Allylic fluorides *via* the cleavage of tertiary cyclopropyl silyl ethers with diethylaminosulfur trifluoride

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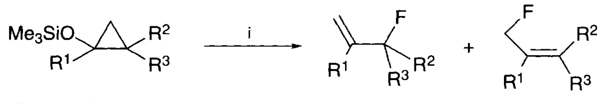
Treatment of tertiary cyclopropyl silyl ethers with diethylaminosulfur trifluoride (DAST) causes ring opening to give allylic fluorides in moderate to high yields.

The introduction of fluorine into organic molecules has become increasingly important in a wide variety of fields, and many kinds of new fluorinating agents have been developed.[1] Among them, DAST, an agent converting aliphatic alcohols or silyl ethers into alkyl fluorides under mild conditions, is one of the most convenient reagents in organic synthesis.[2] Although tertiary cyclopropanols and their silyl ethers are important synthetic intermediates owing to their high reactivity,[3] the systematic study of a reaction of DAST with them has never been examined.

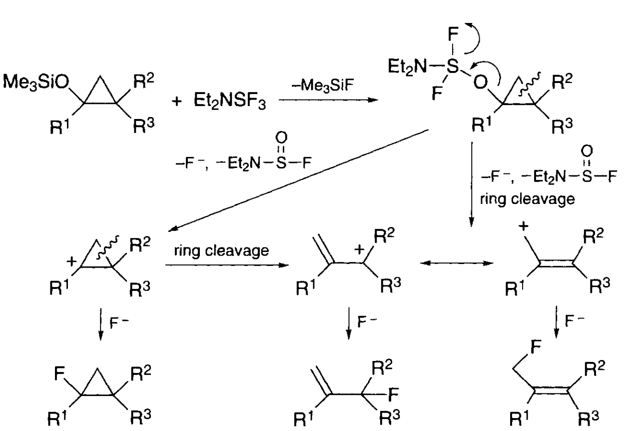
We now report a unique reaction involving the treatment of tertiary cyclopropyl silyl ethers with DAST at room temperature causing ring opening of cyclopropyl groups resulting in the formation of allylic fluorides in moderate to high yields, Scheme 1.†

The results of this reaction are summarized in Table 1. Allylic fluorides were the sole products in most cases. The difference in yield mainly depends on the stability of the products. As noted in runs 6–8, secondary fluorides predominated over primary fluorides. Interestingly, the reaction of DAST with the cyclopropanol silyl ether bearing a strong electron-donating substituent such as α-naphthyl (run 11) did not afford the allyl fluoride but the fluorocyclopropane. These results suggest that the reaction involves a carbocation intermediate.

The plausible reaction mechanism is shown in Scheme 2. The first step is the nucleophilic displacement of a fluorine atom in

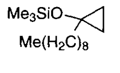
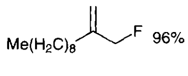
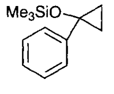
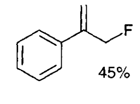
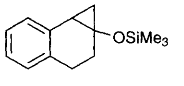
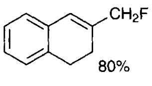
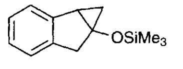
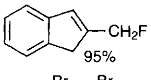
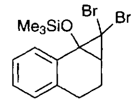
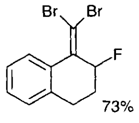
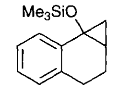
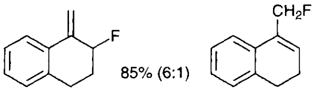
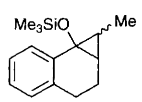
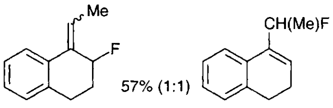
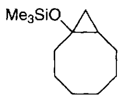
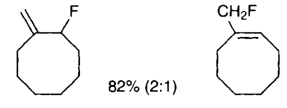
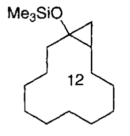
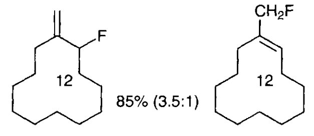
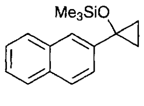
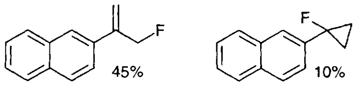
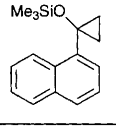
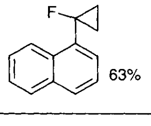


Scheme 1 *Reagents and conditions*: i, DAST, CH_2Cl_2, room temp.



Scheme 2

Table 1

Run	Starting material[a]	Products[b]
1		 96%
2		 45%
3		 80%
4		 95%
5		 73%
6		 85% (6:1)
7		 57% (1:1)
8		 82% (2:1)
9		 85% (3.5:1)
10		 45% 10%
11		 63%

[a] Cyclopropyl silyl ethers were prepared from enol silyl ethers by reaction with diiodomethane in the presence of diethylzinc except for runs 5 and 7. In the case of run 5, the starting material was prepared by the reaction of $CHBr_3$ and potassium *tert*-butoxide with the enol silyl ether. In the case of run 7, 1,1-diiodoethane was used instead of diiodomethane. [b] All compounds were characterized on the basis of mass, IR, ^1H and ^{19}F NMR spectral data. In runs 6–9, the ratio of the products was determined on the basis of ^1H and ^{19}F NMR spectral data.

DAST by the oxygen of the substrate accompanied by elimination of trimethylsilyl fluoride. Next, the elimination of diethylaminosulfino fluoride gives an allylic cation directly or a cyclopropyl cation to be cleaved into the allylic cation. Finally, the fluoride ion attacks the carbocation to afford the product. A stable cyclopropyl cation is attacked by a fluoride ion to produce a fluorocyclopropane.

Footnote

† A typical experimental procedure is as follows: To a solution of cyclopropyl silyl ether (1.0 mmol) in dichloromethane (3 ml) was added DAST (1.0 mmol) at room temp. under an inert atmosphere, and the reaction mixture was stirred for 30 min. Water was added to the reaction mixture and the resulting mixture extracted with dichloromethane. The extract was dried over anhydrous sodium sulfate, filtered and evaporated to afford the crude product. Chromatography on silica gel gave a pure sample.

References

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