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New Nucleophilic Arylating Reagents: Tris(pentafluorophenyl)phosphine, -arsine and -stibine

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Tris(pentafluorophenyl)-substituted pnictogenes (excluding nitrogen) are able to arylate electrophilic compounds containing active halogen atoms in the presence of CsF in bipolar aprotonic solvents.

Pentafluorophenyltrimethylsilane is known to be able to phenylate various electrophiles under the nucleophilic coaction of fluoride ion.[1–3] Recently we have found tris(pentafluorophenyl)bismuth to act in the presence of CsF as the source of pentafluorophenyl anion.[4] Analogous behaviour could also be predicted for the derivatives of the other elements of group 5A (P, As, Sb), because nucleophilic substitution reactions have been widely used for the synthesis of their organic derivatives from the corresponding trihalides. In some cases the action of C-, N- and O-nucleophiles has been observed to lead to the cleavage not only of element–halogen bonds, but also of element–carbon ones.[5–7]

The present work is devoted to the study of the possibility of using $(C_6F_5)_3E$ compounds (E = P, As, Sb) as arylating reagents.

Tris(pentafluorophenyl)phosphine, -arsine and -stibine have already been shown by us, in a similar fashion to tris(pentafluorophenyl)bismuth,[4] to arylate perfluoroalkenes, polyfluoroaromatic and heterocyclic compounds containing active halogen atoms,† as indicated in Scheme 1.

Compound **11** has also been obtained by acidic trimerization of pentafluorobenzonitrile.

The transfer of the pentafluorophenyl group from $(C_6F_5)_3E$ to C-electrophile under the action of fluoride ion probably occurs *via* tetracoordinated intermediate $[(C_6F_5)_3EF]^-$ or a structurally similar species. The electron-withdrawing substituents C_6F_5 and F facilitate the coordination of fluoride ion with heteroatom and the subsequent stepwise transfer of all three pentafluorophenyl groups from $(C_6F_5)_3E$ to the C-electrophile.

In fact, the yields of the products indicate the introduction of up to three pentafluorophenyl groups (in the case of reactions with pentafluoropyridine) from each molecule of compounds **1–3**, as determined by the activity of the electrophilic reagent. The less active alkene **4** and octafluorotoluene **5** have been found to give lower yields because of a

† *General procedure for the synthesis of compounds*. All syntheses were carried out in dry acetonitrile. Caesium fluoride was calcined directly before use. The yields of products were calculated based on the quantity of electrophilic reagents **4–6** consumed.

Compounds **7–9**. A mixture of $(C_6F_5)_3E$ (3 mmol), compound **4** (or **5, 6**) (9 mmol) and CsF (3 mmol) in 50 ml MeCN was maintained under reflux for 10 h (3 h for compounds **5, 6**). The reaction mixture was cooled, poured into water, acidified with HCl and extracted with $CHCl_3$. The organic solution was washed with water, dried with $CaCl_2$ and the solvent distilled off. The residue was distilled *in vacuo* or recrystallized from hexane.

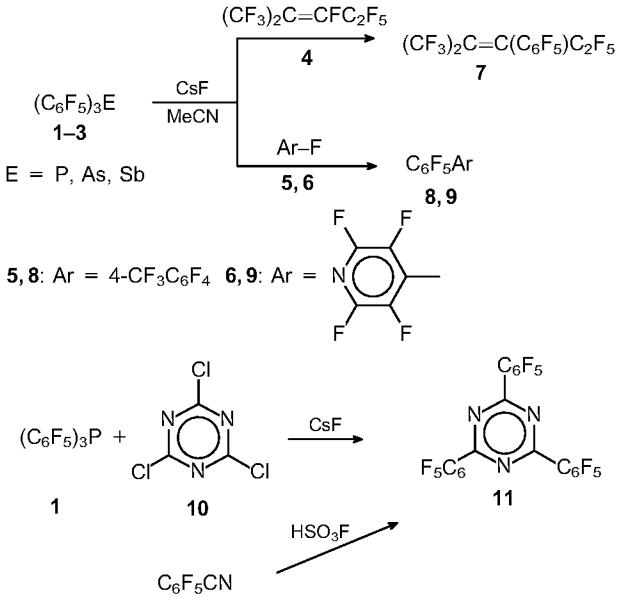
Perfluoro-2-methyl-3-phenylpent-2-ene **7**. Yield: 20% (from **1**), 28% (from **2**), 26% (from **3**); b.p. 64–65 °C/22 Torr. The ^{19}F NMR and IR spectra correspond to those described earlier.[2]

Perfluoro-4-methyldiphenyl **8**. Yield: 30% (from **1**), 36% (from **2**), 33% (from **3**); b.p. 65–66 °C/1 Torr. The ^{19}F NMR spectrum and m.p. correspond to those described earlier.[8]

Perfluoro-4-phenylpyridine **9**. Yield: 82% (from **1**), 75% (from **2**), 77% (from **3**); m.p. 100–102 °C. The ^{19}F NMR spectrum corresponds to that described earlier.[9,10]

2,4,6-*Tris(pentafluorophenyl)*-1,3,5-*triazine* **11**. (*a*) A mixture of compound **1** (6 mmol), compound **10** (6 mmol) and CsF (36 mmol) in 50 ml MeCN was maintained under reflux during 3 h, cooled, poured into water, acidified with HCl and extracted with $CHCl_3$. The organic solution was washed with water, dried with $CaCl_2$ and the solvent distilled off. The residue was recrystallized stepwise from ethanol and hexane. The yield of compound **11** was 40%, m.p. 129–131 °C. ^{19}F NMR ($CHCl_3$, C_6F_6 internal standard): δ 1.80 (2F-*m*), 14.28 (1F-*p*) and 21.66 (2F-*o*). UV spectrum (in heptane): λ_{max} (lg ε) 256 (4.64). MS *m/z* 578.9852 (M^+: calculated for $C_{21}F_{15}N_3$ 578.9852).

(*b*) A solution of 10 mmol of pentafluorobenzonitrile in 10 ml of fluorosulfonic acid was maintained at 20 °C for 6 days then poured onto ice. The residue was filtered and recrystallized from hexane. The yield of compound **11** was 90%.



Scheme 1

side-reaction leading to the formation of pentafluorobenzene.[‡] The latter can probably be connected with the elimination of a proton from the solvent under the action of $C_6F_5^-$ anion. The reactivity of compounds **1–3** in the reaction conditions investigated does not substantially differ in the series from phosphorus to antimony and is comparable with that for tris(pentafluorophenyl)bismuth and pentafluorophenyltrimethylsilane.

[‡] A mixture of compound **1** (3 mmol) and CsF (3 mmol) in 50 ml of MeCN was maintained under reflux during 2 h, then cooled and filtered. As follows from the ^{19}F NMR spectrum of the solution obtained, the main components of the latter (> 50%) are the initial compound **1** and pentafluorobenzene (1:2, mol).

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