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Improved and facile addition reactions of pentafluorosulfanyl bromide

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ABSTRACT

A solution of SF_5Br in CCl_3F (0.5–1 M) was utilized to effect the addition of pentafluorosulfanyl bromide (SF_5Br) to olefins. The reaction of the SF_5Br solution in the presence of triethylborane (0.1 equiv) with an olefin over 20 min at 0 °C gave pentafluorosulfanylated compound **2(a–f)** in high yield (Table 2). An efficient route for the preparation of synthetically useful SF5-containing esters is also described.

Several methods for introduction of pentafluorosulfanyl groups into organic compounds are known. In 1985, Kovacina and DeMarco[1] disclosed a process for the production of mono-pentafluorosulfanyl diacetylene polymers. In a report by Winter and Gard[2] in 2000, the addition of SF_5Br to an acrylic ester was effected in Freon-113 under autologous pressure at 65 °C. In 2001, Winter and Gard[3] reported the reaction of pentafluorosulfanyl chloride with a terminal olefin in the course of preparing SF_5-terminated perfluoroalkyl thiols. In this work, where no solvent was employed, the authors noted that pentafluorosulfanyl bromide yielded only BrF addition products as established by GC analysis. However, in 2004, Gard and co-workers[4] reported that acrylate systems did react with SF_5Br under the same solvent free conditions at 65 °C. These workers also were able to effect the addition of SF_5Br photochemically to allylic acetates in a closed reaction vessel under autologous pressure.[5] Subsequently, Dolbier and co-workers[6] reported that triethylborane dramatically improved the addition reactions of SF_5C1 to alkynes and alkenes in hexane at temperatures ranging from −30 °C to room temperature. In the patent literature,[7] methods for both the catalyzed and uncatalyzed addition reactions of SF_5Br in pentane have been described.

The reactions of SF_5Br have not been widely investigated, and were frequently effected in closed systems such as FEP or metal reaction vessels. To overcome the inconvenience of such systems and to avoid vacuum-transfers of SF_5Br more convenient procedures were developed. As such, we report the use of a standard solution of SF_5Br in normal glassware under an inert atmosphere, such as argon, at ambient pressure and at 0 °C.

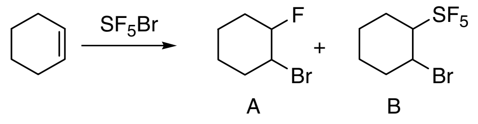
Initially, our investigation into the use of a standard solution of SF_5Br in common glassware gave results similar to those of gaseous SF_5Br addition to the reaction mixture, that is, in dichloromethane, BrF addition to the olefins is the major product. The SF_5Br solutions employed were stable for at least four months under refrigeration and with protection from light and moisture. The addition of KF to the reaction mixture had little or no effect on the reaction[6b] (Table 1).

In a study of the influence of the solvent on the reaction, it was found that the use of polar solvents resulted in BrF addition. The products of SF_5Br addition dominated when nonpolar solvents were employed, with CCl_3F the preferred solvent (Table 1).

As SF_5-containing esters have significant synthetic utility, a search for the most effective route to the preparation of these compounds was undertaken. SF_5Br addition reactions were effected using a SF_5Br solution (0.5–1 M in CCl_3F) and triethylborane (0.1 equiv) in 20 min at 0 °C to form compound **2(a–f)** in high yield[8] (Table 2).

The reaction yielded the SF_5Br addition products cleanly with no evidence of BrF addition. It should be noted that the order of addition of reagents and the temperature of the reaction were critical factors in the success of SF_5Br addition. When the SF_5Br

Table 1
The influence of solvent on pentafluorosulfanyl bromide addition reactions to cyclohexene



Entry	Conditions[a]	Solvent	*A*[b]	*B*
1	KF	CH_2Cl_2	9	1
2	–	CH_2Cl_2	9	1
3	SF_5Br(soln in CH_2Cl_2) and KF	CH_2Cl_2	9	1
4	SF_5Br(soln in CH_2Cl_2)	CH_2Cl_2	9	1
5	KF	Pentane	7	3
6	–	CCl_3F	4	6

[a] All reactions, 0.1 equiv Et_3B, 1.2 equiv SF_5Br, temperature −78 °C to rt.
[b] Product ratio determined by ^{19}F NMR.

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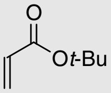
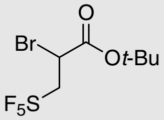
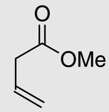
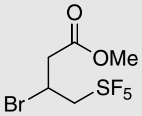
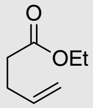
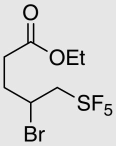
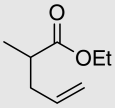
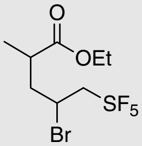
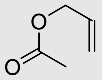
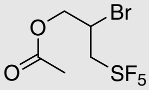
Table 2
Pentafluorosulfanyl bromide addition in CCl_3F

$$A \xrightarrow[\text{Et}_3\text{B (0.1 eq) / 0 °C}]{\text{SF}_5\text{Br (1.3 eq / 0.5 - 1 M in CCl}_3\text{F)}} B$$

Entry	A	B	Reaction time[a]	Yield[b]
1	 **1a**	 **2a**	20	94
2	 **1b**	 **2b**	10	85
3	 **1c**	 **2c**	20	93
4	 **1d**	 **2d**	10	92
5	 **1f**	 **2f**	10	99

[a] In minutes.

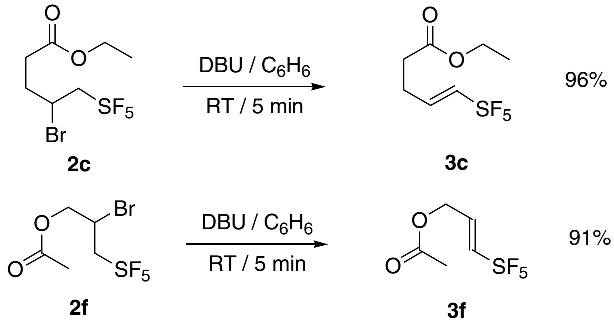
[b] Isolated, purified yield.

solution was added to the solution of starting material and triethylborane at 0 °C, yields of addition product were low and accompanied by side products. On the other hand, addition of the starting material to a stirring solution of SF_5Br solution and triethylborane gave clean products and good yields.

Comparison of the use of SF_5Br solution with that of SF_5Cl was done using **1d**. Reaction using a freshly prepared solution of SF_5Cl in CCl_3F was effected initially at −40 °C. While the expected ethyl 4-chloro-2-methyl-5-pentafluorosulfanylpentanoate, **2e**,[9] was formed, the SF_5Cl reaction required lower temperatures initially and also longer reaction times. It should be noted that the SF_5Cl stock solution in CCl_3F is stable at temperatures below the boiling point of SF_5Cl (bp −21 °C).

To extend the utility of the SF_5Br addition reaction, we also studied the dehydrobromination reaction of the SF_5-containing bromo ester.

As shown in Scheme 1, using DBU, dehydrobromination can be effected (**3c** and **f**) in good yields.[10] In our hands, Schotten–Baumann conditions[11] using KOH to promote dehydrobromination failed.



Scheme 1.

Acknowledgment

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Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.tetlet.2008.07.080.

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8. *Typical procedure:* To a CCl3F solution of SF_5Br (1.3 equiv per mL) at 0 °C was added triethylborane (0.1 eq) followed by the slow addition of starting material (1 equiv). After stirring at 0 °C for 10–20 min, the reaction mixture was quenched with sat. $NaHCO_3$ solution, then extracted with dichloromethane. The combined organic layers were dried over $MgSO_4$ and concentrated. The crude product was purified by Kügelrohr distillation or flash chromatography to afford the liquid, colorless product in good yield.
9. To solution of triethylborane (0.1 equiv) and SF_5Cl solution in CCl3F (1.3 equiv) at −40 °C was added the starting material ester (1 equiv). The mixture was stirred at temperatures between −40 °C and −30 °C for 1 h, and then the bath was removed and the mixture stirred for another hour as it warmed to rt. The reaction was quenched with satd $NaHCO_3$ and extracted with CH_2Cl_2. The organic extracts were washed with water, brine, dried ($MgSO_4$), and filtered.
10. *Typical procedure:* To a solution of the SF_5Br adduct (1 equiv) in benzene (10 mL) was added DBU (1.2 equiv). The mixture was stirred for 5–20 min at room temperature. The reaction mixture was quenched with water, then extracted with dichloromethane. The combined organic layers were dried over $MgSO_4$ and concentrated in vacuo. The crude product was purified by flash chromatography to afford the colorless liquid product in good yield.
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