A Facile Conversion of Alkenes to Alcohols with Benzyltriethylammonium Borohydride–Chlorotrimethylsilane

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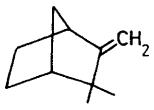
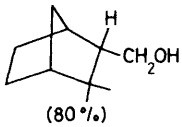
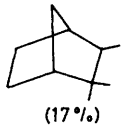
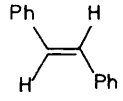
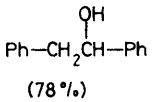
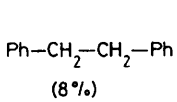
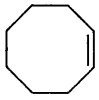
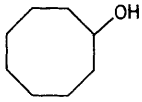
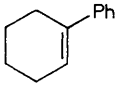
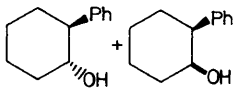
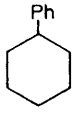
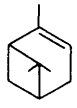
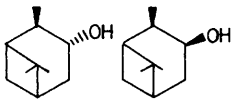
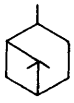
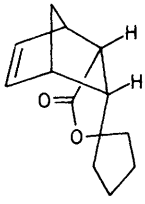
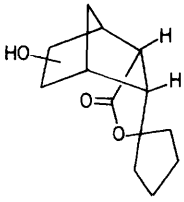
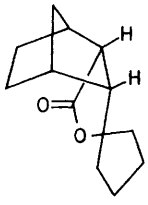
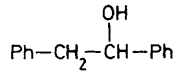
A combination of benzyltriethylammonium borohydride and chlorotrimethylsilane (1 : 1) in dichloromethane at 0 °C has been found to be a convenient reagent system for the conversion of alkenes to alcohols, the hydroxy group of which is introduced in an anti-Markovnikov manner.

Recently, reducing agents formed by a combination of transition metal halide and $NaBH_4$, have been used for reduction of various functional groups; these reactions have attracted considerable attention in organic synthesis.[1—4] For example $SnCl_4$–$NaBH_4$,[2] $TiCl_4$–$NaBH_4$,[3] and $COCl_2$–$NaBH_4$[4] have been found to be useful reagents for effecting the conversion of alkenes to alcohols. Reductive cleavage of acetals and ketals has been reported using Me_3SiCl–$ZnBH_4$[5] whereas Ni_2B–Me_3SiCl[6] has been used for the selective reduction of aldehydes in the presence of ketones.

Table 1. Reaction of alkenes with $PhCH_2N^+(Et)_3{-}BH_4{}^a{-}Me_3SiCl$.

Entry	Alkene	t/h	Alcohol[b,c]	Hydrocarbon
1		3	 (80%)	 (17%)
2		8	 (78%)	 (8%)
3		0.5	 (74%)	 (18%)
4	$Me(CH_2)_6CH{=}CH_2$	0.5	$Me(CH_2)_7CH_2OH$ (72%)	$Me(CH_2)_7Me$ (18%)
5		4	 3 : 1 (84%)	 (9%)
6	 (±)	3	 7 : 1 (82%)	 (11%)
7		2	 (68%)	 (9%)
8	$Ph{-}C{\equiv}C{-}Ph$	10	 (70%)	$Ph{-}CH_2{-}CH_2{-}Ph$ (13%)

[a] Combination of $NaBH_4$ and Me_3SiCl in dry dimethoxyethane (DME) was less effective and produced alcohols in lower yields. [b] All compounds were identified by direct comparison of physical data with those of authentic samples. [c] Yields refer to purified products after chromatography.

During our investigations, a combination of benzyltriethylammonium borohydride[7] and chlorotrimethylsilane (1 : 1) was observed to react readily with alkenes to produce the corresponding alcohols directly in high yields (anti-Markovnikov addition).† The results of this unusual reaction are summarized in Table 1. In all the reactions, apart from the alcohol (major product) a small amount of the corresponding saturated hydrocarbon (7—18%) is also formed. In the reaction of 1-phenylcyclohexene (entry 5) and (±)-α-pinene‡ (entry 6) the corresponding alcohols are formed as a mixture of *cis* and *trans* isomers. Diphenyl acetylene (entry 8) on treatment with this reagent system (10 h) yields 1,2-diphenyl ethanol (70%).§

The mechanism of this unusual reaction remains unclear but hydroboration–oxidation can be excluded as the reactivity of this reagent system is considerably different.¶ The product alcohols may have been formed by air oxidation and/or hydrolysis of some intermediates *via* a radical mechanism.†† It appears that the saturated hydrocarbons formed as minor products arise by deoxygenation of the alcohols.‡‡ Further studies are in progress to delineate the mechanism of this novel reaction and its application to organic synthesis.

We thank C.S.I.R. and D.S.T. (New Delhi) for financial assistance.

Received, 9th January 1989; Com. 9/00137I

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† In a typical reaction, to a stirred solution of the alkene (4 mmol) and benzyltriethylammonium borohydride (4 mmol) in dry dichloromethane (6 ml) at 0 °C was added chlorotrimethylsilane (4 mmol) in dichloromethane (2 ml), and the reaction mixture was stirred for 0.5—4 h. A solution of 10% K_2CO_3 (3 ml) was added and stirred for an additional 0.15 h to produce the alcohol in very good yields.

‡ The reaction of (+)-α-pinene under these reaction conditions, yielded (−)-isopinocampheol (74%) and (+)-neo-isopinocampheol (10%).

§ When the reaction is interrupted after 3 h, a mixture of stilbene (*cis* : *trans*, 1 : 2) can be isolated in 12% yield.

¶ In contrast to hydroboration, this reaction is not stereoselective and diphenylacetylene gives *trans*-stilbene as the major product rather than *cis*-stilbene.

†† Under oxygen-free reaction conditions, alcohols were obtained in lower yields. One of the referees suggested that the reaction can proceed *via* the formation of alkylboranes and further reaction with oxygen to give hydroperoxides which can be subsequently reduced by borohydride to yield the alcohols.

‡‡ When 2-phenylcyclohexanol was treated with benzyltriethylammonium borohydride and Me_3SiCl (1 : 1) at 0 °C for 2 h. Phenylcyclohexane was obtained in 15% yield.