J. inorg. nucl. Chem., 1970, Vol. 32, pp. 1845 to 1846. Pergamon Press. Printed in Great Britain

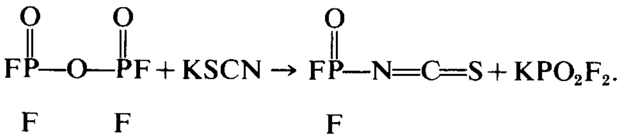
THIOPHOSPHORYL-DIFLUORIDE-ISOCYANATE*

H. W. ROESKY
Anorganisch-Chemisches Institut der Universität, Göttingen, Germany

(*Received* 27 *October* 1969)

Abstract – SPF_2NCO, the isomer of OPF_2NCS, was prepared by the reaction of SPF_3 with $Si(NCO)_4$ at 200°C in an autoclave. The i.r. and ^{19}F-NMR-data of the compound are reported.

RECENTLY we reported the preparation of thiophosphoryl-difluoride-isothio-under cleavage of the Si—N bond[2].



$$\mathrm{F\overset{O}{\underset{F}{\overset{\|}{P}}}{-}O{-}\overset{O}{\underset{F}{\overset{\|}{P}}}F + KSCN \rightarrow F\overset{O}{\underset{F}{\overset{\|}{P}}}{-}N{=}C{=}S + KPO_2F_2.}$$

Thiophosphoryl-trifluoride reacts with silicontetraisocyanate in an autoclave under cleavage of the Si—N bond[2].

$$4SPF_3 + Si(NCO)_4 \rightarrow 4S = PF_2NCO + SiF_4.$$

In a typical experiment 50 g of $Si(NCO)_4$ were reacted with 150 g of SPF_3 in a 300 ml monel autoclave for 12 hr at 200°C. The yield was 8–10 g. At 220°C more OPF_2NCS and $OPF(NCS)_2$ were formed as byproducts along with a polymeric brown solid.

SPF_2NCO can be used for preparing other P, F-compounds. The product is colourless, a bad smelling liquid and inflamable in air. It reacts with traces of water and dissolves Kel-F grease.

The vapour pressures are expressed by the equation $\log p(\mathrm{mm}) = (-1538/T) + 7{\cdot}75$ corresponding to a b.p. of 42·8 ± 1°C, a heat of vaporisation of 7·035 kcal/mole, and a Trouton's constant of 22·3 cal/mole deg. SPF_2NCO was identified by its molecular weight (calc. 143·1, found 142·8 Regnault), i.r., NMR and mass spectrum. The mass cracking pattern is consistent with the proposed structure (in brackets rel. intensities) 143 (100%), 145 (3·2%) molecular ion, 124 (3·2%) $SPFNCO^+$, 115 (4·5%) SPF_2N^+, 111 (1·3%) PF_2NCO^+, 101 (17·4%) SPF_2^+, 92 (1·9%) $PFNCO^+$, 69 (25·8%) PF_2^+, 64 (3·9%) NPF^+, 63 (0·6%) SP^+, 50 (3·2%) PF^+, 32 (2·6%) S^+, 31 (0·6%) P^+, 28 (2·6%) CO^+.

---

*Phosphorverbindungen, 45. Mitteil., 44. Mitteil. H. W. Roesky, *Inorg. & Nucl. Chem. Lett.* In press.

1. H. W. Roesky, *Angew. Chem.* **79**, 61 (1967).
2. M. Murray, and R. Schmutzler, *Z. Chemie* **8**, 241 (1968); O. J. Scherer, *Organometal. chem. Rev.* **A3**, 281 (1968).

The i.r. spectrum (gas, KBr windows) shows absorptions at ≈ 2275 s, 1425 s, 943 vs, 925 s, 812 vs, 735 w, 600 s cm^{-1}: these are tentatively assigned to ν_{as}(NCO) 2275, ν_s(NCO) 1425, ν_{as}(PF) 943, ν_s(PF) 925, ν(P═S), ν(P—N) 812, 600. In the ^{19}F-NMR ($CFCl_3$ external reference) there is found a dublet at $\delta_F = 37{\cdot}2$ ppm with the coupling constant of $J_{F-P} = 1115$ Hz. The isomer has a coupling constant of $J_{F-P} = 1012$ Hz and a chemical shift of $\delta_F = 71{\cdot}6$ ppm.