EXPERIMENTAL

The GLC analysis was run on a Chrom-41 chromatograph, using a 2.5 × 3 mm column packed with 15% Reoplex 400 deposited on Chezasorb (0.20-0.36 mm), a temperature of 100°, nitrogen as the carrier gas, and a flow rate of 20 ml/min.

With stirring, to an ether solution (10 ml) of the Grignard reagent was added in 15 min a solution of the sulfoxide in 10 ml of abs. ether and the mixture was refluxed for 10 h. Then, with cooling, dilute HCl solution was added to dissolve the precipitate. The aqueous layer was extracted with ether (2 × 5 ml). The ether solution was dried over $MgSO_4$ and analyzed by GLC (internal standard - toluene). The total yield of sulfoxides, found in the aqueous layer, was determined by iodometric titration [9]. The sulfoxides were identified and their relative amount was determined after reduction to the sulfides using $NaBH_4$ [10].

CONCLUSIONS

1. Aliphatic sulfoxides RS(O)R' react with R"MgBr to give sulfides (R" +)RSR', which are formally obtained from RSR' by replacing the hydrogen on the α-C atom in R or R' by R", and also RSR', RSR", and R'SR".

2. It was shown that alkyl exchange between RS(O)R' and R"MgBr is possible.

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FORMATION OF TRICHLOROPHOSPHAZOPENTAFLUOROPHENYL FROM PENTAFLUOROANILINE AND ITS TRIHALOACETYL DERIVATIVES

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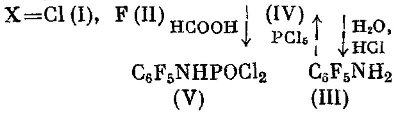
It is known that anilides react with PCl_5 to give arylimidoyl chlorides [1]. The smooth conversion of trichloroacetylpentachloroaniline to N-pentachlorophenyltrichloroacetimidoyl chloride is described in the series of polyhalogenated compounds [2]. We found that the trichloro- (I) and trifluoroacetyl (II) derivatives of pentafluoroaniline (III) react differently with PCl_5 to give only trichlorophosphazopentafluorophenyl (IV). The formation of N-pentafluorophenyltrihaloacetimidoyl chlorides was not detected.



$$\begin{tikzcd}
\mathrm{C_6F_5NHCOCX_3 + PCl_5} \arrow[rr] & & \underset{\mathrm{(IV)}}{\mathrm{C_6F_5N{=}PCl_3}} \arrow[dl, "\mathrm{HCOOH}"'] \arrow[d, shift left, "\mathrm{H_2O,\ HCl}"] \\
\mathrm{X{=}Cl\ (I),\ F\ (II)} & \underset{\mathrm{(V)}}{\mathrm{C_6F_5NHPOCl_2}} & \underset{\mathrm{(III)}}{\mathrm{C_6F_5NH_2}} \arrow[u, shift left, "\mathrm{PCl_5}"]
\end{tikzcd}$$

Based on the ^{19}F NMR spectral data, (II) is converted completely to (IV) when it is heated with either an excess or equimolar amount of PCl_5 at 100°C. Heating with PCl_5 in benzene at 40° gives a mixture of (IV) and the starting compound (II) (1.5:1). The trichloroacetyl

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derivative (I) does not react with PCl_5 in benzene at 40°, but is converted completely to (IV) when heated neat with PCl_5 at 120°. The formation of trichlorophosphazo derivatives, together with imidoyl chlorides, was observed previously only when PCl_5 is reacted with the haloacetyl derivatives of aliphatic amines [3]. The trichlorophosphazophenyls were usually obtained by heating PCl_5 with either the free amines or their hydrochlorides [4]. It was shown by us that (III) reacts with PCl_5 when heated neat to give (IV), and also when heated under milder conditions in either $POCl_3$ or benzene. The analytical data, and also the spectral characteristics, confirm the structure of (IV). As is known [4], the trichlorophosphazophenyls can exist in either the dimeric or monomeric forms. According to [4], a number of trichlorophosphazophenyls, with acceptor substituents in the phenyl ring, exist in the monomeric form. The molecular weight value of (IV), the presence of an intense absorption band at 1360 cm^{-1}, which is characteristic for the N=P bond in monomeric trichlorophosphazo compounds [4], in its IR spectrum, and the value of the ^{31}P chemical shift [5] all testify in support of the fact that (IV) most probably exists in the monomeric form. Also in agreement with this are its solubility in nonpolar solvents and the ease of conversion to phosphoric acid pentafluoroanilide dichloride (V) even by standing in the air or under the influence of HCOOH. The complete hydrolysis of (IV) leads to (III).

The formation of the dimer of trichlorophosphazopentafluorophenyl was observed recently [6] while studying the reaction of N,N-dichloropentafluoroaniline with PCl_3.

EXPERIMENTAL

The ^{19}F NMR spectra were taken on a Varian A56/60A instrument (56.4 MHz) using $POCl_3$ as the solvent and C_6F_6 as the external standard, while the IR spectra were taken on a UR-20 instrument in CCl_4 solution. The molecular weight was determined by mass spectrometry on an MS-902 instrument (energy of electrons = 13 and 70 eV) and also cryoscopically in benzene. The ^{31}P NMR spectra were recorded on a Bruker HX-90 instrument (36.4 MHz) using $POCl_3$ as the solvent and 85% H_3PO_4 as the external standard. The trifluoroacetyl derivative of pentafluoroaniline (II) was obtained as described in [7], mp 94-95°, cf. [7].

Trichloroacetyl Derivative of Pentafluoroaniline (I). A mixture of 2.76 g (15 mmoles) of (III), 8 ml of CCl_3COCl, and 4 drops of conc. H_2SO_4 was refluxed for 34 h in a nitrogen stream. Then the mixture was poured into water, and the obtained precipitate was washed with water and dried to give 4.62 g (93%) of (I), mp 127-128° (from petroleum ether). Found: C 29.00; H 0.41; Cl 32.43; F 29.25; N 3.99%. $C_8HCl_3F_5NO$. Calculated: C 29.00; H 0.32; Cl 32.40; F 28.90; N 4.25%. Infrared spectrum (ν, cm^{-1}): 1500 (C_6F_5), 1750 (C=O), 3420 (N—H). ^{19}F NMR spectrum* (δ, ppm): −0.5 (2F), −8.0 (1F), −16.3 (2F).

Reaction of (I) and (II) with PCl_5. A mixture of 0.4 g (1.2 mmoles) of (I) and 1 g (4.8 mmoles) of PCl_5, or 0.34 g (1.2 mmoles) of (II) and 1 g (4.8 mmoles) of PCl_5, was heated in an evacuated glass ampul for 5 h, and then it was dissolved in $POCl_3$ and the ^{19}F NMR spectrum of the obtained solution was taken.

Reaction of (III) with PCl_5. a) A mixture of 0.36 g (2 mmoles) of (III) and 1.66 g (8 mmoles) of PCl_5 was heated in an evacuated glass ampul for 5 h at 120°, and then it was dissolved in $POCl_3$ and the ^{19}F NMR spectrum was taken. A white crystalline precipitate of (IV) deposited from the solution on standing. It was filtered quickly and washed with a little petroleum ether, mp 101.5-103°. Found: C 23.05; Cl 33.04; F 30.50; N 4.43; P 9.73%; mol. wt. 317 (mass spectroscopy), and 290 (cryoscopically). $C_6Cl_3F_5NP$. Calculated: C 22.7; Cl 33.1; F 29.80; N 4.40; P 9.76%; mol. wt. 317 (for ^{35}Cl). Infrared spectrum (ν, cm^{-1}): 1520 (C_6F_5), 1360 (N=P), 1090 (C—F), 600, 560. ^{31}P NMR spectrum (δ, ppm): +10.5 (cf. [5]). ^{19}F NMR spectrum (δ, ppm): −0.2 (3F), −14.5 (2F). A $POCl_3$ solution of equimolar amounts of (III) and PCl_5, obtained by gentle heating, has a similar ^{19}F NMR spectrum. Compound (III), in its IR spectrum identical with the authentic specimen, was isolated by pouring the solution on ice, followed by neutralization with soda and extraction with ether.

b) To 0.36 g (2 mmoles) of (III) in 2.5 ml of dry benzene was added 0.42 g (2 mmoles) of PCl_5. The reaction goes with gas evolution. To complete the reaction the mixture was warmed gently and left to stand for 4 h. The obtained solution was evaporated *in vacuo* at ∿20° to give 0.49 g (80%) of (IV), mp 95-102°.

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*Using CCl_4 as the solvent and C_6F_6 as the internal standard.

Preparation of Phosphoric Acid Pentafluoroanilide Dichloride (V). The experiment was run the same as described in [8]. To a benzene solution of (IV), obtained as described above, was added 0.05 ml of anhydrous HCOOH in drops. Vigorous gas evolution was observed and the formation of precipitate (V), which was filtered to give 0.24 g of product, mp 84.5-86.5°. An additional 0.26 g of (V) was obtained from the filtrate. The total yield was 85%. Found: C 24.17; Cl 23.56; F 31.05; N 4.60; P 10.41%. $C_6HCl_2F_5NOP$. Calculated: C 24.00; Cl 23.65; F 31.65; N 4.66; P 10.32%. Infrared spectrum (ν, cm^{-1}): 3100, 1520, 1280, 1005. ^{31}P NMR spectrum (δ, ppm): −8.6 (cf. [5], p. 491). ^{19}F NMR spectrum (δ, ppm): −2.7 (2F), −9.8 (1F), −19.9 (2F).

CONCLUSIONS

In contrast to the unfluorinated anilides, the trifluoro- and trichloroacetyl derivatives of pentafluoroaniline form trichlorophosphazopentafluorobenzene when treated with PCl_5. The same compound was obtained by the reaction of pentafluoroaniline with PCl_5.

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CRYOSCOPIC AND ^{11}B NMR SPECTROSCOPIC STUDY OF BROMINE-CONTAINING (DIALKYLAMINO)- AND (DIPHENYLAMINO)BORANES

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It is known that many (dialkylamino)boranes of general formula R_2N-BX_2, where X = H, F, Cl, Br, and R = an alkyl radical, exist not only as monomers, but also have a tendency to form dimers and oligomers [1, 2]. Monomer—dimer equilibrium (1) is observed for some (dialkylamino)boranes [3-5].

$$2R_2N - BX_2 \rightleftarrows (R_2N - BX_2)_2 \tag{1}$$

The ability of aminoboranes to associate depends on many factors, the most important of which is the effect of substituents attached to the B and N atoms. The rapid dimerization of difluoro(dimethylamino)borane $(CH_3)_2NBF_2$ is mentioned in the literature [6]. Replacing a CH_3 group on the N atom by C_2H_5 does not suppress the tendency to dimerize. Thus, difluoro(diethylamino)borane $(C_2H_5)_2NBF_2$ as a melt is found to be in the equilibrium state (1), and as

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