Received: March, 2012

The substitution of the fluorine atoms by the chlorine in the trifluoromethyl group of 4-chlorobenzotrifluoride under the reaction of the chlorination

V.V. Afanasjev, V.F. Golovkov, T.F. Visotscaja, L.V. Kaabak

GosNIIOKhT, Shosse Entuziastov, 23, Moscow, 111024, Russia
e-mail: Dir@gosniiokht.ru

Abstract: *The unusual substitution of the fluorine atoms by the chlorine in the trifluoromethyl group was took place under the reaction of 4-chlorobenzotrifluoride with the aluminum chloride; the last was transformed into the aluminum fluoride.*

Keywords: *aluminum chloride, aluminum fluoride, 4 chlorobenzotrifluoride, 4 chlorobenzotrichloride, chlorination, catalytic agent, trifluormethyl group.*

It is known, that the halogenation of benzene and its derivatives by halogen action is carried out in the presence of catalysts, usually Lewis's acids [1].

Use of catalysts is especially actually at the halogenation of the aromatic compounds steady to electrophilic replacement [2]. In particular, the chlorination of 4-chlorobenzotrifluoride for the purpose of the reception of 3,4-dichlorobenzotrifluoride with the catalysts of chlorination as chloric iron, aluminium chloride, sulfuric acid and Zilberrad reactant (copper monochloride, aluminum chloride, sulfuril chloride) was not successful. Only the use of a complex of chloric iron with phosphorus pentachloride at the molar ratio 4-chlorobenzotrifluoride:chlorine = 1:(1,1-1,2) gave the expected product in 92% yield [3].

At studying of the influence of metals galogenides to chlorination of 4-chlorobenzotrifluoride the feature, consisting that at use as the catalyst of aluminum chloride in the course of chlorination the replacement in of atoms of fluorine on chlorine in trifluoromethyl group took place. It was rather interesting, since concerned only a case of use of aluminum chloride. However this fact at that time has not received development and reaction products in the pure state were not distinguished.

For the purpose of specification of conditions upon the course of such exchange reaction we had been carried out additional researches of products of chlorination of 4-chlorobenzotrifluoride in the presence of aluminum chloride.

For this purpose in a four-necked flask fitted with a stirrer, a bubler, lowered to the flasks bottom, the thermometer and a reflux condenser, placed 180,5 g (1 M) of 4-chlorobenzotrifluoride and 13,35 g (0,1 M) of waterless aluminum chloride.

85,2 g (1,2 M) of chlorine dried in Tischenco bottle passed at 20°C and vigorous stirring for 5 hours. By the end of reaction the temperature in a flask rose to 30°C. The received reaction mixture was distilled in vacuum. Two fractions collected:

A. 3,2 g (1,5 %) 3,4-dihlorbenzotrifluoride. A colourless liquid, b.p. 65-67°C/9, n_D^{20} = 1,4739 (lit. 172,5-173,5°C, n_D^{20}=1,4740 [3]). Anal. Found:38,87; Í 1,36; Cl 33,55; F 26,01. Calcd: C 39,07; Í 1,40; Cl 33,02; F 26,51.

B. 207,0 g (90 %) 4-chlorobenzotrifluoride. A colourless liquid, b.p. 118-120°C /9, n_D^{20} = 1,5724. (Lit. 106,5-106,7°C/6, n_D^{30}=1,5684 [4]). Found: Ñ 35,82; Í 1,54; Cl 62,05. Calcd: Ñ 36,52; Í 1,74; Cl 61,74.

Apparently, in these conditions practically it is not observed the chlorination of 4-chlorobenzotrifluoride, but there is a replacement of atoms of fluorine in trifluoromethyl group on atoms of chlorine. It can testify to favour of that the leading role in the given reaction belongs to aluminum chloride which acts as the main reagent.

For check of such assumption 18,0 g (0,1 M) of 4-chlorobenzotrifluoride and 13,35 g (0,1 ìîëü) of waterless aluminum chloride were heated and stirred in a flask. During the first moment a temperature of the mixture raised to 40°C. Then within 5 hours the temperature was supported by us within 30-40 °C.

After cooling the reaction mixture was filtered on Shota filter and was exposed to vacuum distillation.

We obtained 22,1 g (96 %) 4-chlorobenzotrifluoride. A colourless liquid, b.p. 118-120°C /9, n_D^{20} = 1,5724.

The firm residue on the filter was washed out by ice water, acetone and dried on air. We obtained 8,2 g (97 %) white crystals aluminum fluoride. Found: F 66,90. Calcd: F 67,86.

Reaction of replacement of atoms of chlorine to fluorine in benzotrichloride at action of inorganic compounds of fluorine is known for a long time [5], it is widely used for reception of the corresponding benzotrifluorides [6].

However, as follows from above presented description, in some conditions under the influence of aluminum chloride there can be a replacement of atoms of fluorine unknown earlier by the chlorine in the triftluoromethyl group of 4-chlorobenzotrifluoride.

For an explanation of the mechanism of this reaction it is necessary to consider some role of an atom of the chlorine, being in the fourth position of the benzene ring and, most likely, increasing mobility of the atoms of fluorine in trifluoromethyl group or influences upon a complex of aluminum chloride with 4-chlorobenzotrifluoride formation. Therefore researches will be continued with the other replaced benzotrifluorides.

References

[1] P. Sykes. A Guidebook of Mechanism in Organic Chemistry. M.:Himija. 1997. 320 p.
[2] O.R. Reutov. Teoreticheskie osnovi organicheskoi khimii. M.:MGU. 1964. P.201.
[3] Patent RU 2083544 (1994)
[4] R.H. Myers, M.E. Hobbs, P.M. Gross. J.Am.Chem.Soc., V.76, 1954. P.4737.
[5] A.N. Nesmejanov, N.A. Nesmejanov. Nachala Organicheskoi khimii. M.:Himija. V. II, 1974. P.56.
[6] A.E. Porai-Koshits, L.E. Efros, M.J. Klirova, D.A. Livshits, K.Ju. Marjanovskaja, J.P. Alexandrova, K.E. Ulman. J. pricl.khim.V.XXVII, N.9. P. 969-975.

Recommended for publication by A.F. Eleev