H), 7.40 (d, $J = 12$ Hz, 2 H), 7.10 (d, $J = 12$ Hz, 2 H); $^{13}$C NMR $\delta$ 171.2, 140.4, 123.1, 122.9; IR (KBr) 3210, 1610, 1605, 1550, 1480, 1450, 1410, 1340, 1250, 1200 cm$^{-1}$; MS, $m/e$ 200 (83), 202 (82) [[M]$^{\cdot+}$], 172 (79), 174 (75) [[M – CO]$^{\cdot+}$]; UV ($CHCl_3$) 247 (log $\epsilon$ = 4.2), 318 (infl), 328 (4.0), 366 (3.7), 385 (3.6) nm.

**4-Bromo-2-hydroxy-7-methoxycyclohepta-2,4,6-trien-1-one (20).** The crude reaction mixture obtained from oxidation of diol **10** was allowed to stir at ambient temperatures for 2 h before being worked up as described in the generalized procedure. Recrystallization (hexane/THF) of the crude solid thus obtained afforded tropolone **20** as yellow needles: mp 139–141 °C; $^1$H NMR $\delta$ 7.65 (d, $J = 1.8$ Hz, 1 H), 7.40 (dd $J = 11$ and 1.8 Hz, 1 H), 6.85 (d, $J = 11$ Hz, 1 H), 3.95 (br s, 4 H, $OCH_3$ and $OH$); $^{13}$C NMR $\delta$ 170.6, 159.9, 159.0, 128.8, 124.9, 121.9, 116.9, 56.6; IR (KBr) 3245, 1580, 1550, 1460, 1340, 1240, 1195 cm$^{-1}$; MS, $m/e$ 230 (65), 232 (62) [M]$^{\cdot+}$], 187 (40), 189 (39) [M – [$CH_3\dot{C}O$]$^+$], 51 (100) [$C_4H_3$]$^+$]; HRMS calcd $m/e$ for [M]$^{\cdot+}$ 229.9579, obsd 229.9559; UV ($CHCl_3$) 255 (log $\epsilon$ = 4.83), 320 (infl), 332 (4.15), 372 (4.21), 382 (4.22). Anal. Calcd for $C_8H_7BrO_3$: C, 41.59; H, 3.05; Br, 35.48. Found: C, 41.84; H, 3.20; Br, 34.60.

**2-Hydroxy-5α-cholest-1-en-3-one (21) and 3-Hydroxy-5α-cholest-3-en-2-one (22).**[42] Preparative TLC (silica gel, $CH_2Cl_2/Et_2O$, 95:5) of the crude reaction mixture obtained from oxidation of diol **11** afforded a major chromophoric band ($R_f$ 0.5), which on extraction ($CH_2Cl_2/Et_2O$) gave a white crystalline solid. $^{13}$C and $^1$H NMR analyses of this solid show it to consist of a ca. 2:1 mixture of **21** and **22**. The low-field region in the $^{13}$C NMR spectrum of this mixture was particularly diagnostic displaying two sets of three signals ($\delta$ 195.9, 146.2, 121.1; 195.6, 145.8, 127.2) due to the sp$^2$ hybridized carbons of each isomer. Recrystallization ($CH_3CO_2H$) afforded a ca. 9:1 mixture of **21** and **22** as off-white needles: mp 126–128 °C. $^1$H NMR $\delta$ 5.70 (m, 2 H, $OH$ and vinylic H), 2.60–0.80 (complex m, 36 H), 0.80 (s, 3 H), 0.65 (s, 3 H); $^{13}$C NMR (signals due to major isomer) $\delta$ 195.9, 146.2, 126.2, 56.2, 53.0, 50.3, 45.5, 42.7, 42.1, 39.7, 39.5, 36.2, 35.7, 34.6, 31.8, 28.2, 28.0, 27.2, 24.1, 23.9, 22.8, 22.6, 21.2, 18.7, 12.8, 12.1 (one peak obscured); IR (KBr) 3425, 1662 cm$^{-1}$; MS, $m/e$ 400 (43) [[M]$^{\cdot+}$], 43 (100); UV (hexane) 269 (log $\epsilon$ = 3.45) nm.

**Generalized Procedure for the Oxidation of Diols 2, 5, 6, 8, and 9 Using Oxalyl Chloride "Activated" Dimethyl Sulfoxide.** Dimethyl sulfoxide (108 μL, 2.54 mmol) was added to a stirred solution of oxalyl chloride (67 μL, 0.78 mmol) in $CH_2Cl_2$ (7 mL) maintained at ca. –60 °C (dry ice or liquid nitrogen/$CHCl_3$ bath). After 10 min, a solution of the appropriate diol (0.31 mmol) in $CH_2Cl_2$/dimethyl sulfoxide (1 mL of a 1:1 mixture) was added to the reaction mixture. After 15 min, the reaction mixture was treated with $Et_3N$ (0.44 mL, 3.14 mmol) and allowed to warm to ca. 5 °C and then poured into aqueous 2 M HCl (25 mL) and extracted with $CH_2Cl_2$ (2 × 15 mL). The combined organic extracts were washed with water (1 × 50 mL), dried ($MgSO_4$), filtered, and concentrated under reduced pressure to give the crude oxidation mixture.

Diones **13**, **16** and **18** were purified by the methods detailed under the TFAA/dimethyl sulfoxide oxidation procedure and proved identical in all respects with the materials obtained previously. The tabulated yields for compounds **15** and **19** were estimated by TLC and/or $^1$H NMR analysis of the crude oxidation mixture.

**Reaction of Trifluoroacetic Anhydride with Triethylamine in the Presence of Dimethyl Sulfoxide. Formation of 4-(Dimethylamino)-1,1,1-trifluorobut-3-en-2-one.**[32] TFAA (0.23 mL, 1.63 mmol) was added in a dropwise fashion to a stirred solution of dimethyl sulfoxide (0.5 mL, 0.7 mmol) in $CH_2Cl_2$ (8 mL) maintained at ca. –60 °C under an argon atmosphere. After 10 min at this temperature, the resulting solution was treated with $Et_3N$ (0.3 mL, 2.15 mmol), and stirring was continued at –60 °C for 1.5 h before the cooling bath was removed. When the reaction mixture had warmed to ca. 5 °C, it was quenched with aqueous 2 M HCl (20 mL) and extracted with $CH_2Cl_2$ (20 mL). The organic phase was dried ($MgSO_4$), filtered, and concentrated under reduced pressure to give a colorless oil. Preparative TLC (alumina, $CH_2Cl_2$) of this material afforded a single major chromophoric band ($R_f$ 0.55), which on extraction gave the title enamine (45 mg, 33%) as a colorless oil: $^1$H NMR $\delta$ 7.75 (d, $J = 12$ Hz, 1 H), 5.25 (d, $J = 12$ Hz, 1 H), 3.40 (q, $J = 7$ Hz, 2 H), 3.25 (q, $J = 7$ Hz, 2 H), 1.25 (t, $J = 7$ Hz, 3 H), 1.20 (t, $J = 7$ Hz, 3 H); $^{13}$C NMR $\delta$ 177.6 (q, $J_{^{19}F-^{13}C} = 26.5$ Hz), 154.8, 117.8 (q, $J_{^{19}F-^{13}C} = 218$ Hz), 87.8, 51.2, 43.4, 14.6, 11.5; MS, $m/e$ 195 (10) [[M]$^{\cdot+}$], 126 (100) [[M – $\cdot CF_3$]$^+$]; UV ($CH_3OH$) 311 (log $\epsilon$ = 4.33) nm.

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**Registry No.** **1**, 1119-87-5; **2**, 102064-72-2; **3**, 1460-57-7; **4**, 1792-81-0; **5**, 110045-36-8; **6**, 27607-33-6; **7**, 37163-97-6; **8**, 579-43-1; **9**, 102064-70-0; **10**, 110045-37-9; **10** (acetonide), 110045-45-9; **11**, 20312-09-8; **12**, 110045-38-0; **13**, 110045-39-1; **14**, 10316-66-2; **15**, 110045-40-4; **16**, 3008-37-5; **16** (quinoxaline derivative), 27430-86-0; **17**, 585-25-1; **18**, 134-81-6; **19**, 3172-00-7; **20**, 110076-79-4; **21**, 571-14-2; **22**, 571-13-1; **23**, 110045-41-5; **24**, 110045-42-6; **25**, 110045-44-8; (1α,6α)-8,8-dimethyl-7,9-dioxabicyclo[4.3.3]nona-2,4-diene, 80409-75-2; phenol, 108-95-2; (4aα,8aα)-9,9-dichloro-1,4,5,8-tetrahydro-4a,8a-methanonaphthalene, 39623-22-8; (1α,3β,4α,6α)-4,7,7-tribromobicyclo[4.1.0]heptan-3-ol, 6802-78-4; (1α,3β,4α,6α)-4,7,7-tribromobicyclo[4.1.0]heptan-3-ol, 110045-43-7; triethylamine, 121-44-8; 4-(diethylamino)-1,1,1-trifluorobut-3-en-2-one, 21045-62-5; dimethyl sulfoxide, 67-68-5; trifluoroacetic anhydride, 407-25-0; o-diaminobenzene, 95-54-5.

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# Selective Oxidation of Alcohol Function in Allylic Alcohols to α,β-Unsaturated Carbonyl Compounds Catalyzed by Zirconocene Complexes

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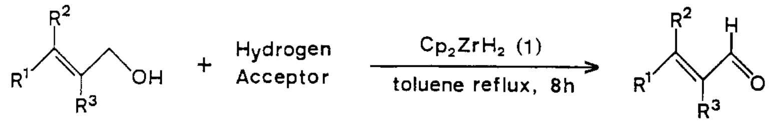
Bis($\eta^5$-cyclopentadienyl)zirconium(IV) complexes, $Cp_2ZrH_2$ (**1**) and $Cp_2Zr(O\text{-}i\text{-}Pr)_2$ (**4**), in the presence of an appropriate hydrogen acceptor such as benzaldehyde or cyclohexanone catalyze the Oppenauer-type oxidation of allylic alcohols to α,β-unsaturated carbonyl compounds. For instance, primary allylic terpenoid alcohols, geraniol and nerol, were oxidized to α- and β-citrals, which are essential compounds in the perfumery industry, in substantial yields without any treatment. Similarly, secondary allylic alcohols such as 3-hexen-2-ol and 2-cyclohexen-1-ol were also oxidized with ease to give 3-hexen-2-one and 2-cyclohexen-1-one in 93% and 89% yields, respectively. But the present OPP-type oxidation by zirconocene complexes is ineffective for propargylic alcohols.

The conversion of allylic alcohols to the corresponding α,β-unsaturated aldehydes or ketones plays an important role in synthetic organic chemistry. Although a variety of methods have been developed for this purpose, most of



(1)

**2a**: $R^1 = H, R^2 = H, R^3 = H$
**2b**: $R^1 = CH_3, R^2 = H, R^3 = H$
**2c**: $R^1 = (CH_2)_2CH_3, R^2 = H, R^3 = H$
**2d**: $R^1 = CH_3, R^2 = CH_3, R^3 = H$
**2e**: $R^1 = (CH_2)_2CH_3, R^2 = H, R^3 = CH_2CH_3$
**2f**: $R^1 = (CH_2)_6CH_3, R^2 = H, R^3 = (CH_2)_5CH_3$
**2g**: $R^1 = (CH_2)_2CH{=}C(CH_3)_2, R^2 = CH_3, R^3 = H$
**2h**: $R^1 = CH_3, R^2 = (CH_2)_2CH{=}C(CH_3)_2, R^3 = H$
**2i**: $R^1 = C_6H_5, R^2 = H, R^3 = H$

**3a**: $R^1 = H, R^2 = H, R^3 = H$
**3b**: $R^1 = CH_3, R^2 = H, R^3 = H$
**3c**: $R^1 = (CH_2)_2CH_3, R^2 = H, R^3 = H$
**3d**: $R^1 = CH_3, R^2 = CH_3, R^3 = H$
**3e**: $R^1 = (CH_2)_2CH_3, R^2 = H, R^3 = CH_2CH_3$
**3f**: $R^1 = (CH_2)_6CH_3, R^2 = H, R^3 = (CH_2)_5CH_3$
**3g**: $R^1 = (CH_2)_2CH{=}C(CH_3)_2, R^2 = CH_3, R^3 = H$
**3h**: $R^1 = CH_3, R^2 = (CH_2)_2CH{=}C(CH_3)_2, R^3 = H$
**3i**: $R^1 = C_6H_5, R^2 = H, R^3 = H$

these necessitate the use of a stoichiometric or excess amount of heavy metal reagents (e.g., Jones reagent,[1] activated manganese oxide,[2] nickel peroxide,[3] etc.) or expensive oxidants (e.g., $Me_3SiOOSiMe_3$,[4] etc.). However, the oxidation of allylic alcohols, especially primary ones, by such reagents frequently causes undesirable side reactions (i.e., formation of carboxylic acids,[5] esters,[5,6] and stereoisomers[7]). In recent years, some convenient methods affected by ruthenium[8] or palladium[9] complexes have appeared, but the oxidation methods, which show high selectivity for a wide variety of allylic alcohols, are scarcely published.

Previously, we have reported that bis($\eta^5$-cyclopentadienyl)zirconium(IV) dihydride, $Cp_2ZrH_2$ (**1**), catalyzes the hydrogen-transfer reaction from alcohols to carbonyl compounds;[10] Meerwein–Ponndorf–Verley (MPV) type reduction of carbonyl compounds and Oppenauer (OPP) type oxidation of alcohols simultaneously proceed under the influence of catalytic amount[11] of **1**. By the use of the above oxidation, primary alcoholic functions are preferentially converted to aldehydes even in the presence of secondary ones. Particularly, it is interesting to note that this method permits the chemoselective oxidation of primary hydroxy functions of diols involving both the primary and secondary hydroxy functions to give hydroxy aldehydes,[12] whose oxidations are difficult to accomplish by usual oxidation methods.

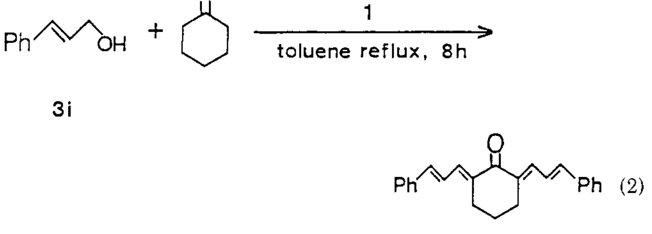
In this paper, we extend the scope of zirconocene-catalyzed OPP-type oxidation by studying the oxidation of a wide variety of allylic alcohols to the corresponding $\alpha,\beta$-unsaturated carbonyl compounds.

Table I shows the results for the zirconocene-catalyzed oxidation of various primary allylic alcohols **2** (eq 1) to $\alpha,\beta$-unsaturated aldehydes **3**.

The oxidation was successfully conducted by the use of a catalytic amount (0.02 equiv) of **1** in the presence of benzaldehyde as hydrogen acceptor in toluene.

Aliphatic allylic alcohols, 2-propen-1-ol (**2a**), *trans*-2-buten-1-ol (**2b**), and *trans*-2-hexen-1-ol (**2c**), were converted to propenal (**3a**), *trans*-2-butenal (**3b**), and *trans*-2-hexenal (**3c**), respectively, in good yields. Similarly, primary allylic alcohols **2d–f** which involve alkyl substituents in their skeletons were also oxidized with ease to the corresponding $\alpha,\beta$-unsaturated aldehydes **3d–f** in 90–95% yields (runs 4–6). The oxidation of a simple terpenoid allylic alcohol, geraniol (**2g**), proceeded with retention of the stereochemistry to form $\alpha$-citral (**3g**) almost quantitatively, but an alternative terpenoid allylic alcohol, nerol (**2h**) having cis configuration, was partly isomerized during the oxidation, giving an isomeric mixture of $\alpha$- and $\beta$-citrals (**3g** and **3h**) in a ratio of 13:87 at 95% conversion (run 8). When the same oxidation was carried out under refluxing benzene, NMR study showed that no isomerization of the double bond occurs to produce **3h** in 77% yield (run 9). The oxidation of cinnamyl alcohol (**2i**) produced cinnamaldehyde (**3i**) in theoretical yield (run 10). These oxidations were also catalyzed by bis($\eta^5$-cyclopentadienyl)zirconium diisopropoxide, $Cp_2Zr(O\text{-}i\text{-}Pr)_2$ (**4**), in good yields (runs 1–7 in Table I), since the zirconocene-catalyzed oxidations seem to proceed via alkoxy zirconium species. However, zirconium tetraisopropoxide, $Zr(O\text{-}i\text{-}Pr)_4$ (**5**), was found to be insufficient as catalyst; the oxidation of **2g** by **5** took place with difficulty to give **3g** in poor yield (21%).

In these oxidations, the carbonyl compounds having an $\alpha$-hydrogen such as acetone or cycloalkanones were inadequate as hydrogen acceptors owing to the formation of aldol condensates between the resulting aldehydes **3** and the starting carbonyl compounds.[13] For instance, the oxidation of **2i** in the presence of cyclohexanone in place of benzaldehyde which permits the selective oxidation to **3i** gave mainly cross-aldol condensate, 2,6-dicinnamylidenecyclohexanone (68%) (eq 2).



3i

(2)

68% Yield

All the secondary allylic alcohols **6** examined were oxidized to the corresponding $\alpha,\beta$-unsaturated ketones **7** in

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(11) Conventional MPV reduction or OPP oxidation by using aluminum alkoxide calls for the use of a stoichiometric or excess amount of reagent to complete the reaction. Furthermore, the resulting aluminum derivatives must be hydrolyzed with acid to generate the products.[21]

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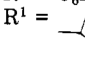
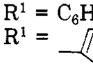
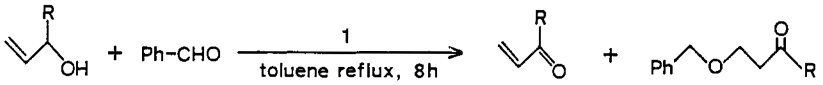
(3)

**6**: $R^1$ = H, $R^2$ = H, $R^3$ = $CH_3$
**6b**: $R^1$ = H, $R^2$ = H, $R^3$ = $(CH_2)_2CH_3$
**6c**: $R^1$ = H, $R^2$ = H, $R^3$ = $(CH_2)_4CH_3$
**6d**: $R^1$ = $CH_3$, $R^2$ = H, $R^3$ = $CH_3$
**6e**: $R^1$ = $CH_3$, $R^2$ = $CH_3$, $R^3$ = $CH_3$
**6f**: $R^1$ = H, $R^2$,$R^3$ = $\{CH_2\}_3$
**6g**: $R^1$ = $CH_3$, $R^2$,$R^3$ = $-CH_2C(CH_3)_2CH_2-$
**6h**: $R^1$,$R^2$,$R^3$ = $\{CH_2)_4-C(CH_3)\{CH_2\}_3$
**6i**: $R^1$ = $C_6H_5$, $R^2$ = H, $R^3$ = $CH_3$
**6j**: $R^1$ = , $R^2$ = H, $R^3$ = $CH_3$

**7a**: $R^1$ = H, $R^2$ = H, $R^3$ = $CH_3$
**7b**: $R^1$ = H, $R^2$ = H, $R^3$ = $(CH_2)_2CH_3$
**7c**: $R^1$ = H, $R^2$ = H, $R^3$ = $(CH_2)_4CH_3$
**7d**: $R^1$ = $CH_3$, $R^2$ = H, $R^3$ = $CH_3$
**7e**: $R^1$ = $CH_3$, $R^2$ = $CH_3$, $R^3$ = $CH_3$
**7f**: $R^1$ = H, $R^2$,$R^3$ = $\{CH_2\}_3$
**7g**: $R^1$ = $CH_3$, $R^2$,$R^3$ = $-CH_2C(CH_3)_2CH_2-$
**7h**: $R^1$,$R^2$,$R^3$ = $\{CH_2)_4-C(CH_3)\{CH_2\}_3$
**7i**: $R^1$ = $C_6H_5$, $R^2$ = H, $R^3$ = $CH_3$
**7j**: $R^1$ = , $R^2$ = H, $R^3$ = $CH_3$



(4)

**6a**: R = $CH_3$
**6b**: R = $(CH_2)_2CH_3$
**6c**: R = $(CH_2)_4CH_3$

**7a**: R = $CH_3$
**7b**: R = $(CH_2)_2CH_3$
**7c**: R = $(CH_2)_4CH_3$

**8a**: R = $CH_3$
**8b**: R = $(CH_2)_2CH_3$
**8c**: R = $(CH_2)_4CH_3$

**Table I. $Cp_2ZrH_2$ (1) or $Cp_2Zr(O\text{-}i\text{-}Pr)_2$ (4) Catalyzed Oxidation of Various Primary Allylic Alcohols 2**[a]

| run | allylic alcohol | product | yield (%)[b] |
|---|---|---|---|
| 1 | **2a** | **3a** | 75 (77) |
| 2 | **2b** | **3b** | 92 (91) |
| 3 | **2c** | **3c** | 93 (90) |
| 4 | **2d** | **3d** | 93 (93) |
| 5 | **2e** | **3e** | 90 (93) |
| 6 | **2f** | **3f** | 93 (94) |
| 7 | **2g** | **3g** | 95 (95) |
| 8 | **2h** | **3g** + **3h** | 12 + 83 |
| 9[c] | | **3h** | 77 |
| 10 | **2i** | **3i** | 95 (95) |

[a] A mixture of **2** (20 mmol), benzaldehyde (40 mmol), and **1** (0.4 mmol) was heated with stirring in refluxing toluene for 8 h. [b] Isolated yields. Numbers in parentheses are the isolated yields when **4** (0.4 mmol) was used as catalyst. [c] In refluxing benzene.

**Table II. $Cp_2ZrH_2$ (1) or $Cp_2Zr(O\text{-}i\text{-}Pr)_2$ (4) Catalyzed Oxidation of Various Secondary Allylic Alcohols 6**[a]

| run | allylic alcohol | hydrogen acceptor[b] | product | yield (%)[c] |
|---|---|---|---|---|
| 1 | **6a** | B.P. | **7a** | 80 (78) |
| 2 | | B.A. | | 59 |
| 3 | **6b** | B.P. | **7b** | 82 (80) |
| 4 | **6c** | B.P. | **7c** | 89 (91) |
| 5 | **6d** | B.A. | **7d** | 87 (90) |
| 6 | **6e** | B.A. | **7e** | 85 (86) |
| 7 | **6f** | B.A. | **7f** | 89 (90) |
| 8 | **6g** | B.A. | **7g** | 83 (81) |
| 9 | **6h** | B.A. | **7h** | 83 |
| 10 | **6i** | B.A. | **7i** | 84 (83) |
| 11 | **6j** | B.A. | **7j** | 90 (88) |

[a] A mixture of **6** (20 mmol), hydrogen acceptor (40 mmol), and **1** (0.4 mmol) was heated with stirring in refluxing toluene for 8 h. [b] B.A.= benzaldehyde, B.P.= benzophenone. [c] Isolated yields. Numbers in parentheses are the isolated yields when **4** (0.4 mmol) was used as catalyst.

satisfactory yields by selecting hydrogen acceptors (eq 3 and Table II).

For instance, secondary allylic alcohols **6a–c** which involve a terminal double bond in their molecules could be oxidized to the corresponding *α*,*β*-unsaturated ketones **7a–c** in 80–89% yields in the presence of cyclohexanone as hydrogen acceptor (runs 1, 3, and 4). Contrary to the oxidation of primary allylic alcohols where benzaldehyde acts as the suitable hydrogen acceptor, in the above oxidations benzaldehyde was less efficient because of formation of undesirable benzyloxy ketones **8a–c**. Thus, **6a** was allowed to react in the presence of benzaldehyde to form **7a** (59%) and a considerable amount of **8a** (33%) (eq 4). The formation of **8a** may be attributed to a subsequent Michael-type addition of the resulting benzyl alcohol to **6a**, since this type of addition takes easily place under acidic or basic conditions.[14] In fact, **7a** was treated in benzyl alcohol under the influence of **1** to form **8a** in 79% yield.

Typical secondary allylic alcohols, *trans*-3-penten-2-ol (**6d**) and *trans*-4-methyl-3-penten-2-ol (**6e**), were easily oxidized without formation of a Michael-type adduct even by the use of benzaldehyde, giving *trans*-3-penten-2-one (**7d**) and mesityl oxide (**7e**) in 87% and 85% yields, respectively. Cyclic allylic alcohols, 2-cyclohexen-1-ol (**6f**) and isophorol (**6g**), were also converted to the corresponding cyclic enones (**7f** and **7g**) in satisfactory yields (runs 7 and 8). Similarly, 10-methyl-$\Delta^{1(9)}$-octalin-2-ol (**6h**) having a steroidal framework was oxidized to 10-methyl-$\Delta^{1(9)}$-octalin-2-one (**7h**) (83%) (run 9). Furthermore, the oxidation of the *α*,*β*-unsaturated alcohols **6i** and **6j** substituted with aromatic groups proceeded smoothly to give the expected enones (**7i** and **7j**) in good yields (runs 10 and 11).

Although the potential of this method for propargylic alcohols (e.g., 2-propyn-1-ol and 1-hexyn-3-ol) was examined, no oxidation product was formed to give the starting alcohols almost quantitatively. Schwartz[15] has reported that a zirconocene complex such as $Cp_2Zr(H)Cl$ reacts readily with alkynyl compounds to give alkenyl zirconium complexes. Therefore, it is probable that the oxidation of the propargylic alcohols is prevented owing to the formation of stable zirconium species by complexation of $Cp_2ZrH_2$ with propargylic alcohols in the reaction system.

In conclusion, the present oxidation possesses several advantages over the conventional methods: (i) the oxidation is completed with only catalytic amounts of $Cp_2ZrH_2$ or $Cp_2Zr(O\text{-}i\text{-}Pr)_2$ without the production of peroxidated or cleaved products by using strong oxidants;[5,6] (II) zirconocene complexes used here are easy to prepare

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and handle in the air; (iii) no special treatment is necessitated to isolate products;[1,4,7] and (iv) the oxidation proceeds with retention of the stereochemistry (e.g., nerol was oxidized to $\beta$-citral in 73% yield without isomerization to $\alpha$-citral as shown in Table I, run 9). Thus, the zirconocene-catalyzed oxidation is a very useful synthetic tool for the selective oxidation of a wide variety of allylic alcohols to $\alpha,\beta$-unsaturated carbonyl compounds.

## Experimental Section

The melting points were determined on a Yanaco-MP52032 apparatus and are corrected. The IR spectra were taken with a JASCO A202 spectrometer and the $^1$H and $^{13}$C NMR spectra were recorded on JEOL PMX-60 and Hitachi R-90H spectrometers with tetramethylsilane as an internal standard, respectively. The GLC analyses were performed on a Yanaco G-1800 instrument with a 3 m × 2.5 mm column packed with 5% Silicon OV-7 on Chromosorb W.

Compounds were commercial grade, and solvents were used after dehydration by conventional methods.

**Zirconium Complexes.** $Cp_2ZrH_2$ (**1**) and $Cp_2Zr(O\text{-}i\text{-}Pr)_2$ (**4**) were prepared by a procedure similar to those described by Wailes.[16] $Zr(O\text{-}i\text{-}Pr)_4$ (**5**) was derived from the reaction of $ZrCl_4$ with an excess amount of $Na(O\text{-}i\text{-}Pr)$.

**1**: mp 304–305 °C (lit.[16] mp 305 °C); IR (KBr) 3100, 1520, 1300, 1020, 840 cm$^{-1}$; $^1$H NMR ($C_6D_6/Me_4Si$) $\delta$ 6.58–6.39 (m, 10 H); $^{13}$C NMR ($C_6D_6/Me_4Si$) 108.2 (s) ppm.

**2**: IR (KBr) 3100, 1015, 840, 770 cm$^{-1}$; $^1$H NMR ($C_6D_6/Me_4Si$) $\delta$ 6.22 (m, 10 H), 2.2–1.4 (m, 14 H); $^{13}$C NMR ($C_6D_6/Me_4Si$) 113.3 (s), 66.6 (d), 25.3 (q) ppm.

**5**: IR (KBr) 3100, 2950, 760 cm$^{-1}$; $^1$H NMR ($C_6D_6/Me_4Si$) $\delta$ 2.3–1.2 (m, 28 H); $^{13}$C NMR ($C_6D_6/Me_4Si$) 68.1 (d), 22.6 (q) ppm.

**Allylic Alcohols 2 and 6.** Commercially available allylic alcohols **2a–d**, and **6a–g,i** were used directly without any treatment. The other allylic alcohols were prepared according to the general methods. *trans*-2-Ethyl-2-hexen-1-ol (**2e**) and *trans*-2-hexyl-2-decen-1-ol (**2f**) were prepared by hydrogenation with $LiAlH_4$ of the corresponding enones derived from aldol condensations of butanal and octanal, respectively. 4-(2-Furyl)-3-buten-2-ol (**6j**) was prepared by hydrogenation of the enone derived from aldol condensation of furfural with acetone. 10-Methyl-$\Delta^{1(9)}$-octalin-2-ol (**6h**) was prepared by reduction of 10-methyl-$\Delta^{1(9)}$-octalin-2-one (**7h**) with $NaBH_4$ in ether.

**2e**: MS, [M$^+$] *m/e* 128; IR (NaCl) 3350, 3000, 2900, 1450, 1400–1200, 1100–930, 890 cm$^{-1}$; $^1$H NMR ($Me_4Si/CDCl_3$) $\delta$ 5.2 (t, 1 H), 2.7–1.4 (m, 8 H), 2.2 (s, 1 H), 1.3 (t, 3 H), 1.1 (t, 3 H); $^{13}$C NMR ($Me_4Si/CDCl_3$) 137.7 (s), 122.4 (d), 57.5 (t), 35.9 (t), 27.7 (t), 22.1 (t), 17.2 (q), 13.7 (q) ppm.

**2f**: MS, [M$^+$] *m/e* 240; IR (NaCl) 3350, 3000, 2900, 1450, 1400–1170, 1120–920, 880 cm$^{-1}$; $^1$H NMR ($Me_4Si/CDCL_3$) $\delta$ 5.3 (t, 1 H), 2.7–1.2 (m, 24 H), 2.5 (s, 1 H), 1.1 (t, 3 H), 1.0 (t, 3 H); $^{13}$C NMR ($Me_4Si/CDCl_3$) 139.1 (s), 122.2 (d), 55.1 (d), 38.0 (t), 29.1 (t), 27.2 (t), 26.0 (t), 25.3 (t), 25.1 (t), 24.7 (t), 23.3 (t), 22.5 (t), 21.9 (t), 20.8 (t), 14.3 (q), 13.9 (q) ppm.

**6h**: MS, [M$^+$] *m/e* 166; IR (NaCl) 3350, 2950, 2900, 1470–1100, 1020, 900, 860, 820 cm$^{-1}$; $^1$H NMR ($Me_4Si/CDCl_3$) 5.5 (s, 1 H), 2.5–1.7 (m, 13 H), 2.4 (s, 1 H), 1.1 (s, 3 H); $^{13}$C NMR ($Me_4Si/CDCl_3$) $\delta$ 140.3 (s), 123.6 (d), 60.0 (d), 50.6 (s), 41.1 (t), 32.6 (t), 30.3 (t), 28.0 (t), 26.0 (t), 25.3 (t), 22.2 (q) ppm.

**6j**: MS, [M$^+$] *m/e* 138; IR (NaCl) 3350, 3030, 2850, 2800, 1480, 1440, 1260, 1170–900, 770 cm$^{-1}$; $^1$H NMR ($Me_4Si/CDCl_3$) $\delta$ 7.3 (d, 1 H), 7.2 (d, 1 H), 6.9 (d, 1 H), 6.2 (d, 1 H), 5.6 (m, 1 H), 4.1 (m, 1 H), 2.3 (s, 1 H), 2.0 (d, 3 H); $^{13}$C NMR ($Me_4Si/CDCl_3$) 149.7 (s), 142.1 (d), 129.4 (d), 120.1 (d), 115.3 (d), 111.9 (d), 67.6 (d), 22.3 (q) ppm.

**General Method for Oxidation of Allylic Alcohols 2 and 6. Catalyzed by $Cp_2ZrH_2$ (1) and $Cp_2Zr(O\text{-}i\text{-}Pr)_2$ (4).** A mixture of **2** or **6** (20 mmol) and benzaldehyde (40 mmol) in dry toluene (30 mL) was allowed to react in the presence of a catalytic amount of **1** (0.4 mmol) or **4** (0.4 mmol) under a nitrogen stream at 110 °C. After the reaction, the catalyst was removed by centrifugation or filtration. The solutions were distilled under reduced pressure and then the products were isolated by MPLC on silica gel (hexane/ethyl acetate = 2–10:1 eluent). Spectral data were compared with those of authentic samples and literature values;[1e,17–20] propenal (**3a**), *trans*-2-butenal (**3b**), $\alpha$-citral (**3g**), $\beta$-citral (**3h**), cinnamaldehyde (**3i**), 1-buten-3-one (**7a**), 1-hexen-3-one (**7b**), 1-octen-3-one (**7c**), 4-methyl-3-penten-2-one (**7d**), 2-cyclohexen-1-one (**7g**), isophorone (**7h**), and 4-phenyl-3-buten-2-one (**7i**). The analytical data of the new compounds are as follows.

***trans*-2-Hexyl-2-decenal (3f)**: MS, [M$^+$] *m/e* 238; IR (NaCl) 2970, 2900, 1760, 1700, 1640, 1470, 1380, 1260, 1180, 1090, 910, 870, 750 cm$^{-1}$; $^1$H NMR ($Me_4Si/CDCl_3$) $\delta$ 9.5 (d, 1 H), 6.2 (t, 1 H), 2.9–1.5 (m, 22 H), 1.0 (t, 3 H), 0.9 (t, 3 H); $^{13}$C NMR ($Me_4Si/CDCl_3$) 193.5 (d), 153.5 (d), 142.8 (s), 44.4 (t), 31.7 (d), 29.3 (t), 29.0 (t), 28.8 (t), 28.6 (t), 28.2 (t), 26.3 (t), 22.8 (t), 22.6 (t), 20.7 (t), 13.9 (q), 13.7 (q) ppm.

**10-Methyl-$\Delta^{1(9)}$-octalin-2-one (7h)**: MS, [M$^+$] *m/e* 164; IR (NaCl) 2950, 2850, 1720, 1660, 1640, 1470–1100, 1020, 900, 860, 820 cm$^{-1}$; $^1$H NMR ($Me_4Si/CDCl_3$) $\delta$ 5.7 (s, 1 H), 2.2–1.7 (m, 12 H), 1.1 (s, 3 H); $^{13}$C NMR ($Me_4Si/CDCl_3$) 199.1 (s), 159.5 (d), 125.6 (s), 51.8 (s), 42.3 (t), 33.2 (t), 30.1 (t), 28.8 (t), 27.2 (t), 25.1 (t), 24.0 (q) ppm.

***trans*-4-(2-Furyl)-3-buten-2-one (7j)**: MS, [M$^+$] *m/e* 136; IR (NaCl) 3050, 2850, 1700, 1620, 1450, 1400, 1350, 1280–1100, 1050–800 cm$^{-1}$; $^1$H NMR ($Me_4Si/CDCl_3$) $\delta$ 7.4 (d, 1 H), 7.0 (d, 1 H), 6.6 (d, 1 H), 6.5 (d, 1 H), 6.4–6.2 (m, 1 H), 2.3 (s, 3 H); $^{13}$C NMR ($Me_4Si/CDCl_3$) 197.5 (s), 150.7 (s), 144.9 (d), 129.3 (d), 124.2 (d), 115.5 (d), 113.7 (d), 27.7 (q) ppm.

**Oxidation of Cinnamyl Alcohol (2i) with Cyclohexanone Catalyzed by $Cp_2ZrH_2$ (1).** A mixture of **2i** (20 mmol) and cyclohexanone (40 mmol) in dry toluene (30 mL) was allowed to react in the presence of **1** (0.4 mmol) under a nitrogen stream at 110 °C for 8 h. After removal of the catalyst by filtration, cinnamaldehyde (**3i**) was isolated by distillation in vacuo. The residue was cooled overnight in a refrigerator, and then 2,6-dicinnamylidenecyclohexanone was deposited as a bright brown crystalline solid in 68% yield.

**2,6-Dicinnamylidenecyclohexanone**: MS, [M$^+$] *m/e* 316; IR (KBr) 3050, 2900, 1690, 1620–1600, 1440, 1250, 1180 cm$^{-1}$; $^1$H NMR ($Me_4Si/CDCl_3$) $\delta$ 7.7–6.6 (m, 16 H), 3.3–2.2 (m, 6 H); $^{13}$C NMR ($Me_4Si/CDCl_3$) 188.7 (s), 152.6 (s), 144.3 (s), 132.9 (d), 123.3 (d), 123.1 (d), 116.1 (d), 115.8 (d), 112.1 (d), 27.9 (t), 21.6 (t) ppm.

**Oxidation of 1-Buten-3-ol (6a) with Benzaldehyde Catalyzed by $Cp_2ZrH_2$ (1).** A mixture of **6a** (20 mmol) and benzaldehyde (40 mmol) in dry toluene (30 mL) was allowed to react in the presence of **1** (0.4 mmol) under a nitrogen stream at 110 °C for 8 h. After the reaction, the catalyst was removed by filtration. 1-Buten-3-one (**7a**) was isolated by distillation under reduced pressure and then 4-(benzyoxy)-2-butanone (**8a**) was separated from the residue by MPLC on silica gel (hexane/ethyl acetate = 10:1 eluent) in 59% yield.

**8a**: MS, [M$^+$] *m/e* 178; IR (KBr) 2900, 1720, 1360, 1110, 920, 770, 680 cm$^{-1}$; $^1$H NMR ($Me_4Si/CDCl_3$) $\delta$ 7.7–7.2 (m, 5 H), 2.7 (s, 2 H), 2.4 (t, 2 H), 1.5 (t, 2 H), 1.4 (s, 3 H); $^{13}$C NMR ($Me_4Si/CDCl_3$) 209.6 (s), 127.1 (s), 124.5 (d), 123.7 (d), 121.1 (d), 72.4 (t), 66.2 (t), 32.9 (t), 21.3 (q) ppm.

**Oxidation of Geraniol (2g) Catalyzed by $Zr(O\text{-}i\text{-}Pr)_4$ (5).** A mixture of **2g** (20 mmol) and benzaldehyde (40 mmol) in dry toluene (30 mL) was allowed to react in the presence of **5** (0.4 mmol) under a nitrogen stream at 110 °C for 8 h. After the reaction, the catalyst was removed by filtration. $\alpha$-Citral (**3g**) was isolated and purified by a similar manner as above.

**Registry No.** **1**, 37342-98-6; **2a**, 107-18-6; **2b**, 504-61-0; **2c**, 928-95-0; **2d**, 556-82-1; **2e**, 38384-38-2; **2f**, 74612-63-8; **2g**, 106-24-1; **2h**, 106-25-2; **2i**, 4407-36-7; **3a**, 107-02-8; **3b**, 123-73-9; **3c**, 6728-26-3; **3d**, 107-86-8; **3e**, 64344-45-2; **3f**, 64935-39-3; **3g**, 141-27-5; **3h**,

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106-26-3; **3i**, 14371-10-9; **4**, 78091-18-6; **5**, 2171-98-4; **6a**, 598-32-3; **6b**, 4798-44-1; **6c**, 3391-86-4; **6d**, 3899-34-1; **6e**, 4325-82-0; **6f**, 822-67-3; **6g**, 470-99-5; **6h**, 26675-10-5; **6i**, 36004-04-3; **6j**, 79380-04-4; **7a**, 78-94-4; **7b**, 1629-60-3; **7c**, 4312-99-6; **7d**, 3102-33-8; **7e**, 141-79-7; **7f**, 930-68-7; **7g**, 78-59-1; **7h**, 826-56-2; **7i**, 1896-62-4; **7j**, 41438-24-8; **8a**, 6278-91-7; $ZrCl_4$, 10026-11-6; Na(O-*i*-Pr), 683-60-3; butanal, 123-72-8; octanal, 124-13-0; furfural, 98-01-1; acetone, 67-64-1; benzaldehyde, 100-52-7; cyclohexanone, 108-94-1; benzophenone, 119-61-9; 2,6-dicinnamylidenecyclohexanone, 18977-40-7.

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# Palladium(II) Chloride Catalyzed Carbonylation of Organic Tellurides with Carbon Monoxide

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Various organic tellurides react with carbon monoxide (1 atm) at room temperature in methanol in the presence of $PdCl_2$ and $Et_3N$ to afford the corresponding methyl carboxylates in good to excellent yields. The reaction is catalytic in $PdCl_2$ when a suitable reoxidant such as $CuCl_2$, $CuCl/O_2$, $FeCl_3$, or $Ce(NH_4)_2(NO_3)_6$ is present. The combination of this carbonylation with phenyltellurenylation of arylacetylenes and propargylic alcohols makes it possible to prepare ring-substituted *cis*-methyl cinnamates and $\Delta^{\alpha,\beta}$-butenolides, respectively. Both monomeric and dimeric palladium complexes, $(Ph_2Te)_2PdCl_2$ and $[(Ph_2Te)PdCl_2]_2$, react readily with CO to give a high yield of methyl benzoate. The key step of the present carbonylation is proposed to be the migration of an organic moiety from Te to Pd (transmetalation) in organic telluride–$PdCl_2$ complexes, presumably formed in situ, to afford organopalladium compounds.

We previously reported that some organotellurium (II or IV) compounds reacted with carbon monoxide (CO) in various organic solvents to give the corresponding carboxylic acids in moderate to quantitative yields in the presence of $PdCl_2$, $PdCl_2/LiCl$, or $Pd(OAc)_2$.[1,2] This was a characteristic reaction of tellurium among the group 16 elements, since the corresponding organosulfur and -selenium compounds scarcely afforded the carbonylation products under similar conditions. In this carbonylation, however, there were several disadvantages as follows: (1) a stoichiometric amount of Pd(II) salt was necessary; (2) after the reaction, an alkaline hydrolysis was needed to obtain the expected acid, and a generally known methoxycarbonylation giving directly its methyl ester occurred only partly even in methanol as the solvent; (3) the kind of organotellurium substrates that can be carbonylated was limited. We attempted to improve this reaction and eventually found that methoxycarbonylation occurs readily for a wide range of organic tellurides under 1 atm CO in methanol when triethylamine was added as a base to the reaction system and the reaction is catalytic in $PdCl_2$ in the presence of a suitable reoxidant. We could prepare *cis*-cinnamates and butenolides from the appropriate acetylenes by the following transformation, and the method may be of interest since the formal addition of PhTeH to acetylenes is facile and highly regio- and stereoselective.[3] The details of the results are herein reported.

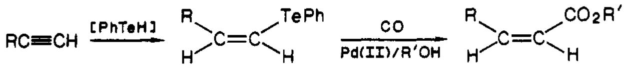

**Table I. Carbonylation of Organotellurium Compounds**[a]

| Te compound | Pd(II)/ additive[b] | product, % yield[c] | |
|---|---|---|---|
| **1a** | A | **2a**, 96 | **3**, 30 |
| **1a** | B | **2a**, 44[d] | **3**, 6[d] |
| **1a** | C | **2a**, 28[e] | **3**, 4[e] |
| **1a** | D | **2a**, 48 | **3**, 24 |
| **1b** | A | **2b**, 71 | **3**, 24 |
| **1c** | A | **2c**, 72 | **3**, 32 |
| **1d** | A | **2d**, 67 | **3**, 17 |
| **1f** | A | **3**, 92 | |
| **1f** | E | **3**, 96 | |
| $(4\text{-}MeOC_6H_4)_2Te$ | A | **2**,[f] 99 | |
| $(4\text{-}MeOC_6H_4)_2TeCl_2$ | A | **2**,[f] 18 | |
| **1g** | E | **2g**, 22[g] | **3**, 98[g] |
| **5a** | A | **6a**, 22[h] | **3'**,[i] 8 |
| **5b** | A | **6b**, 51[h] | **3'**, 3 |
| **5c** | A | **6c**, 43[h] | **3'**, 21 |
| **5d** | A | **6d**, 0 | **3'**, 25 |
| **5e** | A | **6e**, tr | **3'**, 24 |

[a] Carried out with organotellurium compound (1 mmol) and 1 atm CO in MeOH (10 mL) at 25 °C for 5 h to obtain **2** or in $CH_2Cl_2$ (10 mL) at 5–10 °C for 20 h to obtain **6**. [b] Key: A, $PdCl_2$ (1 mmol)/$Et_3N$ (2 mmol); B, $PdCl_2$ (1 mmol)/NaOAc (2 mmol); C, $PdCl_2$ (1 mmol); D, $Pd(OAc)_2$ (1 mmol)/$Et_3N$ (2 mmol); E, $PdCl_2$ (2 mmol)/$Et_3N$ (4 mmol). [c] GLC yield based on Pd(II) salt. [d] Other products: cinnamic acid (46%, $Z/E$ = 97/3) and benzoic acid (11%). [e] Other products: cinnamic acid (44%, $Z/E$ = 100/0) and benzoic acid (8%). [f] R = $4\text{-}MeOC_6H_4$. [g] The yield is based on **1**; other product, 1-dodecene (37%). [h] Isolated yield based on Pd(II) salt. [i] **3'** = $PhCO_2H$.

## Results and Discussion

On treatment of (*Z*)-styryl phenyl telluride (**1a**) with atmospheric pressure of CO and a stoichiometric amount of $PdCl_2$ in methanol in the presence of triethylamine at 25 °C for 5 h, (*Z*)-methyl cinnamate (**2a**) and methyl benzoate (**3**) were obtained in 96% and 30% yields, respectively (eq 1). When sodium acetate was used as a base in place of triethylamine, about half of the products was obtained in acid form (*cis*-cinnamic acid and benzoic acid). In the absence of base the product yield was slightly lower, and the product was mainly obtained as the acid form. The reaction using $Pd(OAc)_2$ and triethylamine gave products completely as methyl esters, but their yields were

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