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THE PENTAFLUOROSULFANYLIMINATION OF ORGANIC AND INORGANIC COMPOUNDS*

A.F. CLIFFORD and A. SHANZER**

Department of Chemistry, Virginia Polytechnic Institute and
State University, Blacksburg, Va. 24061, U.S.A.

To Professor George H. Cady on his 70th birthday

SUMMARY

Reactions of SF_5NCO, SF_5NH_2, $SF_5N{=}SF_2$, $SF_5N{=}SCl_2$ and $SF_5N{=}CCl_2$, with appropriate substrates have produced $SF_5N{=}S(CH_3)_2$, $SF_5N{=}CHC_6H_5$, $SF_5N{=}CCl_2$, $SF_5N{=}SCl_2$, $(SF_5N{=})_2C$, $(SF_5N{=})_2S$ and $SF_5N{=}PCl_3$, some of which are new compounds and some of which represent improved routes to compounds previously reported. The preparations and properties of these are described.

INTRODUCTION

The introduction of novel functional groups into organic molecules has great interest in terms of the effects of such introduction upon the physical and biological properties thus wrought. This paper reports the preparation of a number of new compounds, both organic and inorganic which have been synthesized by reaction of pentafluorosulfanyl isocyanate, SF_5NCO, [1-3], pentafluorosulfanylamine, SF_5NH_2 [4], and

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**Present address: Department of Organic Chemistry, Weizmann Institute of Science, Rehovot, Israel.

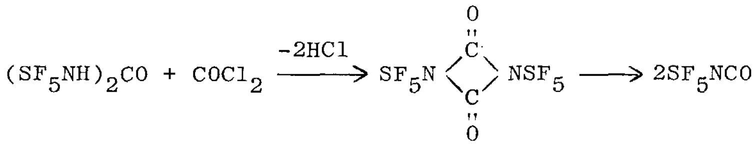
pentafluorosulfanyliminosulfur difluoride [5,6] on appropriate substrates. An improved preparation of the isocyanate is also described.

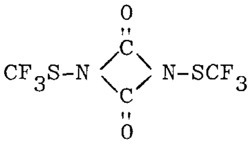
RESULTS AND DISCUSSION

Preparation of Pentafluorosulfanyl Isocyanate, SF_5NCO

The previously reported preparation of SF_5NCO [3] presents problems in purifying the product because of the high solubility of NSF_3 in it and the difficulty of separating them. It was found, however, that the reaction of N,N'-bispentafluorosulfanylurea, $(SF_5NH)_2CO$, [3] which is easily purified by sublimation, with a slight excess of carbonyl fluoride, COF_2, (12 hr at 100°) produced SF_5NCO essentially pure except for a small amount of COF_2 which could easily be separated by trap-to-trap distillation.

When $COCl_2$ was used instead of COF_2, the reaction proceeded much less cleanly. However, the infrared spectrum of the product mixture in addition to indicating the presence of HCl, $COCl_2$, COClF, NSF_3 and SF_5NCO, had peaks about 1390 and 1595 cm^{-1} strongly suggesting a four-membered C-N-C-N ring and urea-type carbonyl groups, respectively. Although it was not isolated, we believe, therefore, that these reactions proceed through an intermediate cyclic compound as follows:



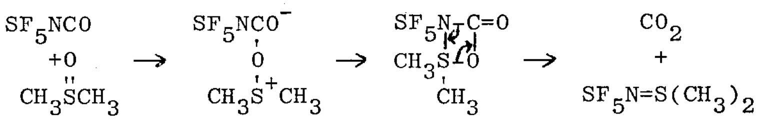
The comparable  has been isolated and identified by Haas [7].

Preparation of Pentafluorosulfanylimino Compounds

Pentafluorosulfanyl isocyanate dissolved in dimethyl sulfoxide reacted with the solvent at room temperature producing a crystalline product after several hours. The only volatile product identified was CO_2. The crystalline product was identified by its H-1 and F-19 NMR and IR spectra as $SF_5N{=}S(CH_3)_2$.

$$SF_5NCO + (CH_3)_2SO \rightarrow SF_5N{=}S(CH_3)_2 + CO_2$$

It is felt that the reaction must proceed by nucleophilic attack of the sulfoxide oxygen on the isocyanate carbon, followed by formation of a four-membered ring and subsequent cleavage.



Similar reactions of electron deficient isocyanates with dimethyl sulfoxide have been reported by King [10], and Roesky and Hoff [11].

Pentafluorosulfanyl isocyanate and freshly distilled benzaldehyde reacted after a few hours at room temperature producing a yellow solution and carbon dioxide. The solution was determined by NMR, IR and mass spectra to contain $SF_5N{=}CHC_6H_5$, a novel, electron-deficient Schiff base.

$$SF_5NCO + C_6H_5CHO \rightarrow SF_5N{=}CHC_6H_5 + CO_2$$

Pentafluorosulfanyl isocyanate and PCl_5 reacted very slowly at room temperature but readily at 60-80° producing $SF_5N{=}CCl_2$ [1,2] and $POCl_3$. The products were identified by NMR and IR spectra.

$$SF_5NCO + PCl_5 \rightarrow SF_5N{=}CCl_2 + POCl_3$$

In contrast to the reaction of $SF_5N{=}SCl_2$ with SF_5NH_2 (see below), the reaction of $SF_5N{=}CCl_2$, carried out under the same conditions as with $SF_5N{=}SCl_2$, was found to proceed with great reluctance and under conditions so far tried has not produced isolable quantities of the expected $SF_5N=C=NSF_5$.

$$SF_5N=CCl_2 + SF_5NH_2 \rightarrow SF_5N=C=NSF_5 + 2HCl$$

However, the infrared spectrum of the product mixture obtained from the reaction carried out at room temperature for 18 hr showed a peak at 2154 cm^{-1} attributable to the N=C=N group (cf. 2150 cm^{-1} for organic carbodiimides found by Khorana [12,13] and 2152-2128 cm^{-1} found by Meakins and Moss [14], for example.) The NMR spectrum exhibited peaks as follows: -60.3 ppm for the basal fluorines and -63.7 ppm for the apical fluorine in a 4:1 ratio respectively and a coupling constant of 152.3 cps. It therefore appears highly probable that $(SF_5N=)_2C$ was formed.

Pentafluorosulfanyliminosulfur difluoride reacted at room temperature with PCl_5 to produce $SF_5N=SCl_2$, a pale yellow liquid whose properties agreed well with those previously reported [8]. This is a reactive compound which rapidly attacked mercury. As previously reported [8], it reacted with AgF_2 to produce $SF_5N=SF_2$. It was also found to react with SF_5NH_2 producing the sulfodiimide, $SF_5N=S=NSF_5$.

$$SF_5N=SCl_2 + SF_5NH_2 \rightarrow SF_5N=S=NSF_5 + 2HCl$$

Pentafluorosulfanyliminosulfur dichloride was also prepared by the reaction

$$2SF_5N=SF_2 + SiCl_4 \rightarrow 2SF_5N=SCl_2 + SiF_4$$

but with somewhat more difficulty than with PCl_5.

Aluminum trichloride also reacted with $SF_5N=SF_2$ at elevated temperature, but the pale yellow liquid obtained contained no fluorine.

Pentafluorosulfanylamine, SF_5NH_2 [4] and PCl_5 reacted at room temperature to give $SF_5N=PCl_3$, a compound presumably containing a multiple bond between nitrogen and phosphorus.

$$SF_5NH_2 + PCl_5 \rightarrow SF_5N=PCl_3 + 2HCl$$

This compound was a pale yellow liquid which reacted rapidly with mercury.

EXPERIMENTAL

Reactions were carried out in equipment similar to that described in previous publications, e.g. [3-5]. The effluent gases were passed over NaF pellets to remove HF and the products were collected and worked up in a conventional vacuum system equipped with both glass and metal sections. Products were stored in Hoke stainless steel cylinders or, if thermally unstable, in Kel-F tubes fitted with vacuum stopcocks and immersed in liquid nitrogen or Dry Ice.

Infrared spectra were obtained on a Beckman IR-20 AX instrument. Nuclear magnetic resonance spectra (H-1 and F-19) were obtained on a JEOL PS-100 spectrometer at 100 MHz and 94 MHz respectively. All F-19 values were referred to Freon-11 and H-1 to tetramethylsilane (TMS). Coupling constants cited were calculated from the spectra by the method of Cady et al. [9]. Mass spectra were obtained on a Perkin-Elmer Hitachi RMU-7 spectrometer. Peaks of less than 10% relative intensity are not reported here unless they have some special significance. Elemental analyses for C, H and N were obtained on a Perkin-Elmer 240 analyzer and for other elements by standard methods by the departmental analyst.

Starting materials were generally used as received except that fluorine was passed over NaF pellets to remove HF and cesium fluoride was dried at 200° in vacuum for 18 hr, crushed and dried again for 6 hr before use. Silver difluoride, originally purchased (technical grade) from Ozark Mahoning, was subsequently regenerated with elemental fluorine.

Thiazyl trifluoride, NSF_3, was prepared as previously described [5], but increased yield was obtained by allowing the reaction to run at room temperature for 8 hr.

N,N'-Bis(pentafluorosulfanyl)urea was prepared as reporte elsewhere [3] using the exact ratio of the reactants required by the equation

$$2NSF_3 + 2HF + COF_2 \rightarrow (SF_5NH)_2CO$$

in quantities of 50, 50 and 25 mmol respectively. The mixture was allowed to stand at room temperature for 7 days in a Kel-F reactor, crystals first being observed to form after only a few hours. About 85% of the expected yield of the urea was recovered from the remaining liquid after this time. The liquid was found to contain HF, NSF_3, SF_5NH_2 and SF_5NCO, all more volatile than the urea. The urea was purified by sublimation at 90° under high vacuum.

Pentafluorosulfanylamine, SF_5NH_2, was prepared as previously described [4].

Preparation of Pentafluorosulfanyl Isocyanate

(a) With $COCl_2$

A slight molar excess of $COCl_2$ was introduced into a 75 ml stainless steel Hoke cylinder containing 0.31 g $(SF_5NH)_2CO$. Reaction did not occur in 12 hr at room temperature or in 22 hr at 80°. Heating for 12 hr at 120° produced a reaction producing a mixture containing HCl, $COCl_2$, COClF, NSF_3 and SF_5NCO.

(b) With COF_2

Carbonyl fluoride (3.1 mmol) was condensed into a Hoke cylinder containing 0.96 g (3.0 mmol) of the urea. After 12 hr at room temperature no appreciable reaction had occurred However, after 12 hr at 100° and a 3 hr sojourn over NaF pellets at room temperature, the gaseous product was found to consist essentially of SF_5NCO contaminated with only a small amount of COF_2. The SF_5NCO was freed of COF_2 easily by trap-to-trap distillation and was identified by infrared and NMR spectra. The yield was 84% based on the urea.

Reaction of SF_5NCO with $(CH_3)_2SO$

Pentafluorosulfanyl isocyanate, 4.2 mmol, was condensed into a Kel-F reactor equipped with a magnetic stirrer and containing 1.1 ml of freshly distilled $(CH_3)_2SO$. The mixture was allowed to warm to room temperature and remain for 5 days with continuous stirring. Crystals were observed to have formed after several hours. After 5 days the reactor was cooled to -45° and the volatile compounds were transferred to an evacuated glass vessel. The volatile components were identified by infrared spectrum to consist mainly of carbon dioxide and traces of SF_5NCO. The reactor was opened in a drybox for examination of the products. This procedure was adopted to avoid getting dimethyl sulfoxide into the vacuum system. The F-19 NMR spectrum, obtained at room temperature on the saturated $(CH_3)_2SO$ product solution, showed the characteristic AB_4 pattern for the SF_5 group. The broad doublet for the basal fluorine atoms, centered at -92.4 ppm relative to external Freon-11, and the 9-line multiplet for the apical fluorine, centered at -113.3 ppm, had the expected intensity ratio of 4 to 1 and a coupling constant of 154 cps. The H-1 NMR spectrum had, in addition to a very broad peak for the hydrogens of the $(CH_3)_2SO$ centered at 2.5 ppm relative to external T.M.S., a peak at 2.98 ppm corresponding to the methyl groups of the $-N{=}S(CH_3)_2$ moiety, in agreement with the methyl chemical shifts observed by Roesky et al. [11], and by Appel et al. [15] for other $N{=}S(CH_3)_2$ containing compounds.

The infrared spectrum of the isolated product showed a broad band at 1250 cm^{-1} assigned to the S(IV)-N stretching vibration and peaks at 3250, 3050, 2950, and 1360 cm^{-1} assigned to the C-H bonds of the methyl groups and at 905, 860, and 602 cm^{-1} assigned to stretching vibrations of the SF_5 group. A weak band observed at 1400 cm^{-1} is probably attributable to some residual $(CH_3)_2SO$.

The crystalline product was very hygroscopic. It melted over a range of several degrees in the vicinity of 72°.

Reaction of SF_5NCO with C_6H_5CHO

In similar fashion SF_5NCO (2.7 mmol) and 1 ml of benzaldehyde were allowed to react at room temperature for 2 days. No crystals appeared but the solution turned yellow after several hours. The products were worked up as before. Carbon dioxide was identified by its infrared spectrum.

The F-19 nuclear magnetic resonance spectrum of the saturated benzaldehyde solution showed the usual AB_4 pattern for the SF_5 group: apical F at -80.4 ppm, basal at -58.8 ppm, coupling constant, 157 cps.

The infrared spectrum (Nujol) exhibited a C=N resonance at 1630 cm^{-1}, higher than for the usual organic C=N frequency, presumably because of the great electron-withdrawing power of the SF_5 group. Characteristic SF_5 bands occurred at 915, 860 and 600 cm^{-1}.

The mass spectrum, which also served to confirm the identity of the compound, follows. The molecule ion peak was observed at m/e 231 (relative intensity 8.5%) with an isotopic distribution consistent with one sulfur atom in the molecule. The largest peak was that of SF_5^+, m/e 127, with the second largest at m/e 230 assigned to $SF_5NCC_6H_5^+$. Peaks at m/e 211 (12.4%) $SF_4NC_7H_5^+$, m/e 153 (17%) SF_5NC^+, m/e 141 (11.2%) SF_5N^+, m/e 103 (18.4%) $C_6H_5CN^+$, m/e 70 (42.6%) SF_2 were also identified.

Reaction of SF_5NCO with PCl_5

Pentafluorosulfanyl isocyanate (3.6 mmol) was condensed into a 75 ml cylinder and allowed to stand successively over night at room temperature, 6 hr at 60°, and 3 hr at 80°, reaction being observed under the last conditions. The usual work-up isolated $POCl_3$, identified by its infrared spectrum.

The infrared spectrum had a peak at 1655 cm^{-1} assigned to C=N absorption, and a doublet at 885 and 915 cm^{-1}, and a singlet at 603 cm^{-1} characteristic of the SF_5 group. The peaks at 800 cm^{-1} and 948 cm^{-1} were assigned to symmetrical and asymmetrical $=CCl_2$ stretchings, respectively. This was in good agreement with the reported values for $FSO_2N=CCl_2$ and $ClSO_2N=CCl_2$ given by Roesky and Biermann [16].

The F-19 NMR spectra exhibited a multiplet for the basal fluorine atoms, centered at -62.6 ppm relative to internal Freon-11, and the apical multiplet, centered at 67.2 ppm with a coupling constant of 156 c.p.s. The spectroscopic results correlated well with those reported by Tullock et al. [1]

Reaction of $SF_5N=CCl_2$ with SF_5NH_2

This reaction was carried out under conditions and in amounts identical to those described below for the reaction of $SF_5N=SCl_2$ with SF_5NH_2. The reactiôn ran much more reluctantly than the latter, never producing isolable amounts of the expected product, $SF_5N=C=NSF_5$. Claim for the preparation is based on the spectral evidence given in the RESULTS AND DISCUSSION.

Reaction of $SF_5N=SF_2$ with PCl_5

Pentafluorosulfanyliminosulfur difluoride (4.2 mmol) was allowed to stand with 3 g PCl_5 at room temperature for 48 hr The fraction collected at -45° was further fractionated yielding a pale yellow liquid identified as $SF_5N=SCl_2$. The yield was 2.7 mmol (65%). The infrared spectrum agreed with that reported earlier [8]: 1235 cm^{-1} (s), N=S stretch (cf. Glemser and Biermann [17]); 910, 855 cm^{-1} and 600 cm^{-1}, SF_5; 475, 415 cm^{-1}, attributed to $=SCl_2$ group, very close to those observed by Lustig [18] for the compound $CF_3N=SCl_2$, and Roesky [16] for the compound $FSO_2N=SCl_2$.

The distillate, dissolved in Freon-11 (1 part to 5) gave a F-19 nmr spectrum with the apical nonuplet of the SF_5 group centered at -73.5 ppm and the basal doublet at -76.6 ppm. The coupling constant was 153.4 cps.

Mass spectral peaks at m/e 210 and 208, in an approximate ratio of 3:1, which were attributed to $S_2F_5NCl^+$, support the assignment of the formula as $S_2F_5NCl_2$.

The dichloride (2.7 mmol) was allowed to stand over 2 g AgF_2 for 6 hr at room temperature and then at 50° for 6 hr A 92% yield (2.5 mmol) of pure SF_5NSF_2 was obtained, identified by its IR spectrum [5].

Reaction of $SF_5N=SF_2$ with $SiCl_4$

Equimolar amounts of $SF_5N=SF_2$ and $SiCl_4$ (4.2 mmol) were held at room temperature for 12 hr with no result. In six hr at 100° partial reaction took place producing $SF_5N{=}SCl_2$, as shown by the IR spectrum. Peaks due to the presence of $SF_5N{=}SF_2$ were still evident even in the product of reaction at 150° for 6 hr. The purified product was shown by IR, NMR and mass spectrum to be identical to that from the PCl_5 reaction.

Reaction of $SF_5N{=}SF_2$ with $AlCl_3$

Pentafluorosulfanyliminosulfur difluoride (4.2 mmol) and 2 g (45 mmol) of anhydrous $AlCl_3$ were held at 100° for 6 hr and then 150° for 2 hr and worked up as usual. Although a pale yellow liquid was collected at -45°, none of the volatile products was found to contain fluorine.

Reaction of $SF_5N{=}SCl_2$ and SF_5NH_2

Pentafluorosulfanyliminosulfur dichloride (2.0 mmol) was condensed with a slight excess of SF_5NH_2 for a 1:2 molar ratio into a Kel-F reactor and allowed to react at room temperature for 18 hr. After the usual work up, the -196° trap contained mainly HCl, identified by its characteristic IR spectrum, and SiF_4. The -131° trap contained thiazyl trifluoride, probably from decomposition of SF_5NH_2. The -45° trap contained a deep yellow liquid subsequently identified as $SF_5N{=}S{=}NSF_5$. The yellow compound was redistilled several times and when the infrared spectrum remained unchanged was subjected to spectroscopic analysis. The yield based on $SF_5N{=}SCl_2$ was 46%.

The infrared spectrum exhibited the following bands: 1445 (vs), 1265 (vs), 1068 (vs) cm^{-1} assigned to N=S=N group vibrations by comparison with related compounds [19]. These bands were also similar to those of SO_2 at 1361 cm^{-1} and 1151 cm^{-1} [20]. The doublet at 915 and 865 cm^{-1} and the strong absorption at 602 are characteristic of the SF_5 group.

The F-19 NMR (external Freon-11) showed a normal AB_4 spin system with the basal fluorines centered at -61.4 ppm and the apical fluorine at -65.0 ppm in a 4:1 ration respectively. The product was a viscous yellow liquid soluble in pentane, diethyl ether and, to a lesser extent, in $CHCl_3$.

Reaction of SF_5NH_2 with PCl_5

Pentafluorosulfanylamine (4.2 mmol) and 3 g (14 mmol) PCl_5 were held at room temperature for 24 hr and the products then worked up as usual. Hydrogen chloride, collected at -196^o, was identified by its IR spectrum. The pale yellow liquid collected at -42^o was identified by its infrared spectrum, F-19 NMR spectrum and mass spectrum as $SF_5N{=}PCl_3$ and was obtained in 84% yield (3.5 mmol). Although it reacted with mercury, it was possible to determine that it had a vapor pressure of approximately 10 mm Hg at room temperature. The infrared spectrum of the vapor showed a shouldered peak at 1230 (m) cm^{-1} assigned to the P=N stretch and a peak at 470 cm^{-1} for the P-Cl stretch in good agreement with other $-N{=}PCl_3$ compounds [21]. The characteristic bands for the SF_5 group appeared at 915 (s), 860 (s) and 600 cm^{-1}.

The F-19 NMR spectrum showed the apical nonuplet centered at -71.8 ppm and the basal doublet at -69.0 ppm. The coupling constant was 754.7 cps.

An attempt to cause the trichlorophosphane to react with SF_5NCO at 80^o (12 hr) was unsuccessful.

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