Catalytic Bromide and Iodide Exchange of Alkyl Chlorides with HBr and HI

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The need to develop efficient methods for the conversion of the generally cheaper, readily available alkyl chlorides to the more reactive, synthetically useful alkyl bromides and iodides is addressed by the use of gaseous HBr and HI in the presence of a ferric halide catalyst. The simple catalytic procedure is especially applicable to secondary and tertiary alkyl chlorides as well as vicinal dichlorides at ambient temperatures in aprotic solvents such as dichloromethane and carbon tetrachloride. The unique role of the $FeBr_3$ catalyst to effect a reversible exchange of bromide via carbenium intermediates is discussed.

Introduction

Alkyl bromides and iodides, owing to their generally enhanced reactivity in comparison with the chloro analogues, are often the reagents of choice for alkylations—as in the preparation of different organometallic reagents (e.g., Grignard and alkyllithium reagents) and in various metal-catalyzed reactions.[1-5] Indeed, the need for the more reactive alkyl bromides and iodides has spawned many attempts at the efficient conversion of the more available alkyl chlorides.[6-23] Basically, these simple transformations have relied on essentially two processes that differ primarily in the source of the newly introduced halogen atom, namely, the classical nucleophilic substitutions on alkyl chlorides by various bromide and iodide salts[6] and the more recent sacrificial transhalogenation of alkyl chlorides with expendable alkyl bromides.[11] However, each has its limitations. For example, the Finkelstein procedure[6] exploits the solubility difference between the halide salts (e.g., NaI and NaCl in acetone) to effect the conversion of organic chlorides to iodides that could proceed to an unfavorable equilibrium were it not for the precipitation of the insoluble chloride salt.[7] Moreover, the difficulties in shifting such equilibria preclude the use of tertiary alkyl chlorides[8] as well as the high conversion of alkyl chlorides to bromides,[9-11] and vice versa.[12] In order to circumvent these problems, a variety of two-phase aqueous systems have been developed with phase-transfer agents such as quaternary ammonium salts[13-15] and crown ethers,[16] and gas-phase processes have been explored by passing the alkyl chlorides directly over metal bromides at elevated temperatures in the absence of solvent.[17,18] Transhalogen exchange between pairs of alkyl halides are promoted by polar solvents[11] or tertiary amines as catalysts.[19] In both, the high conversions to alkyl bromides free from the competitive elimination of alkene are continuing problems.

Catalytic amounts of ferric chloride have been used as a complement to the Finkelstein procedure in the conversion of tertiary alkyl and benzylic chlorides to their iodides with excess NaI in a nonpolar solvent.[20] However, this catalytic system is rather inactive and not effective for secondary and primary alkyl chlorides. An interesting system based on aluminum foil and bromine can be employed to effect halogen exchange between bridgehead halides and halogenated solvents.[24] Antimony pentachloride impregnated in graphite,[23] silver complexes,[22] and oxidative procedures[21] also promote halogen exchange of alkyl iodides in varying degrees to the corresponding bromides and/or chlorides.

None of these processes provide a convenient and highly efficient method for the conversion of secondary and tertiary alkyl chlorides to bromides, particularly without complications from elimination. Our new approach to this classic problem involves the use of gaseous HBr and catalytic amounts of anhydrous ferric bromide in dry dichloromethane.[25] We also describe in this study the application of the same concept to effect the corresponding conversion of alkyl chlorides to iodides.

Results

I. Preparation of Anhydrous Ferric Bromide and Ferric Iodide. Since the catalytic efficiency of the bromide exchange arose from small amounts of ferric bromide, it was prepared under rigorously anhydrous conditions to preclude any iron oxide contaminants. Ac-

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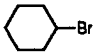
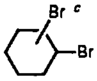
Table I. Catalytic Bromine Exchange of Cyclohexyl Chloride[a]

			products, mmol		
catalyst	HBr, mmol	time,[b] h			 [c]
$FeBr_3$	3	6.0		0.48	
$FeBr_3$	5	2.0		0.72	
$FeBr_3$	8	0.2	*d*	0.98	*d*
$FeBr_3$	8	15	*d*	0.96	*d*
$FeBr_3$[e]	8	0.5	*d*	0.99	*d*
$FeBr_2$[f]	8	48		0.085	

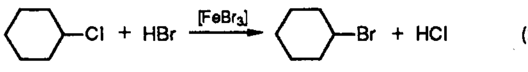
[a] In dichloromethane (8 mL) containing 1 mmol of cyclohexyl chloride and 0.033 mmol of catalyst at 25 °C. [b] Exposure followed by workup. [c] Mixture of mostly 1,2- and 1,3-dibromides by GC-MS analysis. [d] <0.05 mmol. [e] From 0.033 mmol of $Fe(CO)_5$ and 0.09 mmol of Br_2 and irradiation at 360 nm for 60 s. [f] 0.03 mmol added.

cordingly electrolytic iron (prereduced with a stream of hydrogen at 400 °C) was oxidized to ferric bromide with purified bromine in vacuo and then directly sublimed in the sealed tube at 200 °C.[26] Anhydrous $FeBr_3$ prepared in this manner consisted of extremely hygroscopic, dark violet crystals. For catalytic use, however, anhydrous ferric bromide was more conveniently prepared in situ from iron pentacarbonyl and bromine by actinic radiation ($\lambda > 360$ nm) according to the stoichiometry[27]

$$\mathrm{Fe(CO)_5} + \tfrac{3}{2}\mathrm{Br_2} \xrightarrow{h\nu} \mathrm{FeBr_3} + 5\mathrm{CO} \qquad (1)$$

An analogous procedure was used to prepare ferric iodide from either iron pentacarbonyl or diiodotetracarbonyliron(II) and iodine.[30]

II. Optimum Conversion of Cyclohexyl Chloride. Cyclohexyl chloride was selected as the prototypical substrate to establish the optimum reaction conditions for the catalytic bromide exchange under an inert (argon) atmosphere. Typically 1 mmol of cyclohexyl chloride was treated with varying amounts of hydrogen bromide and a saturated solution of ferric bromide ($\sim 4 \times 10^{-3}$ M) in dichloromethane. The conversion was directly proportional to the amount of HBr added, and the results in Table I show that essentially quantitative yields of cyclohexyl bromide were obtained with a 7 molar excess of HBr. Under these conditions the halogen exchange was complete within 15 min, and it could be readily carried out on the preparative scale (see Experimental Section). With less HBr (e.g., 2–4 molar excess), the formation of cyclohexyl bromide was not complete even upon prolonged stirring. Infrared spectral analysis of the atmosphere over the reaction mixture showed the characteristic bands of HCl according to the stoichiometry



(2)

The same bromide exchange could be carried out with a $FeBr_3$ catalyst that was prepared from iron pentacarbonyl and bromine by preirradiation of the dichloromethane solution with a tungsten lamp for a minute (see eq 1). Addition of cyclohexyl chloride and 8 mol of HBr yielded cyclohexyl bromide in 99% yield and only traces of the unreacted chloride. GC-MS analysis also revealed the presence of cyclohexane and isomeric dibromocyclohexanes in small amounts (<1%). The product distribution was unchanged after 15 h, and it indicated that cyclohexyl bromide was stable to the catalytic reaction mixture.

Ferrous bromide under the same conditions was inert, and no exchange of cyclohexyl chloride with HBr was observed. Other chlorinated hydrocarbons such as chloroform and carbon tetrachloride were also used as solvents for the conversion of cyclohexyl chloride. However, owing to a slow catalytic bromide exchange with HBr (vide infra), the least reactive dichloromethane was generally preferred. Ferric bromide was soluble in aromatic hydrocarbons such as benzene and toluene, but the slow bromination of these solvents led to its reductive deactivation.[31] Ferric bromide was also soluble in more polar solvents such as methanol, ethyl ether, dimethylformamide, and acetonitrile, but no catalytic activity was observed. Small amounts of water similarly deactivated the ferric bromide catalyst.

III. Structural Effects of Alkyl Chlorides on the Catalytic Bromine Exchange. A variety of structurally diverse alkyl chlorides was examined to establish the scope and limitations of the catalytic exchange with HBr. The results in Table II generally indicate that high conversions of secondary and tertiary alkyl chlorides could be attained with a standard 7 molar excess of HBr according to the stoichiometry in eq 2. Moreover, the reactive primary alkyl chlorides such as the benzylic and allylic derivatives also incorporated bromine efficiently.

Other primary alkyl chlorides were rather unreactive under the standard conditions. For example, *n*-butyl chloride showed poor conversions even after prolonged exposure to HBr. Bridgehead chlorides like the flexible 1-chloroadamantane reacted upon mixing, but the more constrained 1-chloronorbornane did not react.

Stereochemical retention was observed in the conversion of vicinal dichlorides. Thus *d*,*l*-2,3-dichlorobutane afforded high yields of *d*,*l*-2,3-dibromobutane, and the *meso*-dichloride similarly gave *meso*-2,3-dibromobutane without contamination from the *d*,*l* isomer. Likewise, the mixed chlorobromide *threo*-2-chloro-3-bromobutane yielded only *d*,*l*- and not *meso*-2,3-dibromobutane, and *erythro*-2-chloro-3-bromobutane afforded only *meso*- and not *d*,*l*-2,3-dibromobutane. However, the chlorine atom was not generally replaced stereospecifically since pure *exo*-2-norbornyl chloride afforded a 4:1 mixture of exo:endo bromides.

Rearrangement was observed as a side reaction of *n*-butyl chloride by the production of both *sec*- and *tert*-butyl bromide.[32] Small amounts of the latter were also obtained from *sec*-butyl chloride after prolonged periods of exposure. Skeletal rearrangement of 2,2-dichloronorbornane to a mixture of 1,2-dihalonorbornanes was complete within a short time.[33] Addition of HBr and HCl to an unsaturated bond was a limitation of this method., Thus allyl bromide was only a minor product of allyl chloride, the principal products being the HBr and HCl adducts, 1,2-dibromopropane and 1-bromo-2-chloropropane, respec-

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(27) For the photoinduced conversion of $Fe(CO)_5$ via $Fe(CO)_4Br_2$[28] to $FeBr_2$ and oxidative bromination via Br_2[29], see ref 25.

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(31) For example, $FeBr_3$ (0.51 mmol) and toluene (0.22 mmol) reacted at 25 °C to afford a mixture of *o*- and *p*-bromotoluenes. For the related aromatic chlorinations with $FeCl_3$, see: Kovacic, P.; Brace, N. O. *J. Am. Chem. Soc.* **1954**, *76*, 5491.

(32) Isobutyl bromide was not formed.

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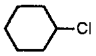
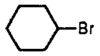
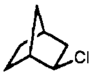
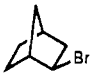
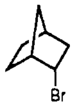
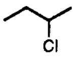
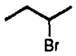
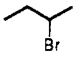
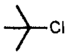
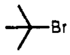
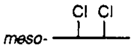
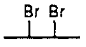
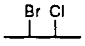
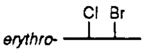
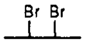
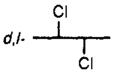
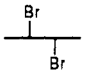
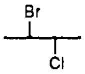
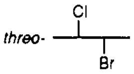
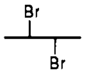
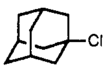
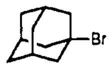
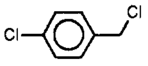
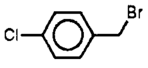
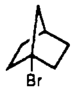
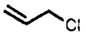
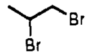
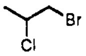
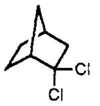
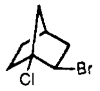
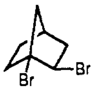
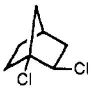
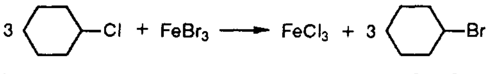
Table II. Reaction of Various Alkyl Chlorides with HBr Catalyzed by Ferric Bromide[a]

alkyl chloride	time, h	alkyl bromide	(%)	byproducts	(%)
	0.3 0.3[b]		(98) (99)	*c* *c*	
	0.3		(81)		(19)[d]
	0.3 15		(99) (97)	*e*	
	15		(5)		(13)[f]
	0.2		(98)		
	1 4		(54) (90)		(2)[g] (0)
	1		(98)	*h*	
	1 4		(46) (82)		(1)[i] (4)
	1		(97)	*h*	
	0.3 15		(78) (77)		(3)[j] (3)
	0.2		(96)	*k*	
	15		(0)		
	0.5 15 15[n]		(79) (93) (15)		(16)[m] (5) (398)[p]
	1[q]		(63)	 (13) 	(14)
	5		(24)[q]	(57)[r]	(2)[s]

[a] In 8 mL of CH_2Cl_2 containing 1 mmol of RCl, 8 mmol of HBr, and 3×10^{-2} mmol of $FeBr_3$ at 25 °C. Yield (%) in parentheses based on stoichiometry in eq 2 and GC analysis with the authentic standard. [b] Catalyst prepared in situ from 0.03 mmol of $Fe(CO)_5$ and 0.09 mmol of Br_2 by irradiation at 360 nm. [c] With traces (<1%) of cyclohexane and $C_6H_{10}Br_2$ (GC-MS). [d] With traces of norbornane and $C_7H_{10}Br_2$ (GC-MS). [e] *tert*-Butyl bromide (2%). [f] *tert*-Butyl bromide (3%). [g] *sec*-Butyl bromide (2%) plus $C_4H_7Br_3$ (1%, GC-MS). [h] Traces *sec*-butyl bromide and $C_4H_7Br_3$ (GC-MS). [i] *sec*-Butyl bromide (2%) plus $C_4H_7Br_3$ (2%), GC-MS. [j] Adamantane (9%) plus 1,3-$C_{10}H_{14}Br_2$ (9%, GC-MS). [k] *p*-$ClC_6H_4CH_3$ (traces) plus $C_7H_5ClBr_2$ (GC-MS). [m] 1-Cl-2-BrC_3H_6 (2%), 1,2-$Cl_2C_3H_6$ (1%), and allyl bromide (2%). [n] 10 mmol of allyl chloride. [p] 1-Cl-2-BrC_3H_6 (4%), 1,2-$Cl_2C_3H_6$ (36%), and allyl bromide (352%). [q] 2,2-Dibromonorbornane (24%). [r] Consisting of 7:3 mixture of exo/endo isomers. [s] 2-Chloronorbornane (4%).

tively. The relative amounts of the latter were time dependent (Table II), and it suggested a bromine-for-chlorine exchange similar to that obtained from *threo*- and *erythro*-2-chloro-3-bromobutane (entries 7 and 9). Another side reaction was the disproportionation of the products to an equimolar mixtue of reduced and dibrominated products, as indicated by the small amounts of cyclohexane as well as dibromocyclohexanes obtained from cyclohexyl chloride (vide supra) and norbornane and dibromonorbornanes from norbornyl chloride. The extent of such an apparent disproportionation was generally minor, except with 1-chloroadamantane, in which as much as 10% adamantane was detected. The disproportionation products appeared to arise in the course of halogen exchange since the product distribution did not change if the reaction mixture was left standing for prolonged times.

IV. Stoichiometric Exchange of Alkyl Chlorides with Ferric Bromide. The catalytic role of ferric bromide was probed directly by treating various alkyl chlorides with stoichiometric amounts of $FeBr_3$ in the absence of added HBr. When a 10–20 molar excess of cyclohexyl chloride was added to the catalyst solution in the absence of HBr, the dark red color of $FeBr_3$ (Figure 1) was quickly bleached to an almost colorless pale yellow-green solution. However, when HBr was introduced, the almost colorless dichloromethane solution gradually regained its original dark red coloration over a 10-min period. Since the pale yellow-green solution was spectrally indistinguishable from a solution prepared from authentic anhydrous $FeCl_3$, we concluded that the stoichiometric exchange occurred as follows (vide infra).[34]


(3)

GC-MS analysis of the reaction mixture indeed revealed the presence of 3 mol of cyclohexyl bromide for each mol of $FeBr_3$ (Table III). When less cyclohexyl chloride (e.g.,

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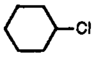
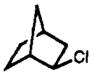
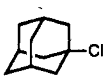
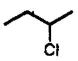
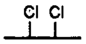
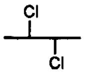
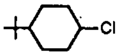
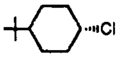
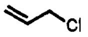
(34) These stoichiometric bromine exchanges also afforded more byproducts (Table III).

Table III. Stoichiometric Bromine Exchange of Alkyl Chlorides with FeBr$_3$[a]

RCl	mmol	FeBr$_3$, mmol	time, h	RBr,[b] mmol	byproducts,[c] mmol		
					R′ClBr		R′Br$_2$
	1.44	0.36	15	0.76	0.01		0.02
	2.50	0.12	0.2	0.35	–		–
	2.11[d]	0.42	24	1.01	0.01		0.02
					RH		R′Br$_2$
	2.02	0.41	1.0	0.49[e]	0.04		0.04
	2.02	0.41	1.5	0.76[e]	0.07		0.07
	2.02	0.41	15	0.95[e]	0.10		0.09
	2.50	0.15	0.2	0.44[e]	<0.05		<0.05
					RH	R′BrCl[g]	R′Br$_2$[g]
	1.52	0.32	1.5	0.41 (0.06)[f]	0.11	0.07	0.02
	1.52	0.32	15	0.64 (0.07)[f]	0.11	0.09	0.05
	1.99	1.58	1.0	1.04 (0.05)[f]	0.06	0.12	0.30
	2.15	1.08[h]	1.5	1.07 (0.09)[f]	0.10	0.19	0.27
					R′Cl$_2$[j]	R′BrCl[k]	R′Br$_2$[j]
	1.80	0.36	1.3	0.60	0.02	0.04	0.01
	1.80	0.36	15	0.84	0.03	0.06	0.03
					R′BrCl[k]	R′Br$_2$[j]	
	1.98	0.37	1.5	<0.05 (0.03)[m]	<0.05	<0.05	
	1.98	0.37	15	0.10 (0.05)[m]	0.03	0.09	
	2.04	0.42	25	0.15	0.78	(erythro RClBr)	
	1.98	0.41	25	0.19	0.73	(threo RClBr)	
	0.77	0.39	17	0.22	0.37	(threo RClBr)	
	cis 1.00	0.33	2	0.16 (0.07)[n]	RCl	(0.18), [0.09][n]	
	trans 1.00	0.32	2	0.09 (0.22)[p]	RCl	(0.16), [0.18][p]	
	2.08	0.42	15	0.70	RHBr$_2$,	etc.[q]	
CCl$_4$	100	3.74	48	1.30	0.03	(CBr$_2$Cl$_2$)	
	100	3.74	168	3.90	0.10	(CBr$_2$Cl$_2$)	

[a] In 8 mL of CH$_2$Cl$_2$ at 25 °C, unless indicated otherwise. [b] R as in column 1. [c] R′ = R(-H). Analysis by GC-MS in Experimental Section. [d] In CHCl$_3$. [e] Exo/endo = 4:1. [f] 2 isomer. [g] Mainly 1,3 isomer. [h] Also contains 0.92 mmol of FeBr$_2$. [j] *meso*/*d,l* mixture. [k] Erythro/threo mixture. [m] 2 isomer. [n] Trans isomer. [p] Cis isomer. [q] Mixture of 1,2-Br$_2$C$_3$H$_6$ (0.03), 1,2-Cl$_2$C$_3$H$_6$ (0.09), and 1-Br-2-ClC$_3$H$_6$ (0.10 mmol) based on GC-MS and reactivity.

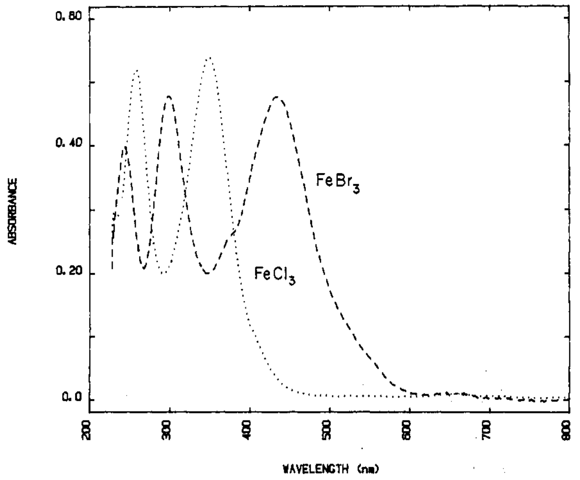


Figure 1. Electronic absorption spectra of 10^{-4} M ferric bromide (---) and ferric chloride (···) in dichloromethane solution.

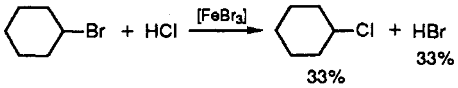
3–4 molar excess) was charged, ~2.4 mol of cyclohexyl chloride reacted with each mol of FeBr$_3$ at 25 °C. From these stoichiometric reactions, we deduced that at some stage of the stepwise replacement of the three bromo ligands on FeBr$_3$, the exchange process was reversible (vide infra).

Although rate measurements were not attempted, qualitative indications of reactivity could be inferred from the product analysis. For example, with a 4 molar excess of *sec*-butyl and 2-norbornyl chlorides, 2 mol of the corresponding bromides were obtained within a 2-h period. The vicinal dichlorobutanes appeared to react slower than *sec*-butyl chloride, but nonetheless proceeded with high selectivity. Even carbon tetrachloride yielded reasonable amounts of bromotrichloromethane over a long period.

The absence of stereochemical retention with 2-norbornyl chloride in the catalytic system (Table II) was confirmed in the stoichiometric exchange. Furthermore *cis*- and *trans*-4-*tert*-butylcyclohexyl chlorides yielded the same cis/trans mixture of bromo derivatives. Except for the slightly enhanced importance of the side reactions, the principal products of the stoichiometric exchange in Table III were largely indistinguished from those obtained in the catalytic system (Table II).

V. Transhalogen Exchange of Alkyl Halides Catalyzed by Ferric Bromide. Three series of reverse transformations were examined in order to establish the reversibility of the catalytic exchange.

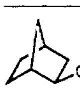
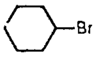
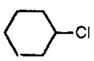
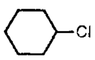
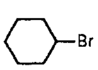
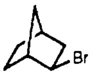
(a) Cyclohexyl bromide was treated with a 7 molar excess of anhydrous HCl in dichloromethane containing 4 × 10^{-3} M FeBr$_3$. Within a 2-h period, an equimolar mixture of cyclohexyl chloride and HBr was observed, Table IV.



(4)

The same treatment of *exo*-2-norbornyl bromide yielded an analogous mixture containing equal yields of 2-nor-

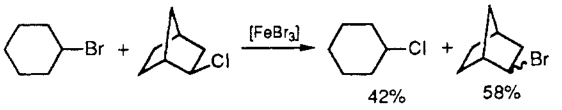
Table IV. Catalytic Transhalogen Exchange of Alkyl Halides[a]

RCl	(mmol)	R′Br	(mmol)	time, h	products, mmol RBr	products, mmol R′Cl
	(1.00)[b]		(1.00)	2 6	0.59[c] 0.59[c]	0.42 0.41
	(1.00)	CBr_4	(5.00)	15	0.79	0.73[d]
	(1.00)	HBr	(8.0)	0.2	0.98	0.98[e,f]
HCl	(8.0)		(1.00)	2 6	0.23[f,g] 0.23[f,g]	0.23 0.23
HCl	(8.00)		(1.00)	2 6	0.25[f,g] 0.27[f,g]	0.25[c] 0.27[c]

[a] In 8 mL of CH_2Cl_2 containing 0.037 mmol of $FeBr_3$ at 25 °C. [b] Exo reactant not analyzed after exchange. [c] Endo/exo mixture. [d] With 0.05 mmol of CBr_2Cl_2. [e] HCl. [f] Estimated from IR spectrum. [g] HBr.

bornyl chloride and HBr. No exchange occurred in the absence of ferric bromide under these conditions.

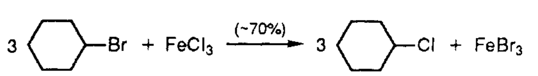
(b) Equimolar quantities of cyclohexyl bromide and *exo*-2-norbornyl chloride were mixed at 25 °C in dichloromethane containing 4 × 10^{-3} M $FeBr_3$. After 2 h, GC-MS analysis indicated that the reaction mixture contained comparable amounts of 2-norbornyl bromide and cyclohexyl chloride.[35]



(5)

Analogously, a mixture of cyclohexyl chloride and carbon tetrabromide slowly produced the same yields of cyclohexyl bromide and bromotrichloromethane as listed in Table IV. No exchange occurred under these conditions in the absence of ferric bromide.

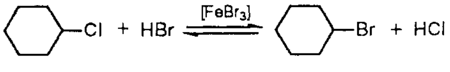
(c) A pale yellow-green solution containing 6 × 10^{-2} M anhydrous $FeCl_3$ was treated with excess cyclohexyl bromide in dichloromethane at 25 °C. The solution immediately turned dark red, and GC-MS analysis within 10 min indicated that 1.8 mol of cyclohexyl chloride were formed for each mol of ferric chloride charged.



(6)

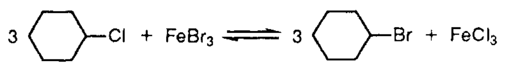
The amount of cyclohexyl chloride did not increase with time, however, and after 15 h, a slightly decreased yield was noted together with small amounts of polyhalogenated byproducts (by GC-MS analysis).

The $FeBr_3$ catalysis of both eq 2 and 4 indicated that the halogen exchange was reversible, i.e.



(7)

Moreover, the stoichiometric exchanges observed in eq 3 and 6 were consistent with a similar high degree of reversibility, i.e.



(8)

The combination of the equilibria in eq 7 and 8 thus added up to the reversible ligation of the iron(III) catalyst, i.e.

$$FeBr_3 + 3HCl \rightleftharpoons FeCl_3 + 3HBr \qquad (9)$$

The rapidity of the ligand exchange in eq 9 was apparent in the instantaneous conversion of the pale yellow-green solution of $FeCl_3$ (see Figure 1) to the characteristic dark red solution of $FeBr_3$ upon the introduction of anhydrous HBr gas. The reverse was also apparent by the bleaching of the dark red solution of $FeBr_3$ in dichloromethane by anhydrous HCl, albeit at a slightly slower rate. Indeed the presence of both HCl and HBr over the catalytic reaction mixture (Tables I and II) was readily observed by IR spectroscopy over the course of the catalytic halogen exchange.

VI. $FeBr_3$-Induced Isomerization, Rearrangement, and Disproportionation of Alkyl Bromides. Owing to the significant amounts of rearranged and disproportionation products that were observed in the catalytic bromide exchange of 2-norbornyl and 1-adamantyl chlorides (Table II), the product stability was independently tested by the exposure of various alkyl bromides to $FeBr_3$ under the reaction conditions.

The addition of pure *exo*-2-norbornyl bromide to $FeBr_3$ in dichloromethane solution at 25 °C led rapidly to the endo isomer in 17% yield (entry 7, Table V). The amount of *endo*-2-norbornyl bromide was comparable to that formed in the catalytic (Table II) and stoichiometric (Table III) exchanges.

The bridgehead derivative, 1-bromoadamantane, was rapidly converted to the 2-bromo isomer (~3%) upon its exposure to $FeBr_3$ in dichloromethane. Moreover, the reverse rearrangement of 2-bromoadamantane by $FeBr_3$ to the bridgehead derivative was effected to high conversion (>80%) within 20 min in dichloromethane solutions. This catalytic rearrangement occurred progressively slower in chloroform and carbon tetrachloride, probably owing to the reduced solubility of $FeBr_3$ in these media.[36] In the latter cases, chloride exchange with the solvent led to discrete amounts of the chloroadamantanes. The mixture of 1- and 2-bromoadamantane in a roughly 20–25 ratio (Table V) was reminiscent of the equilibrium mixture of 1-/2-chloroadamantane $\simeq$ (15–21) obtained from the $FeCl_3$-catalyzed isomerization of either 1- or 2-chloroadamantane in refluxing carbon tetrachloride solutions.[38,39]

In the presence of $FeBr_3$, *cis*-1,2-dibromocyclohexane was slowly converted to the 1,3 and 1,4 isomers in dichloromethane at 25 °C. This isomerization accorded with those observed in the stoichiometric bromine exchange (see, e.g., *tert*-butylcyclohexyl chloride in Table III).

In the course of the catalytic rearrangement of 1- and 2-adamantyl bromides, significant amounts of the disproportionation products, adamantane and dibromoadamantanes, were observed in roughly equimolar amounts (see Table V). An analogous disproportionation to yield norbornane and dibromonorbornane also occurred during the isomerization of *exo*-2-norbornyl bromide, although to a reduced degree.

VII. Catalytic Conversion of Alkyl Chlorides to Alkyl Iodides. Catalytic iodide exchange of alkyl chlorides by the same methodology involved the use of ferric

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[35] The slightly higher yields of norbornyl bromide derive from the profunctional exchange of the chloride with the added $FeBr_3$.

[36] The trend also parallels the decrease in the dielectric constants of CH_2Cl_2, $CHCl_3$, and CCl_4 as 9.08, 4.81, and 2.24, respectively.[37]

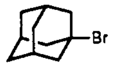
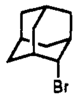
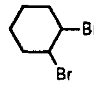
[37] Dean, J. A. *Lange's Handbook of Chemistry*, 13th ed.; McGraw-Hill: New York, 1985; pp 10–103 ff.

[38] Kovacic, P.; Chang, J. H. *J. Org. Chem.* **1971**, *36*, 3138.

[39] Compare also the ratios of 20–50 for the 1/2 isomers in the $AlCl_3$ catalysis at room temperature.[40]

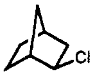
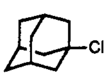
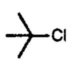
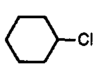
[40] Gerzon, K.; Krumkalns, E. V.; Brindle, R. L.; Marshall, F. J.; Root, M. A. *J. Med. Chem.* **1963**, *6*, 760.

Table V. Catalytic Isomerization, Rearrangement, and Disproportionation of Alkyl Bromides[a]

RBr	(mmol)	$FeBr_3$, mmol	solvent	time, h	products, mmol RH	RBr	R′Br	other
	(1.07)	0.36	CH_2Cl_2	0.4	0.15	0.77	0.04[b]	0.11[c,d]
				21	0.09	0.79	0.03[b]	0.11[c,e]
	(0.76)	0.36	CH_2Cl_2	0.8	0.12	0.03	0.56[f]	0.06[c]
				16	0.20	0.02	0.51[f]	0.10[c]
	(0.69)	0.50	CH_2Cl_2	0.3	0.07	0.02	0.52[f]	0.05[c,h]
				16	0.07	0.02	0.49[f]	0.03[c,i]
	(0.71)	0.38	$CHCl_3$	0.3	0.03	0.61	0.03[f]	0.03[g]
				16	0.04	0.02	0.53[f]	0.06[c,j]
	(0.76)	0.35	CCl_4	0.3	0.01	0.75	<0.01[f]	
				16	0.03	0.57	0.03[f]	0.02[g,k]
	(0.70)	(0.07)[l]	CH_2Cl_2	24	0.03	0.59	0.03[f]	0.03[g]
	(1.01)	0.033	CH_2Cl_2	0.5	0.02	0.81	0.17[m]	0.02[n]
				16	0.02	0.77	0.21[m]	0.02[n]
	(0.96)	0.033	CH_2Cl_2	0.5	0	0.73[o]	0.01[p]	0.22[q]
				4.5	0	0.40[o]	0.05[p]	0.50[q]

[a] In 8 mL of solvent at 25 °C. [b] 2 isomer. [c] Mainly 1,3-dibromoadamantane. [d] With 0.002 mmol of RCl. [e] With 0.02 mmol of RCl and 0.003 mmol of Cl,Br-$C_{10}H_{14}$. [f] 1 isomer. [g] 1,3-Dibromo isomer as minor component. Together with [h] *0*.009, [i] *0*.03, [j] *0*.04, [k] *0*.10 mmol of RCl. [l] $FeBr_2$. [m] Endo isomer based on NMR analysis. [n] Mixture of $Br_2C_7H_{10}$ isomers. [o] 1,2-$Br_2C_6H_{10}$ mixture. [p] 1,3-$Br_2C_6H_{10}$ mixture. [q] 1,4-$C_2H_{10}Br_2$ mixture.

Table VI. Catalytic Iodine Exchange of Alkyl Chlorides[a]

RCl	$Fe(CO)_5/I_2$,[b] mmol/mmol	solvent	temp, °C	time, h	RI, mmol
	0.033/0.098	CH_2Cl_2	25	0.5	1.00[c]
	0.033/0.098	CH_2Cl_2	25	0.5	0.98
	0.033/0.098	CH_2Cl_2	25	0.5	0.98
	0.033/0.098	CH_2Cl_2	25	15	0.03
	0.033/0.098	CCl_4	80	10	0.51
	0.50/1.5	CH_2Cl_2	25	8	0.08
	0.50/1.5	CCl_4	80	6	0.40

iodide and HI. Since FeI_3 is extremely labile,[30] it was prepared in situ from iron pentacarbonyl and iodine by a procedure analogous to that in eq 1, viz.

$$Fe(CO)_5 + {}^3\!/\!_2 I_2 \rightarrow FeI_3 + 5CO \qquad (10)$$

The partial results in Table VI show that the iodide exchange generally followed the reactivity pattern established for the bromide exchange in Table II. Thus the tertiary alkyl chlorides, *tert*-butyl and 1-adamantyl chlorides, were converted to the corresponding iodides in high yields within 30 min at 25 °C. Similarly the rather reactive secondary alkyl chloride *exo*-2-chloronorbornane afforded essentially quantitative yields of 2-iodonorbornane consisting primarily (95%) of the exo isomer. [See the Experimental Section for the preparation of norbornyl iodide on the preparative scale.] However, the conversion of the less reactive secondary alkyl chloride, chlorocyclohexane, was significantly less effective, and it produced only ~50% yields of cyclohexyl iodide in refluxing carbon tetrachloride. Part of the difficulty in achieving high conversions with the less reactive alkyl chloride could be accounted for by the deactivation of the labile ferric catalyst, i.e.[30]

$$2\ FeI_3 \rightarrow 2\ FeI_2 + I_2 \qquad (11)$$

The catalytic iodide exchange had the earmarks of the bromide exchange described above. For example, when

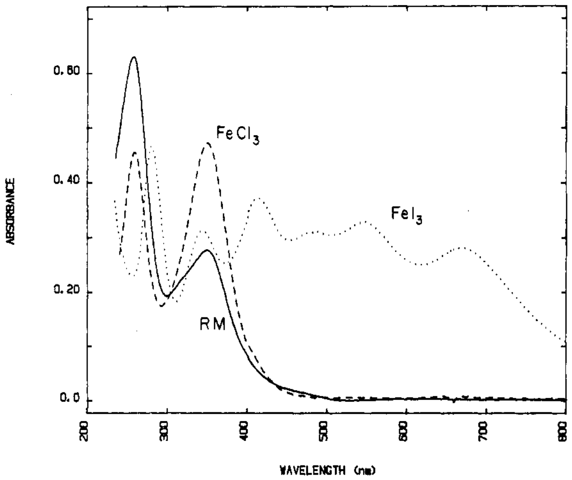
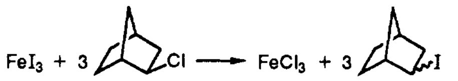


Figure 2. Formation of ferric chloride (—) in the reaction mixture (RM) from the treatment of 10^{-4} M ferric iodide (···) with 20 equiv of norbornyl chloride in dichloromethane at 0 °C. Authentic spectrum of ferric chloride is indicated by (- - -) and note that the excess absorbance at λ ~255 nm is due to absorption by norbornyl iodide (λ_{max} = 256 nm).

a freshly prepared solution of ferric iodide in dichloromethane was treated with norbornyl chloride, it was immediately converted to ferric chloride. Gas chromatographic analysis of the reaction mixture established that 3 mol of norbornyl iodide was produced, i.e.



(12)

The changes in the UV–vis absorption spectrum accompanying the substitution process of ferric iodide (FeI_3) in eq 12 are illustrated in Figure 2. The spectral comparison of the reaction mixture (RM) with that of a dichloromethane solution of authentic ferric chloride ($FeCl_3$) was indeed consistent with the complete replacement of all the iodo ligands when excess norbornyl chloride was employed. The metathesis in eq 12 was also reversible. Thus the treatment of a dilute solution of ferric chloride with excess norbornyl iodide led to norbornyl chloride, accompanied by an immediate darkening of the pale yellow solution to

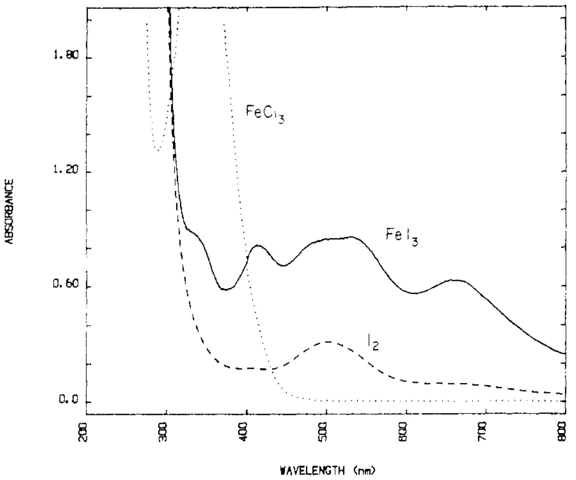


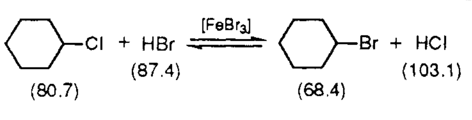
Figure 3. Formation of ferric iodide (b, —) immediately after the addition of 20 equiv of norbornyl iodide to 10^{-4} M ferric chloride (a, ···) in dichloromethane. The same solution after 5 min in the dark (c, - - -) shows the presence of only diiodine (λ_{max} = 504 nm).

a blue-violet ink. The dramatic change in the absorption spectrum of ferric chloride (a) to ferric iodide (b) is illustrated in Figure 3. However, the ferric iodide formed in this manner was rather unstable, and it decomposed readily (~5 min) to a mixture of ferrous iodide and diiodine (λ_{max} = 504 nm) as shown in Figure 3c. Moreover, with the less reactive cyclohexyl chloride, ferric iodide was not observed as a spectral transient. Instead, only the absorption band of diiodine was detected as the ferric iodide disappeared. Clearly the rate of decomposition of ferric iodide under these conditions (eq 11) exceeded its formation according to eq 12 (with cyclohexyl as the alkyl moiety).

Discussion

A variety of secondary and tertiary alkyl chlorides are rapidly converted to the corresponding bromides by exposure to excess HBr in the presence of catalytic amounts of anhydrous ferric bromide in dichloromethane solutions. The procedure for bromide exchange can be considerably facilitated by the in situ preparation of the moisture-sensitive catalyst from $Fe(CO)_5$ and bromine according to eq 1. Furthermore the ready workup of the reaction mixture primarily entails only the simple removal of the gaseous HCl and the excess HBr together with the volatile solvent. The simplicity of the catalytic procedure and its rapidity under mild conditions also recommend it as the method of choice for the conversion of labile tertiary alkyl chlorides to their iodo analogues. However, the added expense to procure anhydrous hydrogen iodide could discourage its use for the less reactive alkyl chlorides.

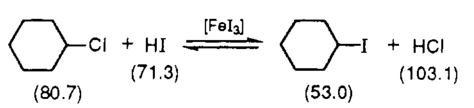
I. Thermodynamics of Halogen Exchange. The presence of a 7 molar excess of HBr is sufficient to drive the bromide exchange of cyclohexyl chloride virtually to completion in eq 2. Conversely, the exposure of cyclohexyl bromide to equivalent amounts of HCl leads to cyclohexyl chloride in 23% conversion according to eq 4. Indeed the limited conversion for the microscopic reverse in eq 4 accords with $\Delta H = -3.4$ kcal mol^{-1} for the reversible process



(13a)

from the thermochemical computation based on the bond dissociation energies indicated by the values in parentheses in eq 13a.[41] Such an overall enthalpy change in essence derives from a bond-energy difference between HBr and HCl (ΔE = 15.7 kcal mol^{-1}) that is larger than that between cyclohexyl chloride and bromide (ΔE = 12.3 kcal mol^{-1}).

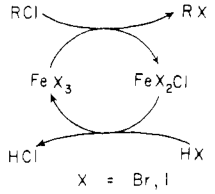
The enthalpy change for iodide exchange is essentially the same as that for the bromide exchange, i.e.



(13b)

since the change in ΔE between HI and HCl relative to the change in ΔE between cyclohexyl iodide and chloride is more or less the same as that for the comparable quantities in bromide exchange in eq 13a.

II. Stepwise Catalytic Mechanism for Halogen Exchange. The stoichiometric exchanges of bromine and iodine between alkyl chloride and ferric bromide and iodide in eq 3 and 12, respectively, support a multistep process for the catalysis. Coupled with the observation of the chlorine transfer in eq 4 and 6, a pair of reversible halogen exchanges can be presented as the catalytic mechanism in eq 14 and 15.



(14)

(15)

According to eq 14 and 15, the catalysis derives from an active ferric halide that remains as FeX_3 as long as sufficient HBr or HI exists to drive the equilibrium in eq 15 (X = Br, I). The extent to which the latter does not pertain (as in the stoichiometric exchanges) leaves open the possibility of halogen exchange by other ferric species, e.g.

$$RCl + FeX_2Cl \rightleftharpoons FeXCl_2 + RX \tag{16}$$

$$RCl + FeXCl_2 \rightleftharpoons FeCl_3 + RX \tag{17}$$

Since the halogen exchange of ferric halides is rapid,[42] i.e.

$$FeX_nCl_m + HX \xrightleftharpoons{\text{fast}} FeX_{n+1}Cl_{m-1} + HCl \tag{18}$$

where $n + m = 3$, we anticipate that the ferric-induced scission of the carbon–chlorine bond as in eq 14, 16, and 17 represents the rate-limiting step in the catalytic cycle. Furthermore the comparable strengths of iron–halogen and carbon–halogen bonds[43] also suggest that the enthalpy changes for eq 14 (16 and 17) are more or less in line with those for the overall process in eq 13. If so, it could account for the unusually facile reversibility that is observed in the catalytic exchange with ferric halides. Contrastingly, the ready conversions of methyl chloride to bromide with aluminum bromide and methyl chloride to iodide with aluminum iodide cannot be carried out in the reverse fashion owing to the high exothermicity of the forward exchange.[44] Indeed mixtures of isopropyl and *n*-propyl

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(41) McMillen, D. F.; Golden, D. M. *Ann. Rev. Phys. Chem.* **1982**, *33*, 493.

(42) (a) As indicated by the rapid color change of $FeCl_3$ to that of $FeBr_3$ on the introduction of HBr. (b) Iron(III) complexes are generally substitution labile. (See: Basolo, F.; Pearson, R. G. *Mechanisms of Inorganic Reactions*, 2nd ed.; Wiley: New York, 1967; p 197 ff.)

(43) Kerr, J. A.; Parsonage, M. J.; Trotman-Dickenson, A. F. In *Handbook of Chemistry and Physics*, 55th ed.; CRC Press: Cleveland, 1974; p F-204.

(44) Brown, H. C.; Wallace, W. J. *J. Am. Chem. Soc.* **1953**, *75*, 6279.

iodides with $AlBr_3$ evolve HBr even at 0 °C.[45] Approximately 2% exchange was also observed for a mixture of methyl bromide and $GaCl_3$ within a 24-h period.

III. Comments on the Alkyl Exchange with Ferric Halide. The facile and reversible halogen exchanges in Tables I–IV underscore the unique role of ferric halide in mediating the catalytic process. Unfortunately the complex series of rapid halogen exchanges described above largely preclude a detailed rate study to establish the precise kinetic order of the ferric species in the rate-limiting step. Accordingly, for purposes of delineating the reactivity patterns, the stereochemistry and the byproduct formation that are pertinent to the catalysis let us focus on only that step in which the alkyl moiety undergoes substitution, that is tentatively identified as eq 14.

The enhanced reactivities of tertiary alkyl, benzylic, and allylic chlorides relative to secondary alkyl chloride, together with the relatively slow exchange of primary alkyl chlorides (Table II), are consistent with the heterolytic scission (as opposed to homolysis) of the alkyl–halogen bond in the course of exchange. Under these circumstances, the role of iron is best accommodated as that of a Lewis acid,[46] e.g.

$$RCl + FeBr_3 \rightarrow R^+ClFeBr_3^- \qquad (19)$$

The stereochemical results, the alkyl rearrangements, and the nature of the byproducts all point to the formation of a discrete carbenium ion or an ion pair as depicted in eq 19. The complete loss of stereochemistry in the bromide exchange with *exo*-2-norbornyl and *cis*- and *trans*-4-*tert*-butylcyclohexyl chlorides preclude any synchronous bond-making/breaking process via an oxidative adduct or a four-center transition state.[47] The remarkably high, if not exclusive, overall stereochemical retention obtained in both (a) the bromide exchange of *threo*- and *erythro*-2-chloro-3-bromobutane and (b) the bis-bromide exchange of *d,l*- and *meso*-2,3-dichlorobutane (see Table II) provides the most compelling evidence that a relatively "free" cation is formed in eq 19. In both cases, the halogen-bridged cations

would represent the intermediates that are responsible for overall stereochemical retention.[48] Indeed the marked difference in reactivity between the bridgehead 1-chloroadamantane and 1-chloronorbornane emphasizes the presence of a substantial driving force that derives from carbenium ion formation in eq 19.[49]

The presence of a cationic intermediate during the catalytic bromine exchange is also indicated by the complete rearrangement of 2,2-dichloronorbornane to a mixture of mainly the exo isomers of 1,2-dichloro-, 1-chloro-2-bromo-, and 1,2-dibromonorbornane (entry, 14, Table II).[33,50] Analogous Wagner–Meerwein rearrangements are apparent in the extensive rearrangement of the 1-adamantyl moiety to the 2-isomer and the reverse transformation described in Table V.[51] Moreover the formation of small but discrete amounts of *tert*-butyl bromide from *sec*-butyl chloride (entry 3) and the preponderance of *sec*-butyl and *tert*-butyl bromides in the slow bromide exchange of *n*-butyl chloride (entry 4) are classical examples in which the rearrangement of carbenium ion intermediates pertains.[52]

The formation of alkanes from the catalytic bromine exchange was most apparent with 2-norbornyl and 1-adamantyl chlorides; a small amount of cyclohexane was also detected by GC-MS analysis of the exchange products from cyclohexyl chloride. Since more or less equivalent amounts of dibromoalkanes accompanied the alkane, the side reaction is best described as a disproportionation, i.e.

$$2RHBr \rightarrow RH_2 + RBr_2 \qquad (20)$$

Such a process can be ascribed to hydride transfer by a reactive carbenium ion, e.g.[53]

$$RHCl + FeBr_3 \rightleftharpoons RH^+FeBr_3Cl^- \qquad (21)$$

$$RH^+ + RHCl \rightarrow RH_2 + RCl^+ \qquad (22)$$

$$RCl^+ + FeBr_3Cl^- \rightleftharpoons RClBr + FeBr_2Cl, \text{ etc.} \qquad (23)$$

where RH = cyclohexyl, 2-norbornyl, 1-adamantyl, etc., examined in this study. Such a catalytic disproportionation appears to be less important in iodide exchange owing to the high yields of tertiary alkyl iodides that are indicated in Table VI. However, significantly lower conversions are attained with the less reactive secondary alkyl chlorides. In these cases, the prolonged reaction times led to dark brown crystals of ferrous iodide by the reductive decomposition of the FeI_3 catalyst according to eq 11. An analogous deactivation of $FeBr_3$ was noted in the course of slow bromide exchanges (>10 h), by the separation of a yellow-brown amorphous solid that could not be reactivated by the further addition of HBr. The deposit was tentatively assigned to ferrous bromide (see Experimental Section) formed by a slow reductive decomposition similar to that described in eq 11. If so, it is promoted by alkyl chlorides, since the dark red solutions of ferric bromide alone in dichloromethane persist for >15 h under comparable conditions.

Experimental Section

Materials. Electrolytic grade iron powder (Glidden metals, SCM Corp.) was pretreated under an atmosphere of dihydrogen at 400 °C for 24 h to remove oxides. Anhydrous ferric bromide ($FeBr_3$) was prepared as shiny dark violet crystals from iron powder and purified bromine in a sealed tube according to the procedure described in the literature.[26] Anhydrous ferrous bromide ($FeBr_2$) was prepared from the decomposition of ferric bromide by heating at 140 °C under a stream of dry nitrogen for 6 h or at 120 °C in vacuo for 10 h. Adamantane and 1-chloro-, 1-bromo-, and 2-bromoadamantane (Aldrich) were purified by sublimation or crystallization from methanol. 1,3-Dibromoadamantane was isolated by silica gel chromatography of the reaction mixture from 1-chloroadamantane (1.7 g) and $FeBr_3$ (1 g) in 50 mL of CH_2Cl_2.[54] 1-Adamantyl iodide was obtained by

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(45) Brown, H. C.; Eddy, L. P.; Wong, R. *J. Am. Chem. Soc.* **1953**, *75*, 6275.

(46) (a) Olah, G. A. *Friedel-Crafts and Related Reactions*; Wiley-Interscience: New York, 1964; Vol. 1, Chapter 4. (b) Olah, G. A. *Friedel-Crafts Chemistry*; Wiley-Interscience: New York, 1973; p 293.

(47) Compare Tsou, T. T.; Kochi, J. K. *J. Org. Chem.* **1980**, *45*, 1930.

(48) See: Capon, B.; McManus, S. P. *Neighboring Group Participation*; Plenum: New York, 1976. (b) de la Mare, P. B. D. *Electrophilic Halogenation*; Cambridge University Press: London, 1976. (c) See: de la Mare and Swedlund in ref 7, p 407. (d) Modena, G.; Scorrano, G. in ref 7, p 301.

(49) For a summary of bridgehead reactivities, see: Hine, J. *Physical Organic Chemistry*, 2nd ed.; McGraw-Hill: New York, 1962; p 165 ff.

(50) For a summary of 2-norbornyl cation rearrangements, see: le Noble, W. J. *Highlights of Organic Chemistry*; Dekker: New York, 1974; p 165 ff.

(51) Schleyer, P. v. R.; Lam, L. K. M.; Raber, D. J.; Fry, J. L.; McKervey, M. A.; Alford, J. R.; Cuddy, B. D.; Keizer, V. G.; Geluk, H. W.; Schlatman, J. L. M. *J. Am. Chem. Soc.* **1970**, *92*, 5246.

(52) For a summary, see: Lowry, T. H.; Richardson, K. S. *Mechanism and Theory in Organic Chemistry*, 2nd ed.; Harper and Row: New York, 1981; Chapter 5.

(53) Compare: Bartlett, P. D.; Condon, F. E.; Schneider, A. *J. Am. Chem. Soc.* **1944**, *66*, 1531.

iodine exchange of 1-adamantyl chloride. *meso-* and *d,l*-2,3-dichlorobutane were prepared by the standard chlorine addition to *trans-* and *cis*-2-butene, respectively. *meso-* and *d,l*-2,3-dibromobutanes were similarly prepared from *trans-* and *cis*-2-butene and bromine.[55] *cis-* and *trans*-4-*tert*-butylcyclohexyl chlorides were prepared from 4-tertbutylcyclohexanol (Aldrich) by treatment with thionyl chloride and tri-*n*-butylamine[56,57] or from the carboxylic acid with lead tetraacetate and lithium chloride.[58] A mixture of *cis-* and *trans*-4-*tert*-butylcyclohexyl bromide was prepared from the alcohol with Br_2 and triphenylphosphine.[57] *exo*-2-Chloronorbornane (Aldrich) was used without further purification. 2,2-Dichloronorbornane was prepared from norcamphor with PCl_3 and PCl_5.[59,60] 2,2-Dibromonorbornane was similarly prepared from norcamphor with PCl_3 and Br_2.[61] 1-Chloronorbornane was prepared from 2,2-dichloronorbornane by treatment with $AlCl_3$ in a isopentane/*n*-pentane mixed solvent.[59,60] The *exo-* and *endo*-2-chloronorbornane mixture was separated by preparative GC from the reaction of *exo*-2-norbornyl bromide and HCl.[62,63] 2-Bromo- and 1,2-dibromonorbornane were similarly isolated from the reaction of *exo*-2-chloronorbornane and HBr.[63,64] Dichloromethane, chloroform, carbon tetrachloride (all of reagent grade quality), and the other solvents were purified by standard procedures and stored under argon.[65]

Analysis. Gas chromatographic analyses were carried out on a Hewlett-Packard 5890A capillary gas chromatograph using a 12.5-m cross-linked dimethyl-silicone column with FI detection. Authentic samples were checked by the internal standard method. Mass spectroscopic fragmentation patterns were measured on a Hewlett-Packard 5970 mass selective spectrometer (EI, 70 eV) interfaced to a 5890A gas chromatograph. Preparative-scale separations were effected on a Gow-Mac 200 series gas chromatograph equipped with a 10 ft × $^1/_4$ in. column packed with 15% XF 1150 on a Chromosorb P and a TC detector. ^1H NMR spectra were recorded on a JEOL FX90Q FT spectrometer. The IR spectra of the gases were measured on a Nicolet DX-10 FT spectrometer. The UV–vis absorption spectra were recorded on a Hewlett-Packard 8450A diode array spectrometer at 25 °C. All inert atmosphere manipulations were carried out under N_2 in a Vacuum Atmospheres MO-41 drybox.

Catalytic Conversion of Alkyl Chlorides to Their Bromides. In a typical procedure, 10 mg (0.033 mmol) of $FeBr_3$ was transferred in a drybox to a Schlenk flask equipped with greaseless Teflon stopcocks and Kel-F O-ring joints. Dichloromethane (8 mL) was introduced with the aid of a hypodermic syringe under a countercurrent of argon. The mixture was stirred magnetically for 10–20 min until the solution became dark red. Alkyl chloride (1.00 mmol) was introduced under an argon atmosphere. With seconary and tertiary alkyl chlorides, an immediate change in color to a pale-yellow green color was noted. Gaseous HBr was introduced by means of a 130-mL ball flask, the flow from which was controlled by a pressure manifold. The solution immediately returned to its original dark red hue upon contact with HBr. The closed system was allowed to react for the prescribed time stated, and it was then quenched with water. The dichloromethane phase was dried with anhydrous $MgSO_4$, and the workup was carried out by standard procedures.

For those catalytic exchanges effected by $FeBr_3$ generated in situ, iron pentacarbonyl (5 μL) was initially added to the Schlenk flask together with dibromine (4.5 μL) and 8 mL of dichloromethane. After the liberation of carbon monoxide subsided, the Schlenk flask and its contents were directly irradiated for 1 min at 360 nm in a Rayonet RPR-100 reactor (Southern New England Ultraviolet Co.) The remainder of the procedure was carried out as described above.

Catalytic Conversion of Alkyl Chlorides to Their Iodides. A Schlenk flask was charged with iron pentacarbonyl (5 μL) and 8 mL of dichloromethane. After diiodine (25 mg) was added under a reverse argon flow, the flask and contents were irradiated at 360 nm for 1 min. To the turbid solution was added 1 mmol of alkyl chloride and gaseous HI (vide supra). After being stirred for the prescribed period, the reaction mixture was quickly quenched with water and the dichloromethane extract dried immediately to minimize hydrolysis of the labile alkyl iodides.

Stoichiometric Conversion of Alkyl Chlorides to Their Bromides. In a typical procedure, a Schlenk flask was charged with 0.3–0.5 mmol of $FeBr_3$ in a drybox. Dichloromethane (8 mL) was added together with 4–5 molar equiv of various alkyl chlorides (Table III). After stirring the mixture for the prescribed period at 25 °C, it was quenched with water and subsequently treated as described above.

Preparative-Scale Conversion of Alkyl Chlorides to Their Bromide and Iodide. To a Schlenk flask was transferred 150 mg (0.5 mmol) of $FeBr_3$ and 60 mL of dichloromethane in a drybox. After stirring for 20 min, cyclohexyl chloride (3.6 mL, 30 mmol) was added under a reverse flow of argon. To the pale yellow-green solution was added gaseous HBr, and the mixture was allowed to stir for ~2 h. Workup yielded 4.7 g (95%) of crude cyclohexyl bromide.

Iron pentacarbonyl (0.5 mmol, 66 μL) was treated with diiodine (1.5 mmol, 380 mg) in 60 mL of dichloromethane. Irradiation at 360 nm for 10 min was followed by the addition of 2-chloronorbornane (3.74 mL, 30 mmol) and 2 L of gaseous HI. After ~2 h of stirring, a solution of 5% aqueous sodium sulfite was added. The dichloromethane extract was washed with water and dried with $MgSO_4$. Upon the removal of the solvent, it yielded 6.3 g (95%) of crude 2-iodonorbornane, which consisted of >95% of the exo isomer (^1H NMR analysis, vide supra).

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Registry No. *dl*-$CH_3CH_2CHClCH_3$, 53178-20-4; $CH_3(CH_2)_3Cl$, 109-69-3; $(CH_3)_3CCl$, 507-20-0; *meso*-$CH_3(CHCl)_2CH_3$, 4028-56-2; *dl-erythro*-$CH_3CHClCHBrCH_3$, 19246-45-8; *dl*-$CH_3(CHCl)_2CH_3$, 2211-67-8; *dl-threo*-$CH_3CHClCHBrCH_3$, 19246-46-9; ClC_{H4}-4-CH_2Cl, 104-83-6; $CH_2{=}CHCH_2Cl$, 107-05-1; *dl*-$CH_3CH_2CHBrCH_3$, 5787-31-5; $CH_3(CH_2)_3Br$, 109-65-9; $(CH_3)_3CBr$, 507-19-7; *meso*-$CH_3(CHBr)_2CH_3$, 5780-13-2; *dl*-$CH_3(CHBr)_2CH_3$, 598-71-0; Cl-C_6H_4-4-CH_2Br, 622-95-7; *dl*-$CH_3CHBrCH_2Br$, 120575-45-3; HBr, 10035-10-6; HI, 10034-85-2; $FeBr_3$, 10031-26-2; $FeBr_2$, 7789-46-0; *dl*-$CH_3CHClCH_2Br$, 120575-46-4; *dl*-$CH_3CHClCH_2Cl$, 26198-63-0; $CH_2{=}CHCH_2Br$, 106-95-6; CCl_4, 56-23-5; CBr_2Cl_2, 594-18-3; HCl, 7647-01-0; CBr_4, 558-13-4; CBr_3Cl, 594-15-0; FeI_3, 15600-49-4; cyclohexyl chloride, 542-18-7; *dl-exo*-2-chloronorbornane, 67844-27-3; 1-chloroadamantane, 935-56-8; 1-chloronorbornane, 765-67-3; *dl*-2,2-dichloronorbornane, 67844-25-1; cyclohexyl bromide, 108-85-0; *dl-exo*-2-bromonorbornane, 67815-05-8; 1-bromoadamantane, 768-90-1; *dl-exo*-1,2-dibromonorbornane, 32763-62-5; *dl-exo*-2-bromo-1-chloronorbornane, 120497-54-3; *dl-endo*-2-bromonorbornane, 67815-06-9; adamantane, 281-23-2; 1,3-dibromoadamantane, 876-53-9; *dl-exo*-1,2-dichloronorbornane, 120497-55-4; *dl-endo*-1,2-dibromonorbornane, 120497-56-5; *dl*-2,2-dibromonorbornane, 67844-24-0; *cis*-4-*tert*-butylcyclohexyl chloride, 13131-74-3; *trans*-4-*tert*-butylcyclohexyl chloride, 13145-48-7; *cis*-4-*tert*-butylcyclohexyl bromide, 5009-36-9; *trans*-4-*tert*-butylcyclohexyl bromide, 5009-37-0; *dl-endo*-2-chloronorbornane, 67844-26-2; 2-bromoadamantane, 7314-85-4; *cis*-1,2-dibromocyclohexane, 19246-38-9; *dl-exo*-2-iodonorbornane, 120497-57-6; 1-iodoadamantane, 768-93-4; $(CH_3)_3CI$, 558-17-8; cyclohexyl iodide, 626-62-0; *dl-trans*-1,2-dibromocyclohexane, 5183-77-7; *cis*-1,3-dibromocyclohexane, 31025-70-4; *dl-trans*-1,3-dibromocyclohexane, 120497-58-7; *cis*-1,4-dibromocyclohexane, 16661-99-7; *trans*-1,4-dibromocyclohexane, 13618-83-2.

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