

Efficient Conversion of Alkyl Chlorides into Bromides

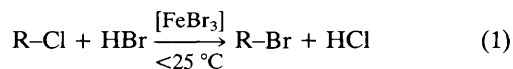
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The convenient and selective catalytic conversion of secondary and tertiary alkyl chlorides into bromides with hydrogen bromide in the presence of small amounts of anhydrous iron(III) bromide is described.

A recent communication¹ has again emphasized the need to develop efficient methods for the conversion of the generally cheaper, readily available alkyl chlorides into the more reactive, synthetically useful alkyl bromides.² Classically this transformation has relied on essentially two procedures, *viz.*, the halogen displacement on alkyl chlorides by various metal bromides,³ and the sacrificial transhalogenation of alkyl chlorides with expendable alkyl bromides.⁴ In both, high conversion into the alkyl bromide free from the competitive elimination of alkene is a continuing problem.

We report a convenient and efficient catalytic procedure based on hydrogen bromide as the readily available bromine source. Typically a solution of the alkyl chloride is exposed to gaseous HBr in the presence of a catalytic amount of iron(III) bromide, *i.e.* reaction (1). The conversion extent is roughly










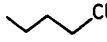














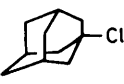
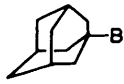

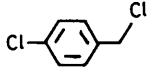
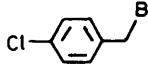



proportional to the amount of HBr, and essentially quantitative yields of the alkyl bromide (Table 1) are obtained within 10–15 min at room temperature using an 8 molar excess of hydrogen bromide. Optimum conditions call for an anhydrous reaction medium, which is easily achieved by the use of nonpolar, aprotic solvents such as dichloromethane and carbon tetrachloride. Since anhydrous iron(III) bromide is quite hygroscopic, the catalyst is more conveniently prepared *in situ* from Fe(CO)₅ and bromine.⁵

The bromide replacement in reaction (1) occurs most readily with secondary and tertiary alkyl chlorides, and it thus serves as a useful adjunct to the more conventional methods.^{1–4} Most noteworthy is the clean conversions of *s*-butyl, cyclohexyl, and *t*-butyl chlorides which occur with minimal complications from elimination, as shown in Table 1. The simplicity of the catalytic method allows these bromide exchanges to be easily expanded to preparative scales. Furthermore, the dichloromethane solvent can be recycled owing to its inertness to the catalyst system.

Stereochemical retention is observed in the conversion of *meso*-2,3-dichlorobutane into the *meso*-dibromide and (±)-2,3-dichlorobutane into the (±)-dibromide.⁶ However the chloride is not generally replaced stereospecifically since pure *exo*-2-norbornyl chloride affords a 4:1 mixture of *exo* and *endo* bromides. The latter suggests a carbonium-type intermediate in the bromide replacement.^{7,8} This is supported by the ready conversion of the bridgehead 1-adamantyl chloride but the unreactivity of the analogous (strained) 1-norbornyl chloride.⁹ Moreover the slow conversion of *n*-butyl chloride is accompanied by the formation of *s*-butyl and *t*-butyl bromides.¹⁰ Interestingly allyl chloride is converted into 1,2-dibromopropane in high yields.

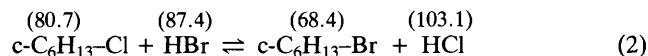
Bromide replacement in reaction (1) is reversible. Thus pure *endo*-2-norbornyl chloride is converted into the same 4:1 mixture of *exo-endo* bromides as obtained from the *exo* isomer (*vide supra*). Cyclohexyl bromide is 23% converted by 8 mol of hydrogen chloride into cyclohexyl chloride by

Table 1. Reaction of various alkyl chlorides with HBr catalysed by FeBr₃.^a

Alkyl chloride	Time/h	Alkyl bromide (% yield)	Byproducts (% yield)
	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)	
 (meso)	1 4	 (54) (90)	 (2) ^g (0)
 (erythro)	1	 (98)	h
 (±)	1 4	 (46) (82)	 (1) ⁱ (4)
 (threo)	1	 (97)	h
	0.3 15	 (78) (77)	 (3) ^j (3)
	0.2	 (96)	k
	0.5 15	 (79) (93)	 (16) ^m (5)

^a In 8 ml of CH₂Cl₂ containing 1 mmol of RCl, 8 mmol of HBr, and 3 × 10⁻² mmol of FeBr₃ at 25°C. Yield (%) in parentheses based on stoichiometry of equation (1) and g.c. analysis with authentic standard. ^b Catalyst prepared *in situ* from 0.03 mmol of Fe(CO)₅ and 0.09 mmol of Br₂ by irradiation at 360 nm. ^c With traces (<1%) of cyclohexane and C₆H₁₀Br₂ (g.c.-mass spectrometry). ^d With traces of norbornane and C₇H₁₀Br₂ (g.c.-m.s.). 1-Norbornyl chloride gave no 1-norbornyl bromide after reaction for 15 h. ^e t-Butyl bromide (2%). ^f Plus t-butyl bromide (3%). ^g Plus s-butyl bromide (2%) plus C₄H₇Br₃ (1%, g.c.-m.s.). ^h Traces of s-butyl bromide and C₄H₇Br₃ (g.c.-m.s.). ⁱ Plus s-butyl bromide (2%) plus C₄H₇Br₃ (2%) (g.c.-m.s.). ^j Plus adamantane (9%) plus 1,3-C₁₀H₁₄Br₂ (9%) (g.c.-m.s.). ^k p-ClC₆H₄CH₂Cl (traces) plus C₇H₅ClBr₂ (g.c.-m.s.). ^m Plus 1-Cl-2-BrC₃H₆ (2%), 1,2-Cl₂C₃H₆ (1%), and allyl bromide (2%).

catalytic amounts of FeBr₃. In the latter, the limited conversions for the microscopic reverse of reaction (1) accords with ΔH = 3.4 kcal mol⁻¹ (cal = 4.184 J) from the thermochemical computation based on bond dissociation energies,¹¹ indicated by the values in parentheses (kcal mol⁻¹) in reaction (2).



The same procedure can be used for the efficient replacement of a similar series of alkyl chlorides by iodide if hydrogen iodide is used in conjunction with iron(III) iodide prepared *in situ* from the actinic irradiation of a mixture of Fe(CO)₅ and iodine.

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