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## Halogen Interchange in Alkyl Halides Using Molybdenum(V) Chloride[1a]

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The interconversion of haloalkane congeners by halide exchange (Finkelstein halide interchange) is a synthetically useful procedure when applied to primary and, to a lesser degree, secondary alkyl halides. Most frequently these interchanges involve the replacement of chloride or bromide with iodide, occur by an SN2 mechanism,[2] and are usually accomplished by treating the alkyl halide with sodium iodide in an appropriate solvent.[3] In general, the replacement of iodide by bromide or chloride, or of bromide by chloride, requires a large excess of the inorganic halide and elevated temperatures.[7,8] Alkyl fluorides do not undergo halide interchange under these conditions.[11,12]

We wish to report that alkyl iodides, bromides, and *fluorides* can be converted to alkyl chlorides in modest to good yields by reaction with molybdenum(V) chloride.

$$RX \xrightarrow[\text{CH}_2\text{Cl}_2]{\text{MoCl}_5} RCl$$
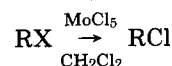
A summary of the results obtained on treatment of various representative substrates is given in Table I.

Several specific points related to the data in Table I deserve brief comment. First, this reaction sequence seems applicable to the conversion of secondary and tertiary alkyl fluorides, bromides, and iodides to the corresponding chloride. As suggested by the nearly quantitative recovery of 1-bromooctane, molybdenum(V) chloride does not affect halogen interchange in primary alkyl bromides. By comparison, 1-iodo- and 1-fluorooctane react readily. This dramatic difference in reactivities suggests the possibility of selective halogen interchange such as, for example, the conversion of a secondary alkyl bromide, iodide, or fluoride to the corresponding chloride in the presence of a primary alkyl bromide (cf. last entry in Table I).

Second, the conversion of 1-iodooctane to 1-chlorooctane is accompanied by the formation of some of the rearranged isomer, 2-chlorooctane. In contrast, the reaction of 1-fluorooctane occurs with extensive rearrangement.

Third, in a effort to probe the mechanism of halogen interchange we have examined the stereochemistry of the product produced by the reaction of molybdenum(V) chloride with (−)-(R)-2-bromooctane[13] (α_{589}^{20} −38.4°, 90% optical purity). The resulting 2-chlorooctane was completely racemic. It is, however, not possible to make a definitive statement concerning the stereochemistry of the carbon–chlorine bond-forming step, since under comparable conditions both optically active 2-chlorooctane[13] (α_{589}^{20} −30.7°, 97% optically pure) and optically active 2-bromooctane are completely racemized in less than 6 min.[14] One conceivable mechanism that accounts for these observations, as well as the 1,2 migrations observed with certain substrates, involves a Lewis acid assisted ionization of the carbon–halogen bond followed by conversion of this carbonium ion to chlorocarbon by reaction with a halometallo–ate complex.

Table I
Reaction of MoCl₅ with Various Alkyl Halides[a]

RX (concn, M)	Registry no.	Alkyl chloride	Registry no.	Yield,[b] % (recovered RX, %)
2-Fluoro-2-methylpropane[c] (2.0)	353-61-7	2-Chloro-2-methylpropane	507-20-0	49
2-Fluorooctane (2.0)	407-95-4	2-Chlorooctane	628-61-5	71
1-Fluorooctane[d] (4.5)	463-11-6	1-Chlorooctane	111-85-3	12
		2-Chlorooctane		58
2-Bromo-2-methylpropane (2.0)	507-19-7	2-Chloro-2-methylpropane		69
2-Bromooctane (2.0)	5978-55-2	2-Chlorooctane	51261-14-4	60
1-Bromooctane (1.0)	111-83-1	1-Chlorooctane		5 (94)
2-Iodo-2-methylpropane (1.5)	558-17-8	2-Chloro-2-methylpropane		48
2-Iodooctane (1.5)	557-36-8	2-Chlorooctane		67
1-Iodooctane (1.0)	629-27-6	1-Chlorooctane		66
		2-Chlorooctane		13
1-Iodo-2-phenylethane (1.5)	17376-04-4	1-Chloro-2-phenylethane	622-24-2	60
Fluorocyclohexane (3.0)	372-46-3	Chlorocyclohexane	542-18-7	62
Bromocyclohexane (2.0)	108-85-0	Chlorocyclohexane		60
1,1-Difluorocyclohexane (1.5)[e]	371-90-4	1,1-Dichlorocyclohexane	2108-92-1	31
1,3-Dibromobutane (2.0)	107-80-2	1-Bromo-3-chlorobutane	56481-42-6	61

[a] Unless otherwise indicated all reactions were carried out in CH₂Cl₂ solution at room temperature under an inert atmosphere of dry nitrogen. The concentration of molybdenum(V) chloride was ~1.0 M. [b] Yields were determined by quantitative vapor phase chromatography and are based on alkyl halide. [c] Carried out at −50°. [d] Performed at −78°. [e] Under similar conditions α,α,α-trifluorotoluene does not react with MoCl₅.

The intermediacy of carbonium ions in the reaction of alkyl halides with molybdenum(V) chloride is supported by the fact that treatment of 1-iodo-2-phenylethane-2,2-d_2[10] (1) with molybdenum(V) chloride produces a 1:1 mixture of 1-chloro-2-phenylethane-2,2-d_2 and 1-chloro-2-phenyleth-ane-1,1-d_2. When this experiment was carried to $\sim$50% completion, the recovered starting halide was found to consist of a 1:1 mixture of 1 and 1-iodo-2-phenylethane-1,1-d_2.[15,16]

Synthetically, the reaction of alkyl halides with molybdenum(V) chloride expands the utility of halogen interconversion to alkyl fluorides in particular, and to tertiary halides in general. Moreover, the conversion of alkyl halides to alkyl chlorides using molybdenum(V) chloride can be accomplished selectively and under conditions that are comparatively milder than those required for the analogous conversion involving displacement by chloride ion. As such, the replacement of fluoride, bromide, and iodide by chloride using molybdenum(V) chloride offers a useful compliment to halide interconversion procedures that proceed by S$_N$2 displacement.

Experimental Section[18]

Molybdenum(V) chloride was prepared by the literature procedure.[19] 2-Fluorooctane,[13] 1-iodo-2-phenylethane,[10] and 1,1-difluorocyclohexane[20] were prepared using known procedures.

Procedures for Halogen Interchange. Similar procedures were used to effect the halogen interchange listed in Table I.

Conversion of 2-Fluorooctane to 2-Chlorooctane. Molybdenum(V) chloride (1.20 g, 4.39 mmol) was placed in a flame-dried, 25-ml flask containing a Teflon-coated stirrer bar. Methylene chloride (3 ml) was added by syringe followed by the slow addition of a solution of 2-fluorooctane (1.16 g, 8.78 mmol) in methylene dichloride (2 ml) over a 5-min period. This mixture was stirred for 2 hr, then cautiously hydrolyzed with water (1 ml). The organic layer was separated, dried (MgSO$_4$), and passed through a short column of alumina. GLC analysis of the eluent indicated a 71% yield of 2-chlorooctane. A collected sample had the retention time and ir spectrum equivalent to that of authentic 2-chlorooctane.

Conversion of 1-Iodo-2-phenylethane to 1-Chloro-2-phenylethane. A solution of 1-iodo-2-phenylethane (2.35 g, 10.1 mmol) in dichloromethane (8 ml) was added by syringe to a solution of molybdenum(V) chloride (4.25 g, 15.6 mmol) in methylene chloride (7 ml) contained in a 25-ml, dried flask equipped with Teflon-coated stirrer bar and capped with a rubber septum. The resulting mixture was stirred for 2 hr at room temperature before cautiously adding water (1 ml). The organic layer was separated, dried (MgSO$_4$), and passed through a short column of alumina. Analysis of the eluent indicated a 60% yield of 1-chloro-2-phenylethane. The infrared spectrum and retention time of sample collected from GLC was equivalent to that of authentic 1-chloro-2-phenylethane.

Conversion of 1,3-Dibromobutane to 1-Bromo-3-chlorobutane. Molybdenum(V) chloride (1.27 g, 4.66 mmol) was placed in a 25-ml, flame-dried flask equipped with a Teflon-coated stirrer bar and capped with a rubber septum. Dichloromethane (3 ml) was added by syringe followed by a solution of 1,3-dibromobutane (1.80 g, 8.32 mmol) in dichloromethane (2 ml). After stirring for 10 hr at room temperature, the reaction mixture was cautiously hydrolyzed with water (1 ml) and the organic layer was dried and passed through a short column of alumina. Analysis of the eluent by GLC indicated the major product (66%) to be 1-bromo-3-chlorobutane: M$^+$ m/e 170; ir (CS$_2$) 803 cm^{-1} [s, ν(C–Cl)]; ^{1}H NMR (CCl$_4$) δ 4.18 (sextet, 1 H), 3.49 (t, 2 H), 2.13 (quart, 2 H), 1.55 (d, 3 H).

Conversion of 1,1-Difluorocyclohexane to 1,1-Dichlorocyclohexane. Molybdenum(V) chloride (1.69 g, 6.20 mmol) was placed in a 25-ml, flame-dried flask equipped with Teflon-coated stirrer bar and capped with a rubber septum. Dichloromethane (3 ml) was added by syringe followed by a similar addition of a solution of 1,1-difluorocyclohexane in methylene chloride (3 ml). After 5 hr and a work-up similar to that described above, the reaction mixture was analyzed by GLC. The principal product (31%) as revealed by its retention time, mass, and infrared spectra, was 1,1-dichlorocyclohexane.[21]

Registry No.—MoCl$_5$, 10241-05-1.

References and Notes

(1) (a) Supported by the Research Corporation, and the donors of the Petroleum Research Fund, administered by the American Chemical Society. (b) Exxon Summer Research Fellow, 1974.
(2) (a) C. K. Ingold, *Q. Rev., Chem. Soc.,* **11**, 1 (1957). (b) Of much more limited use is halogen exchange by free-radical processes; see G. Sosnovsky, "Free Radical Reactions in Preparative Organic Chemistry", Macmillan, New York, N.Y., 1964, pp 308–313.
(3) Typical solvents include acetone,[4] ethanol,[5] or dimethylformamide.[6]
(4) H. B. Hass and H. C. Hoffman, *J. Am. Chem. Soc.,* **63**, 1233 (1941); M. S. Newman and R. D. Closson, *ibid.,* **66**, 1553 (1944); P. Coad et al., *J. Org. Chem.,* **28**, 218 (1963); M. Barash and J. M. Osbond, *J. Chem. Soc.,* 2157 (1959).
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(8) Exchange of bromide or iodide for fluoride can sometimes be carried out by displacement procedures[9] but is more commonly and efficiently performed by reaction with mercury(II) or silver(I) fluoride.[10]
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(13) J. San Filippo, Jr., and L. J. Romano, *J. Org. Chem.,* **40**, 1514 (1975).
(14) Under similar conditions, optically active 2-fluorooctane[13] (α^{20}_{589} −9.44°, 95% optically pure) is 11% racemized by MoCl$_5$ in 1 hr.
(15) Solvolysis studies of 2-phenylethyl derivatives have shown that 1,2-aryl migration proceeds concomitantly with ionization: W. J. Hehre, *J. Am. Chem. Soc.,* **94**, 5919 (1972), and references cited therein.
(16) The interchange of chloride or bromide for fluoride using mercury(II) fluoride also proceeds through the intermediacy of carbonium ions;[10] however, in contrast to the stereochemistry of chloride interchange using molybdenum(V) chloride, the reaction of (−)-(R)-2-bromooctane with mercury(II) fluoride in pentane at 25° yields (+)-(S)-2-fluorooctane (α^{20}_{589} 4.65°, 47% optical purity), indicating that reaction has occurred with a 74% net *inversion* of configuration. Neither optically active 2-bromonor 2-fluorooctane suffers any racemization under these conditions.[17]
(17) J. San Filippo, Jr., and L. Romano, unpublished results.
(18) Infrared spectra were determined within sodium chloride cells on a Perkin-Elmer Model 137 spectrophotometer. NMR spectra were determined with a Varian T-60 NMR spectrometer. Mass spectra were determined on a Hitachi Perkin-Elmer RMU-7E mass spectrometer. Analytical GLC analyses were performed on a Hewlett-Packard Model 5750 flame ionization instrument. Absolute product yields were calculated from peak areas using internal standard techniques with response factors obtained from authentic samples. Dichloromethane was distilled from phosphorus pentoxide immediately prior to use. GLC analysis were determined on a 20 ft × 0.25 in. column of 7.5% SE-30 on Gas-Chrom Z. All reactions and transfers of solids and liquids were performed under a nitrogen atmosphere. Unless otherwise indicated, starting halides and authentic product samples were obtained from commercial sources.
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Introduction of *N*-Vinyl Group into Tautomeric Heterocycles by the Exchange Reaction

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Vinyl exchange between vinyl acetate and a nitrogen heterocyclic compound is a valuable one-step preparation of *N*-vinyl heterocycles, and thus is important in the synthesis of polymers.[1] The reaction is acid catalyzed and is believed to proceed through two successive equilibria[1] as shown in eq 1.