

BORON TRIFLUORIDE PROMOTED REACTIONS OF  
N-HALOELECTROPHILES WITH ALKENES

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**Abstract:** N-Haloelectrophiles react with alkenes in the presence of boron trifluoride etherate to give halofluorides and N-halo adducts.

There is a diverse group of positive halogen compounds containing the nitrogen-halogen bond. The group includes N-haloamines, N-haloamides, and N-haloimides. Although radical reactions of these compounds with alkenes are well-known,<sup>1</sup> their potential for ionic reactions has received little attention. Since we had recently been successful in promoting ionic reactions of another class of sluggish electrophiles, the alkyl hypochlorites, with catalysts such as boron trifluoride<sup>2a-b</sup> and trimethylborate<sup>2c</sup>, we initiated a similar investigation with N-haloelectrophiles.

We wish to report that ionic reactions of many N-halo compounds with alkenes are promoted by BF<sub>3</sub>-etherate in methylene chloride. Since we had found that BF<sub>3</sub> catalyzed reactions of the hypohalites gave halofluorides<sup>2a-b</sup>, we investigated the potential of the N-haloelectrophiles for the preparation of halofluorides. We reasoned that the N-halo compounds might be more useful in the preparation of halofluorides because the other products (amines and amides) could be readily separated.

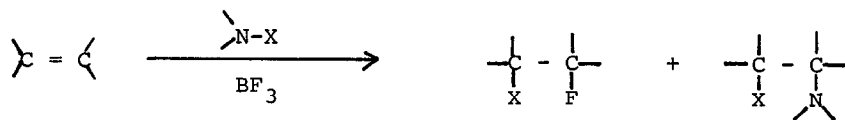


Table I shows yields of halofluorides obtained from 1-hexene (1), cyclohexene (2), and styrene (3) with a variety of N-halocompounds. We examined several N-haloamines in which the basicity of nitrogen, steric bulk of the alkyl group, and electrophilicity of the halogen might be expected to show variation. The best yields of bromo fluorides were obtained with N-bromodimethyl amine. Among the N-chloroamines, N,N-dichloromethyl amine gave more rapid reactions and better yields than the monochloroamines. Trichloramine reacted readily but gave larger amounts of dichloride bi-product.

Table I. Yields<sup>a</sup> of Chloro- and Bromo Fluorides from BF<sub>3</sub>-Promoted Reaction of N-Halo Compounds

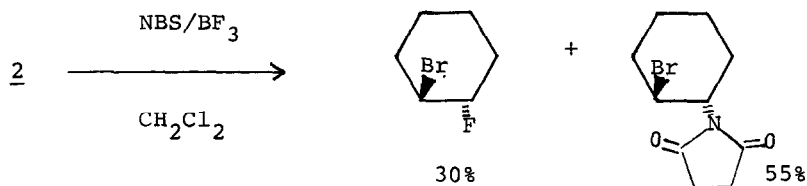
N-X	Alkene	$\begin{array}{c}   \quad   \\ -C-C- \\   \quad   \\ X \quad F \end{array}$ adduct <sup>b</sup>
CH <sub>3</sub> NHCl	<u>1</u>	40
CH <sub>3</sub> NHBr	<u>1</u>	42
(CH <sub>3</sub> ) <sub>2</sub> NCl	<u>1</u>	40
(CH <sub>3</sub> ) <sub>2</sub> NBr	<u>1</u>	45 (35)
(CH <sub>3</sub> ) <sub>2</sub> NBr	<u>2</u>	66 (63)
(CH <sub>3</sub> ) <sub>2</sub> NBr	<u>3</u>	30
N-Chloropiperidine	<u>1</u>	40
N-Bromopiperidine	<u>1</u>	30
CH <sub>3</sub> NCl <sub>2</sub>	<u>1</u>	60 (30)
CH <sub>3</sub> NCl <sub>2</sub>	<u>2</u>	70 (60)
CH <sub>3</sub> NCl <sub>2</sub>	<u>3</u>	10
CH <sub>3</sub> NBr <sub>2</sub>	<u>1</u>	32
(CH <sub>3</sub> ) <sub>3</sub> CNCl <sub>2</sub>	<u>1</u>	35
NCl <sub>3</sub>	<u>1</u>	45
NBS	<u>2</u>	30 (20)
NBA	<u>2</u>	36 (26)
NCS	<u>2</u>	10
CH <sub>3</sub> CON(Br)CH <sub>3</sub>	<u>2</u>	62
CH <sub>3</sub> CON(Br)CH <sub>3</sub>	<u>1</u>	38
C <sub>2</sub> H <sub>5</sub> OCONCl <sub>2</sub> (DCU)	<u>2</u>	41 (33)

<sup>a</sup>Yields were determined by VPC with isolated yields shown in parenthesis.

<sup>b</sup>Markownikoff adducts are obtained from 2 and 3.



product (identified by reported NMR and IR properties<sup>4</sup>).



Halogen-nitrogen adducts probably form from the haloamines also. However, such products were removed by acid extraction during work-up. In the future, work will focus on the scope of haloamine and halamide addition reactions.

Reactions were carried out at room temperature in methylene chloride at alkene concentrations of 0.2 - 0.7 M. The  $\text{BF}_3$ -etherate was added last in molar amounts equal to the electrophile. Reactions were followed by iodometric titration and were usually completed in a few minutes. With dihalo electrophiles such as DCU, reactions were stopped with sulfite after half of the positive halogen was consumed. Halo fluoride products were obtained by distillation or VPC collection and identified by NMR spectra. The haloamines were prepared as dilute solution (ca. 1M) in  $\text{CCl}_4$  or  $\text{CH}_2\text{Cl}_2$  according to a published procedure.<sup>5</sup>

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