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REACTIONS OF AROMATIC IODINE COMPOUNDS TOWARDS ALKALI AND ALKALINE EARTH METAL TETRAFLUOROBROMATES

M.A. Samakbaeva

Scientific supervisors – Ph.D. in Organic Chemistry, Tomsk Polytechnic University, S.P. Zhuravkov;
Doctor of Chemical Sciences, Professor of Tomsk Polytechnic University, M.S. Yusubov;

National Research Tomsk Polytechnic University
634050, Russia, Tomsk, Lenin Avenue 30, madina.samakbaeva@yandex.ru

Intoduction. According to sustainable development strategy, the main goal of investigators is to find, create and implement environmentally friendly processes and materials. The organic chemistry of hypervalent iodine compounds is a big possibility to make greener the processes in chemical technology. Hypervalent iodine reagents are used extensively in organic synthesis as efficient and environmentally benign oxidizing reagents whose chemical properties in many aspects are similar to the derivatives of heavy metals [1]. In this paper we consider on (difluoroiodo) arenes. (Difluoroiodo)arenes, $ArIF_2$, can be prepared by two general approaches:

- oxidative addition of fluorine to iodoarenes using powerful fluorinating reagents
- ligand exchange in iodine (III) compounds, such as ArIO or $ArICl_2$, using HF or SF_4 as a source of fluoride anions [2].

Various fluorinating reagents have been used for the fluorination of iodoarenes. A very clean and selective, although relatively expensive, procedure for the preparation of (difluoroiodo)arenes is based on the fluorination of iodoarenes with xenon difluoride in dichloromethane in the presence of anhydrous hydrogen fluoride (Scheme 1) [3, 4].

This method works well for the fluorination of iodoarenes with electrondonating or electron-withdrawing substituents; the latter, however, require longer reaction times. (Difluoroiodo)arenes are hygroscopic and highly hydrolyzable compounds, which makes their separation and crystallization extremely difficult [2].

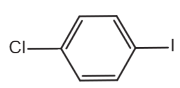
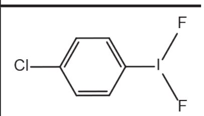
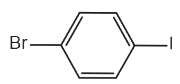
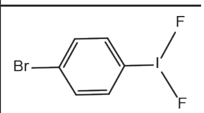
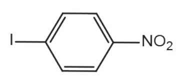
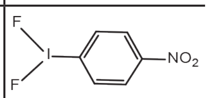
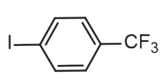
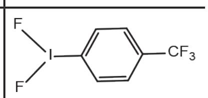
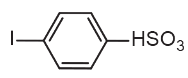
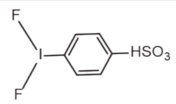
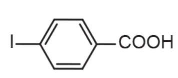
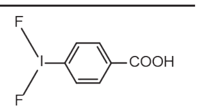
The current work carries out the possibility of safer and more convenient fluorination method development, based on reactions of aromatic iodine compounds with alkali and alkaline earth metal tetrafluorobromates. Sobolev V.I, Filimonov V.D. and coworkers described chemical properties of known fluorobromates: $KBrF_4$, $CsBrF_4$, $RbBrF_4$ and the recently described $Ba(BrF_4)_2$ in reactions with aromatic compounds and pyridine. They found out strong and selective bromination abilities towards aromatic compounds [5]. However, there is no sys-

$$ArI + XeF_2 \xrightarrow[\text{- Xe}]{CH_2Cl_2\text{, HF (anhyd), rt, 1 - 3h}} ArIF_2$$

$$Ar = Ph, 3\text{-}ClC_6H_4, 3\text{-}NO_2C_6H_4, 4\text{-}MeOC_6H_4, 3\text{-}MeOC_6H_4$$

Scheme 1. *Fluorination of iodoarenes with xenon difluoride*

Table 1. Reaction of $Ba(BrF_4)_2$ with hypervalent aromatic compounds

Entry	Substrate	Product
1		
2		
3		
4		
5		
6		

tematic data about reactivity of TFB in fluorination of aromatic compounds.

Methods and materials. As substrates of reactions, we choose following aromatic iodine reagents: CL–Ph–I , Br–Ph–I , NO_2–Ph–I CF_3–Ph–I, SO_3H–Ph–I , COOH–Ph–I. The fluorinating agent is tetrafluorobromate of barium. Tetrafluorobromates of alkali and alkali-earth metals (TFB) are compounds with high fluorinating and brominating ability, they are safer than BF3 in usage.

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METHANE FROM INDUSTRIAL WASTES AS FUEL FOR ROCKETS OF THE FUTURE

T.K. Samatov

Scientific adviser – assistant prof. of FTI NR TPU, Ph.D., A.K. Ustyuzhanina

National Research Tomsk Polytechnic University

634050, Russia, Tomsk, 30 Lenin Avenue, www.tpu.ru

One of the basic problems of space exploration is the development of optimal fuel for rockets and space ships suitable for long flights. In this study the choice of the most resource efficient, safe and less expensive fuel is discussed. The most economic ways of getting it are proposed.

As fuel, rockets use both liquid and solid chemical compounds. The fuel efficiency is assessed by the following criteria: availability, density, cost of production and storage, and specific impulse [1]. The first candidate as fuel for rockets is kerosene. It is one of the most widely used fuels after gasoline. It has a relatively high density, is not particularly toxic and not expensive. And most importantly, it has a high specific impulse, which indicates that such a fuel can accelerate the rocket very well. But there is one important problem: high quality kerosene suitable for rockets can be extracted only from certain grades of oil which are very few nowadays. Thus, we have to consider this candidate not optimal.

The next variant is hydrogen. It is a flammable exploding gas with the highest specific impulse of all our candidates in the list. But its low density spoils the great picture: it takes too much volume to carry enough hydrogen to escape from the Earth's atmosphere. The next big problem is its storage temperature. The liquid hydrogen exists only at temperature of –252 to –259 °C, which means that it will go high storage costs [2].

The third option is heptyl, also known as asymmetric dimethylhydrazine. It has the same properties as kerosene, but it is extremely toxic and dangerous for people and plants. In Soviet times it was widely used but now it can't be used due to its negative characteristics [2].

Thus, the most popular fuels do not meet the criteria of safety and resource efficiency and are not optimal. In this study we propose an alternative fuel for rockets which is more environmentally friendly and economical. It is methane, which was proposed as fuel for the first time in the research works of NPO Energomash named after academician V.P. Glushko, conducted since 1981.

Methane is easily accessible and relatively cheap gas, its density and specific impulse are high enough for both small and large space rockets. The future of space technology is aimed at the multiple use; space ships should be able not only to fly out of the Earth, but also fly back, too, in full force and without damage. In this case, methane could be an optimal fuel as it can be found on the others planets as well as almost on any asteroid which gives the possibility of refueling.

The most important feature of methane is the abundance of ways to get it: by chemical means, from natural gases, and also from industrial wastes.