## SHORT REVIEW

# NEW RESULTS OF THE REACTIONS WITH HEXAFLUOROACETONE AND RELATED COMPOUNDS

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#### SUMMARY

The reaction of hexafluoroacetone (HFA) with CNand SCN-compounds of main group and transition elements is described. The cyclic addition reactions to the CN-moiety is catalyzed by base, preferentially triethylamine. Of particular interest are the adducts of HFA with  $(SCN)_2$  and  $Hg(SCN)_2$ . They are precursors for various new compounds containing sixmembered rings. The elimination of oxygen by the reaction of HFA with N=WCl<sub>3</sub> may be considered as a new Wittig type reaction. The dimer of hexafluorothioacetone inserts into its S-C bond the carbon atom of an isonitrile group to yield five-membered rings. PCl<sub>5</sub> adds to  $(CF_3)_2C=C(CN)_2$ , prepared from HFA and  $CH_2(CN)_2$ , to form a six-membered phosphorus containing ring.

Hexafluoroacetone (HFA) was first prepared in 1941 [1]. It is easily available either by the reaction of hexachloroacetone and anhydrous hydrogen fluoride in the presence of a catalyst 0022-1139/85/\$3.30 © Elsevier Sequoia/Printed in The Netherlands [2] or by the isomerisation of hexafluoropropenoxide in the presence of a Lewis acid [3,4]. We have prepared HFA using hexachloroacetone, anhydrous HF and a  $CrO_x$  catalyst. The reaction proceeds well at 350°C. By-products, which are formed in small amounts, are the very toxic chloropentafluoroacetone and perfluoropropionic acid fluoride. The chloropentafluoro-acetone is easily separated by distillation and the perfluoropropionic acid fluoride by treating the crude product with water. Very pure hexafluoroacetone is obtained by distillation of the HFA  $\cdot$  H<sub>2</sub>O adduct from concentrated sul-furic acid.

The HFA-H $_2$ O adduct is described as having the following cyclic structures a and b [5]:



a (1:1 adduct)



b (2:1 adduct)

Structures of type a and b are not observed in the solid state [6].

The increased acidity of the fluorinated alcohols e.g.  $HFA \cdot H_2O$ over alcohols has been explained on the basis of inductive effects and hydrogen bridge bonding. We were interested in the structure of the  $HFA \cdot H_2O$  adduct and treated it with tetraphenylphosphonium chloride to obtain crystals of composition  $2[(CF_3)_2C(OH)_2 \cdot (CF_3)_2C(O)OH]^- 2PPH_4^+ 1$ . An X-ray single crystal



Fig. 1. The diamion of  $[2 (CF_3)_2 C(OH)_2 \cdot 2 (CF_3)_2 C(O)OH]^2$ .

structure analysis of  $\underline{1}$  indicated that two types of hydrogen bridge bonds are formed. The two hydrogen atoms in the center of the molecule form a symmetric O-H(1)-O bridge, while the other four are non-symmetrically bonded H(2). Fig. 1 shows the dianion of composition [2 (CF<sub>3</sub>)<sub>2</sub>C(OH)<sub>2</sub> · 2 (CF<sub>3</sub>)<sub>2</sub>C(O)OH]<sup>2-</sup>. Reactions of HFA with nitriles and isonitriles of main group elements

Cyanotrimethylsilane exists as an equilibrium with the tautomeric isonitrile form

Me\_SiCN \_\_\_\_\_ Me\_SiNC

At room temperature the nitrile form is much more favoured[7]. The isomers react in different ways with HFA.



The nitrile reacts with insertion of HFA into the siliconcarbon bond to yield the cyanohydrin  $\underline{2}$ . However, when the concentration of HFA is increased, in addition to  $\underline{2}$  the isonitrile adduct  $\underline{3}$  is formed. In the presence of catalytic amounts of triethylamine, an insertion of HFA into the silicon-nitrogen bond is found to yield  $\underline{4}$ . The formation of  $\underline{3}$  and  $\underline{4}$  instead of  $\underline{2}$  is favoured, when an excess of HFA is used. The siliconnitrogen bond in  $\frac{3}{2}$  can be easily cleaved with halides. Ph<sub>2</sub>PCl reacts with  $\frac{3}{2}$  with rearrangement of the five-membered ring to yield the phosphorane 5.



The reaction of  $\underline{3}$  and SeOCl<sub>2</sub> results in the formation of  $\underline{6}$  with elimination of (Me<sub>3</sub>Si)<sub>2</sub>O.



Boron tribromide and  $\underline{3}$  yield  $\operatorname{Br}_2\operatorname{BNC}(\operatorname{HFA})_2 \underline{7}$  as well as  $\operatorname{B[NC(HFA)}_2]_3 \underline{8}$ . On the basis of <sup>19</sup>F-nmr investigations, we assume that in  $\underline{7}$  the boron atom is intramolecular coordinated through oxygen. Because of the nuclear quadrupole moment of <sup>11</sup>B we do not actually observe any fine structure, however, the signal at -72.9 ppm is broader and flatter in shape compared with that at -79.1 ppm.



HFA has been found to be a versatile reagent in phosphorous chemistry [8]. Pseudohalides of phosphorus(III) were reacted with HFA. In general the reactions proceed in the presence of a basic catalyst. Triethylamine has been proved to be the best. T catalyst is probably responsible for a nitrile-isonitrile equilibrium taking place in solution. Insertion into two phosphorus-carbon bonds and cycloaddition to an isonitrile group was observed with  $P(CN)_3$  to yield <u>8</u>.



Substitution of one CN-group by a trifluoromethyl group in  $P(CN)_3$  and its reaction with excess HFA leads to the formation of a chiral phosphane. The X-ray structure determination shows only one enantiomer to be present in the solid state 9 [6].

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A completely different course of reaction has been found with PhP(CN)  $_{2}$ .



The formation of  $\underline{10}$  may be explained by conversion of the nitrile groups to isonitrile groups followed by cycloaddition and insertion of HFA as described for  $\underline{9}$ . In addition one of the fivemembered rings is cleaved at one of the carbon-oxygen bonds with oxidative addition to the phosphorus atom.

In the presence of triethylamine as a catalyst  $P(NCS)_3$  reacts with HFA with complete isomerisation and cycloaddition of all ligands to yield <u>11</u>.



<u>11</u> contains three six-membered diazine rings. As(NCS)<sub>3</sub> and HFA lead to As-S( $-C=N-C(CF_3)_2-O-C(CF_3)_2-O$ )<sub>3</sub> <u>12</u>. The X-ray structure of <u>12</u> has been determined. A fourteen-membered ring <u>13</u> has been found when excess of

As(CN)<sub>3</sub> is reacted with HFA [9].



However, excess of HFA and As(CN)<sub>3</sub> or Sb(CN)<sub>3</sub>, lead to the formation of  $\underline{14}$  and Sb-[O-C(CF<sub>3</sub>)<sub>2</sub>-N=C-O-C(CF<sub>3</sub>)<sub>2</sub>-O-C(CF<sub>3</sub>)<sub>2</sub>]<sub>3</sub>  $\underline{15}$  respectively.

As (CN)<sub>3</sub> + 9 HFA 
$$\longrightarrow$$
 As-
$$\begin{bmatrix} & F_3C & CF_3 \\ & CF_3 & CF_3 \\ & CF_3 & CF_3 \\ & CF_3 & CF_3 \end{bmatrix}_3$$

An oxidative addition to the arsenic or antimony atom in  $\underline{14}$  and  $\underline{15}$  was not observed with HFA.

Cyanate and thiocyanate anions react with HFA to yield an ionic hexafluoropropaneimine  $\underline{16}$  with evolution of  $CO_2$  or COS. Single crystals of the sodium salt were obtained by recrystallisation from dimethoxyethane. The sodium salt crystallizes with two molecules of dimethoxyethane. The X-ray crystal structure shows the anion to be dimeric in the solid state.



NaSCN + 2 HFA 
$$\longrightarrow$$
  $F_3^C$  = N -  $C_1^{F_3}$   $G_2^{F_3}$  -  $G_1^{F_3}$   $G_2^{F_3}$   $G_2^{F$ 

A by-product  $\underline{12}$  of about 7% yield has been found in the HFA-NaSCN reaction. The X-ray structure shows the elimination of all oxygen atoms in HFA and the cleavage of some carbon-carbon bonds. The reaction proceeds at room temperature and it is surprising that at this temperature oxygen is replaced.



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HFA reacts with dithiooxamide with elimination of sulfur to yield the monothiooxamide 18.



The X-ray structure of  $\underline{18}$  shows the  $\begin{array}{c} N \\ O \end{array}$  C - C  $\begin{array}{c} S \\ N \end{array}$  skeleton of the thioxamide to be almost planar [10].

Dicyanodisulfane,  $(SCN)_2$ , as well as dicyanotrisulfane,  $S(SCN)_2$ , react with HFA in the presence of catalytic amounts of tr ethylamine to yield <u>19</u> and  $\overline{O-(CF_3)_2C-O-(CF_3)_2C-N=C}$  ·  $S_3 - \overline{C=N-C-(CF_3)_2-O-C(CF_3)_2-O}$  <u>20</u>.



 $\frac{20}{20}$  is sensitive to heat and is easily converted to  $\frac{19}{20}$  under elimination of sulfur.  $\frac{20}{20}$  was characterized by elemental analysis and mass spectra.

The starting material  $(SCN)_2$  is a red oil at room temperature, it easily polymerizes to yield  $(SCN)_x$ , a brick-red solid.  $(SCN)_2$  is easily cleaved at the sulfur-sulfur bond. In contrast, <u>19</u> shows a remarkable stability at the sulfur-sulfur bond, which is not affected by HFA [11]. The same product is formed when the adduct of HFA and Hg(SCN)<sub>2</sub> is treated with elemental bromine. The S-S bond length in <u>19</u> was found to be 202.0(2)pm, compared with that in  $(S_3N_2O)_2SnCl_4$  of 218.1(3) pm [12].

Cleavage of the sulfur-sulfur bond in <u>19</u> has been achieved with elemental chlorine at  $50^{\circ}$ C in a pressure vessel [13].



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<u>20</u> is a distillable yellow liquid boiling at 69°C/64 mbar. The chlorine atom has been replaced by the following R groups: -CN,  $(C_6H_{11})_2N$ - and  $n-C_4H_9$ .

Derivatives of  $\underline{19}$  with longer sulfur chains are unstable and eliminate sulfur to yield  $\underline{19}$ .

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 $n-C_4H_9-S-C=NC(CF_3)_2-O-C(CF_3)_2-O$  21 eliminates one molecule of HFA by warming up to 120°C for 36 h to form the four-membered ring derivative 22. [13]



In the reaction of HFA with  $Se(CN)_2$  the catalyst, triethylamine, is involved. The product  $\underline{23}$  contains a six- and a five-membered ring bridged by a selenium atom. The five-membered ring is generated by a complete dehydrogenation of an ethyl group.



The structure of  $\underline{23}$  has been established by X-ray crystal analysis. A striking difference to the reactions with cyanate and thiocyanate has been found with potassium selenocyanate. Elemental selenium is precipitated and cyanide ion is the reactive species for the formation of  $\underline{24}$ .



 $\underline{24}$  is generated from an unstable intermediate by a Chapman rearrangement. The structure of the potassium salt a dimethoxyethane adduct was investigated by an X-ray single crystal analysis. The potassium has a coordination number of five through two anions of  $\underline{24}$ .

Mercury dithiocyanate reacts with HFA in the presence of triethylamine with formation of six-membered rings. The generation of six-membered rings was also observed with phosphorus, arsenic and sulfur [14].

$$Hg(SCN)_{2} + 4 HFA \longrightarrow Hg \begin{bmatrix} F_{3}C & CF_{3} \\ N - C & 0 \\ F_{3}C & CF_{3} \end{bmatrix}_{2}$$

 $\underline{25}$  is a white solid and a useful precursor for metathesis reactions with halides accompanied by precipitation of mercury halides, e.g. Cl-S-CF<sub>2</sub>-CF<sub>2</sub>-S-Cl yields  $\underline{26}$ .



The reaction of Hg(CN)<sub>2</sub> with HFA yields a mixture of Hg(CN)<sub>2</sub>. (HFA)<sub>x</sub>, x varies from 2-3. One of the products is the one to two adduct  $\underline{27}$ . Its subsequent reaction with diphenylchloro-phosphane affords the phosphorane  $\underline{28}$ .



HFA, nitridotungsten trichloride and tetraphenylarsonium chloride react to form  $\underline{29}$ .

$$2 \operatorname{Cl}_{3} W = N + HFA + 2 \operatorname{Ph}_{4} \operatorname{As}^{+} \operatorname{Cl}^{-} \longrightarrow [\operatorname{Cl}_{5} W = N - \operatorname{C}^{-} N = W \operatorname{Cl}_{5}]^{2-} 2 \operatorname{Ph}_{4} \operatorname{As}^{+} \operatorname{Cr}_{3} \xrightarrow{2} 2 \operatorname{Ph}_{4} \operatorname{As}^{+} \operatorname{Ph}_{4} \operatorname{Ph}_{$$

Single crystal X-ray structure analysis proves the formation of this interesting compound [15]. The elimination of oxygen by transition metals may be considered as a new Wittig type reaction. The W=N bond of 174.3(15) pm is a little longer than in  $[Cl_5WNC_2Cl_5]$ , which was considered to be a triple bond. Since the geometry at nitrogen is almost linear  $[176.9(14)^{\circ}]$ , a triple bonded resonance form N=W, with a positive formal charge on nitrogen may make a significant contribution. The W-Cl bond trans to N[243.7(7) pm] is larger than the mean of the other four [231.6(8) pm], and the equatorial chlorines are bent away from the nitrogen.

## Reactions of hexafluorothioacetone dimer

The dimer of hexafluorothioacetone, 2,2,4,4-tetrakis(trifluoromethyl)-1,3-dithietane  $\underline{30}$  reacts with P(CN)<sub>3</sub> or As(CN)<sub>3</sub> to yield  $\underline{31}$  and As[N=C-C(CF<sub>3</sub>)<sub>2</sub>-S-C(CF<sub>3</sub>)<sub>2</sub>-S]<sub>3</sub>  $\underline{32}$ .



The structure of  $\underline{32}$  was confirmed by a single crystal X-ray structure analysis.

In the reaction of  $\underline{30}$  with P(CN)<sub>3</sub> in the presence of triethylamine as catalyst, a second product  $\underline{33}$  was isolated in low yield, for which the following structure is suggested by the spectroscopic data; [16,17] FP(S)L<sub>2</sub>, where L is



t-BuAs(CN)<sub>2</sub>, PhP(CN)<sub>2</sub>, and  $\underline{30}$  yield the expected t-BuAsL<sub>2</sub>  $\underline{34}$  and PhPL<sub>2</sub>  $\underline{35}$ . Ge(CN)<sub>4</sub> and  $\underline{30}$  gave the GeL<sub>4</sub>  $\underline{36}$ .

It is well known [18] that HFA adds to CH2 (CN)2. From the adduct water may be eliminated by means of P4010 to yield  $(F_3C)_2C=C(CN)_2$ . By treating  $(F_3C)_2C=C(CN)_2$  with phosphorus pentachloride the cyclic six-membered ring 37 is formed.



37 is a crystalline yellow solid, which may be recovered from the crude material by sublimation [19]. In 37 it is interesting that one of the nitrile groups has been converted to an isonitrile, as shown by <sup>13</sup>C-nmr spectroscopy

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## REFERENCES

1	N. Fukuhara, L.A. Bigelow, J. Am. Chem. Soc. <u>63</u> , 788 (1941).
2	C.G. Krespan, W.J. Middleton, Fluorine Chem. Rev. 1, 145
	(1967).
3	D.E. Morin, Minnesota Mining, US-Pat. 3 231 134 (1965).
4	E.N. Squire, du Pont, US-Pat. 4 302 608 (1981).

- 5 W.J. Middleton, R.V. Lindsey, J. Amer. Chem. Soc. <u>86</u>, 4948 (1964).
- H.W. Roesky, J. Lucas, K.-L. Weber, H. Djarrah, E. Egert,
  M. Noltemeyer, G.M. Sheldrick, Chem. Ber. <u>118</u>, 2396 (1985).
  H.W. Roesky, J. Lucas, K. Keller, K.S. Dhathathreyan,
  M. Noltemeyer, G.M. Sheldrick, Chem. Ber. <u>118</u>, 2659 (1985).
- 7 M.R. Booth, S.G. Frankiss, J.C.S., Chem. Comm. 1968, 1347.
- 8 G.V. Röschenthaler, Z. Naturforsch. <u>33B</u>, 311 (1978); 33B, 131 (1978).
- 9 H.W. Roesky, H. Djarrah, J. Lucas, M. Noltemeyer, G.M. Sheldrick, Angew. Chem. <u>95</u>, 1029 (1983), Angew. Chem. Int. Ed. Engl. <u>22</u>, 1006 (1983).
- 10 H.W. Roesky, H. Hofmann, M. Noltemeyer, G.M. Sheldrick, Z. Naturforsch. 40B, 124 (1985).
- 11 H.W. Roesky, N.K. Homsy, M. Noltemeyer, G.M. Sheldrick, Angew. Chem. <u>96</u>, 1002 (1984), Angew. Chem. Int. Ed. Engl. 23, 1000 (1984).
- 12 H.W. Roesky, M. Kuhn, J.W. Bats, Chem. Ber. 115, 3025 (1982).
- 13 H.W. Roesky, N.K. Homsy, H.G. Schmidt, Z. Anorg. allg. Chem., in press.
- H.W. Roesky, V.W. Pogatzki, K.S. Dhathathreyan, A. Thiel,
   H.G. Schmidt, M. Noltemeyer, G.M. Sheldrick, Chem. Ber. in press
- 15 N.K. Homsy, H.W. Roesky, M. Noltemeyer, G.M. Sheldrick, J. Chem. Soc. Dalton Trans. in press.
- 16 H.W. Roesky, K.S. Dhathathreyan, Chem. Commun. 1984, 1053.
- 17 H.W. Roesky, K.S. Dhathathreyan, M. Noltemeyer, G.M. Sheldrick, Z. Naturforsch. 40B, 240 (1985).
- 18 W.J. Middleton, J. Org. Chem. 31, 3731 (1966).
- 19 H.W. Roesky, K. Keller, unpublished results.