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2,2-Bis(trifluoromethyl)propionic acid. Synthesis and properties

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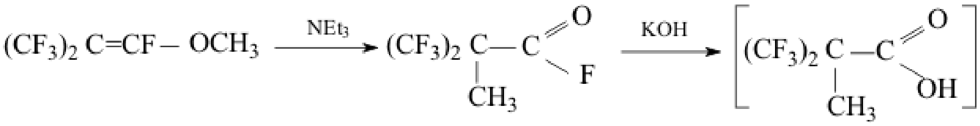
Abstract. *The method for obtaining 2,2-bis(trifluoromethyl)propionic acid from 2-trifluoromethyl-3,3-trifluoropropionic acid is proposed. The resulting substance is characterized by elemental analysis and NMR.*

Keywords: *2,2-bis(trifluoromethyl)propionic acid, fluoroanhydride, Yarovenko reagent.*

Earlier some attempts have been made to obtain 2,2-bis(trifluoromethyl)proionic acid (I) out of corresponding fluoroanhydride (II) by keeping the last one for 6 days with solution of KOH according to the scheme [I]:

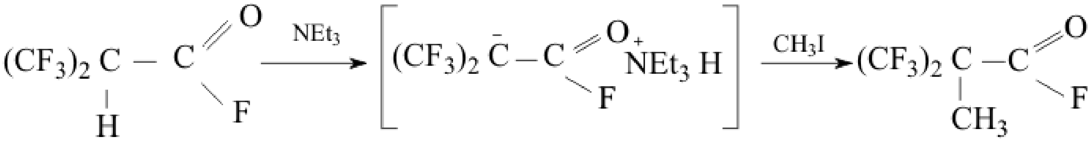


(II) (I)

Physical characteristics of acid (I) are not listed, because, as it is mentioned in the work the formed acid is hydroscopic and it has been isolated in a form of aniline salt [1,2]. For the purpose to work up the acid (I) in its individual form and studying its properties 2-trifluoromethyl-3,3,3-trifluoropropionic acid (□- hydrohexafluoroisobutyric acid) was used for the present work. It is easily transformed into corresponding anhydride (III) with high yield by Yarovenko reagent as described in the work [3], at that it is more convenient to use the reverse mixing of reagents adding 1,1,2-trifluoro-2-chloroethyldiamine to crystal acid and trap the corresponding fluoroanhydride into the collector with potassium fluoride.

(III)

Fluoroanhydride obtained (III) was later mixed with a small excess of triethylamine while cooling and then kept in steel autoclave at room temperature. The next day methyliodide was added to the salt obtained (IV).



(III) (IV) (II)

As a result fluoroanhydride of bis(trifluoromethyl)propionic acid (II) is formed, containing ~ 10-15% of the initial fluoroanhydride (III) b.p.=45-47°C and 31-32°C respectively. When adding fluoroanhydride (III) to aquatic solution of KOH it is easily transformed into 2,2-bis(trifluoromethyl)propioninc acid (I), which after processing of hydrochloric acid solution was extracted by methylene chloride and isolated in the individual form (b.p.=152°C ; m. p. 90-94°C no decomposition). The corresponding ethyl ester (V) was obtained using the known method out of the acid.

Experimental

1. **□-Hydrohexafluoroisobutanoyl fluoride (III)**.

To 196g (1,0 mole) of □-hydrohexafluoroisobutyric acid put into 1,0 litre three-neck flask with a stirrer, drop funnel and gas-outlet tube 190g (0,12 mole) of 1,1,2-trifluoro-2-chloroethyldiamine were added. The mixture was heated with stirring at water bath, evolving products were collected into the trap containing 60g of NaF (1,4 mole). The contents of trap was distilled gathering the fraction with boiling point 30-35°C.

2. **2,2-Bis(trifluoromethyl)propionyl fluoride (II)**.

100g (1,0 mole) of triethylamine were put into the steel autoclave, then it was cooled with dry ice and 180g (0,85 mole) of □-hydrohexafluoroisobutanoyl fluoride were added. The autoclave was sealed and kept for one night at room temperature. The next day the autoclave was opened and 150g (0,1 mole) of iodomethane were added to the slightly cooled mixture. The autoclave was sealed and kept for 24 hours at shaking and opened.

The content of 6 experiments was then united fractioned at the rectification column. 2 fractions were obtained with b.p. = 31-32°C (II) and 45-47°C (III), with the yield of ~ 85%, the fraction (III) was used for the repeated transformation into

52°C (II) and 45-47°C (III), with the yield of ~ 85%, the fraction (III) was used for the repeated transformation into fluoroanhydride (II) according the scheme mentioned above.

3. **2,2-bis(trifluoromethyl)propionic acid.**
130g of KOH in 650ml H_2O were put into 1 litre 4-neck flask equipped with stirrer, reflux condenser, drop funnel and then 210g of fluoroanhydride (II) were gradually added, it was stirred about 2 hours, left for a night. After that 150 ml of HCl were added, the lower layer was separated, the aquatic layer was extracted twice by CH_2Cl_2, dried by $MgSO_4$. Then CH_2Cl_2 was distilled.

In residue ~ 250 g of viscous masses, which were dried in vacuum over P_2O_5 and afterwards distilled. 187g of crystal acid with b.p. = 152°C were obtained. Yield ~72%.
Found: C-28.17, H-2.20, F-55.07%; Calculated: C-28.57, H-1.90, F-54.28%.
NMR ^{19}F spectrum: 6,3 (CF_3) singlet; NMR ^{1}H : 9,5 (OH) singlet

References

1. I. L. Knunianz at all, Izv. Akad. Nauk, Ser. Khim. 1968, 876.
2. I. L. Knunianz at all, Izv. Akad. Nauk, Ser. Khim. 20, 1, 1971, 110-117.
3. A.V. Fokin, A.I. Rabkin at all , Izv. Akad. Nauk, Ser. Khim., 1984, 411-415.

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