Anal. Calcd. for $C_9H_6BrN_3O_2$: C, 40.3; H, 2.3; Br, 29.8; N, 15.7. Found: C, 40.1; H, 2.1; Br, 29.8; N, 15.8.

Treatment of XVIII in the usual way with acetic anhydride–pyridine (1 hr. on the steam bath) afforded XIX in 60% yield as yellow needles. Recrystallized from dimethylformamide m.p. 291–293° dec.

Anal. Calcd. for $C_{11}H_8BrN_3O_3$: C, 42.6; H, 2.6; Br, 25.8; N, 13.6. Found C, 42.4; H, 2.9; Br, 25.7; N, 13.7.

Acknowledgment.—We should like to thank Messrs. J. P. Panella and D. H. Hunneman, who assisted with the experimental work, and Dr. C. K. Fitz who performed the elemental analyses.

The Reaction of Trifluoroacetonitrile with Aliphatic Diamines[1,2]

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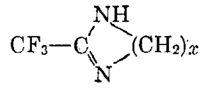
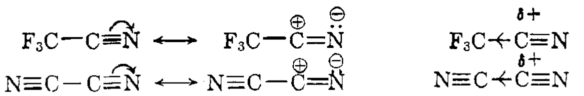
Trifluoroacetonitrile reacts with aliphatic diamines to yield carboxamidines, $CF_3C(=NH)NH(CH_2)_xNH(HN=)CCF_3$, and where $x = 2, 3$, or 4 cyclic compounds as well.



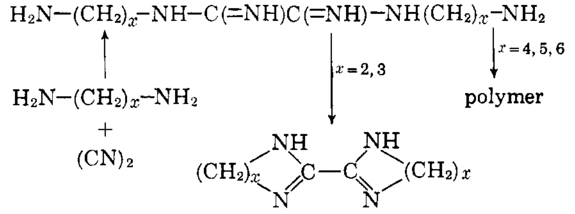
N,N-Dialkylaminoalkylenediamines produce substituted trifluoroacetamidines.

Recent work has indicated a similarity in chemical action of the —CN group in cyanogen and that in trifluoroacetonitrile.[3–6] This has been interpreted as the result of the electron-withdrawing effects of the NC— and CF_3— groups, which enhance the electrophilic character of the CN carbon involved in a resonance hybrid:



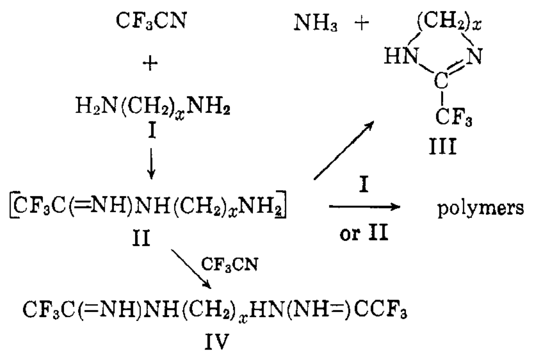
Obviously, in the case of cyanogen, a third resonance structure $(\overset{\oplus}{N}=C=C=\overset{\ominus}{N})$ must reduce somewhat the electrophilicity of the carbon in question and may explain the slower reaction rate observed in some cases.[6]

Extensive studies have been made of the reaction of cyanogen with aliphatic diamines.[7,8] The reaction takes place in two steps. First an oxamidine is formed; then, depending upon the number of carbon atoms in the chain, either an intramolecular reaction results in cyclization or an intermolecular reaction results in polymerization:



No reaction in which cyanogen attacks both NH_2 groups of the diamine is observed.

This investigation has shown that substitution of trifluoroacetonitrile for cyanogen results in a similar sequence of reactions, but introduces a new factor, attack on the second NH_2 group by a second molecule of trifluoroacetonitrile. This presumably is the result of the strong positive character of the reacting $C^{\oplus}$.



The fate of the intermediate (II) depends upon the value of x and, for a particular x, the conditions employed.

Ethylenediamine ($x = 2$).—(1) Ethane-1,2-bis-(trifluoromethyl)carboxamidine (IV. $x = 2$) was isolated when ethylenediamine was added to a solution of trifluoroacetonitrile in ether. (2) 2-Trifluoromethylimidazoline (III. $x = 2$) resulted when either (a) the nitrile was distilled into pure ethylenediamine or into a mixture of the diamine

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[1] From the thesis submitted by Roland N. Johnson in partial fulfillment of requirements for the M.A. degree, June 1962.

[2] This work was supported in part by National Science Foundation Grant, G 9922.

[3] J. C. Grivas and A. Taurins, *Can. J. Chem.*, **39**, 761 (1961).

[4] G. J. Janz and J. J. Stratta, *J. Org. Chem.*, **26**, 2169 (1961).

[5] C. S. Kamper and H. M. Woodburn, unpublished work.

[6] C. S. Kamper and H. M. Woodburn, unpublished work.

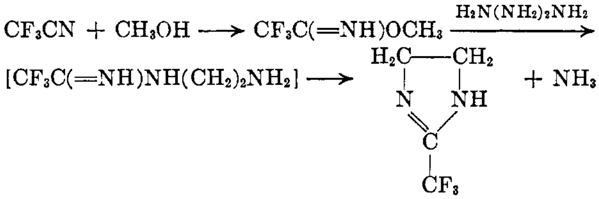
[7] H. M. Woodburn and R. C. O'Gee, *J. Org. Chem.*, **17**, 1235 (1952).

[8] H. M. Woodburn and J. R. Fisher, *ibid.*, **22**, 895 (1957).

and ether; or (b) the diamine in methanol solution was added to liquid nitrile.

The production of the carboxamidine (IV) under condition 1 appears reasonable, since the continuous excess of trifluoroacetonitrile would favor the addition of another molecule of nitrile to the intermediate. Under condition (2)(a), with diamine in continuous excess, time is available for an intramolecular reaction to occur before a second molecule of nitrile can attack the free amino group. Thus the formation of the imidazoline (III) is also reasonable.

More difficult to explain is the formation of imidazoline under condition (2)(b). It seems necessary to assume that in some fashion methanol reduced the reactivity of the nitrile, allowing the intramolecular reaction to take precedence over further addition. This could occur by the rapid formation of an imidate ester which then reacted with the diamine:



However, unpublished studies[9] have shown that a strongly basic catalyst—e.g., sodium methoxide—is needed for the formation of imidate esters from trifluoroacetonitrile; and it would not appear likely that ethylenediamine is sufficiently basic for this purpose.

An untested possibility is the formation of a trifluoroacetonitrile–methanol complex, CF_3CN—$HOCH_3$, which would lower the potential energy of the nitrile, decreasing the rate of formation not only of the intermediate (II) but also of the carboxamidine (IV) relative to the intramolecular reaction.

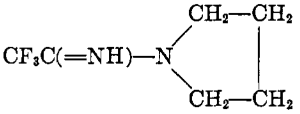
Trimethylenediamine ($x = 3$).—(1) Propane-1,3-bis(trifluoromethyl)carboxamidine (IV. $x = 3$) resulted when an ether solution of trimethylenediamine was added to an excess of trifluoroacetonitrile. (2) 2-Trifluoromethyltetrahydropyrimidine (III. $x = 3$) was the principal product when the nitrile was distilled into an ethanolic solution of trimethylenediamine.

Both results are consistent with the principles outlined above.

Tetramethylenediamine ($x = 4$).—From this compound, **cyanogen** produced only a low yield of oxamidine, followed by the formation of a polymer. However, trifluoroacetonitrile produced an 83% yield of the butane carboxamidine (IV. $x = 4$) when a solution of the diamine in ether was added to the liquid nitrile [condition (1)].

Reversing the addition also gave carboxamidine as the major product but 6% of the cyclic compound (III. $x = 4$), 2-trifluoromethyl-4,5,6,7-tetrahydro-1*H*-1,3-diazepine, was also isolated.

To establish the fact that the cyclic compound was not 1-(trifluoromethylformino)pyrrolidine, the latter was independently synthesized from pyrrolidine and trifluoroacetonitrile.



Pentamethylenediamine, Hexamethylenediamine, and Heptamethylenediamine (x = **5, 6, and 7**).—These diamines produced only carboxamidines when treated with trifluoroacetonitrile. Yields were excellent and mode of addition appeared to have no effect.

In general, the carboxamidines decomposed after several weeks with the evolution of ammonia. In many cases, their hydrochlorides were more satisfactory for storage.

2-Trifluoromethylimidazoline exhibited the ease of hydrolysis characteristic of the imidazoline structure.[10] Attempts to form the hydrochloride from a nonanhydrous ether solution resulted in the formation of ethylenediamine dihydrochloride, while refluxing with water or ethanol for several hours produced ethane-1,2-bis(trifluoromethyl) carboxamide. This unexpected product was identified by synthesizing it independently from ethylenediamine and trifluoroacetic acid.

The reactions of N,N-dimethyl- and N,N-dibutylethylene diamine with trifluoroacetonitrile were also carried out. Eighty percent yields of trifluoroacetamidines resulted.

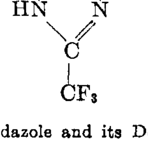
$$CF_3CN + H_2N(CH_2)_2N(CH_3)_2 \longrightarrow CF_3C(=NH)NH(CH_2)_2N(CH_3)_2$$

The amidines were quite unstable and decomposed in a few weeks into tarry residues.

Experimental[11]

Reagents.—Practical ethylenediamine and hexamethylene diamine were purified by the method outlined by Weissberger *et al.*[12] N,N-Di-*n*-butylethylenediamine was dried with sodium hydroxide and redistilled prior to use. Other diamines were purchased and used without further purification. Trifluoroacetonitrile was purchased from Peninsular Chemresearch, Inc.

Reactions of Trifluoroacetonitrile with Diamines. Ethylenediamine. (a) 2-Trifluoromethylimidazoline.—(1) Into



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(9) C. S. Kamper and H. M. Woodburn, unpublished work.

(10) K. Hofmann, "Imidazole and its Derivatives," Interscience, New York, N. Y., 1953, p. 24.

(11) Melting points and boiling points are uncorrected. Chlorine and nitrogen analyses were carried out by standard semimicromethods. Other analyses were made by a commercial laboratory.

(12) Weissberger *et al.*, "Techniques of Organic Chemistry," Vol. VII, Interscience, New York, N. Y., 1955, p. 444.

a trap maintained at the temperature of Dry Ice and trichloroethylene (about −80°) was condensed 14.4 g. (0.15 mole) of trifluoroacetonitrile. The trap was then raised slightly above the cooling mixture so as to permit the gas to pass slowly into a 125-ml. gas washing bottle containing 9.2 g. (0.15 mole) of ethylenediamine. After several minutes, a white solid began to precipitate. The nitrile which did not immediately react passed out of the gas washing bottle into a trap which was maintained at about −80°. The collected nitrile was passed into the diamine and the process was repeated until all the nitrile reacted. Four to five passes were usually sufficient.

The white solid obtained (19.2 g., 94%) was recrystallized from anhydrous methanol giving a product melting at 112–113°.

Anal. Calcd. for $C_4H_5N_2F_3$: N, 20.3. Found: N, 20.45.

The compound was unstable, decomposing into a light yellow oil within a few months.

The **hydrochloride salt** was prepared by dissolving 1.0 g. of the imidazoline in 100 ml. of anhydrous ether. Dry hydrogen chloride gas was then bubbled into the system, producing a white precipitate. This product did not melt, but sublimed at temperatures greater than 250°.

Anal. Calcd. for $C_4H_6N_2ClF_3$: C, 27.52; H, 3.46; N, 16.05; Cl, 20.31; F, 32.65. Found: C, 27.67; H, 3.73; N, 15.71; Cl, 20.50; F, 32.51.

When the imidazoline was dissolved in nonanhydrous ether and dry hydrogen chloride admitted to the system, a precipitate of ethylenediamine dihydrochloride was isolated.

(2) In a flask equipped with a Dry Ice–acetone reflux condenser and a magnetic stirrer was placed 1.3 g. (0.022 mole) of ethylenediamine mixed with 10 ml. of anhydrous ether. Trifluoroacetonitrile (2.9 g., 0.03 mole) was then distilled into this system. The mixture was stirred during the addition of the nitrile (10 min.) and for an hour after. The solvent was evaporated under vacuum leaving 2.0 g. of white solid. Recrystallization from anhydrous methanol gave 1.0 g. of the imidazoline melting at 112–113°. An additional 0.6 g. was obtained from the filtrate. The total yield was 53%.

Anal. Calcd. for $C_4H_5N_2F_3$: N, 20.3. Found: N, 20.26.

(3) Trifluoroacetonitrile (37.0 g., 0.39 mole) was allowed to bubble into a solution of ethylenediamine (16.2 g., 0.27 mole) in 15 ml. of anhydrous ethanol as described above. The white solid (13.8 g., 39%) which precipitated from the reaction mixture was recrystallized from anhydrous methanol and shown to be 2-trifluoromethylimidazoline by a comparison of infrared curves and mixed melting points.

The filtrate from this reaction was distilled leaving 15.7 g. (22%) of ethane-1,2-bis(trifluoromethyl)carboxamide, $CF_3C(=O)NH(CH_2)_2NHC(=O)CF_3$. When recrystallized from anhydrous ethanol, it melted at 195–197°.

Anal. Calcd. for $C_6H_6N_2O_2F_6$: C, 28.58; H, 2.49; N, 11.11; O, 12.69; F, 45.21. Found: C, 28.49; H, 2.35; N, 11.20; O, 12.94 (by difference); F, 45.02.

A similar experiment using methanol as solvent produced both trifluoromethylimidazoline and ethane-1,2-bis(trifluoromethyl)carboxamide.

Ethane-1,2-bis(trifluoromethyl)carboxamide.—(i) 2-Trifluoromethylimidazoline (3.6 g.) was dissolved in 40 ml. of distilled water and refluxed for 5 hr. When the solvent was distilled, a white product remained. This was recrystallized from ethanol to give 0.9 g. (27%) of the carboxamide melting at 196–197°. A small amount of ethylenediamine was isolated from the distillate by forming the derivative, ethylenediamine benzenesulfonamide.

(ii) 2-Trifluoromethylimidazoline (1.5 g.; 0.011 mole) was refluxed with 5 ml. of (presumably) anhydrous ethanol for 11.5 hr. The solvent was evaporated under vacuum giving 0.3 g. (22%) of the carboxamide melting at 195–197°.

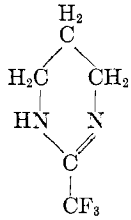
(iii) The carboxamide was obtained in 65.5% yield when 5.0 g. (0.044 mole) of trifluoroacetic acid was slowly added to 1.2 g. (0.02 mole) of ethylenediamine cooled in an ice bath. The yellow solid was heated for an hour to drive off the excess acid and the water which forms during the reaction. When the product was recrystallized from absolute ethanol, it melted at 195–197°. The yield was 3.3 g.

(b) **Ethane-1,2-bis(trifluoromethyl)carboxamidine** [$CF_3C(=NH)NH(CH_2)_2NHC(=NH)CF_3$].—Into a three-necked flask was distilled 7.3 g. (0.077 mole) of trifluoroacetonitrile. Anhydrous ether (10 ml.) was slowly admitted to the system, followed by 1.3 g. (0.022 mole) of ethylenediamine. A white solid was produced. The excess nitrile was distilled into a trap. Dry hexane was added to the reaction mixture to precipitate the product when the flask had come to room temperature. This gave 2.7 g. (50%) of a white solid. The analytical sample, when recrystallized from benzene, melted at 97–97.5°. The product decomposed on standing, presumably with the loss of ammonia. It appeared to be even more unstable if kept in benzene solution for a number of hours or if heated.

Anal. Calcd. for $C_6H_8N_4F_6$: C, 28.81; H, 3.22; N, 22.40; F, 45.57. Found: C, 28.71; H, 3.17; N, 22.18; F, 45.41.

The **hydrochloride salt** was prepared by dissolving 0.7 g. of the carboxamidine in 125 ml. of anhydrous ether and bubbling dry hydrogen chloride gas into the system. This gave an almost quantitative yield of a white product which rapidly decomposed at approximately 190°.

Trimethylenediamine. (a) **2-Trifluoromethyltetrahydropyrimidine.**—Following the method outlined above,



21.6 g. (0.217 mole) of trifluoroacetonitrile was bubbled into a solution containing 15.8 g. (0.217 mole) of trimethylenediamine in 15 ml. of absolute ethanol. The solvent was evaporated under vacuum to leave 17.2 g. (53.5%) of a light yellow product. Sublimation gave a white solid melting at 110–111°.

Anal. Calcd. for $C_5H_7N_2F_3$: C, 39.48; H, 4.64; N, 18.42; F, 37.47. Found: C, 39.22; H, 4.69; N, 18.47; F, 37.31.

The **hydrochloride salt** was formed by dissolving 3.0 g. (0.02 mole) of the pyrimidine in 15 ml. of absolute ethanol and adding 0.7 g. (0.02 mole) of dry hydrogen chloride gas dissolved in 30 ml. of absolute ethanol. The yield of white solid was increased by evaporating the ethanolic solution under vacuum. The analytical sample was recrystallized from absolute ethanol. The salt sublimed but did not melt below 350°.

Anal. Calcd. for $C_5H_8N_2F_3Cl$: C, 31.84; H, 4.28; Cl, 18.80. Found: C, 31.73; H, 4.46; Cl, 18.70.

The same salt was obtained by dissolving 1.5 g. (0.01 mole) of the tetrahydropyrimidine in 15 ml. of 95% ethanol and bubbling dry hydrogen chloride into this solution.

(b) **Propane-1,3-bis(trifluoromethyl)carboxamidine dihydrochloride** [$CF_3C(=NH)NH(CH_2)_3NHC(=NH)CF_3 \cdot 2HCl$].—Using the procedure outlined above, 1.0 g. (0.0135 mole) of 1,3-trimethylenediamine was dissolved in 10 ml. of anhydrous ether and added to 9.5 g. (0.1 mole) of trifluoroacetonitrile. The mixture was allowed to reflux for 45 min. before the excess nitrile was distilled. Addition of dry hexane to the mixture caused the separation of a light yellow oil which would not crystallize. The oil was redissolved in anhydrous ether and added to 70 ml. of ether saturated with dry hydrogen chloride. The white precipitate which formed (1.8 g.; 40%) was filtered, washed with anhydrous ether, and dried *in vacuo* over phosphorus pentoxide. It sublimed, but did not melt below 300°.

Anal. Calcd. for $C_7H_{12}N_4F_6Cl_2$: C, 24.93; H, 3.59; N, 16.62; F, 33.82; Cl, 21.04. Found: C, 25.20; H, 3.71; N, 16.95; F, 33.59; Cl, 21.30.

Tetramethylenediamine. (a) Butane 1,4-bis(trifluoromethyl)carboxamidine [$CF_3C(=NH)NH(CH_2)_4NHC(=NH)CF_3$].—(1) One gram (0.011 mole) of tetramethylenediamine was dissolved in 10 ml. of anhydrous ether and added to 10.1 g. (0.105 mole) of trifluoroacetonitrile maintained at −80°. Immediately a white solid formed. Upon standing for 10 min., the entire mixture had solidified so that stirring could not be maintained. The nitrile was allowed to reflux for 45 min. and then distilled into a trap. At room temperature, the solid redissolved. An oil separated when hexane was added to this solution; however, this oil solidified when kept for 10 hr. at 4°. The white solid which was collected (2.6 g.; 83%) was dissolved in ether and reprecipitated with hexane. It melted at 78.5–80°.

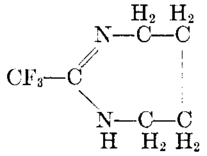
Anal. Calcd. for $C_8H_{12}N_4F_6$: N, 20.01. Found: 20.19.

The **hydrochloride salt** was prepared by dissolving 0.8 g. (0.0023 mole) of the free base in 15 ml. of anhydrous ether and adding this to 50 ml. of anhydrous ether saturated with dry hydrogen chloride. The white precipitate which immediately formed was filtered and dried *in vacuo* over phosphorus pentoxide. The salt decomposed rapidly at approximately 210°.

Anal. Calcd. for $C_8H_{14}Cl_2F_6$: C, 27.36; H, 4.02; N, 15.96; Cl, 20.20; F, 32.47. Found: C, 27.11; H, 3.89; N, 16.04; Cl, 20.40; F, 32.32.

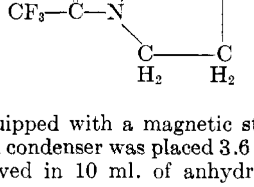
(2) Butane 1,4-bis(trifluoromethyl)carboxamidine was also prepared by slowly distilling 6.1 g. (0.064 mole) of trifluoroacetonitrile into a flask, equipped with a Dry Ice-acetone reflux condenser, containing 2.0 g. (0.023 mole) of tetramethylenediamine dissolved in 20 ml. of anhydrous ether. The solvent was evaporated under vacuum following the removal of excess nitrile. The crude product was dissolved in anhydrous ether, dry hexane was added, and the solution allowed to stand for 10 hr. at room temperature. Three grams (45%) of product melting at 76–78° was recovered.

(b) **2-Trifluoromethyl-4,5,6,7-tetrahydro-1*H*-1,3-diazepine.**—The filtrates from the hexane treatment above were combined and the solvent evaporated under vacuum. The residue, a semisolid, was sublimed twice to give 226 mg. (6%) of a white solid. The melting point was 96–97° (with sublimation).



Anal. Calcd. for $C_6H_9N_2F_3$: C, 43.39; H, 5.46; N, 16.96; F, 34.32. Found: C, 43.38; H, 5.65; N, 17.10; F, 34.09.

In order to prove that the product was not **trifluoromethylforminopyrrolidine** the latter was synthesized.



Into a flask equipped with a magnetic stirrer and a Dry Ice–acetone reflux condenser was placed 3.6 g. (0.05 mole) of pyrrolidine dissolved in 10 ml. of anhydrous ether. Trifluoroacetonitrile (5.0 g.; 0.053 mole) was distilled into the system and allowed to reflux for 1 hr. Fractional vacuum distillation gave 3.2 g. (36%) of a colorless liquid, b.p. 48–48.5°/8 mm.

Anal. Calcd. for $C_6H_9N_2F_3$: C, 43.39; H, 5.46; N, 16.96; F, 34.32. Found: C, 43.19; H, 5.63; N, 16.83; F, 34.07.

Pentamethylenediamine. Pentane-1,5-bis(trifluoromethyl)carboxamidine [$CF_3C(=NH)NH(CH_2)_5NHC(=NH)CF_3$].—(1) Addition of a solution containing 1.2 g. (0.012 mole) of pentamethylenediamine in 5 ml. of anhydrous ether to 7.7 g. (0.081 mole) of liquid trifluoroacetonitrile immediately gave a white solid. The nitrile was refluxed for 45 min. and then removed. This was followed by the addition of dry hexane (20 ml.) to the reaction mixture. The solid was filtered, washed with hexane, and dried to give 3.1 g. (91%) of a white product. This material was dissolved in anhydrous ether (40 ml.) and precipitated with hexane (80 ml.). The melting point was 75.5–76.5°.

Anal. Calcd. for $C_9H_{14}N_2F_3$: C, 36.99; H, 4.83; N, 19.18; F, 39.01. Found: C, 37.12; H, 4.91; N, 19.00; F, 38.87.

The Hydrochloride Salt.—Dry hydrogen chloride was bubbled into a solution containing 1.5 g. (0.0051 mole) of the carboxamidine dissolved in 40 ml. of anhydrous ether. A white product precipitated immediately. The solvent was removed under vacuum. A chloride analysis of the solid was lower than theoretical. Consequently, the material was redissolved in 40 ml. of anhydrous ethanol and again treated with dry hydrogen chloride. Addition of 500 ml. of anhydrous ether caused an oil to separate. This solidified after 12 hr. The yield was 1.5 g. (80%). A definite melting point could not be obtained because the compound rapidly decomposed at approximately 175°.

Anal. Calcd. for $C_9H_{10}N_2Cl_2F_6$: Cl, 19.47. Found: Cl, 19.35.

(2) Into a solution of 4.1 g. (0.04 mole) of pentamethylenediamine in 10 ml. of anhydrous ether was distilled 11.0 g. (0.116 mole) of trifluoroacetonitrile. The nitrile was allowed to reflux for 45 min., then the excess was distilled into a trap maintained at about −80°. The solid produced was dissolved by addition of 70 ml. of anhydrous ether to the reaction mixture. Addition of dry hexane (300 ml.) gave 11.0 g. (95%) of crude pentane 1,5-bis(trifluoromethyl)carboxamidine, melting at 73.5–75°.

Hexamethylenediamine. (a) Hexane-1,6-bis(trifluoromethyl)carboxamidine [$CF_3C(=NH)NH(CH_2)_6NHC(=NH)CF_3$].—A solution of 1.7 g. (0.015 mole) of hexamethylenediamine in 6 ml. of anhydrous ether was added to 9.4 g. (0.099 mole) of liquid trifluoroacetonitrile. The excess nitrile was refluxed for 45 min. and then distilled into a trap. Prior to filtration of the product, 40 ml. of dry hexane was added to the reaction mixture. The white solid (4.2 g.; 91%) was dissolved in 230 ml. of anhydrous ether followed by the addition of 400 ml. of dry hexane. After 52 hr., small starlike crystals had formed on the bottom of the flask. These were filtered to give a solid melting at 103–103.5°.

Anal. Calcd. for $C_{10}H_{16}N_4F_6$: C, 39.21; H, 5.27; N, 18.29; F, 37.22; Found: C, 39.42; H, 5.46; N, 18.40; F, 36.94.

The **hydrochloride salt** was obtained by dissolving 0.1 g. of the product in 40 ml. of anhydrous ether and adding this to 80 ml. of ether saturated with dry hydrogen chloride. Immediately a sticky white precipitate was formed. Most of the ether was decanted; the remainder was evaporated under vacuum. The salt, which rapidly decomposed at about 185°, seemed hygroscopic and was redried prior to analysis.

Anal. Calcd. for $C_{10}H_{18}N_4Cl_2F_6$: Cl, 18.70. Found: Cl, 18.78.

Heptamethylenediamine. (a) Heptane-1,7-bis(trifluoromethyl)carboxamidine [$CF_3C(=NH)NH(CH_2)_7NHC(=NH)CF_3$].—A solution of 1.9 g. (0.016 mole) of heptamethylenediamine in 6 ml. of anhydrous ether was added to 7.4 g. (0.078 mole) of trifluoroacetonitrile. The excess nitrile was allowed to reflux for 45 min. then removed by distillation. Dry hexane (40 ml.) was added and the mixture filtered to give 4.4 g. (88%) of product. This solid was dissolved in 50 ml. of anhydrous ether followed by the addition of 70 ml. of hexane. After 34 hr., a white solid had formed on the bottom of the flask. It melted at 90–91.5°.

Anal. Calcd. for $C_{11}H_{18}N_4F_6$: C, 41.24; H, 5.66; N, 17.49; F, 35.59. Found: C, 41.21; H, 5.56; N, 17.65; F, 35.42.

The Hydrochloride Salt.—Dry hydrogen chloride was bubbled into a solution of 1.0 g. (0.0031 mole) of the free base in 5 ml. of anhydrous ethanol and 20 ml. of anhydrous ether. Then, 50 ml. of anhydrous ether was added to bring about the separation of a colorless oil. After 20 hr., as much as possible of the solvent was decanted. The remainder was removed under vacuum leaving a white solid. It appeared to be extremely hygroscopic and slowly evolved a gas when heated. The analytical sample was dried at 100° *in vacuo* over phosphorus pentoxide.

Anal. Calcd. for $C_{11}H_{20}N_4Cl_2F_6$: Cl, 18.03. Found: Cl, 18.31.

N,N-Dimethylethylenediamine. (a) **N-(β-Dimethylaminoethyl)trifluoroacetamidine [$CF_3C(=NH)NH(CH_2)_2N(CH_3)_2$].**—In a flask equipped with a Dry Ice–acetone reflux condenser and a magnetic stirrer was placed 3.1 g. (0.035 mole) of N,N-dimethylethylenediamine in 10 ml. of anhydrous ether. Trifluoroacetonitrile (5.1 g.; 0.054 mole) was distilled into the system. The nitrile was refluxed for 90 min., then removed. The solid product was recrystallized from chloroform and then sublimed to give 5.1 g. (78%) of a white substance melting at 108–109° (with sublimation). The solid was quite unstable, decomposing into a brown tar.

Anal. Calcd. for $C_6H_{12}N_3F_3$: C, 39.34; H, 6.60; N, 22.94; F, 31.11. Found: C, 36.60; H, 6.68; N, 22.63; F, 29.65.

The **hydrochloride salt** was prepared as follows: A solution containing 285 mg. (0.00156 mole) of the amidine dissolved in 50 ml. of anhydrous ether was added to a solution of anhydrous ether saturated with dry hydrogen chloride. Immediately a white precipitate formed. The mixture was stirred for 20 min. before the solvent was decanted. The product was dried under vacuum. The salt decomposed at approximately 205° (with evolution of a gas). It was hygroscopic.

Anal. Calcd. for $C_6H_{14}N_3Cl_2F_3$: C, 28.14; H, 5.10; Cl, 27.69; F, 22.26. Found: C, 25.38; H, 6.40; Cl, 27.5; F, 18.83.

N,N-Di-*n*-butylethylenediamine. (a) **N-(β-di-*n*-butylaminoethyl)trifluoroacetamidine [$CF_3C(=NH)NH(CH_2)_2N(C_4H_9)_2$].**—Trifluoroacetonitrile (10.5 g.; 0.11 mole) was distilled into a flask (equipped with a Dry Ice–acetone reflux condenser and a magnetic stirrer) containing 8.6 g. (0.05 mole) of N,N-di-*n*-butylethylenediamine dissolved in 10 ml. of anhydrous ether. The excess nitrile was allowed to reflux for 1 hr. and then removed. The solution, light yellow in color, was kept at about 4° for 2 hr. whereupon light yellow crystals formed. The filtrate was evaporated to yield more of the product. The solid was recrystallized from hexane, the analytical sample from a hexane–ether mixture (5:1). The over-all yield was 10.9 g. (81%) of material melting at 50–51°.

Anal. Calcd. for $C_{12}H_{24}N_3F_3$: C, 53.90; H, 9.05; N, 15.73; F, 21.32. Found: C, 53.65; H, 8.86; N, 15.53; F, 21.06.

After a few months, the solid had decomposed into a light yellow liquid.

The **hydrochloride salt** was prepared as above. It melted at 165.5–167°.

Anal. Calcd. for $C_{12}H_{26}N_3Cl_2F_3$: Cl, 20.81. Found: 20.84.

Reduction of the Products of Periodate Oxidation of Carbohydrates. XII. Methylation Studies on Cellulose Polyalcohol[1]

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Cellulose has been oxidized with sodium periodate and the resulting polyaldehyde reduced with sodium borohydride to cellulose polyalcohol. Methylation of this polyalcohol has yielded the corresponding trimethyl ether which upon hydrolysis gave 1,4-di-*O*-methylerythritol and methoxyacetaldehyde. A small proportion of racemic 1-*O*-methylerythritol was also produced, probably as a result of demethylation and its formation is not believed to be of any constitutional significance.

In previous communications[2,3] it was shown that the alcohols derived from the periodate oxidation products (the "dialdehydes") of methyl glycosides by reduction, undergo smooth methylation to give good yields of methylated derivatives whose structures were readily determined by hydrolysis and identification of the products so formed. Thus D′-methoxy-D-hydroxymethyl diethylene glycol, obtained[4] from methyl α-D-glucopyranoside by periodate oxidation followed by reduction, afforded the corresponding tri-*O*-methyl ether which upon hydrolysis furnished 1,3-di-*O*-methylglycerol and methoxyacetaldehyde. As a result of these studies it was pointed out[2,3] that the same general technique should be applicable to the polyalcohols derived from polysaccharides by periodate oxidation followed by reduction and that the procedure might prove useful for investigating the structure of polysaccharides. This technique, already applied to amylopectin polyalcohol,[5] has now been extended to cellulose.

Cellulose (I), in the form of defatted native

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