ISSN 1070-4280, Russian Journal of Organic Chemistry, 2008, Vol. 44, No. 3, pp. 472–473. © Pleiades Publishing, Ltd., 2008.
Original Russian Text © V.V. Levin, A.D. Dil'man, P.A. Belyakov, M.I. Struchkova, 2008, published in Zhurnal Organicheskoi Khimii, 2008, Vol. 44, No. 3, pp. 472–473.

SHORT COMMUNICATIONS

Reaction of Formamides with Fluorotris(pentafluorophenyl)silane

V. V. Levin, A. D. Dil'man, P. A. Belyakov, and M. I. Struchkova

Zelinskii Institute of Organic Chemistry, Russian Academy of Sciences, Leninskii pr. 47, Moscow, 119991 Russia
e-mail: dilman@ioc.ac.ru

Received July 4, 2007

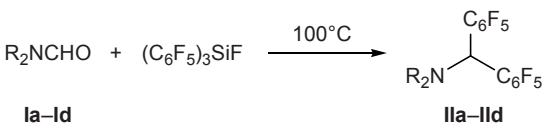
DOI: 10.1134/S1070428008030287

Carboxylic acid amides are weakly reactive toward nucleophiles. In particular, carboxamides are generally inert with respect to organosilicon compounds due to both low electrophilicity of the amide carbonyl group and low polarity of the silicon–carbon bond [1]. However, we can presume that organosilicon reagents with enhanced Lewis acidity of the silicon atom should form complexes with carboxamides in which both electrophilic and nucleophilic components should be activated.

We recently showed that the Lewis acidity of silanes can be enhanced to an appreciable extent via introduction of three electron-withdrawing pentafluorophenyl groups to the silicon atom [2–6]. The most effective reagent for building up new C–C bonds was fluorotris(pentafluorophenyl)silane [5, 6]. We believed it to be interesting to examine the behavior of carboxamides in the presence of $(C_6F_5)_3SiF$.

Fluorotris(pentafluorophenyl)silane reacted with N,N-disubstituted formamides **Ia**–**Id** to give the corresponding *N*,*N*-dialkylbis(pentafluorophenyl)methanamines **IIa**–**IId** (Scheme 1). The reactions were carried out under solvent-free conditions by heating the reactants (formamide–silane ratio 10:1) for several hours at 100°C. Both *N*,*N*-dialkylformamides and cyclic amides can be involved in the process; however, the reaction with morpholine-4-carbaldehyde (**Id**) required longer time, and the yield of compound **IId** was poor.

Scheme 1.

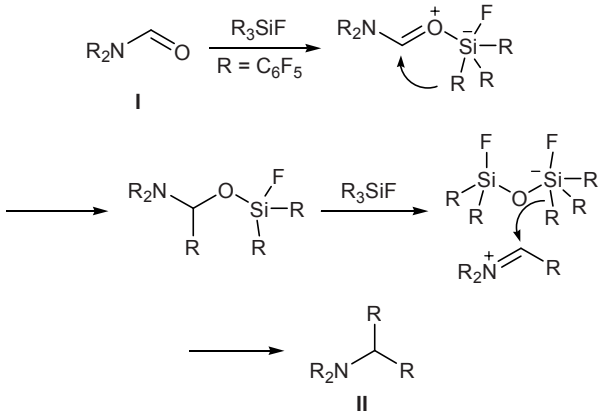


R = Me (**a**), Et (**b**); R_2N = pyrrolidin-1-yl (**c**), morpholino (**d**).

Unfortunately, we failed to isolate and identify products in the reactions of $(C_6F_5)_3SiF$ with *N*,*N*-dimethylacetamide and *N*-methylpyrrolidin-2-one; as a result, intractable mixtures were obtained.

Scheme 2 shows a possible reaction mechanism. Initially, amide **I** reacts with $(C_6F_5)_3SiF$ to give a complex with five-coordinate silicon atom; this complex contains activated carbonyl group and polarized Si–C bond. The subsequent transfer of one pentafluorophenyl group gives hemiaminal intermediate which is capable of undergoing ionization in the presence of the second silane molecule to form iminium cation. In the final step, pentafluorophenyl group is transferred from the five-coordinate silicon complex to iminium cation.

Scheme 2.



Thus we have revealed a new reaction of amides, which is based on the ability of silicon atom to form five-coordinate intermediates. The key specific feature of the process is activation of the amide carbonyl group due to reaction with fluorotris(pentafluorophenyl)silane.

Bis(pentafluorophenyl)methanamines IIa–IId (*general procedure*). A mixture of 548 mg (1 mmol) of $(C_6F_5)_3SiF$ and 10 mmol of formamide **Ia–Id** was heated on a boiling water bath over a period indicated below. The mixture was cooled, 1 ml of a saturated aqueous solution of sodium carbonate and 1 ml of water were added, and the resulting suspension was stirred for 2 min and treated with diethyl ether–hexane (1:1; **IIa**, **IIc**, **IId**) or hexane (**IIb**) (3×7 ml). The extracts were combined, washed with water (2×2 ml), filtered through a layer of Na_2SO_4, and evaporated.

***N*,*N*-Dimethylbis(pentafluorophenyl)methanamine (IIa).** Reaction time 2 h. The product was purified by chromatography using hexane–ethyl acetate (40:1) as eluent. Yield 510 mg (87%),* R_f 0.21 (hexane–EtOAc, 25:1), mp 42–43°C. ^{1}H NMR spectrum (200 MHz, $CDCl_3$), δ, ppm: 2.33 s (6H, CH_3), 5.13 s (1H, CH). ^{13}C NMR spectrum (50 MHz, $CDCl_3$), δ_C, ppm: 44.5 q and 58.1 q (J = 1.6 Hz), 112.9 m, 137.8 d.m (J = 256.6 Hz), 141.1 d.m (J = 255.1 Hz), 145.3 d.m (J = 250.6 Hz). ^{19}F NMR spectrum (188 MHz, $CDCl_3$), δ_F, ppm: –162.3 m (4F, *m*-F); –154.7 t (2F, *p*-F, J = 21.5 Hz), –140.5 d.m (4F, *o*-F, J = 14.5 Hz). Found, %: C 45.87; H 1.81; N 3.49. $C_{15}H_7F_{10}N$. Calculated, %: C 46.05; H 1.80; N 3.58.

***N*,*N*-Diethylbis(pentafluorophenyl)methanamine (IIb).** Reaction time 2 h. The product was purified by chromatography using hexane as eluent, followed by distillation. Yield yield 335 mg (45%), R_f 0.2 (hexane), bp 110–115°C (bath temperature, 0.43 mm). ^{1}H NMR spectrum (200 MHz, $CDCl_3$), δ, ppm: 1.02 t (6H, CH_3, J = 13.9 Hz), 2.65 q (4H, CH_2, J = 13.9 Hz), 5.77 s (1H, CH). ^{13}C NMR spectrum (50 MHz, $CDCl_3$), δ_C, ppm: 12.5, 44.6, 52.8 q (J = 1.6 Hz), 113.6 m, 137.8 d.m (J = 253.6 Hz), 140.9 d.m (J = 255.1 Hz), 145.3 d.m (J = 246.1 Hz). ^{19}F NMR spectrum (282 MHz, $CDCl_3$), δ_F, ppm: –162.6 t (4F, *m*-F, J = 17.8 Hz), –155.4 t (2F, *p*-F, J = 21.7 Hz), –141.1 d.m (4F, *o*-F, J = 19.2 Hz). Found, %: C 48.70; H 2.31; N 3.22. $C_{15}H_7F_{10}N$. Calculated, %: C 48.70; H 2.64; N 3.34.

1-[Bis(pentafluorophenyl)methyl]pyrrolidine (IIc). Reaction time 1 h. The product was purified by chromatography using hexane–ethyl acetate (40:1) as eluent, followed by distillation. Yield 326 mg (52%), R_f 0.31 (hexane–EtOAc, 40:1), bp 112–116°C (bath temperature, 0.42 mm), mp 51–52°C. ^{1}H NMR spectrum (200 MHz, $CDCl_3$), δ, ppm: 1.81–1.93 m [4H, $(CH_2)_2$], 2.48–2.61 m [4H, $N(CH_2)_2$], 5.28 s (1H, CH). ^{13}C NMR spectrum (75 MHz, $CDCl_3$), δ_C, ppm: 23.7, 53.5, 55.7 q (J = 1.2 Hz), 113.6 m, 137.8 d.m (J = 243.1 Hz), 141.2 d.m (J = 243.9 Hz), 145.3 d.m (J = 253.0 Hz). ^{19}F NMR spectrum (188 MHz, $CDCl_3$), δ_F, ppm: –162.8 m (4F, *m*-F), –154.7 t (2F, *p*-F, J = 20.8 Hz), –140.1 m (4F, *o*-F). Found, %: C 48.54; H 2.46; N 3.31. $C_{15}H_7F_{10}N$. Calculated, %: C 48.94; H 2.17; N 3.36.

4-[Bis(pentafluorophenyl)methyl]morpholine (IId). Yield 27% (according to the NMR data using trichloroethylene as reference). By chromatography (hexane–EtOAc, 12:1) we isolated 190 mg of compound **IId** which contained (according to the NMR data) ~10% of an unidentified product which could not be separated by vacuum distillation. bp 132–136°C (bath temperature, 0.36 mm). ^{1}H NMR spectrum (200 MHz, $CDCl_3$), δ, ppm: 2.48 t [4H, $N(CH_2)_2$, J = 4.0 Hz], 3.76 t [4H, $O(CH_2)_2$, J = 4.2 Hz], 5.28 s (1H, CH). ^{13}C NMR spectrum (75 MHz, $CDCl_3$), δ_C, ppm: 52.6, 57.2, 66.8, 112.0 m, 137.8 d.m (J = 253.6 Hz), 140.9 d.m (J = 255.1 Hz), 145.3 d.m (J = 246.1 Hz). ^{19}F NMR spectrum (282 MHz, $CDCl_3$), δ_F, ppm: –162.1 m (4F, *m*-F), –154.3 t (2F, *p*-F, J = 20.8 Hz), –140.1 d.m (4F, *o*-F, J = 15.6 Hz).

The ^{1}H, ^{13}C, and ^{19}F NMR spectra were measured on a Bruker AC-200 spectrometer. All syntheses were performed under dry argon. Kieselgel 60 silica gel (40–63 μm; Merck) was used for chromatography.

This study was performed under financial support by the Ministry of Science of the Russian Federation (project no. MK-4483.2007.3) and by the program of the Presidium of the Russian Academy of Sciences and Foundation for Support of Russian Sciences.

REFERENCES

1. Weber, W.P., *Silicon Reagents for Organic Synthesis*, Berlin: Springer, 1983.
2. Dilman, A.D., Belyakov, P.A., Korlyukov, A.A., Struchkova, M.I., and Tartakovsky, V.A., *Org. Lett*., 2005, vol. 7, p. 2913.
3. Levin, V.V., Dilman, A.D., Belyakov, P.A., Korlyukov, A.A., Struchkova, M.I., Antipin, M.Y., and Tartakovsky, V.A., *Synthesis*, 2006, p. 489.
4. Dil'man, A.D., Arkhipov, D.E., Belyakov, P.A., Struchkova, M.I., and Tartakovskii, V.A., *Russ. Chem. Bull*., 2006, vol. 55, p. 517.
5. Dilman, A.D., Levin, V.V., Karni, M., and Apeloig, Y., *J. Org. Chem*., 2006, vol. 71, p. 7214.
6. Levin, V.V., Dilman, A.D., Belyakov, P.A., Struchkova, M.I., and Tartakovsky, V.A., *Tetrahedron Lett*., 2006, vol. 47, p. 8959.

* Hereinafter, the given yields were calculated assuming transfer of three pentafluorophenyl groups from $(C_6F_5)_3SiF$ molecule.