

mass spectrum (70 eV) m/e (relative intensity) 194 (48), 175 (20), 110 (19), 91 (100), 69 (33). *Anal.* Calcd for $C_6H_4F_6O$: C, 30.94; H, 2.08. Found: C, 30.62; H, 2.07. The third peak was identified as *cis*-1,1,1,4,4,4-hexafluoro-2-methoxy-2-butene (III): ir (vapor) 1680 ($C=C$), 1466 (CH_3), 1400 (CH_3), 1320 (CF), 1269 (CF), 1181 (CF), 1125 (CO), 914 ($C=C<\overset{H}{\text{H}}$); mass spectrum (70 eV) m/e (rel intensity) 194 (48), 175 (14), 110 (19), 91 (100), 69 (36).

Hexafluoro-2-butyne, Methanol, and Sodium Methoxide.—Hexafluoro-2-butyne (1.30 g, 8 mmol) and 8 mmol (0.256 g) of absolute methanol were condensed into a 500-ml reaction vessel containing *ca.* 0.8 mmol (42.9 mg) of sodium methoxide and the resulting solution was allowed to stand (room temperature) for 10 hr. The infrared showed a strong absorption at 1695 cm^{-1} and showed that no butyne was present. The procedure described above was used to isolate the components from the reaction mixture. Two major peaks accounting for 98.6% of the material present were collected by glc and identified as *trans*-1,1,1,4,4,4-hexafluoro-2-methoxy-2-butene (II), 97.8%, and *cis*-1,1,1,4,4,4-hexafluoro-2-methoxy-2-butene (III), 2.2%. No peak corresponding to *trans*-1,1,1,2,4,4,4-heptafluoro-2-butene (IV) appeared.

Attempted Isomerization of *cis*-1,1,1,4,4,4-Hexafluoro-2-methoxy-2-butene (III) with Triethylamine.—*cis*-1,1,1,4,4,4-Hexafluoro-2-methoxy-2-butene (0.0305 g, 0.157 mmol) was sealed in an nmr tube with 0.015 mmol (0.0015 g) of triethylamine and 0.75 mmol of tetramethylsilane. The nmr taken immediately after the sample tube had reached room temperature and the nmr taken after 3 days at room temperature were identical with the spectrum of the *cis*-vinyl ether (III). Then 0.015 mmol (4.8×10^{-4} g) of absolute methanol was condensed into the nmr tube containing the *cis* compound and the triethylamine. After 3 days, the nmr spectrum showed only the *cis* compound III present.

Trifluoromethylacetylene, Methanol, and Triethylamine.—Trifluoromethylacetylene (0.376 g, 4 mmol) and 4 mmol (0.128 g) of absolute methanol were condensed into a 500-ml reaction vessel and allowed to come to room temperature. After 20 hr, infrared analysis showed no reaction. Triethylamine (0.04 g, 0.4 mmol) was then condensed into the reaction vessel. After 7 hr, no reaction could be detected, so another 0.4 mmol (0.04 g) of triethylamine was added. After 39 hr, the reaction mixture had turned brown, but no carbon-carbon double bond could be found in the ir. Unreacted $CF_3C\equiv CH$ (0.229 g, 2.44 mmol) was recovered from the reaction.

Trifluoromethylacetylene, Methanol, and Sodium Methoxide.—Trifluoromethylacetylene (0.780 g, 8.3 mmol) and 8 mmol

(0.256 g) of absolute methanol were condensed into a 1-l. reaction vessel with 1.6 mmol (0.0534 g) of sodium methoxide and allowed to come to room temperature. After 3 hr, an absorbance at 1690 cm^{-1} was observed in the ir. After 45 hr of reaction, the mixture was separated *via* slush baths. The material from a -98° trap [CH_3OH , N_2 (liquid)] was separated *via* glc. Separation was carried out at room temperature. The material isolated from the liquid N_2 trap was unreacted $CF_3C\equiv CH$ (44.5%). Three major peaks were collected by glc of the contents of the -98° trap. The first peak collected was identified as *gem*-trifluoromethylmethoxyethene (VI): ir (vapor) 2941 (CH_3), 1667 ($C=C<\overset{H}{\text{H}}$), 1399 ($C=C<\overset{H}{\text{H}}$), 1370 (CH_3), 1277 (CO), 1205 (CF), 1177 (CF), 1156 (CF), 843 ($C=C<\overset{H}{\text{H}}$); mass spectrum (70 eV) m/e (rel intensity) 126 (100), 107 (8.5), 95 (20), 91 (17), 76 (14), 69 (35), 57 (33), 43 (31), 42 (32). The second peak corresponded to *trans*-1-methoxy-3,3,3-trifluoropropene (V): ir (vapor) 2933 (CH_3), 1672 ($\overset{H}{\text{H}}>C=C<\overset{H}{\text{H}}$), 1454 (CH_3), 1351 ($\overset{H}{\text{H}}>C=C<\overset{H}{\text{H}}$), 1242 (CF), 1178 (CF), 1123 (CF), 953 ($\overset{H}{\text{H}}>C=C<\overset{H}{\text{H}}$); mass spectrum (70 eV) m/e (rel intensity) 126 (100), 111 (6), 107 (19), 95 (42), 91 (33), 77 (34), 76 (18), 69 (38), 57 (18), 37.5 (0.5), 31 (92). The third peak corresponded to *cis*-1-methoxy-3,3,3-trifluoropropene (I): ir (vapor) 2933 (CH_3), 1692 ($\overset{H}{\text{H}}>C=C<\overset{H}{\text{H}}$), 1464 (CH_3), 1280 (CF), 1203 (CF), 1148 (CF), 718 ($\overset{H}{\text{H}}>C=C<\overset{H}{\text{H}}$); mass spectrum (70 eV) m/e (rel intensity) 126 (100), 111 (9), 107 (39), 95 (44), 91 (54), 77 (47), 76 (26), 69 (51), 59 (25), 51 (15), 37.5 (0.5), 31 (57). *Anal.* Calcd for $C_4H_5F_3O$: C, 38.11; H, 4.00. Found: C, 38.38; H, 4.40.

Registry No.—I, 26885-67-6; II, 400-21-5; III, 26885-69-8; IV, 17157-69-6; V, 26885-71-2; VI, 26885-72-3; methanol, 67-56-1; hexafluoro-2-butyne, 692-50-2; trifluoromethylacetylene, 661-54-1.

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The Synthesis of Fluorine-Containing Heterocyclic Nitramines¹

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Trifluoroacetaldehyde reacted readily with ammonia to give 2,4,6-tris(trifluoromethyl)hexahydro-*s*-triazine (1d), which on nitrosation gave the 1,3,5-trinitroso derivative 1e. 2,4,6-Trimethyl-1,3,5-trinitrosohexahydro-*s*-triazine (1f) could not be converted to the trinitro compound; the fluorine-containing trinitroso compound underwent this conversion successfully, although a displacement rather than an oxidation reaction was indicated. 2,2-Diaminohexafluoropropane condensed with formaldehyde and methylenedinitramine to give a mixture of 2,2-bis(trifluoromethyl)-5-nitrohexahydro-*s*-triazine (2b) and 2,2-bis(trifluoromethyl)-5,7-dinitro-1,3,5,7-tetraazacyclooctane (3c). Several *N*-nitroso and *N*-nitro derivatives of these two ring systems were prepared.

Saturated cyclic polyamines with rings composed of alternating carbon and nitrogen atoms, as in Chart I, tend to be unstable. Solutions of formaldehyde and ammonia contain hexahydro-*s*-triazine (1a), but it cannot be isolated from solution and probably is in equilib-

rium with open-chain forms and with ammonia and formaldehyde.^{3,4} Reported derivatives of 1a always have been stabilized by structural features such as the condensed tricyclic system in hexamethylenetetramine, the electronegative groups in RDX (1,3,5-trinitrohexahydro-*s*-triazine (1b), or the C-substituted alkyl groups in 2,4,6-trimethylhexahydro-*s*-triazine (1c); the cyclic

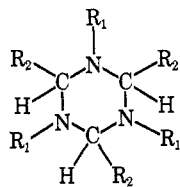
(1) Presented in part at the Third International Fluorine Symposium, Estes Park, Colo., July 24-28, 1967. The work was supported by Detachment 4, Eglin Field, U. S. Air Force.

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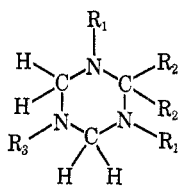
(3) P. Duden and M. Scharf, *Justus Liebig's Ann. Chem.*, **268**, 218 (1895).

(4) H. H. Richmond, G. S. Myers, and G. F. Wright, *J. Amer. Chem. Soc.*, **70**, 3659 (1948).

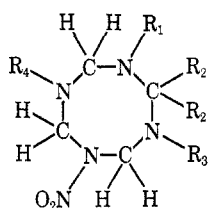
CHART I



- 1a, $R_1 = R_2 = H$
 b, $R_1 = NO_2; R_2 = H$
 c, $R_1 = H; R_2 = CH_3$
 d, $R_1 = H; R_2 = CF_3$
 e, $R_1 = NO; R_2 = CF_3$
 f, $R_1 = NO; R_2 = CH_3$
 g, $R_1 = NO; R_2 = H$
 h, $R_1 = NO_2; R_2 = H$
 i, $R_1 = NO_2; R_2 = CF_3$



- 2a, $R_1 = NO_2; R_2 = H; R_3 = CH_3$
 b, $R_1 = H; R_2 = CF_3; R_3 = NO_2$
 c, $R_1 = NO; R_2 = CF_3; R_3 = NO_2$
 d, $R_1 = R_3 = NO_2; R_2 = CF_3$



- 3a, $R_1 = R_3 = R_4 = NO_2; R_2 = H$
 b, $R_1 = NO_2; R_2 = H; R_3 = R_4 = CH_3$
 c, $R_1 = R_3 = H; R_2 = CF_3; R_4 = NO_2$
 d, $R_1 = NO; R_2 = CF_3; R_3 = H; R_4 = NO_2$
 e, $R_1 = R_3 = NO; R_2 = CF_3; R_4 = NO_2$
 f, $R_1 = R_4 = NO_2; R_2 = CF_3; R_3 = H$

structure of **1c**, "aldehyde-ammonia," has been questioned in the past but has been firmly established by more modern methods such as X-ray^{5,6} and infrared⁷ spectroscopy. A reaction product of chloral and ammonia is also believed to be cyclic. The eight-membered ring system of Chart I is known only in compounds stabilized by nitration or nitrosation of the nitrogen atoms. Two possible routes leading to analogs of RDX and HMX [1,3,5,7-tetraazacyclooctane (**3a**)] are (1) reaction of an aldehyde with an amine to give a cyclic, symmetrically substituted poly(secondary)amine, followed by N-nitration, and (2) condensation of a nitramine with an aldehyde and an amine to give a cyclic polyamine already partially stabilized by the nitramine function. This paper reports the synthesis of new compounds based on the hexahydro-*s*-triazine and 1,3,5,7-tetraazacyclooctane ring systems which are obtained by these two routes.

Trifluoroacetaldehyde reacted readily with ammonia even at -50° . As is the case with hexafluoroacetone, the initial adduct subsequently loses the elements of water rather than of ammonia (spontaneously in the case of trifluoroacetaldehyde); however, where hexafluoroacetone gives the monomeric imine, $(CF_3)_2C=NH$,⁸ trifluoroacetaldehyde gave the trimer, 2,4,6-tris(trifluoromethyl)hexahydro-*s*-triazine (**1d**). The compound was a stable, easily subliming solid.

Treatment of **1d** with dinitrogen tetroxide gave the

trinitroso compound, **1e**, in 58% yield; the corresponding nonfluorinated compound, **1f**, was obtained only in a much lower yield (14%) under somewhat milder conditions by nitrosation of commercial "aldehyde-ammonia." The fluorinated *N*-nitroso compound was the more stable of the two but did decompose at 25° over several days' time.

Oxidation of the C-unsubstituted trinitroso compound **1a** to RDX is well established.⁴ In contrast, the C-methyl compound **1f** failed under all conditions to give a product which could be characterized as the trinitramine **1h**; however, the tris(trifluoromethyl)nitroso compound **1e** was successfully converted to the trinitramine **1i** in 80% yield by treatment with a mixture of 100% nitric acid and trifluoroacetic anhydride. Although this reaction is ostensibly an oxidation, it does not seem to be so in fact, as other oxidizing agents were without effect, even peroxytrifluoroacetic acid, which is a very powerful and specific reagent for the nitrosamine-nitramine oxidation. In such a highly acid medium, a displacement of the nitrosonium ion by the nitronium ion, in an electrophilic attack at the nitrogen atom, seems plausible. The fluorinated trinitramine was also prepared by direct nitration of the hexahydrotriazine **1d**, but the resulting material was less easily purified than that made from the nitroso precursor. When pure, the trinitramine **1i** seemed to be indefinitely stable.

Methylamine condenses with methylenedinitramine (MEDINA) and formaldehyde to give derivatives of the hexahydro-*s*-triazine⁹ and 1,3,5,7-tetraazacyclooctane¹⁰ systems, specifically **2a** and **3b**. We investigated the condensation of alkylamines with MEDINA and trifluoroacetaldehyde, and with trifluoroethylidenedinitramine¹¹ and formaldehyde, in anticipation that a fluorine-containing cyclic compound would be formed in which the *N*-alkyl group might be converted into a nitro group by oxidative nitration. However, in spite of extensive investigation of reaction conditions, no cyclic condensation products were obtained from either of these two systems. A third possibility was the reaction of a fluorinated *gem*-diamine with MEDINA and formaldehyde, and this route proved to be successful.

Two attempts to prepare a fluorinated *gem*-diamine containing a single trifluoromethyl group were unsuccessful. The reduction of trifluoroacetamide, $CF_3C(=O)NH_2$, to 1,1-diamino-2,2,2-trifluoroethane failed, and hydrolysis of $CF_3CH(NHCHO)_2$ to $CF_3CH(NH_2) \cdot HCl$ gave only ammonia and unidentified fluorine-containing substances. The presence of a second trifluoromethyl group, however, stabilizes the *gem*-diamine structure, and $(CF_3)_2C(NH_2)_2$ is accessible by the method of Krespan.⁸ By analogy with the reaction of methylamine, condensation of the fluorinated diamine with MEDINA and formaldehyde would be expected to produce 2,2-bis(trifluoromethyl)-5-nitrohexahydro-*s*-triazine (**2b**) and 2,2-bis(trifluoromethyl)-5,7-dinitro-1,3,5,7-tetraazacyclooctane (**3c**). The condensation proceeded smoothly at 25° , and both of the anticipated products **2b** and **3c** were obtained. These were sep-

(9) F. Chapman, P. G. Owston, and D. Woodcock, *J. Chem. Soc.*, 1638 (1949).

(10) W. J. Chute, D. C. Downing, A. F. McKay, G. S. Myers, and G. F. Wright, *Can. J. Res., Sect. B*, **27**, 218 (1949).

(11) J. A. Krimmel, J. J. Schmidt-Collerus, J. A. Young, G. E. Bohner, and D. N. Gray, *J. Org. Chem.*, **36**, 350 (1971).

(5) N. F. Moerman, *Z. Krist.*, **98**, 447 (1938).

(6) E. W. Lund, *Acta Chem. Scand.*, **12**, 1768 (1958).

(7) A. Novak, *Spectrochim. Acta*, **16**, 1001 (1960).

(8) W. J. Middleton and C. G. Krespan, *J. Org. Chem.*, **30**, 1398 (1965).

arated from unidentified side products by fractional extraction with $\text{CF}_2\text{ClCFCl}_2$ (Freon 113) and were identified by elemental analyses and infrared spectra.

Nitrosation of the hexahydrotriazine derivative **2b** with dinitrogen tetroxide in acetic acid gave a 60% yield of a material whose ir spectrum indicated the absence of N-H and the presence of N=O bonds, presumably the structure **2c**. The material decomposed slowly at room temperature. Nitration of **2b** gave a 70% yield of the stable trinitramine **2d**.

The tetraazacyclooctane ring proved to be less tractable, and neither nitrosation nor nitration gave stable products capable of characterization. Nitrosation of the dinitramino compound **3c** with sodium nitrite and hydrochloric acid, or with nitrosium fluoroborate, was ineffective. The progressively stronger nitrosating systems of sodium nitrite in acetic anhydride¹² and dinitrogen tetroxide with sodium acetate¹³ gave materials which seemed to be, respectively, a dinitromononitroso and a dinitrodinitroso compound, according to their ir spectra, as shown by **3d** and **3e**. Both compounds decomposed slowly on standing, **3e** being somewhat more stable than **3d**. The nitrosoamine groups could not be oxidized to nitramine groups; 100% nitric acid or hydrogen peroxide in acetic acid had no effect, hydrogen peroxide in trifluoroacetic acid led to decomposition, and peroxytrifluoroacetic acid removed both nitroso groups, re-forming **3c**.

Although the stability of cyclic nitramines increases with increasing symmetry, the reactivity of the two nitrogen atoms adjacent to the carbon bearing the trifluoromethyl groups is decreased by both steric and electronic effects, and attempts to obtain a fully nitrated compound with four nitramino groups were unsuccessful, either *via* the nitrosamines described above or by direct nitration of **3c**. Nitration of **3c** with 100% nitric acid in trifluoroacetic anhydride gave a product in good yield whose infrared spectrum indicated that a third nitro group had been introduced (**3f**); however, the material was quite unstable and could not be adequately purified. It precipitated during the nitration reaction, and attempts to circumvent this difficulty by reaction at higher temperatures or in an inert medium failed.

Experimental Section

Infrared absorptions are given, where applicable, for the N-H stretch and N-O (asymmetric) stretch. The N=O (symmetric) stretch cannot be assigned unequivocally since it appears in the same general region as the C-F stretch. Spectra were taken as split mulls on a Beckman IR-8.

1,3,5-Trinitroso-2,4,6-trimethylhexahydro-s-triazine (1f).—A stirred solution of 40 g (0.22 mol) of technical acetaldehyde-ammonia (Eastman) in 175 ml of dry chloroform was cooled to -20° and nitrogen oxide fumes were passed through for 2 hr. The nitrogen oxides, a mixture of N_2O_3 and N_2O_4 , were generated by adding concentrated nitric acid to powdered arsenic sesquioxide and warming as needed to produce a steady gas flow. A precipitate formed as the reaction proceeded. The mixture was poured into water, the chloroform layer removed, and the aqueous layer extracted with additional chloroform. The chloroform layers were combined, washed with water, dried, and concentrated almost to dryness. The precipitate formed by addition of 20 ml of absolute ethanol was filtered and dried: weight 6.5 g (14% yield); mp (after recrystallization from absolute ethanol) 163° (lit.¹⁴ 161°); infrared NH, none, N=O (asymmetric) 1488 cm^{-1} .

(12) E. H. White, *J. Amer. Chem. Soc.*, **77**, 6008 (1955).

(13) W. M. Jones and J. M. Denham, *ibid.*, **86**, 944 (1964).

(14) M. Delepine, *Bull. Soc. Chim. Fr.*, **19**, 15 (1898).

Anal. Calcd for $\text{C}_6\text{H}_{12}\text{N}_6\text{O}_3$: C, 33.3; H, 5.6; N, 38.9. Found: C, 34.0; H, 6.0; N, 39.4.

2,4,6-Tris(trifluoromethyl)hexahydro-s-triazine (1d).—Anhydrous trifluoroacetaldehyde was made by dehydrating the commercial hydrated form (Peninsular ChemResearch) with phosphorus pentoxide and polyphosphoric acid. The anhydrous aldehyde, 66 g (0.68 mol), was added as a gas below the surface of a solution of liquid ammonia, 30 g (1.8 mol), in 140 ml of ether, stirred at -50° . After a short reflux (Dry Ice condenser), the mixture was warmed and the excess ammonia and solvent removed by distillation, heating to a pot temperature of 70° . Benzene (200 ml) was added and the water present removed azeotropically. After removal of the benzene, the semicrystalline residue was filtered, dried, and purified by vacuum sublimation at 40° and recrystallization from cyclohexane and petroleum ether: yield 24 g (36% of theory); mp $83\text{--}84^\circ$; infrared NH, 3315, 3340 cm^{-1} ; N=O none.

Anal. Calcd for $\text{C}_6\text{H}_6\text{F}_9\text{N}_3$: C, 24.8; H, 2.1; F, 58.7; N, 14.4; mol wt, 291. Found: C, 25.1; H, 2.3; F, 59.0; N, 14.2; mol wt, 301 (ebullioscopic in benzene).

On standing for several days, the filtrate from the crude product developed more crystalline material. Each subsequent filtrate likewise crystallized in part, so that the eventual yield probably approaches 50% of theory.

1,3,5-Trinitroso-2,4,6-tris(trifluoromethyl)hexahydro-s-triazine (1e).—To a suspension of 24 g of powdered, freshly fused sodium acetate in 100 ml of glacial acetic acid, cooled to 10° , was added 20 g of liquid dinitrogen tetroxide. With stirring, 9.5 g (0.033 mol) of 2,4,6-tris(trifluoromethyl)hexahydro-s-triazine was added in small portions during a period of 1 hr. After another 1.5 hr at $5\text{--}10^\circ$, the mixture was poured on ice. The precipitated product, after drying, was recrystallized from petroleum ether to give 4.7 g, mp $45\text{--}46^\circ$. Additional material obtained from the mother liquors brought the yield to 58% of theory.

Anal. Calcd for $\text{C}_6\text{H}_6\text{F}_9\text{N}_6\text{O}_3$: C, 19.1; H, 0.1; F, 45.2; N, 22.2. Found: C, 18.4; H, 1.5; F, 42.3; N, 20.2.

Although these analytical data are not in good agreement with theory, the absence of N-H absorption in the infrared as well as the facile conversion of this compound to the trinitro derivative are good evidence that it is the desired trinitrosohexahydro-s-triazine.

1,3,5-Trinitro-2,4,6-tris(trifluoromethyl)hexahydro-s-triazine (1i).—To a nitrating mixture prepared by adding 80 g of absolute nitric acid to 80 g of trifluoroacetic anhydride below 10° , 7.5 g of **1e** was added in small portions over 1 hr at $0\text{--}5^\circ$. The reaction was stirred while warming to room temperature (4 hr) and then was drowned in ice and water. The crude product was filtered, washed with cold water, dried *in vacuo*, and recrystallized from cyclohexane to give 5.7 g (67% of material); mp $117\text{--}118^\circ$; infrared NH, none, N=O (asymmetric) 1625 cm^{-1} .

Anal. Calcd for $\text{C}_6\text{H}_6\text{F}_9\text{N}_6\text{O}_6$: C, 16.9; H, 0.7; F, 40.1; N, 19.7. Found: C, 17.1; H, 0.8; F, 40.0; N, 19.5.

2,2-Bis(trifluoromethyl)-5-nitrohexahydro-s-triazine (2b) and 2,2-Bis(trifluoromethyl)-5,7-dinitro-1,3,5,7-tetraazacyclooctane (3c).—In an open beaker, 65 g (0.48 mol) of MEDINA and 82 g (0.96 mol) of 35% formaldehyde were stirred at $10\text{--}15^\circ$ for 0.5 hr, and 87 g (0.48 mol) of 2,2-diaminohexafluoropropane was then added during a period of 20 min. The mixture was stirred at $10\text{--}15^\circ$ for 1 hr and then for several hours while warming to room temperature, until the two liquid phases which formed could no longer be intimately mixed because of solidification. The contained water was allowed to evaporate at room temperature and the residue was ground and dried *in vacuo* for 16 hr at $25\text{--}30^\circ$ and then extracted continuously with Freon 113. In the first stages of the extraction, before the appearance of crystals (1–3 hr, depending on the efficiency of the extraction), the extract contained mainly **2b**, which was considerably more soluble in Freon 113 than **3c**. Removal of any crystals formed, followed by slight concentration and chilling, gave **2b**. Further extraction of the crude product with Freon 113 gave mainly **3c**, which was only slightly soluble in Freon 113 at room temperature. Pure samples of the two compounds were obtained by repeated fractional extraction and/or recrystallization from Freon 113, using melting points and infrared spectra as criteria of purity. The triazine derivative **2b** melted at 88° and showed complex absorptions at $3300\text{--}3400$ (NH) and $1450\text{--}1510\text{ cm}^{-1}$ (NO); the tetraazacyclooctane derivative **3c** melted at $127\text{--}128^\circ$ and showed sharp absorption bands at 3390 , 3360 (NH), and 1530 cm^{-1} (NO). Reaction in the quantities cited gave 5 g of **2b** and 31 g of **3c**, representing conversions of 4 and 19%, respectively, based on **2,2-**

diaminohexafluoropropane, plus additional impure material. The extraction residue showed no infrared indication of NNO_2 or CF groups.

Anal. Calcd for $\text{C}_2\text{H}_6\text{H}_6\text{N}_4\text{O}_2$ (**2b**): C, 22.4; H, 2.3; F, 42.5; N, 20.9; mol wt, 268. Found: C, 22.6; H, 2.1; F, 36.1; N, 21.0; mol wt, 275 (ebullioscopic in benzene). Calcd for $\text{C}_6\text{H}_3\text{F}_6\text{N}_6\text{O}_4$ (**3c**): C, 21.2; H, 2.4; F, 33.3; N, 24.6; mol wt, 342. Found: C, 21.1; H, 2.5; F, 28.5; N, 24.1; mol wt, 351 (ebullioscopic in benzene).

Nitrosation of 2b.—To a mixture of 5 g of dinitrogen tetroxide, 6.5 g of freshly fused sodium acetate, and 20 ml of acetic acid was added, in small portions, 1.5 g (0.006 mol) of **2b**. After stirring for 1 hr at 10–20° and 0.5 hr at 20–25°, the mixture was poured on ice. The product was filtered, washed, dried, and recrystallized from petroleum ether to give 1.1 g (60% yield) of alleged **2c**, mp 96–97°.

2,2-Bis(trifluoromethyl)-1,3,5-trinitrohexahydro-s-triazine (2d).—**2b** (4 g, 0.015 mol) was added in small portions to a stirred mixture of 7.3 g of 100% nitric acid and 24 g of trifluoroacetic anhydride during a period of 0.5 hr and stirred for an additional 3 hr, all operations being carried out at 5–10°. The precipitated solid was filtered, washed, dried, and recrystallized to give 3.7 g of **2d**: mp 108°, or 70% of theory; infrared NH, none, NO (asymmetric) 1560, 1600, 1620 cm^{-1} .

Anal. Calcd for $\text{C}_5\text{H}_4\text{F}_6\text{N}_6\text{O}_8$: C, 16.8; H, 1.1; F, 31.8; N, 23.5. Found: C, 16.9; H, 1.1; F, 30.6; N, 22.7.

Attempted Nitrosation and Nitration of 3c.—To a stirred solution of 5 g (0.015 mol) of **3c** in 25 ml of acetic acid and 75 ml of acetic anhydride was added slowly 20 g (0.35 mol) of sodium nitrite at 0–5°. After the mixture was stirred for 2 hr, it was poured into 250 ml of ice and water. The solid was filtered, washed, dried, and recrystallized from ethylene dichloride to give 4.3 g of presumed **3d** (79% yield): mp 156–157°; infrared NH, 3390, NO (asymmetric), 1525 (sh), 1535, 1560 cm^{-1} .

Nitrosation of **3c** as in the preparation of **2c** gave a 76% yield of presumed **3e**: mp 151°, infrared NH, none, NO (asymmetric) 1535, 1555 (sh), 1560, 1580 cm^{-1} .

The compound **3c** was nitrated as in the preparation of **2d**. The crude product, obtained in approximately 75% yield, melted at 50–75°. Recrystallization of a small sample from benzene raised this figure to 120–123°, but attempted recrystallization of the main product resulted in progressive deterioration, as indicated by a lowered melting point and the appearance of many new peaks in the infrared spectrum. The recrystallized product after standing 2 weeks at room temperature melted at 105–106°: infrared NH, 3350, NO 1530–1560, 1600 cm^{-1} .

Registry No.—**1d**, 26960-86-1; **1e**, 26960-87-2; **1f**, 27074-73-3; **1i**, 26960-88-3; **2b**, 26960-89-4; **2c**, 26960-90-7; **2d**, 27006-03-7; **3c**, 26960-91-8; **3d**, 26960-92-9; **3e**, 26960-93-0.

Notes

The Synthesis of Fluorine-Containing Aliphatic *gem*-Dinitramines¹

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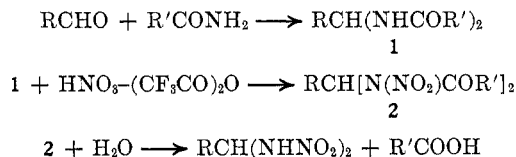
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As part of an extensive program on fluorine-containing *N*-nitro and *C*-nitro compounds, the preparation of a partially fluorinated aliphatic dinitramine related to MEDINA, $\text{CH}_2(\text{NHNO}_2)_2$, was of interest. This paper describes the synthesis of trifluoromethyl-MEDINA, $\text{CF}_3\text{CH}(\text{NHNO}_2)_2$, and its nonfluorinated analog, methyl-MEDINA, $\text{CH}_3\text{CH}(\text{NHNO}_2)_2$.

MEDINA has best been made^{2,3} by condensing formamide with an aldehyde to form an alkylidenebisamide, nitrating the bisamide to an alkylidenebis(*N*-nitroamide), and hydrolyzing the nitramide to the free nitramine, as shown in Scheme I.

This general route was followed in the synthesis of trifluoromethyl-MEDINA and methyl-MEDINA, but variations in properties due to the trifluoromethyl and methyl groups often necessitated considerable modification of reaction conditions. Although the reactions of substituted aldehydes with acetamide and formamide have previously been studied by several workers,^{4–8}

SCHEME I



neither of the bisformamides (**1** ($\text{R} = \text{CH}_3, \text{CF}_3$)) has been reported, and no aldehyde other than formaldehyde has been successfully converted to a *gem*-dinitramine.

Bis(formamido)methane, bis(acetamido)methane, and bis(trifluoroacetamido)methane were made by the method of Sauer,² utilizing a high temperature reaction of hexamethylenetetramine and the appropriate amide. 1,1-Bis(acetamido)ethane was prepared by the method of Noyes and Forman,⁹ but all published techniques for bisamide formation proved unsuccessful in the case of 1,1-bis(formamido)ethane. This compound was prepared by a method similar to that used for bisurethans,¹⁰ the aldehyde and amide being reacted in aqueous solution for brief periods at 25–40° in the presence of hydrochloric acid. 1,1-Bis(formamido)-2,2,2-trifluoroethane and 1,1-bis(acetamido)-2,2,2-trifluoroethane were made by sealed tube reactions at 130°, using anhydrous trifluoroacetaldehyde and the amide. Attempts to prepare a bisamide from propionaldehyde were unsuccessful. A sealed tube reaction of hexa-

(4) G. Pulvermacher, *Ber.*, **25**, 304 (1892).

(5) V. von Richter, *ibid.*, **5**, 477 (1872).

(6) A. Reich, *Monatsh. Chem.*, **25**, 933 (1904).

(7) K. Bulow, *Ber.*, **26**, 1973 (1893).

(8) A. Roth, *Justus Liebig's Ann. Chem.*, **154**, 72 (1870).

(9) W. A. Noyes and D. B. Forman, *J. Amer. Chem. Soc.*, **55**, 3493 (1933).

(10) W. M. Kraft and R. M. Herbst, *J. Org. Chem.*, **10**, 485 (1945).

(1) This work was supported by Detachment 4, Eglin Field, U. S. Air Force.

(2) C. W. Sauer, U. S. Patent 2,713,594 (1955).

(3) C. W. Sauer, U. S. Patent 2,856,429 (1958).