3′-[(Methoxymethyl)oxy]-2,2-dimethylpropionanilide (7). To a mixture of sodium hydride (0.419 g, 17.46 mmol) and 50 mL of dry THF under nitrogen at 0 °C was added phenol **6** (3.067 g, 15.89 mmol). After stirring at 0 °C for 3 h, chloromethyl methyl ether (1.35 mL, 17.78 mmol) was added, and the reaction was allowed to come to room temperature overnight. The solution containing precipitated NaCl was diluted with ether, washed (5% aqueous NaOH, water, brine), and dried (Na_2SO_4), and the solvent was removed at aspirator pressure. Crystallization of the residue (dichloromethane–hexane) yielded 3.092 g (82.1%) of **7** as colorless needles: mp 70–71 °C; IR ($CHCl_3$) 3470, 2960, 1680, 1600, 1520, 1480, 1420, 1140, 1060, 990 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 1.30 (s, 9 H), 3.47 (s, 3 H), 5.16 (s, 2 H), 6.76 (m, 1 H), 7.23 (m, 3 H); ^{13}C NMR (20 MHz, $CDCl_3$) 27.4, 39.5, 55.8, 94.3, 108.1, 112.0, 113.4, 129.5, 139.2, 157.6, 176.5 ppm; MS (70 eV), *m/z* (relative intensity) 237 (M$^+$, 87), 205 (11), 153 (13), 121 (18), 61 (17), 57 (97), 45 (100); UV (MeOH) 209 nm (ε 30 283), 243 (ε 11 465). Anal. Calcd for $C_{13}H_{19}NO_3$: C, 65.82; H, 8.02; N, 5.91. Found: C, 65.82; H, 8.20; N, 5.74.

2′-Carboxy-3′-hydroxy-2,2-dimethylpropionanilide (8). To a solution of **7** (1.519 g, 6.41 mmol) in 75 mL of dry THF at 0 °C under nitrogen was added dropwise 5.3 mL (2.6 M in hexane, 13.8 mmol) of *n*-butyllithium. After the mixture was stirred for 2 h, carbon dioxide was bubbled continuously through the mixture for an additional 2 h. The resulting yellow solution was diluted with ethyl acetate and extracted with two portions of 5% aqueous NaOH. The aqueous layers were combined, acidified to pH 1 (HCl), and extracted twice with ethyl acetate. Combining the organic extracts, washing (H_2O and brine), drying (Na_2SO_4), and concentrating in vacuo gave 1.478 g (97.3%) of **8** as a synthetically pure red-brown oil which crystallized slowly upon standing. A small sample was subjected to preparative TLC on silica gel (10% methanol–ethyl acetate) to afford a clear oil (R_f 0.28–0.41). Crystallization (dichloromethane–hexane) gave colorless crystals: mp 208–209 °C dec; IR (Nujol) 3650–2600, 1675, 1590, 1540, 1290, 1240, 1160, 910 cm^{-1}; ^{1}H NMR ($(CD_3)_2CO$) δ 1.25 (s, 9 H), 6.45 (dd, 1 H, *J* = 8.2 and 1.2 Hz), 7.09 (t, 1 H, *J* = 8.2 Hz), 8.13 (dd, 1 H, *J* = 8.2 and 1.2 Hz), 10.03 (br s, 2 H), 12.88 (s, 1 H); ^{13}C NMR (20 MHz, $(CD_3)_2CO$) 28.1, 40.7, 106.9, 109.4, 111.3, 132.2, 143.6, 164.3, 177.1, 177.6 ppm; MS (70 eV), *m/z* (relative intensity) 193 (M$^+$ − CO_2, 21), 109 (81), 80 (16), 57 (100), 41 (35); UV (MeOH) 222 nm (ε 24 179), 261 (ε 8831). Combustion analysis was performed on the dimethyl derivative, 2′-(carboxymethyl)-3′-methoxy-2,2-dimethylpropionanilide, obtained from the acid by treatment with diazomethane: mp 72.5–74 °C. Anal. Calcd for $C_{14}H_{19}NO_4$: C, 63.40; H, 7.17; N, 5.28. Found: C, 63.47; H, 7.31; N, 5.32.

6-Hydroxyanthranilic Acid (2) Hydrochloride. A. From 4. To a solution of 10 mL of ethanethiol at 0 °C under nitrogen was added sequentially aluminum chloride (0.654 g, 49.2 mmol) and **4** (0.988 g, 3.94 mmol). An immediate precipitate developed and the mixture was diluted with an additional 15 mL of ethanethiol. The mixture was stirred at room temperature for 1.5 h, poured into 5% aqueous HCl, and stirred an additional 20 min. Extracting with three 75-mL portions of dichloromethane, combining the organic extracts, drying (Na_2SO_4), and concentrating at aspirator pressure gave a brown residue. The oil was added to a solution consisting of 6 N HCl (12 mL) and acetic acid (8 mL), heated at 45 °C for 16 h, cooled, and filtered (suction) to yield 0.244 g (30.0%) of **2** as the hydrochloride salt.

B. From 8. To a 24-mL solution of 6 N HCl–acetic acid (1:1) was added **8** (1.454 g, 6.14 mmol). The reaction mixture was stirred at 48 °C for 96 h. It was then cooled to 0 °C, and the resulting crystalline precipitate was collected via vacuum filtration to afford 0.842 g (72.4%) of **2** as a colorless hydrochloride salt, mp 214–216 °C dec [lit.[3] 216 °C dec]; analytical TLC (25% methanol–ethyl acetate) gave one spot at R_f 0.29; IR (KBr) 3350–2200, 1675, 1630, 1560, 1440, 1180, 1130, 1100, 1080, 780 cm^{-1}; ^{1}H NMR ($(CD_3)_2SO$) δ 6.73 (dd, 1 H, *J* = 8.2 and 1.1 Hz), 6.87 (dd, 1 H, *J* = 8.1 and 1.2 Hz), 7.38 (t, 1 H, *J* = 8 Hz[12]), 10.91 (br s, 5 H); ^{13}C NMR (20 MHz, $(CD_3)_2SO$) 105.7, 112.4, 134.3, 139.0, 161.6, 170.6, 180.2 ppm; UV (MeOH) 203 nm (ε 22 601), 234 (ε 13 907).

Acknowledgment. This work was supported by Public Health Service Grant GM31715 from the National Institutes of General Medical Sciences. We are grateful to Mr. John Wityak for NMR spectra and to Mr. Rodger Kohnert for NMR and mass spectra.

Registry No. **1**, 75533-14-1; **2**·HCl, 94596-96-0; **3**, 56619-93-3; **4**, 94596-97-1; **5**, 591-27-5; **6**, 75151-82-5; **7**, 94596-98-2; **8**, 94596-99-3.

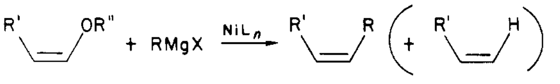
Synthesis of Acyclic, Cis Olefinic Pheromones by Way of Nickel-Catalyzed Grignard Reactions

Ernest Wenkert,* Vitor F. Ferreira,[1] Enrique L. Michelotti, and Marco Tingoli[2]

Department of Chemistry (D-006), University of California-San Diego, La Jolla, California 92093

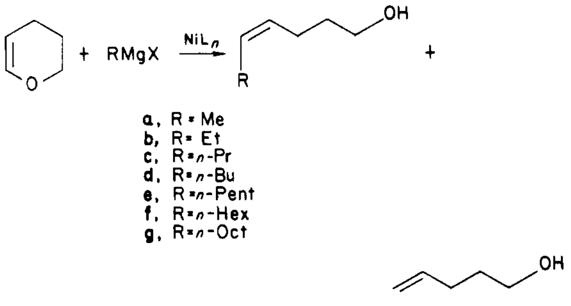
Received July 3, 1984

The recent discovery of an olefin synthesis based on the low-valent, nickel-mediated reactions of Grignard reagents with enol ethers and its application to the preparation of *cis*-olefins (eq 1)[3] suggested the use of this new reaction



(1)

in the field of pheromone synthesis. The reaction appeared to be especially well suited for the construction of acyclic, cis alkenic pheromones, a large group of natural substances the introduction of whose double bonds had been carried out in the past mostly by Wittig reactions or partial hydrogenations of acetylenes.[4] To illustrate its potential, the olefin synthesis scheme was focused on the use of dihydropyran (1), an inexpensive, readily available enol ether, as general starting material[5] and the interaction of the latter with an array of Grignard reagents (eq 2). Several of the resultant olefinic alcohols **2** then were to be converted into pheromones of several structure types.



(2)

3

In an earlier report[3] the reaction of dihydropyran (**1**) with methylmagnesium bromide in the presence of [1,3-bis(diphenylphosphino)propane]nickel dichloride ((dppp)$NiCl_2$) has been shown to yield (*Z*)-4-hexen-1-ol (**2a**) and a similar reaction with ethylmagnesium bromide had led to a ca. 5:1 mixture of (*Z*)-4-hepten-1-ol (**2b**) and 4-penten-1-ol (**3**). This alkylation–reduction ratio now dropped to ca. 1:1 on exposure of dihydropyran (**1**) to the

---

[1] Conselho Nacional de Pesquisas (Brazil) fellowship holder, 1980–1984.

[2] Postdoctoral fellow, 1983, supported by NATO (Grant RG 094.81) and the Consiglio Nazionale delle Ricerche (Italy).

[3] (a) Wenkert, E.; Michelotti, E. L.; Swindell, C. S. *J. Am. Chem. Soc.* **1979**, *101*, 2246. (b) Wenkert, E.; Michelotti, E. L.; Swindell, C. S.; Tingoli, M. *J. Org. Chem.* **1984**, *49*, 4894.

[4] (a) Henrick, C. A. *Tetrahedron* **1977**, *33*, 1845. (b) Rossi, R. *Synthesis* **1977**, 817; (c) **1978**, 413.

[5] For the use of 2,3-dihydrofuran in the same type of reaction leading to two pheromones, see ref 3b.

0022-3263/85/1950-0719$01.50/0

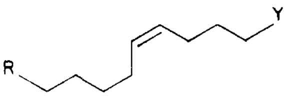
Table I. Carbon Shifts of Alcohols 2 and 3

	C(1)	C(2)	C(3)	C(4)	C(5)	C(6)	C(7)	C(8)	C(9)	C(10)	C(11)	C(12)	C(13)
3	61.2	31.3	29.6	137.8	114.2								
2a	61.6	32.0	22.8	129.5	123.8	12.2							
2b	61.4	32.2	23.1	127.9	131.6	20.0	13.8						
2c	61.7	32.3	23.3	128.8	129.9	28.9	22.5	13.4					
2d	61.7	32.2	23.2	128.5	130.1	26.6	31.6	21.9	13.6				
2e	61.9	32.3	23.3	128.6	130.3	26.9	29.1	31.7	22.3	13.8			
2f	61.8	32.3	23.3	128.6	130.2	26.9	29.4[a]	28.7[a]	31.5	22.4	13.8		
2g	61.8	32.4	23.3	128.6	130.2	27.0	29.5[b]	29.5[b]	29.1[b]	29.1[b]	31.7	22.4	13.8

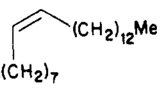
[a,b] Signals in any horizontal row may be interchanged.

Grignard reagents, derived from *n*-propyl, *n*-butyl, *n*-pentyl, *n*-hexyl and *n*-octyl bromides, under similar conditions. The alkylation products, (*Z*)-4-octen-1-ol (**2c**),[6] (*Z*)-4-nonen-1-ol (**2d**),[6] (*Z*)-4-decen-1-ol (**2e**),[6] (*Z*)-4-undecen-1-ol (**2f**), and (*Z*)-4-tridecen-1-ol (**2g**),[7] respectively, were obtained in up to 36% yield and could be separated easily by distillation from the common reduction product 4-penten-1-ol (**3**) (isolated in up to 39% yield). It is noteworthy that the 13-carbon alcohol **2g** has been found recently to be a product of secretion of the preorbital gland of the small neotragine antelope *Raphicerus melanotis* (commonly known as grysbok).[7]

Treatment of alcohol **2g** with methyllithium and the resultant lithium alkoxide with methanesulfonyl chloride yielded a mesylate (**4a**).[8] Exposure of the latter or the equivalent bromide (**4b**), prepared from the sulfonate **4a** by interaction with lithium bromide,[8] to *n*-decylmagnesium bromide in the presence of cuprous cyanide/lithium chloride complex gave (*Z*)-9-tricosene ("Muscalure") (**5**),[9] a sex attractant of the mature female house fly, *Musca domestica*, in 80% overall yield.

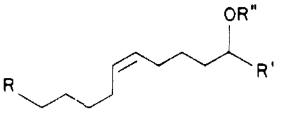


4a, R = *n*-Bu; Y = OSO_2Me
b, R = *n*-Bu; Y = Br
c, R = H; Y = OSO_2Me
d, R = H; Y = Br
e, R = Me; Y = OSO_2Me
f, R = Me; Y = Br

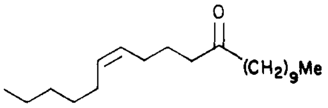


5

Conversion of alcohol **2d** into its bromide (**4d**) by the above two-step procedure and subsequent metal–halogen exchange with *tert*-butyllithium produced an organolithium reagent, whose exposure to gaseous formaldehyde afforded the homologous alcohol **6a**,[6] the product of hydrolysis of one (**6**, R = R′ = H; R″ = Ac) of the sex attractants of the male redbacked cutworm *Euxoa ochrogaster* (Guenée).[10] Acylation of the latter with isovaleryl chloride led to (*Z*)-5-decen-1-yl isovalerate (**6b**), the sex pheromone of the female pine emperor moth *Nudaurelia cytherea cytherea* Fabr.,[11] in 79% overall yield.



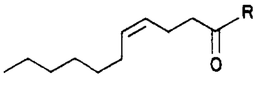
6a, R = R' = R" = H
b, R = R' = H; R" = $COCH_2CHMe_2$
c, R = Me, R' = $(CH_2)_9Me$; R" = H



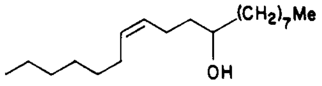
7

Transformation of alcohol **2e** into an organolithium reagent by the above three-step scheme and interaction of the latter with undecanal yielded alcohol **6c**,[4a,12,13] whose oxidation with pyridinium dichromate (PDC) gave (*Z*)-6-heneicosen-11-one (**7**),[4a,12,13] the sex attractant of the female Douglas fir tussock moth *Orgyia pseudotsugata*, in quantitative overall yield.

PDC oxidation of alcohol **2f** produced aldehyde **8a**, a volatile constituent of the anal gland of the male wild rabbit *Oryctolagus cuniculus*,[14] whose reaction with *n*-octylmagnesium bromide afforded alcohol **9**.[15] PDC oxidation of the latter led to (*Z*)-7-nonadecen-11-one (**8b**),[15–17] a sex pheromone of the female peach fruit moth *Carposina niponensis*, in 74% overall yield.[18]



8a, R = H
b, R = $(CH_2)_7Me$



9

Experimental Section

Infrared spectra on liquid films were measured on a Perkin-Elmer Model 1330 spectrophotometer. ^1H NMR spectra of $CDCl_3$ solutions with Me_4Si as internal standard were recorded on a Varian EM-390 spectrometer and a 360-MHz instrument with a highly modified Varian HR-220 console, an Oxford magnet, and a Nicolet 1180-E computer system. ^{13}C NMR spectra of $CDCl_3$ solutions were taken on a Nicolet NT-200 (wide-bore, broad-band, with Oxford magnet) spectrometer, operating at 50.31 MHz in the Fourier transform mode. The carbon shifts are in parts per million downfield from Me_4Si; $\delta(Me_4Si) = \delta(CDCl_3) + 76.9$ ppm.

General Procedure for the Reactions of Grignard Reagents with Dihydropyran. A 2.90 M ethereal solution of methylmagnesium bromide, 2.40 mL (6.00 mmol), was added dropwise to a stirring suspension of 1.63 g (3.00 mmol) of

---

[6] Bestmann, H. J.; Koschatzky, K. H.; Schätzke, W.; Süsz, J.; Vostrowsky, O. *Liebigs Ann. Chem.* **1981**, 1705.

[7] Burger, B. V.; le Roux, M.; Spies, H. S. C.; Truter, V.; Bigalke, R. C.; Novellie, P. A. *Z. Naturforsch. C.: Biosci.* **1981**, *36*, 344.

[8] Huang, W.; Pulaski, S. P.; Meinwald, J. *J. Org. Chem.* **1983**, *48*, 2270.

[9] Previous syntheses: (a) citation in ref 4a. (b) Pop, L. M.; Ghizdavu, I.; Hodosan, F. P. Rom. Pat. *RO 70999* [*Chem. Abstr.* **1982**, *96*, 103958]. (c) Odinokov, V. N.; Tolstikov, G. A.; Galeyeva, R. I.; Kargapol'tseva, T. A. *Tetrahedron Lett.* **1982**, *23*, 1371. (d) Pop, L.; Hodosan, F. *Rev. Roum. Chim.* **1982**, *27*, 545 [*Chem. Abstr.* **1982**, *97*, 127307]. (e) Brown, H. E.; Basavaiah, D. *J. Org. Chem.* **1982**, *47*, 3806.

[10] Struble, D. L. *J. Chem. Ecol.* **1981**, *7*, 615.

[11] Henderson, H. E.; Warren, F. L.; Augustyn, O. P. H.; Burger, B. V.; Schneider, D. F.; Boschoff, P. R.; Spies, H. S. C.; Geertsema, H. *J. Chem. Soc., Chem. Commun.* **1972**, 686.

[12] Smith, R. G.; Daves, G. D., Jr.; Daterman, G. E. *J. Org. Chem.* **1975**, *40*, 1593.

[13] Vig, O. P.; Sharma, M. L.; Verma, N. K.; Malik, N. *Indian J. Chem., Sect. B* **1980**, *19B*, 950.

[14] Goodrich, B. S.; Hesterman, E. R.; Murray, K. E.; Mykytowycz, R.; Stanley, G.; Sugowdz, G. *J. Chem. Ecol.* **1978**, *4*, 581.

[15] Kamikado, T.; Aoki, I. Jpn. Kokai Tokkyo Koho 7981208 [*Chem. Abstr.* **1980**, *92*, 93899].

[16] Yoshida, T.; Saito, S. *Bull. Chem. Soc. Jpn.* **1982**, *55*, 3047.

[17] Yadagiri, P.; Yadav, J. S. *Synth. Commun.* **1983**, *13*, 1067.

[18] Pheromone syntheses based on palladium- or nickel-catalyzed reactions of Grignard reagents with (a) vinyl chlorides or (b) vinyl sulfides [(a) Ratovelomanana, V.; Linstrumelle, G. *Synth. Commun.* **1984**, *14*, 179; (b) Naso, F., private communication] and on reactions of (c) alkenylcopper reagents [(c) Alexakis, A.; Cahiez, G.; Normant, J. F. *Tetrahedron Lett.* **1978**, 2027. Cahiez, G.; Alexakis, A.; Normant, J. F. *Ibid.* **1980**, *21*, 1433. Gardette, M.; Alexakis, A.; Normant, J. F. *J. Chem. Ecol.* **1983**, *9*, 219, 225. Alexakis, A.; Commercon A.; Coulentianos, C.; Normant, J. F. *Tetrahedron* **1984**, *40*, 715].

(dppp)$NiCl_2$ in 80 mL of dry benzene under argon, and the mixture was refluxed for 15 min. After this catalyst reduction, 60.0 mmol of the required Grignard reagent was added and most of the ether removed by distillation. Upon solvent replacement by dry benzene up to a volume of 125 mL and addition of 100 mmol of dihydropyran (1), the mixture was heated at 70 °C for 20 h. It then was cooled, poured into 150 mL of saturated ammonium chloride solution, and extracted with ether. The extract was dried (Na_2SO_4) and evaporated. Distillation of the residue under vacuum separated the liquid products. The yield of alkylation (2) and reduction (3) products combined was ca. 75%.

Spectra of all alcohols **2**: IR OH 3340 (br, m), C=C 1650 (w), 730 (m), 695 (w) cm^{-1}; ^1H NMR δ 0.87 (t, 3, J = 6 Hz, Me), 1.1–2.2 (m, methylenes), 3.62 (t, 2, J = 7 Hz, OCH_2), 5.3–5.5 (m, 2, olefinic Hs); ^{13}C NMR δ in Table I.

(*Z*)-4-Undecen-1-ol (2f), liquid. Anal. Calcd for $C_{11}H_{22}O$: C, 77.57; H, 13.03. Found: C, 77.50; H, 13.10.

General Procedure for the Preparation of Methanesulfonates and Bromides 4. A 1.30 M ethereal solution of methyllithium, 3.46 mL (4.50 mmol), was added dropwise to a stirring solution of 4.20 mmol of any of the alcohols **2d**, **e**, or **g** in 10 mL of dry ether under nitrogen at 0 °C, and the mixture was stirred at this temperature for 30 min. Mesyl chloride, 4.30 mmol, was added slowly at 0 °C, and the resultant suspension was then filtered. The filtrate was washed with 4% sodium hydroxide and saturated brine solutions, dried (Na_2SO_4), and evaporated under vacuum, leading to a quantitative yield of one of the liquid mesylates **4a**, **c**, and **e**.

Spectra of all the mesylates: IR C=C 1650 (w), C-OSO_2 1355 (m), 1175 (m), CH=CH 735 (w), 720 (w), 698 (w) cm^{-1}; ^1H NMR δ 0.86 (t, 3, J = 6 Hz, Me), 1.1–2.3 (m, methylenes), 2.98 (s, 3, $MeSO_2$), 4.18 (t, 2, J = 6 Hz, OCH_2), 5.1–5.5 (m, 2, olefinic Hs); ^{13}C NMR (**4c**) δ 13.6 (C-9), 22.0 (C-8), 22.6 (C-3), 26.5 (C-6), 28.7 (C-2), 31.4 (C-7), 36.8 ($MeSO_2$), 69.2 (C-1), 126.9 (C-4), 130.3 (C-5).

A mixture of 1.80 mmol of any one of the mesylates and 1.10 g (12.6 mmol) of lithium bromide in 20 mL of dry tetrahydrofuran was stirred at room temperature under nitrogen for 48 h and then poured into 100 mL of ether. The suspension was washed twice with 20 mL of water, 25 mL of 4% sodium hydroxide, and 20 mL of saturated brine solutions, dried (Na_2SO_4), and evaporated under vacuum, leading to a quantitative yield of one of the liquid bromides **4b**,[19] **d**,[6] and **f**.[13]

Spectra of all the bromides: IR C=C 1650 (w), 732 (w), 718 (w), 695 w) cm^{-1}; ^1H NMR δ 0.87 (t, 3, J = 6 Hz, Me), 1.1–2.2 (m, methylenes), 3.38 (t, 2, J = 6 Hz, $BrCH_2$), 5.1–5.5 (m, 2, olefinic Hs).

(*Z*)-9-Tricosene (5). Cuprous cyanide, 224 mg, and 106 mg of lithium chloride were dried under vacuum at 100 °C for 12 h. The salts were dissolved in 50 mL of dry tetrahydrofuran and 1 mL of the resultant 50.0 mM solution[20] was added to a stirring mixture of 0.180 mL (0.38 mmol) of a 2.10 M ethereal solution of *n*-decylmagnesium bromide under argon at −10 °C. A solution of 75 mg (0.27 mmol) of sulfonate **4a** in 3 mL of tetrahydrofuran was added and the mixture stirred at −10 °C for 1 h, at 0 °C for 2 h, and at room temperature for 1 h. It then was poured into 35 mL of a saturated ammonium chloride solution and extracted with ether. The extract was dried (Na_2SO_4) and evaporated. Chromatography of the residue on silica gel and elution with hexane gave 70 mg (80 %) of liquid olefin **5**:[9] IR C=C 1650 (w), 712 (w) cm^{-1}; ^1H NMR δ 0.82 (t, 6, J = 6 Hz, methyls), 1.1–2.2 (m, 38, methylenes), 5.2–5.4 (m, 2, olefinic Hs); ^{13}C NMR δ 14.0 (C-1, C-23), 22.6 (C-2, C-22), 31.8 (C-3, C-21), 27.1 (C-8, C-11), 29.3–29.6 (C-4 to C-6, C-12 to C-20), 129.8 (C-9, C-10). The latter was obtained in 65% yield, when the coupling process was carried out on bromide **4b**.

(*Z*)-5-Decen-1-yl Isovalerate (6b). A 1.80 M hexane solution of *tert*-butyllithium, 1.45 mL, was added dropwise to a stirring solution of 267 mg (1.30 mmol) of bromide **4d** in 5 mL of dry ether under nitrogen at 0 °C, and the stirring was continued for 2 h. Excess gaseous formaldehyde was bubbled into the stirring mixture and the stirring was continued at 0 °C for 0.5 h and at room temperature for 0.5 h. The mixture was poured into 60 mL of ether, washed with water, dried (Na_2SO_4), and evaporated, giving 162 mg (80 %) of liquid (*Z*)-5-decen-1-ol (**6a**):[6] ^1H NMR δ 0.85 (t, 3, J = 6 Hz, Me), 1.0–2.2 (m, 12, methylenes), 3.65 (t, 2, J = 6 Hz, OCH_2), 5.2–5.4 (m, 2, olefinic Hs).

A solution of 172 mg (1.10 mmol) of alcohol **6a**, 151 μL (150 mg, 1.25 mmol) of isovaleryl chloride, and 1.2 mL of pyridine in 10 mL of methylene chloride was stirred at room temperature for 18 h. It then was washed with 2 N hydrochloric acid, 4% sodium hydroxide, and saturated brine solutions, dried (Na_2SO_4), and evaporated, yielding 260 mg (98 %) of liquid ester **6b**:[11] IR C=O 1765 (s), C=C 1650 (w), 730 (w), 700 (w) cm^{-1}; ^1H NMR δ 0.90 (d, 6, J = 6 Hz, *i*-Pr Me_2), 0.93 (t, 3, J = 6 Hz, Me), 1.1–2.4 (m, 15, CH, methylenes), 3.98 (t, 2, J = 6 Hz, OCH_2), 5.2–5.4 (m, 2, olefinic Hs).

(*Z*)-6-Heneicosen-11-ol (6c). An organolithium reagent was prepared from 285 mg (1.30 mmol) of bromide **4f** (under the conditions used for the above formation of an organometallic intermediate en route to alcohol **6a**), to whose solution there was added dropwise 267 μL (221 mg, 1.30 mmol) of undecanal at 0 °C. Stirring at 0 °C and subsequently at room temperature and workup as above gave 403 mg (100 %) of liquid alcohol **6c**:[13] IR OH 3360 (br, m), C=C 1650 (w), 740 (w), 728 (w), 702 (w) cm^{-1}; ^1H NMR δ 0.85 (t, 6, J = 6 Hz, Me_2), 1.1–2.2 (m, 32, methylenes), 3.4–3.7 (m, 1, OCH), 5.2–5.4 (m, 2, olefinic Hs).

(*Z*)-6-Heneicosen-11-one (7). A mixture of 620 mg (2.00 mmol) of alcohol **6c** and 752 mg (2.00 mmol) of PDC in 10 mL of methylene dichloride was stirred under nitrogen at room temperature for 41 h. It then was filtered through a short Florisil column and the latter washed with 200 mL of methylene chloride. The combined organic solutions were washed with 1 N hydrochloric acid and saturated sodium bicarbonate solutions, dried (Na_2SO_4), and evaporated, yielding 616 mg (100%) of liquid ketone **7**:[12,13] IR C=O 1712 (s), C=C 1640 (w), 732 (w), 718 (w), 697 (w) cm^{-1}; ^1H NMR δ 0.85 (t, 6, J = 6 Hz, Me_2), 1.1–2.2 (m, 28, methylenes), 2.2–2.5 (m, 4, α-acylmethylenes), 5.2–5.4 (m, 2, olefinic Hs).

(*Z*)-4-Undecenal (8a). Oxidation of 340 mg (2.00 mmol) of alcohol **2f** and workup by the above procedure for the preparation of ketone **7** yielded 286 mg (85%) of liquid aldehyde **8a**:[14] IR CHO 2720 (w), C=O 1726 (s), C=C 1652 (w), 720 (w), 700 (w) cm^{-1}; ^1H NMR δ 0.88 (t, 3, J = 6 Hz, Me), 1.1–2.2 (m, 10, methylenes), 2.3–2.4 (m, 2, 2 H-3), 2.52 (t, 2, J = 6 Hz, CH_2CO), 5.2–5.5 (m, 2, olefinic Hs), 9.78 (t, 1, J = 1 Hz, CHO); ^{13}C NMR δ 13.8 (C-11), 19.8 (C-3), 22.3 (C-10), 26.9 (C-6), 28.7 (C-8 or C-7), 29.3 (C-7 or C-8), 31.5 (C-9), 43.5 (C-2), 126.8 (C-4), 131.3 (C-5), 201.7 (C-1).

(*Z*)-12-Nonadecen-9-ol (9). A 1.56 M ethereal solution of *n*-octylmagnesium bromide, 1.40 mL, was added dropwise to a stirring solution of 272 mg (1.62 mmol) of aldehyde **8a** in 10 mL of dry ether under nitrogen at 0 °C and the mixture then stirred for 15 min and thereafter poured into a saturated ammonium chloride solution. The water phase was extracted with ether and the combined organic solutions were dried (Na_2SO_4) and evaporated, producing 423 mg (93%) of liquid alcohol **9**:[15] IR OH 3355 (m), C=C 1650 (w), 722 (w) cm^{-1}; ^1H NMR δ 0.85 (t, 6, J = 6 Hz, Me_2), 1.1–2.2 (m, 28, methylenes), 3.4–3.7 (m, 1, OCH), 5.2–5.4 (m, 2, olefinic Hs).

(*Z*)-12-Nonadecen-9-one (8b). Oxidation of 564 mg (2.00 mmol) of alcohol **9** and workup by the above procedure for the preparation of ketone **7** yielded 521 mg (93%) of liquid ketone **8b**:[16,17] IR C=O 1711 (s), C=C 1650 (w), 718 (w) cm^{-1}; ^1H NMR δ 0.88 (t, 6, J = 6 Hz, Me_2), 1.2–1.4 (m, 20, methylenes), 2.0–2.1 (m, 2, 2 H-14), 2.2–2.5 (m, 6, 2 H-8, 2 H-10, 2 H-11), 5.2–5.5 (m, 2, olefinic Hs).[21]

Registry No. **1**, 110-87-2; **2a**, 928-91-6; **2b**, 6191-71-5; **2c**, 54393-36-1; **2d**, 59499-28-4; **2e**, 57074-37-0; **2f**, 21676-07-3; **2g**, 75568-01-3; **3**, 821-09-0; **4a**, 94519-25-2; **4b**, 74088-20-3; **4c**, 94519-26-3; **4d**, 59499-29-5; **4e**, 86301-89-5; **4f**, 77899-13-9; **5**, 27519-02-4; **6a**, 51652-47-2; **6b**, 37616-04-9; **6c**, 54844-71-2; **7**, 54844-65-4; **8a**, 68820-32-6; **8b**, 63408-45-7; **9**, 72855-91-5; EtBr, 74-96-4; *n*-PrBr, 106-94-5; *n*-BuBr, 109-65-9; *n*-PentBr, 110-53-2; *n*-HexBr, 111-25-1; *n*-OctBr, 629-04-9; $Me(CH_2)_9Br$, 112-29-8; $Me(CH_2)_9CHO$, 112-44-7.

---

(19) Hennart, C.; Martin, G.; Favreau, J. Ger. Offen. 2931876 [*Chem. Abstr.* **1980**, *93*, 25887].

(20) Tamura, M.; Kochi, J. *Synthesis* **1971**, 303.

(21) The physical constant of all products of known constitution were identical with those cited in the literature.