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SHORT COMMUNICATION

Improved Preparation and Purification of Pentafluorosulfur Bromide

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Pentafluorosulfur bromide is a particularly valuable intermediate for the incorporation of SF_5 groups into molecular structures [1-3], but its attractiveness as a reagent has been diminished by the limitations of available preparative methods. A procedure outlined by Merrill [1], which claims 39% yields of SF_5Br by slow reaction of a corrosive SF_4-BrF_5-Br_2 mixture at 100° and 180 atm. over 5 days, is a formidable undertaking at best, and numerous efforts to duplicate this work have produced yields of 10% or less [4]. On the other hand, the process described by MacDiarmid [5], in which S_2F_{10} is reacted with excess bromine at 138° for 24 hr in a sealed glass tube, is experimentally simpler and easily reproduced [4], but suffers the limitations that (a) owing to poor conversion, yields of SF_5Br are only ~35% based on S_2F_{10} charged, (b) less than half of the SF_5Br is readily recoverable from other materials present, and (c) the "pure SF_5Br" recovered as described [5] is actually contaminated with significant bromine [4].

In this communication we report several simple modifications of the MacDiarmid method which double its efficiency and permit facile recovery of all of the SF_5Br product in a high state of purity.

By replacing Pyrex [5] with Monel reactors and re-using unreacted excess bromine from each synthesis, yields of SF_5Br exceeding 80% (based on S_2F_{10} charged) are routinely obtainable from S_2F_{10}-Br_2 reactions carried out at 150° for 16 hrs. All of the SF_5Br thus produced is easily recoverable in a single

fraction (vide infra) contaminated only with traces of bromine which are readily and quantitatively removed by treatment with mercury. Contrary to an earlier report [5], pure SF_5Br does not react readily with mercury under ambient conditions, and the apparent reactivity observed [5] was most probably the result of Br_2 contamination.

EXPERIMENTAL

The S_2F_{10}, provided by Prof. G. Gard of Portland State University [6], and bromine were used without further purification. Infrared spectra were obtained with a Perkin-Elmer Model 457 instrument. Preliminary S_2F_{10}-Br_2 reactions conducted in Pyrex essentially reproduced the low SF_5Br yields (~35%) described by MacDiarmid [5]. Subsequent reactions, described below, were conducted in 95 cc Monel reactors (Hoke) fitted with stainless steel needle valves.

In a typical preparative sequence, initially Br_2 (250 mmol) and S_2F_{10} (25 mmol) were condensed into the Monel vessel and reacted at 150° for 16 hr. Upon isolation of the reaction products by trap-to-trap fractionation at -78° (Br_2), -116° (SF_5Br + trace Br_2), and -196° (SF_5, SF_6, SOF_2, SiF_4, unreacted S_2F_{10}), it was found that the SF_5Br represented a 46% yield based on the S_2F_{10} charged. The excess Br_2 (-78° trap) was returned to the Monel cylinder, a new charge of S_2F_{10} (25 mmol) was introduced, and the 150°/16 hr/fractionation procedure was repeated as before, with the result that a 65% yield of SF_5Br was obtained. A third repetition of the process, with a 50 mmol charge of S_2F_{10} and the re-used Br_2, provided a 78% yield of SF_5Br. Normally, after the first few sequences of the sort described, yields of SF_5Br around 80% can thenceforth be maintained regularly with subsequent charges of S_2F_{10} and addition of only enough fresh Br_2 to the recycled portion to maintain the Br_2:S_2F_{10} ratio around 4 or 5:1. Variation of the molar ratio Br_2:S_2F_{10} from 10:1 to 4.4:1, as in the series described, has no apparent effect on yields.

Most of the beneficiation of SF_5Br yields appears to result from the removal of a deleterious contaminant in the

Br_2, since a synthesis conducted as before, but with a fresh charge of Br_2, caused the SF_5Br yield to drop to 65%, though subsequent "re-use" of the Br_2 with a fresh sample of S_2F_{10} restored the SF_5Br yield to 81%. However, gas chromatographic, infrared, and mass spectral analysis of fresh bromine samples failed to reveal significant impurities. "Seasoning" of the Monel reactor walls does not appear to be a significant factor, since S_2F_{10} with "pre-used" Br_2 in a fresh Monel cylinder directly produced 80% yields of SF_5Br. On the other hand, the Monel clearly plays a part in the process, since the cited yield increases cannot be obtained in Pyrex reactors.

In the course of this work it was observed that SF_5Br was frequently obtained contaminated with traces of bromine which imparted a reddish color to the liquid and which could not be removed by fractionation. These fractions were readily purified by condensation into a glass bulb fitted with a Teflon stopcock and containing a few cc of mercury. Removal of the bromine was complete after several minutes of agitation at 0°, and the purified SF_5Br (very faintly yellow-colored liquid) was quantitatively recovered; other experiments showed no reaction between SF_5Br and Hg at 25° for 15 minutes.

1 C. Merrill, presented at 3rd International Symposium on Fluorine Chemistry, Munich, August 1965.
2 J. Stewart, L. Kegley, H.F. White, and G. Gard, J. Org. Chem. 34 (1969) 760.
3 A.D. Berry and W.B. Fox, J. Fluorine Chem., 6 (1975) 175.
4 A.D. Berry and W.B. Fox, unpublished results.
5 B. Cohen and A.G. MacDiarmid, Inorg. Chem., 4 (1965) 1782.
6 S_2F_{10} has recently become commercially available through PCR, Inc., Gainesville, Florida.