Sulphur Tetrafluoride–Lithium Hexafluoroisopropylidenimine Rearrangement Reactions

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Summary The isolation of a series of new sulphurdi-imides indicates that irreversible stepwise replacement of labile fluorine atoms accompanied by extensive rearrangement readily occurs during the reaction of SF_4 with $LiN{=}C(CF_3)_2$.

PREVIOUS metathesis reactions of $LiN{=}C(CF_3)_2$ with inorganic chlorides and fluorides proceed in a predictable manner to introduce the unsaturated $-N{=}C(CF_3)_2$ ligand into transition-metal compounds[1] and other inorganic compounds of Groups IIIA—VIA.[2] With SOX_2 ($X = Cl$, F), halogen migration and substitution occur to give the rearranged sulphinylimine, $(CF_3)_2C{=}NC(CF_3)_2N{=}S{=}O$.

Reactions of $LiN{=}C(CF_3)_2$ and SF_4 result in the formation of a series of extensively rearranged compounds.

$(CF_3)_2CFN{=}SF_2$[3]
(I)

$(CF_3)_2CFN{=}S{=}NCF(CF_3)_2$
(II)

$(CF_3)_2CFN{=}S{=}NC(CF_3)_2N{=}C(CF_3)_2$
(III)

$(CF_3)_2C{=}NC(CF_3)_2N{=}S{=}NC(CF_3)_2N{=}C(CF_3)_2$
(IV)

$(CF_3)_2C{=}NC(CF_3)_2N{=}C(CF_3)_2$
(V)

Compounds (I—IV) form a homologous series obtained by replacing F by C_3F_6N- in each of the less substituted members. Further reaction of each of the above pure compounds with $LiN{=}C(CF_3)_2$ produces only the more highly substituted members with none of the lower members being observed, *e.g.*,

$$\begin{aligned} LiN{=}C(CF_3)_2 &+ (I) \longrightarrow (II) + (III) + (IV) + (V) \quad (a)\\ &+ (II) \longrightarrow (III) + (IV) + (V)\\ &+ (III) \longrightarrow (IV) + (V)\\ &+ (IV) \longrightarrow (V)\\ &+ (V) \longrightarrow \text{No reaction.} \end{aligned}$$

When the lithium salt is formed in the usual manner,[2] an interesting side-reaction occurs in (a). A new sulphurimine, $[(CF_3)_2C{=}N-]_2SNH$ (VI), is formed in yields up to 24% in addition to various amounts of (II—V). However, heating the solid lithium salt at 60° under dynamic vacuum removes any trapped $(CF_3)_2C{=}NH$ and almost no (VI) is subsequently formed when (I) reacts with the solid.

Reactions are carried out by condensing pure sulphur tetrafluoride on to an excess of the lithium salt at $-195°$ and warming slowly to 25°. Although product analysis is consistent, yields fluctuate widely over a series of similar reaction conditions, presumably due to the great differences in volatility of the liquid products which affects the ease with which further reaction occurs.

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