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

Anal. Calcd for $C_5H_6H_6N_4O_2$ (**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 $C_6H_8F_6N_6O_4$ (**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 $C_5H_4F_6N_6O_6$: 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*-Dinitramines[1]

John A. Krimmel, Josef J. Schmidt-Collerus,
John A. Young,* George E. Bohner, and Donald N. Gray

*Denver Research Institute, University of Denver,
Denver, Colorado 80210*

Received June 25, 1970

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, $CH_2(NHNO_2)_2$, was of interest. This paper describes the synthesis of trifluoromethyl-MEDINA, $CF_3CH(NHNO_2)_2$, and its nonfluorinated analog, methyl-MEDINA, $CH_3CH(NHNO_2)_2$.

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.

Scheme I

$$RCHO + R'CONH_2 \longrightarrow \underset{1}{RCH(NHCOR')_2}$$

$$1 + HNO_3\text{–}(CF_3CO)_2O \longrightarrow \underset{2}{RCH[N(NO_2)COR']_2}$$

$$2 + H_2O \longrightarrow RCH(NHNO_2)_2 + R'COOH$$

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] neither of the bisformamides **1** (R = CH_3, 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-

---

(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).

(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 Liebigs 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).

fluoroacetone and formamide gave only a 1:1 adduct which dissociated on heating and reverted to free amide and ketone.

MEDINA was prepared from bis(acetamido)methane following the procedure of Brian and Lamberton,[11] but none of the other three bisacetamides **1** (R = CH_3, CF_3, R′ = CH_3; R = CH_3, R′ = CF_3) could be nitrated using either a nitric acid–acetic anhydride or a nitric acid–trifluoroacetic anhydride system. Nitrosyl chloride and dinitrogen pentoxide, both reported to be excellent nitrating agents in anhydrous solvents,[12] also failed to give the desired nitramides. Failure to nitrate 1,1-bis(acetamido)ethane has been reported previously.[11] Sauer[3] succeeded in obtaining good yields of bis(nitroformamides) by the use of 98% nitric acid in either acetic or trifluoroacetic anhydride, and the latter technique was found to be satisfactory with only slight modification for nitration of both 1,1-bis(formamido)-ethane and 1,1-bis(formamido)-2,2,2-trifluoroethane. No nitramides were obtained when acetic anhydride was employed.

The three sets of compounds, bisformamides, bis-(*n*-nitroformamide)s, and dinitramines, constitute a series in which the character of the nitrogen atom is markedly influenced by the atom or group (R = CH_3, H, CF_3) attached to the central carbon atom. This influence was reflected to the greatest extent in the properties of the nitramides. Bis(*N*-nitroformamido)-methane was a fairly stable compound when pure and dry and presented no great difficulty either in isolation from the nitration step or in hydrolysis to the nitramine. 1,1-Bis(*N*-nitroformamido)ethane was quite insoluble in water and fairly stable when dry but was very sensitive to strong acids and decomposed rapidly when left in contact with formic acid. On the other hand, 1,1-bis(*N*-nitroformamido)-2,2,2-trifluoroethane appeared to be rather soluble in water and was unstable at room temperature, although it was much more resistant to decomposition by acids. Consequently, the desired hydrolysis to the substituted nitramines suffered from simultaneous decomposition of the nitramides, hydrolytic in one case and thermal in the other, resulting in lower and more erratic yields of methyl-MEDINA and trifluoromethyl-MEDINA than that of MEDINA itself.

Trifluoromethyl-MEDINA is strongly hydrogen bonded. For the N=O asymmetric stretch in infrared spectra taken on split mulls, MEDINA showed a singlet at 1580 cm^{-1} and methyl-MEDINA showed a main peak at 1581 with a shoulder at 1568 cm^{-1}, while trifluoromethyl-MEDINA showed a doublet at 1688 and 1722 cm^{-1} which reverted to a singlet at 1621 cm^{-1} when the spectrum was taken of a carbon tetrachloride solution. The NH stretch of trifluoromethyl-MEDINA was a broad band at 2950–3250 cm^{-1} in the mull sample but a sharp singlet at 3380 cm^{-1} in the solution.

Experimental Section

1,1-Bis(formamido)-2,2,2-trifluoroethane.—In a high vacuum system, 25 g (0.26 mol) of anhydrous trifluoroacetaldehyde was transferred into a heavy-walled Pyrex tube containing 25 g (0.55 mol) of formamide. The tube was sealed and heated at 120° for 8 hr, cooled to −80°, broken, and reheated until the completely crystalline mass had melted. The contents were poured out and allowed to crystallize. After recrystallization from acetonitrile, the yield of material melting at 193° was 16.2 g or 74% of theory, assuming that 2 mol of aldehyde is necessary to form 1 mol of bisamide plus 1 mol of trifluoroacetaldehyde hydrate. Attempts to prepare trifluoroethylidenebisformamide from the aldehyde hydrate rather than the free aldehyde were completely unsuccessful. Infrared absorptions (split mull, Beckman IR-8) showed NH, 3100, 3280, N=O (asymmetric), none, C=O 1690 cm^{-1}.

Anal. Calcd for $C_4H_5F_3N_2O_2$: C, 28.2; H, 3.0; F, 33.5; N, 16.5. Found: C, 28.4; H, 3.5; F, 34.6; N, 17.3.

1,1-Bis(acetamido)-2,2,2-trifluoroethane.—Reaction of 11.5 g (0.12 mol) of trifluoroacetaldehyde and 11.8 g (0.20 mol) of acetamide for 15 hr at 140°, removal of excess amide by vacuum distillation, and crystallization of the solidified residue from acetonitrile gave 4.1 g (34% of theory) of product: mp 265°; infrared NH, 3115, 3290, NO (asymmetric), none, CO 1678 cm^{-1}.

Anal. Calcd for $C_6H_9F_3N_2O_2$: C, 36.4, H, 4.6; N, 14.1. Found: C, 37.0; H, 4.8; N, 15.7.

1,1-Bis(*N*-nitroformamido)-2,2,2-trifluoroethane.—1,1-Bis-(formamido)-2,2,2-trifluoroethane (5 g, 0.03 mol) was dissolved in 20 g of trifluoroacetic anhydride and 17 g of 100% nitric acid was added slowly with stirring at 5°. After aging for 4 hr at 5 ± 3°, the reaction mixture was poured slowly with vigorous stirring into 100 g of finely crushed ice. The resulting white gummy solid was washed with ice water by decantation, transferred immediately to a small flask, and subjected to high vacuum ($<10\ \mu$) while kept in an ice bath. After about 5 hr, the granular dry, white residue was recrystallized from methylene chloride to give 4.0 g of product. After standing 17 days in a refrigerator at 5°, the material showed a change in melting point from an initial figure of 56° to 35–45°. Because of the instability of the material no elemental analysis was attempted. Infrared showed NH, none, N=O (asym) 1611, 1637, C=O, 1739, 1761 cm^{-1}.

1,1-Dinitramino-2,2,2-trifluoroethane (Trifluoromethyl-MEDINA).—The crude gummy white solid obtained from nitration of 5 g (0.03 mol) of trifluoroethylidenebisformamide was left at room temperature for 1 week, and the partially crystalline residue evaporated under vacuum. After two recrystallizations from chloroform, 1.2 g of product, mp 81°, was obtained for an overall yield, based on bisamide, of 20%. Infrared showed NH, 2950–3250, N=O (asym) 1688, 1722, C=O, none.

Anal. Calcd for $C_2H_3F_3N_4O_4$: C, 11.8; H, 1.5; F, 27.9; N, 27.5. Found: C, 11.9; H, 1.6; F, 25.3; N, 28.1.

1,1-Bis(formamido)ethane.—Formamide (60 g, 1.33 mol) was dissolved in 15 ml of water containing 1.5 ml of concentrated hydrochloric acid, and 30 g (0.68 mol) of monomeric acetaldehyde was added in one portion. The reaction mixture was allowed to stand for 3 hr, during which time the temperature rose to 41° and then subsided. After vacuum distillation, by which 25 g of formamide was recovered, the viscous residue was washed out of the flask with a hot solution of 20 ml of isopropyl alcohol and 60 ml of acetonitrile. The crude product which separated on cooling was recrystallized by dissolving it in the minimum amount of boiling isopropyl alcohol, adding 3 vol of hot acetonitrile, and cooling. The yield of product, mp 119°, was 27 g or 62% based on unrecovered formamide.

Anal. Calcd for $C_4H_8N_2O_2$: C, 41.4; H, 6.9; N, 24.1. Found: C, 41.5; H, 7.2; N, 24.3.

1,1-Bis(*N*-nitroformamido)ethane.—1,1-Bis(formamido)ethane (3.7 g, 0.03 mol) was added in several portions to a stirred mixture of 18 g of 100% nitric acid and 18 g of trifluoroacetic anhydride at 10°. After aging for 2.5 hr, the reaction mixture was added slowly to 200 g of crushed ice, with rapid stirring. After about 5 min a finely divided, almost colorless solid appeared which was filtered and washed once with ice water. The yield of product so obtained averaged about 1.7 g (26% of theory), but yields as high as 60% were sometimes obtained using much larger quantities of trifluoroacetic anhydride. If necessary, the product was recrystallized from a mixture of ethylene dichloride, and ligroin: mp (then) 71°; infrared NH, none, N=O (asym) 1566, 1600, C=O, 1732, 1740 cm^{-1}.

1,1-Dinitraminoethane (Methyl-MEDINA).—To 2.0 g (10 mol) of ethylidenebis(nitroformamide) ten drops of water was added with stirring and the resulting paste allowed to stand at room temperature. After 1 hr the mixture had completely liquefied and the temperature had risen to about 35°. After an additional hour the liquid was filtered, cooled in an ice bath, and filtered again to give 0.5 g (33%) of product, mp 115°. This hydrolysis gave very inconsistent results and the figure cited is the maximum

---

(11) R. C. Brian and A. H. Lamberton, *J. Chem. Soc.*, 1633 (1949).

(12) C. C. Price and C. A. Sears, *J. Amer. Chem. Soc.*, **75**, 3276 (1953).

yield obtained. Infrared showed NH, 3110–3220, N=O (asym), 1568 (sh), 1581, C=O, none.

Registry No.—1,1-Bis(formamido)-2,2,2-trifluoroethane, 26958-24-7; 1,1-bis(acetamido)-2,2,2-trifluoroethane, 27039-91-4; 1,1-bis(*N*-nitroformamido)-2,2,2-trifluoroethane, 26958-25-8; 1,1-dinitramino-2,2,2-trifluoroethane, 26958-26-9; 1,1-bis(formamido)ethane, 20602-52-2; 1,1-bis(*N*-nitroformamido)ethane, 26958-28-1; 1,1-dinitraminoethane, 26958-29-2.

Reactions of Dodecabromopentacyclo[5.3.0.0^{2,6}.0^{3,9}.0^{4,8}]decane with Sodium Methoxide

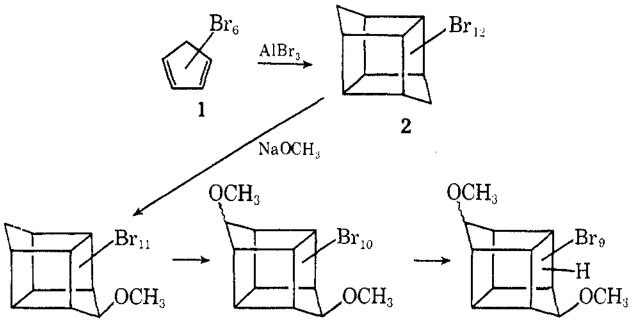
G. A. Ungefug, S. D. McGregor, and C. W. Roberts*[1]

Hydrocarbons and Monomers Research Laboratory, The Dow Chemical Company, Midland, Michigan 48640

Received December 29, 1969

Hexabromocyclopentadiene (1) is dimerized by aluminum tribromide in refluxing bromine to give dodecabromopentacyclo[5.3.0.0^{2,6}.0^{3,9}.0^{4,8}]decane (2).[2] Examination of molecular models leads to the prediction that 2 would be very inert toward nucleophilic attack. The compound has a small cluster of carbon atoms at its center and a large protective outer armor of bromine atoms. Back-side attack at any carbon atom of 2 appears to be impossible. Nevertheless, bromocarbon 2 reacts with sodium methoxide in tetrahydrofuran to give a series of cage compounds.

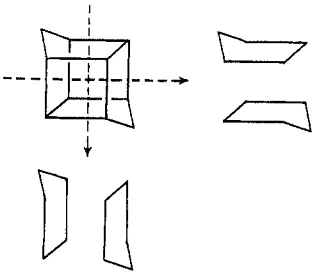
Kinetic control by slow addition of sodium methoxide and patient tlc analysis revealed initial formation of a monomethoxy derivative 3, which was converted to a dimethoxy derivative 4. Most of the starting material 2 and compound 3 disappeared before a third product 5 appeared along with several open cage products which had double bond adsorption in their infrared spectra. Compound 4 was prepared in 70–80% yield by following the reaction by tlc and quenching at a maximum concentration of 4.



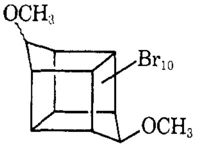
The structures of 3, 4, and 5 are assigned on the basis of their nmr, mass spectra, and relative reaction rates.

Nmr spectra of mixtures of 3 and 4 exhibit two poorly resolved lines at δ 3.97 in DMSO-d_6 with a separation of 0.009 ppm. Thus the environment of the single methyl of 3 is very similar to the environment of the two methyls of 4. Although 5 appears pure by mass spectral analysis, its nmr can only be explained as a mixture. No attempt has been made for an assignment of various isomer ratios of 5 to the nmr spectrum, since the structure is tentative.

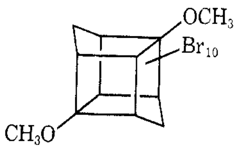
The normal fragmentation pattern observed in mass spectra of bishomocubane compounds is cleavage to two five-carbon rings by the two routes illustrated below.[3]



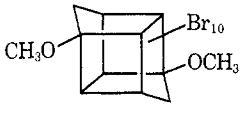
The most intense ion in the mass spectrum of 4 is *m/e* 407 from $C_5Br_4OCH_3^+$. An important feature is the lack of any C_5 fragments from 4 with two OCH_3 groups. Thus the methoxy groups must not be placed on the same five-carbon ring. Compounds **4a–d** satisfy the mass spectrum and the symmetry requirement necessary to give a single line nmr. An alternate structure is the dimethyl ketal 7, which is readily prepared from ketone 6, but 7 has ir, nmr, and mass spectra which are quite different from the spectra of 4.



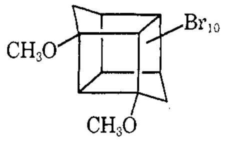
4a



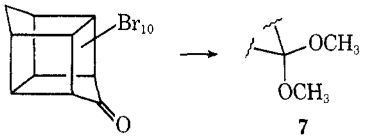
4b



4c

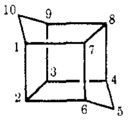


4d



6 7

The structure of 3 is based primarily on its conversion to 4 and on its mass spectrum. Structure **4a** is assigned to 4 on the basis of the reaction rate data. A monomethoxy derivative is formed which reacts with methoxide at about the same rate as bromocarbon 2. Further reaction with methoxide is slower than formation of the first two products. If reaction occurs first at C-10 the activity at C-5 would not be altered, and the product would readily react at C-5 to form 4. After forma-



---

[1] To whom inquiries should be addressed: Textile Department, Clemson University, Clemson, S. C. 29631.

[2] C. W. Roberts and M. B. Chenoweth, U. S. Patent 3,212,973 (1965).

[3] W. L. Dilling and M. L. Dilling, *Tetrahedron*, **23**, 1225 (1967).