(0.5 mmol) in freshly distilled acetonitrile at 0 °C, and then 4-penten-1-ol or 5-hexen-1-ol (1.1 mmol) was added. After 2 h the reaction mixture was poured into water and extracted with ether (10 mL × 3). The organic layer was washed with aqueous solutions of 5% $NaHCO_3$ (10 mL) and saturated NaCl (10 mL) and then dried over anhydrous $MgSO_4$. In the reaction of 4-penten-1-ol, 2-[(phenylthio)methyl]tetrahydrofuran[15] was isolated by column chromatography (Wakogel C-200, eluent; chloroform-/hexane (3-1)) and GPC. In the reaction of 5-hexen-1-ol, cycloetherifications did not occur.

In the reactions of unsaturated carboxylic acids, the following two methods were employed. Method A. 4-Pentenoic or 5-hexenoic acid (1.1 mmol) was added to the resulting solution of diphenyl disulfide (1.0 mmol) and NBSP (0.5 mmol) in acetonitrile (20 mL), and the solution was allowed to stir for 2 h at 0 °C. Method B. NBSP (0.5 mmol) was added to the solution of diphenyl disulfide (1.0 mmol) and 4-pentenoic or 5-hexenoic acids (1.1 mmol) in acetonitrile (20 mL). 5-[(Phenylthio)methyl]dihydrofuran-2-one (7)[15] was isolated from the reaction mixture by column chromatography (Wakogel C-200, eluent, hexane/chloroform (3:1)) and GPC. 6-[(Phenylthio)methyl]tetrahydropyran-2-one (8)[16] was also obtained by column chromatography (Wakogel C-200, hexane/chloroform (1:1)) and GPC.

Registry No. 1, 113345-02-1; 2, 122823-50-1; 3, 137542-98-4; 4, 137542-99-5; 5, 122823-57-8; 6, 137543-00-1; 7, 108078-64-4; 8, 108078-67-7; *m*-NBSP, 6209-71-8; *p*-NBSP, 6209-72-9; $PhTeOSO_2C_6H_4$-*p*-NO_2, 137542-97-3; PhTePh, 32294-60-3; $MeOC_6H_4$-*p*-$(Te)_2$-*p*-C_6H_4OMe, 35684-37-8; $Ph(S)_2Ph$, 882-33-7; $HO(CH_2)_3CH{=}CH_2$, 821-09-0; $HO(CH_2)_4CH{=}CH_2$, 821-41-0; $HO(CH_2)_3CH{=}CHCH_3$, 6126-50-7; $H_2C{=}CHCH_2C_6H_4$-*o*-OH, 1745-81-9; $HO(CH_2)_3CH{=}CH_2$, 591-80-0; $HO_2C(CH_2)_3CH{=}CH_2$, 1577-22-6.

Supplementary Material Available: ^1H and ^{13}C NMR spectra of compound 6, for which elemental analyses were not performed (2 pages). Ordering information is given on any current masthead page.

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Stereoselective Alkene Synthesis via (α-Chloroalkyl)dimethylphenylsilanes and α-Dimethylphenylsilyl Ketones

Anthony G. M. Barrett,* Jason M. Hill, and Eli M. Wallace

Department of Chemistry, Colorado State University, Fort Collins, Colorado 80523

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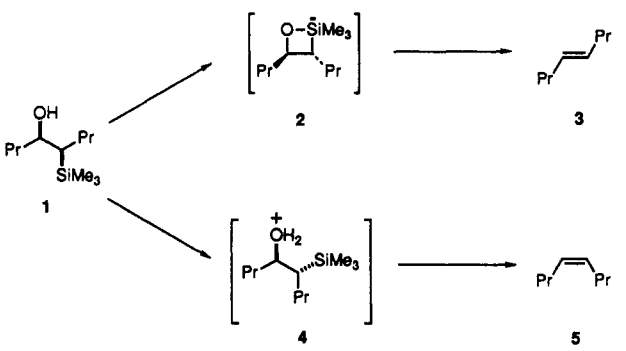
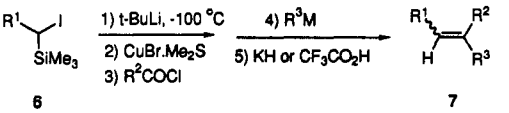
Introduction

The acid or base elimination of a diastereoisomerically pure β-hydroxy silane 1 (the Peterson olefination reaction[1]) provides one of the very best methods for the stereoselective formation of alkenes. Either the *E* or *Z* isomer may be prepared with excellent geometric selectivity from a single precursor (Scheme I). Thus, elimination of the syn diastereoisomer 1 under basic conditions proceeds via a syn manifold and the corresponding pentacoordinate silicate 2. This reaction provides the *E* isomer 3. In contrast, elimination under acid conditions takes place via the anti elimination of the conjugate acid 4 to produce the *Z* isomer 5. There is, however, a major problem that has prevented

Scheme I



Scheme II



the widespread use of the Peterson olefination reaction in synthesis. Unfortunately, there are few experimentally simple methods available for the formation of diastereoisomerically pure β-hydroxy silanes.[2,3] One reliable route is the Cram controlled addition of nucleophiles to α-silyl ketones,[3] but such an approach is complicated by difficulties in the preparation of α-silylalkyllithium species or the corresponding Grignard reagents. In large part, these difficulties would be resolved by the development of a simple method for the preparation and reductive acylation of (α-haloalkyl)silanes. We therefore set out to develop a simple convergent method for the synthesis of α-silyl ketones from aldehydes and acyl chlorides.

Recently, we reported a method for the preparation of both di- and trisubstituted alkenes via the reductive acylation of (α-iodoalkyl)trimethylsilanes 6, the addition of nucleophiles to the resultant α-trimethylsilyl ketones, and elimination.[4] The reductive acylation was carried out by reaction of 6 with *tert*-butyllithium at low temperature (Et_2O, −100 °C), conversion to the organocopper species, and reaction with an acid chloride (Scheme II). However, there are limitations with this methodology. The (α-iodoalkyl)trimethylsilanes 6 were prepared from aldehydes by the addition of hexamethyldisilane in the presence of tetrabutylammonium fluoride, followed by reaction of the resultant (α-hydroxyalkyl)trimethylsilanes with methyltriphenoxyphosphonium iodide. Unfortunately, the intermediate α-hydroxy silanes were formed in only modest yields due to competitive Brook rearrangement.[5] In addition, the conditions for halogen/lithium exchange were inconvenient. Subsequent to this initial publication, we have made significant improvements in this methodology. Herein we report that (α-chloroalkyl)dimethylphenylsilanes and α-dimethylphenylsilyl ketones are useful in-

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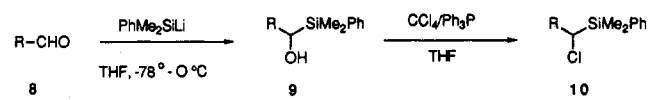
0022-3263/92/1957-0386$03.00/0

Table I. Preparation of (α-Chloroalkyl)dimethylphenylsilanes 10



8 9 10

entry	R	no. (yield (%))	no. (yield (%))
1	C_5H_{11}	**9a** (73)	**10a** (85)
2	C_7H_{15}	**9b** (76)	**10b** (87)
3	Cyc-C_6H_{11}	**9c** (92)	**10c** (82)
4	Ph	**9d** (67)	**10d** (65)

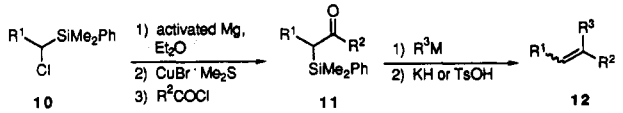
termediates for the synthesis of both di- and trisubstituted alkenes in a highly efficient and convergent manner.

Results and Discussion

Following our work with (α-iodoalkyl)trimethylsilanes, subsequent efforts were directed toward the synthesis of (α-haloalkyldimethylphenylsilanes. It was hoped that the bulkier silyl group would eliminate problems with the Brook rearrangement reaction. Dimethylphenylsilyllithium, unlike trimethylsilyllithium,[6] is readily available from the corresponding chloride and lithium metal,[7] and it adds readily to aldehydes at −78 °C. Following this precedent, a series of aldehydes **8** were smoothly and cleanly converted into the corresponding (α-hydroxyalkyl)silanes **9** in excellent yields (Table I). Much to our delight, significant levels of Brook rearrangement were not observed on chromatographic purification, thereby making isolation much easier than with the trimethylsilyl analogues. However, although conversion of these alcohols into the corresponding iodo compounds could be readily achieved using methyl(triphenoxy)phosphonium iodide,[8] subsequent halogen/metal exchange using *t*-BuLi or various other alkyllithium reagents proved to be highly capricious and of little synthetic utility. In attempting to resolve these difficulties, we investigated the corresponding chlorides **10**. These compounds could be obtained in excellent yields from the (α-hydroxyalkyl)silanes **9** by reaction with carbon tetrachloride and triphenylphosphine[9,10] in refluxing THF (Table I). Unfortunately, the chlorides also did not undergo the necessary halogen/lithium exchange reaction with a variety of alkyllithium reagents.

In an attempt to resolve this problem, our attention turned to the synthesis of corresponding Grignard reagents derived from the chlorides **10**. Activated magnesium[11] in refluxing diethyl ether easily converted the chlorides **10** into the desired Grignard reagents (the first such branched α-silylalkyl Grignard reagents reported). These Grignard reagents are stable for several hours if left over activated magnesium and under argon, but are best utilized immediately. Transmetalation with copper(I) bromide–dimethyl sulfide complex occurred smoothly, and the resultant organocopper species was coupled with various carboxylic acid chlorides at −10 to 0 °C to give excellent yields of α-silyl ketones **11**. These substances proved to be chromatographically unstable and were thus used directly without further purification. Addition of a nucleophile in THF, typically MeLi or *n*-BuLi in the trisubstituted cases or diisobutylaluminum hydride in the disubstituted case, proceeded with excellent Cram control at −78 °C. This was followed by acid (*p*-toluenesulfonic monhydrate) or base (potassium hydride) elimination to furnish the alkenes **12** (Table II). In most cases these were formed with excellent stereoselectivity (85:15 to 99:1).

Table II. Synthesis of Di- and Trisubstituted Alkenes 12



10 11 12

	α-silyl ketone				alkene	
no.	R^1	R^2	R^3M	elim	*E*:*Z*	no. (yield (%))
11a	C_5H_{11}	C_4H_9	MeLi	TsOH	5:95	**12a** (60)
				KH	95:5	**12b** (61)
11b	C_5H_{11}	C_5H_{11}	MeLi	TsOH	8:92	**12c** (67)
				KH	88:12	**12d** (63)
11c	C_5H_{11}	C_7H_{15}	MeLi	TsOH	15:85	**12e** (64)
				KH	94:6	**12f** (62)
11d	C_5H_{11}	Ph	MeLi	TsOH	⟨2:⟩98	**12g** (60)
				KH	⟩98:⟨2	**12h** (69)
11e	C_5H_{11}	*a*	MeLi	TsOH	9:91	**12i** (61)
				KH	99:1	**12j** (62)
11f	C_5H_{11}	C_5H_{11}	BuLi	TsOH	⟨5:⟩95	**12k** (65)
				KH	⟩95:⟨5	**12l** (63)
11g	C_7H_{15}	C_7H_{15}	MeLi	TsOH	10:90	**12m** (54)
				KH	95:5	**12n** (68)
11h	C_7H_{15}	CD_3	BuLi	TsOH	98:2	**12o** (51)
				KH	3:97	**12p** (50)
11i	CyC_6H_{11}	C_7H_{15}	DIBAL	TsOH	8:92	**12q** (61)
				KH	94:6	**12r** (60)

[a] *t*-$BuPh_2SiO(CH_2)_4$.

It is clear from these results that (α-chloroalkyl)dimethylphenylsilanes **10** and the derived Grignard reagents are now readily available and convenient intermediates for the convergent stereocontrolled synthesis of di- and trisubstituted alkenes. The method is experimentally simple and should be of value in the construction of more complex alkene systems.

Experimental Section

THF and diethyl ether were dried by distillation under nitrogen from sodium benzophenone ketyl. All reactions were carried out under dry argon. General procedures are given in detail in the first instance only. Chromatography was carried out on Merck Kieselgel 60 (art. no. 9385). TLC was performed on Merck Kieselgel 60 F254 (art. no. 5715). *E*/*Z* ratios of alkenes were determined by GC/MS.

Preparation of 1-(Dimethylphenylsilyl)-1-hexanol (9a) and 1-Chloro-1-(dimethylphenylsilyl)hexane (10a). A solution of $Me_2PhSiLi$[7] (from $Me_2PhSiCl$ (20 mL, 0.12 mol)) in THF (150 mL) was added dropwise via cannula to a stirred solution of hexanal (13 mL, 0.11 mol) in THF (300 mL) at −78 °C. The reaction mixture was allowed to warm very slowly to 0 °C before being poured into saturated aqueous NH_4Cl and extracted with Et_2O (3 × 300 mL). The combined extracts were dried ($MgSO_4$) and evaporated and the yellow oily residue chromatographed (hexanes/ether (9:1)) to give **9a** (18.77 g, 73%) as a colorless oil: IR (film) 3450, 3069, 2956, 1427, 1248, 1113 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.63–7.6 (m, 2 H), 7.43–7.3 (m, 3 H), 3.55 (m, 1 H), 1.58–1.55 (m, 2 H), 1.34–1.29 (m, 6 H), 1.10 (s, 1 H), 0.91 (t, 3 H, *J* = 7.1 Hz), 0.39, 0.38 (2s, 6 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 136.9, 133.8, 129.3, 127.9, 65.5, 33.4, 31.3, 26.6, 22.7, 13.9, −5.3,

(6) See ref 1d, Chapter 8.
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−5.7; MS (EI) m/z 221 ($M - Me^+$), 203, 165, 135, 105, 75, 43. Anal. Calcd for $C_{14}H_{24}OSi$: C, 71.12; H, 10.23. Found: C, 71.02; H, 10.25.

A solution of **9a** (18.77 g, 0.08 mol) and PPh_3 (27.0 g, 0.10 mol) in THF (300 mL) and CCl_4 (50 mL) was heated at reflux for 6 h. After being cooled, the solvent was removed and the residue extracted with hexanes (3 × 300 mL). Evaporation and chromatography of the residue (hexanes) furnished the chloride **10a** (17.24 g, 85%) as a colorless oil: IR (film) 3070, 2930, 1466, 1378, 1250, 1115 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.56–7.54 (m, 2 H), 7.39–7.24 (m, 3 H), 3.42 (dd, 1 H, J = 2.5, 11.7 Hz), 1.66–1.61 (m, 3 H), 1.29–1.21 (m, 5 H), 0.85 (t, 3 H, J = 7.0 Hz), 0.41 (s, 3 H), 0.40 (s, 3 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 136.0, 134.1, 129.5, 127.8, 51.1, 33.1, 31.0, 27.5, 22.5, 14.0, −4.6, −5.7; MS (EI) m/z 256, 254 ($M^{+\cdot}$), 241, 239, 183, 170, 135, 105, 91, 55, 43. Anal. Calcd for $C_{14}H_{23}ClSi$: C, 65.98; H, 9.10. Found: C, 66.11; H, 9.15.

1-(Dimethylphenylsilyl)-1-octanol (9b): oil (5.19 g, 76%); IR (film) 3425, 3069, 2924, 1465, 1377, 1113 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 7.6–7.57 (m, 2 H), 7.4–7.37 (m, 3 H), 3.52 (m, 1 H), 1.55 (m, 3 H), 1.28 (m, 9 H), 1.13 (s, 1 H), 0.90 (t, 3 H, J = 6.4 Hz), 0.36 (s, 6 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 136.8, 134.1, 129.2, 127.8, 65.4, 33.4, 31.8, 29.4, 29.2, 26.8, 22.6, 14.0, −5.4, −5.7; MS (EI) m/z 249 ($M - Me^+$), 193, 165, 152, 135, 105, 75, 43. Anal. Calcd for $C_{16}H_{28}OSi$: C, 72.66; H, 10.67. Found: C, 72.74; H, 10.89.

(Dimethylphenylsilyl)-1-cyclohexylmethanol (9c): oil (9.43 g, 92%); IR (film) 3450, 3068, 2924, 1449, 1248, 1112 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 7.58–7.53 (m, 2 H), 7.36–7.33 (m, 3 H), 3.32 (d, 1 H, J = 6.0 Hz), 1.80–1.51 (m, 6 H), 1.21–1.04 (m, 6 H), 0.35 (s, 6 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 137.8, 134.0, 129.1, 127.8, 70.9, 42.0, 30.7, 29.5, 26.4, 26.3, 26.2, −3.9, −4.3; MS (EI) m/z 248 ($M^{+\cdot}$), 233, 191, 165, 135, 105, 75, 43. Anal. Calcd for $C_{15}H_{24}OSi$: C, 72.52; H, 9.74. Found: C, 72.12; H, 9.80.

(Dimethylphenylsilyl)-1-phenylmethanol (9d): oil (6.49 g, 67%); IR (film) 3422, 3069, 2959, 1598, 1450, 1249, 1113 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 7.48–7.45 (m, 2 H), 7.38–7.31 (m, 3 H), 7.27–7.22 (m, 2 H), 7.16–7.05 (m, 3 H), 4.68 (s, 1 H), 1.70 (s, 1 H), 0.29 (s, 3 H), 0.25 (s, 3 H); ^{13}C NMR (75 MHz, $CDCl_3$) 143.5, 136.0, 134.3, 129.4, 128.0, 127.8, 125.9, 125.2, 70.0, −5.4, −6.3; MS (EI) m/z 242 ($M^{+\cdot}$), 227, 164, 135, 105, 77, 43. Anal. Calcd for $C_{15}H_{18}OSi$: C, 74.33; H, 7.48. Found: C, 73.98; H, 7.69.

1-Chloro-1-(dimethylphenylsilyl)octane (10b): oil (4.31 g, 87%); IR (film) 3070, 2927, 1466, 1378, 1250, 1115 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 7.60–7.57 (m, 2 H), 7.43–7.39 (m, 3 H), 3.45 (dd, 1 H, J = 3.1, 10.7 Hz), 1.70–1.65 (m, 3 H), 1.31–1.26 (m, 9 H), 0.90 (t, 3 H, J = 6.3 Hz), 0.45 (s, 6 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 135.8, 134.1, 129.5, 127.8, 51.1, 33.1, 31.8, 29.1, 28.8, 27.8, 22.6, 14.1, −4.5, −5.7; MS (EI) m/z 284, 282, ($M^{+\cdot}$), 247, 183, 170, 135, 121, 105, 43; HRMS (EI) calcd for $C_{16}H_{27}ClSi$ ($M^{+\cdot}$) 282.1571, found ($M^{+\cdot}$) 282.1567. Anal. Calcd for $C_{16}H_{27}ClSi$: C, 67.92; H, 9.62. Found: C, 68.03; H, 9.85.

1-Chloro-1-(dimethylphenylsilyl)-1-cyclohexylmethane (10c): oil (7.56 g, 82%); IR (film) 3070, 2928, 2853, 1449, 1250, 1114 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 7.57–7.54 (m, 2 H), 7.37–7.31 (m, 3 H), 3.42 (d, 1 H, J = 4.0 Hz), 1.70–1.07 (m, 11 H), 0.43 (s, 6 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 133.9, 129.4, 127.8, 58.1, 41.4, 32.2, 29.7, 26.3, 26.2, 25.9, −3.0, −3.9; MS (EI) m/z 268, 266 ($M^{+\cdot}$), 231, 183, 135, 105, 91, 67, 43; HRMS (EI) calcd for $C_{15}H_{23}ClSi$ ($M^{+\cdot}$) 266.1258, found ($M^{+\cdot}$) 266.1269. Anal. Calcd for $C_{15}H_{23}ClSi$: C, 67.51; H, 8.69. Found: C, 67.89; H, 9.08.

[Chloro(dimethylphenylsilyl)methyl]benzene (10d): oil (4.20 g, 65%); IR (film) 3069, 2960, 1598, 1494, 1250, 1117 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 7.39–7.05 (m, 10 H), 4.46 (s, 1 H), 0.42 (s, 3 H), 0.32 (s, 3 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 139.6, 134.9, 134.4, 133.0, 129.7, 128.0, 127.6, 127.2, 126.6, 52.3, −5.2; MS (EI) m/z 262, 260 ($M^{+\cdot}$), 225, 135, 105, 89, 63, 43. Anal. Calcd for $C_{15}H_{17}ClSi$: C, 69.07; H, 6.57. Found: C, 69.11; H, 6.67.

Preparation of α-Silyl Ketone 11a. $MgBr_2 \cdot Et_2O$ (2.48 g, 9.6 mmol) and K (0.53 g, 13.6 mmol) in THF (20 mL) were heated at reflux for 3 h to yield a slurry of activated Mg. After cooling and allowing the Mg to settle, the THF was replaced (cannula) with Et_2O (15 mL). A solution of chloride **10a** (0.62 g, 2.4 mmol) in Et_2O (3 mL) was added to the Mg via cannula and the mixture heated at reflux for 1 h. After cooling and allowing the excess Mg to settle, the solution of the Grignard reagent was added via cannula to a stirred slurry of $CuBr \cdot SMe_2$ (0.49 g, 2.4 mmol) in Et_2O (5 mL) at −78 °C. The reaction mixture was allowed to warm to −10 to 0 °C over 45 min, before neat BuCOCl (0.29 mL, 2.4 mmol) was added. After further warming to 25 °C, the reaction mixture was stirred for 1.5 h, filtered through Celite (545), and evaporated. The residual α-silyl ketone **11a** was used in subsequent reactions without further purification.

Preparation of 5-Methyl-5(*Z*)-undecene (12a) and 5-Methyl-5(*E*)-undecene (12b). A. Acidic Elimination. MeLi (2.6 mL, 3.7 mmol, 1.5 equiv based on **10a**) was added to a stirred solution of crude **11a** in THF (10 mL) at −78 °C. After 30 min, the reaction mixture was added via cannula to a stirred solution of p-$TsOH \cdot H_2O$ (2.33 g, 12.2 mmol) in THF (20 mL) at −78 °C and allowed to warm up to 25 °C. After being stirred for an additional 12 h, the reaction mixture was poured into Et_2O (100 mL) and washed with saturated aqueous $NaHCO_3$ (3 × 20 mL) and brine (1 × 20 mL). Drying ($MgSO_4$), evaporation, and chromatography (hexanes) gave alkene **12a** (0.24 g, 60%) (95:5 mixture of Z/E isomers) as a colorless oil.

B. Basic Elimination. MeLi (2.6 mL, 3.7 mmol, 1.5 equiv based on **10a**) was added to a stirred solution of crude **11a** in THF (10 mL) at −78 °C. After 30 min, the reaction mixture was added via cannula to a stirred slurry of KH (excess) and 18-crown-6 (catalytic) in THF (5 mL) at 25 °C, and the mixture was stirred for 16 h. The suspension was poured into Et_2O (100 mL), and excess KH quenched with iso-PrOH (2 mL). Washing with saturated aqueous NH_4Cl (3 × 20 mL) and brine (1 × 20 mL), drying ($MgSO_4$), evaporation, and chromatography (hexanes) gave alkene **12b** (0.25 g, 61%) (95:5 mixture of E/Z isomers) as a colorless oil.

6-Methyl-6(*Z*)-dodecene (12c): oil (0.21 g, 67%); 92:8 mixture of Z/E isomers.

6-Methyl-6(*E*)-dodecene (12d): oil (0.23 g, 63%); 88:12 mixture of E/Z isomers.

Alkenes 12a–d gave IR, ^1H NMR, ^{13}C NMR, and MS data which agree with the reported values.[4,12]

7-Methyl-6(*Z*)-tetradecene (12e): oil (0.46 g, 64%); 85:15 mixture of Z/E isomers; IR (film) 2958, 2926, 2856, 1466, 1377 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 5.1 (t, 1 H, J = 7.4 Hz), 2.01–1.92 (app quintet, 4 H, J = 7.0 Hz), 1.66 (s, 2.77 H), 1.57 (s, 0.23 H), 1.37–1.28 (m, 16 H), 0.88 (t, 6 H, J = 7.0 Hz); ^{13}C NMR (75 MHz, $CDCl_3$) δ 135.4, 125.3, 31.9, 31.8, 31.6, 29.8, 29.3, 28.1, 27.9, 27.8, 23.4, 22.7, 22.6, 15.9, 14.1; MS (EI) m/z 210 ($M^{+\cdot}$), 153, 111, 55. Anal. Calcd for $C_{15}H_{30}$: C, 85.63; H, 14.37. Found: C, 85.72; H, 14.63.

7-Methyl-6(*E*)-tetradecene (12f): oil (0.48 g, 62%); 94:6 mixture of E/Z isomers; IR (film) 2958, 2926, 2856, 1466, 1378, 723 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 5.00 (dt, 1 H, J = 1.2, 7.1 Hz), 1.95 (m, 4 H), 1.66 (s, 0.21), 1.57 (s, 2.79 H), 1.41–1.20 (m, 16 H), 0.87 (t, 6 H, J = 6.3 Hz); ^{13}C NMR (75 MHz, $CDCl_3$) δ 135.1, 124.6, 39.8, 31.9, 31.8, 31.6, 29.6, 29.3, 28.0, 27.9, 23.4, 22.7, 22.6, 15.9, 14.1; MS (EI) m/z 210 ($M^{+\cdot}$), 125, 111, 97, 55. Anal. Calcd for $C_{15}H_{30}$: C, 85.63; H, 14.37. Found: C, 85.60; H, 14.54.

2-Phenyl-2(*Z*)-octene (12g):[4] oil (0.38 g, 60%); >98:<2 mixture of Z/E isomers; IR (film) 3022, 2959, 2855, 1600, 1494, 1376, 1070 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 7.34–7.28 (m, 2 H), 7.23–7.15 (m, 3 H), 5.45 (dt, 1 H, J = 1.3, 7.3 Hz), 2.01 (s, 3 H), 1.99–1.91 (m, 2 H), 1.35–1.18 (m, 6 H), 0.84 (t, 3 H, J = 6.8 Hz); ^{13}C NMR (75 MHz, $CDCl_3$) δ 142.3, 135.9, 128.0, 126.3, 31.5, 29.9, 29.1, 25.6, 22.5, 14.0; MS (EI) m/z 188 ($M^{+\cdot}$), 173, 131, 118, 105, 91, 77, 51, 41. Anal. Calcd for $C_{14}H_{20}$: C, 89.30; H, 10.70. Found: C, 89.24; H, 10.76.

2-Phenyl-2(*E*)-octene (12h):[4] oil (0.45 g, 69%); >98:<2 mixture of E/Z isomers; IR (film) 3057, 2957, 2856, 1597, 1378, 1062 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 7.39–7.17 (m, 5 H), 5.78 (tq, 1 H, J = 1.3, 7.7 Hz), 2.18 (app q, 2 H, J = 7.1 Hz), 2.02 (s, 3 H), 1.49–1.30 (m, 6 H), 0.91 (t, 3 H, J = 7.0 Hz); ^{13}C NMR (75 MHz, $CDCl_3$) δ 144.1, 134.5, 128.8, 128.1, 126.4, 125.6, 31.6, 29.3, 28.8, 22.6, 15.7, 14.1; MS (EI) m/z 188 ($M^{+\cdot}$), 173, 131, 91, 77, 51, 41. Anal. Calcd for $C_{14}H_{20}$: C, 89.30; H, 10.70. Found: C, 89.14; H, 10.95.

1-[(*tert*-Butyldiphenylsilyl)oxy]-5-methyl-5(*Z*)-undecene (12i): oil (0.82 g, 61%); 91:9 mixture of Z/E isomers; IR (film) 3071, 2930, 2858, 1590, 1472, 1112 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 7.70–7.65 (m, 4 H), 7.41–7.33 (m, 6 H), 5.12 (t, 1 H, J

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= 6.4 Hz), 3.66 (t, 2 H, J = 5.4 Hz), 2.02–1.93 (m, 4 H), 1.66 (s, 3 H), 1.56–1.27 (m, 10 H), 1.05 (s, 9 H), 0.88 (m, 3 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 135.6, 135.0, 134.2, 129.5, 127.6, 125.6, 63.8, 32.5, 31.6, 31.4, 29.8, 27.8, 26.9, 24.2, 23.3, 22.6, 19.2, 14.1; MS (EI) m/z 365 (M – t-Bu$^+$) 183, 41. Anal. Calcd for $C_{28}H_{42}OSi$: C, 79.56; H, 10.01. Found: C, 79.78; H, 10.22.

1-[(*tert*-Butyldiphenylsilyl)oxy]-5-methyl-5(*E*)-undecene (12j): oil (0.83 g, 62%); 99:1 mixture of E/Z isomers; IR (film) 3071, 2930, 2858, 1590, 1472, 1112 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.67–7.65 (m, 4 H), 7.43–7.33 (m, 6 H), 5.10 (dt, 1 H, J = 1.2, 7.2 Hz), 3.66 (t, 2 H, J = 6.1 Hz), 1.95 (m, 4 H), 1.66–1.28 (m, 13 H), 1.05 (s, 9 H), 0.88 (t, 3 H, J = 6.7 Hz); ^{13}C NMR (75 MHz, $CDCl_3$) δ 135.6, 134.8, 134.2, 129.5, 127.6, 125.6, 124.8, 63.9, 39.3, 32.1, 31.6, 29.6, 27.9, 26.9, 24.1, 22.6, 19.2, 15.8, 14.1; MS (EI) m/z 365 (M – t-Bu$^+$) 183, 41. Anal. Calcd for $C_{28}H_{42}OSi$: C, 79.56; H, 10.01. Found: C, 79.91; H, 10.24.

6-Butyl-6(*Z*)-dodecene (12k): oil (0.24 g, 65%); >95:<5 mixture of Z/E isomers; IR (film) 2926, 2858, 1560, 1466, 1378, 727 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 5.09, (t, 1 H, J = 7.0 Hz), 1.95 (m, 6 H), 1.40–1.22 (m, 16 H), 0.89 (m, 9 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 139.6, 124.8, 37.0, 36.7, 32.1, 31.7, 30.8, 30.6, 30.0, 29.9, 28.3, 27.7, 22.6, 22.5, 14.1, 14.0; MS (EI) m/z 224 (M$^{\bullet+}$), 182, 167, 154, 41. Anal. Calcd for $C_{16}H_{32}$: C, 85.63; H, 14.37. Found: C, 85.76; H, 14.45.

6-Butyl-6(*E*)-dodecene (12l): oil (0.49 g, 63%); >95:<5 mixture of E/Z isomers; IR (film) 2957, 2927, 2858, 1466, 1378, 727 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 5.09, (t, 1 H, J = 6.8 Hz), 2.01–1.92 (m, 6 H), 1.39–1.22 (m, 16 H), 0.90 (m, 9 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 139.6, 124.8, 37.0, 31.8, 31.7, 30.8, 29.9, 29.8, 28.0, 27.7, 22.9, 22.6, 14.1; MS (EI) m/z 224 (M$^{\bullet+}$), 196, 182, 167, 55. Anal. Calcd for $C_{16}H_{32}$: C, 85.63; H, 14.37. Found: C, 85.85; H, 14.40.

8-Methyl-8(*Z*)-hexadecene (12m): oil (0.39 g, 54%); 90:10 mixture of Z/E isomers; IR (film) 2957, 2855, 1465, 1377, 842, 722 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 5.11 (t, 1 H, J = 7.0 Hz), 2.02–1.92 (m, 4 H), 1.66 (s, 3 H), 1.37–1.27 (m, 20 H), 0.88 (t, 6 H, J = 6.0 Hz); ^{13}C NMR (75 MHz, $CDCl_3$) δ 135.4, 125.3, 31.9, 31.8, 30.2, 29.6, 29.4, 29.35, 29.29, 28.1, 27.8, 23.4, 22.7, 14.1; MS (EI) m/z 238 (M$^{\bullet+}$), 139, 125, 97, 83, 55, 41. Anal. Calcd for $C_{17}H_{34}$: C, 85.63; H, 14.37. Found: C, 85.44; H, 14.73.

8-Methyl-8(*E*)-hexadecene (12n): oil (0.54 g, 68%); 95:5 mixture of E/Z isomers; IR (film) 2925, 2854, 1466, 1378 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 5.11 (tq, 1 H, J = 1.2, 7.0 Hz), 1.97–1.92 (m, 4 H), 1.57 (s, 3 H), 1.39–1.26 (m, 20 H), 0.88 (t, 6 H, J = 6.5 Hz); ^{13}C NMR (75 MHz, $CDCl_3$) δ 135.1, 124.6, 39.7, 31.9, 29.9, 29.30, 29.27, 28.0, 27.9, 22.7, 15.8, 14.1; MS (EI) m/z 238 (M$^{\bullet+}$), 139, 126, 97, 83, 55, 41. Anal. Calcd for $C_{17}H_{34}$: C, 85.63; H, 14.37. Found: C, 85.75; H, 14.79.

5-(Methyl-d_3)-5(*E*)-tridecene (12o): oil (0.33 g, 51%); 98:2 mixture of E/Z isomers; IR (film) 2957, 2856, 2234, 2193, 1466 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 5.11 (t, 1 H, J = 7.1 Hz), 1.98–1.93 (m, 4 H), 1.39–1.23 (m, 14 H), 0.91–0.85 (m, 6 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 135.0, 124.6, 39.4, 31.9, 30.2, 30.0, 29.31, 29.29, 27.9, 22.7, 22.3, 14.1, 14.0; MS (EI) m/z 199 (M$^{\bullet+}$), 171, 157, 142, 129, 114, 86, 72, 58, 41. Anal. Calcd for $C_{14}H_{25}D_3$: C, 85.63; H, 14.37. Found: C, 85.30; H, 14.73.

5-(Methyl-d_3)-5(*Z*)-tridecene (12p): oil (0.38 g, 50%); 97:3 mixture of Z/E isomers; IR (film) 2957, 2856, 2223, 2193, 1466, 1378 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 5.11 (t, 1 H, J = 7.1 Hz), 1.97 (app quintet, 4 H, J = 7.5 Hz), 1.37–1.23 (m, 14 H), 0.93–0.86 (m, 6 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 135.2, 125.3, 31.9, 31.5, 30.4, 30.2, 29.4, 29.3, 27.8, 22.7, 14.09, 14.07; MS (EI) m/z 199 (M$^{\bullet+}$), 171, 157, 142, 129, 114, 86, 72, 58, 41. Anal. Calcd for $C_{14}H_{25}D_3$: C, 85.63; H, 14.37. Found: C, 85.11; H, 14.39.

1-Cyclohexyl-1(*Z*)-nonene (12q): oil (0.41 g, 61%); 92:8 mixture of Z/E isomers; IR (film) 2924, 2852, 1448, 1378, 967, 889 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 5.2 (m, 2 H), 2.25 (app tq, 1 H, J = 3.6, 11.1 Hz), 2.05–1.99 (m, 2 H), 1.72–1.57 (m, 6 H), 1.35–1.02 (m, 14 H), 0.88 (t, 3 H, J = 6.5 Hz); ^{13}C NMR (75 MHz, $CDCl_3$) δ 136.0, 128.1, 36.3, 33.5, 31.9, 30.0, 29.28, 29.25, 29.2, 27.5, 26.18, 26.16, 26.0, 22.7, 14.1; MS (EI) m/z 208 (M$^{\bullet+}$), 180, 166, 152, 124, 109, 96, 81, 67, 41. Anal. Calcd for $C_{15}H_{28}$: C, 86.46; H, 13.54. Found: C, 86.76; H, 13.69.

1-Cyclohexyl-1(*E*)-nonene (12r): oil (0.44 g, 60%); 94:6 mixture of E/Z isomers; IR (film) 2924, 2852, 1448, 1378, 967 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 5.35–5.33 (m, 2 H), 1.98–1.88 (m, 3 H), 1.73–1.60 (m, 6 H), 1.35–1.01 (m, 14 H), 0.88 (t, 3 H, J = 6.5 Hz); ^{13}C NMR (75 MHz, $CDCl_3$) δ 136.4, 127.8, 40.7, 33.3, 32.7, 31.9, 29.7, 29.3, 29.2, 29.1, 26.3, 26.2, 26.0, 22.7, 14.1; MS (EI) m/z 208 (M$^{\bullet+}$), 109, 96, 81, 67, 41. Anal. Calcd for $C_{15}H_{28}$: C, 86.46; H, 13.54. Found: C, 86.47; H, 13.71.

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New Reactions of Potassium Naphthalenide with β-, γ- and δ-Lactones: An Efficient Route to α-Alkyl γ- and δ-Lactones and α,β-Unsaturated Carboxylic Acid Esters

Marek Kowalczuk, Piotr Kurcok, Wojciech Głõwkowski, and Zbigniew Jedliński*

Institute of Polymer Chemistry, Polish Academy of Sciences, 41-800 Zabrze, Poland

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It is known that potassium naphthalenide can transfer a single electron to a suitable organic acceptor molecule.[1] Potassium naphthalenide can also act as a Lewis base (e.g., in its reaction with water[2,3]).

Here, we describe the outcomes of the reactions of the γ-lactones (2-oxotetrahydrofurans) **1a,b**, the δ-valerolactone (tetrahydro-2*H*-pyran-2-one) **1c**, and the β-lactones (2-oxetanones) **3a,b** with potassium naphthalenide and the potassium naphthalenide/18-crown-6 complex.

The potassium naphthalenide/18-crown-6 complex is stable for several days at room temperature, as analysis by ^{39}K NMR and ESR spectroscopy shows.[4]

Potassium naphthalenide, in either the absence or the presence of 18-crown-6, reacts with γ- and δ-lactones (mole ratio 1:1) to yield the lactone enolates which, upon alkylation, give the corresponding α-alkyl γ- and δ-lactones derivatives in high yield (Scheme I, Table I).

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(4) The ^{39}K NMR spectrum of the 0.2 M THF solution of potassium naphthalenide recorded at 20 °C showed a signal due to the potassium cation at δ = 20 ppm. After introduction of the crown ether, the signal remained at the same position, although its line width increased due to complexation of the cation by 18-crown-6. The signal due to the complexed potassium cation retained both its intensity and its line width over 72 h, as repeated measurements showed. The concentration of the naphthalene radical anion in the potassium naphthalenide/18-crown-6 solution remained unchanged as the solution's ESR spectra revealed.

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