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Preparation and Reactions of Heptafluoroazazcyclopentan-2-one

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The pseudohalogen behavior of $NF_2(OSO_2F)$[2] is well demonstrated in reactions with fluorinated olefins, C_2F_4 and C_3F_6, to form (difluoroamino)(fluorosulfato)-substituted fluoroalkanes.[3] The latter are stable materials which, when reacted with alkali metal fluorides, are converted to α-difluoroamino ketones or α-(difluoroamino)acyl fluorides depending on the position of the fluorosulfate group on the chain. Sulfuryl fluoride is also produced.

We now wish to report that $NF_2(OSO_2F)$ also can be reacted with perfluorocyclobutene to form 1-(difluoroamino)-2-(fluorosulfato)hexafluorocyclobutane which undergoes a defluorosulfurylation reaction and concomitant ring expansion when reacted with potassium fluoride to give heptafluoroazacyclopentan-2-one. The ring is further expanded upon reaction with phosphine.

Results and Discussion

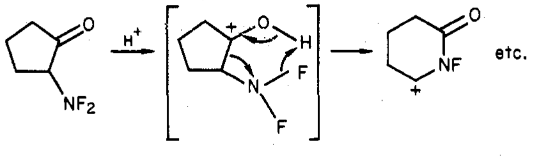
Addition of $NF_2(OSO_2F)$ to the double bond in perfluorocyclobutene requires a higher temperature and longer reaction time than does the analogous reaction with an acyclic perfluoro olefin.[4]

$$\mathrm{NF_2(OSO_2F) + CF_2CF{=}CFCF_2 \xrightarrow[\text{stainless steel, 22 h}]{160\ ^\circ C} \underset{80\%}{NF_2CFCF_2CF_2CF(OSO_2F)}}$$

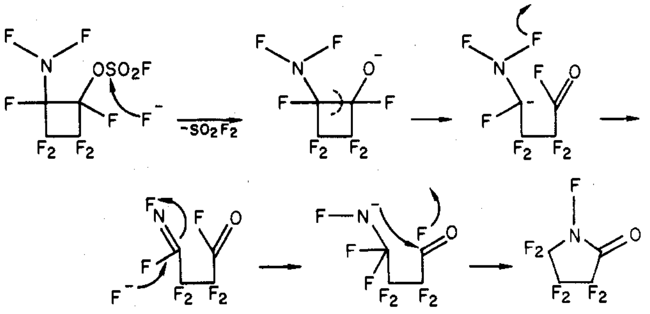
The compound formed is a stable, colorless material which slowly undergoes a defluorosulfurylation reaction at room temperature in the presence of thoroughly dried potassium fluoride to form heptafluoroazacyclopentan-2-one.

$$\mathrm{NF_2CFCF_2CF_2CF(OSO_2F) + KF \xrightarrow[20\ h]{25\ ^\circ C} NFCF_2CF_2CF_2C{=}O + SO_2F_2} \quad (1)$$

Acid-catalyzed ring-expansion reaction routes of a nonfluorinated (difluoroamino)cyclopentane and a (difluoroamino)cyclopentanone have been postulated,[5,6] viz.



In our case, where the reaction is base catalyzed, a likely route can be suggested. Expansion to a five-membered cyclic compound greatly eased the ring strain. This argument is based on the enhanced stability of intermediate A (see discussion concerning KF reaction with (fluorosulfato)heptafluorocyclobutane below). This new cyclic ketone is a volatile, colorless liquid which is stable at 170 °C for at least 30 h. (Trifluoromethyl)hexafluoroazacyclopentan-2-one is synthesized at 350 °C in 70% yield.[7] This great thermal stability is observed also for the unsubstituted hexafluorocyclobutanone, $CF_2CF_2CF_2C{=}O$, which is recovered unchanged after being heated for 12 h at 300 °C.[8] The latter is one of the most reactive ketones ever reported. Its reactivity was attributed to a combination of ring strain and the electron-withdrawing influence of the fluorine atoms.[9]



A

It is interesting to note that when (fluorosulfato)heptafluorocyclobutane, $CF_2CF_2CF_2CF(OSO_2F)$, is defluorosulfurylated in the presence of potassium fluoride, the products include hexafluorocyclobutanone and sulfuryl fluoride.[10] Although the reaction conditions are more rigorous (140 °C) than those used in reaction 1, ring opening does not occur. This lends support to the argument that ring opening is enhanced by the greater stability of intermediate A in the difluoroamino case. An analogous intermediate is not possible for the cyclobutanone.

As might be expected, we find that the behavior of heptafluoroazacyclopentan-2-one with PH_3 is quite different from that of hexafluorocyclobutanone where addition of the relatively acidic PH_3 to the polar form of the ketone occurs. PF_3 is found as one of the major products. In addition, a slightly volatile, oily liquid, which spectral and elemental analyses led us to conclude to be a ten-membered heterocycle (I), is formed

$$\mathrm{NFCF_2CF_2CF_2C{=}O + PH_3 \xrightarrow[2\ days]{25 ^\circ C} \underset{I}{HNCF_2CF_2CF_2C(O)NHCF_2CF_2CF_2C(O)} + PF_3 + \text{orange solid}}$$

in good yield. The liquid is stable to water. Elemental analyses are in excellent agreement with a substance whose empirical formula is C_4F_6HNO, that is, the five-membered monomer of I. However, mass spectral data strongly support the proposed structure—the highest *m/e* is 347 $(M - 2F - H)^+$ and the base peak is 346 $(M - 2F - 2H)^+$. The fragmentation pattern is given in the Experimental Section. The gas-phase infrared spectrum contains bands at 3480 and 1430 cm^{-1} assigned to ν_{NH} and δ_{NH}. A very strong band at 1830 cm^{-1} with 1805 (sh) cm^{-1} is assigned to $\nu_{C=O}$. This is a slight downward shift from the parent ketone. Strong bands are also found in the C–F stretching region.

In $CDCl_3$, the proton NMR spectrum consists of a single broad peak at δ 8.85 and is assigned to N–H. The ^{19}F NMR spectrum has three resonances at ϕ −92.5 (s), −127.6 (tr), and −134.1 (heptet) in the ratio of 1:1:1. The singlet is assigned

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to the CF_2 group adjacent to NH. Although it is surprising that this difluoromethylene group does not couple with adjacent nuclei, similar behavior was noted for $NF_2CF_{2A}CF_{2B}$-(OSO_2F) where CF_{2A} does not interact with either adjacent NF_2 or adjacent CF_{2B}. The triplet is assigned to the CF_2 adjacent to the carbonyl function, the fluorine atoms of which are assumed to couple with the β-CF_2 group ($J = 5.8$ Hz). The resonance assigned to the latter is complex, and although it appears to be either a heptet or a nonet (?) with $J \simeq 2.5$ Hz, the peak height ratios indicate that it is not simple.

These ^{19}F nuclear magnetic resonance spectral assignments are based largely on those observed in the two precursors, i.e., in $NF_2\overline{CFCF_2CF_2CF}(OSO_2F)$, peaks are observed at ϕ −176.5 ($CFOSO_2F$), −133.3 ($CFNF_2$), −126.1 (CF_2), −125.1 (CF_2), +22.0 (NF_2), and +50.5 (SF) in the ratio of 1:1:2:2:2:1 and in $\overline{NFCF_2CF_2CF_2C}{=}O$ at ϕ −130.5 (CF_2), −123.5 (CF_2-CO), −105.2 (CF_2N), and −89.4 (NF) in the ratio of 2:2:2:1. The broad resonance at −89.4 must be assigned to N–F.

The orange solid which is formed has not been characterized. It is common to observe such highly colored materials in reactions involving P(III) compounds.

An equimolar mixture of $\overline{NFCF_2CF_2CF_2C}{=}O$ and NH_3 was reacted at −20 °C to give an involatile white solid (mp 136 ± 1 °C) in a very rapid reaction. This material appears to contain N–F links and on the basis of mass spectral data seems to contain at least two of the initial ketone units. No carbonyl function exists, but ^1H NMR indicates the presence of both NH and OH.

Several other reactions were attempted between $\overline{NFCF_2CF_2CF_2C}{=}O$ and SF_4, COF_2, $CF_3C(O)F$, $S_2O_6F_2$, $SOCl_2$, or H_2S at 25 °C. However, no evidence of reaction and/or interesting products were observed either in the neat experiment or in the presence of polar organic solvents or alkali metal fluorides.

Experimental Section

Reagents. Hexafluorocyclobutene was obtained from PCR, Inc., and was used without further purification. The literature method was used to prepare $NF_2(OSO_2F)$.[2] Other materials were standard shelf reagents, and, with the exception of KF which was dried carefully prior to use, all were consumed as received.

General Procedures. A conventional Pyrex-glass vacuum apparatus which was equipped with a Heise-Bourdon tube gauge and a trap-to-trap distillation system was used for handling gases and volatile liquids and purification of products.

Infrared spectra were recorded on a Perkin-Elmer Model 457 infrared spectrophotometer by using a 10-cm gas cell made of Pyrex glass fitted with KBr windows. Fluorine-19 NMR spectra were determined with a Varian HA-100 spectrometer operating at 94.1 MHz by using CCl_3F as an internal standard, and proton NMR spectra were obtained on a Varian EM-360 with Me_4Si as an internal standard. Fluorine chemical shifts are recorded as negative when upfield from CCl_3F. Mass spectra were obtained with an Hitachi Perkin-Elmer RMU 6E mass spectrometer operating at 17 and 70 eV. Elemental analyses were performed by Beller Laboratories, Göttingen, West Germany.

Preparation of $NF_2\overline{CFCF_2CF_2CF}(OSO_2F)$. Equimolar quantities of hexafluorocyclobutene and $NF_2(OSO_2F)$ (10 mmol) were condensed into a 300-mL stainless-steel cylinder which was fitted with a Hoke needle valve, and the mixture was heated at 160 °C for 20 h.

During trap-to-trap distillation, the compound was condensed into a U-trap and cooled at −50 °C after passing through a −20 °C trap under dynamic vacuum. After purification by means of simple distillation at −35 °C, $NF_2\overline{CFCF_2CF_2CF}(OSO_2F)$ was isolated in 80% yield. The ^{19}F NMR spectrum contained six resonances at ϕ +50.5 (OSO_2F), +22.0 (NF_2), −125.1 (CF_2), −126.1 (CF_2), −133.3 ($CFNF_2$), and −176.5 ($CFOSO_2F$) in the ratio of 1:2:2:2:1:1. The infrared spectrum had absorption bands at 1496 (vs), 1398 (m), 1305 (s), 1241 (vs), 1164 (s), 1140 (ms), 1006 (w), 970 (vs), 930 (vs), 910 (m), 887 (m), 847 (vs), 807 (ms), 772 (w), and 697 (m) cm^{-1}. In the mass spectrum, the molecular ion was absent; however, other fragment peaks such as *m/e* 294 $(M - F)^+$, 194 $(M - C_2F_5)^+$, 164 $(M - CF_3SO_3)^+$, 159 $(M - NF_4SO_2)$, and 100 $(C_2F_4)^+$ were observed. The molecular weight obtained from vapor density measurements was 314 (calcd 313).

Anal. Calcd for $C_4F_9NO_3S$: N, 4.47; S, 10.22; F, 54.6. Found: N, 4.80; S, 10.83; F, 51.4.

Preparation of $\overline{NFCF_2CF_2CF_2C}{=}O$. With use of standard vacuum methods, 5 mmol of $NF_2\overline{CFCF_2CF_2CF}(OSO_2F)$ was condensed onto a large excess of anhydrous KF and the mixture was allowed to stand at 25 °C for 20 h. The compound was retained in a trap at −78 °C. It was contaminated with a small amount of starting material. Roughly 5 mmol of SO_2F_2 was also stopped in a trap at −196 °C. After purification by simple distillation at −50 °C, $\overline{NFCF_2CF_2C\text{-}CF_2CF_2CF_2C}{=}O$ was isolated in 96% yield.

The ^{19}F NMR spectrum contains resonances at ϕ −89.4 (br, NF), −105.2 (complex, CF_2N), −123.5 (s, CF_2CO), and −130.5 (doublet of overlapping quartets ($J_{F_A-F_B} = 5.3$ Hz, $J_{F_A-F_C} = J_{F_A-F_D} = 3.4$ Hz, β-CF_2)). The infrared spectrum is 1848 (vs), 1346 (s), 1312 (s), 1300 (sh), 1201 (vs), 1143 (m), 1056 (m), 992 (s), 970 (s), 847 (w), and 732 (w) cm^{-1}. In the mass spectrum, an intense molecular ion peak at *m/e* 211 is observed. The vapor density molecular weight is 213 (calcd 211). The dendritic crystals melt at −67 ± 1 °C. The vapor pressure of the liquid at 25 °C is 205 mmHg.

Anal. Calcd for C_4F_7NO: C, 22.75; N, 6.64; F, 63.0. Found: C, 22.65; N, 6.87; F, 62.6.

Preparation of $H\overline{NC(O)CF_2CF_2CF_2NHC(O)CF_2CF_2CF_2}$. Into a 70-mL nickel cylinder equipped with a Hoke needle valve were condensed equimolar amounts of $\overline{NFCF_2CF_2CF_2C}{=}O$ and PH_3 (1.0 mmol). The reaction mixture was maintained at 25 °C for 48 h. The resulting mixture was condensed onto finely powdered anhydrous NaF in a 70-mL nickel vessel. A small quantity of orange solid was left in the initial reaction vessel. After 24 h at 25 °C, the volatile products were separated by low-temperature trap-to-trap distillation under dynamic vacuum. A colorless, oily material condensed in a trap at −20 °C (80%), and PF_3 (0.8 mmol) was recovered in a trap at −196 °C. The oily liquid solidified at −25 ± 1 °C. If the raw products were not treated with NaF prior to handling in the glass vacuum system, then very large quantities of SiF_4 were generated. The oily liquid was still obtained. No other volatile phosphorus-containing species were observed, e.g., PF_2H.

The infrared spectrum is as follows: 3480 (m), 1830 (vs), 1805 (m, sh), 1430 (s), 1300 (s), 1190 (vs), 1140 (vs), 1050–1030 (s), 973 (s), and 530 (s) cm^{-1}. The mass spectrum does not contain a molecule ion, but the following fragments are observed at *m/e* 347 $(M - 2F - H)^+$, 346 $(M - 2F - 2H^+$, base), 318 $(M - 2F - CO - 2H)^+$, 296 $(M - CF_4 - 2H)^+$, 268 $(M - CF_4 - 2H - CO)^+$, 246 $(M - C_2F_6 - 2H)^+$, 218 $(M - C_2F_6 - 2H - CO)^+$, 190 $(M - C_2F_6 - 2H^+ - 2CO)^+$, 189 $(C_4F_5N_2OH_2)^+$, 174 $(C_4F_5NOH)^+$, 173 $(C_4F_5NO)^+$, 168 $(C_4F_4N_2O)^+$, 161 $(C_3F_5NO)^+$, 123 $(C_3F_3NO)^+$, and 100 $(C_2F_4)^+$.

Anal. Calcd for $C_8F_{12}N_2O_2H_2$: C, 24.87; H, 0.52; N, 7.25; F, 59.1. Found: C, 24.88; H, 0.56; N, 7.35; F, 58.5.

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Registry No. $NF_2\overline{CFCF_2CF_2CF}(OSO_2F)$, 71486-24-3; $\overline{NFCF_2CF_2CF_2C}{=}O$, 71486-25-4; I, 71486-26-5; $NF_2(OSO_2F)$, 6816-12-2; PH_3, 7803-51-2; hexafluorocyclobutene, 697-11-0.

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Electron Spin Resonance Spectra of Copolymer-Attached Trichloro(η^5-cyclopentadienyl)niobium and Copolymer-Attached Dichlorobis(η^5-cyclopentadienyl)niobium

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Stewart and Porte[1] have reported ESR spectra of some bis(π-cyclopentadienyl) compounds, including dichlorobis(η-cyclopentadienyl)niobium in chloroform–ethanol (9:1) glass at −196 °C. The spin Hamiltonian

$$\hat{\mathcal{H}} = \beta_e[g_{xx}H_x\hat{S}_x + g_{yy}H_y\hat{S}_y + g_{zz}H_z\hat{S}_z] + T_{xx}\hat{I}_x\hat{S}_x + T_{yy}\hat{I}_y\hat{S}_y + T_{zz}\hat{I}_z\hat{S}_z \quad (1)$$

was used[3] in interpreting these spectra.

In this work, ESR spectra of trichloro(η^5-cyclopentadienyl)niobium attached to 20% cross-linked styrene–divinylbenzene copolymer beads (hereafter referred to as copolymer-attached $CpNbCl_3$) and dichlorobis(η^5-cyclopentadienyl)niobium, also attached to 20% cross-linked styrene–divinylbenzene copolymer beads (hereafter referred to as copolymer-attached Cp_2NbCl_2), have been obtained. Spin-Hamiltonian parameters have been determined from these experimental spectra.

Experimental Section

Samples of copolymer-attached $CpNbCl_3$ and copolymer-attached Cp_2NbCl_2 were obtained from Chak-po Lau. Syntheses of these compounds have been described by Lau and by Lee and Brubaker.[2]

Portions of these compounds were transferred into Pyrex tubes in an argon-filled glovebox. After being sealed, these tubes were used as ESR sample tubes. (The ESR absorption due to Pyrex occurs at magnetic field strengths very different from those at which these samples absorb, as Pyrex glass exhibits apparent *g* values of 6.2 and 4.2.)[3]

ESR spectra to be used for quantitative interpretation were obtained by using a Varian V-4500-10A EPR spectrometer. A Hewlett-Packard frequency converter and electronic counter were used to determine microwave frequency accurately. A proton marker was used to determine magnetic field values accurately. ESR spectra were obtained in sections. A typical scan covered only 200–250 G—sometimes less—of the total magnetic field range. Neither of the spectra obtained for quantitative interpretation was obtained entirely in one session. The microwave frequency during a given session was often slightly different from microwave frequencies during other sessions.

For quantitatively interpreted spectral portions for copolymer-attached $CpNbCl_3$, the microwave frequency was between 9.098 and 9.111 GHz. The observed variations in microwave frequency could lead to errors of approximately 0.002 in **g** tensor values and approximately 0.000 04 cm^{-1} in hyperfine tensor values. Some calculated corrections were applied to compensate somewhat for these variations.

The sample temperature was maintained at −126 °C while spectra to be interpreted quantitatively were obtained. This temperature was used for both copolymer-attached $CpNbCl_3$ and copolymer-attached Cp_2NbCl_2. This temperature was determined by calibration with a thermocouple under conditions similar to those in effect when ESR spectra were being obtained for quantitative interpretation. When those quantitative ESR spectra were being obtained, no thermocouple was used; instead, a temperature dial setting and nitrogen gas flow rate corresponding to those used in calibration were employed consistently.

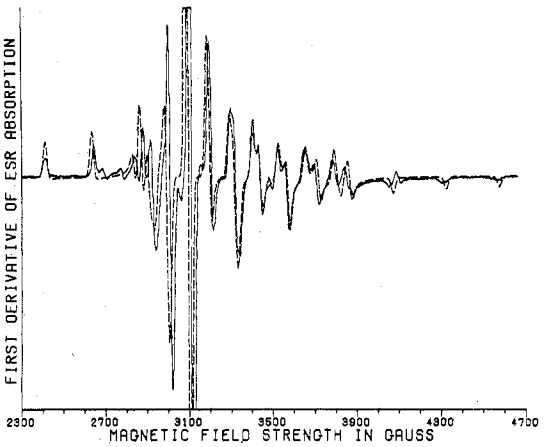

Figure 1. Experimental and simulated ESR spectra of copolymer-attached $CpNbCl_3$.

Data obtained when a standard sample of pitch in KCl was used indicated an error of 0.01% in microwave frequency to magnetic field strength ratio and/or in the procedure used to determine the magnetic field strength of the ESR absorption from a spectrum on chart paper.

Magnetic field strengths were determined at selected points on piecewise experimental spectra. These selected points included relative extrema and points whose vertical coordinates were halfway between those of consecutive relative extrema. Many of these magnetic field strengths were compared later with corresponding values from simulations.

The sections of spectra obtained for accurate interpretation do not provide as aesthetically excellent pictures as desired for illustrations. The illustrated experimental ESR spectra were obtained by use of a Varian E-4 EPR spectrometer, which is a different instrument from the one with which very accurate work was done.

For quantitative spectral portions for copolymer-attached Cp_2NbCl_2, the microwave frequency was between 9.1081 and 9.1092 GHz. This uncertainty of 0.0011 GHz could contribute uncertainties of about 0.0003 to the diagonal elements of the **g** tensor and uncertainties of about 0.000 005 cm^{-1} to the diagonal elements of the hyperfine tensor.

If the magnetic field strengths read from chart paper were perfectly accurate, then the microwave frequency was 9.197 ± 0.010 GHz for the experimental ESR spectrum of copolymer-attached Cp_2NbCl_2 at −126 ± 4 °C shown in Figure 2. For this scan, the magnetic field strengths read from chart paper do seem to be reliable to within 10 G and have been accepted for use in Figure 2.

Results and Discussion

The ESR spectra obtained for both copolymer-attached $CpNbCl_3$ and copolymer-attached Cp_2NbCl_2 are powder pattern spectra; that is, each of these experimental spectra could be considered a superposition of spectra for paramagnetic centers at many orientations relative to the magnetic field. Equations[4,5] appropriate for simulating powder pattern ESR spectra have been incorporated into computer programs that have been written to enable simulation of such spectra and generation of simulated data that can be compared readily with experimental data.

Solutions[4,5] appropriate for the spin Hamiltonian given by eq 1 were used in calculating spectra. The **g** tensor axes have been assumed identical with the corresponding hyperfine (**T**) tensor axes.

For each of these two compounds, the hyperfine parameters T_{xx}, T_{yy}, and T_{zz} all have the same sign. This sign was not determined but is assumed to be negative.

Experimental (solid line) and calculated (dashed line) ESR spectra are presented in Figures 1 and 2. For each compound, a systematic deviation seems to occur near the center of the spectrum. This deviation could be due to a quadupole inter-

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