

ALKALINE AND ALKALINE-EARTH METALS FLUROHALOGENATES IN ORGANIC SYNTHESIS

V.D. Suprunenko, V.I.Sobolev

Scientific Supervisor: PhD, Associate Professor R.V. Ostvald

Language Advisor: Senior teacher U.A. Smirnova

Tomsk Polytechnic University, Russia, Tomsk, Lenin str., 30, 634050

E-mail: vladislav94ru@mail.ru

In recent years, threefluoridebromin is famous fluorinating and bromating agent in chemistry of organic compounds. The main feature of threefluoridebromin is its feature of electrophilyc bromating high-deactivated aromatic compounds. It is known that nitrobenzene forms 3-bromo-nitro benzene with good output. However, threefluoridebromin is a dangerous compound. In this way, using alkaline and alkaline-earth metals fluorohalogenates in organic synthesis is safer.

Tetrafluorobromates are white loose crystal substances, which have low reactivity. Degrading, they form threefluoridebromine which has low decomposition temperature, and possess good fluorinating, and bromating agents. Today chair CTRE is a study on the methods of synthesis tetrafluorobromates and their properties and application. (expand)

Equipment.

Spectrums of gas chromatography-mass-spectrometry (GX-MS) of the interaction products were measured with the help of chromatomass-spectrometers TRACE DSQ on the base of TPU Scientific and Analytical Center. The analysis was performed with the following parameters: expansion coil temperature– 280 °C; thermostatic oven temperature +40 °C - +300 °C; heating speed– 10 °C/min; range of mass scanning– 33-350 a.u.m.

Initial substances

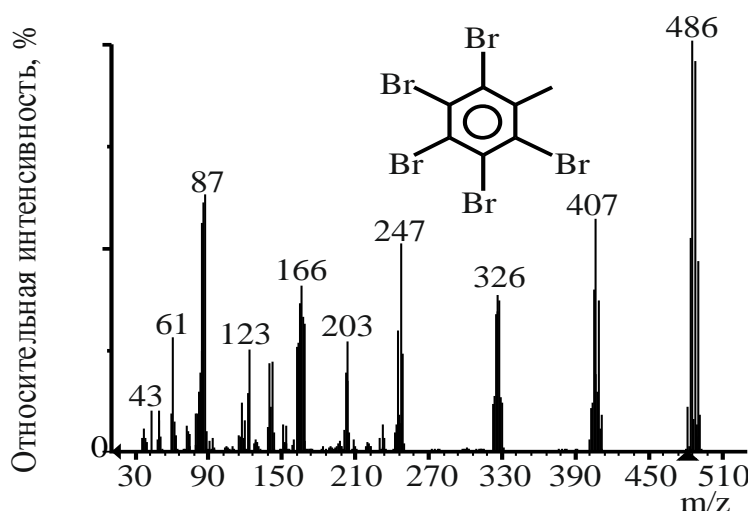
- Kalium tetrafluobromate, KBrF_4
- Barium Tetrafluobromate, $\text{Ba}(\text{BrF}_4)_2$.
- p- Nitrobenzene diazonium tosylate
- Nitrobenzene
- Distilled water
- Calcium chloride, $\text{C}=0,7\text{g/ml}$. solution was prepared immediately before the experiment.
- Siliceous gel, Sigma-Aldrich Silica gel orange, $\geq 99\%$, 10087-2.5KG-R.
- Sodium fluoride, Sigma-Aldrich Sodium fluoride, $\geq 98\%$, 71522-500G.

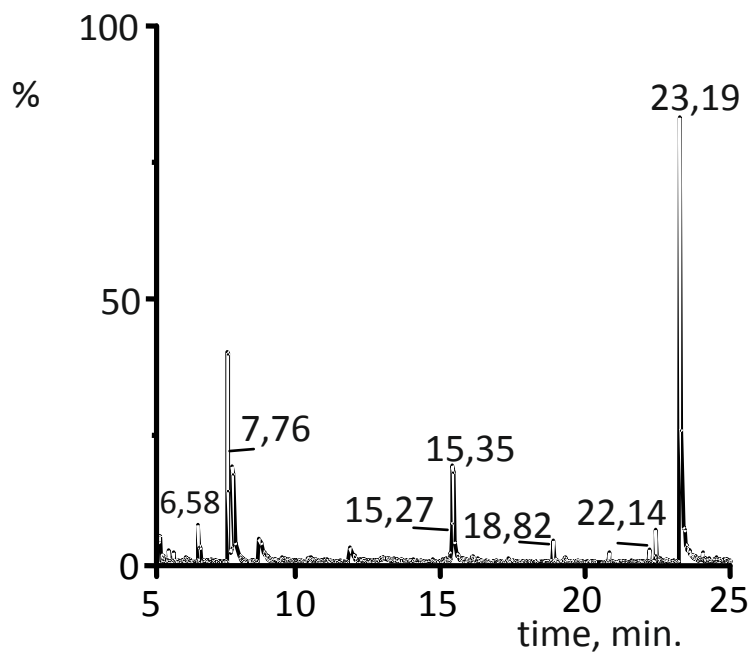
Interaction of KBrF_4 and NBDT in solid state was conducted at following molar ratio of reactants: 3:1; 1:1 and also 3:1:1 in the presence of one mole NaF as an inert diluents. The following reagent samples were used: KBrF_4 - 183 mg (61 mg for a molar ratio 1:1); $\text{Ba}(\text{BrF}_4)_2$ - 420 mg (140 mg a molar ratio 1:1) p-nitrobenzenediazonium tosylate - 100 mg; NaF - 13 mg.

- General experimental techniques for solid substrates are:

- 1. Material samples are placed in an agate mortar and triturated gradually at room temperature in the given proportions.
- 2. This technical product is poured with distilled water and vigorously stirred until complete dispersion in water.
- 3. A concentrated solution of CaCl_2 ($C = 0,7 \text{ g} \setminus \text{ml}$) is added into this slurry to precipitate the free F-ions as an insoluble precipitate of CaF_2 .
- 4. 5ml of ethyl acetate is added into this mixture for extraction of organic substrates into organic phase.
- 5. The aqueous and organic phases are separated using a separatory funnel.
- 6. The organic phase is purified by resinous impurities by filtration through silicagel.

Interaction of KBrF_4 and NBDT . In a 3:1 molar ratio active instantaneous emission of gaseous products is observed as white smoke formation and heating of brown oily substance mixture. The chromatogram of the products of interaction and one of the mass spectra of obtained substances is presented in Figure 2.





Findings

Kalium and barium tetrafluorobromates show high reactivity feature in organic substances in the form of aromatic diazonium salts. Degradation reactions of the diazonium salts to form nucleophilic substitution and electrophilic brominating is predominant over the interaction of reactants This reaction dominates with nitrobenzene, consequently kalium and barium tetrafluorobromate and threefluoridebromine react equally.

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