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S-TRIAZINES

V. Synthesis of Fluoroalkylguanamines by Reaction of Fluoroolefins with Biguanide*

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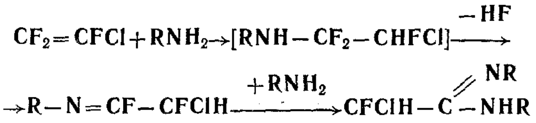
A study is made of the reaction of tetrafluoroethylene, trifluorochloroethylene, and perfluoropropylene with biguanide in dimethylformamide solution. It is shown that these reactions give good yields of guanamines containing the CF_2H, $CFClH$, and CF_3-CFH groups, and also biguanide dihydrofluoride. A reaction mechanism postulating intermediate formation of substituted amidines, is put forward.

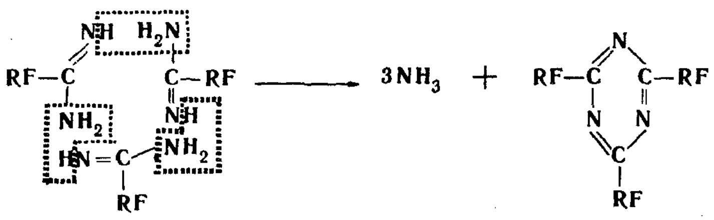
In 1950 Pruett and others investigated the reactions of a number of aliphatic and aromatic amines with trifluorochloroethylene in anhydrous medium. It was first shown that trifluorochloroethylene reacts with aliphatic primary amines to give mixtures of substituted iminofluorides and amidines of fluorochloroacetic acid [1].



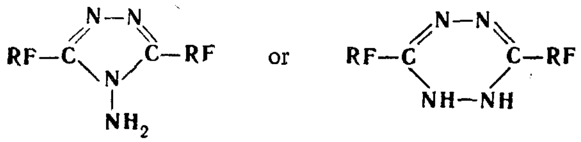
$$CF_2{=}CFCl+RNH_2 \rightarrow [RNH-CF_2-CHFCl] \xrightarrow{-HF}$$
$$\rightarrow R-N{=}CF-CFClH \xrightarrow{+RNH_2} CFClH-C({=}NR)-NHR$$

This showed that amidines of perfluorocarboxylic acids, unlike their hydrogen analogs, are fully stable compounds, which can be successfully used for various syntheses, and in particular for preparing heterocyclic nitrogen compounds.

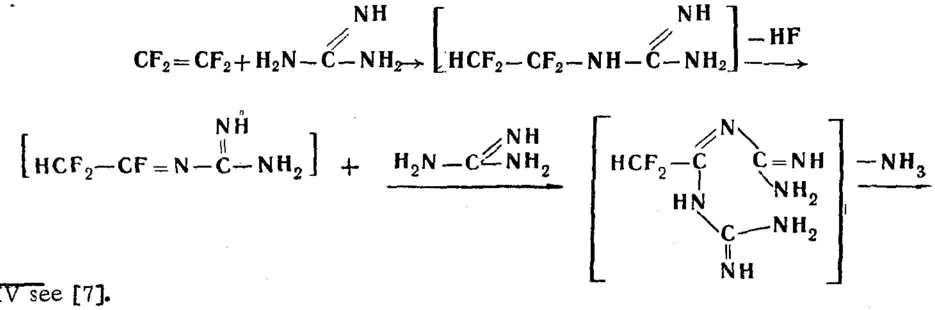
In recent years a number of other authors have synthesized perfluoroalkylamidines from perfluoronitriles of carboxylic acids by treating them with liquid ammonia, primary and secondary amines, hydrazine, and also unsymmetrical dimethylhydrazine [2-5]. Reilly and Brown [6] heated various fluoroalkylamidines at about 125°, and obtained quite satisfactory yields of tris(perfluoroalkyl)-s-triazines.



Treatment of trifluoroacenitrile and prefluoropropionitrile with hydrazine also led to isolation of cyclic products with the following structure [5]:



We investigated the reaction of φ-olefins with guanidine in dry solution, and found that formation of fluoroalkylguanamines proceeds via the intermediate state of formation of the corresponding amidines [7]:



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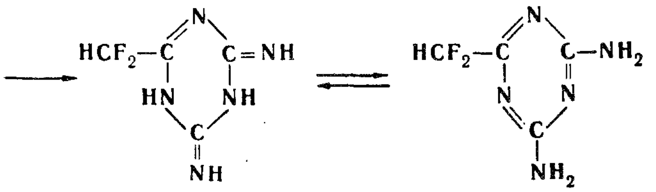
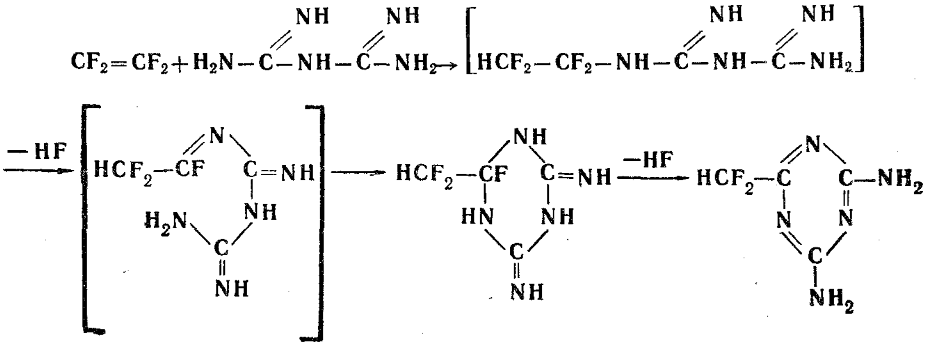
* For Part IV see [7].



The mechanisms of the reaction of φ-olefins with biguanide $-H_2N-C(=NH)-NH-C(=NH)-NH_2$ was of interest in this connection, since it, unlike guanidine, is a diacid base, and also, as experiments showed, the basic reaction products were fluoroalkylguanamines. We consider that formation of s-triazines in this case also proceeds via the substituted amidines stage, thus:



The reaction of φ-olefins with biguanide has been investigated for tetrafluoroethylene, φ-propene, and trifluorochloroethylene. With all φ-olefins reaction is accompanied by a great evolution of heat, and formation of biguanide dihydrofluoride. If tetrafluoroethylene and biguanide react to give a quantitative yield of difluoromethylguanamine, with φ-propene and trifluorochloroethylene, reaction is complicated by extensive resinification, so that yields of s-triazines are considerably cut. Generally s-triazine compounds could not be isolated when using perfluoroisobutene.

Dimethylformamide was used as the solvent in these reactions because guanide and biguanide are soluble only in it and in alcohols. In these reactions use of the latter is precluded.

The constants of the fluoroalkylguanamines prepared are in good agreement with those of guanamines prepared by other methods, particularly by condensing the appropriate φ-olefins with guanidine. They are all readily soluble in dimethylformamide, methanol, acetonitrile, and aqueous solutions of acids, and their analyses, and also the results of spectroscopic investigations, show the names to be correct.

Experimental

Biguanide was prepared by Ostrogovich's method [8], fusing 1 mole dicyanodiamide with 2 moles NH_4NO_3, at 130°.

2-Difluoromethyl-4,6-diamino-s-triazine. 18 g (0.18 mole) biguanide and 50 ml dimethylformamide were placed in a 150 ml 4-necked flask fitted with a stirrer, thermometer, and gas inlet and outlet tubes. The temperature was raised to 60-70°, the mixture energetically stirred, and dry tetrafluoroethylene passed in, so long as the temperature of the reaction mixture remained over 30°, after which it was raised to 80-85°, and tetrafluoroethylene passed in at the rate of 5 l/hr for a further hour. The precipitate (9 g, biguanide dihydrofluoride) was filtered off, washed with ether, and dried. Dimethylformamide was distilled off from the filtrate under reduced pressure. The crystals (12.1 g, 85%) remaining in the flask were washed with 40 ml cold water, and filtered off. Then they were dissolved in 10% HCl, boiled with active charcoal, and neutralized with 10% NaOH. The white crystals precipitated were well washed to free them from NaCl, and dried. MP 277°. Found: F 23.6; N 43.4%. Calculated for $C_4H_5F_2N_5$: F 23.6; N 43.4%.

2-Fluorochloromethyl-4,6-diamino-s-triazine. The experiment was carried out in a way similar to the above. Trifluorochloroethylene was passed, at a rate of 2-3 l/hr, into a solution of 18 g biguanide in 50 ml dimethylformamide, the temperature being kept below 40°. The precipitate of crystals was filtered off, and from the filtrate solvent distilled off under reduced pressure at a temperature not over 50°. The crystals obtained, 6.3 g (40%) were dissolved in 10% HCl, the solution boiled with active charcoal, and made slightly alkaline with 10% NaOH. The crystals precipitated were filtered off with suction, and washed with water until a negative reaction for Cl^- was obtained. 2-Fluoromethyl-

4, 6-diamino-s-triazine formed colorless crystals, decomposing over 300°. Found: C 27.1; H 2.5; F 11.1; Cl 19.6; N 40.0%. Calculated for $C_4H_5FClN_5$: C 27.0; H 2.8; F 10.7; Cl 20.0; N 39.5%.

Picrate, mp 182-183° (ex MeOH). Found: F 5.0; Cl 8.5; N 27.1%. Calculated for $C_{10}H_8FClN_8O_7$: F 4.7; Cl 8.6; N 27.5%.

2-α-Hydroperfluoroethyl-4, 6-diamino-s-triazine. This experiment was carried out similarly. Perfluoropropene was passed, for 4 hr, at the rate of 1.5 *l*/hr, into a solution of 18 g biguanide in 100 ml dimethylformamide held at under 30°. The biguanide dihydrofluoride was filtered off, and the solvent distilled off from the filtrate under reduced pressure, at a temperature not exceeding 40°. Yield of 2-hydroperfluoroethyl-4, 6-diamino-s-triazine, 3.8 g (20%), mp 226° (ex acetonitrile). Found: F 35.8; N 33.8%. Calculated for $C_5H_5F_4N_5$: F 36.0; N 33.2%.

The IR spectra of the above triazines were completely identical with those of the same triazines as prepared by condensing guanidine with fluoroolefins.

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