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A Novel and Unusual Reaction of Enol Ethers with Benzyltriethylammonium Borohydride and Chlorotrimethylsilane

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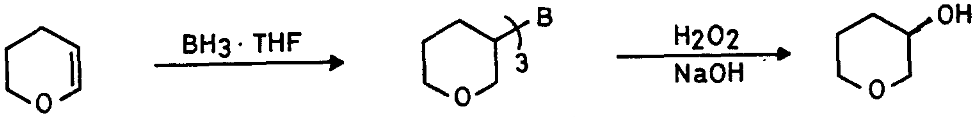
Abstract: Benzyltriethylammonium borohydride-chlorotrimethylsilane reagent system has been found to effect a novel and unusual reaction with cyclic and acyclic enol ethers 1 to give exclusively diols and alcohols 2 respectively in high yields, under very mild reaction conditions.

Hydroboration reaction on electron rich enol ether double bond is highly stereo- and regioselective.[1,2] The hetero atom directs the addition of diborane nearly exclusively to the β-position to give β-hydroxy ether [2] (Scheme-I).

Scheme I



Earlier, we have shown that a combination of benzyltriethylammonium borohydride[3] and chlorotrimethylsilane can be used for the direct conversion of alkenes to alcohols, without involving a formal oxidative work-up.[4] Since this reagent system behaves differently from diborane, we believed it would be of interest to study the reactivity of electron rich enol ether double bonds with this reagent system.

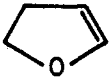
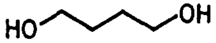
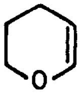
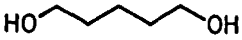
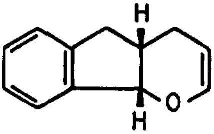
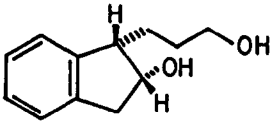
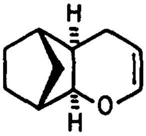
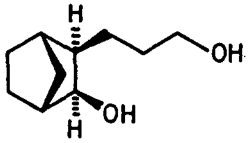
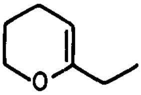
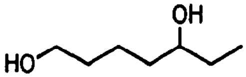
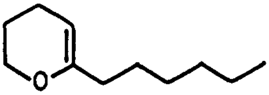
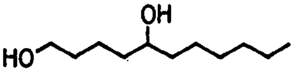
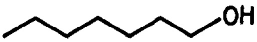
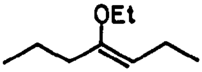
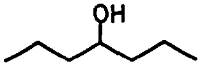
Surprisingly, a combination of benzyltriethylammonium borohydride and chlorotrimethylsilane (1:1) was found to react readily with enol ethers 1 to produce diols or alcohols 2 as the only product in high yields after aqueous work up. In the absence of benzyltriethylammonium borohydride, chlorotrimethylsilane alone does not react with enol ethers. A blank reaction has also been done to rule out the possibility of a simple hydrolysis of the enol ether followed by reduction to give the product. The results of this unusual reaction are summarized in Table I. In all the reactions cyclic enol ethers afforded the corresponding acyclic diols as the only product, whereas acyclic enol ethers 1g-h yielded the corresponding alcohols 2g-h. In contrast to normal hydroboration, this reaction did not yield any β-hydroxy ether or isomeric alcohol.[1,2] 5,6-Indenyldihydro-2H-pyran 1c[5] and 5,6- norbornyl-3,4-dihydro-2H-pyran 1d[6] on treatment with this reagent system yielded the corresponding diols 2c and 2d respectively in high yields. Substituted cyclic enol ethers 1e[7] and 1f[7] reacted with this reagent system to give diols 2e and 2f respectively as the exclusive products.[8]

Based on the experimental observations[9] it appears that simple diborane is not involved in this transformation and silicon probably plays a major role in this reaction[10]. Further work needs to be done to substantiate the mechanism involving this novel reagent system. At the present time, however, this can be used as a useful synthetic methodology for the direct conversion of enol ethers to diols or alcohols in good yields under mild reaction conditions.

In a typical reaction, to a stirred solution of enol ether (4 mmol) and benzyltriethylammonium borohydride (4 mmol) in dry CH_2Cl_2 (6 ml) at 0°C was added Me_3SiCl (distilled over CaH_2)(4 mmol) in CH_2Cl_2 (2 ml), and the reaction mixture was stirred for 6-10 h in the presence of air[9]. A solution of 10 % K_2CO_3 (3 ml) was added and stirred for an additional 0.15 h. After usual work up and chromatographic purification the alcohol or diol was obtained in very good yields.

Table 1

Reaction of enol ethers with $PhCH_2\overset{\oplus}{N}Et_3\overset{\ominus}{B}H_4{}^{-}\text{-}Me_3SiCl$

Entry	Substrate	t/h	Product[a]	Yield[b] %
1	 1a	8.0	 2a	73
2	 1b	8.0	 2b	74
3	 1c	10.0	 2c	83
4	 1d	8.0	 2d	68
5	 1e	7.5	 2e	69
6	 1f	7.0	 2f	72
7	 1g	6.0	 2g	80
8	 1h	3.0	 2h	65

[a] All the products gave satisfactory spectral data and elemental analysis.

[b] Isolated yields.

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References and Notes

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8. When methyl iodide was used (ref 3) instead of chlorotrimethylsilane both β-hydroxy ether and diol were formed.
9. In the presence of 5 mole % of 2,6-di-tert-butyl-1-cresol(BHT) and in the absence of oxygen the enol ethers gave low yields (10-20 %) of the diols.
10. All our attempts to isolate or indirectly study the reactive intermediate have been unsuccessful.

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