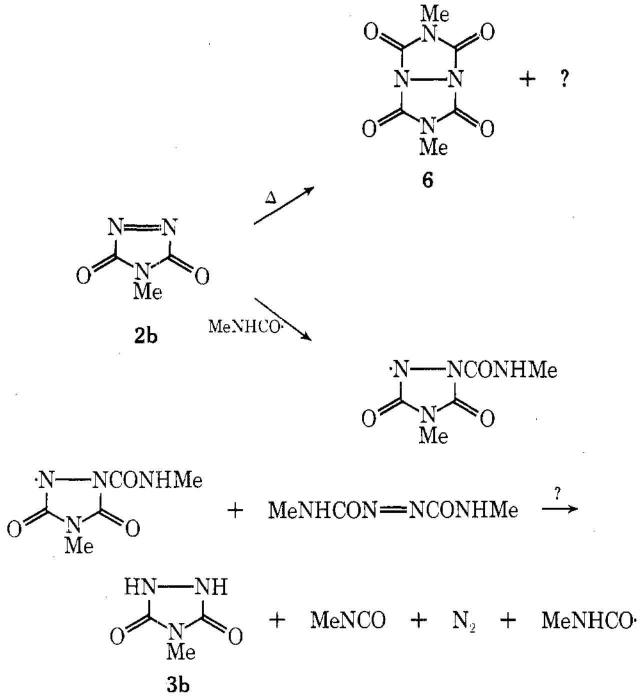
6

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

Thermolysis of *N,N′*-diethyldiazenedicarboxamide (**1b**) in refluxing *o*-dichlorobenzene gave *N,N′*-diethyl-1,2-hydrazinedicarboxamide (**5b**) in 53% yield.

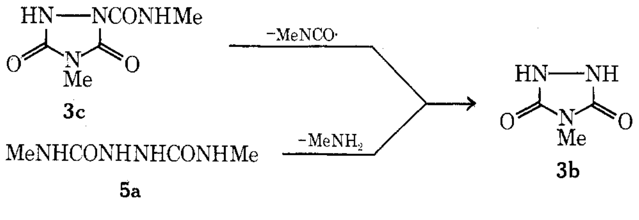
The products obtained from the thermal decomposition of **1c** may be accounted for by assuming that the azo compound initially decomposes by pathways analogous to those proposed for diazenedicarboxamide (**1a**),[4] i.e., trans → cis isomerization followed by cyclization to 4-methyl-3*H*-1,2,4-triazole-3,5(4*H*)-dione (**2b**) and, competitively, thermal decomposition of **1c** to produce nitrogen and methylcarbamoyl radicals. We have conducted control experiments that implicate the triazoline **2b** as an intermediate leading to the formation of both **3c** and **6.**

The reaction of equimolar quantities of **1c** and **2b**[5] in refluxing *o*-dichlorobenzene gave **3c** in 54% yield. This experiment supports the formation of **3c** via addition of methylcarbamoyl radicals to the N=N bond of **2b.** We have designated **1c** as a probable hydrogen donor in the addition reaction. The bicyclic product **6** is apparently formed by thermal decomposition of **2b,** since thermolysis of **2b** in refluxing *o*-dichlorobenzene afforded a tarry reaction mixture from which it was possible to isolate **6.** The latter reaction finds precedence in the previously reported conversion of **2c** to the diphenyl analog of **6.**[6]



The formation of *N,N′*-dimethyl-1,2-hydrazinedicarboxamide (**5a**) may be accounted for by addition of methylcarbamoyl radicals to **1c** to give thermally unstable tris(*N*-methylcarbamoyl)hydrazine (**4b**), which is converted to **5a** by elimination of methyl isocyanate. The latter pathway is analogous to that proposed to account for the formation of biurea from thermal decomposition of **1a.**[4]

When **1c** is thermally decomposed in the absence of solvent by heating at 173°, the temperature of the reaction mixture was observed to rise to 259°. Under these conditions, 4-methylurazole may be formed by either cyclization of *N,N′*-dimethylhydrazinedicarboxamide (**5a**)[7] or by elimination of methyl isocyanate from 1-methylcarbamoyl-4-methylurazole (**3c**), since both **5a** and **3c** are quantitatively converted to 4-methylurazole when heated at 245 and 230°, respectively.



However, control experiments indicate that neither **3c** nor **5b** are reasonable precursors of 4-methylurazole and 4-ethylurazole, respectively, when the thermolysis reactions are conducted in DMSO. DMSO solutions of **3c** and **5b** gave unchanged starting material when heated at 115–120° for 24 hr. Reduction of the triazoline **2b** by methylamine[8] may serve as the source of 4-methylurazole under these conditions.

The formation of 1,3-dimethylurea is most reasonably explained by reaction of methyl isocyanate with either methylamine or moisture.

The formation of 8% carbon monoxide from the neat thermolysis of **1c** suggests an additional pathway for the decomposition of the intermediate triazoline **2b,** i.e., thermal decomposition to methyl isocyanate, carbon monoxide, and nitrogen.[9]

$$\mathbf{2b} \longrightarrow \mathrm{CO} + \mathrm{N_2} + \mathrm{MeNCO}$$

Methyl isocyanate was detected by odor and mass spectrometry and was chemically identified among the volatile products by conversion to 1-methyl-3-phenylurea and trimethyl isocyanurate. Methylamine could not be chemically detected among the volatile thermolysis products. However, the complex mass spectrum of the thermolysis products (200°) displayed a low-intensity methylamine molecular ion (*m/e* 31) and an M − 1 peak of approximately twice the intensity of the molecular ion, which is characteristic of the reported methylamine spectrum.[10]

Experimental Section

Melting points are uncorrected and were determined with a Mel-Temp apparatus. NMR spectra were determined on a Perkin-Elmer R-20 spectrometer utilizing hexamethyldisiloxane as the internal standard. Thin layer chromatography (TLC) was carried out on microscope slides coated with silica gel. Iodine vapor was employed as a visualizing agent. Unless otherwise indicated, chromatograms were developed with ethyl acetate–methanol (5:1).

Neat Thermolysis of *N,N′*-Dimethyldiazenedicarboxamide (1c). The azo compound[11] (12.0 g) was placed in a 100-ml flask fitted with an air condenser and heated at 176° for 5 min. A vigorous, exothermic reaction was observed. In a separate experiment, the temperature of the reaction mixture was observed to rise to 259°. The pungent odor of methyl isocyanate was apparent in the gases evolved. The semisolid residue (9.1 g) was digested with 80 ml of boiling chloroform. Filtration of the cooled suspension afforded 3.6 g (37%) of crude 4-methylurazole (**3b**), mp 215–235°. Recrystallization from water gave white needles, mp 233–235°. Identity was established by elemental analysis and by comparison of the ir spectrum and R_f value (TLC) with data from an authentic sample, mp 235–237° (lit.[7] mp 233°).

Evaporation of the chloroform solution afforded a hygroscopic yellow oil. NMR and TLC revealed a complex mixture with 1,3-dimethylurea as the major component. The 1,3-dimethylurea component of the mixture could be visualized on the TLC plate only after prolonged exposure to iodine vapor.

The oil obtained above was partitioned between 30 ml of chloroform and 30 ml of water. Evaporation of the aqueous solution in vacuo gave an oil which on trituration with 10 ml of ethanol gave 0.29 g of a white solid, mp 150–162° (two components by TLC). Similar treatment of the chloroform residue gave 0.15 g of white solid, mp 195–205°, which was not further investigated. Recrystallization of the material obtained from the aqueous residue from ethanol afforded 1-methylcarbamoyl-4-methylurazole (**3c**) as white crystals: mp 203–206°; ir (KBr) 1700 (s), 1780 cm^{-1} (m); mass spectrum *m/e* 172 (molecular ion); NMR (DMSO-d_6) δ 2.68 (d, ca. 3, *J* = 5 Hz, slowly converted to a singlet on addition of D_2O), 2.80 (s, ca. 3), 7.2–7.8 (broad NH, slow exchange, ca. 2). A low-intensity singlet was observed at δ 2.91 which was also present after D_2O exchange was complete. It is felt that this signal may be due to an additional CH_3NHCO signal caused by restricted rotation about the C–N bond. The other component of the expected doublet could be obscured by the δ 2.80 singlet. Identical results were observed with highly purified **3c** obtained from the reaction of **1c** with **2b**.

Anal. Calcd for $C_5H_8N_4O_3$: C, 34.9; H, 4.7; N, 32.6. Found: C, 35.1; H, 4.8; N, 32.7.

In a separate experiment, 10 g of the azo compound afforded 6.1 g of chloroform-soluble oil and 2.2 g of crude 4-methylurazole, mp 210–220°. A 0.50-g portion of the oil was distilled at 140° (0.1 mm) in a Kügelrohr distillation apparatus to give 0.23 g of colorless distillate which partially crystallized on standing. NMR and TLC established the material to be 1,3-dimethylurea: NMR δ 2.50 (d, J = 4 Hz), 5.8 (broad, NH). Several minor impurity peaks (<10%) were noted between δ 2.9 and 3.4. The extrapolated yield of distilled 1,3-dimethylurea from this experiment is 47%.

Decomposition of 0.25 g (1.7 mmol) of the azo compound at 180° in a flask connected to a gas buret gave 0.61 mmol (36%) of a mixture of CO and N_2. The mixture was determined to consist of 80% N_2 and 20% CO by comparison of peak heights in the high-resolution mass spectrum.

The presence of methyl isocyanate was detected in the gaseous products by carrying out the thermolysis of 1.0 g of **1c** in small portions and leading the effluent gases into a solution of 1.5 g of aniline in benzene. The benzene was evaporated and the residue was treated with 10 ml of 6 *N* HCl. The acid solution was extracted with chloroform. Evaporation of the chloroform gave a gummy residue that separated into two components with TLC. These components had the same R_f values as 1-methyl-3-phenylurea and trimethyl isocyanurate.

The complex mass spectrum of the thermolysis products (70 eV, 200°) included the following significant peaks: *m/e* (rel intensity, assignment) 198 (5, $\mathbf{7}\cdot^+$), 115 (14, $\mathbf{4}\cdot^+$), 88 (5, $CH_3NHCONHCH_3\cdot^+$), 57 (50, $CH_3NCO\cdot^+$), 31 (5, $CH_3NH_2\cdot^+$), 30 (10), 28 (100).

Thermolysis of *N,N'*-Dimethyldiazenedicarboxamide (1c) in *o*-Dichlorobenzene. The azo compound (15 g) was suspended in 300 ml of *o*-dichlorobenzene and the suspension was stirred and heated under reflux for 1.5 hr. Filtration of the hot suspension afforded 6.1 g (41%) of crude *N,N'*-dimethyl-1,2-hydrazinedicarboxamide (**5a**), mp 227–232°. Identity was established by comparison of the ir spectrum and R_f values (TLC) with data from an authentic sample, mp 256° (lit.[7] mp 260°).

The cooled dichlorobenzene filtrate afforded a solid that was suspended in 30 ml of boiling ethanol. Filtration of the hot suspension gave 0.63 g (6%) of 3,7-dimethyl-2,4,6,8-tetraoxo-1,3,5,7-tetraazabicyclo[3.3.0]octane (**6**), mp 300–303°. Recrystallization from aqueous *N,N*-dimethylformamide gave white crystals: mp 303–304°; ir (KBr) 1760 cm^{-1}; mass spectrum *m/e* 198 (molecular ion); NMR (DMSO-d_6) δ 2.88 (s).

Anal. Calcd for $C_6H_6N_4O_4$: C, 36.4; H, 3.1; N, 28.3. Found: C, 36.5; H, 3.0; N, 28.5.

The cooled ethanol filtrate deposited 0.51 g (6%) of crude 1-methylcarbamoyl-4-methylurazole (**3c**), mp 176–182°. After recrystallization from ethanol, white crystals, mp 196–198°, were obtained. Identity was established by comparison of the ir spectrum with that of an authentic sample.

In a separate experiment, 3.0 g of the azo compound was decomposed as described above, giving 1.43 g of solid material which was insoluble in *o*-dichlorobenzene. The filtrate was evaporated in vacuo to give 0.42 g of an oil which partially crystallized on standing. The NMR spectrum of this material revealed it to be a complex mixture with 1,3-dimethylurea as the major component.

Decomposition of 0.50 g (35 mmol) as described above resulted in the evolution of 11 mmol (31%) of water-insoluble gases.

Preparation of 1-Methylcarbamoyl-4-methylurazole (3c). A solution containing 2.15 g (0.019 mol) of **2b**[5] and 2.74 g (0.019 mol) of **1c** in 100 ml of *o*-dichlorobenzene was heated and stirred under reflux for 2 hr. After decantation of the hot solution from a small amount of tarry material the cooled solution deposited 1.78 g (54%) of crude product (mp 164–185°) which on recrystallization from ethanol afforded 0.82 g of white crystals, mp 200–203°. An additional recrystallization raised the melting point to 204–206°. The NMR spectrum of the product was identical with that of the material isolated from the thermolysis of **1c**.

When heated at 230° for 12 hr, **3c** evolved methyl isocyanate and was quantitatively converted to 4-methylurazole, mp 225–228°.

Thermal Decomposition of 4-Methyl-3*H*-1,2,4-triazole-3,5(4*H*)-dione (2b). The triazoline[5] (0.5 g) was suspended in 5 ml of *o*-dichlorobenzene and heated under reflux with stirring for 2 hr. The solution was decanted from tarry material and allowed to evaporate. A yellow powder (0.2 g), mp 240–260°, was obtained which was identified as **6** from its NMR and ir spectra (no impurity peaks were noted in the NMR spectrum).

Thermolysis of *N,N'*-Dimethyldiazenedicarboxamide (1c) in Dimethyl Sulfoxide. A solution of 2.0 g of **1c** in 30 ml of dimethyl sulfoxide was heated at 120° for 22 hr. The solvent was removed in vacuo and the dark residue was treated with 10 ml of chloroform. Filtration yielded 0.55 g (36%) of crude 4-methylurazole (identified by ir and TLC), mp 195–203°. The filtrate deposited 60 mg of unidentified material, mp 225–228°. Evaporation of the chloroform gave a dark oil.

Thermolysis of *N,N'*-Diethyldiazenedicarboxamide (1b) in *o*-Dichlorobenzene. The azo compound[12] (1.5 g) was suspended in 30 ml of *o*-dichlorobenzene and heated under reflux with stirring for 1 hr. Stirring was continued at room temperature overnight. Filtration afforded 0.8 g of crude *N,N'*-diethylhydrazinedicarboxamide (**5b**), mp 230–235°. Identity was established by comparison of the ir spectrum with that obtained from an authentic sample,[13] mp 247–249°. Evaporation of the filtrate gave an uncharacterized oil.

Acknowledgment. We thank the donors of the Petroleum Research Fund, administered by the American Chemical Society, and the Research Foundation of State University of New York for support of this project. We are indebted to Professors Martin S. Gibson and Albert Padwa for providing the mass spectra. We also wish to acknowledge the cordial cooperation of Drs. J. E. Herweh and R. M. Fantazier in providing preprints of their diazenedicarboxamide results and valuable discussions.

Registry No.—**1b**, 18880-19-8; **1c**, 18880-14-3; **2b**, 13274-43-6; **3b**, 16050-65-0; **3c**, 55029-97-5; **5a**, 2937-76-0; **5b**, 2937-75-9; **6**, 55029-98-6; 1,3-dimethylurea, 96-31-1; 1-methyl-3-phenylurea, 1007-36-9; trimethyl isocyanurate, 827-16-7.

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Nucleosides. XVII. Benzylation–Debenzylation Studies on Nucleosides

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The present study was prompted by an internal need to develop a facile blocking–deblocking sequence of the –CONH– moiety in uridine (1) and guanosine (3) so that the corresponding (blocked) intermediates would be amenable to purification via anion exchange chromatography.