Transformatiom of Propargylic Alcohols into Enones

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α,α-Disubstituted propargylic alcohols were transformed into enones by the catalysis with Ag(I) or Ag(I)–Me_3SiCl under the mild conditions. This procedure provides a new synthetic method of α,β-unsaturated ketones having an oxygen function at α' position from 2-butyne-1,4-diol derivatives. 3-Acetoxy-1,4,4-triphenyl-3-buten-2-one was obtained from 4-acetoxy-1,1,4-triphenyl-2-butyn-1-ol by the catalysis with tin(IV) chloride or aluminium chloride.

Transformation of propargylic alcohols into enones has been known as Meyer–Shuster rearrangement which is carried out under strong acidic conditions[1,2] or at high temperature.[3,4] As an improved approach, the method using Re(VII)–TsOH has recently been developed.[5]

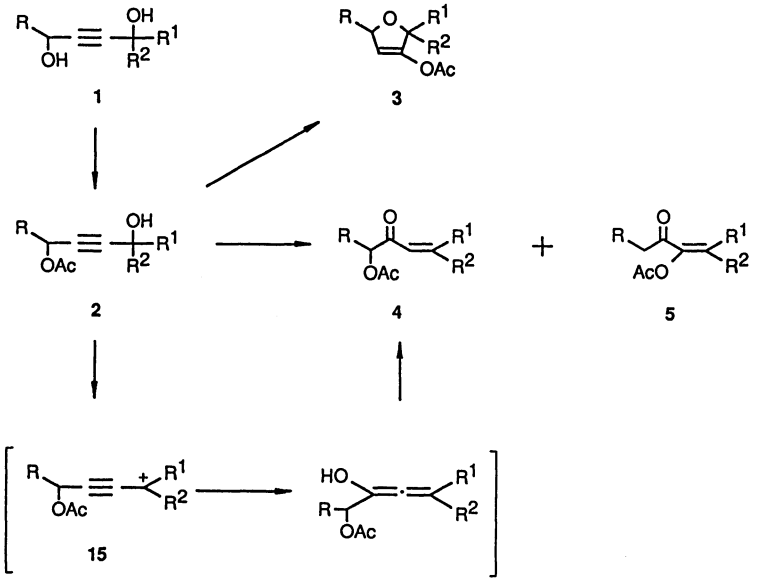
Previously, we reported that transformation of enantiomerically enriched 2-butyne-1,4-diols **1** into dihydrofurans **3** with complete enantiospecificity was achieved by Ag(I)-catalyzed rearrangement and cyclization.[6] Herein we report Ag(I)-mediated transformation of α,α-diaryl-substituted propargylic alcohols into the corresponding enones under the mild conditions. Furthermore, we found a novel catalyst, silver tetrafluoroborate–trimethylchlorosilane, for the transformation of α,α-dialkyl-substituted 2-butyne-1,4-diol derivatives into enones **4**.

Results and Discussion

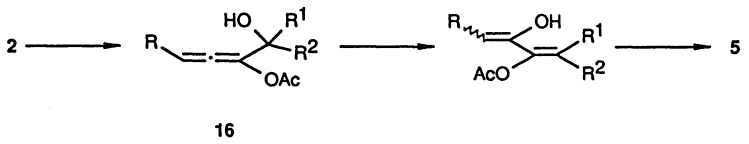
Reactivity of the Hydroxyl Group in Propargylic Alcohols. As shown in Table 1 (Run 1 and 9), α,β-unsaturated α'-acetoxy enones **4a** and **4d** were obtained in high yields by the Ag(I)-catalyzed transformation (Method A) of monoacetates **2a** and **2d**, which were prepared from corresponding 2-butyne-1,4-diol derivatives. Although an enone **4a** was obtained from a propargylic alcohol **2a** having two aromatic substituents (Run 1), **2b** having alkyl substituents (Run 3) gave a dihydrofuran **3b**.[6,7] These results suggest that high stability of benzylic carbocation (Scheme 1, **15**) produced by Ag(I)-mediated elimination[8] of the tertiary hydroxyl group accelerates the formation of enones.

In the case of **2e**, α-acetoxyenone **5e** was produced along with **4e** (Run 10). Formation of **5** was explained by rearrangement of the acetoxyl group as shown in Scheme 2. In comparison with the reaction of **2d**, the electron withdrawing group (Cl) in **2e** made the intermediate **15** less stable. Therefore, formation of **16**[6] from **2e** could compete with that of **15**.

Tetrahydropyranyl (THP) ether **6** was also transformed into the enone **7**, but the THP group was

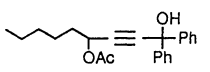
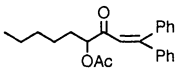
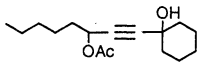
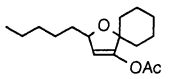
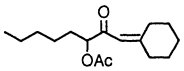
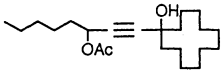
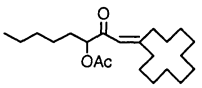
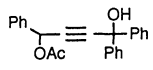
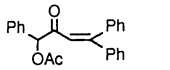
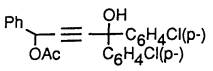
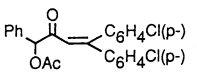
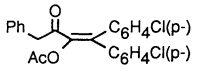
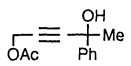
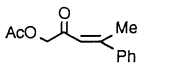
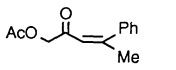
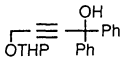
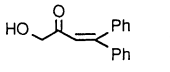
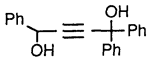
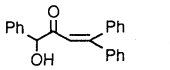
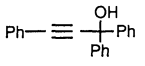
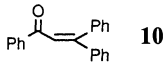
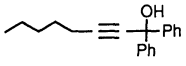
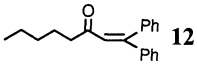
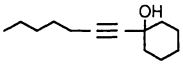
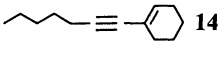


Scheme 1.



Scheme 2.

Table 1. Transformation of Propargyl Alcohol Derivatives[a)]

Run	Acetylenic alcohol		Method	Time/h	Product		Yield/%		Yield/%
1		**2a**	A	13.5		**4a**	96		
2			D	0.3			91		
3		**2b**	A	5.5		**3b**	84		
4			B	24			68		
5			C	24			38		
6			D (25 °C)	120		**4b**	32		
7			E	2			52		
8		**2c**	B	1.1		**4c**	54		
9		**2d**	A	1		**4d**	93		
10		**2e**	A (60 °C)	2		**4e**	43	 **5e**	10
11		**2f**	A (50 °C)	5		**4f**	32	 **4f'**	68
12			B	0.5			82		
13		**6**	A	0.5		**7**	53		
14		**1d**	F	5.5		**8**	84		
15		**9**	A	2		**10**	89		
16		**11**	A	0.5		**12**	84		
17		**13**	B	3.5		**14**	61		

a) Method A: $AgBF_4$ (5—11 mol%), benzene, 80 °C; Method B: $AgBF_4$ (8—11 mol%), Me_3SiCl (8—20 mol%), 1,2-dichloroethane, 50 °C; Method C: $AgClO_4$ (9 mol%), Me_3SiCl (9 mol%), 1,2-dichloroethane, 50 °C; Method D: $SnCl_4$ (10 mol%), 1,2-dichloroethane, 0 °C; Method E: Me_3SiOTf (10 mol%); Method F: $AgBF_4$ (31 mol%), acetone, 56 °C.

removed. When the diol **1d** was treated with silver tetrafluoroborate (Run 14), the corresponding enone **8** was obtained in a good yield. Though propargylic alcohols **9** and **11** could be converted into enones, **13** gave only the enyne **14**. Comparison of Run 4 with Run 17 suggests neighboring group participation of the acetoxyl group to stabilize the cationic intermediate like **17**. Furthermore, in the case of secondary propargylic

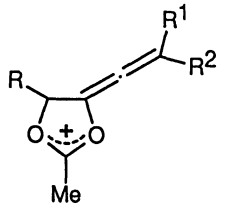


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Table 2. Transformation of 4-Acetoxy-1,1,4-triphenyl-2-butyn-1-ol into Enones with Various Lewis Acids[a]

Reagent	mol%	Temp °C	Yield/% 4d	5d
$AgBF_4$[b]	15	30	86 (90%ee)[c]	0
$AgBF_4$–Me_3SiCl	7/7	25	72	15
H_2SO_4[d]	152	25	62	23
$TiCl_4$[e]	10	25	37	19
$Et_2O \cdot BF_3$	10	0	0	42
$AlCl_3$	14	25	0	49
$SnCl_4$	10	0	0	53

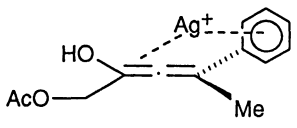
a) Solvent, 1,2-dichloroethane; time, 0.3 h. b) Starting alcohol **2d**, 90%ee; solvent, benzene; time, 56 h. c) At 70 °C, **4d** (70%ee) was obtained. d) Solvent, acetic acid; Ref. 11. e) Time, 24 h.

alcohols, corresponding enones were not obtained.

In addition, treatment of **2d** (90%ee) with $AgBF_4$ at 30 °C gave **4d** without loss of optical purity (Table 2, Run 1). When this transformation was carried out at 70 °C, epimerization at α' position of the enone **4d** was observed.

Comparison of Various Catalysts. $AgBF_4$–Me_3SiCl was found to be effective for the transformation of **2b** into the corresponding enone **4b** (Table 1, Method B). Although the reaction of **2b** with $AgBF_4$ alone activated the triple bond[6] to give dihydrofuran **3b** (Run 3), the catalysis of $AgBF_4$–Me_3SiCl or $AgClO_4$–Me_3SiCl promoted the elimination of the tertiary hydroxyl group to yield **4b** (Runs 4 and 5). In addition, Me_3SiClO_4 was reported to be obtained from Me_3SiCl and $AgClO_4$.[9,10] Therefore, the catalyst for the enone formation by Method B would not be silver ion but cationic trimethylsilyl species formed in situ. This sequence was also supported by the fact that transformation of **2b** into **4b** was carried out by the catalysis of trimethylsilyl triflate providing Me_3Si^+ (Run 7). By Method B, **4c** was also obtained from **2c** (Run 8).

When **2f** having an aromatic substituent was treated with $AgBF_4$ (Run 11), both (*E*)- and (*Z*)-isomers (**4f** and **4f'**) were obtained, while only (*E*)-isomer **4f** was formed by Method B (Run 12). As described above, trimethylsilyl group-mediated elimination of the hydroxyl group initiated the transformation in Method B, in which the less strained (*E*)-isomer was produced. In contrast, at the stage of a proposed intermediate **18**, silver ion would be placed at the same side with the phenyl group (Run 11). Therefore, protonation proceeded mainly from the opposite side of the phenyl group in Method A.



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As shown in Table 2, 3-acetoxy-1,4,4-triphenyl-3-buten-2-one (**5d**) was produced by the catalysis of $AlCl_3$ or $SnCl_4$. Under the acidic conditions (H_2SO_4–AcOH)[11] or other conditions, a mixture of **4d** and **5d** was formed. But the enones **5** were not formed in the case of **2** having an alkyl substituent (Scheme 1). Therefore, Lewis acids would accelerate elimination of the acetoxyl group at the benzylic position, followed by formation of the rearranged intermediate **16** (Scheme 2).

While $AgBF_4$ and $SnCl_4$ gave similar results in the formation of **4a** (Table 1, Runs 1 and 2), the proposed catalyst, $AgBF_4$–Me_3SiCl, was more effective for the synthesis of **4b** than $SnCl_4$ (Table 1, Runs 4 and 6).

Experimental

Melting points and boiling points are uncorrected. ^1H NMR and ^{13}C NMR spectra in $CDCl_3$ (tetramethylsilane as an internal standard) were recorded on a JEOL JNM-GX270 spectrometer. IR data of neat liquid film samples (unless otherwise noted) were recorded on a Shimadzu FTIR-4200 spectrometer, and mass spectra on a JEOL JMS-DX303 spectrometer at 70 eV. Preparative TLC plates were prepared with Merck Kieselgel 60 PF_{254}. Column chromatography and flash chromatography were performed on silica gel (Wakogel C-200 and C-300), respectively. Benzene was distilled from sodium benzophenone ketyl and 1,2-dichloroethane from P_2O_5.

Preparation of Propargyl Alcohol Derivatives and Their Acetates. The diols **1** and acetylenic alcohols **6**, **9**, **11**, and **13** were prepared from corresponding ketones by the modification reported previously.[7] Yields(%) and the starting ketones were as follows: **6** (76%, benzophenone), **9**[12] (93%, benzophenone), **11** (82%, benzophenone), **13**[13] (72%, cyclohexanone). According to the reported method,[7] the diols **1** were monoacetylated to give following acetates (yield, %): **2a** (79% yield from 1-octyn-3-ol), **2b** (80% yield from cyclohexanone), **2c** (77% yield from cyclododecanone), **2d** (77% yield from 1-phenyl-2-propyn-1-ol), **2e** (92% yield from 4,4'-dichlorobenzophenone), **2f** (43% yield from acetophenone). Physical and spectral data of these alcohols and acetates are summarized below.

1,1-Diphenyl-2-nonyne-1,4-diol (1a) and 4-Acetoxy-1,1-diphenyl-2-nonyn-1-ol (2a). 1a: Mp 97.1—97.5 °C; ^1H NMR δ=0.89 (3H, t, J=6.8 Hz), 1.27—1.79 (8H, m), 2.09 (1H, br s), 3.03 (1H, br s), 4.48 (1H, t, J=6.4 Hz), 7.21—7.59 (10H, m); IR (KBr) 3300, 1490, 1450, 1140 cm^{-1}; MS m/z (%) 308 (M^+, 1), 217 (20), 105 (100), 77 (70). Found: C, 81.86; H, 7.87%. Calcd for $C_{21}H_{24}O_2$: C, 81.78; H, 7.84%.

2a: ^1H NMR δ=0.88 (3H, t, J=6.8 Hz), 1.27—1.85 (8H, m), 2.07 (3H, s), 3.03 (1H, br s), 5.49 (1H, t, J=6.8 Hz), 7.22—7.59 (10H, m); IR 3400, 1730, 1240 cm^{-1}; MS m/z (%) 350 (M^+; 5), 307 (99), 79 (100). Found: C, 78.77; H, 7.50%. Calcd for $C_{23}H_{26}O_3$: C, 78.83; H, 7.48%.

1-(3-Hydroxy-1-octynyl)cyclohexanol (1b) and 1-(3-Acetoxy-1-octynyl)cyclohexanol (2b). 1b: Bp 152—160 °C (bath temp)/0.30 mmHg (1 mmHg=133.322 Pa); ^1H NMR δ=0.90 (3H, t, J=6.8 Hz), 1.29—1.93 (18H, m), 4.41 (1H, t, J=6.8 Hz); IR 3300, 1430, 1230 cm^{-1}; MS m/z (%) 224 (M^+, 9), 135 (63), 55 (100).

2b: Bp 137—145 °C (bath temp)/0.38 mmHg; ^1H NMR δ=0.89 (3H, J=6.8 Hz, t), 1.31—1.73 (18H, m), 2.07 (3H, s),

5.39 (1H, t, J=6.8 Hz); IR 3400, 1740, 1230 cm^{-1}; MS m/z (%) 266 (M^+, 13), 137 (100). Found: C, 71.90; H, 9.88%. Calcd for $C_{16}H_{26}O_3$: C, 72.14; H, 9.84%.

1-(3-Hydroxy-1-octynyl)cyclododecanol (1c) and 1-(3-Acetoxy-1-octynyl)cyclododecanol (2c). 1c: ^{1}H NMR δ=0.90 (3H, t, J=6.84 Hz), 1.23—1.92 (30H, m), 2.26 (2H, br s), 4.38 (1H, t, J=6.35 Hz).

2c: ^{1}H NMR δ=0.89 (3H, t, J=6.8 Hz), 1.35—1.83 (30H, m), 2.07 (3H, s), 5.38 (1H, t, J=6.8 Hz); IR 3450, 1740, 1235 cm^{-1}. Found: C, 75.32; H, 10.66%. Calcd for $C_{22}H_{38}O_3$: C, 75.38; H, 10.93%.

1,1,4-Triphenyl-2-butyne-1,4-diol (1d) and 4-Acetoxy-1,1,4-triphenyl-2-butyn-1-ol (2d). 1d:[14] Mp 141.8—142.4 °C; ^{1}H NMR δ=2.28 (1H, br s), 2.86 (1H, br s), 5.62 (1H, d, J=5.9 Hz), 7.24—7.62 (15H, m); IR (KBr) 3250, 1490, 1450cm^{-1}; MS m/z (%) 296 (M^+-H_2O, 9), 182 (26), 105 (100).

2d: ^{1}H NMR δ=2.07 (3H, s), 6.61 (1H, s), 7.22—7.60 (15H, m); IR 3450, 3050, 1740, 1490, 1370, 1230 cm^{-1}; MS m/z (%) 296 ($M^+-CH_3CO_2H$, 100), 280 (89), 105 (61). Found: C, 80.42; H, 5.72%. Calcd for $C_{24}H_{20}O_3$: C, 80.88; H, 5.66%.

1,1-Bis(4-chlorophenyl)-4-phenyl-2-butyne-1,4-diol (1e) and 4-Acetoxy-1,1-bis(4-chlorophenyl)-4-phenyl-2-butyn-1-ol (2e). 1e: ^{1}H NMR δ=2.49 (1H, br s), 3.14 (1H, br s), 5.57 (1H, s), 7.21—7.58 (13H, m). Found: C, 68.79; H, 4.20; Cl, 18.79%. Calcd for $C_{22}H_{16}Cl_2O_2$: C, 68.94; H, 4.21; Cl, 18.50%.

2e: ^{1}H NMR δ=2.11 (3H, s), 6.56 (1H, s), 7.25—7.53 (13H, m); IR 3400, 1740, 1490, 1230 cm^{-1}; MS m/z (%) 424 (M^+, 17). Found: C, 67.59; H, 4.48%. Calcd for $C_{24}H_{18}O_3Cl_2$: C, 67.78; H, 4.27%.

4-Phenyl-2-pentyne-1,4-diol (1f) and 5-Acetoxy-2-phenyl-3-pentyn-2-ol (2f). 1f: ^{1}H NMR δ=1.75 (3H, s), 4.31 (2H, s), 7.24—7.40 (3H, m), 7.59—7.66 (2H, m).

2f: ^{1}H NMR δ=1.73 (3H, s), 2.10 (3H, s), 4.73 (2H, s), 7.10—7.73 (5H, m); IR 3450, 1750, 1450, 1380, 1360, 1230 cm^{-1}; MS m/z (%) 203 (M^+-CH_3, 100). Found: C, 71.69; H, 6.58%. Calcd for $C_{13}H_{14}O_3$: C, 71.54; H, 6.47%.

1,1-Diphenyl-4-(tetrahydro-2-pyranyloxy)-2-butyn-1-ol (6). Mp 74.1—75.1 °C; ^{1}H NMR δ=1.46—1.83 (6H, m), 3.39—3.52 (1H, m), 3.80—3.87 (1H, m), 4.41 (2H, br s), 4.84 (1H, t, J=3.0Hz), 7.22—7.61 (10H, m); IR (KBr) 3400, 1490, 1450, 1340, 1200, 1140, 1120, 1020 cm^{-1}; MS m/z (%) 220 (M^+−THP−OH, 92), 191 (100), 105 (63). Found: C, 78.20; H, 6.83%. Calcd for $C_{21}H_{22}O_3$: C, 78.23; H, 6.88%.

1,1,3-Triphenyl-2-propyn-1-ol (9).[12] ^{1}H NMR δ=7.22—7.38 (10H, m), 7.48—7.53 (2H, m), 7.65—7.70 (3H, m).

1,1-Diphenyl-2-octyn-1-ol (11). ^{1}H NMR δ=0.90 (3H, t, J=7.1 Hz), 1.19-1.66 (6H, m), 2.33 (2H, t, J=7.1 Hz), 2.70 (1H, br s), 7.19—7.38 (6H, m), 7.57—7.63 (4H, m); IR 3450, 1490, 1450 cm^{-1}; MS m/z (%) 278 (M^+, 28), 221 (100), 143 (65). Found: C, 86.20; H, 8.04%. Calcd for $C_{20}H_{22}O$: C, 86.29; H, 7.97%.

1-(1-Heptynyl)cyclohexanol (13).[13] ^{1}H NMR δ=0.90 (3H, t, J=7.1 Hz), 1.12—1.91 (17H, m), 2.20 (2H, t, J=7.1 Hz).

Transformation of Propargyric Alcohols into Enones. Method A and F. According to the reported procedure,[7] the acetylic alcohols were treated with silver tetrafluoroborate (5—31 mol%).

4-Acetoxy-2-pentyl-1-oxaspiro[4,5]dec-3-ene (3b).[6] ^{1}H NMR δ=0.88 (3H, t, J=6.8 Hz), 1.14—1.62 (18H, m), 2.18 (3H, s), 4.77 (1H, dt, J=1.5, 5.8 Hz), 5.72 (1H, d, J=1.5 Hz); ^{13}C NMR δ=13.0, 20.3, 20.9, 21.2, 21.6, 23.8, 24.1, 30.9, 33.3, 35.0, 36.5, 80.4, 82.9, 107.9, 149.6, 180.4; IR 1780, 1760, 1660, 1196 cm^{-1}. Found: m/z 224.1706. Calcd for $C_{14}H_{24}O_2$: M−CH_2C=O, 224.1774.

Method B, C, D, and E (A Typical Procedure). 3-Acetoxy-1-cyclohexylidene-2-octanone (4b). A 1,2-dichloroethane (1.4 ml) solution of **2b** (104 mg, 0.39 mmol) was heated at 50 °C in the presence of silver tetrafluoroborate (7 mg, 9 mol%) and trimethylsilyl chloride (18 mol%) for 24 h in the dark under a nitrogen atmosphere. The reaction mixture was then diluted with dichloromethane (15 ml) at room temperature and washed with saturated aqueous sodium hydrogencarbonate solution (5 ml). Concentration of the organic phase gave the crude product, which was purified by preparative TLC (hexane–ethyl acetate 3 : 1) to afford **5b** (71 mg, 68% yield). ^{1}H NMR δ=0.89 (3H, t, J=6.59 Hz), 2.03 (3H, s), 2.20 (2H, t, J=6.1 Hz), 2.80 (2H, s), 4.97 (1H, dd, J=5.1, 8.1 Hz), 6.01 (1H, s); ^{13}C NMR δ=13.9, 20.7, 22.3, 24.9, 26.1, 27.9, 28.8, 29.6, 30.3, 30.7, 31.4, 38.4, 79.0, 116.9, 165.6, 170.5, 197.1; IR 1750, 1700, 1620 cm^{-1}; MS m/z (%) 266 (M^+, 22), 143 (70), 136 (86), 95 (100). Found: m/z 266.1795. Calcd for $C_{16}H_{26}O_3$: M, 266.1880.

4-Acetoxy-1,1-diphenyl-1-nonen-3-one (4a). ^{1}H NMR δ=0.88 (3H, t, J=6.8 Hz), 1.29—1.76 (8H, m), 2.11 (3H, s), 5.03 (1H, dd, J=4.4, 8.3 Hz), 6.65 (1H, s), 7.18—7.39 (10H, m); ^{13}C NMR δ=14.0 (d), 20.7 (q), 22.4 (t), 25.1 (t), 30.8 (t), 31.4 (t), 78.8 (d), 121.1 (d), 128.1 (d), 128.4 (d), 128.6 (d), 129.4 (d), 129.8 (d), 138.7 (s), 141.1 (s), 157.0 (s), 170.5 (s), 196.1 (s); IR 1735, 1695, 1585, 1240, 1070 cm^{-1}; MS m/z (%) 350 (M^+, 37), 290 (78), 77 (100). Found: C, 78.97; H, 7.48%. Calcd for $C_{23}H_{26}O_3$: C, 78.83; H, 7.48%.

3-Acetoxyl-1-cyclododecylidene-2-octanone (4c). ^{1}H NMR (60 MHz) δ=0.87 (3H, m), 1.17—1.93 (28H, m), 2.10 (3H, s), 2.20—3.07 (2H, m), 5.02 (1H, t, J=6.0 Hz), 6.20 (1H, s); IR 1750, 1700, 1620, 1240 cm^{-1}; MS m/z (%) 350 (M^+, 22), 308 (24), 290 (77), 207 (97), 143 (99), 42 (100). Found: C, 75.26; H, 11.14%. Calcd for $C_{22}H_{38}O_3$: C, 75.38; H, 10.93%.

1-Acetoxy-1,4,4-triphenyl-3-buten-2-one (4d).[15] ^{1}H NMR δ=2.15 (3H, t, J=6.8 Hz), 6.07 (1H, s), 6.58 (1H, s), 7.03—7.43 (15H, m+s (δ 7.40)); ^{13}C NMR δ=20.7 (q), 80.9 (d), 120.7 (d), 128.0 (d), 128.3 (d), 128.5 (d), 128.9 (d), 129.1 (d), 129.2 (d), 129.7 (d), 133.5 (s), 138.4 (s), 140.9 (s), 157.2 (s), 170.1 (s), 192.4 (s); IR (KBr) 1740, 1710, 1610, 1600, 1370, 1240 cm^{-1}; MS m/z (%) 356 (M^+, 6), 296 (33), 167 (74), 165 (100). Found: C, 80.86; H, 5.66%. Calcd for $C_{24}H_{20}O_3$: C, 80.88; H, 5.66%.

1-Acetoxy-4,4-bis(4-chlorophenyl)-1-phenyl-3-buten-2-one (4e). ^{1}H NMR δ=2.16 (3H, s), 6.07 (1H, s), 6.56 (1H, s), 6.95—7.14 (13H, m); IR 1740, 1700, 1560, 1490 cm^{-1}; MS m/z 364 (M^+−AcOH) with an isotopic pattern of dichlorine. Found: C, 67.50; H, 4.23; Cl, 16.46%. Calcd for $C_{24}H_{18}O_3Cl_2$: C, 67.78; H, 4.27; Cl, 16.67%.

3-Acetoxy-4,4-bis(4-chlorophenyl)-1-phenyl-3-buten-2-one (5e). ^{1}H NMR δ=2.11 (3H, s), 3.54 (2H, s), 6.92—7.41 (13H, m); IR 1760, 1700, 1590, 1490 cm^{-1}; MS m/z 364 (M^+−AcOH) with an isotopic pattern of dichlorine. Found: C, 68.00; H, 4.23; Cl, 16.83%. Calcd for $C_{24}H_{18}O_3Cl_2$: C, 67.78; H, 4.27; Cl, 16.67%.

1-Acetoxy-4-phenyl-3-peten-2-one (4f) and (4f'). Configuration of the olefin was determind by analysis of NOE data and chemical shifts of the olefin proton. ^{1}H NMR of **4f** δ=2.20 (3H, s), 2.59 (3H, d, J=1.5 Hz), 4.78 (2H, s), 6.46 (1H, d, J=1.0 Hz), 7.38—7.51 (5H, m); ^{1}H NMR of **4f'** δ=2.08 (3H, s), 2.22 (3H, d, J=1.5 Hz), 4.34 (2H, s), 6.15 (3H, d, J=1.5 Hz), 7.21—7.39 (5H, m); IR (KBr) 1740, 1700, 1600, 1240, 1060 cm^{-1}; MS m/z (%) 218 (M^+, 100). Found: C, 71.79; H,

6.47%. Calcd for $C_{13}H_{14}O_3$: C, 71.54; H, 6.47%.

1-Hydroxy-4,4-diphenyl-3-buten-2-one (7). ^{1}H NMR δ= 3.28 (1H, br s), 4.00 (2H, s), 6.67 (1H, s), 7.20—7.46 (10H, m); ^{13}C NMR δ=68.3, 121.7, 128.4, 128.5, 128.9, 129.0, 129.6, 130.1, 138.5, 140.1, 157.1, 199.0; IR 3450, 1690, 1650, 1500 cm^{-1}; MS *m/z* (%) 238 (M^+, 3), 220 (7), 208 (70), 179 (100). Found: C, 80.43; H, 5.85%. Calcd for $C_{16}H_{14}O_2$: C, 80.65; H, 5.92%.

1-Hydroxy-1,4,4-triphenyl-3-buten-2-on (8). ^{1}H NMR δ= 4.42 (1H, br s), 5.15 (1H, br s), 6.54 (1H, s), 7.04—7.49 (15H, m); IR 3500, 2950, 1690, 1600, 1500, 1380, 1060 cm^{-1}; MS *m/z* (%) 314 (M^+, 10), 209 (100), 167 (59). Found: C, 84.15; H, 6.00%. Calcd for $C_{22}H_{18}O_2$: C, 84.05; H, 5.77%.

Solvolysis of **4d** with NaOMe in Methanol (0.01 mol dm^{-3}) at room temperature also gave **8** (83% yield).

1,1,3-Triphenyl-2-propen-1-one (10).[12] ^{1}H NMR δ=7.11 (1H, s), 7.14—7.50 (13H, m), 7.88—7.93 (2H, m).

1,1-Diphenyl-1-octen-3-one (12). ^{1}H NMR δ=0.83 (3H, t, *J*=7.1 Hz), 1.06—1.29 (4H, m), 1.49 (2H, m), 2.22 (2H, t, *J*=7.6 Hz), 6.57 (1H, s), 7.16—7.42 (10H, m); IR 1690, 1660, 1590, 1570, 1440 cm^{-1}; MS *m/z* (%) 278 (M^+, 48), 207 (100). Found: C, 86.29; H, 8.21%. Calcd for $C_{20}H_{22}O$: C, 86.29; H, 7.97%.

1-(1-Heptynyl)cyclohexene (14).[16] ^{1}H NMR δ=0.90 (3H, t, *J*=7.1 Hz), 1.23—1.43 (4H, m), 1.47—1.68 (6H, m) , 2.02—2.14 (4H, m), 2.27 (2H, t, *J*=7.1 Hz), 6.00 (1H, m).

Transformation of Enatiomerically Enriched Alcohol 2d. According to the reported procedure,[17] **1d** was prepared from (*R*)-1-phenyl-2-propyn-1-ol (**19**) (90%ee) and benzophenone, and then converted into monoacetate **2d** (90% ee, 51% yield from **19**), which was transformed into **4d** by Method A. Enantiomeric excess (%) was estimated by the examination of Eu(hfc)$_3$ shifted ^{1}H NMR spectra of the acetates **2d** and **4d**.

Preparation of 3-Acetoxy-1,4,4-triphenyl-3-buten-2-one (5d). A typical procedure is as follows. A 1,2-dichloroethane (1.3 ml) solution of **2d** (99 mg, 0.28 mmol) was stirred at 0 °C in the presence of tin(IV) chloride (0.28 mmol) for 15 min under a nitrogen atmosphere. The reaction mixture was diluted with dichloromethane (15 ml) and washed with saturated aqueous sodium hydrogencarbonate (5 ml) and concentrated. Purification of the crude product by preparative TLC (hexane-ethyl acetate 3 : 1) afforded **5d** (53 mg, 53% yield). ^{1}H NMR δ=2.09 (3H, s), 3.48 (2H, s), 6.92—6.95 (2H, m), 7.14—7.44 (13H, m); ^{13}C NMR δ=20.5 (q), 48.0 (t), 126.9 (d), 128.3 (d), 128.4 (d), 128.9 (d), 129.1 (d), 129.5 (d), 129.6 (d), 130.0 (d), 130.6 (d), 134.2 (s), 138.1 (s), 139.4 (s), 170.2 (s), 197.7 (s); IR 1760, 1696 cm^{-1}; MS *m/z* (%) 355 (M^+, 6), 296 (33), 165 (100). Found: *m/z* 297.1221. Calcd for $C_{22}H_{17}O$: M–AcO, 297.1277.

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References

1) S. Swaminathan and K. V. Narayanan, *Chem. Rev.*, **71**, 429 (1971).
2) M. Edens, D. Boerner, C. R. Chase, D. Nass, and M. D. Schiavelli, *J. Org. Chem.*, **42**, 3403 (1977).
3) P. Chabardes, E. Kuntz, and J. Varagnat, *Tetrahedron*, **33**, 1775 (1977).
4) H. Pauling, D. A. Andrews, and N. C. Hindley, *Helv. Chim. Acta*, **59**, 1233 (1976).
5) K. Narasaka, H. Kusama, and Y. Hayashi, *Chem. Lett.*, **1991**, 1413.
6) Y. Shigemasa, M. Yasui, S. Ohrai, M. Sasaki, H. Sashiwa, and H. Saimoto, *J. Org. Chem.*, **56**, 910 (1991).
7) H. Saimoto, T. Hiyama, and H. Nozaki, *Bull. Chem. Soc. Jpn.*, **56**, 3078 (1983).
8) T. Wakamatsu, K. Hashimoto, M. Ogura, and Y. Ban, *Synth. Commun.*, **8**, 319 (1978).
9) U. Wannagat and W. Liehr, *Angew. Chem.*, **69**, 783 (1957).
10) H. Vorbrüggen and K. Krolikiewicz, *Angew. Chem., Int. Ed. Engl.*, **14**, 421 (1975).
11) M. Apparu and R. Glenat, *Bull. Soc. Chem. Fr.*, **1968**, 1106.
12) K. H. Meyer and K. Schuster, *Ber. Dtsch. Chem. Ges. B*, **55**, 819 (1922).
13) D. Reisdorf and H. Normant, *Organomet. Chem. Syn.*, **1**, 393 (1972); B. M. Trost and M. Lautens, *J. Am. Chem. Soc.*, **109**, 1469 (1987).
14) E. V. Dehmlow and A. R. Shamout, *Justus Liebigs Ann. Chem.*, **1982**, 1750.
15) T. Abe, T. Tsukihara, M. Yasui, H. Saimoto, and Y. Shigemasa, *Acta Crystallogr., Sect. C*, **45**, 1459 (1989).
16) B. M. Trost and S. J. Martin, *J. Am. Chem. Soc.*, **106**, 4263 (1984).
17) M. M. Midland, A. Tramontano, A. Kazubski, R. S. Graham, D. J. S. Tsai, and D. B. Cardin, *Tetrahedron*, **40**, 1371 (1984), and Ref. 6.