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Preliminary Note

The reaction of tetrafluoroethylene with arsenic trifluoride

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Tetrafluoroethylene under pressure has been found to react with arsenic trifluoride in the presence of antimony pentafluoride to give the compounds $As(C_2F_5)_3$ and $FAs(C_2F_5)_2$. A previously reported synthesis of arsenic trispentafluoroethyl involved the reaction of pentafluoroethyl iodide with arsenic[1].

In the present synthesis, antimony pentafluoride seems to act as a catalyst. The compound $F_2AsC_2F_5$ was not isolated and is presumably unstable with respect to the disproportionation

$$2F_2AsC_2F_5 \rightarrow AsF_3 + FAs(C_2F_5)_2$$

The olefin trifluorochloroethylene, $F_2C{=}CFCl$, reacted in a similar manner to give the compound $FAs(CFClCF_3)_2$ b.p. 116–119°. The orientation of the addition was proved by hydrolysis which produced the compound CF_3CFClH. The olefin hexafluoropropene did not appear to react with arsenic trifluoride in the presence of antimony pentafluoride. The nature of the catalysis of the reaction by antimony pentafluoride has not been elucidated. However the 1:1 adduct of arsenic trifluoride and antimony pentafluoride when melted reacts with tetrafluoroethylene to produce mainly $As(C_2F_5)_3$. The adduct is thought to contain the species $AsF_2^+SbF_6^-$. Possibly the mechanism involves the attack of tetrafluoroethylene by AsF_2^+. As the proportion of SbF_5 in the AsF_3/SbF_5 mixture is reduced, more of the compound $FAs(C_2F_5)_2$ is produced.

In a typical reaction, arsenic trifluoride (75 ml) and antimony pentafluoride (19 g) were charged into a 300 ml autoclave fitted with a stirring device. The vessel was pressurized at room temperature with tetrafluoroethylene to 260 psi. A pressure drop commenced immediately and the tetrafluoroethylene pressure was continually brought back to 260 psi. The temperature rose to 30° during the course of the reaction which lasted 1 h. The product appeared to consist of two layers. The upper layer was distilled and gave $FAs(C_2F_5)_2$, 96 g, b.p. 66° and $As(C_2F_5)_3$, 11 g, b.p. 92–94°.

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Reaction of the compounds $As(C_2F_5)_3$ and $FAs(C_2F_5)_2$ with iodine and tetrafluoroethylene under pressure at 220° gave perfluoroalkyl iodides $F(C_2F_4)_nI$ with $n = 1$–4. This presumably occurs by cleavage to give perfluoroethyl iodide, C_2F_5I, which then telomerizes with tetrafluoroethylene.

Hydrolysis of the compound $FAs(C_2F_5)_2$ gave the product $(C_2F_5)_2As{-}O{-}As(C_2F_5)_2$.

REFERENCE

1 P. B. Ayscough and H. J. Emeléus, *J. Chem. Soc.*, (1954) 3381.