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9. BIS(TRIFLUOROMETHYL) SULFOXIDE

$$CF_3SCl + AgOCOCF_3 \longrightarrow CF_3SOCOCF_3 + AgCl$$

$$CF_3SOCOCF_3 \xrightarrow{h\nu} CF_3SCF_3 + CO_2$$

$$CF_3SCF_3 + 2ClF \xrightarrow[10\text{ hr.}]{-78°\text{C. to }25°\text{C.}} CF_3SF_2CF_3 + Cl_2$$

$$CF_3SF_2CF_3 + HCl \xrightarrow{\text{Pyrex}} [CF_3SCl_2CF_3] + 2HF$$

$$4HF + SiO_2 \longrightarrow 2H_2O + SiF_4$$

$$[CF_3SCl_2CF_3] + H_2O \longrightarrow CF_3S(O)CF_3 + 2HCl$$

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Bis(trifluoromethyl) sulfoxide has been prepared[1] previously by the direct fluorination of bis(trifluoromethyl) sulfide at −78°C. in hexafluoroethane followed by hydrolysis of the bis(trifluoromethyl)sulfur difluoride (difluorobis(trifluoromethyl)sulfur). This method suffers because elemental fluorine must be used, and the yields are low.

Oxidation of bis(trifluoromethyl) sulfide with commercially obtainable chlorine monofluoride in the absence of solvent yields bis(trifluoromethyl)sulfur difluoride in >90% yield.[2,3] Pure bis(trifluoromethyl)sulfur difluoride is resistant to hydrolysis and is stable in Pyrex glass at 25°C. for extended periods of time. Reaction of bis(trifluoromethyl)sulfur difluoride with anhydrous

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hydrogen chloride in a clean Pyrex bulb results in the formation of bis(trifluoromethyl) sulfoxide in good yield. This preparative method has been extended and results in the preparation of $CF_3S(O)C_2F_5$, $CF_3S(O)C_3F_7$, and $C_2F_5S(O)C_2F_5$.[2,3]

Bis(trifluoromethyl) sulfide was prepared by the photolysis of *S*-trifluoromethyl trifluoromonothioperoxyacetate (trifluoroacetic trifluorosulfenic anhydride).[4] Other preparative methods[5,6] have been difficult to reproduce, or they produce the monosulfide in small yield. Oxidation of bis(trifluoromethyl) sulfide with chlorine monofluoride proceeds smoothly when the metal reactor containing the mixture is slowly warmed from −78 to 25°C. over 10 hours. No cleavage products are formed, and the desired bis(trifluoromethyl)sulfur difluoride is isolated in >90% yield. The reaction of the sulfur difluoride with anhydrous hydrogen chloride to produce bis(trifluoromethyl) sulfoxide is presumed to proceed through the bis(trifluoromethyl)sulfur dichloride intermediate. Since hydrogen fluoride is produced when hydrogen chloride reacts with bis(trifluoromethyl)sulfur difluoride in Pyrex glass, water is formed, which results in hydrolysis of the bis(trifluoromethyl)-sulfur dichloride intermediate. Attempts to isolate the sulfur dichloride intermediate by reaction of hydrogen chloride and bis(trifluoromethyl)sulfur difluoride in the presence of sodium fluoride in a nickel bomb resulted in the formation of bis(trifluoromethyl) sulfide and chlorine quantitatively.

A. *S*-TRIFLUOROMETHYL TRIFLUOROMONOTHIOPEROXYACETATE

(Trifluoroacetic Trifluorosulfenic Anhydride)

Procedure

Ten mmoles of trifluoromethanesulfenyl chloride,* CF_3SCl, is allowed to react with excess silver trifluoroacetate* at 25°C. for

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10 minutes in a 1-l. Pyrex vessel to produce *S*-trifluoromethyl trifluoromonothioperoxyacetate, $CF_3SOCOCF_3$. The reaction is quantitative. The $CF_3SOCOCF_3$ may be freed from trace amounts of trifluoromethanesulfenyl chloride, CF_3SCl, by passage through a −78°C. Dry Ice-acetone bath, which retains the pure CF_3-$SOCOCF_3$.

Properties

S-Trifluoromethyl trifluoromonothioperoxyacetate is a colorless liquid at 25°C. The ^{19}F n.m.r. resonances occur at 47.3 p.p.m. (CF_3S) and 76.5 p.p.m. ($CF_3C(O)O$) relative to CCl_3F. No coupling is observed between the trifluoromethyl groups.[4] The infrared spectrum consists of bands at 1835(m), 1805(w,sh), 1317(w), 1246(m-s), 1202(vs), 1190(s,sh), 1120(m-s), 1069(s), 835(w), 765(w-m), and 720(w) cm^{-1}.

B. BIS(TRIFLUOROMETHYL) SULFIDE

■ ***Caution.*** *The volatile reactants and products are toxic and contact with these reagents should be avoided.*

Procedure

Ten mmoles of *S*-trifluoromethyl trifluoromonothioperoxyacetate are photolyzed for $\frac{3}{4}$ hour through Pyrex glass with a Hanovia Utility ultraviolet quartz lamp (140 watts), which produces bis(trifluoromethyl) sulfide and carbon dioxide quantitatively. Pure bis(trifluoromethyl) sulfide is retained in a −120°C. slush bath (diethyl ether) while carbon dioxide slowly sublimes into a −183°C. bath during trap-to-trap distillation.

Properties

Bis(trifluoromethyl) sulfide exists as a colorless gas at room temperature and condenses to a colorless liquid. The vapor pressure of bis(trifluoromethyl) sulfide is given by the equation $\log P_{\text{mm.}} = 7.82 - 1239.1/T$, from which the b.p. is calculated as −22.2°C.[5] The ^{19}F n.m.r. spectrum consists of a single resonance at 38.6 p.p.m. relative to CCl_3F. The infrared spectrum contains bands at 1220(s), 1198(vs), 1160(s), 1078(vs), 758(m), and 475(w) cm^{-1}.

C. BIS(TRIFLUOROMETHYL)SULFUR DIFLUORIDE

■ ***Caution.*** *Chlorine monofluoride is toxic and exceedingly damaging to the skin.*

Procedure

Reaction of bis(trifluoromethyl) sulfide with chlorine monofluoride* is carried out in a 75-ml. stainless-steel Hoke bomb. The bomb is evacuated, and in a typical preparation, 10 mmoles of bis(trifluoromethyl) sulfide and 22 mmoles of chlorine monofluoride are added at −183°C. The vessel is warmed to −78°C. and allowed to warm slowly to 25°C. over a 10-hour period. The product mixture is first separated by fractional condensation. The bis(trifluoromethyl)sulfur difluoride ($CF_3SF_2CF_3$) is retained in a −98°C. slush bath, while any unreacted CF_3SCF_3, ClF, and Cl_2 pass into a −183°C. bath. The $CF_3SF_2CF_3$ may be purified further by gas chromatography utilizing a 17-ft., 20% Kel-F oil† on Chromasorb P column. Final purification gives $CF_3SF_2CF_3$ in >90% yield based on the amount of monosulfide used.

Properties

At 25°C. bis(trifluoromethyl)sulfur difluoride is a colorless gas which condenses, on cooling, to a colorless liquid. A boiling point of

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21°C. is calculated from the Clausius-Clapeyron equation $\log P_{\mathrm{mm.}} = 8.00 - 1507/T$. The ^{19}F n.m.r. resonances at 58.0 (CF_3) and 14.2 p.p.m. (SF_2) relative to CCl_3F integrate to the proper 6:2 ratio with $J_{SF_2-CF_3} = 19.5$ Hz. The infrared spectrum contains bands at 1281(vs), 1260(s), 1215(m–s), 1144(m), 1081(vs), 766(m), 677(s), and 507(m) cm^{-1}.

D. BIS(TRIFLUOROMETHYL) SULFOXIDE

Procedure

Four mmoles of bis(trifluoromethyl)sulfur difluoride react with 16 mmoles of anhydrous hydrogen chloride* in a clean, 1-l. Pyrex vessel for 24 hours to give bis(trifluoromethyl) sulfoxide in 70% yield. The bis(trifluoromethyl) sulfoxide is purified by fractional condensation. The desired sulfoxide is retained in a −78°C. bath while unreacted hydrogen chloride and bis(trifluoromethyl)sulfur difluoride pass into a −183°C. bath. Further purification by gas chromatography, utilizing a 17-ft., 20% Kel-F oil on Chromasorb P column, enables isolation of pure $CF_3S(O)CF_3$. When the reaction is carried out in a metal bomb, no sulfoxide is formed. The products isolated were identified as CF_3SCF_3, chlorine, and unreacted hydrogen chloride.

Properties

Bis(trifluoromethyl) sulfoxide is a colorless liquid at 25°C. A normal boiling point of 37.3°C. is calculated from the Clausius-Clapeyron equation $\log P_{\mathrm{mm.}} = 7.66 - 1483/T$. Confirmatory spectral properties include a molecular ion in the mass spectrum (2.1%) and a single ^{19}F resonance at 64.5 p.p.m. relative to CCl_3F. The infrared spectrum contains bands at 1244(vs), 1191, 1187 (doublet, s), 1121(m–s), 1105(vs), 752(w), and 468(w) cm^{-1}.

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10. ALUMINUM TRIHYDRIDE-DIETHYL ETHERATE

(Etherated Alane)

$$3LiAlH_4 + AlCl_3 \xrightarrow{\text{diethyl ether}} 4[AlH_3 \cdot 0.3(C_2H_5)_2O] + 3LiCl$$

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Methods for the preparation of aluminum trihydride-diethyl etherate, $AlH_3 \cdot 0.3[(C_2H_5)_2O]$,‡ have been published,[1,2] but the absence of complete experimental details makes duplication difficult. The following procedure is a modification of that reported by Finholt, Bond, and Schlesinger.[1] Problems inherent in previous methods, such as premature precipitation, decomposition of the alane, and lithium chloride contamination, are avoided.

Premature precipitation is controlled by maintaining a low temperature (−5°C.) in the reaction mixture. Purified reactants, as well as minimal exposure to light and higher temperatures,

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‡Ebulliometric molecular weight determinations obtained in diethyl ether (concentration range, 0.25-1.0 *M*) indicates molecular weights only slightly higher than 30. This is consistent with studies reported by Wiberg and Uson.[3] It must be assumed that in solution, AlH_3 exists essentially as the monomeric form.