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An improved and facile preparation of SF_5Br

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Abstract

A high yield and facile preparation of SF_5Br is described. This preparation is carried out either at room temperature or with slight heating in a one-pot procedure. © 1998 Elsevier Science S.A. All rights reserved.

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1. Introduction

Pentafluorosulfur bromide (SF_5Br) was first prepared in small amounts by reacting SF_4 with Br_2 and BrF_5 at 100°C and under pressure [1]. In 1965, another method involving reacting S_2F_{10} and Br_2 at 138°C was reported [2]. This method was further studied in order to improve both yield and purity [3,4]. In 1977, SF_5Br was prepared by the reaction of SF_4, BrF and CsF at 80–90°C for 24 h; the authors did not provide any additional information other than the temperature and time [5]. A later report used a similar procedure [6]; in this case, the BrF is performed from Br_2 and BrF_3 and then transferred into a main metal reactor containing CsF; after addition of SF_4 the reaction mixture is heated to 90°C for 15 h. The yield of the SF_5Br with respect to SF_4 was only 36% [6]. We now describe an improved synthesis of SF_5Br that is carried out in a single reaction vessel at room temperature or with slight heating.

This compound (SF_5Br) offers an important and effective method for incorporating the SF_5 group into organic compounds. The introduction of SF_5 groups into organic molecular systems can bring about significant changes in their physical, chemical, and biological properties. These properties are manifested by various applications such as solvents for polymers, perfluorinated blood substitutes, surface-active agents, fumigants, a low energy surface film, and as thermally and chemically stable systems (see for example Refs. [7–14]).

2. Results and discussion

The preparation of SF_5Br is carried out in situ by first reacting Br_2 with BrF_3 at room temperature for 6–11 days in the presence of CsF:

$$Br_2 + BrF_3 = 3BrF.$$

Upon addition of SF_4, the reaction mixture stands for 36 days at room temperature or for 20 days with moderate heating:

$$BrF + SF_4 \xrightarrow{CsF} SF_5Br.$$

The product is vacuum-transferred from the reaction mixture cooled to −78°C to a Carius tube (150 ml) containing mercury and cooled to −196°C; the material that is collected in the first 5–10 min may contain some impurities (SF_4, SF_6, Br_2, BrF). The Carius tube is warmed to 10–15°C and shaken in order to remove any bromine and bromine fluorides. The yields for the room temperature and heated sample were 99.6% and 88.2%, respectively. The quantity of the SF_5Br was tested by reaction with CH_2=CHBr and CHF=CF_2 [15,16]. While we have used this method to prepare amounts up to 150 g of SF_5Br, it should be possible to scale up the procedure to kilogram quantities. We found that it was not necessary to preform the BrF in a separate vessel in order to obtain good yields of SF_5Br [6]. The CsF must be replaced or regenerated by heating in vacuo after two complete runs in order to maintain high yields.

3. Experimental details

The reactants BrF_3, Br_2, SF_4 and CsF were obtained from Ozark-Mahoning, MCB, Matheson Gas Products and PCR,

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respectively, and used as received. Infrared spectra of reactants and products were obtained on a Perkin Elmer 2000 FTIR operating at 1.0 cm^{-1} resolution using KBr windows.

3.1. Preparation of SF_5Br at room temperature

To a dry 500 ml Monel vessel, 20.0 g (132 mmol) of powdered CsF was added. The vessel was then equipped with a Whitey stainless steel valve and the CsF was dried in vacuo at 100°C, 24 h. After drying, bromine trifluoride, 56.58 g (413.3 mmol) and bromine, 97.41 g (609 mmol) were vacuum-transferred into the cold vessel (−196°C) and allowed to warm to room temperature. After 11 days, the reaction vessel was cooled to −196°C; 54.03 g (500 mmol) of SF_4 was added. After 6 days at room temperature, an additional 24.62 g (227.8 mmol) of SF_4 was added. The reactants were stored at room temperature for 30 days after which the SF_5Br was removed at −78°C. The yield of the product after treatment with mercury was (150 g, 725 mmol) 99.6% based on the amount of SF_4. The infrared spectrum of SF_5Br agreed with the literature [5].

3.2. Preparation of SF_5Br with heating

To a dry 150 ml stainless steel vessel, 5.00 g (32.9 mmol) of CsF was added. The vessel was equipped with a Whitey stainless steel valve, and the CsF was dried in vacuo at 100°C, 24 h. After drying, bromine trifluoride, 4.88 g (35.6 mmol) and bromine, 10.05 g (62.89 mmol) were vacuum-transferred into the cold vessel (−196°C) and allowed to warm to room temperature. After 6 days, the reaction vessel was cooled to −196°C; 10.54 g (97.54 mmol) of SF_4 was added. The reaction vessel was allowed to stand at room temperature for 6 days then the lower quarter portion of the reaction vessel was warmed in a sand bath at 50°C for 6 days and then at 76°C for 14 days. The SF_5Br was removed at −78°C and freed of impurities as described above. (17.8 g, 86.0 mmol). The yield of the product was 17.8 g (86.0 mmol); 88.2% based on the amount of SF_4. The infrared spectrum of SF_5Br agreed with the literature [5].

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