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SHORT COMMUNICATION

Synthesis of a Bis(pentafluorosulfur) Ethane

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Although pentafluorosulfur bromide, SF_5Br, has been less extensively investigated than its homolog SF_5Cl, recent studies have shown that the bromide is significantly more reactive than the chloro compound with respect to olefin additions [1-3]. In reactions with the comparatively deactivated double bonds of simple haloolefins [2] and vinylsilanes [3], addition of SF_5Br occurs readily under ambient conditions, whereas the corresponding additions of SF_5Cl, where they occur at all, require prolonged heating or photolysis [3-6].

This enhanced reactivity of SF_5Br suggested its possible utility for the synthesis of the first bis(pentafluorosulfur) ethanes by addition to pentafluorosulfur ethylenes, a relatively unfamiliar class of compounds whose behavior would be expected to resemble that of haloolefins:

$$SF_5Br + SF_5CH{=}CH_2 \rightarrow SF_5CHBrCH_2SF_5 \text{ or } (SF_5)_2CHCH_2Br$$

In the case of $SF_5CH{=}CH_2$, addition of SF_5Br produced the desired bis(pentafluorosulfur) ethane in high yields, though heating to 70° was required. Surprisingly, more highly halogenated pentafluorosulfur ethylenes ($SF_5CH{=}CHF$, $SF_5CH{=}CHBr$, $SF_5CH{=}CF_2$, $SF_5CF{=}CFH$, $SF_5CF{=}CF_2$) did not undergo SF_5Br addition to a measurable extent, even under more stringent conditions. It is significant to note that, unlike SF_5Br, bromine adds readily to the perfluorovinyl compound $SF_5CF{=}CF_2$ at room temperature under free radical conditions [7,8]. This suggests that the reaction of SF_5Br with $SF_5CH{=}CH_2$ and with simple haloolefins [2] proceeds via a different pathway than the (presumably) free-radical addition of Br_2, possibly one involving electrophilic addition of the more polar SF_5Br. This process would be energetically less favorable for more highly halogenated $SF_5C=C$ structures. This issue is currently being pursued in a careful examination of the stereochemistry of addition of SF_5Br to cis- and trans-difluoroethylenes.

The SF_5Br - $SF_5CH=CH_2$ addition product, which we believe to be the first example of a bis(pentafluorosulfur) ethane, is a stable, colorless liquid with a vapor pressure of approximately 5 torr at 22°. Of the two possible isomers, $SF_5CHBrCH_2SF_5$ and $(SF_5)_2CHCH_2Br$, the 1,2-bis(pentafluorosulfur)-1-bromoethane structure seems most likely on the basis of a degradation reaction with aqueous base which cleaved one SF_5-group and produced the known compound $SF_5CBr=CH_2$ [6] with its bromine atom geminal to the remaining SF_5-group. Moreover, the 1,2-arrangement of SF_5-groups in the disubstituted ethane would be consistent with the direction of addition observed in other SF_5Br reactions [1]. Unfortunately, neither the NMR spectrum nor mass spectrometry (see experimental section) permitted a more direct and unambiguous structural assignment, though the existence of two SF_5-groups was confirmed by the NMR study.

Experimental

All reactant manipulations were conducted in a Pyrex system equipped with greaseless Kontes glass/Teflon valves. Infrared spectra were recorded on a Perkin-Elmer Model 457 Spectrophotometer using a 10 cm. cell with KBr windows. ^{19}F-NMR spectra were obtained with a JEOL MH-100 spectrometer at 94.1 MHz. Proton spectra were recorded with a Varian HA-100 instrument. The mass spectral measurements employed a Hewlett-Packard Model 5930A Quadrupole Spectrometer.

Pentafluorosulfur bromide was prepared by the bromination of disulfur decafluoride [9]; the vinyl derivative $SF_5CH=CH_2$ was prepared by addition of SF_5Cl (Peninsular Chem-Research) to ethylene (Matheson), followed by dehydrohalogenation with KOH [6]. Similar SF_5Cl addition-dehydrohalogenation sequences involving $CH_2=CF_2$, $CHF=CHF$, and $CHF=CF_2$ were used to prepare $SF_5CH=CF_2$, $SF_5CF=CHF$, and $SF_5CF=CF_2$, respectively. The bromoolefin $SF_5CH{=}CHBr$ was prepared by gas-phase addition of SF_5Br to acetylene (Air Products) at 25° and was converted to $SF_5CH{=}CHF$ by reaction with KF in "crown" ether.

Preparation of 1,2-bis(pentafluorosulfur)-1-bromoethane

In a typical experiment, pentafluorosulfur bromide and $SF_5CH{=}CH_2$ (one mmol each) were condensed into a 3 ml Pyrex tube fitted with a Kontes valve, and the mixture was heated to 70° for 8 hours. Fractional condensation of the reaction mixture through traps at -45°, -96°, and -196° led to the recovery of 0.42 mmols of unreacted SF_5Br and 0.34 mmols of $SF_5CH{=}CH_2$ in the -196° and -96° traps, and 0.57 mmols of the $SF_5CHBrCH_2SF_5$ adduct (91% yield based on 60% of SF_5Br consumed) in the -45° trap. (Calc. for $S_2F_{10}C_2H_3Br$:C, 6.65; H, 0.84; F, 52.63. Found: C, 6.67; H, 0.92; F, 60.26.)

The clear, colorless liquid exhibited a vapor pressure of 5 torr; a gas-phase infrared spectrum at that pressure showed absorptions (relative intensities in parentheses) at 1420 (0.4), 1375 (0.7), 1175 (1.1), 950 (3.9), 895 (4.8), 865 (10.0), 845, (sh), 670 (1.0), 595 (2.3), 580 (5.0), and 555 (3.4) cm^{-1}. The bands at 895, 865, and 580 cm^{-1} are characteristic of SF_5-groups [10]. The ^{19}F-NMR spectrum clearly showed separate AB_4 patterns from the two SF_5-groups in a 1:1 ratio, with chemical shifts of -55.2 (SF_4), -75.0 (SF), -66.3 (SF_4'), and -78.8 (SF′) ppm relative to internal $CFCl_3$; J(F-F) was 145 Hz in both cases. The proton NMR spectrum, an ABC pattern comprised of three complex multiplets centered at $\tau = 5.74, 5.21, 4.17$ *vs* internal TMS, was not readily interpretable in structural terms. Mass spectral analysis showed fragments at m/e values (relative intensities in parentheses) as follows: 234, $SF_5C_2H_3Br$ (4); 232, $SF_5C_2H_2Br$ (4); 133, SF_4C_2H (5); 127, SF_5 (100); 125, C_2H_3BrF (56); 108, C_2H_3Br (10); 107, C_2H_2Br (27); 106, C_2H_3Br (10); 105, C_2H_2Br (27); 89, SF_3 (89); 70, SF_2 (20).

Attempted Dehydrobromination of 1,2-bis(pentafluorosulfur)-1-bromoethane

In a typical experiment, 0.57 mmols of $SF_5CHBrCH_2SF_5$ was treated at 0° for 30 min. with 1.8 mmols of KOH dissolved in 0.2 ml of a 1:1 water-methanol mixture. The volatile product was dried over P_2O_5 for 15 min. and fractionated to obtain unreacted $SF_5CHBrCH_2SF_5$ (0.16 mmol) and the degradation product $SF_5CBr{=}CH_2$ (0.29 mmol, 50% yield based on reactant consumed). Identity of the $SF_5CBr{=}CH_2$ was confirmed by its molecular weight (calc. 233.0, found 228.2) and by comparison of its infrared, NMR, and mass spectra with those of an authentic sample prepared by the dehydrobromination of $SF_5CHBrCH_2BR$ [6].

Attempted Addition of SF_5Br to Other Pentafluorosulfur Ethylenes

Reactions of SF_5Br with $SF_5CF{=}CF_2$, $SF_5CH{=}CF_2$, $SF_5CF{=}CFH$, $SF_5CH{=}CHF$, and $SF_5CH{=}CHBr$ were attempted over a range of conditions (reaction temperatures of 120 to 180°, times of 18 hr to 7 days, SF_5Br:olefin ratios of 2:1 and 1:2). No reaction ensued at the shorter times and lower temperatures, and at the maximum times/temperatures, reactants were still 90-95% unchanged, with the minor consumption attributable mainly to the onset of reactant decomposition (e.g., appearance of S_2F_{10}, Br_2, olefin dimer, etc.). In the case of SF_5Br + $SF_5CF{=}CF_2$, reactants were 96% unchanged after 7 days at 170-180° although the NMR spectrum of a trace product showed two ^{19}F doublets in the SF_4 region; however their ratio was 1:2 rather than 1:1. Photochemical irradiation (2537 Å) of SF_5Br and $SF_5CH{=}CHBr$ (2:1) for 1 hour produced nearly complete destruction of the SF_5Br, forming S_2F_{10}, SiF_4, and SOF_2, but left the olefin unchanged.

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