Revisit the Reduction of Propargyl Alcohol by Deuterium NMR

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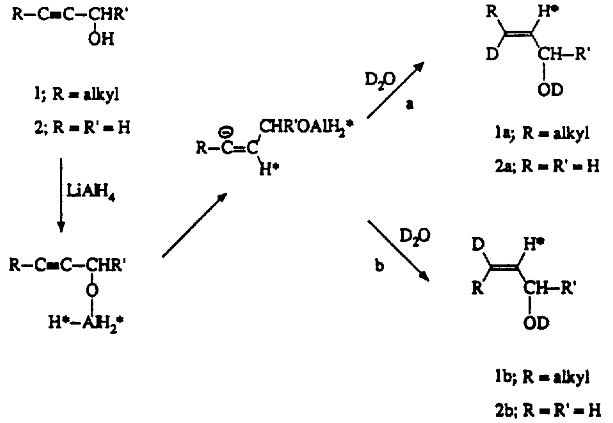
Since the discovery of the deuterium in 1933, deuterium labelling experiment became one of the most useful ways of studying reaction mechanisms as a fact of the low natural abundance of ^2H (1.6×10^{-4}) with respect to ^1H.[1] Although the statistical or selective replacement of hydrogen atoms by deuterium often requires difficult or tedious synthetic procedures, the use of deuterium labelling studies on chemistry has been sparked by the advent of modern high field superconduct NMR, which has solved the problems occurred by sensitivity and quadrupole moment.

The triple bond of propargylic alcohols has been widely used as a precursor of the isotopically labeled allylic compounds[2] and as a synthon for the stereospecific olefins.[3] There is a general agreement in early works on this area that the reduction proceeded *via* a specific hydride transfer from the aluminum bound to oxygen to the β carbon of the triple bonds, leading to the exclusive *trans* olefin (**1a**) after hydrolysis (Scheme 1).[4]

Since then, several authors reported contradictory results.[3,5] More specifically, Lewis basicity of the solvent and the addition of Lewis acids or bases changed the ratio of *cis* and *trans* reduction and the position of the initial hydride transfer, respectively. These workers obtained data from the integration of ^1H NMR intensities and did not mention about taking any special precautions.[6]

We have now reinvestigated the reduction of propargyl alcohol using deuterium NMR on what we believe to get rid of the systematic errors caused by the proton impurities of the solvents and deuterium compounds and by the integration of the overlapped proton peaks.[6] Diethyl ether and tetrahydrofuran (THF) were chosen as the solvents since the two solvents showed a significant solvent effect on the ratio of *cis* and *trans* reduction (THF; 0:100, Ether; 40:60).[5] The reduction was done by the previously reported procedures[5] at 0 °C and the product was purified by short column distillation (Yields; 70-80%).



Scheme 1

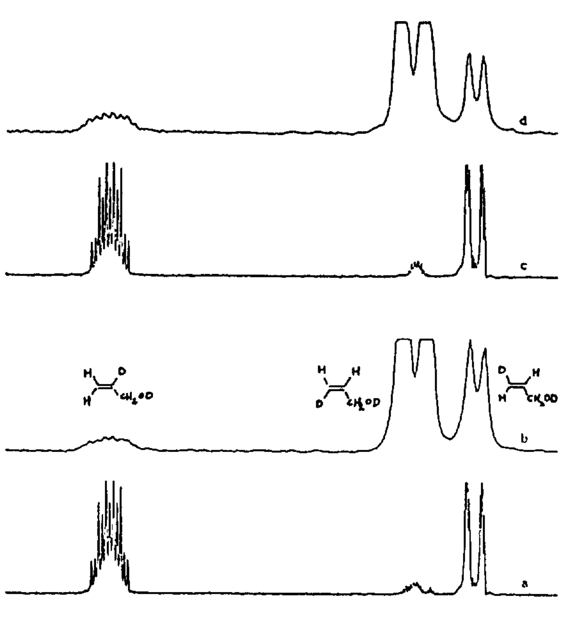


Figure 1. The partial ^2H (at 46.07 MHz, in $CHCl_3$) and ^1H (at 300.13 MHz, in $CDCl_3$) NMR spectra. (a) ^1H NMR of products from ether (b) ^2H NMR of products from ether (c) ^1H NMR of products from THF (d) ^2H NMR of products from THF.

Table 1. Percent Ratios[a] of Products from the Reduction[b] of 2

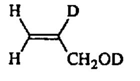
	2a	**2b**	**3**
THF	73.9(± 5.9)	17.8(± 1.6)	8.3(± 0.3)
Diethyl ether	70.1(± 6.3)	24.3(± 1.7)	5.6(± 0.3)

[a] determined by 46.07 MHz ^2H NMR integration. [b] reaction temperature at 0 °C.

The representative partial deuterium NMR Spectra obtained on a Bruker AM-300 spectrometer at 46.07 MHz are shown in Figure 1 with corresponding proton NMR spectra at 300.13 MHz. The deuterium spectra were recorded in an unlocked mode. The proton decoupling was not applied to avoid the NOE.[7] A short pulse width (30° tilt angle) and much longer pulse repetition time (4.2 s) than the deuterium T_1[1] were employed to avoid saturation. In order to minimize the field or homogeneity drifts, the temperature of 10 mm broad-band probe was elevated to 27 °C which was 5 °C higher than the room temperature.

From the proton NMR spectra (Figure 1a and c), which were collected by 30° pulse and 16.7 s repetition time, it was almost impossible to calculate the ratio of the *trans* (**2a**) and *cis* (**2b**) reduction products because of the overlapped peaks. Thus, the methine proton (δ 6.0-5.9) of vinyl group in **2a** and **2b** has almost the same chemical shift. The multiplet peaks at δ 5.3-5.2 and δ 5.15-5.07 are due to the terminal one proton of vinyl group in **2b** and **2a**, respectively. These peaks, however, overlapped with the protons of **3** and small amount (<1%) of non-deuterated allyl alcohol produced by proton impurities of solvent and D_2O. Furthermore it was impossible to know whether the first hydride transfer was proceeded to the γ carbon of the triple bond to yield β deutero compound (3). However, the deuterium NMR (Figure 1b and d) clearly show the individual deuterium peaks as assigned in the Figure and solved the problems of the proton NMR. The fact that the individual deuterium NMR peaks are from the mono-deuterated compounds on the olefin bonds (**2a, 2b, 3**) was easily determined by the EIMS (*m/z* 60.0577, 3.2 mmu error). Table 1 shows the yields of each compound from diethyl ether and THF solvents.

It may thus be concluded that in contrast to the previous results,[3,5] 1) the Lewis basicity of solvent is not totally responsible for the *cis* and *trans* reduction route, 2) without adding Lewis acid, a significant amount of hydride transfer to the γ carbon of the triple bond proceeds.



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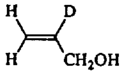

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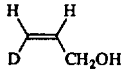

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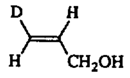

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The other interesting results have been observed which is also an additional evidence for a non-specific hydride transfer. When the reduction of alcohol 2 was done by the $LiAlD_4$, the expected deuterium compound 4 and 6% of 5 were obtained after hydrolysis with H_2O. The compound 6 was not observed even in diethyl ether.

On the basis of these results, further studies are currently being pursued to unravel the reduction mechanism.

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Catalysis of the Reduction of Dioxygen by N-Hexadecyl-N'-Methyl Viologen(+1) Monomolecular Films at Glassy Carbon Electrodes

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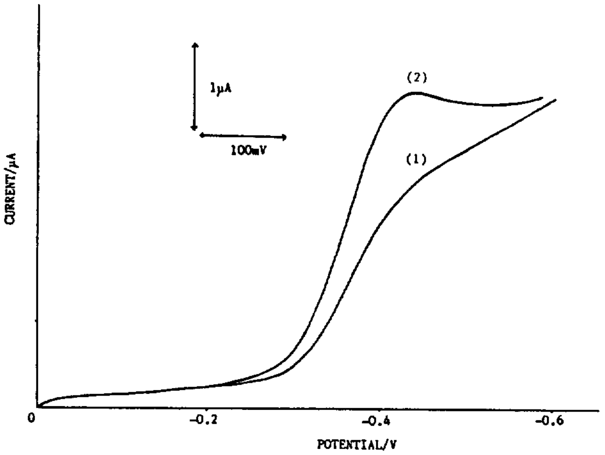

Figure 1. Voltammetric response at glassy carbon electrode in a 5 μM $C_{16}MV^{2+}$ aqueous solution of 0.1M NaCl + 40 mM KH_2PO_4 + 40 mM CH_3COOH (pH 5.3) under nitrogen atmosphere. Electrode area = 0.071 cm^2. Scan rate = 4 mV/s. Potentials are given with respect to saturated calomel reference electrode. Exposure time, (1); 1 min, (2); 10 mins.

Viologens have been extensively used as electron mediators in biological and photoelectrochemical systems[1] and active functional group in electrochromic displays[2]. Recently Anson showed that poly(xylylviologen) catalyzed the electroreduction of dioxygen to hydrogen peroxide[3]. In that study, polymeric viologens were used as a catalytic form because polymeric catalyst coatings on electrode surfaces can provide very high concentrations of redox catalyst sites at positions where they can be easily cycled between oxidation states electrochemically. However, the advantages inherent with polymeric coatings were not apparent in ref. 3 because the rate of the cross reaction between dioxygen and the viologen radical cations proceeded more slowly within the polyelectrolyte film than in homogeneous solution and thus only the outermost monolayer participated in the catalysis. On the other hand, Bard has shown that N-hexadecyl-N'-methyl viologen(+2), $C_{16}MV^{2+}$, forms a monomolecular film on glassy carbon surfaces in the concentration range of 1-20 μM in aqueous solutions of 50 mM NaCl[4]. Therefore, we thought that the monomolecular film formed at glassy carbon could be used as a more effective catalyst for the electroreduction of dioxygen, thereby designing a better electrocatalytic system for activating dioxygen reduction.

Figure 1 shows a voltammetric response at glassy carbon electrode immersed in 5 μM $C_{16}MV^{2+}$ aqueous solution of 0.1M NaCl under nitrogen atmosphere. As was shown previously[4], $C_{16}MV^{2+}$ strongly adsorbs at glassy carbon surfaces due to the hydrophobicity originating from the long alkyl chain introduced intentionally. When the same experiment was performed under oxygen atmosphere, the current response increased sharply because the reduced form of the viologen, $C_{16}MV^{1+}$, at electrode surfaces catalyzed the electroreduction of dioxygen. Little change from background current was observed with identical experimental conditions of methyl viologen(+2) instead of $C_{16}MV^{2+}$. To investigate the kinetics of the electrode reaction, rotating disk voltammetric techniques were employed[5]. Rotation rates were varied between 700 and 900 rpm, and between 1400 and