p-$BrC_6H_4COCF_3$, 16184-89-7; $PhCH_2COCF_3$, 350-92-5; c-$C_6H_{11}COCF_3$, 6302-04-1; $Me(CH_2)_5COCF_3$, 400-60-2; CH=CH-CH=C(COCF$_3$)S, 651-70-7; (2-$C_4H_3S)_2C(OH)CF_3$, 35320-32-2; $PhCOCH_2F$, 450-95-3; $Ph_2C(OH)CH_2F$, 337-72-4; $PhCOCH_2OMe$, 4079-52-1; $Ph_2C(OH)CH_2OMe$, 14704-09-7; PhC(OH)Me, 599-67-7; $Ph_2C(OH)(CF_2)_2CF_3$, 559-54-6; p-$MeSC_6H_4MgBr$, 18620-04-7; p-FC_6H_4MgBr, 352-13-6; m-FC_6H_4MgBr, 17318-03-5; m-$CF_3C_6H_4MgBr$, 402-26-6; EtO_2CCO_2Et, 95-92-1; $PhCOCO_2Et$, 1603-79-8; p-$MeC_6H_4COCO_2Et$, 5524-56-1; p-$MeOC_6H_4COCO_2Et$, 40140-16-7; p-$MeSC_6H_4COCO_2Et$, 62936-31-6; p-$FC_6H_4COCO_2Et$, 1813-94-1; m-$FC_6H_4COCO_2Et$, 110193-59-4; p-$CF_3C_6H_4COCO_2Et$, 73790-06-4; m-$CF_3C_6H_4COCO_2Et$, 110193-60-7; SCH=CHCH=CCOCO$_2$Et, 4075-58-5; $BuCOCO_2Et$, 677-22-5; CD_3MgI, 41251-37-0; c-$C_3H_5C_6H_4Li$, 110205-34-0; p-CH_2=CHC_6H_4Li, 7442-12-8; p-$Me_3SiC_6H_4Li$, 17881-54-8; p-$Me_3SiCH_2C_6H_4Li$, 110193-61-8; t-$BuCOCO_2Et$, 5333-74-4; $EtCOCO_2Et$, 15933-07-0; CD_3COCO_2Et, 66966-38-9; c-$C_3H_5C_6H_4COCO_2Et$, 110205-35-1; p-CH_2=$CHC_6H_4COCO_2Et$, 110193-62-9; p-$Me_2NC_6H_4COCO_2Et$, 41116-24-9; p-$Me_3SiC_6H_4COCO_2Et$, 110193-63-0; p-$Me_3SiCH_2C_6H_4COCO_2Et$, 109088-72-4; MeLi, 917-54-4; BuLi, 109-72-8; 1-naphthyllithium, 14474-59-0; (1-naphthylcarbonyl)trifluoromethane, 6500-37-4.

Facile Reduction of Saturated and Unsaturated Carboxylic Acids and Their Salts to Aldehydes by Thexylbromoborane–Dimethyl Sulfide[1]

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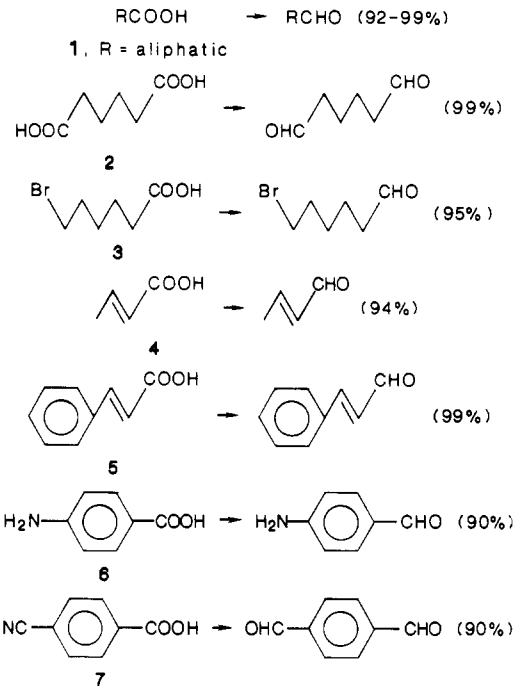
Thexylchloroborane–dimethyl sulfide appears to be an ideal reagent for the direct transformation of acyclic and alicyclic carboxylic acids into aldehydes so long as alkene functions are not present.[2,3] In the course of a systematic study of the reducing characteristics of thexylbromoborane–dimethyl sulfide,[4] we have found that this reagent as well selectively converts carboxylic acids and their sodium and lithium salts to the corresponding aldehydes in the presence of several functionalities, including carbon–carbon double bonds. This paper describes this facile reduction.

Results and Discussion

Thexylbromoborane–dimethyl sulfide (ThxBHBr–SMe_2) is readily prepared by hydroborating 2,3-dimethyl-2-butene (tetramethylethylene) in methylene chloride[5] with monobromoborane–dimethyl sulfide, which in turn is easily prepared by treating borane–dimethyl sulfide with $^1/_2$ equiv of bromine in carbon disulfide.[6]

Chart I



The reagent reduces aliphatic carboxylic acids **1**, regardless of structural type, to aldehydes in almost quantitative yield within 1 h at room temperature. Even aliphatic diacids **2** are converted to the dialdehydes in yields of 93–99%. The reagent tolerates many organic functionalities, viz., esters, acid chlorides, epoxides, halides, and nitro compounds. For example, halo aliphatic acids **3** provide the corresponding halo aldehydes in good yields (85–95%). However, the most useful feature of this reagent is its reluctance to hydroborate carbon–carbon double bonds, an advantage of this reagent over thexylchloroborane–dimethyl sulfide, which readily adds to alkenes. Thus, α,β-unsaturated carboxylic acids such as methacrylic, crotonic (**4**), and cinnamic (**5**) acids are readily converted to the corresponding olefinic aldehydes in yields of 94–99% (Chart I).

The rate of reduction of aromatic carboxylic acids is sluggish, requiring 3 equiv of the reagent and 9 h at room temperature. The yields are significantly lower than those in the aliphatic series and appear to be influenced by substituents on the aromatic ring. For example, the yields from both benzoic and α-naphthoic acids were ca. 50%, whereas the yields from *m*-nitro-, *o*-chloro-, *m*-chloro-, and *p*-aminobenzoic (**6**) acids were 75–93%. The reduction of terephthalic acid with 6 equiv of the reagent gave the corresponding dialdehyde in 95% yield. This reagent also reduces the nitrile function partially.[7] Thus, the reaction of *p*-cyanobenzoic acid (**7**) with 3.1 equiv of the reagent gave terephthalaldehyde in a yield of 90%. These results are summarized in Table I.

The reagent thexylbromoborane–dimethyl sulfide also reduces sodium and lithium carboxylates to the corresponding aldehydes at room temperature in high yields. This facile reduction is due to the simple substitution for

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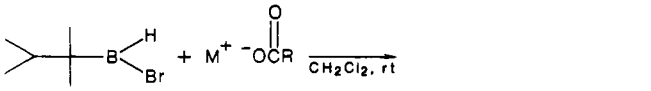
Table I. Yields of Aldehydes in the Reduction of Representative Carboxylic Acids with Thexylbromoborane-Dimethyl Sulfide in CS_2[a]-CH_2Cl_2 at Room Temperature[b]

acid	yield of aldehyde,[c] %	acid	yield of aldehyde,[c] %
acetic	87	cyclohexanecarboxylic	99 (89)[e]
butyric	92	chloroacetic	95
hexanoic	94	bromoacetic	85
decanoic	94	6-bromohexanoic	95
stearic	98 (92)[d]	methacrylic	94
isobutyric	99	crotonic	94
isopentanoic	98	cinnamic	99 (87)[e]
pivalic	89	benzoic	49
phenylacetic	90	α-naphthoic	45
diphenylacetic	89	terephthalic	95
triphenylacetic	95	*m*-nitrobenzoic	75
succinic	93	*o*-chlorobenzoic	93
adipic	99	*m*-chlorobenzoic	81
1,10-decanedicarboxylic	99	*p*-aminobenzoic	90
cyclopropanecarboxylic	99	*p*-cyanobenzoic[f]	90 (81)[d]

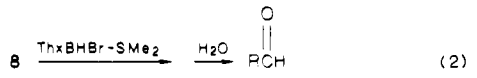
[a] Essential solvent for the hydrogen evolution step; less than 50 vol % in total reaction mixture. [b] Aliphatic carboxylic acids were reacted with 5% excess reagent (2.1 equiv for monocarboxylic and 4.2 equiv for dicarboxylic acids) for 1 h and aromatic carboxylic acids with 50% excess reagent (3 equiv for monocarboxylic and 6 equiv for dicarboxylic acids) for 9 h, both at room temperature, after the hydrogen evolution at −20 °C. [c] Analysis with (2,4-dinitrophenyl)hydrazine. [d] Yields are based on the analytically pure aldehydes isolated after evaporation of solvent, following treatment of the bisulfite adduct with formaldehyde.[2] [e] Yields of distilled product, following treatment of the bisulfite adduct with formaldehyde.[2] [f] Reacted with 3.1 equiv of reagent; only terephthalaldehyde formed.

the bromo group of the reagent by a carboxylate to form thexyl(acyloxy)borane **8**, the acyloxy group of which is readily reduced to aldehyde by another 1 equiv of thexylbromoborane (eq 1 and 2). This substitution reaction occurs readily in methylene chloride with precipitation of the metal bromide even under the heterogeneous conditions.



(1)

8



(2)

This system reduces both sodium and lithium salts of most aliphatic carboxylic acids **9**, including diacids, to aldehydes (Chart II) in approximately 3 h at room temperature in yields of 85–99%, as shown in Table II. In almost all cases the yields for sodium and for lithium salts are similar, with no obvious generalizations to be drawn about the differences (the largest differences observed was 16%, and the average, about 5%). Just as in the reduction of α,β-unsaturated carboxylic acids by this reagent,[2] the reduction of their salts, such as cinnamic (**10**) and crotonic (**11**) acid salts, gives the corresponding aldehydes in good yields, without attack on the double bond. The yields of aldehydes in the reduction of aromatic carboxylic acid salts are significantly lower and vary with the substitutents, cf. benzoic, *p*-methoxybenzoic, and *p*-chlorobenzoic versus

Chart II

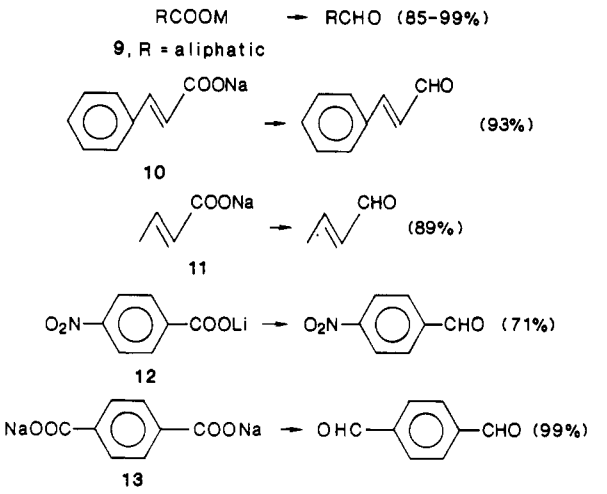


Table II. Yields of Aldehydes in the Reduction of Representative Sodium and Lithium Salts of Carboxylic Acids by Thexylbromoborane-Dimethyl Sulfide in CH_2Cl_2 at Room Temperature[a]

acid salt	yield of aldehyde,[b] % Na salt	Li salt
butyric	90	89
hexanoic	92 (77)[c]	86
decanoic	87	89
stearic	92 (88)[d]	92
isobutyric	88	86
isopentanoic	90	87
pivalic	85[e]	
cyclopropanecarboxylic	87	77
cyclohexanecarboxylic	86	76
diphenylacetic	83	99 (91)[d]
6-bromohexanoic	72	76
α-camphoric	88	87
1,10-decanedicarboxylic	85	92 (87)[d]
cinnamic	93	82
crotonic	89	81
benzoic	49	47
p-methoxybenzoic	42	31
p-chlorobenzoic	44	43
p-nitrobenzoic	70	71
terephthalic	99	94

[a] Reacted with 2 equiv of reagent for monocarboxylic and 4 equiv for dicarboxylic acid salts for 3 h at room temperature. [b] Analysis with (2,4-dinitrophenyl)hydrazine. [c] An isolated yield of distilled product, following treatment of the bisulfite adduct with formaldehyde.[2] [d] Yields are based on the analytically pure products after evaporation of solvent, following treatment of the adduct with formaldehyde.[2] [e] Reacted for 6 h.

p-nitrobenzoic (**12**) and terephthalic (**13**) acid salts (Table II).

The bisulfite adduct procedure for the isolation of aldehyde products, adopted for reduction of carboxylic acids with thexylchloroborane,[2] appeared also to be broadly applicable to this case.

Experimental Section[8]

Preparation of Thexylbromoborane–Dimethyl Sulfide (ThxBHBr–SMe_2) in CH_2Cl_2. Monobromoborane–dimethyl sulfide (1.5 mol) in 66 mL of CH_2Cl_2 and 15 mL of Me_2S was

(8) All reactions were performed under a dry N_2 atmosphere. All chemicals used were commerical products of the highest purity available; CH_2Cl_2 and CS_2 were stirred for 1 day under N_2 over P_4O_{10} and distilled; Me_2S was dried over 4-Å molecular sieves and distilled from sodium–benzophenone ketyl prior to use. ^{11}B NMR spectra were recorded on a Bruker FT-80 spectrometer, and the chemical shifts are reported in parts per million downfield from $BF_3{\cdot}OEt_2$.

placed in an oven-dried, 500-mL flask fitted with a side arm and a bent adaptor connected to a Hg bubbler. The flask was immersed in an ice-water bath, and to this was added 196 mL of precooled 2,3-dimethyl-2-butene (1.65 mol) dropwise over a period of 1 h via a double-ended needle. The reaction mixture was stirred for an additional 2 h at 0 °C, followed by stirring overnight at room temperature. The resulting CH_2Cl_2 solution was found to be 3.34 M in ThxBHBr–SMe_2, and ^{11}B NMR showed a clean doublet centered at δ 5.16 (J_{BH} = 123 Hz).

Reduction of Carboxylic Acids and Isolation of Products. The following procedure for the reduction of cyclohexanecarboxylic acid is illustrative. An oven-dried, 100-mL flask, fitted with a side arm and a bent adaptor connected to a Hg bubbler, was charged with 6.79 g (53 mmol) of cyclohexanecarboxylic acid and 35 mL of CS_2.[9] The flask was immersed in a cold bath and maintained at −20 °C. A precooled 3.2 M solution of ThxBHBr–SMe_2 in CH_2Cl_2 (16.6 mL, 53.1 mmol) was added dropwise with stirring. After complete evolution of the H_2, the cold bath was removed, and the reaction mixture was warmed to room temperature. An additional 1.1 eqiv of the reagent (18.3 mL, 58.3 mmol, 10% excess) was added, and the reaction mixture was stirred for 1 h at room temperature. Analysis of an aliquot with (2,4-dinitrophenyl)hydrazine indicated a yield of 99%.

The rest of the reaction mixture (50 mmol) was transferred via a double-ended needle to a flask containing 50 mL of cold water in an ice–water bath and was then hydrolyzed with vigorous stirring for 1 h at room temperature. The mixture was saturated with NaCl, and the separated organic layer was subjected to the $NaHSO_3$ isolation procedure.[2] The yield of pure distilled cyclohexanecarboxaldehyde was 5.0 g (89%): bp 160–161 °C (761 mm); n_D^{20} 1.4498.

Reduction of Carboxylic Acid Salts and Isolation of Products. The following procedure is for the larger scale reaction. In the assembly previously described were placed 10.9 g of lithium diphenylacetate (50 mmol) and 17 mL of CH_2Cl_2. Into the reaction mixture was injected 33.3 mL of the 3 M reagent solution (100 mmol), and the slurry was stirred for 3 h at room temperature. The reaction mixture was then hydrolyzed with 50 mL of cold water by stirring vigorously for 1 h at room temperature. The mixture was saturated with NaCl. After neutralization with a small amount of $NaHCO_3$, the separated organic layer was poured into 75 mL of a saturated aqueous $NaHSO_3$ solution, and 70 mL of THF was added. The mixture was stirred for 1 h, by which time the crystalline bisulfite adduct of diphenylacetaldehyde had precipitated. The solution was cooled in an ice–water bath to ensure complete crystallization of the adduct, which was then collected by filtration and washed with 3 × 25 mL of pentane. The adduct was placed in 40 mL of water, and then 50 mL of THF and 8 mL of a 37% CH_2O solution were added. The mixture was stirred for 1 h and saturated with $MgSO_4 \cdot 7H_2O$. The organic layer was separated and dried. Evaporation of volatiles gave 8.93 g of analytically pure diphenylacetaldehyde (91%), n^{20}_D 1.5892.

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Registry No. 1 (R = CH_3), 64-19-7; 1 (R = CH_3, aldehyde), 75-07-0; 1 (R = $H_2C{=}C(CH_3)$, 79-41-4; 1 ($H_2C{=}C(CH_3)$), 78-85-3; 1 (R = $(CH_2)_2CH_3$), 107-92-6; 1·Na (R = $(CH_2)_2CH_3$), 156-54-7; 1-Li (R = $(CH_2)_2CH_3$), 21303-03-7; 1 (R = $(CH_2)_2CH_3$, aldehyde), 123-72-8; 1 (R = $(CH_2)_4CH_3$), 142-62-1; 1·Na (R = $(CH_2)_4CH_3$), 10051-44-2; 1·Li (R = $(CH_2)_4CH_3$), 16577-51-8; 1 (R = $(CH_2)_4CH_3$, aldehyde), 66-25-1; 1 (R = $(CH_2)_8CH_3$), 334-48-5; 1·Na (R = $(CH_2)_8CH_3$), 1002-62-6; 1·Li (R = $(CH_2)_8CH_3$), 20336-95-2; 1 (R = $(CH_2)_8CH_3$, aldehyde), 112-31-2; 1 (R = $(CH_2)_{16}CH_3$), 57-11-4; 1·Na (R = $(CH_2)_{16}CH_3$), 822-16-2; 1·Li (R = $(CH_2)_{16}CH_3$), 4485-12-5; 1 (R = $(CH_2)_{16}CH_3$, aldehyde), 638-66-4; 1 (R = $CH(CH_3)_2$), 79-31-2; 1·Na (R = $CH(CH_3)_2$), 996-30-5; 1·Li (R = $CH(CH_3)_2$), 25179-23-1; 1 (R = $CH(CH_3)_2$, aldehyde), 78-84-2; 1 (R = $CH_2CH(CH_3)_2$), 503-74-2; 1·Na (R = $CH_2CH(CH_3)_2$), 539-66-2; 1·Li (R = $CH_2CH(CH_3)_2$), 556-25-2; 1 (R = $CH_2CH(CH_3)_2$, aldehyde), 590-86-3; 1 (R = $C(CH_3)_3$), 75-98-9; 1·Na (R = $C(CH_3)_3$), 1184-88-9; 1 (R = $C(CH_3)_3$, aldehyde), 630-19-3; 1 (R = $C_6H_5CH_2$), 103-82-2; 1 (R = $C_6H_5CH_2$, aldehyde), 122-78-1; 1 (R = $(C_6H_5)_2CH$), 117-34-0; 1·Na (R = $C_6H_5)_2CH$), 1716-11-6; 1·Li (R = $(C_6H_5)_2CH$), 25017-18-9; 1 (R = $(C_6H_5)_2CH$, aldehyde), 947-91-1; 1 (R = $(C_6H_5)_3C$), 595-91-5; 1 (R = $(C_6H_5)_3C$, aldehyde), 42365-04-8; 1 (R = $HO_2C(CH_2)_2$), 110-15-6; 1 (R = $HO_2C(CH_2)_2$, aldehyde), 638-37-9; 1 (R = $(CH_2)_8CO_2H$), 693-23-2; 1·2Na (R = $(CH_2)_8CO_2H$), 17265-14-4; 1·2Li (R = $(CH_2)_8CO_2H$), 19370-86-6; 1 (R = $(CH_2)_8CHO$, dialdehyde), 38279-34-4; 1 (R = $ClCH_2$), 79-11-8; 1 (R = $ClCH_2$, aldehyde), 107-20-0; 1 (R = $BrCH_2$), 79-08-3; 1 (R = $BrCH_2$, aldehyde), 17157-48-1; 1 (R = C_6H_5), 65-85-0; 1·Na (R = C_6H_5), 532-32-1; 1·Li (R = C_6H_5), 553-54-8; 1 (R = C_6H_5, aldehyde), 100-52-7; 1 (4-$HO_2CC_6H_4$ = R), 100-21-0; 1·2Na (4-$HO_2CC_6H_4$ = R), 10028-70-3; 1·2Li (4-$HO_2CC_6H_4$ = R), 42596-02-1; 1 (R = 4-$OHCC_6H_4$, aldehyde), 623-27-8; 1 (R = 3-$O_2NC_6H_4$), 121-92-6; 1 (R = 3-$O_2NC_6H_4$, aldehyde), 99-61-6; 1 (R = 2-ClC_6H_4), 118-91-2; 1 (R = 2-ClC_6H_4, aldehyde), 89-98-5; 1 (R = 3-ClC_6H_4), 535-80-8; 1 (R = 3-ClC_6H_4, aldehyde), 587-04-2; 2, 124-04-9; 2 (aldehyde), 1072-21-5; 3, 4224-70-8; 3·Na, 50530-06-8; 3·Li, 51568-15-1; 3 (aldehyde), 57978-00-4; 4, 3724-65-0; 4·Na, 21988-86-3; 4·Li, 110419-20-0; 4 (aldehyde), 4170-30-3; 5, 621-82-9; 5·Na, 538-42-1; 5·Li, 110419-19-7; 5 (aldehyde), 104-55-2; 6, 150-13-0; 6 (aldehyde), 556-18-3; 7, 619-65-8; 7 (aldehyde), 105-07-7; 4-$H_3COC_6H_4CHO$, 123-11-5; 4-$H_3COC_6H_4CO_2Na$, 536-45-8; 4-$H_3COC_6H_4CO_2Li$, 16090-04-3; 4-ClC_6H_4CHO, 104-88-1; 4-$ClC_6H_4CO_2Na$, 3686-66-6; 4-$ClC_6H_4CO_2Li$, 16090-16-7; 4-$O_2NC_6H_4CHO$, 555-16-8; 4-$O_2NC_6H_4CO_2Na$, 3847-57-2; 4-$O_2NC_6H_4CO_2Li$, 18393-32-3; Me_2S, 75-18-3; $(H_3C)_2C{=}C(CH_3)_2$, 563-79-1; cyclopropanecarboxylic acid, 1759-53-1; cyclopropanecarboxaldehyde, 1489-69-6; cyclopropanecarboxylic acid sodium salt, 155-22-6; cyclopropanecarboxylic acid lithium salt, 110419-17-5; cyclohexanecarboxylic acid, 98-89-5; cyclohexanecarboxaldehyde, 2043-61-0; cyclohexanecarboxylic acid sodium salt, 136-01-6; cyclohexanecarboxylic acid lithium salt, 16090-10-1; α-naphthoic acid, 86-55-5; α-naphthaldehyde, 66-77-3; α-camphoric acid disodium salt, 74543-12-7; α-camphoric acid dilithium salt, 110419-18-6; α-camphoraldehyde, 69804-91-7; thexylbromoborane–dimethyl sulfide complex, 109620-28-2; monobromoborane–dimethyl sulfide complex, 55652-52-3.

(9) We have observed that CS_2 seems to be essential in the solvent for the H_2 evolution step. CS_2 readily disssolves HBr, which is formed from the reaction of carboxylic acid and reagent. The dissolved HBr then reacts with thexyl(acyloxy)borane, the undesired intermediate, and thus converts it into the desired intermediate thexyl(acyloxy)bromoborane.

One-Step Preparation of the 3,3′-Dimer of Precocene II

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The antijuvenile hormones precocenes I (1) and II (2) have been shown to induce precocious metamorphosis when applied to larval stages of insects.[1,2] As a consequence of this effect several analogues of both compounds have been synthesized in a search for compounds with better activity.[3,4] We have prepared several dimers,[5,6] the

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