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Unusual interaction of perfluoroaromatic organozinc compounds with benzoyl chloride and DMF

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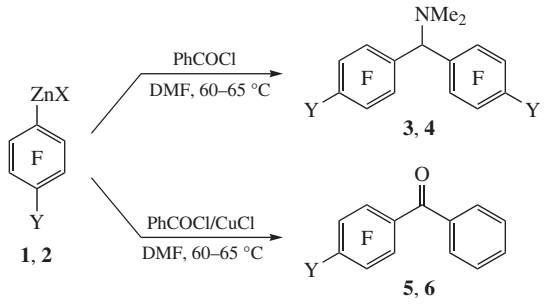
The organozinc compounds obtained from chloropentafluorobenzene and octafluorotoluene in reactions with benzoyl chloride and DMF form *N*,*N*-dimethylbis(perfluoroaryl)methylamines; the addition of CuCl changes the direction of reaction towards the formation of corresponding polyfluoroaromatic ketones.

Recently, the methods of obtaining polyfluoroaromatic organozinc compounds from chloropolyfluoroarenes, perfluoroarenes and Zn in DMF have been developed.[1–4] DMF was an effective reaction medium for the preparation of these organozinc compounds. With the participation of polyfluoroaromatic organozinc compounds, hydro- and bromopolyfluoroarenes, perfluorobiaryls[1–3] and allylpolyfluoroarenes[4] have been obtained. Polyfluoroarenes containing the carbonyl group and, in particular, polyfluoroaromatic ketones are other important polyfluoroaromatic functional derivatives. However, polyfluoroaromatic ketones are not easily accessible. In this connection, polyfluoroaromatic organozinc compounds are of interest to synthesise polyfluoroaromatic ketones in reactions with carboxylic acid chlorides. In this communication, the results of interactions of polyfluoroaromatic organozinc compounds with benzoyl chloride in DMF are reported. C_6F_5ZnX (X = Cl, C_6F_5) **1** and 4-$CF_3C_6F_4ZnX$ (X = Cl, 4-$CF_3C_6F_4$) **2** under the action of benzoyl chloride in DMF gave *N*,*N*-dimethylbis(perfluoroaryl)-methylamines **3** and **4** instead of expected polyfluoroaromatic ketones.† At the same time, in the presence of small amounts of CuCl (~0.01 mol), polyfluoroaromatic ketones **5**‡ and **6**§ were the main products (Scheme 1). These reactions were performed in an argon atmosphere.[4]



1 X = Cl or C_6F_5, Y = F
2 X = Cl or 4-$CF_3C_6F_4$, Y = CF_3
3, **5** Y = F
4, **6** Y = CF_3

Scheme 1

Reagent **1** is obtained from chloropentafluorobenzene,[4] whereas reagent **2** is synthesised from octafluorotoluene.[2,4] The treatment of reagent **2** with calcium chloride for binding fluoride ions (CaF_2) when synthesising compounds **4** and **6** can preserve reactive PhCOCl (unlike inactive PhCOF) in a reaction mixture. PhCOF could be formed by the action of ZnF_2 on PhCOCl.[5]

The formation of amines **3** and **4** probably occurs with the assistance of Vilsmeier reactants (Scheme 2).

Organocopper compounds probably take part in the synthesis of polyfluoroaromatic ketones **5** and **6** (Scheme 3) *via* the transformation of reagent **1**. Earlier, it was noticed that polyfluoroaromatic ketones are formed from C_6F_5Cu and acyl chlorides.[6]

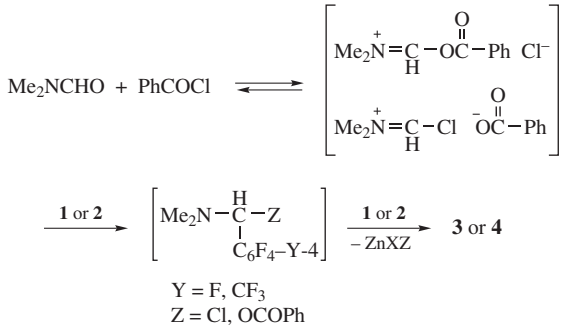
The synthesis of amines **3**, **4** and ketones **5**, **6** is accompanied by formation of the corresponding hydropolyfluoroarenes (C_6F_5H and 4-$CF_3C_6F_4H$).

The structure of new compounds was confirmed by elemental analysis, IR, UV, ^1H and ^{19}F NMR spectroscopy and mass spectrometry.†

† ^{19}F and ^1H NMR spectra were recorded on a Bruker AC-200 instrument (188.3 and 200 MHz, respectively) for the reaction mixtures containing organozinc compounds in DMF and for solutions of compounds **3**, **4** in CCl_4; ^{19}F and ^1H NMR spectra of compounds **5**, **6** (solutions in CCl_4) were recorded on a Bruker AV-300 instrument (282.4 and 300 MHz, respectively). Chemical shifts are given in δ/ppm from CCl_3F and TMS; the internal standards were C_6F_6 (–162.9 ppm from CCl_3F) and $(Me_3Si)_2O$ (0.04 ppm from TMS). IR spectra were taken on a Bruker Vector 22 IR spectrophotometer. UV spectra were measured on a Hewlett Packard 8453 UV spectrophotometer. The molecular masses of the compounds were determined by high-resolution spectrometry on a Finnigan MAT 8200 instrument (EI, 70 eV). GC-MS analyses were performed with a Hewlett-Packard G1800A apparatus (30 m capillary column, HP-5). GLC analyses were carried out on a Hewlett-Packard HP 5980 instrument (30 m capillary column, HP-5).

Organozinc compounds **1** and **2** were obtained from chloropentafluorobenzene and octafluorotoluene, respectively, by reaction with zinc in DMF in the presence of the catalyst $SnCl_2$.[2,4]

Synthesis of N,N-*dimethylbis(perfluoroaryl)methylamines (general procedures).* To a solution of perfluoroaromatic organozinc compounds, benzoyl chloride (3.52 g, 25.0 mmol) was added, the mixture was heated at 60–65 °C for 4 h and cooled to room temperature. According to ^{19}F NMR, the reaction mixture contained 43–44% of amines **3**, **4**, 40–42% of hydropolyfluoroarenes (C_6F_5H and 4-$CF_3C_6F_4H$). To a reaction mixture 50 ml of water was added, the organic products were extracted with $CHCl_3$ (3×5 ml). The combined extracts were washed with 50 ml of a 10% solution of Na_2CO_3 and 50 ml of water and dried over K_2CO_3. $CHCl_3$ was distilled off. In reaction with compounds **1** distilled off $CHCl_3$ contained C_6F_5H (^{19}F NMR). The rest further was subjected to distillation *in vacuo* (~3 Torr). HCl was passed through a solution of fractions in 10 ml of diethyl ether before the termination of a precipitation of a hydrochloride. In reaction with compound **2**, 10 ml of diethyl ether was added to the rest, and HCl was passed before the termination of a precipitation of a hydrochloride. The hydrochloride precipitate was filtered off and washed with 5–10 ml of diethyl ether. For preparation of amines **3**, **4**, 50 ml of 10% solution of Na_2CO_3 was added to a precipitate and a mixture was heated at 90–100 °C (10 min). The precipitate of amine was filtered off and washed with 50 ml of water.



Scheme 2

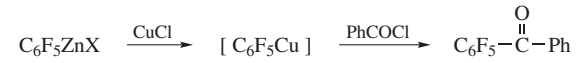
N,N-*Dimethylbis(pentafluorophenyl)methylamine* **3**. From a solution of organozinc compounds **1**[4] (7.14 g, 10 mmol, 91% compound **1** with an impurity of 9% C_6F_5H) a fraction (1.32 g) with bp 117–127 °C containing (GLC) amine **3** (90%) and a fraction (0.88 g) with bp 172–173 °C containing (GC-MS) amine **3** (8%), PhCOOH (4%), $(PhCO)_2O$ (84%) were obtained. The ^{19}F NMR spectrum of the residue (0.21 g) does not contain signals of fluorine atom. A hydrochloride (1.01 g) and then amine **3** (0.86 g, yield 44%, ~99% purity by GLC) were isolated from fractions.

3: mp 53–54 °C. IR (CCl_4, ν/cm^{-1}): 2995, 2961, 2874, 2828, 2779, 1651, 1522, 1505, 1124, 1006, 804. UV [EtOH, λ_{max}/nm (lg ε)]: 204 (4.14), 210 (4.14), 263 (3.25). ^1H NMR, δ: 2.27 (s, 6H, Me), 5.12 (s, 1H, CH). ^{19}F NMR, δ: –162.3 (m, 4F, F-3, F-5), –154.8 (t, 2F, F-4, $^3J_{3,4}$ 21 Hz, $^3J_{4,5}$ 21 Hz), –140.5 (m, 4F, F-2, F-6). HRMS: found, 391.03999; calc. for $C_{15}H_7F_{10}N$, 391.04187. HRMS, *m/z* (%): 391 (M^+, 47), 347 ($M^+ - NMe_2$, 62), 278 (25), 224 ($M^+ - C_6F_5$, 100), 42 (17), 28 (12). Found (%): C, 46.2; H, 1.7; F, 48.0; N, 3.6. Calc. for $C_{15}H_7F_{10}N$ (%): C, 46.0; H, 1.8; F, 48.6; N, 3.6.

N,N-*Dimethylbis(4-trifluoromethyl-2,3,5,6-tetrafluorophenyl)methylamine* **4**. Prepared by a published method[4] solution of organozinc compounds **2** was treated with an equimolar quantity of $CaCl_2$ (calcined at 250–300 °C for 3 h). The resulting mixture was stirred at room temperature for 3 h. Then, the solution of organozinc compounds was decanted. From a decanted solution of organozinc compounds **2** (7.84 g, 8.15 mmol, relative content **2** – 85% with an impurity of 4-$CF_3C_6F_4H$ – 15%) a hydrochloride (1.04 g) and then amine **4** (0.90 g, yield 45%, ~98% purity by GLC) were isolated.

4: mp 58–60 °C. IR (CCl_4, ν/cm^{-1}): 2995, 2963, 2882, 2830, 2782, 1656, 1497, 1332, 1191, 1159, 1016. UV [EtOH, λ_{max}/nm (lg ε)]: 205 (4.25), 220 (4.21), 280 (3.72). ^1H NMR, δ: 2.33 (s, 6H, Me), 5.29 (s, 1H, CH). ^{19}F NMR, δ: –140.4 (m, 4F), –138.5 (m, 4F), –58.0 (t, 6F, $2CF_3$, $^4J_{CF_3–F(3)}$ 21.5 Hz, $^4J_{CF_3–F(5)}$ 21.5 Hz). HRMS: found, 491.03553; calc. for $C_{17}H_7F_{14}N$, 491.03548. HRMS, *m/z* (%): 491 (M^+, 27), 447 ($M^+ - NMe_2$, 13), 274 ($M^+ - CF_3C_6F_4$, 100), 42 (11). Found (%): C, 41.3; H, 1.5; F, 54.0; N, 3.0. Calc. for $C_{17}H_7F_{14}N$ (%): C, 41.6; H, 1.4; F, 54.1; N, 2.9.

‡ *Synthesis of phenyl(2,3,4,5,6-pentafluorophenyl)ketone* **5**. The mixture of organozinc compounds **1** (8.47 g, 10.0 mmol, 96% compound **1** with an impurity of 4% C_6F_5H), benzoyl chloride (2.11 g, 15.0 mmol) and CuCl (15 mg, 0.15 mmol) was heated at 60–65 °C for 4 h under argon atmosphere and cooled to room temperature. To a reaction mixture, 10 ml of water was added and then it was steam distilled. The organic layer was separated and dried over $MgSO_4$. A mixture (2.13 g), which contained (GLC) 90% of ketone **5** (yield 70%), 7% of C_6F_5H, was obtained. The analytical sample of ketone **5** (~99% purity by GC-MS) was prepared by distillation of this mixture *in vacuo*, bp 108–110 °C (~4 Torr), mp 32.5–34 °C (lit.,[7] mp 33–34 °C). IR (CCl_4, ν/cm^{-1}): 1689 (C=O), 1519 and 1499 (aromatic ring). ^1H NMR, δ: 7.47 (m, 2H, H-3, H-5), 7.61 (m, 1H, H-4), 7.78 (m, 2H, H-2, H-6). ^{19}F NMR, δ: –161.2 (m, 2F, F-3, F-5), –152.4 (t, 1F, F-4, $^3J_{3,4}$ 20.3 Hz, $^3J_{4,5}$ 20.3 Hz), –141.2 (m, 2F, F-2, F-6). Spectral data are in agreement with published data.[7–9] GC-MS: 272 $[M]^+$, 195 $[C_6F_5CO]^+$, 167 $[C_6F_5]^+$, 117, 105 $[PhCO]^+$, 77 $[Ph]^+$, 51.



Scheme 3

Reactions of polyfluoroaromatic organozinc compounds with carboxylic acid chlorides in DMF in the absence or the presence of CuCl can be used for the synthesis of other *N*,*N*-dimethylbis-(polyfluoroaryl)methylamines or polyfluoroaromatic ketones.

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§ *Synthesis of phenyl(4-trifluoromethyl-2,3,5,6-tetrafluorophenyl)ketone* **6**. The mixture of organozinc compounds **2** (15.95 g, 14.0 mmol, 85% compound **2** with an impurity of 15% 4-$CF_3C_6F_4H$), benzoyl chloride (2.17 g, 15.4 mmol) and CuCl (15 mg, 0.15 mmol) was heated at 60–65 °C for 4 h under argon atmosphere and cooled to a room temperature. To a reaction mixture, 10 ml of water was added and then it was steam distilled. The organic layer was separated and dried over $MgSO_4$. A mixture (3.80 g), which contained (GLC) 85% of ketone **6** (72% yield) and 7% of 4-$CF_3C_6F_4H$, was obtained. The analytical sample of ketone **6** (~99% purity by GC-MS) was prepared by distillation *in vacuo*, bp 114–115 °C (~4 Torr), mp 31–32 °C (lit.,[10] mp 31.5–32.5 °C). IR (CCl_4, ν/cm^{-1}): 1689 (C=O), 1486 (aromatic ring). ^1H NMR, δ: 7.51 (m, 2H, H-3, H-5), 7.65 (m, 1H, H-4), 7.81 (m, 2H, H-2, H-6). ^{19}F NMR, δ: –139.9 (m, 2F), –139.5 (m, 2F), –57.8 (t, 3F, CF_3, $^4J_{CF_3–F(2)}$ 21.6 Hz, $^4J_{CF_3–F(6)}$ 21.6 Hz). Spectral data are in agreement with published data.[10] GC-MS: 322 $[M]^+$, 245 $[CF_3C_6F_4CO]^+$, 217 $[CF_3C_6F_4]^+$, 105 $[PhCO]^+$, 77 $[Ph]^+$, 51.