PCC oxidation of organoboranes obtained using acetoxyborohydride

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The selective hydroboration with acetoxyborohydride of dienes and functionalized olefins followed by PCC oxidation afford the corresponding carbonyl derivatives.

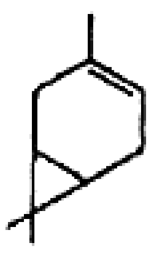
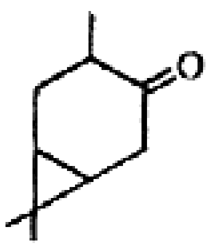
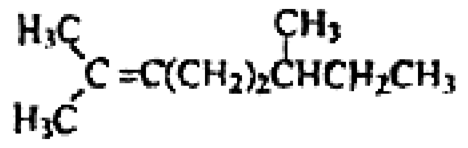
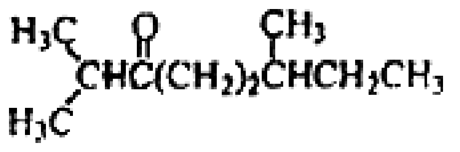
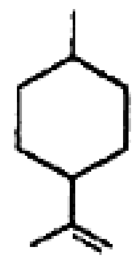
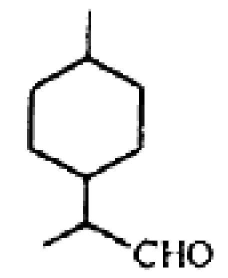
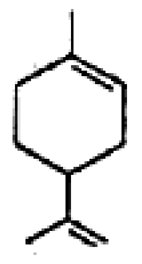
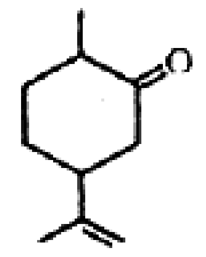
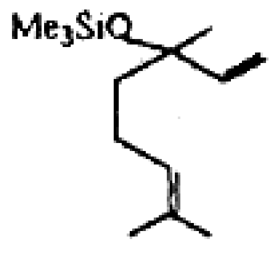
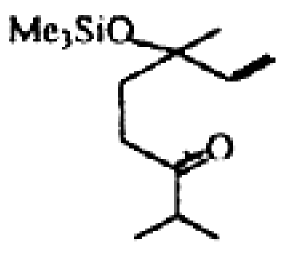
Organoboranes, obtained via hydroboration[1] of carbon-carbon multiple bonds, are versatile synthetic intermediates which can virtually be converted to any functionality[2]. Acetoxyborohydride ($CH_3COO\overline{B}H_3$) can be conveniently obtained[3] from sodium borohydride and mercuric acetate. We have reported that this reagent selectively hydroborates an internal or more substituted carbon-carbon double bond of diene or triene[4], and hydroborates only carbon-carbon double bond of functionalized olefins[5] without effecting functionalities like OTs, OMs, halogens, lactones etc. The above advantages of acetoxyborohydride to synthesize functionalized and unsaturated organoboranes prompted us to explore the other utilities of this hydroborating reagent. Brown *et al.*[6,7] reported that organoboranes can be conveniently converted to the corresponding ketones and aldehydes upon PCC oxidation. Consequently, organoboranes prepared from acetoxyborohydride when treated with PCC undergo oxidation to afford, in good yields, the corresponding aldehydes and ketones (eqns. 1, 2) (Table 1). As reported[4], the reagent selectively hydroborates the more substituted C=C and PCC oxidation of the resulting organoborane intermediate affords the corresponding enones (sl. nos. 8, 9, Table 1).

$$X\text{–}(CH_2)_n\text{–}CH{=}CH_2 \xrightarrow[\text{ii) PCC}]{\text{i) } CH_3COO\overline{B}H_3} X\text{–}(CH_2)_n\text{–}CH_2CHO \qquad (1)$$

$$X\text{–}CH{=}CH_2 \xrightarrow[\text{ii) PCC}]{\text{i) } CH_3COO\overline{B}H_3} X\text{–}(CH_2)_n\text{–}CHO \qquad (2)$$

X = Ether or esters or R–CH=CH–

Table 1. Hydroboration-PCC oxidation of alkenes to corresponding carbonyl compounds

Sl. no.	Alkene	Product	Yield(%)
1			79
2	$H_3COOC(CH_2)_8CH{=}CH_2$	$H_3COOC(CH_2)_8CH_2CHO$	85
3			81
4	$H_3C(CH_2)_{14}CH{=}CH_2$	$H_3C(CH_2)_{14}CH_2CHO$	83
5	$H_3C(CH_2)_8CH{=}CH_2$	$H_3C(CH_2)_8CH_2CHO$	84
6	 $\mathrm{(H_3C)_2C{=}C(CH_2)_2\overset{CH_3}{C}HCH_2CH_3}$	 $\mathrm{(H_3C)_2CH\overset{O}{\overset{\|}{C}}(CH_2)_2\overset{CH_3}{C}HCH_2CH_3}$	80
7			81
8			79
9			80

Sl. nos. 2, 3, 4, 5 and 9 also yielded Markownikov products (6–13%) while no product could be isolated in other cases.

Experimental

Preparation of organoborane[4] : Dry THF was added to sodium borohydride (2.5 mmol) under nitrogen. The contents were kept in an ice bath and mercuric acetate (1.25 mmol) was added slowly under blanket of nitrogen. The mixture was stirred for 1 h at 0°. It was brought to room temperature, an alkene (2.5 mmol) in THF (2 ml) was added dropwise, and further stirred at room temperature for 16 h to afford organoborane from which THF was distilled off under reduced pressure.

PCC oxidation of organoborane[6,7] : PCC[8] (3.75 mmol) dissolved in anhydrous dichloromethane (6.5 ml) was transferred to the above freshly prepared organoborane, preventing entry of air. The reaction mixture was refluxed for 1 h, then cooled to room temperature, dichloromethane (10 ml) was added, followed by brine solution. The organic layer was separated. The aqueous layer was washed with dichloromethane (2 × 10 ml) and the combined organic layer was dried over magnesium sulfate. The evaporation of the solvent yielded a thick brown liquid whose TLC showed completion of the reaction and formation of single product. This crude reaction mixture was chromatographed over silica gel and eluted with benzene : ethyl acetate with increasing percentage of ethyl acetate. Each pure carbonyl compound was then identified by IR and NMR spectral analyses.

Spectral analysis of products (sl. nos. 6, 7 and 9) are given below (products sl. nos. 1[9], 2[10], 3[10], 4[11], 5[11] and 8[12] are known compounds) : sl. no. 6, b.p. 210°, δ 2.3 (3H, m), 1.4 (3H, d, *J* 6 Hz), 1.3 (6H, d, *J* 6.3 Hz), 1.0 (5H, m), 0.9 (3H, m), ν_{max} 2920, 1710 (C=O), 1450, 1400, 1380, 1310 cm^{-1}; sl. no. 7, b.p. 170–172°, δ 9.7 (1H, d, C*H*O), 2.2 (1H, m), 1.4 (3H, d, *J* 5.9 Hz), 1.2 (1H, m), 1.0–0.9 (9H, m), 0.8 (3H, d, *J* 6.1 Hz), ν_{max} 2940, 2750 (O=C–*H*), 1760 (C=O), 1480, 1410, 1370, 1300 cm^{-1}; sl. no. 9, b.p. 232–235°, δ 5.97 (1H, m, C*H*=CH_2), 5.20 (2H, m, CH_2=CH), 2.1 (3H, m), 1.20 (3H, s), 1.0 (2H, m), 0.8 (6H, d, *J* 5.9 Hz), ν_{max} 3040, 2930, 1740 (C=O), 1630, 1460, 1380, 1300 cm^{-1}.

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