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# Replacement of an oxygen atom by chlorine atoms in the reaction of pentafluorobenzaldehyde with $CCl_3$-substituted compounds in the presence of $AlCl_3$

***T. D. Petrova,* V. E. Platonov, and L. M. Pokrovskii***

*N. N. Vorozhtsov Novosibirsk Institute of Organic Chemistry,*
*Siberian Branch of the Russian Academy of Sciences,*
*9 prosp. Lavrent´eva, 630090 Novosibirsk, Russian Federation.*
*Fax: +7 (383 2) 34 4752. E-mail: petrova@nioch.nsc.ru*

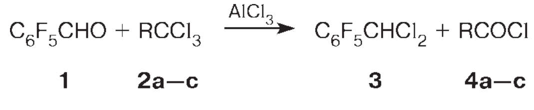
The interaction of pentafluorobenzaldehyde with $RCCl_3$ (R = Cl, Ph, $C_6F_5$) in the presence of threefold molar excess of $AlCl_3$ proceeds with replacing the oxygen atom of the aldehyde group by two chlorine atoms from the $CCl_3$ group and results in the formation of pentafluorobenzylidene chloride. The electrophilic mechanism of the reaction is proposed.

**Key words**: pentafluorobenzaldehyde, $CCl_4$, $AlCl_3$, benzotrichloride, pentafluorobenzotrichloride, pentafluorobenzylidene chloride, electrophilic mechanism.

The reactions of pentafluorobenzaldehyde (**1**), pentafluoroacetophenone and decafluorobenzophenone with $CCl_4$ (**2a**), benzotrichloride (**2b**), and pentafluorobenzotrichloride (**2c**) in the presence of excess $AlCl_3$ as a continuation of our investigations into the electrophilic polyhaloalkylation of polyfluoroaromatic N-, S-, and O-functional derivatives by $R—CX_3$ (X = Cl, F; R = alkyl, aryl) compounds[1—5] were studied in the present paper.

It was established that on the interaction of aldehyde **1** with $CCl_4$ and trihalomethyl derivatives **2b,c** in the presence of threefold molar excess of $AlCl_3$ in respect to **1** the replacement of the oxygen atom from the aldehyde group by two chlorine atoms resulting in pentafluorobenzylidene chloride (**3**) and of benzoyl and pentafluorobenzoyl chlorides (**4b,c**, respectively) takes place (Scheme 1).

**Scheme 1**



$$\underset{\mathbf{1}}{C_6F_5CHO} + \underset{\mathbf{2a-c}}{RCCl_3} \xrightarrow{AlCl_3} \underset{\mathbf{3}}{C_6F_5CHCl_2} + \underset{\mathbf{4a-c}}{RCOCl}$$

R = Cl (**a**); Ph (**b**); $C_6F_5$ (**c**)

In the case of benzaldehyde, this reaction is realized only in the course of its interaction with benzotrichloride **2b** (but not with $CCl_4$) in the presence of Lewis acid in catalytic amounts (0.2 wt.%).[6]

The interaction of aldehyde **1** with $CCl_4$ and excess of $AlCl_3$ proceeds at the boiling point of the reaction mixture and causes dichloride **3** formation in 54% yield (the known procedure for obtaining **3** from **1** in 80% yield includes heating **1** in the presence of $PCl_5$ [7]). The reaction does not take place at room temperature, in the presence of catalytic amounts of $AlCl_3$ or at heating **1** together with $AlCl_3$ in the absence of $CCl_4$. On the contrary, aldehyde **1** and benzotrichloride **2b** begin to interact already at 0 °C, and almost fully convert into dichloride **3** at room temperature. The reaction of **1** with **2c** also proceeds at room temperature. By GC/MS analysis α-chloro-2,3,4,5,6-pentafluorobenzyl benzoate (**5**) as well as isomeric trichloromethyldiphenyldichloromethanes $PhCCl_2C_6H_4CCl_3$ (**6**) and the products of their hydrolysis, *viz*., trichloromethylbenzophenones $PhCOC_6H_4CCl_3$ (**7**), which are likely resulted from a transformation of the initial benzotrichloride **2b**, were found in the products of the reaction of aldehyde **1** with benzotrichloride **2b**. According to $^{19}F$ NMR analysis, the proportion of the compounds **3** and **5** is equal to ~4.7 : 1.

Pentafluoroacetophenone and decafluorobenzophenone give no fluorine-containing products in their reactions with $CCl_4$ or with **2b**. In the case of **2b**, the reaction mixtures contain besides unreacted initial ketone compounds **6** and **7** as well.

Taking into account the data about electrophilic properties of polyhalomethanes in the presence of Lewis acids and about the generation of the cationoid intermediates on the interaction of $CCl_4$ with $SbF_5$ [8—12] and of com-

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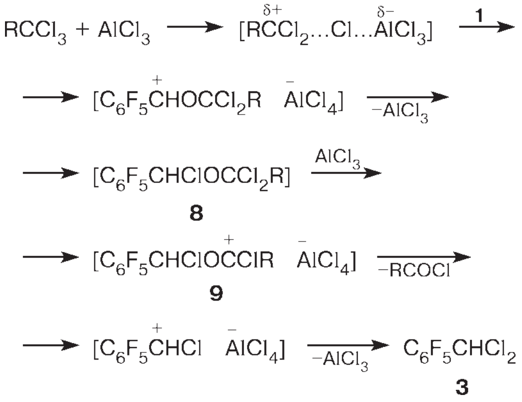
pound **2b** with $AlCl_3$ under Friedel—Crafts reaction conditions,[13] as well as our data about electrophilic character of interaction of the $RCCl_3$—$AlCl_3$ system with polyfluoroaromatic functional derivatives[1—4], one can propose the following scheme of the transformation of aldehyde **1** into dichloride **3** in the presence of $AlCl_3$ excess (Scheme 2).

**Scheme 2**



The conversion **8** → **9** seems to be occur more easily when R = Ph or $C_6F_5$, than when R = Cl, because in former two cases the relatively stable intermediates with cationic centers in benzyl position are generated. This can explain the fact that compound **3** is formed from aldehyde **1** in the course of its interaction with trichloromethyl derivatives **2b** and **2c** under milder conditions than with $CCl_4$.

Electrophilic character of the processes under study is confirmed by the formation of diphenyldichloromethane derivatives **6** which seem to be the products of alkylation of the initial **2b** by phenyldichloromethyl cationoid intermediate formed from **2b** in the presence of $AlCl_3$.

## Experimental

The compositions of the reaction mixtures were determined by $^{19}F$ NMR spectrometry and GC/MS techniques. The $^{19}F$ NMR spectra were recorded with a Bruker WP-200SY spectrometer (188.28 MHz), hexaflourobenzene (+162.9 ppm from $CCl_3F$) was used as the internal standard. The GC/MS analysis was carried out on a Hewlett-Packard G 1081A instrument with a HP 5890 series II gas chromatograph and an HP 5971 mass-selective detector (EI, 70 eV) with the HP5 capillary column (diphenyl (5%)—dimethylsiloxane (95%)): 30 m × 0.25 mm × 0.25 μm. The He flow (1 mL $min^{-1}$) was used as a carrier gas. The following temperature regime program was applied: 2 min at 50 °C, 50→280 °C with the rate of 10 deg $min^{-1}$, 5 min at 280 °C. Evaporator temperature was 280 °C. Temperature of ion source was 173 °C. The scanning velocity was 1.2 scan $s^{-1}$ in the mass interval 30—650 amu.

**Interaction of polyfluoroaromatic carbonyl compounds with $RCCl_3$ in the presence of $AlCl_3$.** ***A.*** The polyfluorinated carbonyl compound (2 mmol), fresh sublimated $AlCl_3$ (6 mmol), and 4 mL of anhydrous $CCl_4$ (2 g of **2b** or **2c**) were stirred for 6 h at the corresponding temperature. The reaction mixture was decomposed with cold water, extracted with ether. The ether layer was dried over $CaCl_2$, and then the ether was evaporated. The residue was analyzed by $^{19}F$ NMR and GC/MS techniques.

***B.*** **Pentafluorobenzylidene chloride 3.** Aldehyde **1** (1.2 g, 6 mmol), $AlCl_3$ (2.4 g, 18 mmol), and $CCl_4$ (10 mL) were heated at 80 °C for 6 h. After the reaction mixture was treated as described above, the residue was distilled *in vacuo*. The yield of **3** was 0.81 g (54%), b.p. 77 °C (25 Torr) (*cf.* Ref. 7: 82—84 °C b.p. (30 Torr)).

In the experiments with benzotrichloride (**2b**) the formation of presumably α-chloro-2,3,4,5,6-pentafluorobenzyl benzoate (**5**) and two isomeric trichloromethyldiphenyldichloromethanes **6** and trichloromethylbenzophenones **7** along with unreacted initial compounds was detected by GC/MS technique

In MS of compound **5** fragment ions with $m/z$ ($I_{rel}$ (%)): 336 $[M]^+$ (0.05), 301 $[M - Cl]^+$ (13.9), 215 $[M - OCOC_6H_5]^+$ (6.72), 195 $[M - COC_6H_5—HCl]^+$ (6.47), 167 $[C_6F_5]^+$ (2.66), 105 $[C_6H_5CO]^+$ (100), 77 $[C_6H_5]^+$ (24.13) were observed. The values of chemical shifts of fluorine atoms in the $^{19}F$ NMR spectrum of this compound ($2F_o$ 21.58 ppm, $F_p$ 11.18 ppm, $2F_m$ 1.62 ppm) were close to the corresponding values for dichloride **3** ($2F_o$ 21.72 ppm, $F_p$ 11.32 ppm, $2F_m$ 1.63 ppm).

For major isomer **6** $m/z$ ($I_{rel}$ (%)): 319 (100), 317 $[M - Cl]^+$ (77.82), 282 $[M - 2\ Cl]^+$ (5.78), 247 $[M - 3\ Cl]^+$ (20.53), 212 $[M - 4\ Cl]^+$ (36.19), 176 $[M - 4\ Cl - HCl]^+$ (35.40), 165 $[M - 2\ Cl - CCl_3]^+$ (65.33); for **7**, respectively: 298 $[M]^+$ (6.74), 263 $[M - Cl]^+$ (100), 165 $[M - 3\ Cl - CO]^+$ (16.07), 158 $[M - Cl - C_6H_5CO]^+$ (10.40), 123 $[M - Cl_2 - C_6H_5CO]^+$ (23.77), 105 $[C_6H_5CO]^+$ (88.93), 77 $[C_6H_5]^+$ (56.98).

Experiments with polyfluorinated ketones were carried out at 80 °C. In the reactions with $CCl_4$ the obtained reaction mixtures contained only initial ketone.

**Interaction of benzotrichloride 2b with $AlCl_3$.** Aluminum chloride (0.4 g, 3 mmol) was added to benzotrichloride **2b** (1 g, 5 mmol) and the mixture was stirred for 6 h at ~20 °C. Then the reaction mixture was decomposed as described above. After ether evaporation, 0.88 g of the residue was obtained. According to the GC/MS analysis, the residue contained compounds **6** and **7** along with initial benzotrichloride **2b**.

## References

1. T. I. Savchenko, I. V. Kolesnikova, T. D. Petrova, and V. E. Platonov, *J. Fluorine Chem.*, 1983, **22**, 439.
2. I. V. Kolesnikova, T. D. Petrova, A. G. Ryabichev, and V. E. Platonov, *Bull. Acad. Sci. USSR, Div. Chem. Sci.*, 1988, **37**, 1466 (Engl. Transl.).
3. T. D. Petrova, V. E. Platonov, and A. M. Maksimov, *J. Fluorine Chem.*, 1999, **98**, 17.

4. T. D. Petrova, A. G. Ryabichev, T. I. Savchenko, I. V. Kolesnikova, and V. E. Platonov, *Zh. Org. Khim.,* 1988*,* **24***,* 1513 [*J. Org. Chem. USSR*, 1988, **24** (Engl. Transl.)].
5. T. D. Petrova, V. E. Platonov, I. S. Popova, and I. V. Kolesnikova, *J. Fluorine Chem*., 1991, **54**, P50.
6. B. F. Filimonov, G. S. Litvinenko, G. F. Dvorko, and S. A. Mramornova, *Zh. Obshch. Khim.,* 1979, **49**, 1098 [*J. Gen. Chem. USSR*, 1979, **49** (Engl. Transl.)].
7. A. K. Barbour, M. W. Buxton, R. L. Coe, R. Stephens, and J. C. Tatlow, *J. Chem. Soc.*, 1961, 808.
8. I. S. Akhrem and A. V. Orlinkov, *Russ. Chem. Bull.*, 1998, **47**, 740 (Engl. Transl.).
9. G. A. Olah, L. Heiliger, and Q. K. S. Prakash, *J. Am. Chem. Soc.*, 1989, **111**, 8020.
10. G. A. Olah, G. Rasul, A. K. Yudin, A. Burrichter, G. K. S. Prakash, A. L. Chistyakov, I. V. Stankevich, I. S. Akhrem, N. P. Gambaryan, and M. E. Vol´pin, *J. Am. Chem. Soc.*, 1996, **118**, 1446.
11. G. A. Olah, G. Rasul, L. Heiliger, and G. K. S. Prakash, *J. Am. Chem. Soc.*, 1996, **118**, 3580.
12. G. Frenking, S. Fau, Ch. M. Marchand, and H. Grützmacher, *J. Am. Chem. Soc.*, 1997, **119**, 6648.
13. N. R. Ayyangar, R. J. Lahoti, K.V. Srinivasan, and T. Daniel, *Synthesis*, 1991, 322.

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