A THIOPHILIC PATHWAY FOR THE SYNTHESIS OF PERFLUORINATED α,β-UNSATURATED THIOCYANATES

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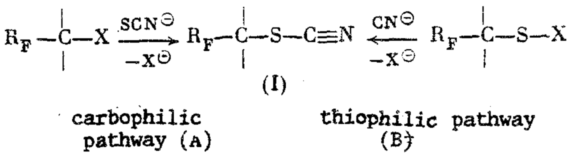
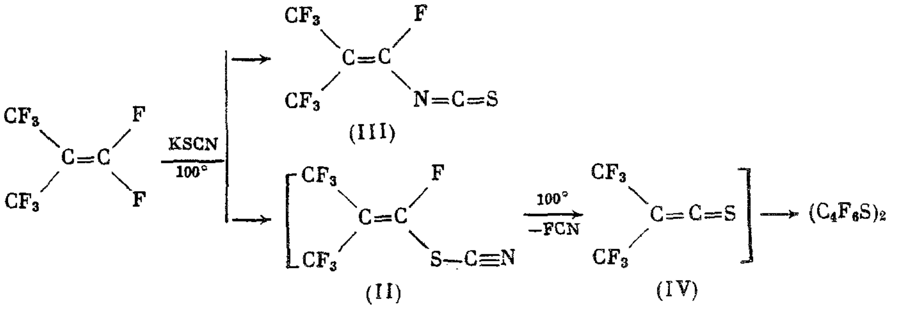
413.5'16'151:547.279.1

While perfluoroalkyl thiocyanates (I) are readily available from both carbophilic and thiophilic substitution reactions (pathway A [1,2] or B [3]), the corresponding α,β-unsaturated thiocyanates (II) have been exceedingly difficult to obtain.

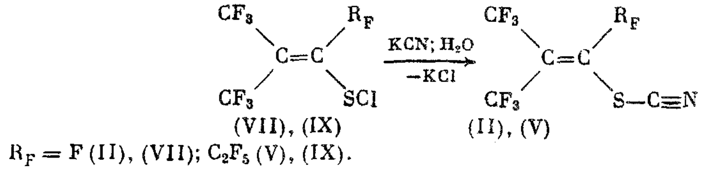


The difficulty in obtaining this class of compounds using the previously investigated carbophilic pathway (1) is a consequence of 1) the formation of isomeric derivatives (III) and 2) the accompanying decomposition with the formation of thioketene (IV) under the vigorous conditions for substitution at the carbon atom [4] (see the review of Zeifman et al. [5]). The only example of such a compound, namely, 1,2-dithiocyano-3,3-difluoro-1-cyclopropene was described only in a specific series of electron-deficient small rings [6].

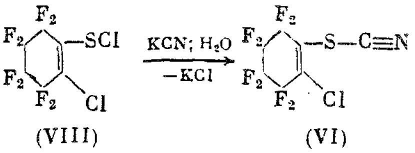


(1)

In the present work, we showed that the thiophilic pathway (reactions (2) and (3)) may be used to obtain perfluoro-α,β-unsaturated thiocyanates of both linear ((II) and (V)) and cyclic structure ((VI)). This pathways entails the reaction of readily available perfluorinated α,β-unsaturated sulfenyl chlorides (VII), (VIII) [7], and (IX) [8] with KCN in water.



(2)



(3)

The proposed reaction is carried out at 5-10°C for 20 min and gives 50-70% yields with the absence of isomerization, leading to the formation of the desired products, which are colorless liquids with bp 70°C (90 mm) (II), 73-75°C (65 mm) (V), and 65-66°C (10 mm) (VI). The structures of these products were established by ^{19}F NMR spectroscopy and elemental analysis.

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THE FLUORINATION OF SILYLATED PHOSPHITES BY PERFLUOROPROPYLENE OXIDE

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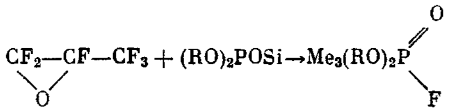
The chemical properties of perfluoroolefin oxides have not been studied extensively. We have found that silyl ethers of dialkyl phosphites undergo oxidative fluorination efficiently by perfluoropropylene oxide (I) under mild conditions to give the corresponding dialkyl fluorophosphates. This reaction has not been described previously.



(I) (II) (IIIa—c)

R = Me (a), Et (b), Pr (c)

General Procedure. A sample of 0.01-0.015 mole phosphite (II) was added to a steel test tube and a 1.5-fold excess of (I) was condensed at from −50 to −40°C. The test tube was sealed, brought to room temperature, and maintained for 10 h. After opening, the reaction mixture was distilled in vacuum to give dialkyl fluorophosphates (III). (IIIa): bp 39-44°C (9 mm), δP (H_3PO_4, ppm): −6.3, J_{P-F} = 972 Hz, δF (CF_3CO_2H, ppm): −9.9, J_{P-F} = 976 Hz (37%) [1]. (IIIb): bp 58-65°C (9 mm), δP) −8.5, J_{P-F} = 976 Hz, δF) −4.7, J_{P-F} = 976 Hz (56%) [1]. (IIIc): bp 79-92°C (9 mm), δP) −8.3, J_{P-F} = 977 Hz, δF) −5.3, J_{P-F} = 970 Hz (45%) [1].

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