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Rearrangement of Allylic and Propargylic Alcohols Catalyzed by the Combined Use of Tetrabutylammonium Perrhenate(VII) and *p*-Toluenesulfonic Acid

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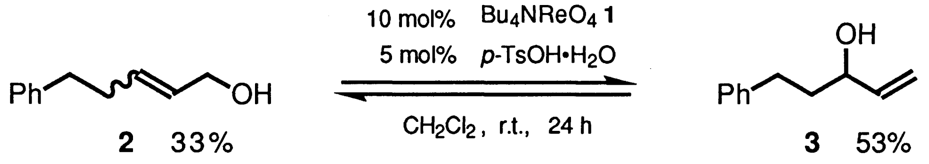
Allylic rearrangement and/or dehydration of allylic alcohols proceed by the use of a catalytic amount of tetrabutylammonium perrhenate and *p*-toluenesulfonic acid. Treatment of propargylic alcohols with the above reagents affords the rearranged products, α,β-unsaturated carbonyl compounds.

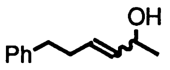
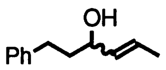
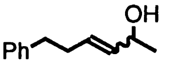
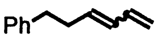
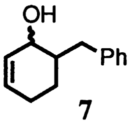
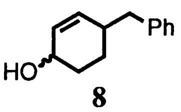
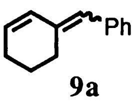
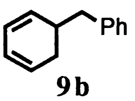
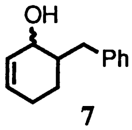
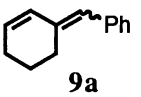
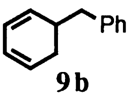
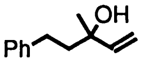
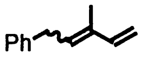
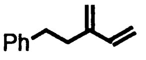
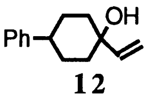
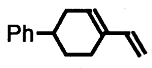
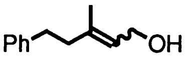
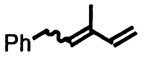
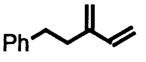
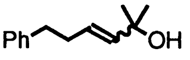
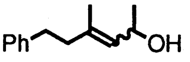
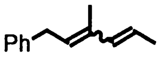
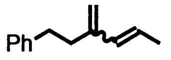
Allylic rearrangement of allylic alcohol derivatives is one of the important transformations in synthetic organic chemistry, and various methods for effecting such a transposition have been reported. The rearrangement of allylic acetates or carbamates is performed by the use of transition metal compounds such as palladium(II)[1)] and mercury(II).[2)] As for the rearrangement of allylic alcohol itself, the strong Brϕnsted acids were conventionally used as catalysts[3)] and, as an improved approach, the $VO(acac)_2$-$Me_3SiOOSiMe_3$ catalyzed method has recently been developed.[4)] Herein, we wish to report the allylic rearrangement and/or dehydration of allylic and propargylic alcohols catalyzed by the combined use of tetrabutylammonium perrhenate (Bu_4NReO_4, **1**)[5)] and *p*-toluenesulfonic acid hydrate (*p*-$TsOH{\cdot}H_2O$).

The rearrangement of a primary allylic alcohol, 5-phenyl-2-penten-1-ol (**2**), did not occur with either Bu_4NReO_4 **1** or *p*-$TsOH{\cdot}H_2O$ but proceeded with the combined use of the two reagents. After screening the reaction conditions, it was found that the treatment of **2** with 10 mol% of **1** and 5 mol% of *p*-$TsOH{\cdot}H_2O$ in dichloromethane at room temperature for 24 h afforded the rearranged product **3** in 53% yield along with 33% of the starting material **2**. At this point, the mixture was thought to be at equilibrium because the ratio of **2** and **3** did not change after longer reaction time.



In the reactions of secondary and tertiary allylic alcohols, it was found that not only the allylic rearrangement but also the dehydration proceeded considerably by the treatment with **1** and *p*-$TsOH{\cdot}H_2O$ (Table 1). When the secondary allylic alcohols **4** and **7** were treated with the catalysts for 5 min, the rearranged secondary allylic alcohols **5** and **8**, respectively, were obtained with the starting materials (Entries 1 and 3). But the dehydration reaction gradually proceeded to give the corresponding conjugated dienes **6a,b** and **9a,b** after prolonged reaction time (Entries 2 and 4). When the tertiary allylic alcohols **10**, **12**, and **16** were employed, the dehydration reaction occurred to afford the conjugated dienes **11a,b**, **13**, and **17**, respectively, in high yields and the rearranged allylic alcohols were not detected (Entries 5, 6, and 8). Furthermore, none of the rearranged tertiary allylic alcohols were detected during the reaction of **14** and **18** and the 1,3-dienes **15a,b** and **19a,b**, respectively, were obtained exclusively (Entries 7 and 9). These results indicate that the dehydration reaction of tertiary allylic alcohols rapidly proceeds under the present reaction conditions.

Table 1. The Reactions of Various Allylic Alcohols Catalyzed by Bu_4NReO_4 and p-$TsOH{\bullet}H_2O$[a)]

Entry	Starting material	Time	Products, Yield (Recovery)
1	 **4**	5 min	 40% (56%) **5**
2	 **4**	18 h	 66% **6a**  17% **6b**
3	 **7**	5 min	 49% (33%) **8**  + **9a**  10% **9b**
4	 **7**	23 h	 + **9a**  75% **9b**
5	 **10**	2 h	 68% **11a**  23% **11b**
6	 **12**	3 h	 86% **13**
7	 **14**	4 h	 53% **15a**  17% **15b**
8	 **16**	0.5 h	 95% **17**
9	 **18**	0.5 h	 82% **19a**  12% **19b**

a) All reactions were carried out by the use of 10 mol% of Bu_4NReO_4 and 5 mol% of p-$TsOH{\bullet}H_2O$ in dichloromethane at room temperature.

The representative experimental procedure (Table 1, Entry 1) was as follows: To a dichloromethane solution (2 ml) of the allylic alcohol **4** (57.7 mg, 0.33 mmol), a dichloromethane solution (1.5 ml) of **1** (16.6 mg, 0.033 mmol) and *p*-TsOH•H_2O (3.3 mg, 0.017 mmol) were added at room temperature. After the mixture was stirred for 5 min, diethyl ether and saturated aqueous sodium hydrogencarbonate were added and the mixture was stirred for 5 min. The organic materials were extracted with diethyl ether and the combined extracts were washed with brine and dried over Na_2SO_4. After the solvent was removed in vacuo, the crude materials were purified by thin-layer chromatography (silica gel, hexane:ethyl acetate=5:1) to give the rearranged product **5** (23.1 mg, 40% yield) and the starting material **4** (32.5 mg, 56%).

This catalytic system was then applied to the rearrangement of propargylic alcohols to prepare α,β–unsaturated ketones. As shown in Table 2, α-phenyl-substituted propargylic alcohols (Entries 1-3) and tertiary propargylic alcohols (Entries 4 and 5) smoothly rearranged to the corresponding α,β–unsaturated carbonyl compounds in high yields by the use of catalytic amounts of **1** and *p*-TsOH•H_2O at room temperature. On the other hand, the rearrangement of secondary propargylic alcohols proceeded slowly at room temperature (Entry 6), but the rearranged products generated smoothly by carrying out the reaction in refluxing dichloroethane. Under the refluxing reaction conditions, the β,γ–unsaturated ketones were initially formed as major products, which were then gradually isomerized to give the α,β–unsaturated ketones in good yields as shown in Entries 7 and 8. In the Entries 6-8, the α,β–unsaturated carbonyl compounds were contaminated with the corresponding β,γ–isomers in 3%, 6%, and 1%, respectively. The primary propargylic alcohol, however, hardly rearranged even by the use of equimolar amounts of the catalysts (Entry 9). As compared with allylic alcohols, the dehydration reaction of propargylic alcohols proceeded rather slowly, and the conjugated enynes were produced as by-products.

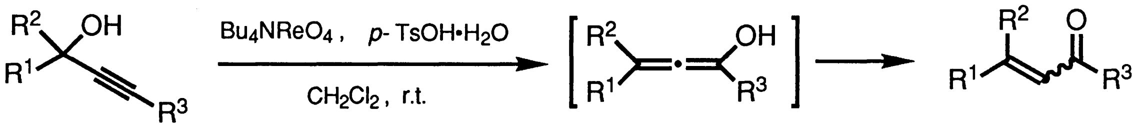


Table 2. The Rearrangement of Propargylic Alcohols into α,β-Unsaturated Carbonyl Compounds

Entry	R^1	R^2	R^3	**1**, x/mol%	*p*-TsOH, x/mol%	Time, t/h	Yield[a], x/%
1	Ph	H	H	10	10	2	92
2	Ph	H	Bu	10	10	2	83
3	Ph	H	$SiMe_3$	10	10	2	75
4	$Ph(CH_2)_2$	Me	H	20	20	27	81 (12)
5	$Ph(CH_2)_2$	Me	Bu	20	20	18	80 (14)
6	$Ph(CH_2)_2$	H	Bu	20	20	27	22 (10)
7[b]	$Ph(CH_2)_2$	H	Bu	10	10	25	73 (12)
8[b]	Bu	H	Ph	10	10	15	61 (35)
9	H	H	$Ph(CH_2)_2$	100	100	28	trace

a) The figures in parentheses are the yields of conjugated enynes. b) The reactions were carried out in refluxing dichloroethane.

The rearrangement of propargylic alcohols into α,β–unsaturated carbonyl compounds has been reported by several workers,⁽⁶⁾ but all of them require high reaction temperature (>120 °C) and most of those methods cannot be applied to secondary propargylic alcohols such as the compounds in Entries 6-8 of Table 2. On the other hand, the combined use of Bu_4NReO_4 **1** and *p*-TsOH•H_2O effectively catalyzes the rearrangement of such propargylic alcohols.

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5) Tetrabutylammonium perrhenate **1** was prepared according to the literature procedure and was purified by repeating recrystallization three times. For the synthesis of **1**, see: S. J. Compton, D. D. Cox, P. E. Reed, and J. M. Williams, *Inorg. Synth.*, **26**, 391 (1989).
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