## Use of tris(pentafluorophenyl)bismuth as an arylating reagent

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It has been shown that tris(pentafluorophenyl)bismuth arylates polyfluorinated electrophilic compounds in the presence of cesium fluoride.

**Key words:** tris(pentafluorophenyl)bismuth; cesium fluoride; perfluoro-2-methyl-2-pentene; perfluoro-5-aza-4-nonene; pentafluoropyridine.

It is known that pentafluorophenyltrimethylsilane arylates perfluoroolefins, perfluoroazaalkenes, and poly-fluoroarenes in the presence of cesium fluoride.<sup>1-3</sup> In the present work, the possibility of arylation of some perfluorinated compounds with tris(pentafluorophenyl)-bismuth (1) was shown for the first time.

Compound 1 reacts with perfluoro-2-methyl-2-pentene (2) on heating in acetonitrile to give perfluoro-2methyl-3-phenyl-2-pentene (3) in a low yield (Scheme 1).

Pentafluoropyridine (4) or perfluoro-5-aza-4-nonene (6) react with compound 1 under mild conditions to give arylation products 5 or 7, respectively. All of the  $C_6F_5$  groups successively participate in the formation of the products. It may be assumed that the reaction proceeds *via* the intermediate formation of a tetra-coordinate bismuth anion generated by the action of the fluoride anion on compound 1.

Thus, tris(pentafluorophenyl)bismuth is an efficient carrier of all of the  $C_6F_5$  groups, and its reactivity is comparable to that typical of pentafluorophenyltrimethylsilane.

## Experimental

<sup>19</sup>F NMR spectra were recorded on a Bruker WP-200 SY spectrometer at 188.28 MHz using  $C_6F_6$  as the internal standard. IR spectra were obtained on a Specord IR-75 spectrophotometer. Reagent 1 prepared by the known procedure<sup>4</sup> was purified by recrystallization from heptane (yield 60 %).

Reactions of tris(pentafluorophenyl)bismuth (1) with polyfluorinated compounds. a. A mixture of compound 1 (4.0 g, 5.6 mmol), olefin 2 (5.1 g, 17 mmol), and freshly calcined CsF (0.9 g) in dry MeCN (50 mL) was stirred for 10 h in a flask with a reflux condenser at 50–55 °C. The reaction mixture was cooled, poured into water, and acidified with HCl. The lower layer was separated, washed with water, and dried with CaCl<sub>2</sub>. The unreacted olefin 2 was distilled off, and the residue was distilled *in vacuo* to give 1.15 g (15 %) of compound 3, b.p. 64–65 °C (22 Torr). The <sup>19</sup>F NMR and IR absorption spectra were in agreement with Ref. 2.

**b.** A mixture of compound 1 (1.9 g, 2.7 mmol), azaalkene 6 (3.7 g, 8.5 mmol), and CsF (0.4 g) in MeCN (25 mL) was

Scheme 1



stirred at 20 °C for 3 h, refluxed for 15 min, cooled, and treated as described above to give 3.0 g (64 %) of compound 7, b.p. 86-88 °C (14 Torr). The <sup>19</sup>F NMR and IR absorption spectra were in agreement with Ref. 3.

c. A mixture of compound 1 (1.5 g, 2.1 mmol), pentafluoropyridine 4 (1.1 g, 6.5 mmol), and CsF (0.4 g) in MeCN (25 mL) was stirred at 20 °C for 3 h, refluxed for 15 min, cooled, poured into water, and acidified with HCl. The lower layer was separated and washed with water. The crystalline product was filtered off, dried, and sublimed at 80 °C (2 Torr) to give 1.64 g (82 %) of compound 5, m.p. 100–102 °C (from heptane). The <sup>19</sup>F NMR spectrum was in agreement with Refs. 5 and 6.

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