



**Table 1.** Reduction of Acrylic Acid (**1**), Propiolic Acid (**5**), and Propargyl Alcohol (**6**) with  $\text{LiAlH}_4$  in Diethyl Ether

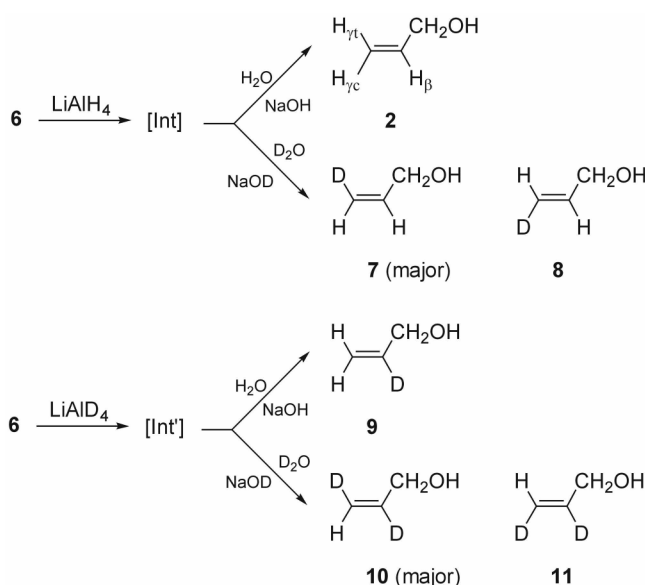
Exp.	Subs. <sup>a</sup>	$\text{LiAlH}_4^b$	Conditions	Products (%) <sup>c</sup>
1	1.32	44	1 to LAH at 0° reflux 18 h	2 (5), 3 (42), 1 (5) <sup>d</sup> , 4 (45)
2	1.87	66	1 to LAH at 0° reflux 8 h	2 (8), 3 (34), 1 (15) <sup>d</sup> , 4 (35)
3	5.49	98	5 to LAH at 0° 0° 2 h, reflux 8 h	2 (44), 3 (50), 6 (6)
4	5.49	98	5 to LAH at 0° reflux 2 h	2 (40), 3 (51)
5	6.52	39	5 to LAH at 0° RT 20 h, reflux 6 h	2 (35), 6 (60)
6	6.34	34	5 to LAH at 0° reflux 48 h	2 (70), 6 (5)
7	6.68	34	5 to LAH at 0° RT 20 h, reflux 6 h	2 (40), 6 (50)

<sup>a</sup>Mmole. <sup>b</sup>Relative percentage. <sup>c</sup>Recovery percent.

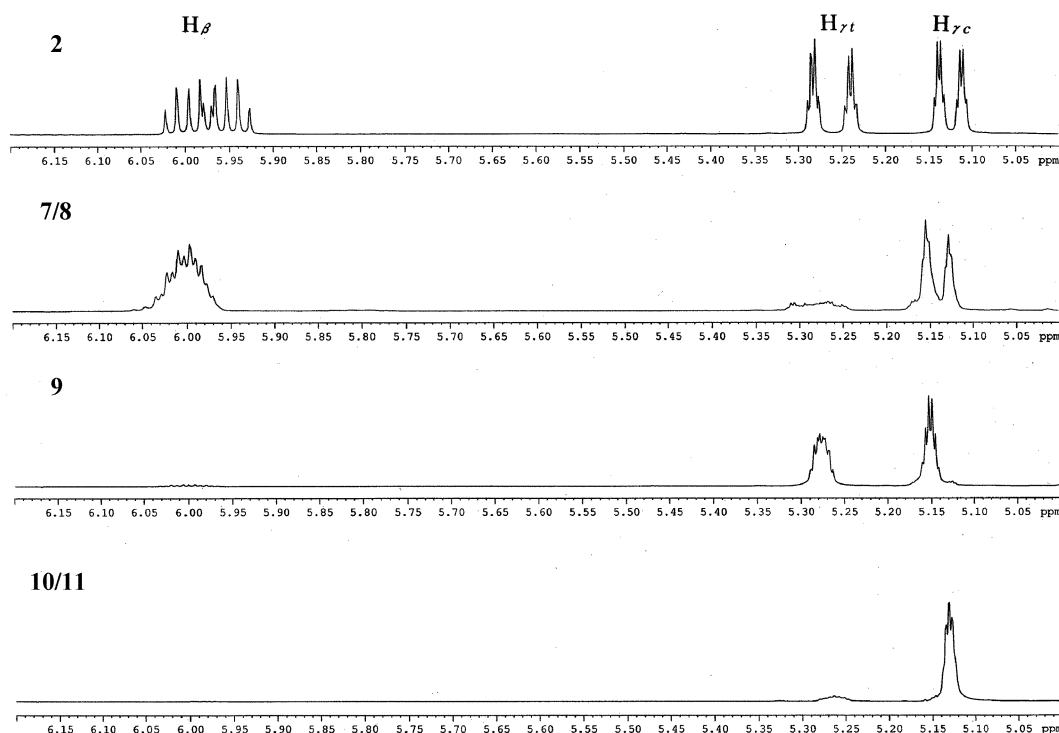
The apparent failure to obtain **2** from **1** or **5** led us to investigate an alternative method, which is the reduction of **6** to **2**. There are a few reports<sup>6-8</sup> related to similar reaction with alkynols of  $\text{HO-CR}^1\text{R}^2\text{C}\equiv\text{C-R}^3$  to allyl alcohols  $\text{HO-CR}^1\text{R}^2\text{CH}=\text{CH-R}^3$ , but reduction of **6** ( $\text{R}^1=\text{R}^2=\text{H}$ ) to **2** has not been reported. Since we have to have a dideuterated allyl alcohol, any procedure by which  $\text{D}_2$  component should add to a C-C triple bond should be useful, and naturally, we became interested in the mechanism of the conversion of **6** to **2**.

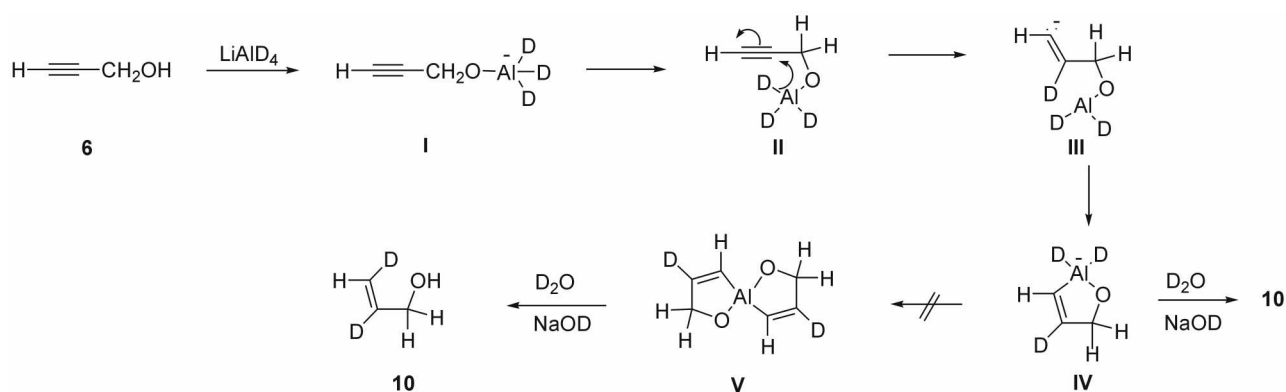
When a mixture of **6** and  $\text{LiAlH}_4$  (1 : 1 mole ratio) in diethyl ether was heated at reflux for 48 h and then quenched

with aqueous NaOH, **2** was the sole product in 70% yield (Table 1, Entry 6). On the other hand, quenching with NaOD in  $\text{D}_2\text{O}$  gave 3-deuterioallyl alcohols, **7** and **8** in a ratio of 10 : 1. Similar reaction of **6** with  $\text{LiAlD}_4$  and subsequent quenching with aqueous NaOH gave 2-deuterioallyl alcohol **9**. Alternatively, quenching with NaOD in  $\text{D}_2\text{O}$  gave a mixture of 2,3-dideuterioallyl alcohols **10** and **11** in a ratio of 9 : 1.



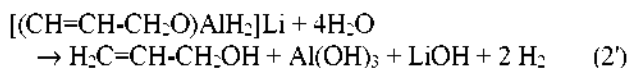
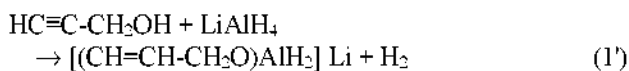
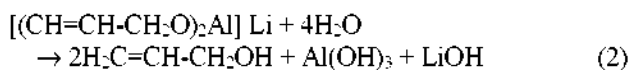
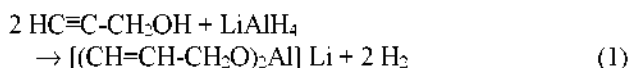
The structures of the reduction products were readily confirmed by NMR spectroscopy as shown in Figure 1. The signal of  $\text{H}_\beta$  appears in the most downfield region ( $\delta$  5.97) as an overlapping *ddt* with coupling constants of 17.2 ( $J_{\beta,\gamma}$ ),

**Figure 1.** NMR spectra of the vinyl portion of allyl and deuterated allyl alcohols.



10.5 ( $J_{\beta,\gamma}$ ) and 5.1 ( $J_{\beta,\alpha}$ ) Hz. The signals of  $H_\gamma$  and  $H_\alpha$  appear at  $\delta$  5.26 and 5.13, respectively. The disappearance of the signals in Figure 1 clearly shows the position of deuterium atom in the allyl alcohols 7-11.

The positions of deuterium atoms in 7-11 strongly suggest a mechanism in which a hydride transfer from aluminum hydride to  $\beta$ -C of 6 like II as shown in Scheme 1. Once an  $sp^2$ -hybridized carbanion forms, it may form a complex IV. Apparently, the complex IV is not reactive enough to form a bis-allyl complex such as V. Instead it survives until being quenched by aqueous NaOH. We tested the possibility by measuring the hydrogen gas evolved. During the stage of addition of 6 (68 mmol) to  $LiAlH_4$  (34 mmol) in diethyl ether, 1 equiv. (34 mmol) of hydrogen gas was evolved, but further generation of the gas was not observed during the reflux. Upon quenching about 2 equiv. (68 mmol) of the gas was evolved. The quenched mixture was extracted with diethyl ether to give a mixture of 2 in 40% yield and 6 which together accounted for about 50% of the starting material. The result may be explained by two sets of stoichiometric equations as follows:

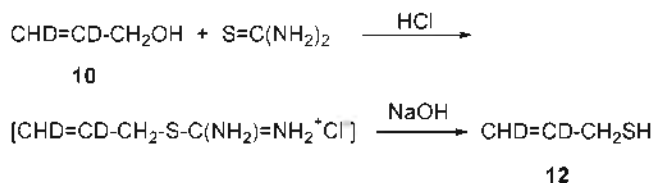


If the reduction is to take place by Eqns. (1) and (2), quantitative amount of  $\text{H}_2$  gas should be formed during the stage of addition and reflux. On the other hand, Eqns. (1') and (2') indicate that one equiv. of  $\text{H}_2$  should be formed at first and then two equiv. of the gas should be evolved during the quenching stage. Our observation is consistent with the latter.

It is known that alkynes which are not activated by an adjacent hydroxyl group react much more slowly with  $LiAlH_4$ .<sup>9</sup> Our observation that the H atom of the terminal

alkyne does not exchange with D atom when  $LiAlD_4$  was used as reducing agent and a solution of NaOD in  $D_2O$  was used for quenching clearly indicates that the hydride transfer from  $LiAlH_4$  to C-C triple bond is intramolecular as for II and not intermolecular. If it is intermolecular, the hydride should attack  $\gamma$ -C preferably on the grounds of stereoelectronic effect. Therefore, H-D exchange is likely to take place.

Finally, conversion of 10 to 2,3-dideuterioallyl mercaptan (12) was achieved by reacting with thiourea in aqueous HCl solution at 80 °C for 24 h and subsequently quenching with aqueous NaOH solution. The final product was purified by distillation to give 46% yield.



## Experimental Section

**General.** Nuclear magnetic resonance (NMR) spectra were recorded on a Bruker DPX-400 FT NMR spectrometer in the Central Lab of Kangwon National University at 400 MHz for  $^1\text{H}$  and 100 MHz for  $^{13}\text{C}$  and were referenced to tetramethylsilane. Infrared spectra were recorded on a JASCO FT/IR-460 Plus spectrophotometer. Mass spectra were obtained using Micromass Autospec M363.

**Materials.** Acrylic acid (1), propiolic acid (5), propargyl alcohol (6),  $LiAlH_4$ ,  $LiAlD_4$  and NaOD in  $D_2O$  were used as received as the commercial products. Diethyl ether was distilled from over sodium metal prior to use.

**Reduction of Acrylic Acid (1): A Representative Procedure.** A mixture of  $LiAlH_4$  (2.5 g, 66 mmol) and diethyl ether (120 mL) was cooled to 0 °C. Acrylic acid (96.0 mL, 87 mmol) was added in drops while the generated  $\text{H}_2$  gas was collected in a graduated cylinder. The mixture was heated at reflux for 8 h and then cooled in an ice-water bath. Water (2.5 mL), 15% NaOH (2.5 mL), and then water (7.5 mL) were added in sequence, and the resulting mixture

was extracted with ether (3 × 50 mL). The pooled ethereal extract was dried over MgSO<sub>4</sub>. Then the ether was removed by fractional distillation using a Vigreux column. The residual liquid was analyzed by NMR spectroscopy showing that it was a mixture of allyl alcohol (**2**) and 1-propanol (**3**) in a ratio of 1 : 8, and unidentified compounds. The aqueous layer was acidified with 2M-HCl to pH 4 and then extracted with ether to give the starting acid and propionic acid (**4**) in a ratio of 1 : 9.

**Reduction of Propiolic Acid (**5**):** The procedure is essentially similar to the reduction of **1**. The acid **5** (3 mL, 49 mmol) was added to a mixture of LiAlH<sub>4</sub> (3.72 g, 98 mmol) in ether (130 mL) at 0 °C, and the resulting mixture was heated at reflux for 12 h. Quenching with aqueous NaOH and extraction with ether gave a mixture of **6** (6%), **2** (40%), and **3** (51%).

**Reduction of Propargyl Alcohol (**6**): A Representative Procedure.** The alcohol **6** (2 mL, 34 mmol) was added to LiAlH<sub>4</sub> (2.20 g, 52 mmol) in ether (100 mL) at 0 °C and the resulting mixture was heated at reflux for 12 h. Quenching with aqueous NaOH and subsequent extraction with ether gave a mixture of **2** (75%) and **6** (20% recovery).

**Preparation of  $\beta$ -deuterioallyl alcohol (**9**).** The alcohol **9** was prepared by following the procedure for the reduction of **6** above except the quenching with NaOD-D<sub>2</sub>O in 50% yield.

**Preparation of *trans*- $\beta,\gamma$ -dideuterioallyl alcohol (**10**).** The alcohol **10** was prepared by following the procedure for the reduction of **6** above using LiAlD<sub>4</sub> in same scale and subsequent quenching with NaOD-D<sub>2</sub>O. The isolated product (44%) was a mixture of **10** and **11** in a ratio of 9 : 1 by NMR. Repeated column chromatography with silica gel with hexane-EtOAc (9 : 1) gave essentially pure form of **10**.

**Preparation of  $\beta,\gamma$ -dideuterioallyl mercaptan (**12**).** Conc. HCl (2.2 mL) was added to a solution of thiourea (1.81 g, 24 mmol) in water (2 mL).  $\beta,\gamma$ -Dideuterioallyl alcohol (**10**, 1.4 g, 23 mmol) was slowly added to the

solution. The resulting solution was heated at 80 °C for 24 h. After cooling to room temperature, a solution of NaOH (1.50 g) in water (2 mL) was added slowly. The solution was fractionally distilled to give **12** as a colorless liquid in 46% yield. IR (neat): 3079 (w, =C-H), 2923 (ms. CH<sub>2</sub>), 2558 (w, S-H), 1617 (ms. C=C), 1410 (ms. CH<sub>2</sub>), 1220 (m. C-S), 919 (s, C=C-H); <sup>1</sup>H-NMR (CDCl<sub>3</sub>)  $\delta$  1.43 (t, 1 H, S-H, *J* = 7.7 Hz), 3.17 (d, 2H, CH<sub>2</sub>, *J* = 7.6 Hz), 5.01 (brs. 1H, C=C-H); <sup>13</sup>C-NMR (CDCl<sub>3</sub>) ppm 27.45 (CH<sub>2</sub>), 115.16 (t. CHD, *J* = 23.4 Hz), 136.90 (t. CD, *J* = 24.0 Hz); Mass. m/z (%) 152 (100, dimeric M<sup>+</sup>), 108 (84, dimeric M<sup>+</sup> - CH<sub>2</sub>S), 75 (74, CHD=CD-CH<sub>2</sub>S<sup>-</sup>).

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