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Silica Gel Supported Zinc Borohydride.[1] A Novel Reagent for Hydration of Unactivated Alkenes and Alkynes

Brindaban C. Ranu,* Arunkanti Sarkar, Manika Saha and Rupak Chakraborty

Department of Organic Chemistry, Indian Association for the
Cultivation of Science, Jadavpur, Calcutta - 700 032, India.

Abstract : A simple and general procedure for hydration of unactivated alkenes and alkynes producing less substituted alcohols selectively has been achieved by the reaction of the corresponding alkenes or alkynes on silica gel support with zinc borohydride in 1,2-dimethoxyethane.

Supported reagents are of growing use in organic synthesis.[2] Advantages frequently claimed in favour of supported reagents compared with their homogeneous counterparts are increased yields, mild conditions, and clean and rapid reactions. In addition to these advantages regio-, stereo-, and chemoselective control using supported reagents is also being achieved.[3] We have recently introduced silica gel suupported zinc borohydride for the regio- and stereoselective reductive cleavage of unsymmetrical epoxides,[1,4] and regioselective 1,2-reduction of conjugated ketones and aldehydes,[5] and we herein wish to disclose another application of this reagent for regioselective hydration of unactivated alkenes and alkynes.[6]

Hydration of alkenes or alkynes to alcohols is one of the most useful reactions in organic synthesis. In principle, an unsymmetrical alkyl-substituted carbon-carbon double or triple bond on such reaction can produce the more substituted carbinol or the less substituted alcohol depending on the mode of hydration. In general, oxymercuration-demercuration[7] of alkenes produces more substituted alcohols and, hydroboration-oxidation leads to less substituted alcohols.[8] Recently, various combinations of Lewis acids and borohydrides, e.g. $SnCl_4$-$NaBH_4$,[9] $TiCl_4$-$NaBH_4$,[10] $CoCl_2$-$NaBH_4$,[11] Me_3SiCl-$PhCH_2N^+(Et)_3\,^-BH_4$[12] and $TiCl_4$-$PhCH_2N^+(Et)_3\,^-BH_4$[13] have also been reported to effect hydration of olefins providing less substituted alcohols. On the other hand, alkynes on usual hydroboration with diborane followed by oxidation with alkaline hydrogen peroxide[14] or by modified procedure with rhodium(III) porphyrin as catalyst[15] undergo hydration to produce the less substituted alcohols predominantly.

As a part of our continuing efforts to utilize surface-mediated reactions for useful synthetic transformations,[16] we have discovered that in general, the reaction of zinc borohydride in 1,2-dimethoxyethane with alkenes or alkynes on a silica gel support furnished clean regioselective hydration to produce the less substituted alcohols in excellent yields.

$$\begin{matrix} R-CH=CH_2 \\ \text{or} \\ R-C\equiv CH \end{matrix} \xrightarrow[\text{DME, RT}]{SiO_2/Zn(BH_4)_2} RCH_2CH_2OH$$

In a general procedure, a solution of zinc borohydride in DME was added to alkene or alkyne uniformly adsorbed on activated silica gel and the reaction was continued at room temperature under stirring till completion (TLC). The reaction mixture was then decomposed with water and filtered. The filtrate was extracted with ether and the extract was evaporated to leave the product. A wide range of structurally varied alkenes and alkynes were treated by this procedure and were found to undergo clean regioselective hydration to give the corresponding less substituted alcohols in high yields. The results are presented in Table 1.

For alkenes, the regioselectivity, in general, is good. Less substituted alcohols are formed exclusively from all alkenes except styrene which produced about 20% of the more substituted alcohol, 1-phenylethanol (entry 2). This may be due to the electronic influence of the adjacent phenyl ring.

The results with alkynes are very interesting. Among the terminal acetylenes, 1-hexyne and 1-octyne produced 1-hexanol and 1-octanol respectively as the sole isolable products (entries 11,12), whereas phenyl acetylene led to a mixture of 2-phenylethanol and 1-phenylethanol, the more substituted alcohol, 1-phenyl ethanol being the major product (entry 13). In the reactions of internal acetylenes a modest selectivity for hydration at the acetylenic carbon next to tertiary or secondary carbon centre has been observed.

The reactions are reasonably fast and no side products other than regio- or stereoisomeric alcohols have been isolated. An important observation regarding this reaction is that silica gel or zinc borohydride alone failed to promote any hydration. Replacement of zinc borohydride with other zinc salts like zinc acetate, zinc sulfate, zinc oxide and zinc chloride also produced no alcohols. A combination of zinc borohydride and silica gel is essential for the reaction to proceed.

The mechanism of this reaction is not very clear to us. A possibility of surface-generated borane has been considered. To investigate this, for comparison all the alkenes and alkynes were subjected to hydroboration followed by oxidation with alkaline hydrogen peroxide by standard procedure.[8] It was found that distribution of stereo-, and regioisomeric alcohols obtained by our procedure differ for many substrates from that achieved by hydroboration-oxidation (Table 1). In some cases (entries 9,13,17) this difference is very significant. On the other hand, in the present reaction no oxidizing agent has been used. That same result was obtained when the reaction was carried out under argon with careful exclusion of oxygen or air also disapproves the possibility of aerial oxidation. These observations indicate that the present reaction with silica gel supported zinc borohydride may not follow the same course as in normal hydroboration-oxidation process.

Table 1. Hydration of Alkenes and Alkynes with Silica Gel Supported Zinc Borohydride

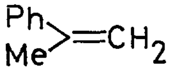
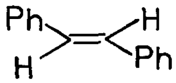
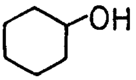
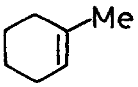
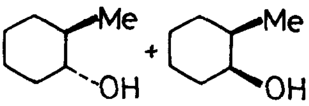
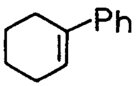
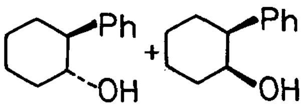
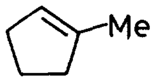
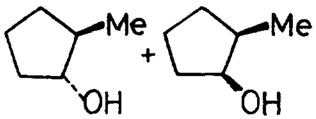
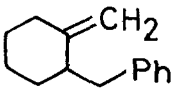
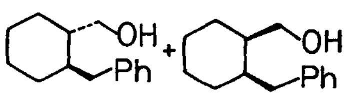
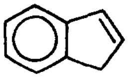
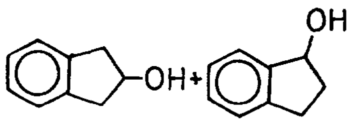
Entry	Substrate	Time (h)	Products (ratio)^a		Yield(%)^b
1	$CH_3(CH_2)_6CH=CH_2$	0.5	$CH_3(CH_2)_7CH_2OH$		95
2	$PhCH=CH_2$	1	$PhCH_2CH_2OH$ + $PhCH(OH)CH_3$	(80:20) (81:19)^c	85
3		1.5	$PhCH(Me)CH_2OH$		90
4		24	$PhCH(OH)CH_2Ph$		70
5		0.5			85
6		0.5		(70:30) (98:02)^c	80
7		24		(75:25) (95:05)^c	70
8		0.5		(70:30) (95:05)^c	70
9		1		(55:45) (97:03)^c	90
10		1		(75:25) (86:14)^c	90

Table 1. (Contd.)

Entry	Substrate	Time(h)	Products (ratio)[a]		Yield(%)[b]
11	$CH_3(CH_2)_3C{\equiv}CH$	1	$CH_3(CH_2)_4CH_2OH$		75
12	$CH_3(CH_2)_5C{\equiv}CH$	1	$CH_3(CH_2)_6CH_2OH$		85
13	Ph-C≡C-H	1.5	$PhCH(OH)CH_3$ + $PhCH_2CH_2OH$	(60:40) (25:75)[c]	90
14	$PhC{\equiv}C\text{-}CH_3$	1.5	$PhCH(OH)CH_2CH_3$ + $PhCH_2CH(OH)CH_3$	(62:38) (50:50)[c]	93
15	$PhC{\equiv}C\text{-}CH_2CH_3$	1.5	$PhCH(OH)CH_2CH_2CH_3$ + $PhCH_2CH(OH)CH_2CH_3$	(72:28) (66:34)[c]	96
16	PhC≡C-Ph	24	$PhCH(OH)CH_2Ph$		75
17	$CH_3(CH_2)_3C{\equiv}C\text{-}CH_3$	1.5	$CH_3(CH_2)_3CH(OH)CH_2CH_3$ + $CH_3(CH_2)_4CH(OH)CH_3$	(80:20) (30:70)[c]	80

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[a] The ratio was estimated by ^{1}H NMR and GC.

[b] All yields refer to isolated pure products.

[c] The ratio refers to that obtained by usual hydroboration-oxidation.

In conclusion, whatever be `the exact nature of reaction-path, the present combination of zinc borohydride and silica gel provides an efficient methodology for the hydration of alkenes and alkynes producing selectively the corresponding less substituted alcohols. The usefulness of this reagent system lies in its ease of use, good yields, simple work-up, and mildness of reaction condition.

Experimental

General : ^{1}H NMR spectra were recorded at 60 MHz on EM 360 spectrometers of Varian Associates in CCl_4 or $CDCl_3$ solutions with Me_4Si as an internal standard. IR spectra were recorded on a Perkin Elmer 298 spectrometer. Thin layer chromatography was done on precoated silica gel plates (E. Merck). Silica gel (60-120 mesh) used for column chromatography and silica gel HF 254, used in reaction were supplied by SRL, India. Zinc borohydride in 1,2-dimethoxyethane (DME) was prepared from zinc chloride and sodium borohydride following a reported procedure.[17] Alkenes and alkynes used for this investigation are mostly commercial materials and a few have been prepared by standard procedures. All reagents were distilled before use.

General Procedure for Hydration : The alkene or alkyne (1 mmol) was adsorbed on silica gel (HF 254 for TLC, activated by heating at 180°C for 3 h under vacuum, 1 g per mmol of substrate) under stirring for 5 mins. A solution of zinc borohydride (1.5 mmol) in DME (3 ml) was then added to the silica gel impregnated with alkene or alkyne at room temperature and the mixture was sitrred for a certain period of time as required for completion (monitored by TLC). The reaction mixture was then decomposed by careful dropwise addition of water and filtered. The filtrate was extracted with ether and the extract was washed with aqueous sodium hydrogen carbonate and brine, dried (Na_2SO_4) and then evaporated to leave the product. The product was purified and when mixture, was separated by column chromatography over silica gel. The products are all known compounds and were easily identified by comparison of IR and ^{1}H NMR spectra with those of authentic samples.[18]

Although the procedure was written in 1 mmol scale, gram-scale reactions were also carried out and found to afford the corresponding products in anologously good yields.

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