

Available online at [www.sciencedirect.com](http://www.sciencedirect.com)

ScienceDirect

Procedia Chemistry 11 (2014) 88 – 91

---

---

**Procedia**  
Chemistry

---

---

1st International Symposium on Inorganic Fluorides: Chemistry and Technology, ISIF 2014

## Electrophilic bromination of nitrobenzene using barium tetrafluorobromate (III)

V.I. Sobolev\*, V.B. Radchenko, R.V. Ostvald, V.D. Filimonov, I.I. Zherin

*National Research Tomsk Polytechnic University, 30 Lenina Avenue, Tomsk 634050, Russia*

---

### Abstract

It has been shown that Ba (BrF<sub>4</sub>)<sub>2</sub> acted as a highly-active brominating agent. In case of interaction with nitrobenzene, the pure 3-bromo-nitrotoluene is formed. It has been shown that typical electrophilic bromination of the aromatic compound with electron-donating and electron-accepting substituents occurred without any catalysts or hard conditions.

© 2014 The Authors. Published by Elsevier B.V. This is an open access article under the CC BY-NC-ND license (<http://creativecommons.org/licenses/by-nc-nd/3.0/>).

Peer-review under responsibility of the National Research Tomsk Polytechnic University

*Keywords:* Synthesis ; bromine trifluoride ; fluorohalogenates ; bromination; chromatography ; calorimetry ; fluorine

---

### 1. Introduction

Brominated aromatic compounds are important in various fields of industry; they are commonly used as biocides, fire extinguishing agents, herbicides, and as different intermediates in organic synthesis. Most aromatic bromination processes are carried out in presence of different catalysts such as various Lewis acids. The main disadvantage of these methods is the fact that they require anhydrous conditions and especially large amount of catalyst. This often results in substantial amounts of effluents discharged, raising serious disposal problems. Furthermore, bromination of aromatic compounds, in particular non-activated ones, is a time-consuming process with relatively low yields. The other well-known way is based on the diazotation of the corresponding anilines, followed by thermal decomposition in the presence of bromide ion. This usually requires relatively long reaction times and a suitable aniline derivative which is not always easily available<sup>1,2</sup>.

---

\* Corresponding author. Tel.: +7-913-846-2548.

E-mail address: [vsobolev1989@tpu.ru](mailto:vsobolev1989@tpu.ru)

Shlomo Rosen suggests a different way for such bromination processes using  $\text{BrF}_3$ <sup>3</sup>. This method shows excellent yields even at low temperatures in presence of considerable quantities of solvents without any catalysts<sup>4</sup>. The main disadvantage of this method is the extremely high reactivity of  $\text{BrF}_3$  and the requirement of using elemental bromine as a carrier for  $\text{BrF}_3$ <sup>5</sup>.

Not so long ago we have suggested another way for selective bromination of various aromatic compounds, even extremely deactivated ones. In order to conduct a more detailed research of these processes, the process of nitrobenzene bromination using  $\text{Ba}(\text{BrF}_4)_2$  has been researched.

## 2. Experiments

### 2.1. Equipment and methods

<sup>1</sup>H NMR and <sup>13</sup>C NMR spectra have been recorded with a Bruker AVANCE AV 300 (Bruker, Germany) spectrometer at 300MHz with  $\text{CDCl}_3$  as a solvent and  $\text{Me}_4\text{Si}$  as an internal standard.

IR spectra have been recorded on a Thermo Nicolet 5700 FT-IR spectrometer (Thermo Fisher Scientific, USA)<sup>4</sup>.

Powder X-ray diffraction (XRD) patterns have been obtained with a Stadi-P-Diffractometer (Stoe, Germany) using  $\text{Cu-K}\alpha$  radiation, a germanium monochromator, and a Mythen1K detector<sup>6</sup>. The data have been handled using the WINXPOW software<sup>7</sup>. The compounds have been filled into Lindemann capillaries and flame-sealed. Le Bail profile fitting and Rietveld refinement have been executed in the Jana2006 software<sup>8</sup>.

The solid precipitate's energy dispersive X-ray fluorescence analysis (EDXRF) has been carried out with an ARL QUANT'X EDXRF spectrometer (Thermo Scientific, USA) equipped with a Peltier cooled Si (Li) detector. The measurements have been done in two steps with different experimental conditions in order to get primary lines for both barium and bromine. In the case of the barium line measurement a Cu thick filter together with 50 kV voltage on the X-ray tube have been used. Whereas for the bromine determination, we have employed a Pd thick filter and 28 kV on the tube. The durations of the measurement in both cases have been the same and equal to 120 seconds of lifetime<sup>4</sup>. All measurements have been done in air atmosphere. The sample of solid precipitate has been introduced into the device in a solid form. The sample holders have been covered with thin layers of Prolene® Film (Chemplex Industries, USA)<sup>9</sup>.

GC-MS has been performed using a gas chromatograph Agilent 7890A (Agilent Technologies, USA) combined with a mass-spectrometer Agilent 5975C (Agilent Technologies, USA) under the following conditions – the temperature of the liner was 230°C; the temperature of thermostat was changing from 50 to 250°C; heating rate was 10°C/min; mass scan area was from 33 to 350.

Melting point of the pure organic product has been determined by the MP 50 Melting point system (Mettler Toledo, Switzerland).

### 2.2. Reagents and sample preparation procedure

Organic compounds and solvents were of commercially grade and were not additionally purified. Barium fluorobromate  $\text{Ba}(\text{BrF}_4)_2$  has been obtained by a method described in<sup>6</sup> and held in a Teflon container. In order to decrease the reaction's intensity, the solution of alkane and Freon R113 has been used to run the reaction. The Freon R113 reacts with neither  $\text{BrF}_3$  nor  $\text{Ba}(\text{BrF}_4)_2$  that's why it is very convenient for such processes.

A flask with a mixture of nitrobenzene and Freon-113 with the 1:30 volume ration has been cooled down to -25°C. Then the flask has been equipped with a magnetic stirrer and condenser and heated up to 45°C and held for 6 hours with vigorous stirring and with no light. The solution color change from pale yellow to intensive orange has been observed during the stirring. The TLC analysis has been held during the entire experiment, the product with  $R_f=0.36$  has been observed.

After previous steps the excess of Freon-113 has been evaporated and the crude product has been dissolved in ethyl acetate. The product solution has been filtered through a silica gel filter in order to remove the possible presence of sludge products. The crude organic mixture has been quantitatively analyzed by a GC internal standard program. Pure bromo-aromatic compound has been separated from crude organic mixture by a preparative column chromatography method on a silica gel. The n-hexane-ethyl acetate mixture with a 5/2 volume ratio has been used as

an eluent. The yields were based on the reacted aromatic derivatives, and the conversions were practically quantitative in the sense that 2 mol/equiv of an aromatic compound was consumed for every mol/equiv of  $\text{Ba}(\text{BrF}_4)_2$ . The physical and spectral properties of all products completely matched those of authentic samples or those appearing in the literature.

### 3. Results and discussion

The reaction scheme is showed in Fig. 1. It demonstrates a typical electrophilic bromination mechanism of aromatic compounds; the total yield amounted to 75%. It is completely constituent with the results of S. Rosen<sup>1</sup> obtained using bromine trifluoride.

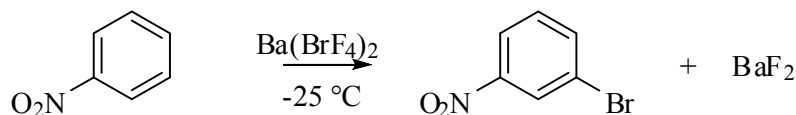


Fig. 1. Interaction scheme of nitrobenzene with  $\text{Ba}(\text{BrF}_4)_2$

Such reactivity of barium fluorobromate could be explained in the way of its decomposition process<sup>9</sup>. Its decomposition products are barium fluoride and bromine trifluoride, in other words, bromine trifluoride is forming *in situ* instead of the S. Rosen way<sup>1-3</sup>.

This fact explains  $\text{Ba}(\text{BrF}_4)_2$  is a quite more selective and less reactive reagent than  $\text{BrF}_3$  or its solution in bromine under the same conditions. The pure organic product after purification has been analyzed according to several methods after the steps mentioned above<sup>10</sup>. The prepared compound as described above has been analyzed by  $^1\text{H}$  NMR – signals at 7.439 ppm (1 H, t), 7.841-7.812 ppm (1 H, d,  $J=8.7\text{Hz}$ ), 8.180-8.149 ppm (1 H, d,  $J=9.3\text{Hz}$ ), 8.365 ppm (1 H, s).  $^{13}\text{C}$  NMR – signals at 122.108; 122.818; 126.667; 130.646; 137.598; 148.72 ppm. IR – 3097.9; 1530.4; 1345.8  $\text{cm}^{-1}$ . The determined melting point of pure organic compound was 53°C. It is in good agreement with literature data for *m*-bromonitrobenzene<sup>12</sup>. Thus, we can conclude that *m*-bromonitrobenzene is formed during the process of nitrobenzene interaction with  $\text{Ba}(\text{BrF}_4)_2$ .

The solid precipitate of  $\text{BaF}_2$  is formed during the reaction because of the interaction process of  $\text{Ba}(\text{BrF}_4)_2$  and *p*-nitrotoluene. It has been analyzed by X-ray powder diffraction and X-ray fluorescence spectrometry; both analysis techniques told us that there was pure  $\text{BaF}_2$  formed as the only solid product of the interaction of  $\text{Ba}(\text{BrF}_4)_2$  and nitrobenzene.

The EDXRF spectrum of  $\text{Ba}(\text{BrF}_4)_2$  is shown in Fig. 2.

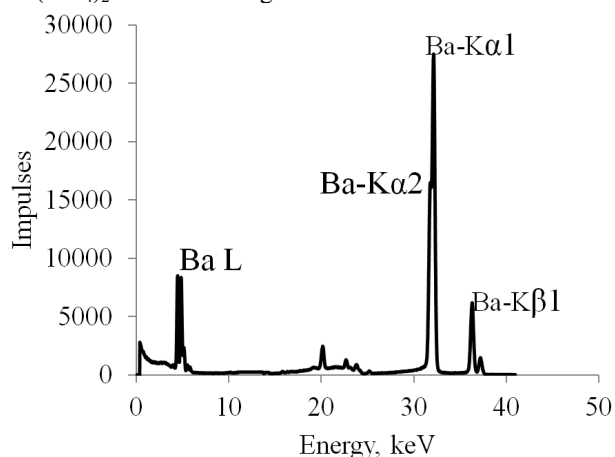


Fig. 2. EDXRF spectrum of  $\text{Ba}(\text{BrF}_4)_2$

EDXRF shows characteristic lines of barium ( $L\alpha=4.51$  keV,  $L\beta=4.91$  keV,  $L\gamma_1=5.61$  keV,  $L\gamma_3=5.81$  keV) and characteristic lines of rhodium ( $K\alpha=20.15$  keV,  $K\beta_1=22.69$  keV,  $K\beta_2=23.31$  keV) which is explained by using rhodium cathode in the X-ray tube. Fluorine cannot be detected due to some restrictions of this method. So, both analysis methods have shown that pure barium fluoride was formed as a solid precipitate.

In conclusion, we would like to propose a new and efficient procedure for the preparation of *m*-bromonitrobenzene using Ba (BrF<sub>4</sub>)<sub>2</sub>. We agree with S. Rozen and his co-workers that fluorine chemists should not shy away from BrF<sub>3</sub> since under the right conditions it can be a useful and versatile reagent<sup>1,2</sup>; also if you're still shy away from BrF<sub>3</sub> you should try fluorobromates of alkali and alkali-earth metals for the same processes, these reagents are more mild and more safe for use than BrF<sub>3</sub>. Also Ba (BrF<sub>4</sub>)<sub>2</sub> could be considered as a potentially high-effective brominating agent for complex electron-accepting aromatic systems.

## References

1. S. Rosen. General Method for the Preparation of *b,b*-Difluoroacrylates Using BrF<sub>3</sub>. *Journal of Organic Chemistry* 2004; 69; 8786–8788.
2. S. Rosen. Attaching the Fluorine Atom to Organic Molecules Using BrF<sub>3</sub> and Other Reagents Directly Derived from F<sub>2</sub>. *Accounts of Chemical Research* 2005; 8; 803–812.
3. S. Rosen. Selective Reactions of Bromine Trifluoride in Organic Chemistry. *Advanced Synthesis & Catalysis* 2010; 352; 2691–2707.
4. V. Sobolev, V. Radchenko, R. Ostvald, V. Filimonov, I. Zherin. *p*-Nitrotoluene Bromination Using Barium Fluorobromate Ba(BrF<sub>4</sub>)<sub>2</sub>. *Advanced Materials Research* 2014; 1040; 337-341.
5. A. G. Sharpe, H. J. Emeleus. Chemistry of the Inter-halogen Compounds. Part I. The Reaction of Bromine Trifluoride with Metallic Halides. *J. Chem. Soc.* 1948; 2135.
6. S. Ivlev, P. Woidy, V. Sobolev, I. Zherin, R. Ostvald, F. Kraus. On Tetrafluorobromates (III): Crystal Structures of the Dibromate CsBr<sub>2</sub>F<sub>7</sub> and the Monobromate CsBrF<sub>4</sub>. *Zeitschrift für anorganische und allgemeine Chemie* 2013; 639 (15); 2846–2850.
7. STOE WinXPOW, Stoe & Cie GmbH, Darmstadt, 2011.
8. V. Petricek, M. Dusek, L. Palatinus, Jana 2006, *The Crystallographic Computing System*, Praha, Czech Republic, 2006.
9. S. Ivlev, P. Woidy, F. Kraus, I. Gerin and R. Ostvald. Tetrafluorobromates for Urban Mining of Noble Metals: A Case Study on Iridium Metal. *Eur. J. Inorg. Chem.* 2013; 28; 4984–4987.
10. V. Sobolev, I. Zherin, R. Ostvald, S. Ivlev, V. Filimonov, P. Postnikov Halon 1301 synthesis by using fluoroxidants. *Proceedings - 2012 7th International Forum on Strategic Technology*, IFOST 2012.