Highly Selective Conversion of Terminal Olefins into Aldehydes[1]

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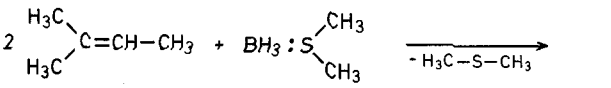
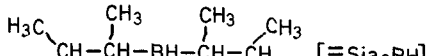
The convenient conversion of a terminal olefin into the corresponding aldehyde is a highly useful synthetic transformation. We recently reported[2] such a conversion involving the hydroboration of a terminal olefin with borane:dimethyl sulfide [$BH_3:S(CH_3)_2$][3,4] followed by the oxidation of the resulting organoborane with pyridinium chlorochromate ($Pyr\cdot HCl\cdot CrO_3$)[5]. This is the first convenient method available for the one-pot conversion of terminal olefins into aldehydes. However, there are some significant limitations to this procedure. First, the hydroboration of terminal olefins with borane:dimethyl sulfide exhibits a 94:6 regioselectivity[3]. Oxidation then produces the aldehyde with approximately 6% of the corresponding methyl ketone as an impurity[2]. Secondly, certain functional groups are not inert toward borane:dimethyl sulfide. Consequently, in the hydroboration of olefins containing such functional groups, considerable amounts of undesirable products can be formed. Finally, borane:dimethyl sulfide 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.

These difficulties can be circumvented with the highly selective hydroborating agent, bis[3-methyl-2-butyl]borane (disiamylborane), derived from 2-methyl-2-butene (Scheme **A**)[6].





Scheme **A**

Disiamylborane exhibits enhanced regioselectivity (≥99%) in the hydroboration of terminal olefins[6]. It also exhibits major differences in the rates of reactions with different types of olefins, permitting in dienes the selective hydroboration of terminal double bonds in the presence of internal C=C linkages[7]. A high selectivity is exhibited by disiamylborane in the hydroboration of olefins containing typical functional groups[8,9]. Therefore, we undertook to explore the synthesis of aldehydes **2** from terminal olefins **1** utilizing the exceptional selectivity of disiamylborane. Indeed, we discovered that the disiamylborane derivatives are readily converted into aldehydes by the pyridinium chlorochromate oxidation in refluxing dichloromethane (Scheme **B**).

The resulting aldehyde containing traces (<1%) of the methyl ketone can usually be separated without difficulty from the volatile side product, 3-methyl-2-butanone, see e.g. Scheme **C**.

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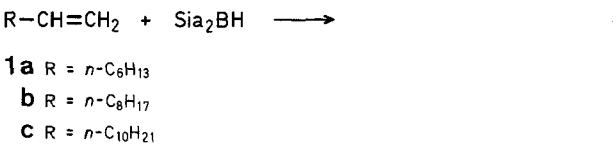
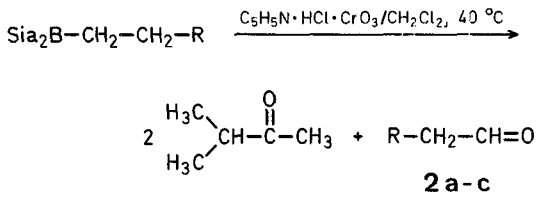
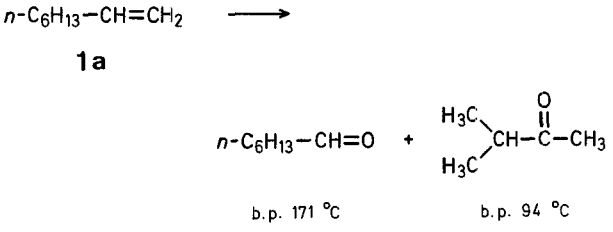


1a R = *n*-C_6H_{13}
b R = *n*-C_8H_{17}
c R = *n*-$C_{10}H_{21}$

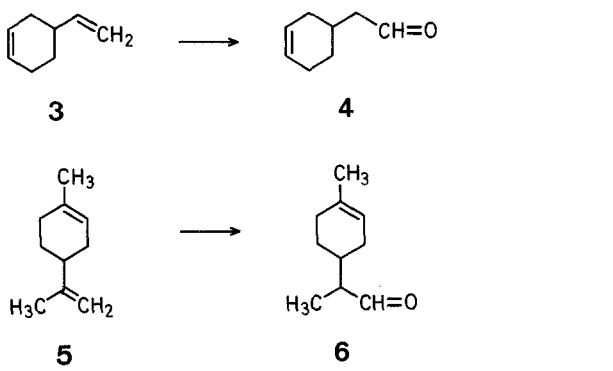


Scheme **B**



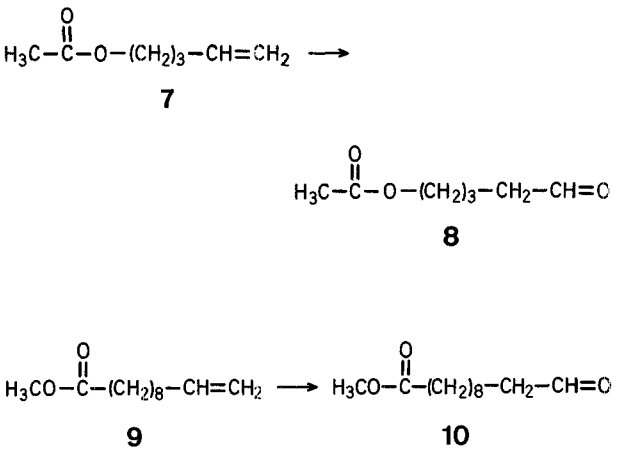
Scheme **C**

The exceptional selectivity of this method is demonstrated by the conversion of 4-vinylcyclohexene (**3**) into 3-cyclohexenylacetaldehyde (**4**) and of *d*-limonene (**5**) into *p*-menth-1-en-9-al (**6**; Scheme **D**).



Scheme **D**

The inertness of ester groups toward disiamylborane[9] was utilized in the conversion of typical unsaturated esters e.g. **7** and **9** into 5-acetoxypentanal (**8**) and methyl 11-oxoundecanoate (**10**), Scheme **E**.



Scheme **E**

The method proved to be applicable to an aromatic compound containing the labile methylenedioxy linkage, as shown by the conversion of safrole (**11**) to the corresponding aldehyde (**12**), Scheme **F**.

Scheme **F**

The results with these and other representative olefins are summarized in the Table.

This development makes available a valuable new procedure for the conversion of terminal double bonds in compounds containing other types of double bond or reducible functional groups into the corresponding aldehydes.

Table. Synthesis of Aldehydes via Disiamylborane Hydroboration

Olefin	Aldehyde[a]	Yield [%][b]	b.p./torr		n_D^{20}		Reference
			observed	reported	observed	reported	
1a	**2a**	71 (89)	65–66 °C/15	171 °C/760	1.4185	1.4183	11
1b	**2b**	72 (88)	118–119 °C/18	208 °C/760	1.4278	1.4280	11
1c	**2c**	69	115–116 °C/4	185 °C/100	1.4337	1.4344	11
3	**4**	67	82–83 °C/15	46–52 °C/3.7	1.4836	—	12
5	**6**	67 (74)	49–51 °C/0.3	33–34 °C/0.001	1.4745	1.4759	13
7	**8**	63	108–110 °C/15	63–65 °C/2	1.4280	1.4311	14
9	**10**	62	110–112 °C/0.2	—	1.4432	1.4430	15
11	**12**[c]	55	104–106 °C/0.25	—	1.5386	—	—

[a] The products were characterized by ^{1}H-N.M.R. The G.L.C. analysis using 12 ft × 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 × 1/8 in column packed with 10% SE-30 on Varaport-30 revealed that the products were >97% pure.

[b] Yield of isolated products; values in the parentheses are G.L.C. yields.

[c] Satisfactory microanalytical values and ^{13}C-N.M.R. spectra were obtained. ^{1}H-N.M.R.: δ = 9.67 (partly resolved t, 1H, J = 1.5 Hz); 6.60 (m, $3H_{arom}$); 5.80 (s, 2H, O—CH_2—O); 2.60 ppm (distorted t, 4H, CH_2—CH_2).

***n*-Octyldisiamylborane; Typical Procedure:**
In an oven-dried, nitrogen-flushed 100-ml round bottom flask[10] fitted with a septum inlet, magnetic stirring bar, and a connecting tube leading to a mercury bubbler is placed borane:dimethyl sulfide (6.63 ml, 65 mmol, neat reagent is 9.8 molar in borane). The flask is cooled in an ice/salt mixture (−12 °C) and 2-methyl-2-butene (14.3 ml, 135 mmol) is added dropwise with stirring. The reaction mixture is brought to 0 °C after 15 min and maintained at this temperature for 1.5 h with stirring. Ether (10 ml) is 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 is stirred for an additional hour, and then added dropwise through a double-ended needle to 1-octene (9.42 ml, 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 requires 2 h at 0 °C. At the end of this period, ether and dimethyl sulfide are removed under aspirator vacuum and *n*-octyldisiamylborane is dissolved in dichloromethane (25 ml).

Oxidation of *n*-Octyldisiamylborane with Pyridinium Chlorochromate; Typical Procedure:
In a 1000-ml reaction flask[10] equipped with a reflux condenser are placed pyridinium chlorochromate (108 g, 500 mmol) and dichloromethane (400 ml). With vigorous stirring, the solution of *n*-octyldisiamylborane is added dropwise (exothermic reaction). After the initial vigorous reaction has subsided, the mixture is heated under reflux for 2 h, cooled to room temperature, and diluted with ethyl ether (200 ml). The clear solution is filtered through 100–200 mesh Florisil (200 g) contained in a 350-ml sintered glass funnel. The residue in the flask is washed with ether (3 × 100 ml) and filtered through the same Florisil pad. The combined filtrates are concentrated on a rotary evaporator, and distilled under reduced pressure to give octanal; yield: 5.5 g (71%); b.p. 65–66 °C/15 torr. The G.L.C. analysis (see Table) indicates that the product is essentially pure, containing traces of 2-octanone.

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[2] C. Gundu Rao, S. U. Kulkarni, H. C. Brown, *J. Organometal. Chem.* **172**, C20 (1979).
[3] C. F. Lane, *J. Org. Chem.* **39**, 1437 (1974).
[4] Available from Aldrich Chemical Co., Milwaukee, Wisconsin.
[5] E. J. Corey, J. W. Suggs, *Tetrahedron Lett.* **1975**, 2647.
[6] H. C. Brown, G. Zweifel, *J. Am. Chem. Soc.* **83**, 1241 (1961).
[7] H. C. Brown, A. W. Moerikofer, *J. Am. Chem. Soc.* **83**, 3417 (1961).
[8] H. C. Brown, K. A. Keblys, *J. Am. Chem. Soc.* **86**, 1791 (1964).
[9] H. C. Brown, K. A. Keblys, *J. Am. Chem. Soc.* **86**, 1795 (1964).
[10] H. C. Brown, *Organic Syntheses via Boranes*, Wiley-Interscience, New York, 1975. See Chapter 9 for details.
[11] *Catalog Handbook of Fine Chemicals*, Aldrich Chemical Co., Milwaukee, Wisconsin, U.S.A.
[12] N. A. LeBel, N. D. Ojha, J. R. Menke, R. J. Newland, *J. Org. Chem.* **37**, 2896 (1972).
[13] G. Ohloff, W. Giersch, K. H. Schulte-Ette, E. Kovats, *Helv. Chim. Acta* **52**, 1531 (1969).
[14] A. A. Shamschurin, B. G. Kovalev, A. P. Donya, *Dokl. Akad. Nauk SSSR* **190**, 1362 (1970); *Engl. Trans.* **190**, 169 (1970).
[15] C. G. Tomecko, R. Adams, *J. Am. Chem. Soc.* **49**, 528 (1927).

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