Tetrahedron Letters, Vol. 33, No. 46, pp. 6903-6906, 1992
Printed in Great Britain

0040-4039/92 $5.00 + .00
Pergamon Press Ltd

Reaction of Alkylhypochlorites and Xenon Difluoride with Cyclohexene

Dale F. Shellhamer,* Mark J. Horney, Andrew L. Toth and Victor L. Heasley

Department of Chemistry
Point Loma Nazarene College, San Diego, CA 92106, USA

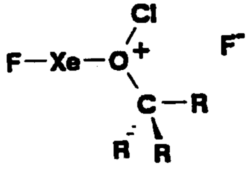
Reactions of alkylhypochlorites and xenon difluoride with cyclohexene give primarily 1-chloro-2-fluorocyclohexanes *via* formation of a complex between xenon difluoride and the alkylhypochlorite.

Key Words: Xenon difluoride; methylhypochlorite; t-butylhypochlorite; triethylcarbinylhypochlorite; 1-chloro-2-fluorocyclohexane; 1-chloro-2-hydroxycyclohexane.

Alkylhypohalites[1] (ROCl) and xenon difluoride[2] (XeF_2) are electrophiles that react very slowly with alkenes in aprotic solvents without acid catalyst. On the other hand, these electrophiles and alkenes do react with or without catalyst in protic solvents[3] or in aprotic solvents under radical reaction conditions.[4]

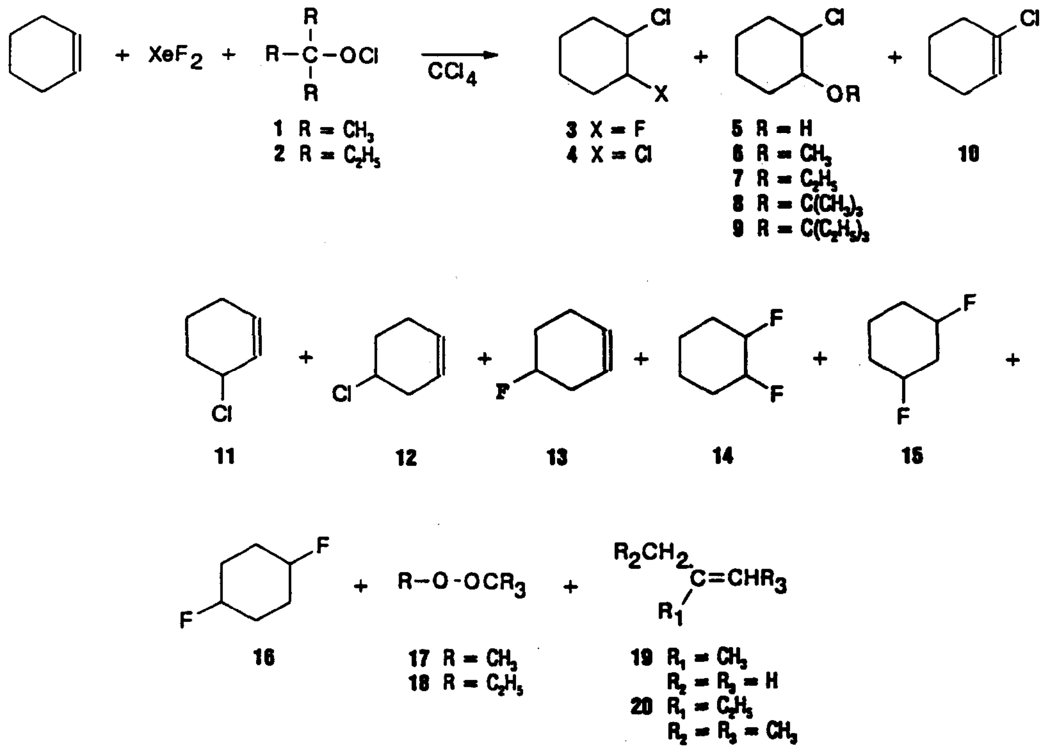
We were surprised to observe a smooth reaction when cyclohexene in carbon tetrachloride was treated with a mixture of t-butylhypochlorite (1) and xenon difluoride (Scheme). This reaction did not occur when the alkyl hypochlorite or xenon difluoride were added separately to cyclohexene in carbon tetrachloride. Product distributions for ROCl (1 R = t-Bu-; 2 R = $(C_2H_5)_3C$-) and XeF_2 with cyclohexene are given in the Table.

We suggest that the products are formed *via* a complex such as **21a** or **21b**. The evidence for a complex is listed below:



21a R = CH_3
21b R = C_2H_5

GENERAL REACTION SCHEME



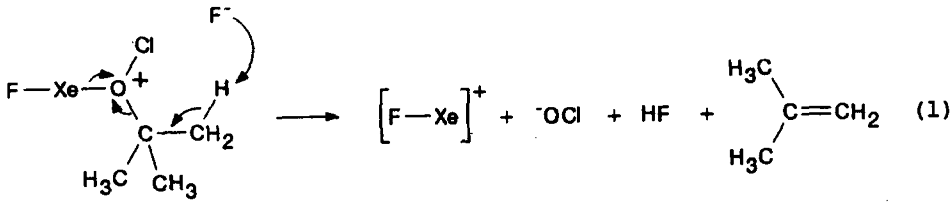
TABLE

PRODUCT RATIOS FOR CYCLOHEXENE + XeF_2 IN CCl_4 WITH

$(CH_3)_3COCl$		$(C_2H_5)_3COCl$	
Product	**Ratio**	**Product**	**Ratio**
3 trans	49.4	3 trans	54.5
3 cis	0.3	3 cis	0.3
4 trans	1.3	4 trans	1.6
5 trans	7.2	5 trans	3.2
6 trans	4.5	7 trans	0.6
8 trans	7.6	9 trans	5.4
8 cis	0.2	9 cis	0.3
10	4.7	10	1.6
11	14.8	11	11.0
12	0.4	12	0.0
13	3.3	13	6.0
14, 15, and 16 (trans & cis)	3.2	14, 15, and 16 (trans & cis)	6.0
17	3.3	18	a
19	a	20	9.5

[a]unable to quantify

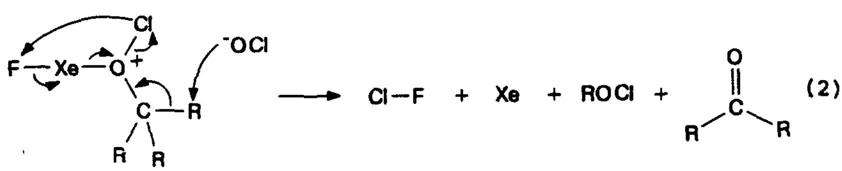
a. Production of alkenes **19** and **20**, and the chlorohydrin **5**, are consistent with complex formation as shown in equation 1 with **21a**. The alkenes and chlorohydrin **5** are not observed when tetrabutyl ammonium fluoride and the alkylhypohalites are reacted with cyclohexene without XeF_2.[5] This indicates that the complex is required for elimination to the alkenes.



21a

$$^{-}OCl + HF \longrightarrow HOCl + \text{cyclohexene} \longrightarrow \mathbf{5}$$

b. Formation of the unexpected products **6** and **7** from **1** and **2** respectively can best be explained from a complex. We suggest that the hypochlorite anion ($^{\ominus}OCl$, eq 1) attacks the complex to form CH_3OCl from **21a** and C_2H_5OCl from **21b** (equation 2). Apparently a complex is required because methyl hypochlorite (CH_3OCl) and acetone are not formed when $(CH_3)_3COCl$ is treated with calcium hypochlorite in THF.



$$ROCl + \text{cyclohexene} \xrightarrow{[HF]} \mathbf{6} \text{ or } \mathbf{7}$$

c. Chlorine monofluoride (ClF) is formed (equation 2) and can be swept with nitrogen into an adjacent flask containing cyclohexene to give **3** under conditions which do not carry XeF_2 or $(C_2H_5)_3COCl$ from the reaction vessel.

We are continuing to study this reaction with other hypohalites and N-haloelectrophiles.

Acknowledgment. Support for this work was provided by the National Science Foundation CHE 8919000, and by Research Associates of Point Loma Nazarene College.

REFERENCES AND NOTES

1. Heasley, V.L.; Gipe, R.K.; Martin, J.L.; Wiese, H.C.; Oakes, M.L. and Shellhamer, D.F. *J. Org. Chem.* **1983**, 48, 3195 and references therein.
2. Shellhamer, D.F.; Conner, R.J.; Richardson, R.E.; Heasley, V.L. and Heasley, G.E. *J. Org. Chem.* **1984**, 49, 5015. Filler, R. *Isr. J. Chem.* **1978**, 17, 71. Chemistry of Halides, Pseudohalides and Azides, Part I, Chapter 15, pp. 657-679, S. Patai, editor; Wiley 1983.
3. For xenon difluoride see: Shellhamer, D.F.; Carter, D.L.; Chua Chiaco, M.; Harris, T.E.; Henderson, R.D.; Low, W.S.C.; Metcalf, B.T.; Willis, M.C.; Heasley, V.L. and Chapman, R.D. *J. Chem. Soc. Perkin Trans 2*, **1991**, 401 and references therein. For alkyl hypohalites see: Heasley, G.E.; Emery III, W.E.; Hinton, R.; Shellhamer, D.F.; Heasley, V.L. and Rogers, S.L. *J. Org. Chem.* **1978**, 43, 361 and references therein.
4. For xenon difluoride see: Shellhamer, D.F.; Ragains, M.L.; Gipe, B.T.; Heasley, V.L. and Heasley, G.E. *J. Fluorine Chem.* **1982**, 20, 13. Hildreth, R.A.; Druelinger, M.L.; and Shackelford, S.A. *Tetrahedron Lett.* **1982**, 1059. For alkyl hypohalites see reference 1.
5. Chlorohydrin products are also formed when $(CH_3)_3COCl$ and boron trifluoride etherate are treated with alkenes to give fluorohalide products.[1] In this previous paper, we assumed the chlorohydrin products formed were due to moisture. Reinvestigation of this reaction under anhydrous conditions and with moisture added did not change the amount of chlorohydrin products. Thus we believe that a complex is also formed between alkyl hypohalites and boron trifluoride.

(Received in USA 23 June 1992; accepted 21 July 1992)