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SHORT COMMUNICATIONS

Dedicated to the memory of Doctor Duc Le Van

Synthesis of 2,6- and 2,3-Difluorophenyldimethyl(thio)phosphines

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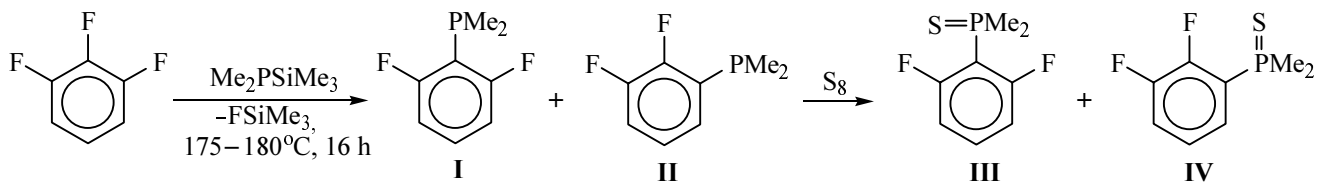
Fluorine substitution in polyfluoroarenes C_6F_5X (X = H, F, Cl, CF_3 etc.) and pentafluoropyridine by PMe_2 groups effected by Me_3SiPMe_2 is a convenient and efficient method of synthesis of polyfluoro-aryldimethylphosphines [1, 2]. These phosphines like their less fluorinated analogs are of interest as potential ligands of catalytically active complexes of transition metals and as initial substances for preparation of biologically active phosphorus-containing heterocyclic and other compounds [3]. By an example of formation of 2,6-difluorophenyldimethylphosphine (**I**) and 2,3-difluorophenyldimethylphosphine (**II**) from 1,2,3-trifluorobenzene we showed the opportunity of applying this approach to less active partly fluorinated substrates.

The reaction was carried out practically without solvent (only a little C_6D_6 was present required for registering NMR spectra) and gave under the conditions indicated on the scheme a mixture of phosphines **I** and **II** in a ratio 1.0 : 1.1 with the degree of conversion about 80%. In the NMR spectra the following signals belong to isomer **I**, δ, ppm, ^{1}H: 1.34 d.t (6H, CH_3, $^2J_{PH}$ 4.8, $^5J_{FH}$ 1.3 Hz); ^{19}F: –101.6 d.m ($^3J_{PF}$ ~30 Hz); ^{31}P{^{1}H}: –54.8 t ($^3J_{PF}$ ~30 Hz). Signals in the NMR spectra of isomer **II** are as follows, δ, ppm, ^{1}H: 1.17 d.d (6H, CH_3, $^2J_{PH}$ 3.9, $^5J_{FH}$ 1.1 Hz); ^{19}F: –135.1 m (1F, ^{2}CF), –156.8 m (1F, ^{3}CF); ^{31}P{^{1}H}: –51.1 d ($^3J_{PF}$ 30.4 Hz).

By treating with excess sulfur the isomer mixture of compounds **I** and **II** was converted into a mixture of 2,6-difluorophenyldimethyl(thio)-phosphine (**III**) and 2,3-difluorophenyldimethyl(thio)phosphine (**IV**), that were isolated in 35 and 24% respective yields calculated on Me_3SiPMe_2.

The observed regioselectivity of the fluorine replacement made it possible to prepare both isomeric substitution products. The mentioned ratio of phosphines **I** and **II** originating from the concurrent nucleophilic attack of Me_3SiPMe_2 on positions C^2–F and C^1–F in the 1,2,3-trifluorobenzene respectively is essentially different from the ratio 1:4 in the corresponding products of the methoxydefluorination of 1,2,3-$F_3C_6H_3$ effected by MeONa in a mixture DMSO–MeOH, 9:1 by volume [4]. This result was understood as originating from stronger stabilization of the transition state in reaction of S_NAr type by a fluorine from the *meta*-position than from the *ortho*-position, taking also in account the statistical factor [4, 5]. In this connection it is presumable that the stabilization of the transition state in the reaction under study is affected by some additional factor. This may be



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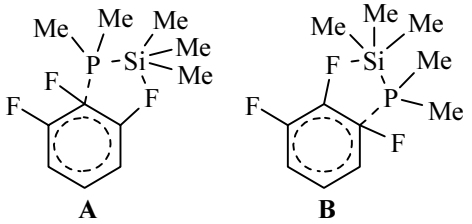
a coordination of the electrophilic $SiMe_3$ with the fluorine atom in the *ortho*-position with respect to the substitution site, as shown by structures **A** and **B** for nucleophilic attack on positions *2* and *1* respectively.

This interaction, analogous to the effect of the "built-in solvation" [6] was observed for a number of groups, including those like $P(S)Me_2$ [2], $P(S)Ph_2$, and $P(O)Ph_2$ [7]. The ability of fluorine to take part in coordination of this type was formerly assumed for understanding the kinetics of alkoxy- and piperidinodefluorination of the hexafluorobenzene and its derivatives [8]. We formerly [9] (cf. [5]) reported that 1,2,3-trifluorobenzene reacted with Me_3SiPMe_2 faster than 1.3,5-trifluorobenzene; this fact also was consistent with the assumption of Si←F coordination in the transition state.

Dimethylthiophosphinyl-2,6-difluorobenzene (III) and dimethylthiophosphinyl-2,3-difluorobenzene (IV). Into an ampule cooled with liquid nitrogen was condensed in a vacuum (0.05 mm Hg) 0.24 g (1.8 mmol) of 1,2,3-trifluorobenzene, 0.20 g (1.5 mmol) of Me_3SiPMe_2, and 0.1 ml of C_6D_6. The ampule was sealed, heated to 175–180°C for 16 h, cooled to 20°C, and the composition of the reaction mixture was analyzed by NMR spectroscopy (see above). The ampule was opened under argon atmosphere, and the reaction mixture was transferred into a flask charged preliminary with 0.06 g (2.0 mmol) of sulfur. The mixture obtained was heated at 100°C for 1 h. The volatile products were removed in a vacuum (0.05 mm Hg), and compounds **III** and **IV** were isolated by TLC on Silica gel 60 F_{254} plates (Merck),eluent $CHCl_3$.

Compound III. Yield 0.108 g (35%), colorless crystals, mp 83–85°C. ^{1}H NMR spectrum, δ, ppm: 7.3–7.6 (1H, CH). 6.8–7.1 (2H, CH). 2.18 d.t (6H, CH_3, $^2J_{PH}$ 14.0, $^5J_{FH}$ 2.5 Hz). ^{19}F NMR spectrum, δ, ppm: –102.3 m. ^{31}P NMR spectrum, δ, ppm: 28.0 m. Mass spectrum, *m/z* (I_{rel}, %): 206 $[M]^+$ (100), 191 $[M - CH_3]^+$ (61), 173 $[M - S - H]^+$ (21). Found, *m/z*: $[M^+]$ 206.01305. $C_8H_9F_2PS$. Calculated: *M* 206.01306.

Compound IV. Yield 0.075 g (24%), colorless oily substance. ^{1}H NMR spectrum, δ, ppm: 7.9–8.1 (1H, CH), 7.3–7.4 (1H, CH), 7.2–7.3 (1H, CH), 2.05 d.d (6H, CH_3, $^2J_{PH}$ 13.6, $^5J_{FH}$ 1.6 Hz). ^{19}F NMR spectrum, δ, ppm: –131.5 m (1F, C*2*F), –139.3 m (1F, C*3*F). ^{31}P NMR spectrum, δ, ppm: 31.7 m. Mass spectrum, *m/z* (I_{rel}, %): 206 $[M]^+$ (100), 191 $[M - CH_3]^+$ (73), 173 $[M - S - H]^+$ (17). Found, *m/z*: $[M]^+$ 206.01314. $C_8H_9F_2PS$. Calculated: *M* 206.01306.



NMR spectra were registered on a spectrometer Bruker AC 200 at operating frequencies 200.13 (^{1}H), 188.31 (^{19}F), and 81.02 (^{31}P) MHz in $CDCl_3$ (δ 7.25 ppm), external references CCl_3F, 85% H_3PO_4. Mass spectra were measured on Varian MAT-212 instrument.

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