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ORGANOBORANES FOR SYNTHESIS. 4. OXIDATION OF ORGANOBORANES WITH PYRIDINIUM CHLOROCHROMATE. A DIRECT SYNTHESIS OF ALDEHYDES FROM TERMINAL ALKENES VIA HYDROBORATION

HERBERT C. BROWN,* SURENDRA U. KULKARNI,[3a] C. GUNDU RAO[3b]
and VEMANNA D. PATIL[3c]

Richard B. Wetherill Laboratory, Purdue University
West Lafayette, Indiana 47907 USA

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Abstract. The oxidation of trialkylboranes containing primary alkyl groups with pyridinium chlorochromate (PCC) in methylene chloride provides the corresponding aldehydes in good yields. The stoichiometry for the oxidation of alcohols, borate esters and trialkylboranes with PCC has been examined. In view of the poor regioselectivity (only 94% primary alkyl groups) and functional group tolerance observed in the hydroboration with borane (BH_3·THF or $BH_3·SMe_2$), a more selective hydroborating agent, bis(3-methyl-2-butyl)borane (disiamylborane), was utilized for the preparation of aldehydes from terminal alkenes. However, the formation of 3-methyl-2-butanone as a by-product, and the requirement of six moles of PCC per mole of aldehyde are major disadvantages in this method. This difficulty was circumvented by employing monochloroborane-dimethyl sulfide for hydroboration. This reagent exhibits high regioselectivity (> 99% primary alkyl groups) in the hydroboration of terminal alkenes. Oxidation of the resulting dialkylchloroborane following hydrolysis affords the desired aldehydes in satisfactory yields. Consequently, the hydroboration of terminal alkenes, followed by PCC oxidation, represents a direct convenient method for the transformation of alkenes into the corresponding aldehydes.

Organoboranes react cleanly and quantitatively with alkaline hydrogen peroxide to produce alcohols, representing a general method for the conversion of alkenes into the corresponding *anti*-Markovnikov alcohols.[4] Similarly, the oxidation of organoboranes derived from internal alkenes afford ketones upon oxidation with aqueous chromic acid.[1] Unfortunately, the direct conversion of organoboranes containing primary alkyl groups into the corresponding aldehydes via aqueous chromic acid oxidation has thus far been unsuccessful.[5] Although it is possible to oxidize such organoboranes, first, with alkaline hydrogen peroxide, followed by oxidation of the resulting primary alcohols into aldehydes by known methods[6,7] (eq 1), the direct conversion of terminal alkenes into the corresponding aldehydes would be a highly useful synthetic transformation.

$$RCH{=}CH_2 \xrightarrow{BH_3} (RCH_2CH_2)_3B \longrightarrow RCH_2CH_2OH \longrightarrow RCH_2CHO \qquad (1)$$

In view of the instability of aldehydes under strongly acidic or basic conditions, we sought a reagent that could be used under mild conditions. Customarily, aldehydes are prepared from primary alcohols using Collins' reagent.[6] However, Corey and Suggs[7] have developed a new reagent, pyridinium chlorochromate ($C_5H_5N·HCl·CrO_3$, PCC), for the oxidation of alcohols to carbonyl compounds. PCC is a readily available, stable reagent, which oxidizes a wide variety of alcohols to carbonyl compounds under mild conditions.[7] The slightly acidic character of this reagent can be modified by buffering the reaction mixture with powdered anhydrous sodium acetate, which renders the reagent stable to acid-labile groups such as tetrahydropyranyl ethers.

The use of PCC in the synthesis of ketones from organoboranes derived from cycloalkenes has been reported recently.[8] Consequently, we undertook to examine the application of PCC oxidation for the preparation of aldehydes from terminal alkenes via hydroboration.

RESULTS AND DISCUSSION

Although PCC has been widely used since its discovery for the oxidation of alcohols to carbonyl compounds, no systematic study of the stoichiometry of this reaction is reported in the literature.[9,10] Consequently, we examined the stoichiometry of oxidation with PCC.[11]

Stoichiometry of PCC Oxidation. In a typical experiment, 15 mmol of 1-octanol was added to a well-stirred suspension of varying amounts (10, 15, 16.5 and 22.5 mmol) of PCC in 15 mL of methylene chloride and the mixture was heated under reflux. The progress of the reaction was followed by analyzing the reaction mixture for octanal by GC (Figure 1). It is evident that when 10 mmol of PCC was used, only 64% of octanal was formed. On the other hand, 15 mmol of PCC produced 94% octanal. Both 16.5 and 22.5 mmol of PCC provided quantitative yields of the aldehyde. Considering the purity of commercial PCC (98%, specified), it appears that 15 mmol is the theoretical amount required to oxidize 15 mmol of octanol.[12] Therefore, we conclude that the oxidation of primary alcohols to aldehydes by PCC under the conditions employed (CH_2Cl_2, reflux) involves the transfer of only two electrons (eq 2). This is contrary to the three-electron transfers observed in aqueous chromic acid oxidations.[13] Some examples of two-electron oxidations with Cr(VI) compounds have been reported in the past.[14] In the oxidation of isopropyl alcohol with chromic acid, the Cr(IV) species once formed is completely inert as an oxidant in the absence of at least a minimal amount of water.[15]

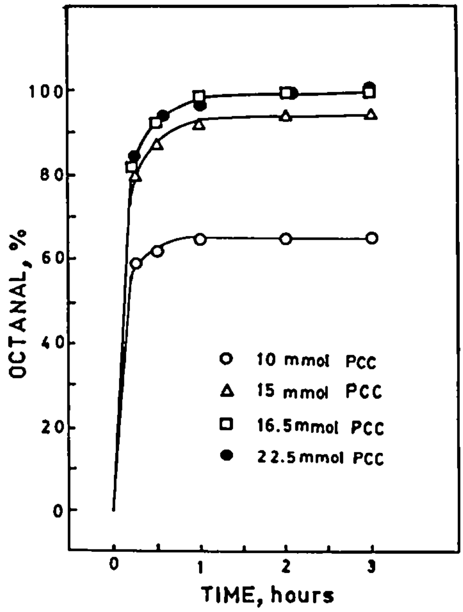


Figure 1. Oxidation of 15.0 mmol of *n*-octanol with different quantities of PCC in 15 mL of refluxing methylene chloride

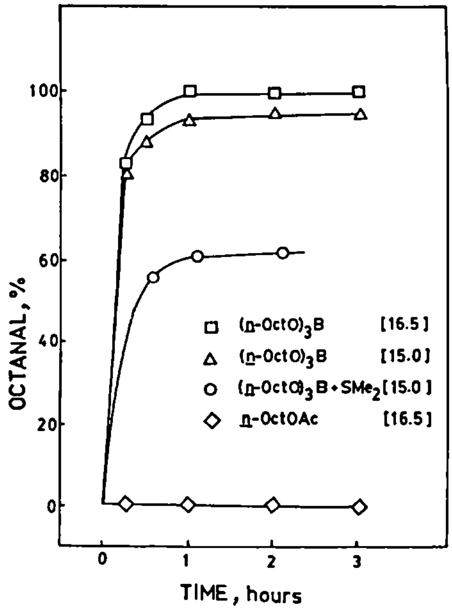


Figure 2. Reaction of tri-*n*-octyl borate (5.0 mmol) and *n*-octyl acetate (15.0 mmol) with PCC (16.5 mmol) in 15 mL of refluxing CH_2Cl_2. Competitive oxidation of tri-*n*-octyl borate (5.0 mmol) in the presence of SMe_2 (5.0 mmol) with PCC (15 mmol).

$$RCH_2OH + C_5H_5N\cdot HCl\cdot CrO_3 \longrightarrow RCHO + C_5H_5N\cdot HCl + CrO_2 + H_2O \qquad (2)$$

Similarly, the experiments with trioctylborate clearly established that three moles of PCC are required for the oxidation of one mole of trioctylborate (eq 3). Since borane-dimethyl sulfide ($BH_3\cdot SMe_2$, BMS) is a convenient and commonly used hydroborating agent, the organoboranes prepared using this reagent contain dimethyl sulfide. Therefore, it was determined that one mole of SMe_2 consumes one mole of PCC. Consequently, either it is removed under reduced pressure, or sufficient excess PCC was used for oxidation. The inertness of the oxidation conditions toward a common functional group, ester, was established by the treatment of octyl acetate with PCC (Figure 2).

$$(C_8H_{17}O)_3B + 3\ C_5H_5N\cdot HCl\cdot CrO_3 \longrightarrow 3\ C_7H_{15}CHO + B(OH)_3 + 3\ C_5H_5N\cdot HCl + 3\ CrO_2 \qquad (3)$$

The amount of PCC required for the complete oxidation of trialkylboranes to aldehydes was determined in the same manner. It is evident that one mole of trialkylborane is oxidized by six moles[12] of PCC to provide three moles of aldehyde (Figure 3).

Oxidation of Trialkylboranes With PCC. The terminal alkenes were transformed into the corresponding organoboranes by treatment with BMS in methylene chloride[16] and the resulting organoboranes without isolation were oxidized with excess PCC in the same solvent. Representative aldehydes were prepared in good yields and excellent purities (Table 1). Since the regioselectivity in the hydroboration of straight chain terminal alkenes with BMS is 94:6, the organoboranes contain approximately 6% of the secondary alkyl groups, which give rise to methyl ketones upon oxidation (eq 4).

The oxidation of organoboranes with PCC proceeds via the formation of borate esters, as observed by the ^{11}B NMR spectrum of aliquots from an incomplete reaction. This has been further substantiated by observation of the facile oxidation of borate esters by PCC.[2b]

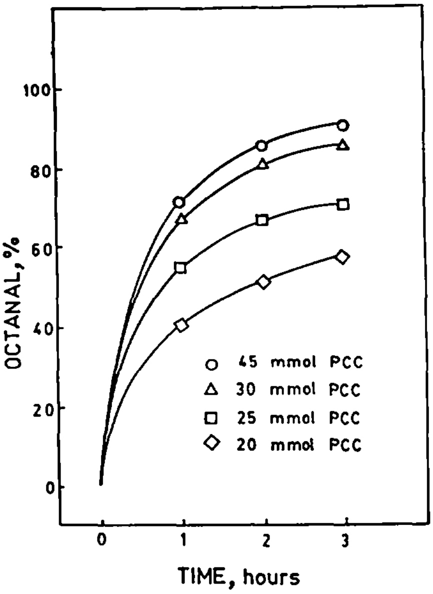


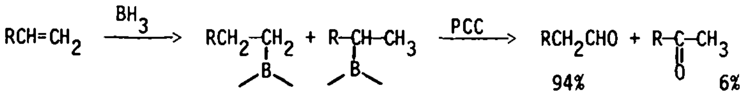
Figure 3. Reaction of 5.0 mmol of tri-*n*-octylborane with different quantities of PCC in 30 mL CH_2Cl_2 under reflux

This is the first convenient method available for the direct conversion of organoboranes into aldehydes. However, there are some limitations to this procedure. First, the aldehyde obtained from terminal monosubstituted alkenes contains up to 6% of the corresponding methyl ketones (eq 4). Secondly certain functional groups are not totally inert toward BMS. Consequently, in the hydroboration of alkenes containing such functional groups, considerable amounts of undesired products can be formed. Finally, BMS does not distinguish efficiently between various types of double bonds in dienes, making it difficult to achieve the selective hydroboration of a specific double bond.

Table 1. Preparation of Representative Aldehydes by the Oxidation of Trialkylboranes With Pyridinium Chlorochromate

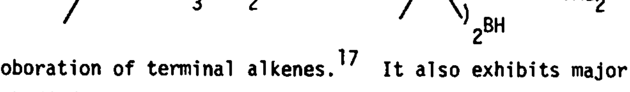
		Yield[c]	Bp, °C/mm		$n^{20}D$	
Alkene	Aldehyde[a,b]	%	Obs.	Rep.	Obs.	Rep.
1-hexene	hexanal	72	76-78/45	128/760[d]	1.4029	1.4039[d]
1-octene	octanal	70	65-66/15	72/20[d]	1.4185	1.4183[e]
1-decene	decanal	74	61-63/3	81/7[d]	1.4285	1.4287[d]
1-dodecene	dodecanal	78	70-72/2	100/3.5[d]	1.4355	1.4350[d]
3,3-dimethyl-1-butene	3,3-dimethylbutanal	64	102/745	102-103/750[f]	1.4145	1.4150[d]
methylenecyclohexane	cyclohexylcarboxaldehyde[g]	71	58-60/18	161-163/760[e]	1.4509	1.4500[e]

[a] The aldehydes were identified by comparison of ^1H NMR spectra, bp, $n^{20}D$ and GC retention times with those of authentic samples. [b] GC analysis on 12 ft x 1/8 in column packed with 5% QF-1 on Varaport-30 revealed the presence of < 5% of minor products, the corresponding methyl ketones. [c] Overall isolated yields of > 95% pure aldehydes based on the starting alkenes; all reactions were carried out on 60 mmol of alkenes. [d] Taken from "Handbook of Chemistry and Physics," 60th edition; Chemical Rubber Co., Cleveland, 1980. [e] Taken from "Catalog Handbook of Fine Chemicals," Milwaukee, 1981-82. [f] Taken from L. Schmerling, *J. Am. Chem. Soc.*, 68, 1650 (1946).



$$RCH=CH_2 \xrightarrow{BH_3} RCH_2\text{-}\underset{\diagup B \diagdown}{CH_2} + R\text{-}\underset{\diagup B \diagdown}{CH}\text{-}CH_3 \xrightarrow{PCC} \underset{94\%}{RCH_2CHO} + \underset{6\%}{R\text{-}\overset{}{\underset{O}{\underset{\|}{C}}}\text{-}CH_3} \quad (4)$$

Oxidation of Alkyldisiamylboranes. The difficulties associated with the use of BMS can be circumbented by employing the highly selective hydroborating agent, bis(3-methyl-2-butyl)borane (disiamylborane), derived from 2-methyl-2-butene (eq 5).[17] Disiamylborane exhibits enhanced regioselectivity (> 99%) in the hydroboration of terminal alkenes.[17] It also exhibits major differences in the rates of reactions with different types of alkenes, permitting in dienes the selective hydro-

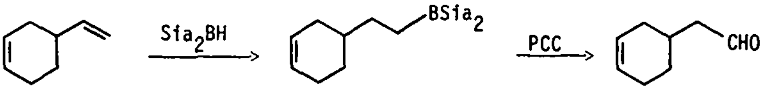


(5)

boration of terminal double bonds in the presence of internal C=C linkages.[18] A high selectivity is exhibited by disiamylborane in the hydroboration of alkenes containing typical functional groups.[19] Consequently, we examined the oxidation of alkyldisiamylboranes as a route for efficient aldehyde synthesis. Indeed, the reaction of alkyl disiamylborane with PCC was clean, providing the desired aldehydes, along with 3-methyl-2-butanone (eq 6). The resulting aldehyde can usually be

$$RCH{=}CH_2 \xrightarrow{Sia_2BH} RCH_2CH_2BSia_2 \xrightarrow{PCC} RCH_2CHO + 2(CH_3)_2CHCOCH_3 \qquad (6)$$

separated without difficulty from the volatile side-product. The exceptional selectivity of this method is demonstrated by the conversion of 4-vinylcyclohexene into 3-cyclohexenylacetaldehyde (eq 7). The inertness of ester groups toward disiamylborane[19] was utilized in the conversion of typical



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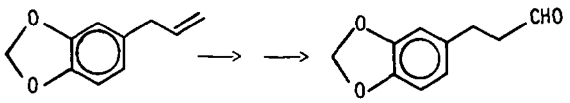
unsaturated esters into 5-acetoxypentanal (eq 8) and methyl 11-oxoundecanoate (eq 9). The method

$AcO(CH_2)_3CH{=}CH_2 \longrightarrow \longrightarrow AcO(CH_2)_4CHO$ (8) $MeOOC(CH_2)_8CH{=}CH_2 \longrightarrow \longrightarrow MeOOC(CH_2)_9CHO$ (9)

proved to be applicable to an aromatic compound containing a methylenedioxy linkage, as shown by the conversion of safrole to the corresponding aldehyde (eq 10). The results of these and other



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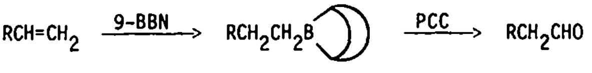
representative alkenes are summarized in Table 2.

Table 2. Preparation of Aldehydes via Hydroboration With Disiamylborane

Alkene	Aldehyde[a]	Yield[b] %	Bp, °C/mm Obs.	Bp, °C/mm Rep.	n^{20}_D Obs.	n^{20}_D Rep.
1-octene	octanal	71(89)	65-66/15	171/760[c]	1.4185	1.4183[c]
1-decene	decanal	72(88)	118-119/18	208/760[c]	1.4278	1.4280[c]
4-vinylcyclohexene	3-cyclohexenyl-acetaldehyde	67	82-83/15	46-52/3.7[d]	1.4836	
d-limonene	*p*-menth-1-ene-9-al	67(74)	49-51/0.3	33-34/0.001[e]	1.4745	1.4759[e]
4-pentenyl acetate	5-acetoxypent-anal	63	108-110/15	63-65/2[f]	1.4280	1.4311[f]
methyl 10-undecenoate	methyl 11-oxo-undecanoate	62	110-112/0.02		1.4432	1.4430[g]
safrole	3-(3,4-methylene-dioxyphenyl)-propanal	55	104-106/0.25		1.5386	

[a] The products were characterized by ^{1}H NMR. GC analysis using 12 ft x 1/8 in column packed with 5% QF-1 on Varaport-30 indicated the presence of traces of methyl ketones. The analysis on 12 ft x 1/8 in column packed with 10% SE-30 on Varaport-30 revealed that the products were > 97% pure. [b] Isolated yields. The values in parentheses are GC yields. [c] Taken from "Catalog Handbook of Fine Chemicals,: Aldrich Chemical Co., Milwaukee, 1981-82. [d] N. A. LeBel, N. D. Ojha, T. R. Menke and T. Newland, *J. Org. Chem.*, 37, 2896 (1972). [e] G. Ohloff, W. Giersch, K. H. Schulte-Ette and E. Kovats, *Helv. Chim. Acta*, 52, 1531 (1969). [f] A. A. Shamschurin, B. G. Kovalev and A. P. Donya, *Dokl. Akad. Nauk SSSR*, 190, 1362 (1970). [g] D. G. Tomecko and R. J. Adams, *J. Am. Chem. Soc.*, 49, 528 (1927).

Oxidation of *B*-Alkyl-9-BBN. 9-Borabicyclo[3.3.1]nonane (9-BBN) is a highly regioselective hydroborating agent possessing exceptional functional group selectivity as well.[20] Therefore, we examined the PCC oxidation of *B*-alkyl-9-BBN, prepared conveniently by the hydroboration of alkenes with 9-BBN (eq 11). Octanal was obtained from 1-octene in 82% yield (GC). However, the side-products,



(11)

cyclooctanone, cyclooctene and bicyclo[3.3.0]octene, derived from the bicyclooctyl moiety,[21] severely limit the application of this method for the preparation of aldehydes. Consequently, no attempt was made to prepare aldehydes from *B*-alkyl-9-BBN derivatives.

Oxidation of Dialkylchloroboranes. The need for large amounts of PCC (six moles for the preparation of one mole of aldehyde) for the oxidation of alkyldisiamylborane can be avoided by using dialkylhaloboranes. The hydroboration of a terminal alkene with monochloroborane proceeds with excellent regioselectivity, providing the dialkylchloroborane containing > 99% of primary alkyl groups (eq 12).[22] Dialkylchloroborane prepared in this way was hydrolyzed and the solvent, along with

$$2\ RCH{=}CH_2 + H_2BCl\cdot SMe_2 \longrightarrow (RCH_2CH_2)_2BCl\cdot SMe_2 \qquad (12)$$

SMe_2, was removed under reduced pressure (eq 13). The hydrogen chloride generated in the process

$$2(RCH_2CH_2)_2BCl\cdot SMe_2 + H_2O \longrightarrow (RCH_2CH_2)_2BOB(CH_2CH_2R)_2 + 2\ HCl + 2\ SMe_2 \qquad (13)$$

was neutralized with pyridine. Oxidation of the resulting borinic acid (or anhydride) with PCC provided the corresponding aldehyde.

In the attempted monohydroboration of a representative diene, *d*-limonene, with $BH_2Cl\cdot SMe_2$, a considerable amount of dihydroboration was observed, as revealed by the formation of diol and the presence of unreacted *d*-limonene upon hydrogen peroxide oxidation. Such dihydroboration of dienes with $BH_2Cl\cdot OEt_2$ has been observed in the past.[23] This difficulty was circumvented by the use of a new monofunctional hydroborating agent, thexylchloroborane (ThxBHCl)[24] for the selective monohydroboration of the diene (eq 14). The results with the preparation of aldehydes from dialkylchloroboranes are summarized in Table 3.

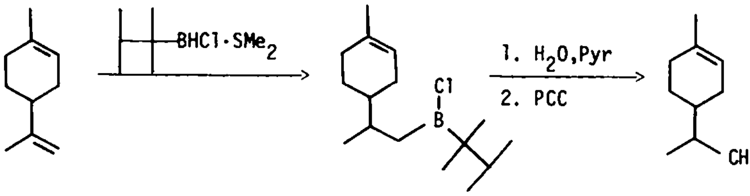


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Table 3. Preparation of Aldehydes via Hydroboration With Monochloroborane and Thexylchloroborane

		Yield	Bp, °C/mm		$n^{20}D$	
Alkene	Aldehyde[a]	%	Obs.	Rep.	Obs.	Rep.
1-octene[b]	octanal	68	75-76/27	171/760[d]	1.4187	1.4183[d]
1-decene[b]	decanal	66	112-113/27	207-209/760[d]	1.4282	1.4280[d]
4-vinylcyclohexene[c]						
d-limonene[c]	*p*-menth-1-en-9-al	68	59-61/0.4	33-34/0.001[e]	1.4749	1.4759[e]
[c]						
[c]						
[c]						

[a] GC analysis indicated > 97% purity. [b] $H_2BCl\cdot SMe_2$ was used for hydroboration. [c] $ThxBHCl\cdot SMe_2$ was used for hydroboration. [d] See footnote *c* in Table 2. [e] See corresponding footnote in Table 2.

We had hoped to obtain high yields (80-90%) of aldehydes using monochloroborane for hydroboration. Unfortunately, only 60-70% was realized. Presumably there is loss of a considerable amount of aldehyde in the reduced chromium tar.

Preparation of Ketones by PCC Oxidation. Organoboranes containing secondary alkyl groups are oxidized directly to ketones by aqueous chromic acid.[1] Such organoboranes are also oxidized by PCC to the corresponding ketones.[8] We examined the oxidation of dialkylchloroboranes derived from cyclic alkenes. Indeed, the ketones were obtained in excellent yields (eq 15). Representative cyclic ketones were prepared in order to demonstrate the generality of PCC oxidation of organoboranes (Table 4).

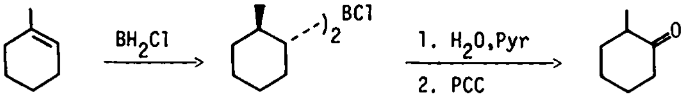

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Table 4. Preparation of Cyclic Ketones via Hydroboration With Monochloroborane

		Yield[b]	Bp, °C/mm		$n^{20}D$	
Alkene	Ketone[a]	%	Obs.	Rep.	Obs.	Rep.
cyclohexene	cyclohexanone	74	55-56/25	47/15	1.4512	1.4507
cycloheptene	cycloheptanone	83	68-70/20	71/19	1.4599	1.4608
cyclooctene	cyclooctanone	72	110-111/40	74/12	1.4689	1.4694
1-methylcyclohexene	2-methylcyclohexanone	81	55-56/16	167-168/735	1.4480	1.4483
1-methylcyclopentene	2-methylcyclopentanone	68	40-42/20	44/18	1.4369	1.4364
α-pinene	isopinocamphone	80	54-55/0.9	69-70/5[d]	1.4752	1.4745[d]

[a] Identified by ^1H NMR and GC retention times by comparison with the authentic samples. [b] Isolated yields of > 98% pure distilled products. [c] See footnote *d* in Table 1. [d] Taken from H. C. Brown and G. Zweifel, *J. Am. Chem. Soc.*, 83, 2544 (1961).

CONCLUSIONS

The rapid reaction of alkenes with a number of hydroborating agents provides a variety of organoboranes. These organoboranes can be readily oxidized with PCC under mild anhydrous conditions to afford the corresponding carbonyl compounds. Organoboranes derived from internal alkenes produce ketones in excellent yields[8] (Table 4). However, those obtained from terminal alkenes produce aldehydes in moderate yields. The present study deals mainly with the preparation of aldehydes from alkenes via hydroboration, followed by oxidation with PCC. Representative ketones have been prepared from cyclic alkenes via hydroboration with monochloroborane in order to demonstrate the generality of the oxidation of organoboranes with PCC.

The high yields, anhydrous reaction conditions and easy workup procedure make this a highly convenient method for the conversion of terminal alkenes into aldehydes.

EXPERIMENTAL SECTION

General Comments. The techniques employed in handling air-sensitive borane reagents are described elsewhere.[25] All glassware was oven-dried at 140°C, assembled hot and cooled under a stream of dry nitrogen. The transfer of all liquids and solutions were carried out using hypodermic syringes fitted with stainless steel needles. All reactions were carried out under a static pressure of nitrogen.

Materials. Methylene chloride (Aldrich, Gold Label) was dried over molecular sieves under nitrogen. BMS from Aldrich was used directly. Disiamylborane,[26] monochloroborane-dimethyl sulfide[22] and thexylchloroborane[24] were prepared as described elsewhere. All alkenes were the standard laboratory chemicals and were used after confirming their purities (by GC, ^{1}H NMR, n^{20}D). Pyridinium chlorochromate (Aldrich) was dried in a vacuum dessicator prior to use. 1-Octanol (Aldrich) was distilled from calcium hydride.

Analyses. The gas chromatographic analyses were carried out on a Varian 1400 instrument using a 8 ft x 1/8 in column packed with 5% SE-30 on Varaport-30. The separation of aldehydes from ketones was achieved on a QF-1 column (12 ft x 1/8 in). ^{1}H NMR and ^{11}B NMR spectra were recorded on Varian T-60 and FT-80A spectrophotometers respectively.

Determination of Stoichiometry. (A) Oxidation of 1-Octanol. In an oven-dried, nitrogen-flushed, 100-mL, round-bottom flask equipped with a magnetic stirring bar, a septum inlet, reflux condenser and a connecting tube leading to a mercury bubbler were placed 2.16 g (10 mmol) of PCC, 15 mL of CH_2Cl_2 and 1.3 mL (5 mmol) of *n*-tetradecane (internal standard for GC analysis). To the well-stirred mixture was added 2.36 mL (15 mmol) of 1-octanol and the mixture was heated under reflux. At definite intervals of time, 0.5 mL of the supernatant liquid was withdrawn and added to a vial containing 2 mL of ether in order to quench the reaction. The clear ether solution was analyzed by GC for the amount of octanal. The experiments were repeated with 3.24 (15 mmol), 3.56 (16.5 mmol) and 4.86 g (22.5 mmol) of PCC. The results are summarized in Figure 1.

(B) Oxidation of Tri-*n*-octyl Borate. The reaction was carried out as described above, except that 5.0 mmol of tri-*n*-octylborate (prepared from BMS and 1-octanol[27]) was added to the specified amounts of PCC in 15 mL CH_2Cl_2. In one experiment, 5.0 mmol of SMe_2 was mixed with the borate prior to oxidation. In another experiment, the stability of the ester group to the conditions of PCC oxidation was determined by treating 15 mmol of *n*-octyl acetate with 16.5 mmol of PCC in 15 mL of CH_2Cl_2. The results are summarized in Figure 2.

(C) Oxidation of Tri-*n*-octylborane. The reaction was carried out as described above for the borate ester, except that 5.0 mmol of tri-*n*-octylborane was treated with 20, 25, 30, 45 mmol of PCC in 30 mL CH_2Cl_2 and the formation of octanal was followed by GC. The results are summarized in Figure 3.

Preparation of Octanal From Tri-*n*-octylborane. Procedure A. In an oven-dried, nitrogen-flushed, 100-mL, round-bottom flask fitted with a septum inlet, magnetic stirring bar and a connecting tube leading to a mercury bubbler were placed 2.04 mL of BMS (20 mmol, neat reagent was 9.8 *M* in BH_3) and 20 mL of methylene chloride. To this solution was added 9.4 mL of 1-octene (60 mmol) dropwise with vigorous stirring. The reaction mixture was stirred for 1 h at room temperature and then the solvent and dimethyl sulfide were removed using a water aspirator. The resulting trialkylborane was added dropwise to a well-stirred suspension of 38.3 g of PCC (180 mmol) in 150 mL of methylene chloride, taken in a 500-mL round-bottom flask fitted with a septum inlet, a magnetic stirring bar and a reflux condenser with a connecting tube leading to a mercury bubbler. After the initial vigorous reaction subsided, the mixture was refluxed for 4 h with stirring. It was then cooled to room temperature, diluted with 200 mL of dry ethyl ether and filtered through 100 g of 100-200 mesh Florisil contained in a 350-mL sintered glass funnel. The residue in the flask was extracted with ether (3 x 50 mL) and the solvents removed on a rotary evaporator. The resulting liquid, on distillation under reduced pressure, gave 5.4 g (70% yield) of octanal, bp 65-66°/15 mm, n^{20}D 1.4185 [lit. bp 171°/760 mm, n^{20}D 1.4183]. GC analysis on QF-1 column revealed the presence of $\sim$ 5% 2-octanone. Other aldehydes were prepared in the same manner (Table 1).

Procedure B. The oxidation reaction was carried out in the same manner as described in Procedure A. To the reaction mixture after refluxing for 4 h was added 50 mL of water. Steam distillation provided a condensate consisting of methylene chloride, aldehyde and water. The organic layer was separated, the aqueous layer extracted with ether (2 x 50 mL), dried over anhydrous magnesium sulfate and the solvent removed. Distillation under reduced pressure afforded 5.3 g of octanal (a yield of 69%), bp 65-66°/15 mm, n^{20}D 1.4185.

Preparation of *n*-Octyldisiamylborane. In a 100-mL reaction flask[25] cooled in an ice-salt mixture (-12°C) was placed 6.63 mL of BMS (65 mmol) and 14.3 mL of 2-methyl-2-butene (135 mmol) was added dropwise with stirring. The reaction mixture was brought to 0°C after 15 min and maintained at this temperature for 1.5 h with stirring. Ether (10 mL) was added to the flask through the connecting tube to wash disiamylborane sticking to the sides of the flask. This also converts the slurry into a homogeneous solution, convenient for transfer. The mixture was stirred for an additional hour and then added dropwise through a double-ended needle to 9.42 mL of 1-octene (60 mmol) contained in another 100-mL reaction flask immersed in an ice bath. This mode of addition--borane-to-olefin--is particularly essential with dienes and olefins containing other functional groups. Hydroboration of 1-octene required 2 h at 0°C. At the end of this period, ether and methyl sulfide were removed under aspirator vacuum and *n*-octyldisiamylborane was dissolved in dichloromethane (25 mL).

Preparation of Octanal From *n*-Octyldisiamylborane. In a 1000-mL reaction flask equipped with a reflux condenser were placed 108 g of PCC (500 mmol) and 400 mL of dichloromethane. With vigorous stirring, the solution of *n*-octyldisiamylborane was added dropwise (exothermic). After the initial vigorous reaction subsided, the mixture was heated under reflux for 2 h, cooled to room temperature and diluted with 200 mL of ethyl ether. The clear solution was filtered through 100-200 mesh Florisil (200 g) contained in a 350-mL sintered glass funnel. The residue in the flask was washed with ether (3 x 100 mL) and filtered through the same Florisil pad. The combined filtrates were concentrated on a rotary evaporator and distilled under reduced pressure to obtain 5.5 g (71% yield) of octanal, bp 65-66°/15 mm. The GC analysis indicated that the product is essentially pure, containing traces of 2-octanone. Other aldehydes were prepared in the same manner (Table 2).

Preparation of Octanal From Di-*n*-octylchloroborane. In a 100-mL reaction flask fitted with a reflux condenser, 15 mL of a 1 *M* solution of $BH_2Cl\cdot SMe_2$ (15 mmol) was cooled to 0°C and 4.7 mL of 1-octene (30 mmol) was added dropwise with stirring. The mixture was stirred for 2 h at room temperature to ensure complete formation of dialkylchloroborane. To the well-stirred mixture was added 0.54 mL of water (30 mmol) and heated under reflux for 0.5 h. The HCl generated was neutralized by adding 1.5 mL of pyridine and the volatile materials were removed under the aspirator vacuum. The residue was dissolved in 10 mL of CH_2Cl_2 and added dropwise to a well-stirred suspension of 19.2 g of PCC (90 mmol) in 60 mL CH_2Cl_2 taken in a 500-mL reaction flask. The stirred mixture was heated under reflux for 3 h and octanal was isolated as described above. Yield: 2.63 g (68%), bp 75-76°/27 mm, $n^{20}D$ 1.4187. Other aldehydes were prepared in the same way (Table 3).

Preparation of Cyclohexanone. Dicyclohexylchloroborane was prepared from 3.1 mL of cyclohexene (30 mmol), hydrolyzed with 0.54 mL (30 mmol) of water and treated with 1.5 mL of pyridine, as described above. The oxidation with PCC was also carried out in the same manner. The usual workup, followed by distillation, provided 2.2 g (74% yield) of cyclohexanone, bp 55-56°/25 mm. Other ketones were also prepared in the same manner (Table 4).

Preparation of *p*-Menth-1-ene-9-al Using Thexylchloroborane. A stock solution of thexylchloroborane was prepared by adding 39.2 mL (330 mmol, 10% excess) of 2,3-dimethyl-2-butene to a mixture of 33 mL $H_2BCl\cdot SMe_2$ (300 mmol, the neat liquid was 9.1 *M* in the reagent), 4.4 mL of SMe_2 (60 mmol) and 73 mL of CH_2Cl_2 at 0°C. After complete addition, the mixture was allowed to attain 25°C and stirred for 1.5 h. The resulting solution was 2.0 *M* in $ThxBHCl\cdot SMe_2$. To a solution of 4.9 mL of *d*-limonene (30 mmol) in 10 mL CH_2Cl_2 was added 15 mL of the $ThxBHCl\cdot$solution (30 mmol) at 0°C and the mixture was stirred for 1 h at 25°C when the ^{11}B NMR showed a single resonance at δ 80 (uncomplexed R_2BCl). The solvent was removed under reduced pressure, the residue was dissolved in 15 mL of THF and 0.54 mL (30 mmol) of water was added. The mixture was stirred for 1 h at 25°C, 15 mL of pyridine was added dropwise. THF was removed under reduced pressure and the residue was dissolved in 20 mL of CH_2Cl_2. Oxidation was carried out with 29.2 g of PCC (135 mmol) mixed with 10 g of anhydrous NaOAc (in order to prevent possible migration of the double bond). The usual workup provided 3.1 g (68% yield) of *p*-menth-1-en-9-al, bp 59-61°C/0.4 mm, $n^{20}D$ 1.4749. Other unsaturated aldehydes were prepared in the same way.

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