distilled and purified by preparative TLC on Silica Gel L 100/160 μm (eluant= 10:1 benzene–acetone).

CONCLUSIONS

The S-β-aryl(benzyl)mercaptoethyl esters of the diethyl- and dihexylthiophosphoric acids, and of the O-ethyl-, O-butyl-, O-cyclohexylmethyl-, and O-ethylphenylthiophosphonic acids, were synthesized.

LITERATURE CITED

1. A. P. Brestkin and N. N. Godovikov, Usp. Khim., 47, 1609 (1978).
2. M. Kh. Berkhamov, L. M. Zakharova, L. G. Grineva, V. M. Kuzamyshev, G. G. Ol'khovaya, M. Kh. Bekanov, R. S. Agabekyan, N. N. Godovikov, and M. I. Kabachnik, Izv. Akad. Nauk SSSR, Ser. Khim., 879 (1981).
3. L. G. Grineva, G. G. Ol'khovaya, V. M. Kuzamyshev, M. Kh. Bekanov, A. Z. Taubulatova, T. M. Musukaeva, M. Kh. Berkhamov, and N. N. Godovikov, in: Chemistry of Physiologically Active Compounds [in Russian], Vol. 2, Nalchik (1978), p. 9.
4. B. V. Kopylova, Ya. V. Yashkina, Sh. A. Karapet'yan, and R. Kh. Freidlina, Izv. Akad. Nauk SSSR, Ser. Khim., 5 (1975).
5. N. A. Karbanov, V. M. Kuzamyshev, L. G. Grineva, M. Kh. Bekanov, G. G. Ol'khovaya, Z. A. Shavaeva, M. Kh. Berkhamov, and N. N. Godovikov, in: Chemistry of Physiologically Active Compounds [in Russian], Vol. 2, Nalchik (1978), p. 21.
6. G. Schrader, German Patent 961,083 (1954).

1,1-BIS(TRIFLUOROMETHYL)HYDRAZINE

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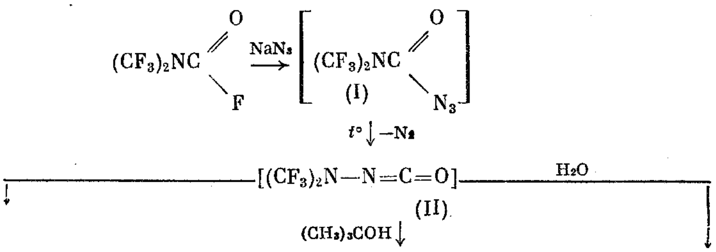
UDC 542.91:547.234'161

Previously it was reported that bis(trifluoromethyl)carbamic acid azide (I) (obtained by reacting bis(trifluoromethyl)carbamoyl fluoride with a suspension of NaN_3 in xylene) decomposes to give the unstable bis(trifluoromethyl)amino isocyanate (II), which spontaneously trimerizes to (III) [1].

In order to synthesize 1,1-bis(trifluoromethyl)hydrazine* the decomposition of azide (I) was run in the presence of either tert-butanol or water. In the first case tert-butyl bis(trifluoromethyl)-carbamate (IV) is formed, whose pyrolysis at 270-300°C gave 1,1-bis(trifluoromethyl)hydrazine (V). However, it is more convenient to obtain hydrazine (V) by the decomposition of azide (I) in the presence of water.



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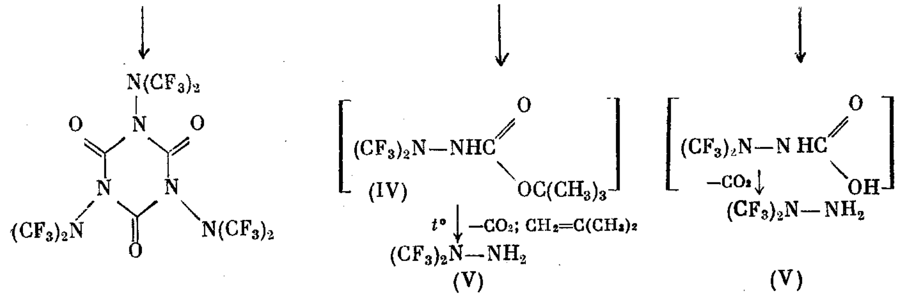
*We were unable to obtain 1,1-bis(trifluoromethyl)hydrazine either by the reduction of bis(trifluoromethyl)nitrosamine or by the reaction of bis(trifluoromethyl)chloramine with ammonia.

A. N. Nesmeyanov Institute of Heteroorganic Compounds, Academy of Sciences of the USSR, Moscow. Translated from Izvestiya Akademii Nauk SSSR, Seriya Khimicheskaya, No. 2, pp. 436-438, February, 1984. Original article submitted May 16, 1983.



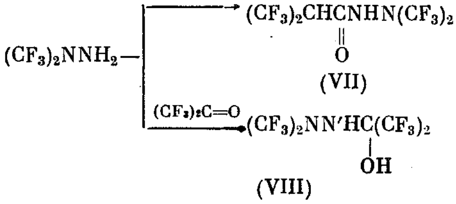
Hydrazine (V) is stable, does not form salts with either CF_3COOH or HCl, but reacts easily with electrophilic reagents. Thus, in the reaction with perfluoro-2-azapropene both of the hydrogen atoms of hydrazine (V) react to give N,N-bistrifluoromethyl-N',N'-bis(tetrafluoro-2-azapropenyl)hydrazine (VI).

$$(CF_3)_2N{-}NH_2 \xrightarrow[-(CF_3)_2NH]{2CF_3N=CF_2} [(CF_3)_2N{-}NH{-}CF{=}N{-}CF_3]$$

$$\xrightarrow[(CF_3)_2NH]{2CF_3N=CF_2} (CF_3)_2N{-}N'(CF{=}N{-}CF_3)_2$$

(VI)

Hradrazine reacts smoothly with carbonyl compounds. Thus, it adds in quantitative yield to bis(trifluoromethyl)ketene [$(CF_3)_2C{=}C{=}O$] and hexafluoroacetone to respectively give α-monohydrohexafluoroisobutyric acid bis(trifluoromethyl)hydrazide (VII) and N,N-bis(trifluoromethyl)-N'-α-hydroxyhexafluoroisopropylhydrazine (VIII).


$(CF_3)_2NNH_2 \rightarrow (CF_3)_2CHC(=O)NHN(CF_3)_2$ (VII)

$(CF_3)_2NNH_2 \xrightarrow{(CF_3)_2C=O} (CF_3)_2NN'HC(OH)(CF_3)_2$ (VIII)

The dehydration of hydrazine (VIII) with oleum gave hexafluoroacetone bis(trifluoromethyl)hydrazone (IX), the first member of the fully fluorinated hydrazones.

$$(VIII) \xrightarrow[-H_2O]{H_2SO_4\cdot SO_3} (CF_3)_2NN{=}C(CF_3)_2$$

(IX)

EXPERIMENTAL

The IR spectra were taken on a Perkin-Elmer-225 instrument, the ^{19}F NMR spectra were taken on a Perkin-Elmer R-20 instrument (56.46 MHz, standard = CF_3COOH), and the mass spectra were taken on a Varian MAT CH-8 instrument.

A solution of bis(trifluoromethyl)carbamic acid azide (I) was obtained by adding bis(trifluoromethyl)carbamoyl fluoride to a suspension of NaN_3 in o-xylene at 5-10°C.

1,1-Bis(trifluoromethyl)hydrazine (V). Method A. To a xylene solution of azide (I) (from 10 g of bis(trifluoromethyl)carbamoyl fluoride and 5 g of NaN_3) was added 3.7 g of tert-butanol and the mixture was heated on the steam bath, gradually raising the temperature to 90-100°C. After the N_2 evolution had ceased a part of the xylene was vacuum-distilled. The residue was cooled with solid CO_2. The obtained crystals of tert-butyl bis(trifluoromethyl)aminocarbamate (IV) were filtered and distilled to give 5.3 g (34.6%) of (IV), bp 245-247°. Found: C 30.36; H 3.41; N 10.28; F 43.20%. $C_7H_{10}O_2N_2F_6$. Calculated: C 31.34; H 3.73; N 10.44; F 42.53%. Infrared spectrum (ν, cm^{-1}): 1750 (C=O), 3100 (NH). ^{19}F NMR spectrum (δ, ppm): —15.6 s ($(CF_3)_2N$) mass spectrum 253 $[M - CH_3]^+$. Pyrolysis of (IV). The vapors of (IV) (10.5 g) were passed in a helium stream through a glass tube heated at 270-300°C. Fractional distillation of the pyrolysis product gave 1.8 g (81%) of isobutylene (bp —7°C) and 3 g (45%) of (V), bp 39-40°, n_D^{20} 1.2850, d_4^{20} 1.4803. Found: C 14.67; H 1.21; N 16.41% $C_2H_2N_2F_6$. Calculated: C 14.28; H 1.19; N 16.41%. ^{19}F NMR spectrum: 10.00 ppm, s. PMR spectrum: 3.5 ppm, s. Mass spectrum: 168 M^+, 149 $[M - F]^+$, 129 $[M - F - HF]^+$.

Method B. To a xylene solution of azide (I) (from 10 g of 1,1-bis(trifluoromethyl)-carbamoyl fluoride) was added 5 ml of water and the vigorously stirred mixture was heated at 70-90°C until the N_2 evolution ceased. Here product (V) was collected in a receiver cooled in solid CO_2. After distillation over zeolite we obtained 4.5 g (54%) of (V), bp 39-40°, n_D^{20} 1.2855, ^{19}F NMR = 10.1 ppm, s.

N,N-Bis(trifluoromethyl)-N'-bis(tetrafluoro-2-azapropenyl)-hydrazine (VI). A mixture of 3.4 g of (V) and 4 ml of perfluoro-2-azapropene was shaken in a glass ampul at ∿20°C for 6 h. Then the bis(trifluoromethyl)amine was distilled off (bp —6°C) and we obtained 3.5 g (59%) of (VI), bp 96-97°, n_D 1.2990. Found: C 18.22; N 14.24; F 67.34%. $C_6N_4F_{14}$. Calculated: C 18.27; N 14.21; F 67.51%. Infrared spectrum: 1740 cm^{-1} (C=N). ^{19}F NMR spectrum (δ, ppm): —43.7 m (CF), —20.63 d (CF_3N), —20.56 d (CF_3N), —16.4 m ($(CF_3)_2N$). Mass spectrum: 394 M^+, 228 $[C_4N_2F_8]^+$, 114 $[C_2NF_4]^+$.

2-Monohydrohexafluorosiobutyric Acid Bis(trifluoromethyl)hydrazide (VIII). To a solution of 2 g of bis(trifluoromethyl)ketene in dry ether at —10 to —15°C was added 2 g of (V) and the mixture was allowed to stand overnight. After distilling off the ether we obtained 3.3 g (80%) of (VII) as white needle crystals, mp 160-162°C (decompn.) (from diisopropyl ether). Found: C 20.60; H 0.54; N 7.89; F 65.19%. $C_6H_2H_2OF_{12}$. Calculated: C 20.80; H 0.57; N 8.09; F 65.89%. ^{19}F NMR spectrum (δ, ppm): —13.5 s (CF_3N), —12.4 (CF_3), J_{F-H} = 8 Hz.

N,N-Bis(trifluoromethyl)-N'-α-hydrohexafluoroisopropylhydrazine (VIII). A mixture of 3.4 g of (V) and 3.4 g of hexafluoroacetone in a glass ampul was shaken for 12 h and then distilled to give 3.3 g (83%) of (VIII), bp 96-97°; n_D^{20} 1.990. Found: C 17.93; H 0.69; N 8.71; F 67.74%. $C_5H_2N_2OF_{12}$. Calculated: C 17.96; H 0.59; N 8.38; F 68.26%. Mass spectrum: 334 M^+. ^{19}F NMR spectrum (δ, ppm): —13.3 (CF_3), 1.5 s (CF_3).

Hexafluoroacetone Bis(trifluoromethyl)hydrazine (IX). With stirring, 5.2 g of (VIII) was added to oleum. The fraction with bp 48°C was distilled off by heating on the steam bath. After shaking with H_2SO_4 and redistillation we obtained 3.8 g (78%) of (IX), bp 48°, n_D^{20} 1.280. Found: F 71.77%. $C_5N_2F_{12}$. Calculated: F 72.15%. ^{19}F NMR spectrum (δ, ppm): —12.8 m (CF_3N), —12.0 m (CF_3). Mass spectrum: 316 M^+, 297 $[M - F]^+$, 247 $[M - CF_3]^+$, 28 $[M - F - CF_3]^+$.

CONCLUSIONS

1. The stable 1,1-bis(trifluoromethyl)hydrazine was synthesized by the thermal decomposition of either tert-butyl bis(trifluoromethyl)carbamate or a solution of bis(trifluoromethyl)carbamic acid azide in the presence of water, and its reaction with perfluoro-2-azapropene, bis(trifluoromethyl)ketene, and hexafluoroacetone was studied.

2. The dhydration of the adduct of 1,1-bis(trifluoromethyl)hydrazine with hexafluoroacetone by oleum gave hexafluoroacetone bis(trifluoromethyl)hydrazone, the first member of the perfluorohydrazones.

LITERATURE CITED

1. A. F. Gontar, É. G. Bykhovskaya, A. S. Vinogradov, and I. L. Knunyants, Izv. Akad. Nauk SSSR, Ser. Khim., 2632 (1981).