

Sulphur Tetrafluoride-Lithium Hexafluoroisopropylideneimine Rearrangement Reactions

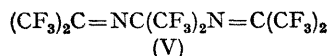
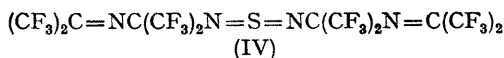
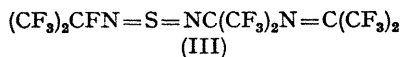
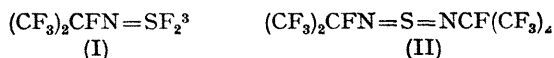
By RICHARD F. SWINDELL and JEAN'NE M. SHREEVE*

(Department of Chemistry, University of Idaho, Moscow, Idaho 83843)

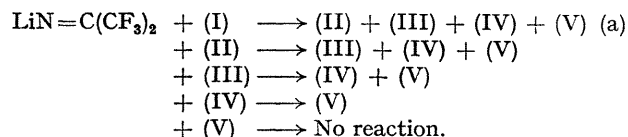
Summary The isolation of a series of new sulphurdi-imides indicates that irreversible stepwise replacement of labile fluorine atoms accompanied by extensive rearrangement readily occurs during the reaction of SF₄ with LiN=C(CF₃)₂.

PREVIOUS metathesis reactions of LiN=C(CF₃)₂ with inorganic chlorides and fluorides proceed in a predictable manner to introduce the unsaturated -N=C(CF₃)₂ ligand into transition-metal compounds¹ and other inorganic compounds of Groups IIIA—VIA.² With SOX₂ (X = Cl, F), halogen migration and substitution occur to give the rearranged sulphinylimine, (CF₃)₂C=NC(CF₃)₂N=S=O.

Reactions of LiN=C(CF₃)₂ and SF₄ result in the formation of a series of extensively rearranged compounds.



Compounds (I—IV) form a homologous series obtained by replacing F by C₃F₆N- in each of the less substituted members. Further reaction of each of the above pure compounds with LiN=C(CF₃)₂ produces only the more highly substituted members with none of the lower members being observed, *e.g.*,



When the lithium salt is formed in the usual manner,² an interesting side-reaction occurs in (a). A new sulphurimine, [(CF₃)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 (CF₃)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.

Fluorine research at the University of Idaho is supported by the National Science Foundation and the Office of Naval

Research. R.F.S. is a National Defense Education Act Fellow; J.M.S. is an Alfred P. Sloan Foundation Fellow.

(Received, July 12th, 1971; Com. 1191.)

¹ B. Cetinkaya, M. F. Lappert, and J. McMeeking, *Chem. Comm.*, 1971, 215.

² R. F. Swindell, T. J. Ouellette, D. P. Babb, and J. M. Shreeve, *Inorg. and Nuclear Chem. Letters*, 1971, 7, 239.

³ O. Glemser and S. P. von Halasz, *Chem. Ber.*, 1969, 102, 3333.