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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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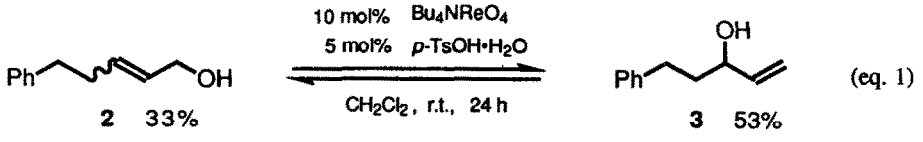
Key Words
tetrabutylammonium perrhenate; *p*-toluenesulfonic acid; allylic rearrangement; dehydration; propargylic rearrangement

Abstract: *Allylic rearrangement and/or dehydration reaction of allylic alcohols proceeds smoothly by the use of catalytic amounts of tetrabutylammonium perrhenate and p-toluenesulfonic acid hydrate. Treatment of propargylic alcohols with the catalysts at room temperature affords the rearranged products, α,β-unsaturated carbonyl compounds, while β,γ-unsaturated ketones are obtained as main products by the reaction in refluxing 1,2-dichloroethane. The application of this catalytic system is also described for the preparation of some synthetic intermediates.*

1,3-Allylic rearrangement of allylic alcohols is one of the important transformations in organic syntheses and various methods for effecting such a transposition have been reported. The rearrangement of allylic acetates or carbamates is performed by the use of metal compounds such as palladium(II)[1] and mercury(II).[2] As for the rearrangement of an allylic alcohol itself, the strong Brønsted acid catalyzed reactions[3] were conventionally used and, as an improved approach, the $VO(acac)_2$-$Me_3SiOOSiMe_3$ catalyzed method has recently been developed.[4] The rearrangement of propargylic alcohols into α,β–unsaturated carbonyl compounds has also been reported by several workers.[5] However, all of them are carried out at high reaction temperature (>120 °C) and, moreover, most of those methods cannot be applied to the rearrangement of primary and secondary propargylic alcohols. We have reported that the 1,3-rearrangement of allylic and propargylic alcohols are catalyzed by the combined use of tetrabutylammonium perrhenate (Bu_4NReO_4, **1**)[6] and *p*-toluenesulfonic acid hydrate (*p*-TsOH•H_2O) under mild reaction conditions.[7] In this report, the full details of these reactions and the further applications of this catalytic system are summarized.

Firstly, the allylic rearrangement between a primary alcohol and a secondary alcohol was examined and it was found that the treatment of 5-phenyl-2-penten-1-ol (**2**) with 10 mol% of Bu_4NReO_4 **1** and 5 mol% of *p*-TsOH•H_2O at room temperature for 24 hours afforded the rearranged secondary allylic alcohol **3** in 53% yield with the recovery of the starting material **2** in 33% (eq. 1). At this point, the mixture was at equilibrium because

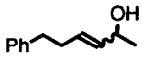
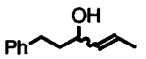
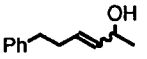
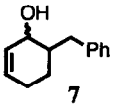
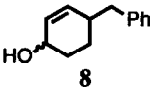
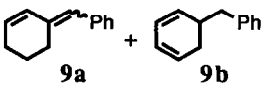
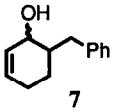
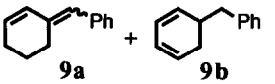
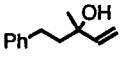
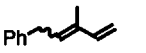
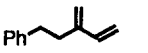
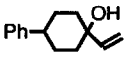
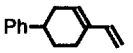
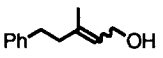
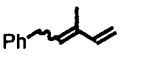
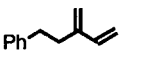
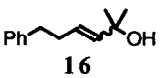
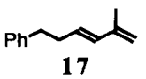
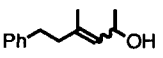
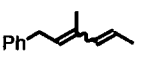
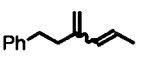


(eq. 1)

the ratio of **2** and **3** did not change after longer reaction time.

This reaction proceeded only by the combined use of Bu_4NReO_4 **1** and *p*-TsOH•H_2O and the combinations of **1** with other acids such as acetic acid and pyridinium *p*-toluenesulfonate were less effective. As for the solvent, the reaction in dichloromethane gave the best result and the allylic rearrangement hardly proceeded in tetrahydrofuran, acetonitrile, and N,N-dimethylformamide.

Table 1. The Reactions of Various Allylic Alcohols Catalyzed by Bu_4NReO_4 and *p*-TsOH•H_2O[a)]

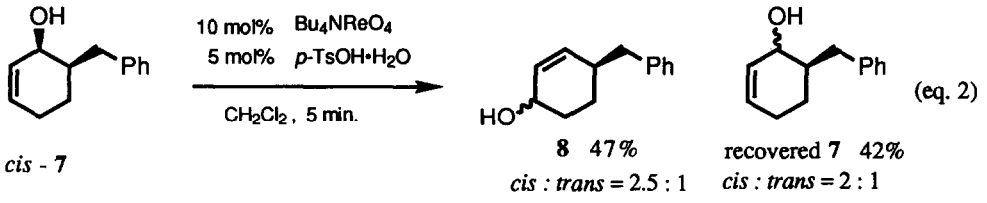
Entry	Starting material	Time	Products, Yield
1	 **4**	5 min	 **5** 40% (**4**, 56%)
2	 **4**	18 h	 **6a** 66%  **6b** 17%
3	 **7**	5 min	 **8** 49% (**7**, 33%)
			 **9a** + **9b** 10%
4	 **7**	23 h	 **9a** + **9b** 75%
5	 **10**	2 h	 **11a** 68%  **11b** 23%
6	 **12**	3 h	 **13** 86%
7	 **14**	4 h	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

a) All reactions were carried out by the use of 10 mol% of Bu_4NReO_4 and 5 mol% of *p*-TsOH•H_2O in dichloromethane at room temperature.

In the reaction of secondary allylic alcohols, the rearrangement occurred very smoothly with the catalysts but also the dehydration of the allylic alcohols proceeded gradually to give the conjugated dienes. For example, when the secondary allylic alcohols **4** and **7** were treated for a short time with the catalysts at room temperature, the rearranged secondary allylic alcohols **5** and **8**, respectively, were obtained with the starting materials **4** and **7** (Table 1, Entries 1 and 3). But the reaction for prolonged reaction time gave the corresponding conjugated dienes **6a,b** and **9a,b** in good yields (Entries 2 and 4). In the reaction where the starting materials or the rearranged products were tertiary allylic alcohols, the dehydration reaction occurred immediately to afford the conjugated dienes exclusively and none of the rearranged allylic alcohols was detected (Entries 5-9).

When the acetates of the allylic alcohols **2** and **3** were employed instead of the allylic alcohols, allylic rearrangement and/or dehydration did not occurred with the catalysts under the same reaction conditions, suggesting the possibility that the reaction proceeds via the allylic esters of perrhenic acid.

The steric course of the reaction was investigated in the rearrangement of the *cis*- and *trans*-cyclohexenols **7** and **8** (eq. 2 and 3). The treatment of the *cis*-**7** with the catalysts afforded both of the rearranged products (*cis*-**8** and *trans*-**8** in the ratio of 2.5 : 1, 47% yield) and the starting material (*cis*-**7**: *trans*-**7**= 2 : 1, 42% yield) as diastereomer mixtures. In the reaction of the *trans*-**7**, the rearranged product and the starting material were also isolated as mixtures of diastereomers. These results indicate that the allylic alcohols do not rearrange completely in a stereoselective manner, but some part of the reaction occurrs through the allylic cation as an intermediate.

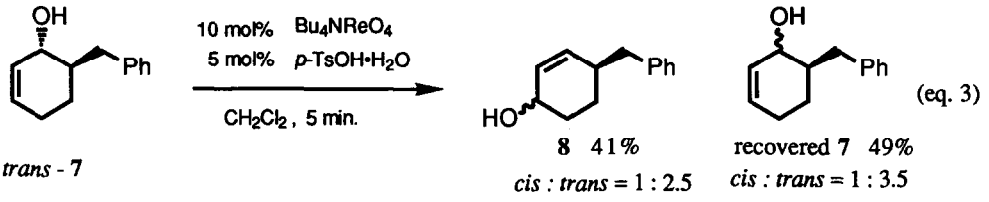


cis - **7**

8 47%
cis : *trans* = 2.5 : 1

recovered **7** 42%
cis : *trans* = 2 : 1

(eq. 2)

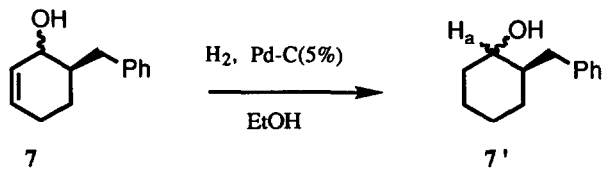


trans - **7**

8 41%
cis : *trans* = 1 : 2.5

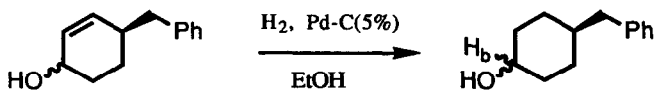
recovered **7** 49%
cis : *trans* = 1 : 3.5

(eq. 3)



7 **7'**

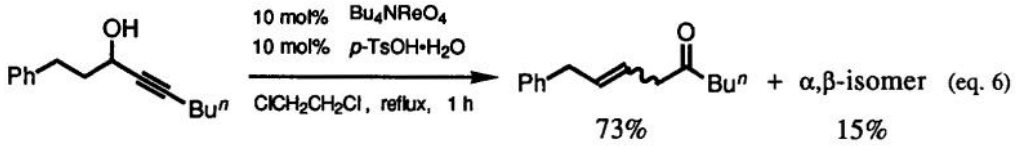
(eq. 4)



8 **8'**

(eq. 5)

By using the catalysts, Bu_4NReO_4 - *p*-TsOH•H_2O, the rearrangement of propargylic alcohols was examined to prepare α,β–unsaturated ketones. As shown in Table 2, α-phenyl 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 at room temperature. On the other hand, the rearrangement of secondary propargylic alcohols proceeded very slowly at room temperature (Entry 6), but the rearrangement was considerably accelerated by carrying out the reaction in refluxing 1,2-dichloroethane. Under the more vigorous reaction conditions, the β,γ–unsaturated ketones were initially formed as major products (Entry 7 and eq. 6), that were then gradually isomerized under the reaction conditions to the corresponding α,β–unsaturated ketones in good yields as shown in entries 8 and 9.



In the entries 6, 8 and 9, the α,β–unsaturated carbonyl compounds were contaminated only with small amounts of the corresponding β,γ–isomers in 3%, 6%, and 1%, respectively. The primary propargylic alcohol, however, hardly rearranged by the use of equimolar amounts of the catalysts (Entry 10) even under the refluxing conditions. As compared with allylic alcohols, the propargylic alcohols were dehydrated rather slowly and the conjugated enynes were produced as by-products.

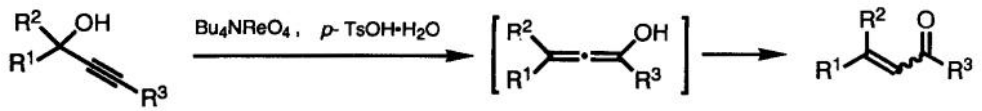
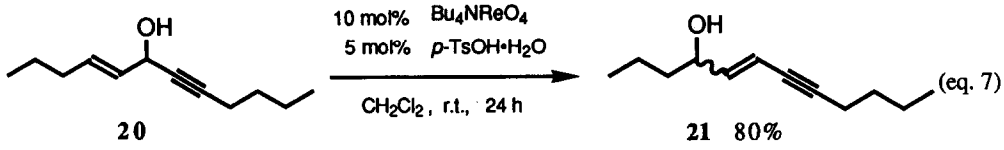


Table 2. The Rearrangement of Propargylic Alcohols[a)]

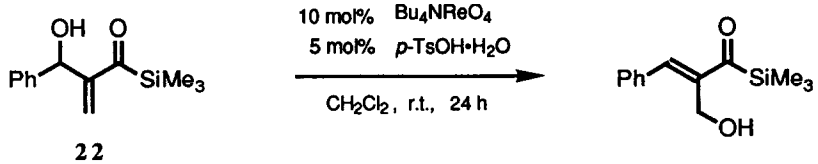
Entry	R^1	R^2	R^3	Bu_4NReO_4 mol%	*p*-TsOH mol%	Time h	Yield / % α,β–enone	β,γ–enone	enyne
1	Ph	H	H	10	10	2	92		
2	Ph	H	Bu	10	10	2	83		
3	Ph	H	$SiMe_3$	10	10	2	75		
4	$Ph(CH_2)_2$	Me	H	20	20	27	81		12
5	$Ph(CH_2)_2$	Me	Bu	20	20	18	80		14
6	$Ph(CH_2)_2$	H	Bu	20	20	27	19	3	10
7[b)]	$Ph(CH_2)_2$	H	Bu	10	10	1	15	73	12
8[b)]	$Ph(CH_2)_2$	H	Bu	10	10	25	67	6	12
9[b)]	Bu	H	Ph	10	10	15	60	1	35
10[b)]	H	H	$Ph(CH_2)_2$	100	100	28	trace		

a) The reactions were carried out in dichloromethane at room temperature, otherwise noted.
b) The reactions were carried out in refluxing 1,2-dichloroethane.

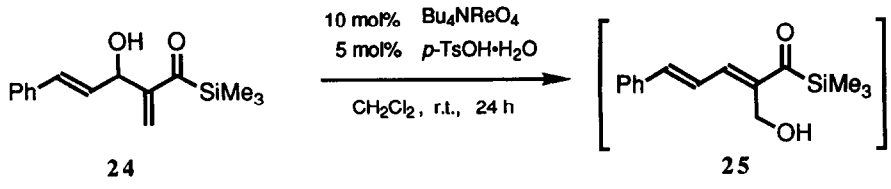
This catalytic system was applied to the rearrangement of some allylic alcohols where the products are thermodynamically more stable as compared with the starting materials. Treatment of the enyne alcohol **20** with the catalysts resulted in the regioselective rearrangement toward the direction of the olefinic moiety, giving the conjugated alcohol **21** in high yield (eq. 7). The α-methylene β-hydroxy acylsilanes **22** and **24**[8] were readily rearranged to the more stable conjugated forms (eq. 8 and 9). Particularly, in the reaction of **25**, the successive *in situ* cyclization reaction afforded the α-methylene cyclopentenone **26** in good yield.



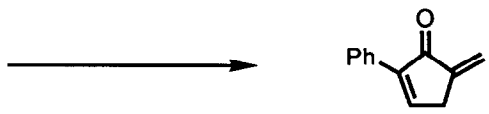
20 **21** 80% (eq. 7)



22 **23** 70% (eq. 8)



24 **25**



26 67% (eq. 9)

Experimental

General. NMR spectra in $CDCl_3$ were recorded on Bruker AM500 spectrometer using tetramethylsilane as the internal standard, otherwise noted. IR spectra were measured with Horiba FT-300S spectrometer. High-resolution mass spectra were measured for the new compounds with JEOL JMS-D300 mass spectrometer operating at 70 eV. Column chromatography was conducted on silica gel (Merck, 7734, 70-230 mesh) and medium pressure column chromatography was performed with the YFLC-254 system of YAMAZEN Corp. Preparative thin-layer chromatography (TLC) was carried out on a silica gel (Wakogel B-5F). Dichloromethane and 1,2-dichloroethane were distilled from P_2O_5, then from CaH_2, and dried over MS 4A.

The compounds **22** and **24** were prepared by the reaction of 1-trimethylsilyl-1-methylthio-1,2-propadiene with benzaldehyde and 3-phenylpropanal, respectively, in the presence of $BF_3•Et_2O$ in dichloromethane at -78 °C.[8]

General Procedure for the Rhenium Catalyzed Allylic and Propargylic Rearrangement at Room Temperature (Table 1, Entry 1) Under an argon atmosphere, 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 to a dichloromethane solution (2 ml) of the allylic alcohol **4** (57.7 mg, 0.33 mmol) at room temperature. After the mixture was stirred for 5 min, diethyl ether and saturated aqueous sodium hydrogen carbonate 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 (hexane:ethyl acetate=5:1) to give the rearranged product **5** (23 mg, 40% yield) and the starting material **4** (33 mg, 56%).

Rearrangement of Propargylic Alcohols under 1,2-Dichloroethane Refluxing Conditions (Table 2, Entry 8) Under an argon atomosphere, to a 1,2-dichloroethane solution (2 ml) of the 1-phenyl-4-nonyn-3-ol (19.0 mg, 0.09 mmol), a 1,2-dichloroethane solution (1.5 ml) of **1** (4.9 mg, 0.01 mmol) and *p*-TsOH•H_2O (2.2 mg, 0.01 mmol) were added and the mixture was heated to reflux. After the mixture was refluxed for 25 hour, the same workup as the above case was carried out and 1-phenyl-3-nonen-5-one was isolated in 67% yield and 1-phenyl-2-nonen-5-one in 6% yield.

Assignment of the Stereochemistry of the Compounds 7 and 8 Each stereoisomer of **7** was hydrogenated (5% Pd-C, H_2 1atm, rt, in EtOH) to give a single stereoisomer, respectively (eq. 4). The alcohol having the axial H_a proton (3.28 ppm, ddd, J= 4.3, 9.8, 9.8 Hz) was assigned as the *trans*-**7'** and the another isomer having the equatorial H_a proton (3.78 ppm, broad singlet) was assigned as the *cis*-**7'**. In the case of the rearranged compounds **8**, the inseparable mixture of the both isomers was converted to **8'** by hydrogenation and the each isomer was separated by thin-layer chromatography (eq. 5). The *trans*- structure , *trans*-**8'**, was confirmed by the existence of the axial H_b proton (3.54 ppm, dddd, J= 4.3, 4.3, 10.8, 10.8 Hz) and the *cis*-**8'** showed the equatorial H_b proton at 3.96 ppm as a broad singlet.

Spectral Data

5-Phenyl-1-penten-3-ol (3) IR (neat) 3348, 1603, 1496, 1452, 1425 cm^{-1}; ^1H NMR (60 MHz, CCl_4) δ= 1.5-2.0 (2H, m), 2.4 (1H, bs), 2.5-2.8 (2H, m), 3.7-4.2 (1H, m), 4.8-5.3 (2H, m), 5.8 (1H, ddd, J= 6, 9, 17 Hz), 7.0 (5H, s).

1-Phenyl-4-hexen-3-ol (5) IR (neat) 3383, 1603, 1495, 1450, 1404 cm^{-1}; ^1H NMR δ= 1.58 (1H, bs), 1.70 (3H, dd, J= 1.4, 6.4 Hz), 1.75-1.89 (2H, m), 2.62-2.73 (2H, m), 4.05 (1H, q, J= 7.0 Hz), 5.51 (1H, ddq, J_d= 7.0, 15.3 Hz, J_q= 1.4 Hz), 5.66 (1H, dq, J_d= 15.3 Hz, J_q= 6.4 Hz), 7.15-7.28 (5H, m); ^{13}C NMR δ= 17.65, 31.75, 38.72, 72.40, 125.75, 127.16, 128.32, 128.37, 128.41, 141.99.

1-Phenyl-2,4-hexadiene (6a) Two stereoisomers (2:1 ratio) were obtained as an inseparable mixture (stereochemistry was not determined). major isomer: ^1H NMR δ= 1.73 (3H, d, J= 6.3 Hz), 3.39 (2H, d, J= 6.9 Hz), 5.60-5.79 (2H, m), 6.01-6.11 (2H, m), 7.17-7.30 (5H, m); minor isomer: ^1H NMR δ= 1.80 (3H, d, J= 6.9 Hz), 3.52 (2H, d, J= 7.7 Hz), 5.60-5.79 (2H, m), 6.01-6.11 (2H, m), 7.17-7.30 (5H, m).

6-Phenyl-1,3-hexadiene (6b) One isomer (stereochemistry was not determined) ^{1}H NMR δ= 2.41 (2H, dt, J_d= 10.3 Hz, J_t= 7.8 Hz), 2.71 (2H, t, J= 7.8 Hz), 4.97 (1H, d, J= 11.2 Hz), 5.10 (1H, d, J= 15.0 Hz), 5.43-5.48 (1H, m), 6.30 (1H, dt, J_d= 16.9 Hz, J_t= 10.3 Hz), 6.43-6.48 (1H, m), 7.17-7.30 (5H, m)

***cis*-6-Benzyl-2-cyclohexen-1-ol (*cis*-7)** ^{1}H NMR δ= 1.33 (1H, bs), 1.43-1.54 (2H, m), 1.79-1.85 (1H, m), 1.93-2.01 (1H, m), 2.07-2.13 (1H, m), 2.59 (1H, dd, J= 7.7, 13.5 Hz), 2.84 (1H, dd, J= 7.7, 13.5 Hz), 3.89-3.91 (1H, bs), 5.81-5.88 (2H, m), 7.16-7.29 (5H, m); ^{13}C NMR δ= 22.33, 25.85, 37.98, 41.43, 65.30, 125.81, 128.28, 128.70, 129.17, 131.58, 140.86; HRMS Calcd. for $C_{13}H_{16}O$-H_2O: M-H_2O, 170.1096. Found: m/z 170.1089.

***trans*-6-Benzyl-2-cyclohexen-1-ol (*trans*-7)** ^{1}H NMR δ= 1.24-1.31 (1H, m), 1.61 (1H, bs), 1.68-1.79 (2H, m), 1.94-2.03 (2H, m), 2.42 (1H, dd, J= 9.0, 13.5 Hz), 3.03 (1H, dd, J= 4.8, 13.5 Hz), 3.92-3.96 (1H, m), 5.63-5.67 (1H, m), 5.76-5.78 (1H, m), 7.17-7.20 (3H, m), 7.26-7.29 (2H, m); ^{13}C NMR δ= 24.43, 24.82, 38.80, 43.91, 71.04, 125.94, 128.29, 129.28, 129.82, 129.87, 140.51; HRMS Calcd. for $C_{13}H_{16}O$: M, 188.1202. Found: m/z 188.1233.

4-Benzyl-2-cyclohexen-1-ol Two stereoisomers, *cis*- and *trans*-**8**, were obtained as an inseparable mixture. *cis*-isomer (*cis*-**8**) ^{1}H NMR δ= 1.38-1.46 (1H, m), 1.53 (1H, bs), 1.58-1.63 (1H, m), 1.65-1.72 (1H, m), 1.73-1.79 (1H, m), 2.27-2.33 (1H, m), 2.58 (1H, dd, J= 8.2, 13.4 Hz), 2.66 (1H, dd, J= 7.3, 13.4 Hz), 4.12-4.14 (1H, m), 5.73-5.76 (1H, m), 5.77-5.80 (1H, m), 7.13-7.29 (5H, m); ^{13}C NMR δ= 23.95, 30.23, 37.42, 41.89, 64.60, 125.99, 128.29, 129.03, 129.08, 135.04, 140.30; *trans* isomer (*trans*-**8**) ^{1}H NMR δ= 1.22-1.30 (1H, m), 1.38-1.46 (1H, m), 1.53 (1H, bs), 1.73-1.79 (1H, m), 2.01-2.06 (1H, m), 2.37-2.42 (1H, m), 2.50 (1H, dd, J= 8.1, 13.3 Hz), 2.61 (1H, dd, J= 7.0, 13.3 Hz), 4.20-4.23 (1H, m), 5.65-5.70 (2H, m), 7.13-7.29 (5H, m); ^{13}C NMR δ= 26.63, 31.65, 37.29, 42.17, 66.91, 125.98, 128.25, 129.08, 130.64, 133.63, 140.13; HRMS Calcd. for $C_{13}H_{16}O$-H_2O: M-H_2O, 170.1096. Found: m/z 170.1106.

3-Methyl-5-phenyl-1,3-pentadiene (11a) Two stereoisomers (2:1 ratio) were obtained as an inseparable mixture (stereochemistry was not determined). major isomer: ^{1}H NMR δ= 1.85 (3H, s), 3.50 (2H, d, J= 7.5 Hz), 4.98 (1H, d, J= 10.7 Hz), 5.15 (1H, d, J= 17.3 Hz), 5.67 (1H, t, J= 7.5 Hz), 6.40 (1H, dd, J= 10.7, 17.3 Hz), 7.15-7.31 (5H, m); minor isomer: ^{1}H NMR δ= 1.87 (3H, d, J= 1.0 Hz), 3.52 (2H, d, J= 8.0 Hz), 5.09 (1H, d, J= 10.8 Hz), 5.28 (1H, d, J= 17.3 Hz), 5.56 (1H, t, J= 7.8 Hz), 6.91 (1H, dd, J= 10.8, 17.3 Hz), 7.15-7.31 (5H, m).

3-Methylene-5-phenyl-1-pentene (11b) One isomer (stereochemistry was not determined) ^{1}H NMR δ= 2.52 (2H, t, J= 8.1 Hz), 2.81 (2H, t, J= 8.1 Hz), 5.01 (1H, bs), 5.04 (1H, bs), 5.13-5.23 (2H, m), 7.15-7.31 (6H, m).

4-Phenyl-1-vinyl-1-cyclohexene (13) ^{1}H NMR δ= 1.75-1.84 (1H, m), 2.02-2.10 (1H, m), 2.20-2.46 (4H, m), 2.78-2.84 (1H, m), 4.95 (1H, d, J= 10.7 Hz), 5.10 (1H, d, J= 17.5 Hz), 5.84 (1H, m), 6.41 (1H, dd, J= 10.7, 17.5 Hz), 7.18-7.32 (5H, m); ^{13}C NMR δ= 24.40, 29.53, 33.94, 40.20, 110.33, 126.06, 126.84, 128.38, 129.09, 135.89, 139.61, 146.78; HRMS Calcd. for $C_{14}H_{16}$: M, 184.1253. Found: m/z 184.1247.

***trans*-2-Methyl-6-phenyl-1,3-hexadiene (17)** IR (neat) 1606, 1521, 1495, 1452 cm^{-1}; ^{1}H NMR δ= 1.82 (3H, s), 2.42 (2H, q, J= 7.1 Hz), 2.72 (2H, t, J= 7.1 Hz), 4.87 (2H, s), 5.70 (1H, dt, J_d= 15.7 Hz, J_t= 7.1 Hz), 6.18 (1H, d, J= 15.7 Hz), 7.17-7.21 (3H, m), 7.26-7.29 (2H, m); ^{13}C NMR δ= 18.66, 34.83, 35.92, 114.60, 125.81, 128.30, 128.37, 129.84, 133.29, 141.89, 142.04.

3-Methyl-1-phenyl-2,4-hexadiene (19a) Two stereoisomers (10:7 ratio) were obtained as an inseparable mixture (stereochemistry was not determined). major isomer: ^{1}H NMR δ= 1.77 (3H, d, J= 7.2 Hz), 1.83 (3H, s), 3.47 (2H, d, J= 7.4

Hz), 5.53 (1H, t, J= 7.4 Hz), 5.65 (1H, dq, J_d= 15.6 Hz, J_q= 7.2 Hz), 6.11 (1H, d, J= 15.6 Hz), 7.16-7.30 (5H, m); minor isomer: ^{1}H NMR δ= 1.85 (3H, s), 1.83 (3H, d, J= 7.7 Hz), 3.50 (2H, d, J= 7.7 Hz), 5.40 (1H, t, J= 7.7 Hz), 5.75-5.82 (1H, m), 6.57 (1H, d, J= 15.4 Hz), 7.16-7.30 (5H, m).

4-Methylene-6-phenyl-2-hexene (19b) One isomer (stereochemistry was not determined) ^{1}H NMR δ= 1.80 (3H, d, J= 7.1 Hz), 2.47-2.50 (2H, m), 2.78-2.81 (2H, m), 4.85 (1H, bs), 4.90 (1H, bs), 5.75-5.82 (1H, m), 7.16-7.30 (6H, m).

***cis*-2-Benzylcyclohexan-1-ol (*cis*-7')** ^{1}H NMR δ= 1.19-1.25 (1H, m), 1.30 (1H, bs), 1.38-1.47 (3H, m), 1.53-1.60 (2H, m), 1.61-1.69 (2H, m), 1.72-1.78 (1H, m), 2.53 (1H, dd, J= 7.7, 13.4 Hz), 2.70 (1H, dd, J= 7.5, 13.4 Hz), 3.77-3.79 (1H, bs), 7.15-7.18 (3H, m), 7.24-7.27 (2H, m); ^{13}C NMR δ= 20.32, 25.27, 26.38, 33.25, 38.68, 43.54, 68.55, 125.73, 128.22, 129.13, 141.01.

***trans*-2-Benzylcyclohexan-1-ol (*trans*-7')** ^{1}H NMR δ= 0.88-0.93 (1H, m), 1.05-1.11 (1H, m), 1.21-1.29 (2H, m), 1.45-1.65 (4H, m), 1.68-1.71 (1H, m), 1.94-1.98 (1H, m), 2.34 (1H, dd, J= 9.2, 13.3 Hz), 3.14 (1H, dd, J= 4.0, 13.3 Hz), 3.28 (1H, ddd, J= 4.3, 9.8, 9.8 Hz), 7.15-7.18 (3H, m), 7.25-7.27 (2H, m); ^{13}C NMR δ= 24.89, 25.41, 30.00, 35.82, 39.00, 47.03, 74.54, 125.74, 128.16, 129.40, 140.75.

***cis*-4-Benzylcyclohexan-1-ol (*cis*-8')** ^{1}H NMR δ= 1.30-1.62 (8H, m), 1.67-1.73 (2H, m), 2.53 (2H, d, J= 7.3 Hz), 3.95-3.97 (1H, bs), 7.12-7.18 (3H, m), 7.25-7.27 (2H, m); ^{13}C NMR δ= 26.70, 32.23, 38.42, 42.75, 66.99, 125.68, 128.13, 129.11, 141.12; HRMS Calcd. for $C_{13}H_{18}O$: M, 190.1358. Found: m/z 190.1358.

***trans*-4-Benzylcyclohexan-1-ol (*trans*-8')** ^{1}H NMR δ= 0.96-1.05 (2H, m), 1.15-1.24 (2H, m), 1.43-1.60 (2H, m), 1.70-1.73 (2H, m), 1.91-1.95 (2H, m), 2.47 (2H, d, J= 7.1 Hz), 3.54 (1H, dddd, J= 4.3, 4.3, 10.8, 10.8 Hz), 7.10-7.18 (3H, m), 7.24-7.27 (2H, m); ^{13}C NMR δ= 31.01, 35.48, 38.78, 43.24, 71.06, 125.75, 128.13, 129.07, 141.03; HRMS Calcd. for $C_{13}H_{18}O$: M, 190.1358. Found: m/z 190.1359.

1-Phenyl-1-hepten-3-one The *cis*- and *trans*-isomers were separated by TLC (*cis* : *trans* = 2 : 5). *cis*-form: IR (neat) 1689, 1606, 1570, 1493, 1456, 1408 cm^{-1}; ^{1}H NMR δ= 0.86 (3H, t, J= 7.4 Hz), 1.23-1.31 (2H, m), 1.53-1.59 (2H, m), 2.44 (2H, t, J= 7.4 Hz), 6.18 (1H, d, J= 12.8 Hz), 6.81 (1H, d, J= 12.8 Hz), 7.32-7.34 (3H, m), 7.49-7.52 (2H, m); ^{13}C NMR δ= 13.77, 22.20, 26.24, 43.28, 128.17, 128.63, 129.05, 129.49, 135.33, 139.52, 203.49; *trans*-form: IR (neat) 1658, 1612, 1454, 1406 cm^{-1}; ^{1}H NMR δ= 0.94 (3H, t, J= 7.4 Hz), 1.35-1.42 (2H, m), 1.64-1.70 (2H, m), 2.66 (2H, t, J= 7.4 Hz), 6.73 (1H, d, J= 16.1 Hz), 7.37-7.39 (3H, m), 7.54 (1H, d, J= 16.1 Hz), 7.53-7.55 (2H, m); ^{13}C NMR δ= 13.87, 22.42, 26.45, 40.64, 126.25, 128.20, 128.89, 130.33, 134.58, 142.28, 200.65.

***trans*-3-Phenyl-1-trimethylsilyl-2-propen-1-one** IR (neat) 1635, 1579, 1450 cm^{-1}; ^{1}H NMR δ= 0.31 (9H, s), 6.88 (1H, d, J= 16.4 Hz), 7.36-7.38 (3H, m), 7.42 (1H, d, J= 16.4 Hz), 7.52-7.54 (2H, m); ^{13}C NMR δ= -2.06, 128.19, 128.91, 130.42, 131.24, 134.85, 142.90, 212.34; HRMS Calcd. for $C_{12}H_{16}OSi$: M, 204.0971. Found: m/z 204.0971.

3-Methyl-5-phenyl-2-pentenal The geometry of the olefin was determined by the chemical shift of the methyl group.[9] The *cis*- and *trans*-isomers were separated by TLC (*cis* : *trans* = 2 : 3). *cis*-form: IR (neat) 1674, 1633, 1606, 1496, 1452 cm^{-1}; ^{1}H NMR δ= 2.00 (3H, d, J= 1.2 Hz), 2.86 (4H, s), 5.86 (1H, dq, J_d= 8.1 Hz, J_q= 1.2 Hz), 7.15-7.31 (5H, m), 9.71 (1H, d, J= 8.1 Hz); ^{13}C NMR δ= 25.05, 34.80, 34.94, 126.49, 128.35, 128.58, 128.83, 140.18, 162.62, 190.41; *trans*-form: IR (neat) 1672, 1633, 1608, 1495, 1448 cm^{-1}; ^{1}H NMR δ= 2.19 (3H, d, J= 1.2 Hz), 2.51-2.54 (2H, m), 2.81-2.85 (2H, m), 5.90

(1H, dq, J_d= 8.0 Hz, J_q= 1.2 Hz), 7.15-7.31 (5H, m), 9.99 (1H, d, J= 8.0 Hz); ^{13}C NMR δ= 17.71, 33.52, 42.17, 126.28, 127.58, 128.20, 128.53, 140.52, 162.82, 191.18.

3-Methyl-1-phenyl-4-nonyn-3-ol IR (neat) 3390, 2239, 1712, 1603, 1496, 1456 cm^{-1}; ^{1}H NMR δ= 0.93 (3H, t, J= 7.1 Hz), 1.40-1.54 (4H, m), 1.52 (3H, s), 1.90-2.01 (2H, m), 2.04 (1H, bs), 2.23 (2H, t, J= 7.1 Hz), 2.81-2.89 (2H, m), 7.17-7.23 (3H, m), 7.27-7.30 (2H, m); ^{13}C NMR δ= 13.54, 18.24, 21.87, 30.31, 30.76, 31.30, 45.66, 68.12, 83.67, 84.25, 125.73, 128.34, 128.36, 142.11; HRMS Calcd. for $C_{16}H_{22}O$: M, 230.1672. Found: m/z 230.1694.

3-Methyl-1-phenyl-3-nonen-5-one The geometry of the olefin was determined by the chemical shift of the methyl group.[9] The *cis*- and *trans*-isomers were separated by TLC (*cis* : *trans* = 2 : 3). *cis*-form: IR (neat) 1728, 1682, 1614, 1495, 1454 cm^{-1}; ^{1}H NMR δ= 0.91 (3H, t, J= 7.5 Hz), 1.32 (2H, sext, J= 7.5 Hz), 1.56 (2H, quint, J= 7.5 Hz), 1.86 (3H, d, J= 1.2 Hz), 2.38 (2H, t, J= 7.5 Hz), 2.76 (2H, dd, J= 6.3, 9.3 Hz), 2.86 (2H, dd, J= 6.3, 9.3 Hz), 6.08 (1H, d, J= 1.2 Hz), 7.16-7.29 (5H, m); ^{13}C NMR δ= 13.90, 22.39, 25.66, 26.38, 34.47, 35.95, 44.10, 124.16, 125.85, 128.28, 128.31, 128.42, 128.50, 141.78, 157.84, 200.90; *trans*-form: IR (neat) 1714, 1685, 1618, 1495, 1454 cm^{-1}; ^{1}H NMR δ= 0.90 (3H, t, J= 7.5 Hz), 1.29 (2H, sext, J= 7.5 Hz), 1.53 (2H, quint, J= 7.5 Hz), 2.17 (3H, d, J= 1.1 Hz), 2.37 (2H, t, J= 7.5 Hz), 2.42 (2H, dd, J= 7.7, 8.5 Hz), 2.78 (2H, dd, J= 7.7, 8.5 Hz), 6.01 (1H, d, J= 1.1 Hz), 7.16-7.30 (5H, m); ^{13}C NMR δ= 13.86, 19.32, 22.36, 26.36, 33.95, 42.92, 44.12, 123.62, 126.06, 128.28, 128.37, 141.05, 156.79, 201.52; HRMS Calcd. for $C_{16}H_{22}O$: M, 230.1672. Found: m/z 230.1683.

***trans*-1-Phenyl-3-nonen-5-one** IR (neat) 1707, 1672, 1630, 1495, 1456 cm^{-1}; ^{1}H NMR δ= 0.91 (3H, t, J= 7.4 Hz), 1.32 (2H, sext, J= 7.4 Hz), 1.57 (2H, quint, J= 7.4 Hz), 2.50 (2H, t, J= 7.2 Hz), 2.53 (2H, dt, J_d= 1.5 Hz, J_t= 7.2 Hz), 2.78 (2H, t, J= 7.4 Hz), 6.10 (1H, dt, J_d= 16.0 Hz, J_t= 1.5 Hz), 6.84 (1H, dt, J_d= 16.0 Hz, J_t= 7.2 Hz), 7.17-7.31 (5H, m); ^{13}C NMR δ= 13.92, 22.46, 26.47, 34.16, 34.52, 39.96, 126.25, 128.39, 128.54, 130.82, 140.80, 145.86, 200.93; HRMS Calcd. for $C_{15}H_{20}O$: M, 216.1515. Found: m/z 216.1524.

1-Phenyl-2-nonen-5-one The geometry of the olefin was not determined. IR (neat) 1714, 1603, 1495, 1456 cm^{-1}; ^{1}H NMR δ= 0.88 (3H, t, J= 7.4 Hz), 1.28 (2H, sext, J= 7.4 Hz), 1.54 (2H, quint, J= 7.4 Hz), 2.40 (2H, t, J= 7.4 Hz), 3.12 (2H, d, J= 6.8 Hz), 3.36 (2H, d, J= 6.4 Hz), 5.57-5.70 (2H, m), 7.15-7.19 (3H, m), 7.25-7.28 (2H, m); ^{13}C NMR δ= 13.82, 22.29, 25.79, 39.01, 41.98, 46.55, 123.58, 126.07, 128.42, 128.49, 133.37, 140.15, 207.40.

***trans*-1-Phenyl-2-hepten-1-one** IR (neat) 1670, 1622, 1448 cm^{-1}; ^{1}H NMR δ= 0.91 (3H, t, J= 7.3 Hz), 1.37 (2H, sext, J= 7.3 Hz), 1.46-1.52 (2H, m), 2.30 (2H, dq, J_d= 1.4 Hz, J_q= 7.0 Hz), 6.85 (1H, dt, J_d= 15.3 Hz, J_t= 1.4 Hz), 7.05 (1H, dt, J_d= 15.3 Hz, J_t= 7.0 Hz), 7.43-7.54 (3H, m), 7.89-7.91 (2H, m); ^{13}C NMR δ= 13.81, 22.30, 30.27, 32.52, 125.90, 128.49, 128.50, 132.53, 138.04, 150.11, 191.00.

***trans*-4-Dodecen-7-yn-6-ol (20)** ^{1}H NMR δ= 0.89 (3H, t, J= 7.1Hz), 0.91 (3H, t, J= 7.4 Hz), 1.34-1.54 (6H, m), 1.84 (1H, bs), 2.02-2.06 (2H, m), 2.22-2.25 (2H, m), 4.80-4.82 (1H, m), 5.60 (1H, ddt, J_d= 6.3, 15.3 Hz, J_t= 1.0 Hz), 5.85 (1H, ddt, J_d= 1.0, 15.3 Hz, J_t= 6.6 Hz); ^{13}C NMR δ= 13.52, 13.61, 16.40, 21.89, 22.04, 30.64, 33.93, 63.16, 79.69, 86.71, 129.73, 133.28; HRMS Calcd. for $C_{12}H_{20}O$: M, 180.1515. Found: m/z 180.1500.

5-Dodecen-7-yn-4-ol (21) The *cis*- and *trans*-isomers were obtained as an inseparable mixture (*cis* : *trans* = 1 : 2). IR (neat) 3357, 2216, 1462, 1433 cm^{-1}; ^{1}H NMR *trans*-form δ= 0.85-0.93 (6H, m), 1.23-1.60 (8H, m), 1.81 (1H, bs), 2.25-2.31 (2H, m), 4.10 (1H, q, J= 6.5 Hz), 5.64 (1H, dd, J= 1.5, 15.8 Hz), 6.01 (1H, dd, J= 6.5, 15.8 Hz); *cis*-form δ= 0.85-0.93 (6H,

m), 1.23-1.60 (8H, m), 1.81 (1H, bs), 2.25-2.31 (2H, m), 4.63 (1H, q, J= 7.8 Hz), 5.49 (1H, d, J= 10.8 Hz), 5.77 (1H, dd, J= 7.8, 10.8 Hz).

2-Hydroxymethyl-3-phenyl-1-trimethylsilyl-2-propen-1-one (23) IR (neat) 3448, 1597, 1572, 1450, 1412 cm^{-1}; ^1H NMR δ= 0.37 (9H, s), 2.71 (1H, bs), 4.44 (2H, s), 7.37-7.51 (5H, m), 7.61 (1H, s); ^{13}C NMR δ= -0.95, 56.98, 126.53, 128.34, 128.72, 129.55, 129.66, 134.54, 144.82, 146.81, 239.05; HRMS Calcd. for $C_{13}H_{18}O_2Si$: M, 234.1076. Found: m/z 234.1053.

5-Methylene-2-phenyl-2-cyclopenten-1-one (26) IR (neat) 1689, 1645, 1593, 1491, 1444, 1417 cm^{-1}; ^1H NMR δ= 3.32 (2H, d, J= 1.2 Hz), 5.53 (1H, d, J= 0.9 Hz), 6.24 (1H, d, J= 0.9 Hz), 7.34-7.42 (3H, m), 7.75-7.79 (3H, m); ^{13}C NMR δ= 31.74, 117.70, 126.97, 128.43, 128.53, 131.89, 142.09, 144.73, 152.30, 193.90.

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