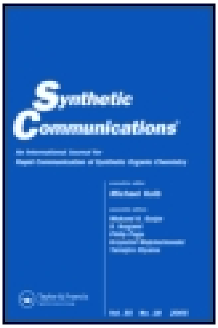

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Facile One-Pot Synthesis of Polyfluorinated Diarylacetonitriles

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FACILE ONE-POT SYNTHESIS OF POLYFLUORINATED DIARYLACETONITRILES

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Abstract: Polyfluorinated diarylacetonitriles were obtained by the reaction of polyfluoroaromatic compounds with acetonitrile in the presence of $Me_3SnN(SiMe_3)_2$ and CsF.

Polyfluorinated diarylacetonitriles can be obtained by the interaction of polyfluoroarylacetonitriles with polyfluoroaromatic compounds in the presence of strong bases with ~ 80 % yield [1]. Polyfluoroarylacetonitriles, in turn, can be synthesized by the reaction of polyfluorobenzyl halides with the cyanides of alkaline metals (yield ~ 80 %) [2], or by the reaction of polyfluoroaromatic compounds with cyanoacetic ester in the presence of strong bases and subsequent hydrolysis of the obtained polyfluoroarylcyanoacetic ester (yield ~ 70 %) [3].

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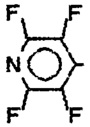
In the present communication we show, that polyfluoroaromatic compounds are able to react with acetonitrile in the presence of 1,1,1-trimethyl-N,N-bis(trimethylsilyl)stannaneamine and CsF to give polyfluorodiarylacetonitriles with high yield:

$$2\ \mathrm{ArF} + \mathrm{CH_3CN} + 3\ \mathrm{Me_3SnN(SiMe_3)_2} + \mathrm{CsF} \longrightarrow$$

$$\longrightarrow \mathrm{Ar_2C(Cs)CN} + 3\ \mathrm{FSnMe_3} + 3\ \mathrm{HN(SiMe_3)_2}$$

$$\mathrm{Ar_2C(Cs)CN} \xrightarrow{\mathrm{H_2O,\ HCl}} \mathrm{Ar_2CHCN}$$

Ar = C_6F_5-; 4-$CF_3C_6F_4$-;  .

The fluoride ion presumably attacks on the tin to form $FSnMe_3$ and the non-nucleophilic base $CsN(SiMe_3)_2$. Alkali amides are sufficiently strongly basic to generate the C-anions from weak CH-acids [4]. The acidities of hexamethyldisilazane and acetonitrile protons are close: 25,8 (in THF) [5] and 31.3 (in DMSO) [6] respectively. Therefore, cesium hexamethyldisilylamide in CH_3CN is expected to be in equilibrium with the acetonitrile anion (compare [4]).

$$\overset{+}{\mathrm{Cs}}\cdot\overset{-}{\mathrm{N}}\mathrm{(SiMe_3)_2} + \mathrm{CH_3CN} \rightleftarrows \mathrm{HN(SiMe_3)_2} + \overset{+}{\mathrm{Cs}}\cdot\overset{-}{\mathrm{C}}\mathrm{H_2CN}$$

The reaction of the generated C-anion with the other molecules of acetonitrile to form the corresponding "dimer" $CH_3C(NH_2)=CHC{\equiv}N$ is, in principle, also possible [7]. But the rate of its reaction with polyfluoroaromatic compounds is probably higher than that with acetonitrile. The polyfluorinated acetonitrile, being formed by that way, reacts further as shown before [1].

Sodium hexamethyldisilylamide has been shown earlier to give polyfluorinated diarylamines in the reaction with polyfluoroaromatic compounds under mild conditions in THF [8]. But in the present case the products of N-substitution of fluorine atoms in aromatic ring were not found.

Experimental

The ^1H and ^{19}F NMR spectra were recorded on a Bruker WP 200 SY spectrometer at frequencies of 200 and 188.28 MHz respectively with internal standards - CH_3CN (δ 2.00) and C_6F_6; IR spectra on Specord M 80 instrument; mass spectra on Finnigan MAT MS-8200 mass-spectrometer (EI, 70 eV).

$Me_3SnN(SiMe_3)_2$ was synthesized according to [9]. Cesium fluoride was calcined directly before use. All syntheses were carried out in dry acetonitrile in a nitrogen atmosphere.

Bis-(p-heptafluorotolyl)acetonitrile. A mixture of $Me_3SnN(SiMe_3)_2$ (3.24 g, 0.01 mol) and octafluorotoluene (2.36 g, 0.01 mol) was added dropwise to a boiling suspension of CsF (0.61 g, 0.004 mol) in CH_3CN (40 ml). The reaction mixture was boiled during 1 hr, cooled, filtered to remove $FSnMe_3$ (IR spectrum is identical to that, presented in [10]) and CsF. The NMR (^1H and ^{19}F) spectra were recorded. The ^{19}F NMR spectrum of the solution consists of 7 signals. The signals at 107.6 (3F), 22.4 (2F), 15.4 (1F) and 2.7 (2F) ppm were assigned to octafluorotoluene and the signals at 109.2 (3F), 18.9 (2F) and 16.0 (2F) ppm - to $(p\text{-}CF_3C_6F_4)_2\overline{C}\text{-}CN$ anion (compare with the data in [11]). The molar ratio was near to 1 : 1. The ^1H NMR spectrum contains, besides CH_3CN signal, the signal of hexamethyldisilazane (0.07 ppm). The solution was poured into water, acidified with HCl, extracted with diethyl ether, the organic solution dried with $CaCl_2$ and the ether distilled off. The residue was sublimed in vacuum at 90 °C/1 Torr and the sublimate was recrystallized from petroleum ether (70 - 100 °C). The yield of the product was 1.30 g (82 %). M/z M^+: 472.9887 (found) and 472.9885 (calculated).

Decafluorodiphenylacetonitrile and bis-(2,3,5,6-tetrafluoropyridyl)acetonitrile were synthesized by the same method with 73 % and 77 % yield, respectively. M/z M^+: found (calculated) - 372.9934 (372.9949) and 339.0046 (339.0042).

The spectral characteristics and m.p. of the obtained compounds correspond to those, described in [12].

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