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SHORT COMMUNICATION

Derivatives of Pentafluorophenyldisulfane

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In a continuing study of the preparation and reactions of compounds containing the pentafluorophenylthio group, C_6F_5S, [1], some derivatives of pentafluorophenyldisulfane, C_6F_5SSX, have been prepared. The disulfanes, C_6F_5SSR (R = alkyl, aryl), are well known [2]. The preparation of three possible precursors to further derivatives of pentafluorophenyldisulfane were investigated. These were chloro(pentafluorophenyl)disulfane, $C_6F_5SS\ell$, pentafluorophenyldisulfane, C_6F_5SSH, and (diethylamino)(pentafluorophenyl)-disulfane, $C_6F_5SSNEt_2$.

Chloro(pentafluorophenyl)disulfane has been obtained from the reaction of pentafluorothiophenol and freshly distilled sulfur dichloride, either in a sealed tube or in hexane as a solvent. Chloro(trifluoromethyl)disulfane has been prepared analogously [3], or from the reaction of CF_3SSNR_2 with hydrogen chloride [4], or by chlorination of trifluoromethyldisulfane [5]. Chloro(pentafluorophenyl)disulfane is a yellow liquid, b.p. 32-34°C/0.15mm. It is somewhat thermally unstable, forming disulfur dichloride and, presumably, the disulfane $(C_6F_5S)_2$ and must be distilled in high vacuum. Bromo(trifluoromethyl)disulfane decomposed analogously at room temperature to disulfur dibromide and bis(trifluoromethyl)disulfane [4].

The reactions of chloro(pentafluorophenyl)disulfane should be similar to those of a sulfenyl chloride [6] and also to those reported for chloro-(trifluoromethyl)disulfane [7]. With n-propanethiol and diethylamine, n-propyl(pentafluorophenyl)trisulfane and (diethylamino)(pentafluorophenyl)-disulfane respectively were formed. Mixed products, presumably due to the lack of stability of the anticipated products, were obtained in the reactions of the chlorodisulfane with hydrogen sulfide (expected product

$(C_6F_5)_2S_5$) and phenyl magnesium bromide (expected product $C_6F_5SSC_6H_5$). In the mass spectrum of the hydrogen sulfide reaction products the sulfanes $(C_6F_5)_2S_x$ x = 2, 3 were observed, and in the phenyl magnesium bromide reaction $C_6H_5.C_6H_5$, $C_6H_5\ SC_6H_5$, and $C_6H_5SC_6F_5$ were found.

In an attempt to prepare the disulfane C_6F_5SSH, the reaction of pentafluorobenzenesulfenyl chloride with an equimolecular amount of hydrogen sulfide was studied. The results indicated that rather than the formation of the disulfane or the trisulfane, $C_6F_5SSSC_6F_5$, pentafluorothiophenol and sulfur were formed. This reaction presumably proceeded through the formation of pentafluorophenyldisulfane.

$$\begin{array}{l} C_6F_5SC\ell \ + \ H_2S \ \rightarrow \ [C_6F_5SSH] \ + \ HC\ell \\ \qquad\qquad\qquad\qquad\qquad \downarrow \\ \qquad\qquad\qquad\qquad C_6F_5SH \ + \ 1/8S_8 \end{array}$$

Trifluoromethyldisulfane slowly decomposes at room temperature to sulfur and trifluoromethanethiol [8]. Trifluoromethyldisulfane has recently been prepared by the controlled low temperature reaction of hydrogen sulfide and trifluoromethanesulfenyl chloride [8], although the trisulfane, CF_3SSSCF_3, was the only product isolated from earlier reactions [9].

A large number of compounds such as $RS_xNR'_2$ (often thioimides, x = 1,2) have been used as synthetic intermediates due to the ready fracture of the S-N bond by a variety of nucleophiles [10]. The disulfane derivatives $RSSNR'_2$ can be prepared from chloro(dialkylamino)sulfane and the mercury derivative of the thiol [4]. The compound C_6F_5SSNEt has been obtained from chloro(diethylamino)sulfane and the mercury derivative $Hg(SC_6F_5)_2$. Its reactions have not been studied.

EXPERIMENTAL

Most reagents were available commercially and were dried before use. Chloro(diethylamino)sulfane [11], pentafluorobenzenesulfenyl chloride [12], and bis(pentafluorophenyl)mercury [13] were prepared by literature methods. Sulfur dichloride was purified immediately prior to use [14].

Microanalyses were performed by the Butterworth Microanalytical Consultancy Ltd.. Infrared spectra were recorded as films or KBr discs on a Perkin-Elmer model 457 spectophotometer. Proton NMR spectra were obtained on a Perkin-Elmer model 457 spectrophotometer in $CDC\ell_3$ with TMS as internal standard. Mass spectra were recorded on a DuPont/CEC model 21-104 mass spectrometer using direct introduction.

Chloro(pentafluorophenyl)disulfane was prepared by the slow addition of 40 mmoles of C_6F_5SH in 50 ml. hexane to a solution of 40 mmoles of $SC\ell_2$ in 50 ml. hexane. After removal of the solvent golden yellow $C_6F_5SSC\ell$ could be distilled off, b.p. 32-34°C/0.15 mm., n_D^{25} 1.5481, ρ 1.8876 g/ml. Found: C, 26.7; H,<0.2; Cℓ, 13.1; S, 24.3%. Calcd. for $C_6C\ell F_5S_2$: C, 27.0; H, 0; Cℓ, 13.3; S, 24.0%. A peak at 473m cm^{-1} in the IR spectrum may be assigned as $\upsilon(S\text{-}C\ell)$. The same product was obtained by the reaction of equimolecular amounts of $SC\ell_2$ and C_6F_5SH in a sealed tube. Some $S_2C\ell_2$ was formed on heating a sample of $C_6F_5SSC\ell$ in a sealed tube at 110°C for 20 h.

Excess Et_2NH (20 mmoles) in hexane reacted with $C_6F_5SSC\ell$ (10 mmoles) to form yellow $C_6F_5SSNEt_2$ (yield 52%), b.p. 42-46°C/0.04mm., n_D^{25} 1.5130. Found: C, 39.7; H, 3.10; N, 4.84%. Calcd. for $C_{10}H_{10}F_5NS_2$: C, 39.6; H, 3.32; N, 4.62%. Two peaks at 2.81 (quartet) and 1.06 (triplet) ppm were observed for the methylene and methyl groups in the ^1H NMR spectrum (J(H-H) 6.8 Hz.).

$C_6F_5SSC\ell$ (10 mmoles) reacted with excess <u>n</u>-PrSH (20 mmoles) in hexane to yield <u>n</u>-$PrSSSC_6F_5$ (yield 59%), b.p. 48-52°C/0.03mm., n_D^{25} 1.5403. Found: C, 35.3; H, 2.6%. Calcd. for $C_9H_7F_5S_3$: C, 35.3; H, 2.3%. The ^1H NMR spectrum showed three peaks, ratio 2:2:3, at 2.86(triplet), 1.76(multiplet) and 1.02(triplet) ppm respectively (J(H-H) = 6.7 Hz.).

In a sealed tube approximately 4.3 mmoles of H_2S were reacted with 8.6 mmoles of $C_6F_5SSC\ell$. On opening the tube 8.3 mmoles of HCℓ were recovered. No trace of H_2S was found (IR spectrum). The mass spectrum of the solid residue showed it to be primarily $(C_6F_5)_2S_x$ x = 2,3.

The Grignard reagent PhMgBr in Et_2O was slowly added to a solution of $C_6F_5SSC\ell$ (6.3 mmoles) in Et_2O. A liquid product was recovered, the mass spectrum of which showed large amounts of $C_6F_5SC_6H_5$, $C_6H_5SC_6H_5$ and $C_6H_5C_6H_5$.

The reactions of an equimolar and a two fold excess of H_2S and $C_6F_5SC\ell$ were studied in sealed tubes. The only product other than HCℓ isolated from the equimolar reaction was $(C_6F_5)_2S_3$, m.p. 47-50°C, lit. m.p. 57°C [15]. Found: S, 21.6%. Calcd. for $C_{12}F_{10}S_3$: S, 22.3%. Sulfur, m.p. 114-6°C, lit. m.p. 113°C [16] and C_6F_5SH, b.p. 22°C/0.03 mm., n_D^{25} 1.4618; lit. b.p. 143°C/atm. [17], n_D^{25} 1.4620 (Found: S, 16.3%. Calcd. for C_6HF_5S: S, 16.0%) were the only non gaseous products from the excess H_2S reaction.

Pentafluorophenyl(diethylamino)disulfane was also prepared from the reaction of $Et_2NSC\ell$ (10.8 mmoles) and $Hg(SC_6F_5)_2$ (5.4 mmoles) in dry ether.

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