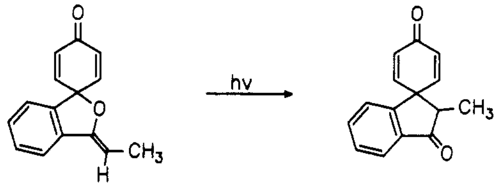

2b **3b**

conditions. Since the dienone carbonyl group of **3** is protected as a ketal, selective chemistry of the indanone portion of the molecule should be facilitated. The success of the **4** → **5** reaction derives from selective quenching of the secondary photochemistry of the product by piperylene. In contrast, the unexpected photochemical stability of the 2,5-cyclohexadienone product accounts for the high-yield **2b** → **3b** reaction. We defer discussion on the relatively high photochemical stability of **3b** relative to other simple 2,5-cyclohexadienones. However, reactions analogous to **2b** → **3b** would complement the earlier described thermal route to spirodienones since the photochemical reaction can be effected at room temperature.[13]

Acknowledgment. We acknowledge partial support from the National Science Foundation.

Supplementary Material Available: ^1H NMR spectra of **5a–g** and **3b** and the ^{13}C NMR spectrum of **5g** (9 pages). Ordering information is given on any current masthead page.

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[13] All compounds showed IR and ^1H NMR spectra in agreement with the assigned structures and showed exact mass measurements within 3 millimass units of calculated values. Compounds **5a**,**b** were colorless oils, and the remaining products showed the following melting points: **5c**, 111–112 °C; **5d**, 97–99 °C; **5e**, 113–116 °C; **5f**, 191–191.5 °C; **5g**, 188–189 °C.

Hydroboration with Boron Halides and Trialkylsilanes

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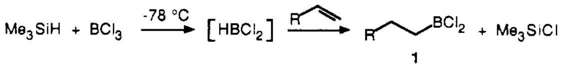
Received January 26, 1990

Summary: Mixtures of alkenes and trialkylsilanes added to boron trichloride at −78 °C result in quantitative hydroboration, presumably via dichloroborane, to alkyldichloroboranes, which with trialkylsilanes at 25 °C hydroborate alkenes to dialkylchloroboranes.

Dichloroborane was prepared from boron trichloride and hydrogen and shown to be an effective hydroborating agent 30 years ago,[1] though the high-temperature reaction and rapid quench required would be cumbersome for laboratory use. More recently dichloroborane has been prepared as etherate or dimethyl sulfide complexes, which can be dissociated with boron trichloride to hydroborate olefins, though the reactions are slow.[2] Direct reaction of methylnaphthylphenylsilane with boron trichloride has yielded diborane and the halosilane with retention of configuration at silicon,[3] and other reactions of haloboranes with silanes have yielded diborane,[4] but no hydrohaloborane products have ever been noted.

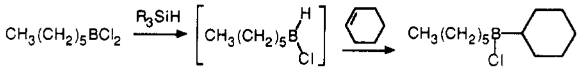
We have now found that mixing trialkylsilanes, boron trichloride, and alkenes neat or in pentane results in rapid, quantitative hydroboration of the alkene to the corresponding alkyldichloroborane (1), presumably via dichloroborane as an intermediate. Results are summarized in Table I.



1

Trimethylsilane was added to 1-hexene and boron trichloride at −78 °C, the mixture was transferred via cannula to an NMR tube kept at −78 °C, and the 64-MHz ^{11}B NMR spectrum was taken within 5 min. The formation of 1-hexyldichloroborane (**1a**) (δ 62.0)[5] [lit.[6] $RBCl_2$ δ 61–64] was already complete.[7] Triethylsilane and tributylsilane are similarly effective, but the trialkylsilyl chlorides have high enough boiling points to complicate separation from **1**. Boron tribromide can be used in place of boron trichloride to generate alkyldibromoboranes.

Trialkylsilanes reduce **1** at 25 °C to alkylchloroboranes. For example, **1a** with cyclohexene and trimethylsilane in a few minutes (or tributylsilane more slowly) shows a few percent conversion to **2** (^{11}B NMR δ 42, broad), which disappears as 1-hexylcyclohexylchloroborane (**3**) forms during ~2 h.[8]



1a **2** **3**

With 2 mol of trialkylsilane, cyclohexyldichloroborane is converted to cyclohexylborane dimer, ^{11}B NMR δ 23.7 [lit.[9] $(RBH_2)_2$ δ 22–24],[5] ^1H coupled: broad d ($J = 105$ Hz), bridge H couplings not resolved.

The preferred procedure for reaction of acid-sensitive alkenes with dichloroborane or dibromoborane is to mix the silane and alkene first. Addition of an equimolar mixture of 1-hexyne and trimethylsilane to boron trichloride at −78 °C yielded only 1-hexenyldichloroborane (**4**) and no detectable 1,1-bis(dichloroboryl)hexane (**5**).

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[5] External boron trifluoride etherate reference.

[6] Brown, H. C.; Sikorski, J. A. *Organometallics* **1982**, *1*, 28–37.

[7] The rapidity was further demonstrated by layering diethylsilane on top of 1-hexene/BCl_3 in a 5-mm NMR tube encased in a 14-mm tube at −98 °C. After 5 min the reactants remained unmixed, BCl_3 δ 47, but after one inversion of the tube and return to the −98 °C bath in 2–3 s, the ^{11}B NMR within 1 min showed only **1a**, δ 62.

[8] Generation of **2** in the absence of alkene yielded R_2BCl (^{11}B δ 78.3), B_2H_5Cl (for NMR data see ref 12), B_2H_6, and other unidentified products. However, **1a** + cyclohexene led to **3** [50-MHz ^{13}C NMR δ 14.1, 22.7, 24.6, 26.8, 27.4, 28.1, ~28 (broad, obscured by sharp peaks, B*C*), 31.8, 32.1, 37.7 (broad, B*C*')], which may have contained ≤5% di-*n*-hexylchloroborane [δ 14.1, 22.7, 24.6, 29.4 (broad, B*C*), 31.9, 32.0] and ≤5% dicyclohexylchloroborane [δ 26.7, 27.2, 27.8, 36.4 (broad, B*C*)].

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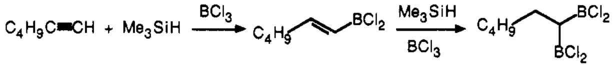
Table I. Results of Addition of Trimethylsilane to Unsaturated Compounds and Boron Halides[a]

B compd	unsat compd	product	^{11}B NMR, δ	yield, %	other data
BCl_3	1-hexene	$CH_3(CH_2)_5BCl_2$	62.0	95 isol[b]	bp 65–68 °C (23 Torr)
BCl_3	cyclohexene	cyclohexyl-BCl_2	63.5	95 isol[c]	bp 72–73 °C (15 Torr)
BCl_3	1-hexyne	$C_4H_9CH{=}CHBCl_2$	53.2	–	$RCH(BCl_2)_2$, < 2%
$2BCl_3$	1-hexyne[d]	$C_5H_{11}CH(BCl_2)_2$	60.8	83 ester[d]	1,2-isomer, ≤3%
BCl_3	allyl-Cl	$Cl(CH_2)_3BCl_2$	62.6	95 ester[e]	
BCl_3	allyl-Br	$Br(CH_2)_3BCl_2$	–	80 ester[e]	
BCl_3	(+)-α-pinene[f]	(ipc)-BCl_2[f]	62.0	95 (ipc)-OH	
BCl_3	α-pinene[f,g]	(ipc)$_2$BCl	72.0	88 (ipc)-OH	
BBr_3	1-hexene	$CH_3(CH_2)_5BBr_2$	64.5	95 isol[h]	bp 54–56 °C (0.8 Torr)
1-hexylBCl_2	cyclohexene	(1-hex)BCl(*c*-hex)	72.1	97 GC	(ROH + R′OH)
c-hexBCl_2	1-hexene	(1-hex)BCl(*c*-hex)	72.1	97 GC	(ROH + R′OH)
1-hexBBr_2	1-hexene	$[CH_3(CH_2)_5]_2BBr$	78.3	98 isol	bp 82–84 °C (0.2 Torr)
1-hexBCl_2	1-hexene	$[CH_3(CH_2)_5]_2BCl$[i]	77.9	–	

[a] The alkene and boron halide were mixed neat at −78 °C and the Me_3SiH was added via cannula, mol ratio 1:1:1. After 5–10 min the mixture was allowed to warm to 25 °C, and the NMR spectrum was taken. Boron halides were isolated by vacuum distillation or converted to the indicated derivative. [b] R_2BCl <1%. On workup with H_2O_2, 1-hexanol was obtained in 98% GC yield, 2-hexanol 0.4%. [c] R_2BCl <1%. The hydride source was Me_2SiClH, reaction time 8 h at 25 °C; alternatively, Me_3SiH reacted rapidly, yield not measured. [d] Et_3SiH (2 mol) was used in place of Me_3SiH, and the propanediol boronic ester was isolated (see text). [e] Pinanediol ester, 200-MHz NMR same as reported.[9] [f] A mixture of (+)-(α)-pinene and Me_3SiH was added to the boron trichloride at −78 °C; (ipc) = isopinocampheyl. [g] $1BCl_3{:}2$(+)-(α)-pinene:$2Me_3SiH$. [h] R_2BBr <2%. [i] *m/e* calcd 216.1816, found 216.1810; ^{13}C NMR, see ref 8.

This result contrasts with the mixtures of mono- and dihydroboration product obtained from 1-hexyne with dichloroborane etherate and boron trichloride at higher temperatures.[2] With an additional mole of trimethylsilane and boron trichloride, **4** was quantitatively converted to **5**, which was converted to the propanediol boronic ester, identical with an authentic sample[10] by 200-MHz ^{1}H NMR spectroscopy except for the presence of ~2–3% of presumed 1,2-isomer (δ 0.61, d, CH_2B).



4 **5**

The mildness of the procedure is confirmed by the conversions of (+)-α-pinene (98% ee) to (isopinocampheyl)dichloroborane (*m/e* calcd 218.0800, found 218.0779) and (diisopinocampheyl)chloroborane (*m/e* calcd 320.2442, found 320.2440), structures confirmed by ^{13}C NMR spectroscopy. The latter with hydrogen peroxide yielded isopinocampheol, mp 54–56 °C, $[\alpha]^{23}_D$ −32.5° (*c* 10, benzene) (lit.[11] mp 57 °C, $[\alpha]^{20}_D$ −32.0°).

Boron trichloride with equimolar diethylsilane in the range −78 °C to −20 °C apparently formed a few percent of free chloroborane and mainly its disproportionation products 1,2-dichlorodiborane and BCl_3 as indicated by ^{11}B NMR data.[12] At 0 °C only chlorodiborane (^{11}B NMR known[13]) and diborane persisted. Either the (postulated) $B_2H_4Cl_2$ or the B_2H_5Cl solutions readily hydroborated cyclohexene or 1-hexene to alkyldichloroborane, but mixtures of diborane and boron trichloride with or without trialkylsilyl chloride failed to hydroborate alkenes. Monomeric boranes are the active intermediates in hydroborations,[14] and the foregoing observations are consistent with the hypothesis that $B_2H_4Cl_2$ dissociates to $2BH_2Cl$, or B_2H_5Cl to BH_2Cl and BH_3, much more easily than B_2H_6 dissociates to $2BH_3$.[15] *CAUTION*: The use of preformed chloroborane mixtures is not recommended for synthetic purposes. Some diborane is always formed and may have been a factor in the pressure buildup, septum expulsion, and *spontaneous combustion* observed when boron trichloride and triethylsilane were mixed at −78 °C, 1-hexene was then added, and the solution was warmed toward 20 °C.

A typical experimental procedure leading to isolation of a boronic ester follows. (*CAUTION*: An inert atmosphere is required for all reactions of silanes with boron halides, which produce spontaneously flammable boranes.) Trimethylsilane (1.73 g, 23.3 mmol) was condensed under argon at −78 °C and mixed with allyl chloride (1.81 g, 23.3 mmol), and this mixture was added via cannula to boron trichloride (2.74 g, 23.3 mmol) stirred at −78 °C under argon. On completion of the addition the formation of $Cl(CH_2)_3BCl_2$ was indicated by the typical $RBCl_2$ peak[6] at δ 62.6 in the ^{11}B NMR spectrum.[5] Volatile byproducts were removed at 25 °C (100 Torr) for 1 h. The residue was cooled in an ice bath, and a solution of (*S*)-pinanediol[16] (3.97 g, 23.3 mmol) in diethyl ether (15 mL) was added. After being stirred 10 min, the mixture was distilled. The yield of (*S*)-pinanediol (3-chloropropyl)boronate, bp 130 °C (0.5 Torr), was 5.7 g (95%). The ^{1}H NMR spectrum was similar to that previously reported.[17]

Acknowledgment. We thank the National Science Foundation for support, Grant CHE-8618762, and the Boeing Corporation for part of the cost of the Nicolet NT-200 NMR instrument.

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(11) Shin-Piaw, C. *Compt. Rend.* **1936**, *202*, 127.

(12) 64-MHz, ^{1}H coupled: BCl_3, δ 46.8 (s); assigned $HBCl_2$, δ 56.1, d, J_{BH} = 204 Hz; assigned cis and trans $ClHB(H_2)BHCl$, δ 14.3 and 16.2 (overlapping d's of t's); also some B_2H_5Cl, δ 9.07 (t of t's, J = 45 Hz and J = 138 Hz) and 24.89 (d, J = 164 Hz, of t's, J = 55 Hz); B_2H_6, δ 18.55 (t, J = 47 Hz, of t's, J = 138 Hz); other minor constituents also observed. One H of Et_2SiH_2 was utilized.

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(15) Hydroboration with BH_2Cl to form RBHCl would be followed by hydride–chloride exchange with BCl_3 to produce $RBCl_2$. Hydroboration of 1-hexene with presumed $B_2H_4Cl_2$ led after oxidation to 1-hexanol containing 0.8% 2-hexanol, double the amount seen under the preferred conditions (Table I), which suggests possible competition between less selective BH_2Cl and $HBCl_2$. Selectivities of borane and haloboranes: Brown, H. C.; Ravindran, N.; Kulkarni, S. U. *J. Org. Chem.* **1979**, *44*, 2417–2425.

(16) Chemical Abstracts name: [1*S*-(1α,2β,3β,5α)]-2,6,6-trimethylbicyclo[3.1.1]heptane-2,3-diol. This compound was purchased from the Aldrich Chemical Co.

(17) Matteson, D. S.; Jesthi, P. K.; Sadhu, K. M. *Organometallics* **1984**, *3*, 1284–1288.