Fluorination of p-chlorobenzotrifluoride by manganese trifluoride.

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A great number of papers have been devoted to the fluorination of aromatic hydrocarbon compounds by higher fluorides of metals of a variable valence. At the same time most of these investigations were devoted to study of the processes of fluorination by cobalt trifluoride.

In this paper we focus on the reaction of p-chlorobenzotrifluoride with manganese trifluoride . The experiments were carried out in the temperature range of 300-350°C. Manganese trifluoride was produced before the synthesis just in a reactor by manganese difluoride treatment with elemental fluorine at 250-300°C.

Fluorination of p-chlorobenzotrifluoride was carried out by means of passing vapors of organic substance through the vertical reactor with manganese trifluoride at the given temperature.

The reaction products were collected in a cooled trap and after neutralization from hydrogen fluoride they were analyzed by gas-liquid chromatography (GLC), NMR and mass-spectroscopy methods.

It has been determined that below 300°C p-chlorobenzotrifluoride negligibly reacted with manganese trifluoride. So, when 80 gr. of p-chlorobenzotrifluoride was passing through the reactor at 290°C only 48 gr. of fluorination products was collected, among them the following were identified:

trifluoromethyl-4-chloropolyfluorocyclohexenes and 1 -trifluoromethyl-4-chloropolyfluorocyclohexadienes with a number of fluorine atoms in the ring from 2 to 5. The remaining reaction products were supposed to remain in the reactor, this was confirmed indirectly by the behavior of further regeneration of manganese fluorides with elemental fluorine.

At increasing the temperature to 500°C the yield of fluorination reaction products was increased substantially. So, at 500°C when 80gr of p-chlorobenzotrifluoride was fed to the reactor there was collected 105 gr. of the reaction products in the cooled trap. GLC analysis has shown the presence of 11 main components. As a result of mass-spectrum analysis, it was assumed that among the fluorination products there were 1-trifluoromethyl -4-chloropentafluorocyclohexane and isomers of 1 - trifluoromethyl-4-chloro-tetrafluorocyclohexene. The investigations conducted on dehydrohalo-genation have shown the presence of the following substances in the reaction products: 1-trifluoromethyl-4-chloropentafluorocyclohexane, isomers of 1-trifluoromethyl-4-chlorotetrafluorocyclohexene, isomers of 1 -trifluoromethyl-4-chloropentafluorocyclohexene, isomers of l-trifluoromethyl-4-chloroheptafluorocyclohexane.

The study conducted on dehydrohalogenation of the above mentioned compounds is in agreement with our assumption on the structure of the main reaction products. The main reaction products were the following isomers:

l-trifluoromethyl-4-chlorodifluorobenzene

1 -trifluoromethyl-4-chlorotrifluorobenzene

l-trifluoromethyl-4-chlorotetrafluorobenzene confirmed by ^{19}F, ^{1}H NMR and mass spectroscopy. Besides, after dehydrofluorination, in raw material there were uncovered and identified products of fluorotoluenes decomposition to fluorochlorobenzenes.

Experimental.

Manganese difluoride (970 g) freshly calcined at 300°C is fed into a flow -type reactor made of Ni (800 mm long, 36 mm in diameter) equipped with a two-region electrical heating and 4 thermo couples installed along the reactor length. The reactor is heated in a nitrogen flow to the temperature of 300°C and feeding elemental fluorine is started at a rate of 25 l/hour (125 I total). During the fluorination process the temperature in the reaction zones increases spontaneously up to 450°C. The indication of the fluorination reaction completion is a temperature drop in the last zone to the initially set value (300oC) and fluorine passage through the reactor. Manganese trifluoride prepared in the such way is blown with nitrogen for 1 h, then the temperature is raised to 450°C and p-chlorobenzotrifluoride is feeding at a rate of 25 g/hour (91 g total). During the fluorination the temperature in the reaction zones is rising consequently up to 520-550°C. The fluorination products are captured in a trap cooled to minus 20°C. The raw material in amount of 105 g has been produced after washing. According to the data of ^{19}F, ^{1}H NMR and mass spectroscopy the main reaction products were shown to be polyfluorinated chlorotrifluoromethylcyclohexenes, the starting p-chlorobenzotrifluoride was absent.

To confirm the assumed structure of fluorocyclohexenes produced , their dehydrofluorination was carried out. Dehydrofluorination was conducted in a flow-type reactor of 800 mm long and 25 mm in diameter filled with a carrier with a developed surface at the temperature of 500°C.

105 g of the fluorination products was passed during 3 hours. 65 g of the pyrolysis product was produced which consisted mainly of polyfluorobenzo-trifluorides with addition of polyfluorobenzenes according to the-data ^{19}F, ^{1}H NMR and mass spectrocsopy.