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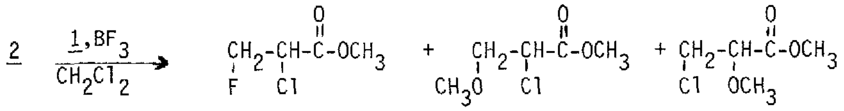
REACTION OF METHYL HYPOCHLORITE WITH CERTAIN OLEFINS IN THE PRESENCE OF BORON TRIFLUORIDE

Victor L Heasley*, Dale F Shellhamer, Robert K Gipe, Harry C Wiese, Melanie L Oakes
Department of Chemistry, Point Loma College, San Diego, CA 92106
Gene E Heasley
Department of Chemistry, Bethany Nazarene College, Bethany OK 73008

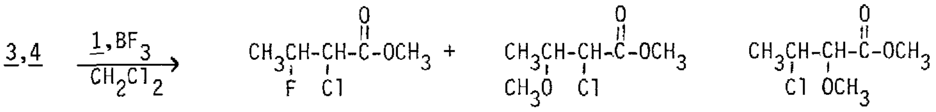
Abstract Fluoro chlorides are major products in the reaction of methyl hypochlorite with certain olefins in the presence of boron trifluoride

We would like to report an unexpected reaction of methyl hypochlorite (CH_3OCl,1) with certain olefins in methylene chloride containing a small amount of boron trifluoride, BF_3[1,2] We observed that 1 reacted with methyl acrylate (2), methyl crotonate (3), and methyl isocrotonate (4) to produce fluoro chlorides by the addition of the elements of Cl, F The expected methoxychloro regioisomers were also formed



$$\underline{2} \xrightarrow[CH_2Cl_2]{1,BF_3} \underset{F\quad\ Cl}{CH_2\text{-}CH\text{-}\overset{O}{\overset{\|}{C}}\text{-}OCH_3} + \underset{CH_3O\quad Cl}{CH_2\text{-}CH\text{-}\overset{O}{\overset{\|}{C}}\text{-}OCH_3} + \underset{Cl\quad OCH_3}{CH_2\text{-}CH\text{-}\overset{O}{\overset{\|}{C}}\text{-}OCH_3}$$

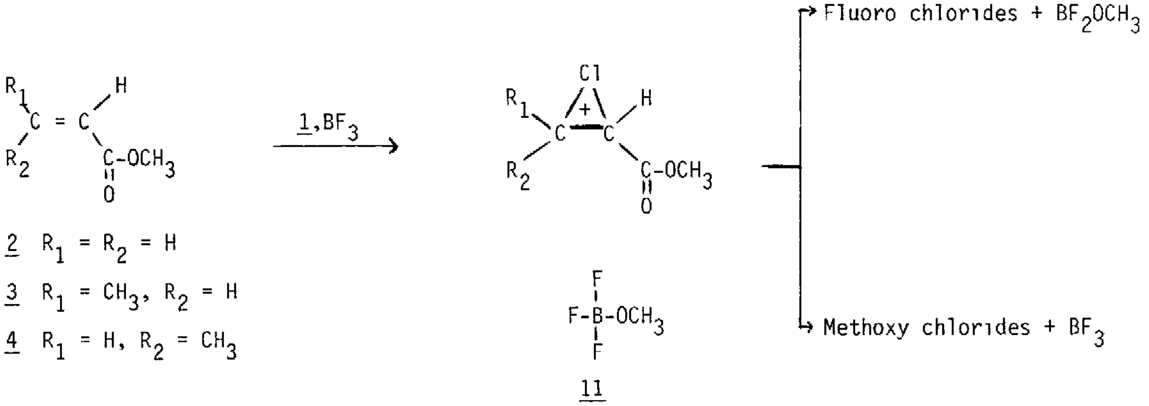
5 - 36% 6a - 26% 6b - 21%



$$\underline{3},\underline{4} \xrightarrow[CH_2Cl_2]{1,BF_3} \underset{F\quad Cl}{CH_3CH\text{-}CH\text{-}\overset{O}{\overset{\|}{C}}\text{-}OCH_3} + \underset{CH_3O\quad Cl}{CH_3CH\text{-}CH\text{-}\overset{O}{\overset{\|}{C}}\text{-}OCH_3} \quad \underset{Cl\quad OCH_3}{CH_3CH\text{-}CH\text{-}\overset{O}{\overset{\|}{C}}\text{-}OCH_3}$$

From 3	7(erythro)-59%	8a(erythro)-22%	8b(erythro)-9%
From 4	9(threo)-53%	10a(threo)-14%	10b(threo)-3%

We suspect that the mechanism involves formation of intermediate ion-pair 11 which collapses to products either by release of fluoride or methoxide ion from the methoxytrifluoroborate anion



2 $R_1 = R_2 = H$

3 $R_1 = CH_3$, $R_2 = H$

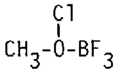
4 $R_1 = H$, $R_2 = CH_3$

There is little information in the literature on the stability or reactivity of an anion such as in 11, and we can only speculate on its existence[3].

The completely stereospecific, anti ring-opening of the chloronium ion in 11 by both methoxide ion and fluoride ion is understandable from the standpoint of bonding in the chloronium ion. Because of the electron-withdrawing ability of the carbonyl group, the bridging in the chloronium ion should be quite symmetrical,[4,5] thereby necessitating backside (anti) attack on the α or β carbons of 11.

The difference in regiospecificity between the methoxide and fluoride ions is difficult to explain. Perhaps fluoride does attack the α-carbon, but the resulting α-fluoro, β-chloro product is unstable to the reaction conditions and loses HF. Small amounts of unidentified compounds were present in the vpc analyses. Also, the β-chloroolefins resulting from elimination may polymerize in the presence of BF_3. Perhaps the same explanation can be used to account for the results with styrene. Reaction of 1 and styrene under the same conditions as for 2, 3 and 4 produced only a low yield of β-chlorostyrene and β-chloro-α-methoxy addition product. Conceivably 1-phenyl-1-fluoro-2-chloroethane is unstable to the reaction conditions[6].

We also considered the possibility that methyl hypochlorite (1) is not the actual chlorinating agent. Another possibility is a boron trifluoride-methyl hypochlorite complex such as 12. To investigate this possibility, we saturated a solution of 1 in CH_2Cl_2 with gaseous BF_3 and observed the methyl proton singlet in the nmr. We speculated that if 12 were formed, the absorption for 1 should decrease and a new absorption should appear downfield for 12. When



$$CH_3\text{-}\overset{Cl}{O}\text{-}BF_3$$

12

BF_3 was passed into a solution of 1, no new peak appeared. Only the absorption for 1 at 3.93 ppm was observed. These data cast doubt on the involvement of 12, but do not prove that a trace of it, in equilibrium with 1, is not the chlorinating agent.

Chlorine monofluoride, ClF, formed as shown below, is another possible halogenating agent.

$$1 + BF_3 \longrightarrow ClF + BF_2OCH_3$$

The formation of ClF, however, cannot occur to any significant extent since 1 on the basis of the nmr studies is apparently unreactive towards BF_3[7].

We plan to extend the mechanistic and synthetic implications of these reactions by studying other alkenes where loss of HF is impossible or at least less likely, substituting other trifluorides for BF_3(AlF_3,InF_3), examining the reactions of other hypochlorites (bulky t-butyl hypochlorite may give only fluoro chloride), extending the study to hypobromites, hypoiodites, and positive halo-nitrogen systems (NCS,NBS,NIS).

A typical reaction is illustrated with methyl acrylate (2): To a stirred solution of 6.63 mmol of 2 in 5 mL of CH_2Cl_2 in the dark was added approximately 6 drops of BF_3-etherate followed by 1.28 mmol of 1 (a 1.28 M solution of 1 in CH_2Cl_2). The reaction was completed in approximately 5 min., and the products were analyzed by vpc, 12' x 0.125" ss column packed with 1.5% DNP. All products were isolated by preparative vpc, and their structures were established by nmr. Nmr spectra were obtained for 5, 7, and 9. 5. ^{1}H, δ3.80 (s,3H), 4.00-5.41 (m,3H-complex multiplet, neither H,H or H,F coupling constants are interpretable), ^{19}F, δ3.56 (triplet of doublets, J=45.6Hz and 15.5Hz,1H). 7. ^{1}H, δ1.50(dd,J=22.5Hz and 6.8Hz,3H), 3.83 (s,3H), 4.22 (t,J=6.8Hz,1H), 4.90(doublet of quintets, J=46.5Hz and 6.8Hz,1H), ^{19}F, δ6.20(doublet of quartets of doublets, J=46.5Hz, 22.5Hz, 6.8Hz,1F). 9. ^{1}H, δ1.45(d,d,1H), J=22.0Hz and 6.0Hz,3H), 3.81(s,3H), 4.24(dd,J=17.0Hz and 6.0Hz,1H), 4.98(doublet of quintets, J=45.0Hz and 6.0Hz,1H).

We suggest that the additions of Cl,F are anti, giving erythro from 3 and threo from 4, because (a) a completely stereospecific syn addition would be unprecedented, and (b) the most stable conformer from anti addition to 3 would have the F and H on C#2 in a gauche configuration-the smaller H,F coupling, whereas the most stable conformer from anti addition to 4 would have the F and H on C#2 in an anti configuration - the larger H,F coupling. The structures of 6ab, 8ab, and 10ab are confirmed by nmr, these data will be presented elsewhere.[8]

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2. Both boron trifluoride etherate, $BF_3 \cdot O(C_2H_5)_2$ and gaseous BF_3 were used without apparent difference in the product ratios.
3. Oxytrifluoroborates have been prepared and are reported to be fairly stable. In general, the B-F bond is stronger than the B-X bond (BF_3X^-).

   Ion pairs analogous to 11 have been postulated for the following BF_3 catalyzed reactions: Addition of H_2S to olefins, in alkylations of aromatics with alkyl chlorides, polymerizations, addition of cyanogen halides to olefins, and nitrations with nitryl chloride. Fluoride formation was not reported in any of these studies. See: "Advances in Fluorine

Chemistry", M Stacey, J C Tatlow, and A G Sharpe, Academic Press, Vol 1, 1960, p 112-118, and other references therein

4 We have recently observed that the brominations of methyl crotonate and methyl isocrotonate are highly stereospecific V L Heasley, D W Spaite, D F Shellhamer, and G E Heasley, *J Org Chem.*, **44**, 2608 (1979)

5. Tightly bridged chloronium ions are known to be involved in the chlorinations of cyclopentene V.L Heasley, G E Heasley, P D Davis, D M Ingle, and K D Rold , *J. Org Chem* , **39**, 736 (1974) and in the chlorination of di-t-butylethylene R C Fahey, *J Am Chem Soc* , **88**, 4681 (1967)

6 As far as we can determine, this compound has not been reported in the literature

7 It seems doubtful that molecular ClF is involved in the reactions since it is known to react explosively with hydrocarbons Furthermore, ClF should replace all of the hydrogens, as well as add to the double bond, resulting in many products This was not observed For a discussion of the reactions and properties of ClF see reference 3, p 18-19

8 A manuscript is in preparation on the reactions of **1** with **2**, **3**, and **4** in methanol to give **6ab**, **8ab**, and **10ab**

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