Reactions of Organoboranes with Ferric Chloride and Thiocyanate. Convenient Syntheses of Alkyl Chlorides and Thiocyanates from Olefins *via* Hydroboration

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(Received March 13, 1974)

The reactions of trialkylboranes with ferric chloride and thiocyanate in an aqueous tetrahydrofuran solution give the corresponding alkyl chlorides and thiocyanates in good yields. It was found that two equivalents of ferric salts per alkyl group of organoborane are required, and not only the first alkyl group of trialkylborane but other alkyl groups are also used.

Many reports have appeared on new applications of organoboranes to the synthesis of various organic compounds.[1] Alkyl halide synthesis has also been reported. For example, the reaction of organoboranes with *N*-chlorodialkylamines gives the corresponding alkyl chlorides in 30—53% yields based on trialkylboranes.[2]

It was shown that concurrent polar and radical processes occur to give amine and alkyl chlorides, respectively, as follows.[3]

$$R_3B + R_2NCl \begin{cases} \xrightarrow{\text{polar}} RNR_2 + R_2BCl \\ \xrightarrow{\text{radical}} RCl + R_2BNR_2 \end{cases} \quad (1)$$

However, this reaction is unsuitable for efficient preparation of alkyl chlorides, since the four products are formed in approximately equal yields.

On the other hand, alkyl bromides and iodides are produced readily *via* organoboranes. For instance, the reaction of organoboranes with bromine in dichloromethane gives the corresponding alkyl bromides in yields exceeding 80% based on R_3B.[4,5] Treatment of trialkylboranes with bromine in the presence of sodium methoxide also gives the corresponding alkyl bromides in excellent yields,[6] the three alkyl groups in trialkylborane being almost consumed by the reaction.

Organoboranes similarly react with iodine in the presence of base to produce alkyl iodides in relatively good yields.[7] Alkyl iodides are synthesized by the reaction of organoboranes with allylic or benzylic iodides in tetrahydrofuran in the presence of air.[8]

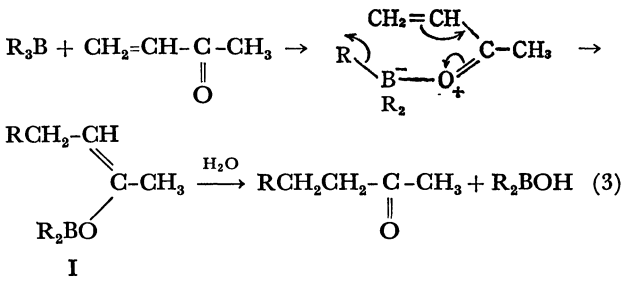
Lane reported an interesting synthetic procedure for alkyl chlorides and bromides by the reaction between trialkylboranes and cupric halides in 43—92% yields based upon R_3B:[9]

$$R_3B + 2CuX_2 \rightarrow RX + R_2BOH + Cu_2X_2 + HX \quad (2)$$
$$(X=Br, Cl)$$

During the course of studies on oxygen-induced addition reactions of organoboranes with α,β-unsaturated carbonyl compound,[10] it was found that the above reactions are enhanced in the presence of the Fenton reagent (hydrogen peroxide–ferrous sulfate),[11] and that when ferrous chloride is used instead of sulfate in the Fenton reagent, alkyl chlorides are obtained in high yield from the corresponding organoboranes.[12] We wish to report herewith our results, since they differ from and have certain advantages over those given by Lane.[9]

Results and Discussion

Reaction of Trialkylboranes with Fenton Reagent (Ferrous Chloride–Hydrogen Peroxide). It was reported that organoboranes react smoothly with methyl vinyl ketone through a co-ordination process.[10a]



In the absence of water or other protonolyzing species, the reaction product seemed to be enol borinate (I). Actually, such an intermediate was found to be readily isolated by distillation under reduced pressure.[13] Intermediate (I) was rapidly hydrolyzed to ketone by addition of water. However, the mechanism (Eq. 3) was later revised and it was reported that the reaction should proceed through a radical-chain mechanism.[10] Brown and Kabalka[14] confirmed that oxygen acts as a powerful radical initiator.

In connection with this work, we examined the reactions with α,β-unsaturated ketones in the presence of hydrogen peroxide–iron salt (Fenton reagent), since the reagent is known to form hydroxy radicals and could be considered to act as a radical initiator. Tricyclohexylborane was treated with crotonaldehyde in aqueous tetrahydrofuran in the presence of hydrogen peroxide–ferrous chloride at 40 °C. The reaction mixture was analyzed by glpc. It was found that the expected 4-methyl-4-cyclohexylbutyraldehyde was obtained in 91% yield, based on the organoborane, in addition to which cyclohexyl chloride was also produced in 70% yield.[12] We have attempted to find the synthetic procedure of alkyl chlorides. The results of representative reactions are summarized in Table 1.

It was found that more than one single alkyl group in trialkylborane seem to be involved in this reaction, contrary to general aspects of the organoborane reaction, in which only one alkyl group is used as the alkyl source.

Reaction of Trialkylboranes with Ferric Chloride. In

Table 1. Reaction[a] of trialkylboranes with ferrous chloride-hydrogen peroxide

R_3B from olefin	Reaction time, hr	Product	Yield,[b] %
1-Hexene	48	1-Chlorohexane	168[c] (153)[d]
		2-Chlorohexane	15[c] (9)[d]
Cyclohexene	24	Chlorocyclohexane	183[c] (156)[d]
Cyclooctene	48	Chlorocyclooctane	180[c]

a) Carried out at 55 °C by using R_3B (8 mmol), $FeCl_2$ (48 mmol) and H_2O_2 (48 mmol). b) Based on the trialkylborane, R_3B used. c) Determined by glpc. d) Isolated by distillation.

Table 2. Reaction[a] of trialkylboranes with ferric chloride

R_3B from olefin	Reaction time, hr	Product	Yield,[b] %
1-Pentene	24	1-Chloropentane	177[c] (144)[d]
		2-Chloropentane	12[c] (6)[d]
1-Hexene	48	1-Chlorohexane	180[c] (162)[d]
		2-Chlorohexane	15[c] (12)[d]
1-Octene	48	1-Chlorooctane	165[c]
		2-Chlorooctane	12[c]
Cyclohexene	48	Chlorocyclohexane	219[c] (195)[d]
Cyclooctene	48	Chlorocyclooctane	81[c]

a) Carried out at 55 °C by using R_3B (8 mmol) and $FeCl_3$ (48 mmol). b) Based on the trialkylborane used. c) Determined by glpc. d) Isolated by distillation.

Table 3. Reaction[a] of trialkylboranes with cupric halides

R_3B from olefin	Cupric halide	Reaction time, hr	Product	Yield,[b] %
1-Hexene	$CuCl_2$	48	1-Chlorohexane	186[c]
			2-Chlorohexane	12[c]
Cyclohexene	$CuCl_2$	48	Chlorocyclohexane	186[c]
cis-2-Butene	$CuBr_2$	24	2-Bromobutane	165[c]
1-Pentene	$CuBr_2$	24	1-Bromopentane	216[c] (195)[d]
			2-Bromopentane	15[c] (12)[d]
1-Hexene	$CuBr_2$	48	1-Bromohexane	258[c] (234)[d]
			2-Bromohexane	12[c] (9)[d]
1-Octene	$CuBr_2$	48	1-Bromooctane	153[c]
			2-Bromooctane	9[c]
Cyclohexene	$CuBr_2$	48	Bromocyclooctane	249[c]
Cyclooctene	$CuBr_2$	48	Bromocyclooctane	24[c]

a) Carried out at 55 °C by using R_3B (8 mmol) and CuX_2 (48 mmol). b) Based on the trialkylborane used. c) Determined by glpc. d) Isolated by distillation.

the reaction of organoboranes with ferrous chloride-hydrogen peroxide, color change was observed. The brown color due to ferric ion gradually turned pale yellowish green, suggesting the reduction of Fe^{3+} ion to Fe^{2+} ion. Thus we examined the direct reaction between trialkylboranes and ferric chloride. The reaction proceeded smoothly. The results are given in Table 2. In the case of tricyclohexylborane, cyclohexyl chloride was obtained in a 219% yield based on tricyclohexylborane, indicating that not only the first and second alkyl groups in R_3B but also a part of the third alkyl group takes part in the reaction.

Table 4. Stoichiometric study of the reaction[a] of tricyclohexylborane with ferric chloride

$FeCl_3$, mmol	Product	Yield,[b] mmol (%)[c]
2.0	0.9	(11)
4.0	1.9	(24)
8.0	3.9	(49)
16.0	7.4	(93)
48.0	17.4	(219)

a) Carried out at 55 °C for 48 hr by using 8 mmol of tricyclohexylborane. b) Determined by glpc. c) Based on tricyclohexylborane.

Reaction of Trialkylboranes with Other Metal Halides. Other metal halides, including manganese chloride, cobalt chloride, cuprous chloride, cupric chloride, stannic chloride, mercuric chloride, ferrous bromide, cuprous bromide and cupric bromide, were examined as regards their activities in the reactions. Cuprous chloride–hydrogen peroxide, cupric chloride, cuprous bromide–hydrogen peroxide and cupric bromide were found to be powerful reactants. The results of the reactions of typical organoboranes with cupric chloride and bromide are summarized in Table 3.

Stoichiometric Study on the Reaction of Tricyclohexylborane with Ferric Chloride. In order to clarify stoichiometry in the reaction, we carried out reactions using tricyclohexylborane with various amounts of ferric chloride. The results are given in Table 4. We see that the use of two equivalents of ferric chloride for each equivalent of tricyclohexylboranes gave rise to an almost quantitative conversion of a single alkyl group into cyclohexyl chloride. Consequently, the reaction is considered to obey stoichiometry (Eq. 4), as pointed out by Lane[9] and Ainley and Challenger.[15] It was also observed that the use of 48 mmol of ferric chloride for 8 mmol of tricyclohexylborane gives 17.4 mmol of the product. Lane reported that a single alkyl group of a trialkylborane is converted into the corresponding alkyl halide in a reasonable length of time. However, our results demonstrate that not only the first alkyl group of the organoborane but also the second and third cyclohexyl groups react with ferric chloride (Eq. 5)

$$R_3B + 2FeCl_3 + H_2O \longrightarrow RCl + R_2BOH + 2FeCl_2 + HCl \quad (4)$$

$$R_3B + 6FeCl_3 + 3H_2O \longrightarrow 3RCl + B(OH)_3 + 6FeCl_2 + 3HCl \quad (5)$$

No mechanistic investigation was carried out for the reaction. However, the mechanism through an alkyl radical from organoborane by an electron transfer reduction of metal salts, proposed by Lane,[9] is apparently reasonable.

Reaction of Trialkylboranes with Ferric Thiocyanate. We attempted to extend the reaction to synthesize alkyl thiocyanates by using metal thiocyanates, instead of metal halides. Although potassium and cupric thiocyanates did not react smoothly with such trialkylboranes, the reaction with ferric thiocyanate gave the

Table 5. Reaction[a] of trialkylboranes with ferric thiocyanate

Exp. no	R_3B from olefin mmol	$Fe(NH_4)(SO_4)_2$ mmol	KSCN mmol	Product	Yield[b] mmol (%)	Bp, °C (mmHg)
	1-Butene					
1	1.7	10.2	30.6	1-BuSCN	3.8 (226)[c]	
				2-BuSCN	0.2 (14)[c]	
	2-Butene					
2	1.7	0	30.6	None		
3	1.7	10.2	30.6	2-BuSCN	3.7 (217)[c]	
4	8.5	51.0	153.0	2-BuSCN	17.0 (200)[d]	93(66)
	1-Hexene					
5	1.7	0	30.6	None		
6	1.7	10.2	30.6	1-HexSCN	3.9 (230)[c]	
				2-HexSCN	0.3 (17)[c]	
7	8.5	51.0	153.0	1-HexSCN	20.3 (239)[d]	110(17)
	Cyclohexene					
8	1.7	10.2	30.6	CyclohexSCN	3.4 (200)[c]	
				CyclohexNCS	0.3 (15)[c]	
9	8.5	51.0	153.0	CyclohexSCN	16.2 (191)[d]	85 (4)
				CyclohexNCS	0.6 (7)[d]	
	2-Methyl-2-butene					
10	1.7	10.2	30.6	3-Me-2-BuSCN	1.7 (98)[c]	

a) Carried out at 55 °C for 24 hr. b) Based on the trialkylborane employed. c) Determined by glpc. d) Isolated by distillation.

corresponding alkyl thiocyanates in good yields. When a mixture of ferric ammonium sulfate (6 equiv. to each organoborane) and potassium thiocyanate (18 equiv.) in water was gradually added to a solution of tricyclohexylborane in tetrahydrofuran and refluxed for 24 hr, formation of a mixture of cyclohexyl thiocyanate and cyclohexyl isothiocyanate was shown by glpc in yields of 200% and 15%, respectively, based on R_3B. Representative results of the reaction are summarized in Table 5. In the preparative scale experiments 4, 7 and 9, the products were readily separated by extraction with petroleum ether, followed by distillation.

Experimental

Materials. Commercial 1-pentene, 1-hexene, 1-octene, cyclohexene and cyclooctene were dried over Molecular Sieve-5A, and 30%-hydrogen peroxide, metal halides and thiocyanates(Wako Chemical Co.) were used. Ferrous chloride was used after analysis by the usual *o*-phenanthroline method.

Reaction between Trialkylboranes and Metal Halides. The following procedure for the preparation of cyclohexyl chloride is representative. A dry 50-ml flask equipped with a magnetic stirring bar, septum inlet and reflux condenser was flushed with nitrogen. The flask was charged under nitrogen with 8 mmol of tricyclohexylborane in 5 ml of dry THF and 48 mmol of ferric chloride in 10 ml of water. The reaction mixture was stirred at 55 °C for 48 hr. After the completion of the reaction, the lower aqueous layer was separated and extracted with ether. The combined upper layer and extracts were washed with saturated aqueous sodium chloride solution, and finally analyzed by glpc, demonstrating that cyclohexyl chloride was obtained in a yield of 219% based on tricyclohexylborane.

All the products were confirmed either by comparison with authentic samples or examination of analytical and spectral data in accordance with assigned structures.

Reaction of Trialkylboranes with Ferric Thiocyanate. The following procedure is representative. A 100-ml flask, fitted with the same equipment as mentioned above, was charged with 8.5 mmol of the tri-2-butylborane obtained by hydroboration of 2-butene with diborane. To the solution was slowly added 8 ml (51 mmol) of aqueous solution of ferric ammonium sulfate and 40 ml (153 mmol) of aqueous solution of potassium thiocyanate. The mixture was refluxed at 55 °C for 24 hr under stirring. After cooling, the reaction mixture was extracted with petroleum ether several times. The combined extracts were washed with water and dried over anhydrous magnesium sulfate, and then distilled at 93 °C under 66 mmHg. Thus, 17.0 mmol (200%) of 2-butyl thiocyanate were obtained in a pure state. All the products were identified by direct comparison with authentic samples.

References

1) (a) A. Suzuki, *Yuki Gosei Kagaku Kyokai Shi*, **28**, 288 (1970). (b) A. Suzuki, *ibid.*, **29**, 995 (1971). (c) H. C. Brown and M. M. Rogić, *Organometal. Chem. Syn.*, **1**, 305 (1972). (d) H. C. Brown and M. M. Midland, *Angew. Chem. Int. Ed. Engl.*, **11**, 692 (1972). (e) H. C. Brown, "Boranes in Organic Chemistry," Cornell Univ. Press, Ithaca, 1972.

2) J. G. Sharefkin and H. D. Banks, *J. Org. Chem.*, **30**, 4313 (1965).

3) A. G. Davies, S. C. W. Hook, and B. P. Roberts, *J. Organometal. Chem.*, **23**, C11 (1970).

4) C. F. Lane and H. C. Brown, *J. Amer. Chem. Soc.*, **92**, 7212 (1970).

5) C. F. Lane and H. C. Brown, *J. Organometal. Chem.*, **26**, C51 (1971).

6) H. C. Brown and C. F. Lane, *J. Amer. Chem. Soc.*, **92**, 6660 (1970).

7) H. C. Brown, M. W. Rathke, and M. M. Rogić, *J. Amer. Chem. Soc.*, **90**, 5038 (1968).
8) A. Suzuki, S. Nozawa, M. Harada, M. Itoh, H. C. Brown, and M. M. Midland, *ibid.*, **93**, 1508 (1971).
9) C. F. Lane, *J. Organometal. Chem.*, **31**, 421 (1971).
10) (a) A. Suzuki, A. Arase, H. Matsumoto, M. Itoh, H. C. Brown, M. M. Rogić, and M. W. Rathke, *J. Amer. Chem. Soc.*, **89**, 5708 (1967). (b) A. Suzuki, S. Nozawa, M. Itoh, H. C. Brown, E. Negishi, and S. K. Gupta, *Chem. Commun.*, **1969**, 1009. (c) G. W. Kabalka, H. C. Brown, A. Suzuki, S. Honma, A. Arase, and M. Itoh, *J. Amer. Chem. Soc.*, **92**, 710 (1970). (d) A. Suzuki, S. Nozawa, M. Itoh, H. C. Brown, G. W. Kabalka, and G. W. Holland, *ibid.*, **92**, 3503 (1970).
11) Presented at the 14th Symposium on Essential Oil and Terpene Chemistry of the Chemical Society of Japan, Kitami, September 5, 1970.
12) Presented at the Hokkaido Local Meeting of the Chemical Society of Japan, Tomakomai, August 7, 1971.
13) N. Miyaura, M. Harada, M. Itoh, and A. Suzuki, *Chem. Lett.*, **1973**, 1145.
14) H. C. Brown and G. W. Kabalka, *J. Amer. Chem. Soc.*, **92**, 714 (1970).
15) A. D. Ainley and F. Challenger, *J. Chem. Soc.*, **1930**, 2171.