0040-4039/85 \$3.00 + .00 ©1985 Pergamon Press Ltd.

## BORON TRIFLUORIDE PROMOTED REACTIONS OF N-HALOELECTROPHILES WITH ALKENES

Gene E. Heasley\*, J. Mark Janes, Stephen R. Stark, Brian L. Robinson Department of Chemistry, Bethany Nazarene College, Bethany, OK 73008

Victor L. Heasley and Dale F. Shellhamer Department of Chemistry, Point Loma College, San Diego, CA 92106

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 in-vestigation with N-haloelectrophiles.

We wish to report that ionic reactions of many N-halo compounds with alkenes are promoted by  $BF_3$ -etherate in methylene chloride. Since we had found that  $BF_3$  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.

$$c = \zeta \xrightarrow{N-X} - \zeta - \frac{l}{C} + -\frac{l}{C} - \frac{l}{C}$$

Table I shows yields of halofluorides obtained from 1-hexene  $(\underline{1})$ , cyclohexene  $(\underline{2})$ , and styrene  $(\underline{3})$  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.

		-c-c-
N-X	Alkene	x F adduct <sup>b</sup>
CH3NHC1	<u>1</u>	40
CH <sub>3</sub> NHBr	<u>1</u>	42
(CH <sub>3</sub> ) 2NC1	<u>1</u>	40
(CH <sub>3</sub> ) 2 <sup>NBr</sup>	<u>1</u>	45 (35)
(CH <sub>3</sub> ) <sub>2</sub> NBr	2	66 (63)
(CH <sub>3</sub> ) 2 <sup>NBr</sup>	<u>3</u>	30
N-Chloropiperidine	<u>1</u>	40
N-Bromopiperidine	<u>1</u>	30
CH3NC12	<u>1</u>	60 (30)
CH <sub>3</sub> NC1 <sub>2</sub>	2	70 (60)
CH <sub>3</sub> NC1 <sub>2</sub>	3	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
NC13	<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
C2 <sup>H</sup> 5 <sup>OCONC1</sup> 2 <sup>(DCU)</sup>	<u>2</u>	41 (33)

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

<sup>a</sup>Yields were determined by VPC with isolated yields shown in parenthesis. <sup>b</sup>Markownikoff adducts are obtained from <u>2</u> and <u>3</u>.

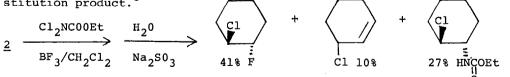
\_

We were surprised to find that rearranged fluorides were formed from 1-hexene:

$$\frac{1}{1} \xrightarrow{CH_{3}NCl_{2}}_{BF_{3}/CH_{2}Cl_{2}} \xrightarrow{CH_{2}CH(CH_{2})_{3}CH_{3}}_{Cl_{F}} + \xrightarrow{CH_{2}CH_{2}CH_{2}CH_{2}CH_{2}}_{Cl_{F}} \xrightarrow{CH_{2}CH_{2}CH_{2}}_{Cl_{F}} + \xrightarrow{CH_{2}CH_{2}CH_{2}}_{Cl_{F}} \xrightarrow{CH_{2}CH_{2}CH_{2}}_{Cl_{F}} + \xrightarrow{CH_{2}CH_{2}CH_{2}}_{Cl_{F}} \xrightarrow{CH_{2}CH_{2}CH_{2}}_{Cl_{F}} + \xrightarrow{CH_{2}CH_{2}}_{Cl_{F}} +$$

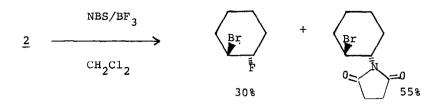
The rearranged products are not formed from equilibration of the vicinyl chloro fluoride. Presumably the products arise from hydride shifts in the intermediate carbocation:

Perhaps the most promising aspect of this study is that the use of  $BF_3$  may provide a facile method for the electrophilic addition to the carboncarbon double bond of the N-halocompounds themselves. In several instances N-halo adducts are found in major amounts. An example is the reaction of N,N-dichlorourethane (DCU). An immediate reaction occurs between <u>1</u> and DCU in methylene chloride in the presence of an equivalent of  $BF_3$ -etherate. In addition to the chloro fluoride, and a small amount of 3-chlorocyclo-hexene, the <u>trans</u>-chlorourethane adduct is obtained after work-up (identified<sup>3</sup> by VPC, NMR, and m.p.). In contrast, when DCU reacts with <u>2</u> by a radical mechanism in refluxing benzene, both <u>cis</u>- and <u>trans</u>- chlorourethane are obtained in 6% and 28% yield respectively, along with 28% of the substitution product.<sup>3</sup>



Both NBS and N-chlorosuccinimide(NCS) react rapidly with  $\underline{1}$  and  $\underline{2}$  to give adducts: NBS and  $\underline{2}$  reacted within a minute in methylene chloride with an equivalent of BF<sub>3</sub> to afford the bromo succinimidyl adduct as the major

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 BF<sub>3</sub>-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 CCl<sub>4</sub> or CH<sub>2</sub>Cl<sub>2</sub> according to a published procedure.<sup>5</sup>

## REFERENCES

- R.S. Neale, <u>Synthesis</u>, <u>1971</u>, 1; F. Minisci and A. Citterio, "Advances in Free Radical Chemistry", Vol. 6, pp 65-153, G.H. Williams, Ed., Heyden, 1980; O.E. Edwards, G. Bernath, J. Dixon, J.M. Paton, D. Vocelle, Can. J. Chem, 1974, 52, 2123
- (a) V.L. Heasley, D.F. Shellhamer, R.K. Gipe, H.C. Wiese, M.L. Oakes, G.E. Heasley, Tetrahedron Lett., 1980, 21, 4133;
  - (b) V.L. Heasley, G.E. Heasley, R.K. Gipe, J.L. Martin, M.L. Oakes,
     B.L. Robinson, D.F. Shellhamer, H.C. Wiese, <u>J. Org. Chem.</u>, <u>1983</u>, <u>48</u>, 3195.
  - (c) G.E. Heasley, M. Duke, D. Hoyer, J. Hunnicutt, M. Lawrence, M.J. Smolik, V.L. Heasley, D.F. Shellhamer, <u>Tetrahedron Lett.</u>, <u>1982</u>, <u>23</u>, 1459.
- 3. T.A. Foglia and D.Swern, J. Org Chem., 1966, 31, 3625.
- Fu-Lung Lu, Y.M.A. Naguib, M. Kitadani, and Y.L. Chow, <u>Can. J. Chem.</u>, 1979, 57, 1967

5. V.L. Heasley, P. Kovacic, R.M. Lange, <u>J. Org. Chem.</u>, <u>1966</u>, <u>31</u>, 3050.

Acknowledgements: Support for this work was provided by the donors of the Petroleum Research Fund, administered by the American Chemical Society, the Catalysts of Bethany Nazarene College, and the Research Associates of Point Loma College.

(Received in USA 1 October 1984)