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

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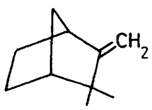
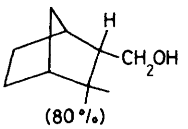
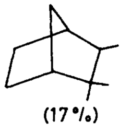
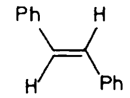
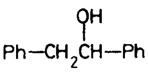
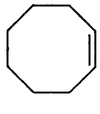
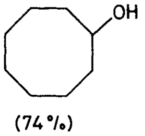
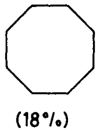
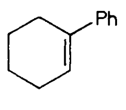
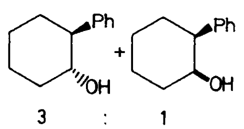
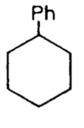
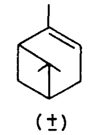
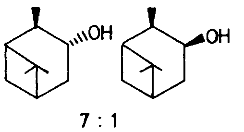
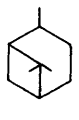
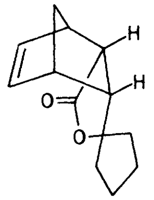
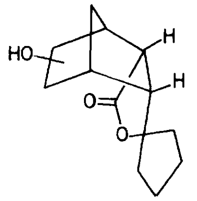
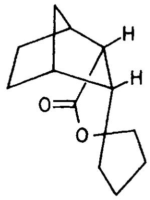
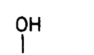
A combination of benzyltriethylammonium borohydride and chlorotrimethylsilane (1 : 1) in dichloromethane at 0 °C has been found to be a convenient reagent system for the conversion of alkenes to alcohols, the hydroxy group of which is introduced in an anti-Markovnikov manner.

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	 $Ph{-}CH_2CH(OH){-}Ph$ (78%)	$Ph{-}CH_2{-}CH_2{-}Ph$ (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	 $Ph{-}CH_2{-}CH(OH){-}Ph$ (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.

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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.