Notes

Synthesis of Tri- and Tetrasubstituted Olefins from α-Silyl Esters[1]

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We have reported that ethyl (trimethylsilyl)acetate and ethyl (diphenylmethylsilyl)acetate react with Grignard reagents to give, after elimination, 1,1-disubstituted ethylenes in a regiospecific manner (eq 1), making these

$$\underset{\mathbf{1}}{R_3SiCH_2CO_2Et} \xrightarrow[\text{2. KO-}t\text{-Bu or BF}_3\text{OEt}_2\text{ or H}_2\text{SO}_4]{\text{1. R}^2\text{MgX}} \underset{\mathbf{2}}{CH_2{=}CR^2_2} \qquad (1)$$

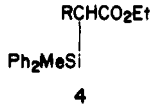
α-silyl acetates ethylene dication, **3**, equivalents.[3] We report herein on the extension of this reaction to the synthesis of tri- and tetrasubstituted olefins via vinyl dication equivalents **4** and **6**, respectively.[4]

$R_3SiCH_2CO_2Et$

1

$CH_2{=}C^{+}_{+}$

3

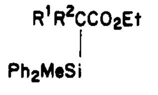


4

$\underset{Ph_2MeSi}{RCHCO_2Et}$

$RCH{=}C^{+}_{+}$

5



6

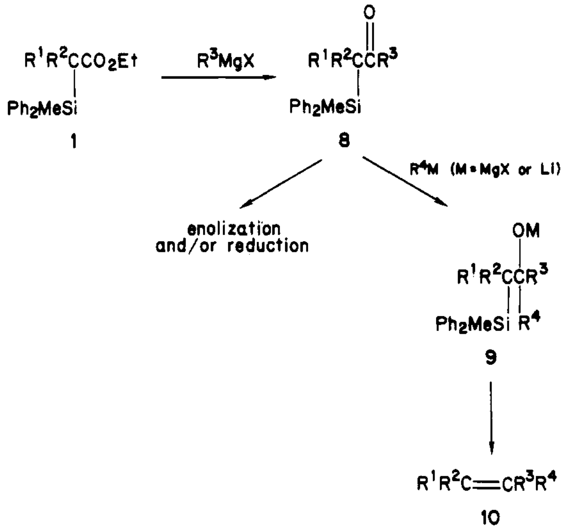
$\underset{Ph_2MeSi}{R^1R^2CCO_2Et}$

$R^1R^2C{=}C^{+}_{+}$

7

As is clear from Scheme I the success of the reaction will depend on the ability of the second equivalent of organometallic to add to the rather hindered β-keto silane formed in the initial step.[5] Thus, enolization or reduction are possible alternatives to addition to the carbonyl of the β-keto silane. It would be expected, therefore, that increased steric demand on either the ester or the organometallic (R^4M) would lead to lower yields of the olefins and higher yields of β-keto silanes or ketones.[5] That this is the case can be seen from the results shown in Table I.

Scheme I



Not surprisingly the best results are obtained with the α-silylpropionate ester **4** (R = Me) (entries 1–4). This provides good to excellent yields of the trisubstituted olefins with only the use of a Grignard reagent. As seen from entries 1 and 2 it is possible to use the α-trimethylsilyl esters as well, but these must be prepared by alkylation of ethyl (trimethylsilyl)acetate and are therefore less readily available.[6] A comparison of entries 2 and 3 indicates that the trimethylsilyl group holds no particular advantage over the diphenylmethylsilyl group in the reaction.

Increasing the size of the R group from methyl to n-octyl has a strong effect on the reaction. For example, the reaction of the α-diphenylmethylsilyl ester **4** (R = n-C_8H_{17}) with methylmagnesium iodide (entry 7) gives only a 39% yield of the desired olefin and the yield of olefin drops off precipitously with the use of ethyl- or n-propylmagnesium bromide (entries 9 and 10).

The best yields of the 1,1-dimethyl olefins, important in terpenes,[7] were obtained by a sequential addition of methylmagnesium iodide and methyllithium wherein the yields are about 55% (entries 8 and 14). It is interesting to note that the n-octyl group displays a greater steric influence on the reaction than two methyl groups (**6**, $R^1 = R^2$ = Me) as seen from the direct comparisons of entries 6 and 12 with 15 and 16, respectively. This therefore represents a regiospecific introduction of the dimethylethylidene unit of acylic terpenes. Allylmagnesium bromide reacts very well with the n-octyl ester (entry 11).[8] The exclusive use of an organolithium reagent gives several

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[1] The chemistry of α-silyl carbonyl compounds, part 9.

[2] MARC Faculty Fellow on leave from Bayamon Regional College. Taken in part from the Ph.D. Thesis of D. H.

[3] Larson, G. L.; Hernandez, D. *Tetrahedron Lett.* **1982**, *23*, 1035. For other silicon-containing vinyl cation equivalents, see ref. 10 and (a). Hudrlik, P. F.; Peterson, D. *Tetrahedron Lett.* **1972**, 1785. (b) Ruden, R. A.; Gaffney, B. L. *Synth. Commun.* **1975**, 5, 15. (c) Hudrlik, P. F.; Kulkarni, A. K. *J. Am. Chem. Soc.* **1981**, *103*, 6251. (d) Ohnuma, T.; Hata, N.; Fujiwara, H.; Ban, Y. *J. Org. Chem.* **1982**, *47*, 4713.

[4] For reviews on the synthesis of olefins, see (a). Faulkner, D. J. *Synthesis* **1971**, 175. (b) Reucroft, J.; Sammes, P. G. *Q. Rev. Chem. Soc.* **1971**, *25*, 135. (c) Marfat, A.; McQuirk, P. R.; Helquist, P. *J. Org. Chem.* **1979**, *44*, 3888. (d) Arora, A. S.; Ugi, I. K. In "Methoden der Organische Chemie (Houben-Weyl)", 4th ed; Muller, E., Ed.; Georg Thieme Verlag: Stuttgart, 1972; Vol. V., Part 1B, pp 728–945. (e) Gosney, I.; Rowley, A. G. In "Organophosphorus Reagents in Organic Synthesis"; Cadogen, J. I. G., Ed.; Academic Press: New York, 1979, (f). For methods compiled for computer-assisted synthetic analysis, see: Corey, E. J.; Long, A. K. *J. Org. Chem.* **1978**, *43*, 2208.

[5] β-Keto silanes are the principal products with the use of Grignard reagents only and with relatively sterically hindered cases. Larson, G. L.; Montes de Lopez-Cepero, I.; Torres, L. E. *J. Org. Chem.* **1984**, *25*, 1673. Protodesilylation of the crude β-keto silanes results in the preparation of ketones from esters. Larson, G. L.; Hernandez, H.; Montes de Lopez-Cepero, Torres, L. M. *J. Am. Chem. Soc.*, submitted for publication.

[6] For excellent applications of the alkylation of α-silyl esters, see: Helmchen, G.; Schmierer, R. *Tetrahedron Lett.* **1983**, *24*, 1235.

[7] For reviews, see: (a), "The Total Synthesis of Natural Products"; ApSimon, J., Ed.; Wiley-Interscience: New York, 1973; Vol. 2 (articles by A. F. Thomas; C. H. Heathcock; and J. W. ApSimon and J. W. Hooper). (b) Thomas, A. F.; Bessiere, Y. In "The Total Synthesis of Natural Products"; ApSimon, J. W., Ed.; Wiley-Interscience: New York, 1981; Vol 4.

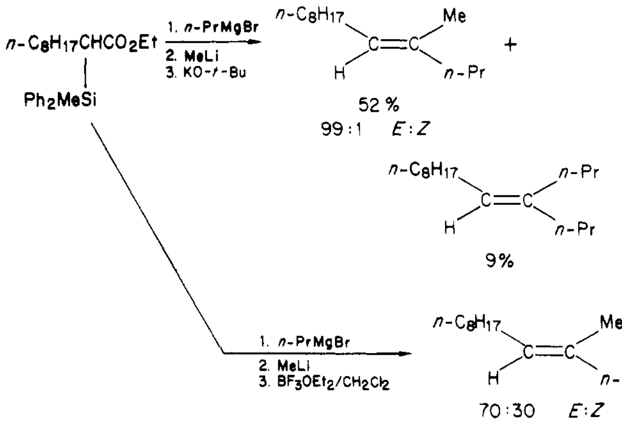
[8] Barluenga, J.; Yus, M.; Concellon, J. M.; Bernad, P. *J. Org. Chem.* **1983**, *48*, 609.

0022-3263/84/1949-4285$01.50/0

products and is a synthetically useless reaction under the present conditions.

Consistent with the anticipated and observed steric effect on the reaction, the formation of tetrasubstituted olefins proceeds best with the dimethyl system **6** ($R^1 = R^2 = Me$) as seen from entries 15–17. The only other system investigated, the n-octyl methyl system **6** ($R^1 = Me$, $R^2 = n$-$^{1}C_8H_{17}$) gave only 12% of 2,3-dimethylundec-2-ene (entry 18).

In one attempt to prepare a mixed trisubstituted olefin in a single-flask operation, α-diphenylmethylsilyl ester **4** ($R = n$-C_8H_{17}) was treated sequentially with n-propylmagnesium bromide, methyllithium, and potassium *tert*-butoxide (conditions for a syn elimination of a β-oxido silane[9]). This gave a 61% yield of a mixture of 85% 4-methyltridec-4-ene, which was shown to be greater than 99% *E* isomer, consistent with a Cram addition of methyllithium to the β-keto silane formed.[10] Unfortunately, when this sequence was carried out as above, the reaction mixture was hydrolyzed rather than being treated with potassium *tert*-butoxide and the crude reaction product was treated with boron fluoride etherate (conditions for anti elimination of β-hydroxy silanes[9]), the olefin was isolated as a 70:30 *E*:*Z* mixture. Apparently the syn elimination of the β-oxido (diphenylmethylsilane) is a rather facile process giving rise to considerable *E* product before the addition of the boron fluoride etherate. These results are summarized in eq 2. Clearly the synthesis of mixed trisubstituted olefins will best be accomplished via the reaction of organometallics with purified β-keto silanes rather than in a single-flask operation. Studies toward this end are underway in our laboratory.



(2)

Conclusions

α-Diphenylmethylsilyl esters can be reacted with organomagnesium halides or a sequential combination of an organomagnesium halide and an organolithium reagent followed by elimination to give tri- and tetrasubstituted olefins and are therefore synthetically equivalent to vinyl dications. The reaction is sensitive to steric factors but requires only readily available starting materials and is simple to perform.

Experimental Section

General Considerations. All reactions were run in a flame-dried, standard apparatus under an atmosphere of nitrogen. Spectra were recorded on Perkin-Elmer 283 (IR), JEOL FX90Q (NMR), and Hewlett-Packard 5995A (MS) spectrometers. Mass spectra were recorded at 70 eV and are reported as m/e (relative intensity). The monosubstituted α-diphenylmethylsilyl esters were prepared via direct silylation of the lithium ester enolate according to our published procedure.[11] The disubstituted α-silyl esters were prepared by methylation of the lithium enolate of the monosubstituted α-silyl esters. Grignard and lithium reagents were prepared from the appropriate halide and titrated prior to use. Magnesium was of greater than 99.99% purity.[3] Solvents were dried by standard procedures prior to use.

Preparation of 1,1-Diphenylpropene (11). Phenylmagnesium bromide (18 mmol) was prepared in ether as an approximate 0.5 M solution. To this was added 1.04 g (6 mmol) of ethyl 2-(trimethylsilyl)propionate in 10 mL of THF, and the resulting mixture was refluxed for 24 h. The excess Grignard reagent was hydrolyzed with water at 0 °C and the mixture further diluted with ether and washed with water (3 × 15 mL). The organic layer was concentrated at reduced pressure and the crude β-hydroxysilane dissolved in THF and treated with 1 mL of sulfuric acid at room temperature overnight. The reaction mixture was then diluted with ether (15 mL), washed sequentially with water, 10% sodium bicarbonate, and water, dried, and concentrated at reduced pressure. The crude material was chromatographed on silicon gel, eluting with hexane, to give 0.98 g (85%) of the title compound; mp 45–47 °C (uncorrected) (lit.[12] mp 52 °C); IR (neat) 1595 cm^{-1}; ^{1}H NMR δ 7.03 (m, 10 H) 6.18 (q, 1 H, $J = 7.0$ Hz), 1.70 (d, 3 H, $J = 7.0$ Hz).

2-*n*-Pentyl-2-octene (12). Treatment of ethyl 2-(trimethylsily)propionate with n-pentylmagnesium bromide as above gave a 54% yield of the title olefin: n_D^{20} 1.4371; ^{1}H NMR δ 5.25 (q, 1 H, $J = 7.0$ Hz), 2.20–1.70 (m, 4 H), 1.55, (d, 3 H, $J = 7.0$ Hz), 1.27 (bs, 12 H), 0.87 (bt, 6 H); ^{13}C NMR δ 140.8, 118.1, 37.1, 32.1, 31.9, 29.9, 28.1, 22.7, 14.0, 13.1; MS, 182 (5), 70 (100).

3-*n*-Hexyl-2-nonene (13). Treatment of ethyl 2-(diphenylmethylsilyl)propionate with n-hexylmagnesium bromide as above gave the title compound in 66% yield: n_D^{20} 1.4455; IR (neat) 1665 cm^{-1}; ^{1}H NMR δ 5.18 (q, 1 H, $J = 6.6$ Hz), 1.97 (m, 4 H), 1.57 (d, 3 H, $J = 6.6$ Hz), 1.27 (bs, 16 H), 0.88 (t, 6 H); ^{13}C NMR δ 140.7, 118.0, 37.1, 31.9, 29.8, 29.5, 29.3, 28.2, 22.7, 14.1, 13.2; MS, 210 (5), 70 (100). Anal. Calcd for $C_{15}H_{30}$: C, 85.71; H, 14.29. Found: C, 85.67; H, 14.32.

1,1-Dibenzylpropene (14). Following the above procedure with benzylmagnesium chloride gave a 37% yield of the title compound: n_D^{20} 1.5679; IR (neat) 1600 cm^{-1}; ^{1}H NMR δ 7.17 (bs, 10 H), 5.45 (q, 1 H, $J = 7.0$ Hz), 3.25 (s, 2 H), 3.15 (s, 2 H), 1.70 (d, 3 H, $J = 7.0$ Hz); ^{13}C NMR δ 140.2, 140.0, 138.4, 129.1, 128.6, 128.3, 128.2, 125.2, 122.2, 43.1,35.1; MS, 222 (15), 91 (100).

1,1-Diphenyl-1-butene (15). The title compound was formed in 55% yield; IR (neat) 1595 cm^{-1}; ^{1}H NMR δ 7.30, (bs, 10 H), 6.14 (t, 1 H, $J = 7$ Hz), 2.1 (dq, 2 H, $J = 7$ and 7 Hz), 1.0 (t, 3 H, $J = 7$ Hz); ^{13}C NMR δ 143.0, 141.3, 131.6, 130.0, 128.2, 127.3, 126.9, 23.2, 14.4; MS, 208 (73), 115 (100).

1,1-Diphenyl-1-decene (16). The title compound was formed in 20% yield: n_D^{20} 1.5485; ^{1}H NMR δ 7.28 (bs, 10 H), 6.13 (t, 1 H, $J = 7.6$ Hz), 2.27–1.83 (m, 2 H), 1.22 (bs, 12 H), 0.85 (m, 3 H) (lit.[13] for ^{1}H NMR); ^{13}C NMR δ 142.9, 141.7, 140.3, 131.5, 130.3, 129.9, 128.7, 128.0, 127.2, 126.8, 122.5, 31.9, 30.0, 29.8, 29.4, 29.3, 22.7, 14.1; MS, 292 (18), 115 (100).

2-Methylundec-2-ene (17). Title compound produced in 54% yield: n_D^{20} 1.4360 (lit.[14] n_D^{20} 1.4250); ^{1}H NMR δ 5.13 (t, 1 H, $J = 7.1$ Hz), 2.15–1.78 (m, 2 H), 1.67 (bs, 3 H), 1.59 (bs, 3 H), 1.27 (bs, 12 H), 0.88 (bt, 3 H); ^{13}C NMR δ 131.0, 125.1, 32.1, 30.1, 29.7, 29.5, 28.2, 25.7, 22.9, 17.7, 14.2; MS, 168 (14), 69 (100).

3-Ethyldodec-3-ene (18). Reaction of 30 mmol of ethylmagnesium iodide with 6 mmol of ethyl 2-(diphenylmethylsilyl)caprate gave after KO*t*-Bu elimination 0.11 g (9%) of the title compound: n_D^{20} 1.4492; ^{1}H NMR δ 5.13 (t, 1 H, $J = 7.1$ Hz), 2.00 (bq, 6 H), 1.29 (bs, 12 H), 1.13–0.87 (m, 9 H); ^{13}C NMR δ

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(9) For a review of this topic, see: Colvin, E. "Silicon in Organic Synthesis"; Butterworths: Boston, MA, 1981; pp 142–152. For definitive studies, see: Hudrlik, P. F.; Peterson, D.; Rona, R. J. *J. Org. Chem.* **1975**, *40*, 2263. Hudrlik, P. F.; Peterson, D. *J. Am. Chem. Soc.* **1975**, *97*, 1464.

(10) For an example of Cram addition of methyllithium to a β-keto silane: Utimoto, K.; Obayashi, M.; Nozaki, Ah. *J. Org. Chem.* **1976**, *41*, 2940. Obayashi, M.; Utimoto, K.; Nozaki, H. *Tetrahedron Lett.* **1977**, 1807.

(11) Larson, G. L.; Fuentes, L. M. *J. Am. Chem. Soc.* **1981**, *103*, 2418.

(12) Horner, L.; Hoffmann, H.; Wippel, H. G. *Ber.* **1958**, *91*, 61.

(13) Grant. D. W.; Shitton, R. *J. Chem. Soc., Perkin Trans. I* **1974**, 135.

(14) Frank, R. L.; Smith, P. V.; Woodward, F. E.; Reynolds, W. B.; Canterino, P. J. *J. Polym. Sci.* **1948**, *3*, 39.

Table I. Tri- and Tetrasubstituted Olefins from α-Silyl Esters

entry (cmpd)	R^1	R^2	R^{3}M	R^{4}M	olefin	yield,[a] %
1 (**11**)	Me[b]	H	PhMgBr	PhMgBr	MeCH=CPh$_2$	85
2 (**12**)	Me[b]	H	n-C$_5$H$_{11}$MgBr	n-C$_5$H$_{11}$MgBr	MeCH=C(n-C$_5$H$_{11}$)$_2$	54
3 (**13**)	Me	H	n-C$_6$H$_{13}$MgBr	n-C$_6$H$_{13}$MgBr	MeCH=C(n-C$_6$H$_{13}$)$_2$	66
4 (**14**)	Me	H	PhCH$_2$MgCl	PhCH$_2$MgCl	MeCH=C(CH$_2$Ph)$_2$	37
5 (**15**)	Et	H	PhMgBr	PhLi	EtCH=C(Ph)$_2$	55
6 (**16**)	n-C$_8$H$_{17}$	H	PhMgBr	PhLi	n-C$_8$H$_{17}$CH=C(Ph)$_2$	20
7 (**17**)	n-C$_8$H$_{17}$	H	MeMgI	MeMgI	n-C$_8$H$_{17}$CH=C(Me)$_2$	39
8 (**17**)	n-C$_8$H$_{17}$	H	MeMgI	MeLi	n-C$_8$H$_{17}$CH=(Me)$_2$	54
9 (**18**)	n-C$_8$H$_{17}$	H	EtMgI	EtMgI	n-C$_8$H$_{17}$CH=C(Et)$_2$	9
10 (**19**)	n-C$_8$H$_{17}$	H	n-C$_3$H$_7$MgBr	n-C$_3$H$_7$MgBr	n-C$_8$H$_{17}$CH=C(n-C$_3$H$_7$)$_2$	8
11 (**20**)	n-C$_8$H$_{17}$	H	C$_3$H$_5$MgBr	C$_3$H$_5$MgBr	n-C$_8$H$_{17}$CH=C(allyl)$_2$[c]	84
12 (**21**)	n-C$_8$H$_{17}$	H	n-C$_4$H$_9$MgBr	n-C$_4$H$_9$Li	n-C$_8$H$_{17}$CH=C(n-C$_4$H$_9$)$_2$	19
13 (**22**)	n-C$_8$H$_{17}$	H	n-C$_3$H$_7$MgBr	MeLi	n-C$_8$H$_{17}$CH=C(n-C$_3$H$_7$)Me[d]	55
14 (**23**)	CH$_2$=CH(CH$_2$)$_7$	H	MeMgBr	MeLi	CH$_2$=CH(CH$_2$)$_7$CH=C(Me)$_2$	56
15 (**24**)	Me	Me[e]	PhMgBr	PhLi	Me$_2$C=C(Ph)$_2$	70
16 (**25**)	Me	Me[e]	n-C$_4$H$_9$MgBr	n-C$_4$H$_9$Li	Me$_2$C=C(n-C$_4$H$_9$)$_2$	60
17 (**26**)	Me	Me[e]	n-C$_6$H$_{13}$MgBr	n-C$_6$H$_{13}$MgBr	Me$_2$C=C(n-C$_6$H$_{13}$)$_2$	44
18 (**27**)	n-C$_8$H$_{17}$	Me[f]	MeMgI	MeLi	(n-C$_8$H$_{17}$)MeC=CMe$_2$	12

[a] Isolated yields. [b] Ethyl (trimethylsilyl)propionate prepared via methylation of ethyl (trimethylsilyl)acetate used in these reactions. [c] The allyl Grignard has been shown to add twice to other hindered esters. [d] Product is greater than 99:1 *E*:*Z* when elimination is carried out with KO-*t*-Bu. [e] Prepared by methylation of the lithium enolate of **4** (R = Me). [f] Prepared by methylation of **4** (R = n-C$_8$H$_{17}$).

142.5, 123.3, 32.0, 30.3, 29.6, 29.4, 29.2, 27.6, 23.2, 22.8, 14.1, 13.3, 13.0; MS, 196 (9), 55 (100). The major product was 3-dodecanone (71%).

4-Propyltridec-4-ene (19). The title compound was produced in 8% yield as above: ^{1}H NMR δ 5.2 (t, 1 H, J = 7.1 Hz), 2.1–1.9 (m, 6 H), 1.3 (bs, 12 H), 0.85 (m, 9 H); ^{13}C NMR δ 139.0, 125.3, 39.1, 32.1, 31.9, 30.2, 29.6, 29.4, 29.3, 27.7, 22.7, 21.7, 21.4, 14.2, 14.1, 14.0; MS, 224 (17), 70 (100). The major product was 4-tridecanone formed in 78% yield.

4-Allyltrideca-1,4-diene (20). The reaction of 6 mmol of allylmagnesium bromide with 2 mmol of **4** (R = n-C$_8$H$_{17}$) at reflux for 21 h gave 84% of the title compound: $n_D{}^{20}$ 1.4621; IR (neat) 1635 cm^{-1}; ^{1}H NMR δ 6.15–5.51 (m, 2 H), 5.24 (t, 1 H, J = 6.1 Hz), 5.25–5.05 (m, 2 H), 5.00 (m, 2 H), 2.82–2.67 (bt, 2 H, J = 5.3 Hz), 2.20–1.80 (m, 2 H), 1.26 (bs, 12 H), 0.82 (bt, 3 H); ^{13}C NMR δ 137.1, 136.2, 135.0, 127.5, 115.7, 115.1, 41.4, 34.6, 32.0, 30.0, 29.6, 29.4, 27.9, 14.1; MS, 220 (not observed) 41 (100). Anal. Calcd for C$_{16}$H$_{28}$; C, 87.27; H, 12.73. Found: C, 87.09; H, 12.85.

General Procedure for Reaction with a Grignard Reagent Followed by an Organolithium Reagent. The α-silyl ester was reacted with 2 equiv of Grignard reagent in THF at reflux, the reaction was cooled to 0 °C, and 3 equiv of lithium reagent in ether were added followed by a 24-h reflux period. The reaction was cooled to room temperature and 9 equiv of KO-*t*-Bu was added, and the reaction was refluxed for 1 h. Workup as before gave the olefins.

5-Butyltetradec-5-ene (21). Title compound produced in 19% yield: $n_D{}^{20}$ 1.4495; ^{1}H NMR δ 5.17 (t, 1 H, J = 7.0 Hz), 2.21–1.70 (m, 6 H), 1.26 (bs, 20 H), 1.05–0.73 (m, 9 H); ^{13}C NMR δ 139.5, 124.8, 36.8, 32.0, 30.9, 30.6, 30.3, 29.8, 29.6, 29.4, 27.8, 23.0, 22.8, 22.6, 14.1; MS, 252 (25), 55 (100). 5-Tetradecanone was produced in 78% yield.

(*E*)-4-Methyltridec-4-ene (22). Treatment of **4** (R = n-C$_8$H$_{17}$) with n-propylmagnesium bromide followed by methyllithium as above gave 55% yield of the title compound: $n_D{}^{20}$ 1.4420; ^{1}H NMR δ 5.14 (tq, 1 H, J = 7.0 Hz, 1.22 Hz), 1.97 (t, 4 H), 1.60 (s, 3 H), 1.36 (bs, 14 H), 0.90 (bt, 3 H); ^{13}C NMR δ 134.8, 124.8, 41.9, 31.9, 30.0, 29.6, 29.4, 27.9, 22.7, 21.0, 15.8, 14.1, 13.7; MS, 196 (24), 55 (100). Anal. Calcd for C$_{14}$H$_{28}$: C, 85.71: H, 14.29. Found, C, 85.63: H, 14.35. GC–MS analysis with a capillary columnm (15 m SE-30) showed the sample to have an *E*:*Z* ratio of greater than 99:1. This same column separated a 70:30 *E*:*Z* mixture formed by boron fluoride etherate elimination (see text).

11-Methyldodeca-1,10-diene (23). The title compound was formed in 56% yield: $n_D{}^{20}$ 1.4479; ^{1}H NMR δ 6.02–5.59 (m, 1 H), 5.21–4.86 (m, 3 H), 2.30–1.75 (m, 4 H), 1.68 (bs, 3 H), 1.59 (bs, 3 H) 1.30 (bs, 10 H); ^{13}C NMR δ 139.2, 131.0, 125.0, 114.2, 33.9, 30.0, 29.5, 29.4, 29.3, 29.0, 28.1, 25.7, 17.7; MS, 180 (7), 69 (100).

1,1-Diphenyl-2-methylpropene (24). The title compound was formed in 70% yield: $n_D{}^{16}$ 1.5950; ^{1}H NMR δ 7.22 (s, 10 H), 1.78 (s, 6 H); ^{13}C NMR δ 143.3, 137.2, 135.3, 130.9, 129.8, 128.7, 127.8, 127.1, 126.0, 22.4, MS, 208 (80), 115(100).

2-Methyl-3-butylhept-2-ene (25). The title compound was formed in 60% yield: $n_D{}^{20}$ 1.4415; ^{1}H NMR δ 2.20–1.89 (m, 4 H), 1.64 (s, 6 H), 1.48–1.07 (m, 8 H), 0.88 (bt, 6 H); ^{13}C NMR δ 133.2, 123.9, 32.3, 31.2, 23.0, 20.2, 14.1; MS, 168 (17), 83 (100). Anal. Calcd for C$_{12}$H$_{24}$: C, 85.71: H, 14.29. Found: C, 85.61: H, 14.36.

2-Methyl-3-*n*-hexylnon-2-ene (26). The title compound was formed in 44% yield, purified by preparative GLC (3% SE-30); $n_D{}^{20}$ 1.4540; ^{1}H NMR δ 2.20–1.7 (m, 4 H), 1.64 (s, 6 H), 1.28 (bs, 16 H), 1.05–0.70 (bt, 6 H); ^{13}C NMR δ 133.2, 123.9, 32.6, 31.9, 29.7, 28.9, 22.7, 20.2, 14.1; MS, 224 (41), 8 (100). Anal. Calcd for C$_{16}$H$_{32}$: C, 85.71: H, 14.29. Found: C, 85.54; H, 14.32.

2,3-Dimethyl-2-undecene (27). This compound was formed in 12% yield and identified by GC–MS only.

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Registry No. **4** (R = Me), 77772-22-6; **4** (R = Et), 89638-15-3; **4** (R = n-C$_8$H$_{17}$), 89638-16-4; **4** (R = CH$_2$ = CH(CH$_2$)$_7$), 89968-59-2; **6** (R^1 = R^2 = Me), 91413-17-1; **6** (R^1 = n-C$_8$H$_{17}$, R^2 = Me), 91586-15-1; **11**, 778-66-5; **12**, 91586-16-2; **13**, 91586-17-3; **14**, 40558-71-2; **15**, 1726-14-3; **16**, 1530-27-4; **17**, 56888-88-1; **18**, 68066-08-0; **19**, 91586-18-4; **20**, 91586-19-5; **21**, 91586-20-8; (*E*)-**22**, 91586-21-9; (*Z*)-**22**, 91586-22-0; **23**, 18625-77-9; **24**, 781-33-9; **25**, 91586-23-1; **26**, 91586-24-2; **27**, 91586-25-3; PhBr, 108-86-1; n-C$_5$H$_{11}$Br, 110-53-2; n-C$_6$H$_{13}$Br, 111-25-1; PhCH$_2$Cl, 100-44-7; MeI, 74-88-4; EtI, 75-03-6; n-C$_3$H$_7$Br, 106-94-5; C$_3$H$_5$Br, 106-95-6; n-C$_4$H$_9$Br, 109-65-9; PhLi, 591-51-5; MeLi, 917-54-4; n-C$_4$H$_9$Li, 109-72-8; ethyl 2-(trimethylsilyl)propionate, 13950-55-5.

Oxidation of 4-Aryl-Substituted Isoxazolin-5-ones. A New Synthesis of 2,5-Diaryl-1,3-oxazin-6-ones

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The oxidation of a large number of 3,4-disubstituted isoxazolin-5-ones has been achieved with active manganese dioxide as well as with peroxyformic acid. In the first case