

## ALIPHATIC FLUORO DIAZO COMPOUNDS

## COMMUNICATION 1. SOME NEW REACTIONS OF 2-DIAZO-1,1,1-TRIFLUOROETHANE

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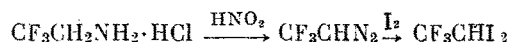
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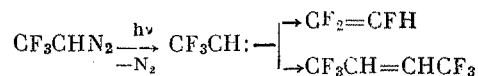
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2-Diazo-1,1,1-trifluoroethane  $\text{CF}_3\text{CHN}_2$  was prepared in 1943 by Gilman and Jones [1]; they showed that its reaction with iodine led to 1,1,1-trifluoro-2,2-diiodoethane:



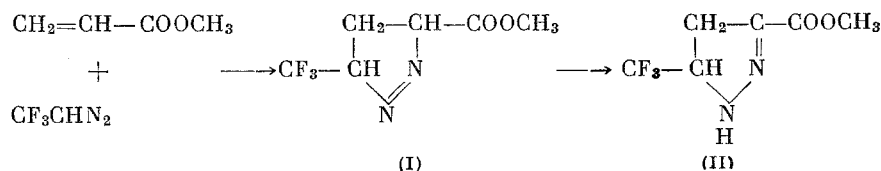
In 1960 Fields and Haszeldine [2] studied the photochemical decomposition of diazotrifluoroethane and found that the (trifluoromethyl)carbene then formed became stabilized in two ways: isomerization into trifluoroethylene and dimerization into 1,1,1,4,4,4-hexafluoro-2-butene:



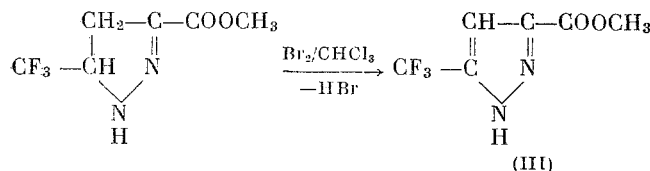
To obtain a more complete view of the reactivity of (perfluoroalkyl)diazomethanes and of the possibilities for the synthesis from these of various types of organofluorine compounds, we investigated some characteristic reactions of diazoalkanes in their application to 2-diazo-1,1,1-trifluoroethane. It was of interest to determine to what extent the powerful electron-accepting effect of the trifluoromethyl group, which determines the high stability of diazotrifluoroethane, lowers and limits the reactivity of the latter in comparison with other classes of aliphatic diazo compounds.

As would be expected, many reactions which go vigorously with dilute solutions of diazomethane will go only in concentrated solutions or in absence of solvents in the case of diazotrifluoroethane. We therefore worked mainly with pure diazotrifluoroethane, which its stability and boiling point (+13.5°) make quite feasible. Moreover, the lower activity of diazotrifluoroethane makes the rapid and reliable determination of its concentration in solution practically impossible by the methods developed for diazomethane, and in those cases in which it was necessary to work in solutions they had to be prepared from the pure substance.

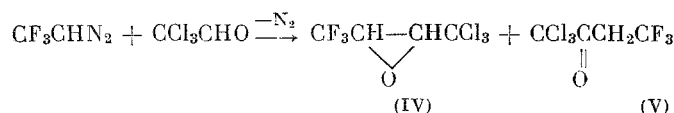
We carried out reactions of diazotrifluoroethane with compounds containing a carbon-carbon double bond (methyl acrylate), a carbonyl group (chloral), a carboxy group (dichloroacetic acid), a mercapto group (benzenethiol), a sulfonyl chloride group (p-chlorobenzenesulfonyl chloride), and a mercury-chlorine bond (mercuric chloride). Diazotrifluoroethane reacts very readily with methyl acrylate in solution at low temperature. In petroleum ether at -10° a liquid addition product is formed, and when kept at room temperature this substance is gradually converted into a crystalline isomer. The conversion is accelerated by heating, and also in presence of polar solvents. When the liquid isomer is dissolved in ethanol, ether, or carbon tetrachloride with subsequent evaporation of solvent the crystalline isomer is obtained, and it is also formed by the reaction of diazotrifluoroethane with methyl acrylate in petroleum ether at room temperature and in diethyl ether, even when cooled. According to the results of infrared spectroscopy the liquid adduct is methyl 5-(trifluoromethyl)-1-pyrazoline-3-carboxylate (I) and the crystalline adduct is the corresponding 2-pyrazoline isomer (II). The spectrum of (I) contains absorption bands due to  $\text{C}=\text{O}$  at  $1744\text{ cm}^{-1}$  and  $\text{N}=\text{N}$  (weak) at  $1554\text{ cm}^{-1}$ , and the spectrum of (II) contains an intense  $\text{C}=\text{N}$  band at  $1558\text{ cm}^{-1}$ , a  $\text{C}=\text{O}$  absorption band (displaced as a result of conjugation with  $\text{C}=\text{N}$ ) at  $1680\text{ cm}^{-1}$ , and an  $\text{N}-\text{H}$  absorption band at  $3300\text{ cm}^{-1}$ .



The comparative stability of the isomer (I) is explained by the effect of the trifluoromethyl group on the adjacent nitrogen atom, which shows itself in the reduced basicity of the latter. The usual rearrangement of (I) into (II), which consists in the transfer of a proton from carbon to nitrogen, is consequently retarded. A similar effect explains the high stability of (II): this compound can be distilled at atmospheric pressure at 245° with only slight decomposition. The oxidation of (II) with bromine in chloroform gives methyl 5-(trifluoromethyl)pyrazole-3-carboxylate (III) quantitatively:

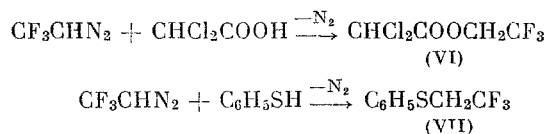


The reaction of diazotrifluoroethane with chloral was carried out in absence of solvent at room temperature with subsequent heating in a water bath. It gave 1,1,1-trichloro-2,3-epoxy-4,4,4-trifluorobutane (IV) and 1,1,1-trichloro-4,4,4-trifluoro-2-butanone (V):

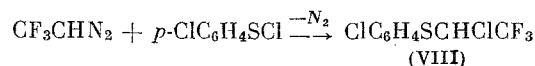


The structure of (V) was confirmed by the presence of an intense C = O absorption band at 1780 cm<sup>-1</sup> in its infrared spectrum.

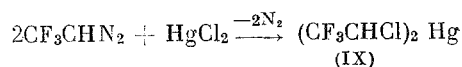
The reactions of diazotrifluoroethane with compounds containing a mobile hydrogen atom, e.g. dichloroacetic acid and benzenethiol, go smoothly at low temperature in absence of solvents with formation, respectively, of 2,2,2-trifluoroethyl dichloroacetate (VI) and phenyl 2,2,2-trifluoroethyl sulfide (VII):



Similarly, reaction with p-chlorobenzenesulfonyl chloride gives p-chlorophenyl 1-chloro-2,2,2-trifluoroethyl sulfide (VIII):



A particularly interesting possibility is the synthesis of fluorine-containing heteroorganic compounds from aliphatic fluoro diazo compounds, which we demonstrated for the case of the preparation of bis(1-chloro-2,2,2-trifluoroethyl)mercury (IX) from diazotrifluoroethane and mercuric chloride. This reaction goes in ethereal solution at 30°:



## EXPERIMENTAL

2-Diazo-1,1,1-trifluoroethane was prepared by Gilman and Jones's procedure [1], somewhat modified. A mixture of 13.5 g of 2,2,2-trifluoroethylamine hydrochloride, 20 ml of water, and 125 ml of bis-2-chloroethyl ether was prepared in a thick-walled 250-ml bottle. The mixture was cooled to  $-15^{\circ}$ , a solution of 8 g of sodium nitrite in 15 ml of water cooled to  $0^{\circ}$  was added, and finally 1 ml of 10% sulfuric acid was added. The mixture was shaken for 10 min and then cooled to  $-15^{\circ}$ , the organic layer was separated and set aside at  $-15^{\circ}$ , and 1 ml of 10% sulfuric acid and 75 ml of bis-2-chloroethyl ether were added to the aqueous layer, which was shaken at room temperature for 1 h. The mixture was treated as indicated above, and the operation was repeated with 25 ml of bis-2-chloroethyl ether. The combined organic extracts were washed with a little 5% sodium carbonate solution and dried over anhydrous calcium chloride. Diazotrifluoroethane was driven off from a water bath ( $70-90^{\circ}$ ) at 180-200 mm and was collected in a trap cooled to  $-78^{\circ}$ , in front of which there was placed a trap cooled to a temperature of from  $-15$  to  $-20^{\circ}$ . The yield of diazotrifluoroethane was 4.9-5.0 ml (7.4-7.5 g, 67-68%). The diazotrifluoroethane so obtained was used on the same day. On one occasion, when there was a sudden loss of vacuum in the course of the vacuum distillation, an explosion occurred.

Methyl 5-(Trifluoromethyl)-1-pyrazoline-3-carboxylate (I). 5.85 g of diazotrifluoroethane was added to a solution of 4.58 g of methyl acrylate in 40 ml of dry petroleum ether at  $-15^{\circ}$ , and the mixture was kept at from  $-15$  to  $-10^{\circ}$  for about 5 h. The reaction product, which was insoluble in petroleum ether, separated as a lower layer. The mixture was left at room temperature for 12 h, and the lower layer was then separated and vacuum-distilled. Yield 9.0 g (86.5%); b.p.  $55-56^{\circ}$  (0.25 mm);  $n_D^{20}$  1.4045;  $d_4^{20}$  1.3742. Found: C 36.66, 36.72; H 3.74, 3.58; F 28.76, 28.56; N 14.50, 14.80%; MR 34.94.  $C_6H_7F_3N_2O_2$ . Calculated: C 36.74; H 3.60; F 29.12; N 14.28%; MR 34.90.

Methyl 5-(Trifluoromethyl)-2-pyrazoline-3-carboxylate (II). 6.24 g of diazotrifluoroethane was added with cooling to a solution of 5.3 g of methyl acrylate in 40 ml of dry petroleum ether. The temperature of the mixture was brought up to that of the room, and the mixture was then left for 12 h. The crystals that came down were filtered off, and we obtained 9.4 g of a substance (86.4%) of m.p.  $109-109.5^{\circ}$  (from benzene or water). Found: C 36.76, 36.96; H 3.59, 3.68; F 29.07, 29.35; N 14.62, 14.52%.  $C_6H_7F_3N_2O_2$ . Calculated: C 36.74; H 3.60; F 29.12; N 14.28%.

Methyl 5-(Trifluoromethyl)pyrazole-3-carboxylate (III). Bromine was added dropwise to 1 g of (II) in 5 ml of chloroform until the color persisted. Vigorous liberation of hydrogen bromide was observed. Chloroform was evaporated, and we obtained a quantitative yield of (III), m.p.  $134.5-135^{\circ}$  (from chloroform). Found: C 37.14, 37.22; H 2.55, 2.54; F 29.53, 29.35; N 14.34, 14.31%.  $C_6H_5F_3N_2O_2$ . Calculated: C 37.12; H 2.60; F 29.36; N 14.53%.

Reaction of 2-Diazo-1,1,1-trifluoroethane with Chloral. 7.3 g of chloral was introduced into a 20-ml flask provided with reflux condenser cooled to  $-78^{\circ}$  and connected through a column containing calcium chloride to a gas buret for the collection of the nitrogen liberated, and with cooling to  $-78^{\circ}$ , 6.9 g of diazotrifluoroethane was added. Nitrogen soon began to come off, at first extremely quickly so that it was necessary to cool the reaction mixture from time to time with a mixture of solid carbon dioxide and acetone. After 2-3 h the reaction slowed down. The mixture was left overnight at room temperature and then heated for 4 h in a water bath. As a result of vacuum distillation we obtained: 1) 1,1,1-trichloro-2,3-epoxy-4,4,4-trifluorobutane (IV); b.p.  $52-56^{\circ}$  (55 mm); yield 6.1 g (53.8%). After redistillation it had: b.p.  $63^{\circ}$  (102 mm);  $n_D^{20}$  1.3990;  $d_4^{20}$  1.5731. Found: C 20.84, 20.82; H 0.95, 1.07; F 24.25, 24.29%; M 225.1 (determined cryoscopically in benzene); MR 35.28.  $C_4H_2F_3Cl_3O$ . Calculated: C 20.94; H 0.88; F 24.85%. M 229.4; MR 35.14. 2) 1,1,1-Trichloro-4,4,4-trifluoro-2-butanone (V), b.p.  $69-70^{\circ}$  (55 mm); yield 3.6 g (31.7%). After redistillation it had: b.p.  $72^{\circ}$  (60 mm);  $n_D^{20}$  1.4100;  $d_4^{20}$  1.5977. Found: C 21.20, 21.16; H 0.57, 0.52; F 24.90, 24.67%; M 228.3 (determined cryoscopically in benzene); MR 35.58.  $C_4H_2F_3Cl_3O$ . Calculated: C 20.94; H 0.88; F 24.85%; M 229.4; MR 35.70.

2,2,2-Trifluoroethyl Dichloroacetate (VI). The procedure was similar to that of the preceding experiment. For reaction we took 9.3 g of dichloroacetic acid and 7.2 g of diazotrifluoroethane. The mixture was washed with sodium bicarbonate solution, dried with calcium chloride, and distilled. We obtained 10 g (72.5%) of (VI); b.p.  $138.5^{\circ}$ ;  $n_D^{20}$  1.3858;  $d_4^{20}$  1.5262. Found: C 22.49, 22.60; H 1.59, 1.52; F 26.90, 27.20%; MR 32.44.  $C_4H_3F_3Cl_2O_2$ . Calculated: C 22.77; H 1.43; F 27.02%; MR 32.48.

Phenyl 2,2,2-Trifluoroethyl Sulfide (VII). This was prepared similarly from 4.9 g of benzenethiol and 5.4 g of diazotrifluoroethane. Yield 7.6 g (89%); b.p.  $49^{\circ}$  (3 mm);  $n_D^{20}$  1.4890;  $d_4^{20}$  1.2642. Found: C 50.04, 49.88; H 3.59, 3.67; F 28.96, 29.49%; MR 43.85.  $C_8H_7F_3S$ . Calculated: C 50.02; H 3.67; F 29.68%; MR 43.96 ( $AR_S$  was taken to be 8.00).

p-Chlorophenyl 1-Chloro-2,2,2-trifluoroethyl Sulfide (VIII). This was prepared similarly from 5.38 g of p-chlorobenzenesulfenyl chloride and 4.5 g of diazotrifluoroethane; yield 6.5 g (77.2%); b.p. 89-91° (3 mm). After redistillation it had: b.p. 82.5° (2 mm);  $n_D^{20}$  1.5170;  $d_4^{20}$  1.4602. Found: C 36.68, 36.86; H 1.87, 2.02; F 21.42, 20.88%; MR 54.05.  $C_8H_5F_3Cl_2S$ . Calculated: C 36.80; H 1.93; F 21.83%; MR 53.70 ( $AR_S$  was taken to be 8.00).

Bis(1-chloro-2,2,2-trifluoroethyl)mercury (IX). A mixture of 17.6 g of mercuric chloride, 16 g of diazotrifluoroethane, and 25 ml of dry ether was introduced into a 50-ml flask provided with reflux condenser cooled to -78° and connected through a column containing calcium chloride to a gas buret. The mixture was warmed in a water bath up to 30°, and when the liberation of nitrogen had stopped it was filtered. Ether was driven from the filtrate and the residue was distilled. A substance came over at 205-220°; it solidified; yield 12.8 g (45.5%). It was redistilled in a vacuum [115-120° (6 mm)] over a little concentrated sulfuric acid, and was then crystallized from hexane; m.p. 82-83°. Found: C 10.78, 10.73; H 0.37, 0.45; F 26.48, 26.78%.  $C_4H_2F_6Cl_2Hg$ . Calculated: C 11.02; H 0.46; F 26.17%.

#### SUMMARY

For the case of 2-diazo-1,1,1-trifluoroethane it was shown that (perfluoroalkyl)diazomethanes can be applied in the synthesis of various classes of organofluorine compounds.

#### LITERATURE CITED

1. H. Gilman and R. G. Jones, J. Amer. Chem. Soc., 65, 1458 (1943).
2. R. Fields and R. N. Haszeldine, Proc. Chem. Soc., No. 1, 22 (1960).