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SHORT COMMUNICATION

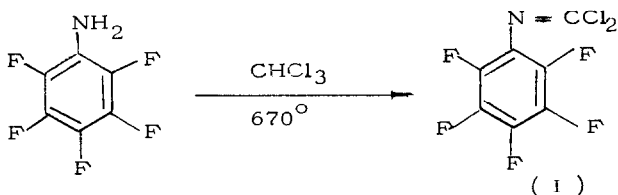
Formation of 2,3,4,5,6-Pentafluorophenylcarbonimidoyl Dichloride by
Copyrolysis of 2,3,4,5,6-Pentafluoroaniline with Chloroform

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Interaction of aniline and some of its derivatives with dichloro-
carbene generated from chloroform and bases results in the formation
of phenylisocyanides [1]. Attempts at the preparation of 2,3,4,5,6-
pentafluorophenyl isocyanide from 2,3,4,5,6-pentafluoroaniline were
unsuccessful [2]*.

During the course of our investigations of thermolytic reactions
of polyfluoroaromatic compounds in the presence of sources of di-
halocarbenes, in this paper we describe the interaction of 2,3,4,5,6-
pentafluoroaniline with chloroform in flow system at 670°. The main
polyfluorinated compound in the reaction mixture was 2,3,4,5,6-penta-
fluorophenylcarbonimidoyl dichloride (I).



*Our attempts to prepare this compound by interaction of $\text{C}_6\text{F}_5\text{NH}_2$
and CHCl_3 in the presence of various bases were also unsuccess-
full. Only traces of isocyanide were identified in reaction mixture
together with the initial amine.

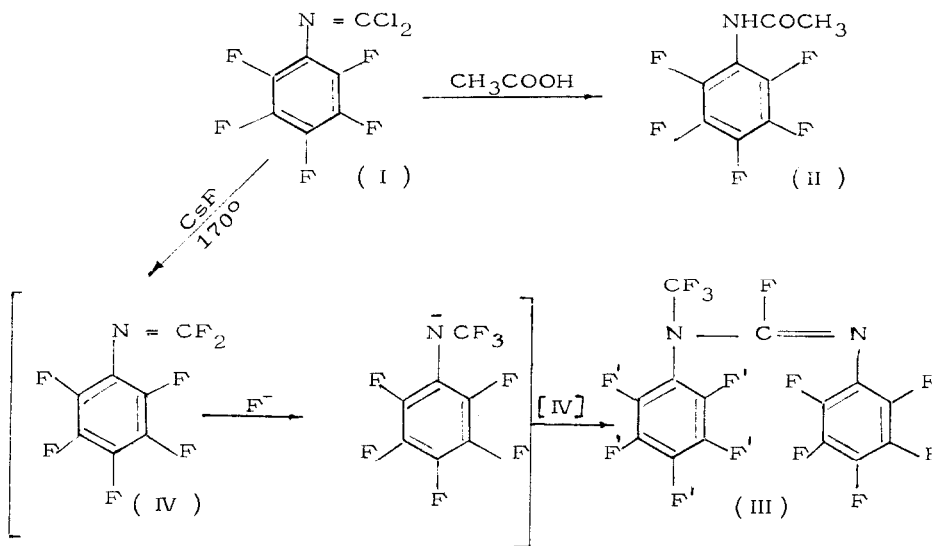
At the same time copolyrolysis of 2,3,4,5,6-pentafluoroaniline with sources of difluorocarbene results in the predominantly formation of perfluoroindan [3].

The mechanism of formation of compound (I) is not quite clear yet, but one of the possible pathways can be chlorination of the intermediate 2,3,4,5,6-pentafluorophenyl isocyanide. Such a method of preparation of phenylcarbonimidoyl dichlorides from phenylisocyanides is known [4].

The structure of compound (I) has been confirmed by elemental analysis, mass spectrometric determination of molecular weight, IR, UV and ^{19}F NMR spectra data and some reactions. The IR spectrum shows characteristic bands at 1520 cm^{-1} (C_6F_5) and 1665 cm^{-1} ($\text{N}=\text{C}$); in ^{19}F NMR spectrum are three signals of fluorine atoms adjacent to aromatic ring with chemical shifts at $+0,2$ (2 m-F), $+3,8$ (1 p-F), $+12,8$ (2 o-F) ppm; UV spectrum, $\text{nm}:\lambda_{\text{max}} 217$ ($\log\epsilon 3,67$), 270 ($\log\epsilon 3,31$).

Compound (I) when boiled with glacial acetic acid forms the well known 2,3,4,5,6-pentafluoroacetanilide, like the formation of acetanilide from the nonfluorinated analog of (I) [6].

Dimer (III) was formed under the action of CsF on compound (I). Probably this transformation proceed via fluoride ion catalysed reaction of intermediate pentafluorophenyl difluoride. Such a reaction with CsF is known for phenylcarbonimidoyl difluoride [7].



EXPERIMENTAL

^{19}F NMR spectra were recorded on a "Varian A-56/60A" instrument with C_6F_6 as internal standard. IR spectra were recorded on a "UR-20" instrument for 5% solutions in CCl_4 . UV spectra were recorded on a "Specord UV VIS" instrument for solutions in hexane. GLC analysis has been conducted on a "IHM-7A" apparatus with a catharometer; linear programming of the temperature (10^0 per min). The stationary phase was methylphenylsilicon SE-54, 15% on Chromosorb W; gas carrier was He.

Copyrolysis of 2,3,4,5,6-pentafluoroaniline with chloroform

A mixture of pentafluoroaniline (10g) and CHCl_3 (32g) in a stream of N_2 (25 l/hr) were passed through silica tube placed in an electric oven at 670^0 . The reaction mixture was distilled with steam, the organic layer was separated, dried over MgSO_4 and analysed by GLC. The reaction mixture (14g) contains: compound (I) (nc) - 30%; $\text{C}_6\text{F}_5\text{CN}$ - 7% ; $\text{C}_6\text{F}_5\text{Cl}$ - 5%; $\text{C}_6\text{F}_5\text{-C}_6\text{F}_5$ - 4%; tetrachloroethylene - 22%; octachloropropane - 6%; hexachlorobutadiene - 9%. The sum of unidentified compounds - 17%. Compound (I) has been isolated by rectification (b.p. $94^0/40$ mmHg) and then purified by preparative scale GLC. Analysis: Found: C, 31.88 ; Cl, 27.00; F, 36.18; N, 5.20%. $\text{C}_7\text{Cl}_2\text{F}_5\text{N}$ requires C, 31.82; Cl, 26.90; F, 35.98; N, 5.30 %.

Reactions of compound (I)(a) Acetolysis

Solution of 0.2g compound (I) in 4 ml glacial acetic acid was boiled for 4 hr. Pentafluoroacetanilide (II) was obtained. Yield 0.1g (56%), m.p. $131\text{-}132^0$; lit, m.p. $131\text{-}132^0$ [6] .

(b) Reaction with CsF

Compound (I) (0.18g) and anhydrous CsF (1.1g) were heated in a sealed tube for 4 hr at 170^0 . The reaction mixture was extracted by ether, then dried over MgSO_4 . Evaporation of ether yielded 0.11g (70%) of compound (III) (nc) with m.p. $31\text{-}32^0$ (sublimation). Mol. weight 462 (mass spectrum) (calculated 462).

IR spectrum, cm^{-1} : 1520 (C_6F_5), 1740 ($\text{C}=\text{N}$). ^{19}F NMR spectrum (acetone) : -0,5 (2 m-F), +2,5 (1 p-F, 2 m-F'), +13,0 (2 o-F), +14,4 (1 p-F'), +18,9 (2 o-F'), + 107,0 [CF_3 , a doublet of triplets , J (CF_3 -CF), 16,5 Hz], + 122,0 ppm [CF, quadruplet with broadened lines, J (CF_3 -CF), 16,5 Hz].

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