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Some features of the chlorination of 4-chlorobenzotrifluoride

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Abstract: The optimal conditions for the chlorination of 4-chlorobenzotrifluoride for trifluoromethyl-3,4-dichlorobenzene obtaining in the presence of a complex $[PCl_4]^+[FeCl_4]^-$ were found with yield up to 92%. It was found that under certain conditions under the influence of aluminum chloride previously unknown substitution of fluorine atoms for chlorine in trifluoromethyl group of trifluoromethyl-4-chlorobenzene could occur.

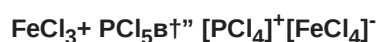
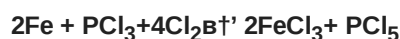
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It is known that the halogenation of benzene and its derivatives in the ring of the action of the halogen is in the presence of catalysts, usually Lewis acids [1]. The use of catalysts is especially true in case of the halogenation of aromatic compounds resistant to electrophilic substitution such as benzene nucleus containing the trifluoromethyl group [2].

In this aspect of particular interest is the investigation of conditions of chlorination of 4-chlorobenzotrifluoride to synthesize trifluoromethyl-3,4-dichlorobenzene - starting material for synthetic pyrethroid tau fluvalinate (Mauritius), approved for use in Russia [3].

In this context, we studied the effect of different catalysts to the chlorination process of 4-chlorobenzotrifluoride: $FeCl_3$, $AlCl_3$, H_2SO_4 , Zilberad's reagent (monochloride copper, aluminum chloride, sulfurylchloride) as well as a mixture of $Fe + PCl_3$. An abridged version of the results previously discussed in [4, 5].

The theoretical prerequisites to the use of iron and phosphorus trichloride as catalyst of were chlorination were concluded our assumption that the complex formation $[PCl_4]^+[FeCl_4]^-$ by passing chlorine through a medium containing a mixture of $Fe + PCl_3$.



Probably the electrophilic chlorination of 4-chlorobenzotrifluoride carries out by active cation chlorine eliminated from PCl_4^+ , and anion $FeCl_4^-$ contributes to the stabilization of the resulting π -complex.

Chlorination was carried out at room temperature by passing an excessive amount of chlorine in 4-chlorobenzotrifluoride in the presence of a suitable catalyst. The molar ratio of trifluoromethyl 4-chlorobenzene: chlorine is within the values of 1: (1,1-1,2). Catalysts of chlorination were added in an amount of 2% to 6,2 % for the complex of ferric chloride with phosphorus pentachloride, this value was defined as the sum of $Fe + PCl_3$. The try to increase the amount of catalyst up to 10% did not result in increased yield of the desired product, but significantly impeded its isolation from the reaction mass. Conditions and the results of the research are presented in the table.

Table. 4-Chlorobenzotrifluoride results chlorination with chlorine in the presence of various catalysts

# exp.	Catalyst	Amount, gram-atom or mole	Ratio Fe/PCl_3	Temperature, $^{\circ}C$	Yield of 3, 4-dichlorobenzotrifluoride, %	Annotation
1	$FeCl_3$	0,02	-	18	12	
2	$AlCl_3$	0,02	-	18	1,5	Trichloromethyl-4-chlorobenzene is formed as a main product.
3		0,02	-	18	trace	

	H ₂ SO ₄					
4	Zilberrad's reagent	0,02	-	18	trace	
5	Fe (cuttings)+PCl ₃	0,02+0,011	0,55	18	91	Trifluoromethyl-2,4-dichloro-benzene is formed as a main product.
6		0,04+0,022	0,55	18	92	
7		0,02+0,0011	0,05	5	90	
8		0,02+0,0011	0,05	40	83	

In experiments 1-4 desired product did not separated out, its concentration in the reaction mass was determined by chromatography. In experiments 5-8 trifluoromethyl-3,4-dichlorobenzene was recovered in pure form and identified by chromatographic methods (spectrometry mass, ¹H-NMR and IR spectroscopy). In addition, physical constants of the samples were in agreement with literature data [6]. From the results presented in the table shows that chlorination trifluoromethyl-4-chlorobenzene in the presence of ferric chloride, aluminum chloride, sulfuric acid, Zilberrad's reagent do not yield satisfactory results and the yield of trifluoromethyl-3,4-dichlorobenzene does not exceed 12% (Test 1).

At the same time, the use of a complex of ferric chloride with phosphorus pentachloride afforded the desired product in yields up to 92%. The investigation of the chlorination under these conditions (experiments 5-8) show that the change in the amount of catalyst from 2,11% to 6,2%, as well as the change in the ratio Fe/PCl₃ from 0,05 to 0,55 do not affect significantly the yield of the title product which is in the range 83-92%.

However, increasing the reaction temperature to 40 °C, considerably reducing the output of the trifluoromethyl-3,4-dichlorobenzene, which in this case amounted to 83% (exp. 8).

When chlorination trifluoromethyl-4-chlorobenzene in the presence of Fe+PCl₃ as a reaction byproduct was isolated trifluoromethyl-2,4-dichlorobenzene, as well as the part of the starting material. Thus, the reaction proceeds in two directions:



When studying the effect of metal halide chlorination trifluoromethyl-4-chlorobenzene was established the feature consisting in that when using aluminum chloride as a catalyst in the chlorination observed substitution in the trifluoromethyl group fluorine atoms to chlorine. It was very interesting, because relate only to the use of aluminum chloride.

In order to clarify the conditions for the occurrence of such an exchange reaction, we carried out additional studies the products of chlorination of trifluoromethyl-4-chlorobenzene in the presence of aluminum chloride.

For this in a four necked flask equipped with a stirrer, a bubbler, lowered to the bottom of the flask, thermometer and reflux condenser were placed 180,5 g (1 mole) of trifluoromethyl-4-chlorobenzene and 13,35 g (0,1 mole) of anhydrous aluminum chloride. After that 85,2 (1,2 mole) of chlorine dried by sulfuric acid in Tishenco bottle passed at 20 °C and vigorous stirring for 5 hours. At the end of reaction, the temperature in the flask rose to 30 °C.

The reaction mixture was dispersed in vacuo. Two fractions identified:

A. 3,2 g (1,5%) trifluoromethyl-3,4-dichlorobenzene. Colorless liquid. Bp 65-67 °C/9 mm Hg, n_D^{20} 1,4739 (Lit. b.p. 172,5 - 173,5 °C, n_D^{20} 1,4740 [3]). Found, %: C 35,87; H 1,36; Cl 33,55; F 26,01. C₇H₃Cl₂F₃. Calculated, %: C 39,07; H 1,40; Cl 33,02; F 26,51.

B. 207,0 g (90%) of trichloromethyl-4-chlorobenzene. Colorless liquid, bp 118-120 °C/9 mmHg, n_D^{20} 1,5724. (Lit. b.p. 106,5-106,7 °C/6 mmHg, n_D^{30} 1,5684 [7]). Found, %: C 35,82; H 1,54; Cl 62,05. C₇H₄Cl₄. Calculated, %: C 36,52; H 1,74; Cl 61,74.

As seen in these conditions practically it is not observed a chlorination of trifluoromethyl-4-chlorobenzene in the ring, but there is a replacement of fluorine atoms in trifluoromethyl group on atoms of chlorine. This may be evidence in favour of the fact that the main role in this reaction belongs to aluminum chloride, which acts as the main agent.

To verify this assumption, we heated with stirring in a flask, 18,0 g (0,1 mole) of trifluoromethyl-4-chlorobenzene and 13,35 g (0,1 mole) of anhydrous aluminum chloride. Thus, for the moment of mixing the reactants warming of the reaction mixture to 40 °C was observed. Then, the temperature was maintained between 30-40 °C within 5 hours.

After cooling, the reaction mass was filtered on a Shot's filter and was subjected to vacuum distillation.

We received 22,1 g (96%) of trichloromethyl-4-chlorobenzene. A colorless liquid, b.p. 118-120 °C/9 mmHg, n_D^{20} = 1,5724.

The solid filter residue was washed out by ice water, acetone and dried in air.

Was received 8,2 g (97%) of white crystals of aluminum fluoride. Found, %: F 66,90. Calculated, %: F67,86.

The substitution reaction of chlorine atoms by fluorine in benzotrifluoride with the action of inorganic fluorine compounds known for the long time [8] , it is widely used in the preparation of homologous benzotrifluoride [9] as well as the conversion of phenyltrichlorosilane into phenyltrifluorosilane [10].

However, as follows from the description provided above aluminum chloride in the certain conditions replaces of fluorine atoms to chlorine in the trifluoromethyl group of trifluoromethyl-4-chlorobenzene. This reaction was unknown previously.



For an explanation of the mechanism of this reaction it is necessary to consider a possible role of the chlorine atom placed in the fourth position of the benzene ring, and apparently increasing the mobility of fluorine atoms in trifluoromethyl group thanks to participating in the formation of a complex of aluminum chloride with trifluoromethyl-4-chlorobenzene.

Conclusions

1. The optimal conditions for chlorination of 4-chlorobenzotrifluoride to obtain trifluoromethyl-3,4-dichlorobenzene in the presence of an offered complex $[\text{PCl}_4]^+[\text{FeCl}_4]^-$, providing the desired product yield up to 92 %, are discovered.

2. It was found for the first time that previously unknown substitution of fluorine for chlorine in trifluoromethyl group of trifluoromethyl-4-chlorobenzene could occur under influence of aluminum chloride.

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