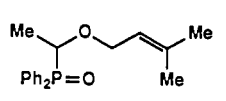
The stereospecific enzymic conversion of **4** to **5** implies the intermediacy of cation **6** for this cyclization and suggests an analogous intermediate (**7**) for the enzymic conversion of 2,3-oxidosqualene to lanosterol. This finding removes the need to invoke covalent binding of C(20) to the cyclase in lanosterol biosynthesis from 2,3-oxidosqualene, since the initially formed conformation of the protosterol C(20) cation can lead to the natural C(20) configuration via a least motion pathway involving only a small (<60°) rotation about the C(17)-C(20) axis.



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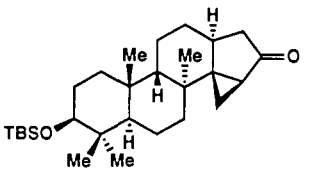

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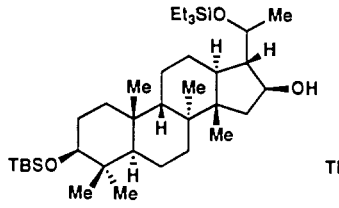
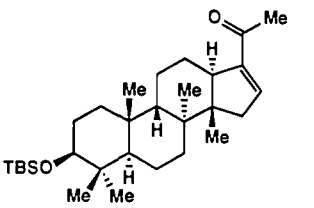


11



12

Substrate **4** was synthesized from epoxy aldehyde **8**[5b,11] and phosphine oxide **9**[12] by the following sequence: (1) conversion of **9** to the lithio derivative (LDA in THF at -90 °C) and reaction with the aldehyde **8** at -90 °C for 15 min to give after extractive isolation a 1.3:1 mixture (88% yield) of two diastereomeric β-hydroxy phosphine oxides; (2) chromatographic separation on silica gel-1% H_2O using ether-H_2O (100:1) to elute the minor diastereomer, R_f 0.51 (ether), and the major diastereomer, R_f 0.35 (ether); (3) reaction of the major diastereomer with NaH-NaOH-THF at 23 °C for 24 h to form **4** stereoselectively in 93% yield.[13] Radiolabeled **4** containing tritium at C(18) was synthesized from 1-tritiated aldehyde **8**.

The enzymic cyclization product **5** was synthesized as the 3-TBS ether from the previously synthesized protosterol precursor **10**.[6] Ketone **10** was converted to the triol derivative **11** by existing methodology[6] using acetaldehyde as an aldol component. Intermediate **11** was transformed into enone **12** in 88% overall yield by the following sequence: (1) mesylation ($MeSO_2Cl$, Et_3N, CH_2Cl_2, 0 °C, 1h); (2) cleavage of triethylsilyl (1% CF_3CO_2H in THF-H_2O, 23 °C, 6 h); (3) oxidation (pyridinium chlorochromate-Al_2O_3, CH_2Cl_2, 23 °C, 6 h); and (4) elimination (KO-*t*-Bu-THF, 23 °C, 3 h). Reduction of enone **12** by 4 equiv of lithium in 1:1 THF-liquid NH_3 containing 2 equiv of H_2O[6] at -35 °C for 2 min afforded the 3-TBS ether of **5** (30%) and the less polar 17α-epimer (52%, mp 190-192 °C).[14]

In conclusion, this work has revealed that the enzymic conversion of 2,3-oxidosqualene (**1**) to lanosterol proceeds by the cyclization of **1** to a protosterol intermediate having a β-oriented side chain at C(17), as in **7**. The long-held alternative **2**[2] is untenable, and it is unnecessary to postulate covalent attachment[3] of the intermediate protosterol to the cyclase enzyme.[15]

Supplementary Material Available: Syntheses of **8** and **4** from squalene, enzymic preparation of **5** and identification of its *tert*-butyldimethylsilyl ether derivative, and preparation of totally synthetic *tert*-butyldimethylsilyl ether derivatives of **5** and 17α-acetylprotosterol (21 pages). Ordering information is given on any current masthead page.

(11) A convenient large-scale synthesis of **8** is described in the supplementary material.

(12) (a) The phosphine oxide **9** was synthesized by the following sequence: (1) reaction of 3-methyl-2-butenyl vinyl ether (Boeckman, R. K., Jr.; Ko, S. S. *J. Am. Chem. Soc.* **1982**, *104*, 1033-1041) with triphenylphosphonium bromide in THF at 23 °C and (2) treatment with aqueous NaOH at 45 °C (see: Ley, S. V.; Lygo, B.; Organ, H. M.; Wonnacott, A. *Tetrahedron* **1985**, *41*, 3825-3836). (b) See also: Ceruti, M.; Viola, F.; Dosio, F.; Cattel, L.; Bouvier-Navé, P.; Ugliengo, P. *J. Chem. Soc., Perkin Trans. 1* **1988**, 461-469.

(13) The *Z* isomer of **4** was similarly obtained from the minor diastereomeric β-hydroxy phosphine oxide. The stereochemistries of **4** and the *Z* isomer were assigned from NOE experiments.

(14) The R_f values for **5** and the 17-epimer determined by using silica gel with 1:3 ether-hexane were 0.53 and 0.49, respectively. The configuration at C(17) of **5** follows from the quantitative base-catalyzed conversion to the 17-epimer and also from X-ray diffraction data, to be published separately.

(15) We are indebted to Mr. Seiichi P. T. Matsuda for his assitance in the preparation of microsomal cyclase and to Prof. Ian Scott of Texas A and M University for information on the stability of the yeast cyclase as a function of pH. This research was assisted financially by a grant from the National Institutes of Health and an NSF graduate fellowship to S.C.V.

Highly Enantioselective and Diastereoselective Ireland-Claisen Rearrangement of Achiral Allylic Esters

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The Ireland-Claisen rearrangement of allylic esters, as silyl enol ethers,[1] has found broad application in synthesis especially because of its diastereoselectivity when two adjacent stereocenters are produced. Reported here is the first enantioselective version of this process with achiral esters, which depends on a readily available and recyclable chiral boron reagent.[2] A number of other approaches to enantioselective aza-Claisen and acetal Claisen rearrangements, mainly using chiral substrates, have been described recently.[3-5]

The chiral bromoborane **1** (or its enantiomer) has been employed previously for the conversion of propionate esters to either of the isomeric enolates.[2a] In a similar way, the reagent **1** can be used to convert (*E*)-crotyl propionate (**2**) to either the (*E*,*E*)-enolate (**3**) or the (*E*,*Z*)-enolate (**4**) simply by a change of the solvent and the tertiary amine used for enolate formation (Scheme I). The (*E*)-enolate **3** [formed in 24 h at -78 °C in CH_2Cl_2 with $(i\text{-Pr})_2NEt$ as base] and the (*Z*)-enolate **4** (formed in 24 h at -78 °C in 1:2 toluene-hexane with Et_3N as base) undergo Claisen rearrangement upon storage at -20 °C for 14 days to afford Claisen rearrangement products in good yield after aqueous workup, along with the recovered bis-sulfonamide precursor of bromoborane **1**, which was efficiently recovered for reuse. The reaction in CH_2Cl_2 via **3** produced the threo acid **5** (75% yield) of >97% ee and with 99:1 threo-erythro selectivity, whereas the reaction in toluene-hexane via **4** gave the erythro acid **6** (65%) in 96% ee and with 90:10 erythro-threo selectivity.[6]

The scope of this enantioselective Claisen rearrangement was evaluated by the study of the examples summarized in Tables I and II. The Claisen rearrangements of various allylic propionate and butyrate esters generally proceed with remarkably high enantioselectivity, and in many cases the analytical method could not detect enantiomeric contamination. Lower enantioselectivities

(1) Ireland, R. E.; Mueller, R. H.; Willard, A. K. *J. Am. Chem. Soc.* **1976**, *98*, 2868-2877.

(2) (a) Corey, E. J.; Kim, S. S. *J. Am. Chem. Soc.* **1990**, *112*, 4976-4977. (b) Corey, E. J.; Imwinkelried, R.; Pikul, S.; Xiang, X. B. *J. Am. Chem. Soc.* **1989**, *111*, 5493-5495.

(3) Aza-Claisen rearrangement: (a) Kurth, M. J.; Decker, O. H. W.; Hope, H.; Yanuck, M. D. *J. Am. Chem. Soc.* **1985**, *107*, 443-448. (b) Bailey, P. D.; Harrison, M. J. *Tetrahedron Lett.* **1989**, *30*, 5341-5344.

(4) Phosphonate anion Claisen rearrangement: Denmark, S. E.; Marlin, J. E. *J. Org. Chem.* **1987**, *52*, 5742-5745.

(5) Catalytic Claisen silyl vinyl ether rearrangement: Maruoka, K.; Banno, H.; Yamamoto, H. *J. Am. Chem. Soc.* **1990**, *112*, 7791-7793.

(6) The determination of the ratio of erythro-threo diastereomers was made by GC analysis of the benzyl esters. The absolute configuration of **5** was determined by conversion to (*S*,*S*)-(-)-2,3-dimethylsuccinic anhydride; see: Berner, E.; Leonardsen, R. *Justus Liebigs Ann. Chem.* **1939**, *538*, 1-43. The absolute configuration of **6** is assigned by analogy with similar examples which follow.

0002-7863/91/1513-4026$02.50/0

Scheme I

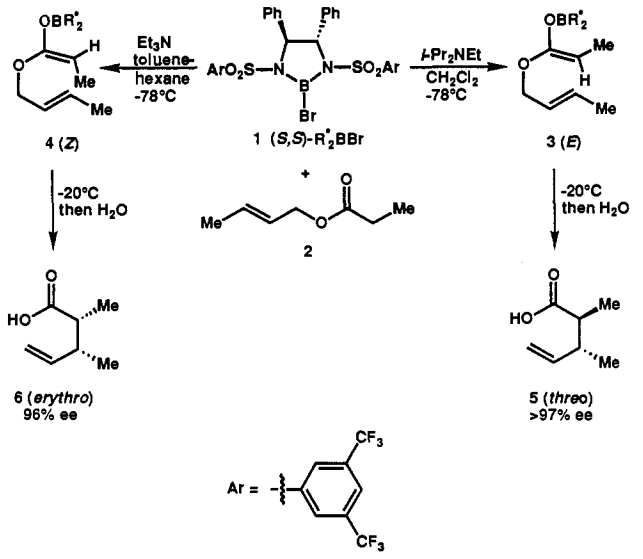
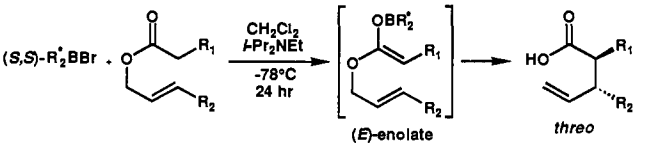


Table I. Enantioselective Claisen Rearrangement in CH_2Cl_2 via (*E*)-Boron Enolate



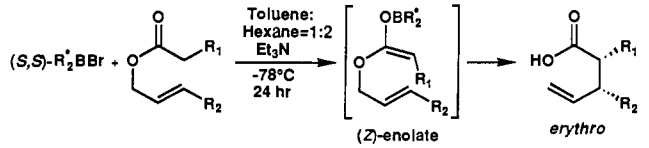
entry	R_1	R_2	yield,[a] %	threo:erythro[b]	ee,[c] %
1	Me	Me	75	99:1	>97[f]
2	Et	Me	79	98:2	95[d]
3	Me	Ph	75	91:9	95[f]
4	Et	Ph	72	91:9	>97[f]
5	Ph	Ph	100	23:77	>97[f]
6	SPh	Me	52	39:61	>97[f]
7	CH_2Ph	H	70		82[e]
8	CH_2-1-naphthyl	H	48		77[e]

[a] Reaction times at −20 °C: 14 days for entries 1, 2, 5, 7, and 8; 7 days for entries 3, 4, and 6. [b] Diastereomeric ratios determined by GC analysis of benzyl (entry 1) or methyl esters (entries 3–6) or by ^1H NMR analysis of benzyl ester (entry 2). [c] Ee values determined after reductioin to the corresponding primary alcohol and conversion to the MTPA ester by ^1H NMR (entries 1–5, 7, and 8) (see: Dale, J. A.; Mosher, H. S. *J. Am. Chem. Soc.* **1973**, *95*, 512–519) or by HPLC analysis of the methyl ester using a Daicel OJ column (entry 6). [d] Absolute configuration determined by ozonolysis and esterification to (2*S*,3*S*)-(+)-2-methyl-3-ethylsuccinic acid *p*-bromophenacyl ester and rotational correlation; see: Brockmann, H., Jr.; Muller-Enoch, D. *Chem. Ber.* **1971**, *104*, 3704–3710. [e] Correlated with a synthetic sample prepared by alkylation with $ArCH_2Br$ of the lithio derivative of 3-(4-pentenoyl)-4(*S*)-methyl-5(*R*)-phenyl-1,3-oxazolidin-2-one; see: Evans, D. A.; Ennis, M. D.; Mathre, D. J. *J. Am. Chem. Soc.* **1982**, *104*, 1737–1739. [f] Absolute configuration assigned by analogy with entries 2, 7, and 8.

were observed in the case of esters of allyl alcohol itself (entries 7 and 8 in Table I and entries 8 and 9 in Table II). In addition, for the rearrangement of esters of phenylacetic acid and α-(phenylthio)acetic acid via (*E*)-enolates (entries 5 and 6 in Table I), only moderate diastereoselectivities were found, although the rearrangements of the corresponding (*Z*)-enolates (entries 5–7 in Table II) proceeded with very good diastereoselectivity. Despite these occasional limitations, it is apparent that the methodology presented here is highly useful because of the very high stereoselectivity that can be realized and the easy recoverability of the chiral reagent.

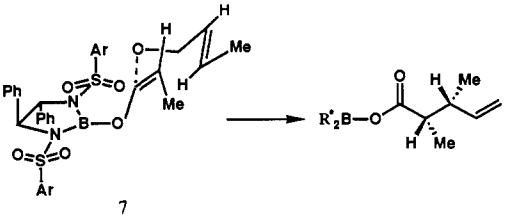
The diastereoselectivity of the Claisen rearrangements presented in Tables I and II is consistent with the assigned geometry of the intermediate boron enolate[2a] and the expectation of a preferred chair geometry for the transition state.[7] The absolute configuration of the rearrangement products agrees with predictions based upon the sterically more favorable chair transition state, which for the *S,S* boron reagent **1** is easily discerned from inspection of molecular models to be that shown in formula **7**.

Table II. Enantioselective Claisen Rearrangement in Toluene–Hexane via (*Z*)-Boron Enolate



entry	R_1	R_2	yield,[a] %	erythro:threo[b]	ee,[c] %
1	Me	Me	65	90:10	96[h]
2	Et	Me	79	89:11	>97[d]
3	Me	Ph	88	96:4	>97[h]
4	Et	Ph	69	95:5	>97[h]
5	Ph	Ph	100	98:2	>97[e]
6	SPh	Me	56	95:5	>97[f]
7	SPh	Ph	45	91:9	>97[f]
8	CH_2Ph	H	57		84[g]
9	CH_2-1-naphthyl	H	63		79[g]

[a] Reaction times at −20 °C: 14 days for entries 1, 2, 5, and 7–9; 7 days for entries 3, 4, and 6. [b] Diastereomeric ratios determined by GC analysis of benzyl (entry 1) or methyl esters (entries 3–6), by ^1H NMR analysis of benzyl ester (entry 2), or by HPLC analysis of methyl ester using Du Pont Zorbax silica gel column (entry 7). [c] Ee values determined after reduction to the corresponding primary alcohol and conversion to the MTPA ester by ^1H NMR (entries 1, 3, 4, 5, 8, and 9) or by GC analysis (entry 2) (see: Dale, J. A.; Mosher, H. S. *J. Am. Chem. Soc.* **1973**, *95*, 512–519) or by HPLC analysis of the methyl ester using a Daicel OJ column (entry 6 and 7). [d] Absolute configuration determined by ozonolysis and esterification to (2*S*,3*R*)-(−)-2-methyl-3-ethylsuccinic acid *p*-bromophenacyl ester and rotational correlation; see: Brockmann, H., Jr.; Muller-Enoch, D. *Chem. Ber.* **1971**, *104*, 3704–3710. [e] Absolute configuration determined by ozonolysis, reduction, and lactonization to (2*S*,3*R*)-(−)-2,3-diphenylbutyrolactone, epimerization to (2*R*,3*R*)-(−)-2,3-diphenylbutyrolactone, and rotational correlation; see: Berova, N. D.; Kurter, B. J. *Tetrahedron* **1969**, *25*, 2301–2311. [f] Absolute configuration determined by conversion to (3*R*)-(−)-3-methyl- or -phenyl-1-pentyl benzoate and rotational correlation with synthetic samples, which were prepared from the commercially available (2*S*)-(−)-2-methyl-1-butanol or (2*S*)-(+)-2-phenyl-1-butyric acid. [g] Correlated with a synthetic sample prepared by alkylation with $ArCH_2Br$ of the lithio derivative of 3-(4-pentenoyl)-4(*S*)-methyl-5(*R*)-phenyl-1,3-oxazolidin-2-one; see: Evans, D. A.; Ennis, M. D.; Mathre, D. J. *J. Am. Chem. Soc.* **1982**, *104*, 1737–1739. [h] Absolute configuration assigned by analogy with entries 2 and 5–9.



7

Although the Claisen rearrangement is slow at −20 °C, as indicated in Tables I and II, we have found in our most recent experiments that rearrangement of several substrates cited in these tables can be conducted at +4 °C and for shorter times with no significant loss of stereoselectivity. For example, the reaction of entry 3 in Table I requires only 3.5 days at +4 °C and affords threo product in >97% ee, and the reaction corresponding to entry 5 in Table II requires only 2 days at +4 °C and provides erythro product in >97% ee. The following procedure is illustrative.

(2*S*,3*R*)-Diphenyl-4-pentenoic Acid. To a 10-mL, flame-dried, nitrogen-filled, round-bottomed flask was added rapidly (*S,S*)-1,2-bis[[3,5-bis(trifluoromethyl)phenyl]sulfonylamino]-1,2-diphenylethane (100 mg, 0.13 mmol), and the flask was closed with

(7) For a review, see: Hill, R. K. In *Asymmetric Synthesis*; Morrison, J. D., Ed.; Academic Press: New York, 1984; Vol. 3, pp 503–572.

a dry septum. After three cycles of evacuation and flushing with nitrogen, the sulfonamide was dissolved in dry dichloromethane (3 mL), boron tribromide solution in dichloromethane (0.5 M solution, 0.50 mL) was added, and the reaction mixture was stirred at room temperature for 24 h to form bromoborane **1**. Solvent was evaporated completely at 25 mmHg through calcium chloride and sodium hydroxide traps, and dry dichloromethane (3 mL) was added and evaporated in vacuo. After admission of nitrogen, toluene (4 mL) was added and the flask was warmed with a heat gun to dissolve **1**. After cooling to −78 °C (dry ice–acetone), cinnamyl phenylacetate (29.7 mL, 0.9 equiv) was added, the bath was removed to dissolve the solidified ester, and the mixture was recooled to −78 °C. Triethylamine (18.6 μL, 1.0 equiv) was added slowly at −78 °C. The reaction mixture was stirred at −78 °C for 24 h and stored at +4 °C for 2 days. The reaction mixture was quenched with aqueous acid (pH ca. 1) and stirred for 30 min. The organic layer was washed with water and extracted with dilute sodium hydroxide solution. Evaporation of the organic layer and silica gel chromatography furnished >85% recovery of the starting bis-sulfonamide. The aqueous layer was washed with ether, acidified with 10% hydrochloric acid, and extracted with ether. The organic layer was dried and evaporated to produce pure (2*S*,3*R*)-diphenyl-4-pentenoic acid (29.6 mg, 99%). This acid was transformed into the corresponding methyl ester with diazomethane.

R_f: 0.54 (hexane:ethyl acetate = 5:1). $[\alpha]_D$: +119.9° (*c* 1.46, $CHCl_3$). Mp: 127–128 °C. GC (DB1-30W capillary column from J & W Scientific, 25 m): 24.81 min at 140 °C. HPLC (Du Pont Zorbax silica gel): 8.62 min (hexane:ethyl acetate = 100:1, 2mL/min). IR (neat): 1736, 1266, 1180, 734 cm^{-1}. ^1H NMR (500 MHz, $CDCl_3$): δ 3.34 (s, 3 H), 3.92 (d, J = 11.6 Hz, 1 H), 4.00 (m, 1 H), 4.68 (d, J = 17 Hz, 1 H), 4.79 (d, J = 10 Hz, 1 H), 5.67 (m, 1 H), 7.20–7.40 (m, 10 H). FABMS: *m/e* 267 ($M + H^+$).[8]

Supplementary Material Available: Physical data on Claisen rearrangement products and experimental procedures for correlation of absolute configuration (22 pages). Ordering information is given on any current masthead page.

(8) This research was assisted financially by grants from the National Institutes of Health and the National Science Foundation.

Importance of Lewis Acid Mediated Electron Transfer in Mukaiyama–Michael Reaction of Ketene Silyl Acetals

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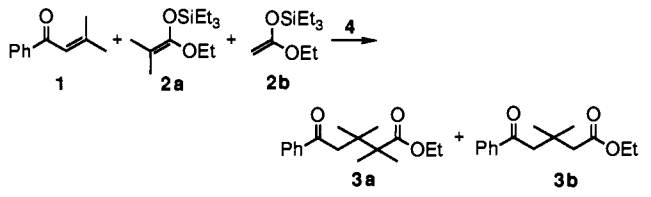
Ketene silyl acetals have received increasing attention in organic synthesis.[1] The Mukaiyama–Michael reaction of these compounds, in particular, offers a convenient route for 1,5-keto esters.[2] The importance of Lewis acids in promotion of this reaction has led one quite naturally to postulate initial nucleophilic attack of the ketene silyl acetal (or its transmetalation species) toward electrophiles. We disclose herein that this postulate is not always the case. Initial electron transfer plays a key role on some occasions, thus allowing smooth connection of contiguous quaternary carbon centers which would otherwise be difficult to achieve.[2,3]

Scheme I[a]



promotor **4**	yield,% **3a**	**3b**	**3a/3b**
4a (0.05 equiv)	85	0	100:0
4b (0.10 equiv)	95	0	100:0
4c (0.10 equiv)	93	0	100:0
4d (1.0 equiv)	98	2.4	97:3

[a] Reaction conditions: α-enone:ketene acetal:ketene acetal = 1:1:1, CH_2Cl_2, −78 °C, 4 h.

In the context of synthetic applications of organotin triflates as functional Lewis acids,[4] we conducted the crossover reaction of an equimolar mixture of ketene silyl acetal **2b** and its β,β-disubstituted derivative **2a** with a hindered α-enone **1** in the presence of a catalytic amount of $Bu_2Sn(OTf)_2$ (**4a**) (Scheme I). More sterically demanding **2a** reacted exclusively to give the adduct **3a** bearing contiguous quaternary carbon centers. The preference holds with other promotors, $SnCl_4$ (**4b**), Et_3SiClO_4 (**4c**),[5] and $TiCl_4$ (**4d**).[6]

These results cannot be interpreted in terms of the nucleophilic attack of ketene silyl acetals which should favor the coupling between less hindered carbons. In fact, RajanBabu revealed that the relevant thermal reaction in highly polar solvents which proceeds through nucleophilic attack of an ester enolate ion toward an α-enone exhibited a quite different tendency: crossover reaction of β,β-disubstituted and β-monosubstituted ketene silyl acetals with 2-cyclopentenone gave rise to the adducts derived from the respective ketene silyl acetals in a nearly equal ratio.[7] Since the preferred connection of more hindered carbons is characteristic of radical coupling,[3o] a plausible explanation is put forth by assuming an initial electron transfer. Scheme II representatively

(1) Gennari, C. *Selectivities in Lewis Acid Promoted Reactions*; Schinzer, D., Ed.; Kluwer Academic Publ.: Dordrecht, 1989; Chapter 4, p 53.

(2) Saigo, K.; Osaki, M.; Mukaiyama, T. *Chem. Lett.* **1976**, 163. Kobayashi, S.; Mukaiyama, T. *Chem. Lett.* **1986**, 1805. Kobayashi, S.; Mukaiyama, T. *Chem. Lett.* **1987**, 1183. Hashimoto, Y.; Sugumi, H.; Okauchi, T.; Mukaiyama, T. *Chem. Lett.* **1987**, 1691. Minowa, N.; Mukaiyama, T. *Chem. Lett.* **1987**, 1719. Kobayashi, S.; Tamura, M.; Mukaiyama, T. *Chem. Lett.* **1988**, 91.

(3) Coupling of α-keto or α-alkoxycarbonyl radicals: (a) Kharasch, M. S.; Mcbay, H. C.; Urry, W. H. *J. Am. Chem. Soc.* **1948**, *70*, 1269. (b) Moore, C. G. *J. Chem. Soc.* **1951**, 236. (c) Ansell, M. F.; Hickinbottom, W. J.; Holton, P. G. *J. Chem. Soc.* **1955**, 349. Coupling of enolates: (d) Rathke, M. W.; Lindert, A. *J. Am. Chem. Soc.* **1971**, *93*, 4605. (e) Chassin, C.; Schmidt, E. A.; Hoffmann, H. M. R. *J. Am. Chem. Soc.* **1974**, *96*, 606. (f) Ito, Y.; Konoike, T.; Saegusa, T. *J. Am. Chem. Soc.* **1975**, *97*, 649. (g) Kobayashi, Y.; Taguchi, T.; Morikawa, T.; Tokuno, E.; Sekiguchi, S. *Chem. Pharm. Bull.* **1980**, *28*, 262. (h) Inaba, S.-I.; Ojima, I. *Tetrahedron Lett.* **1977**, 2009. Oxidative coupling of α-lithiated allylic sulfones: (i) Julia, M.; Le Thuillier, G.; Roland, C.; Saussine, L. *Tetrahedron Lett.* **1982**, *23*, 2453. (j) Baudin, J.-B.; Julia, M.; Roland, C.; Verpeaux, J.-N. *Tetrahedron Lett.* **1984**, *25*, 3203. (k) Büchi, G.; Freidinger, R. M. *Tetrahedron Lett.* **1985**, *26*, 5923. (l) Amatore, C.; Thiebault, A.; Verpeaux, J.-N. *J. Chem. Soc., Chem. Commun.* **1989**, 1543. Friedel–Crafts reaction: (m) Chan, T. H.; Paterson, I.; Pinsonnault, J. *Tetrahedron Lett.* **1977**, 4183. (n) Baran, J.; Mayr, H. *J. Org. Chem.* **1988**, *53*, 4626. Substitution of nitro compounds: (o) Kornblum, N. *Angew. Chem., Int. Ed. Engl.* **1975**, *14*, 734. Claisen rearrangement: (p) Denmark, S. E.; Harmata, M. A. *Tetrahedron Lett.* **1984**, *25*, 1543. (q) Kraus, G. A.; Thomas, P. J. *J. Org. Chem.* **1986**, *51*, 503. (r) Gilbert, J. C.; Kelly, T. A. *J. Org. Chem.* **1986**, *51*, 4485. Addition of benzyllithiums to olefins: (s) Krief, A.; Barbeaux, P. *Synlett* **1990**, 511.

(4) Sato, T.; Otera, J.; Nozaki, H. *J. Am. Chem. Soc.* **1990**, *112*, 901. Sato, T.; Wakahara, Y.; Otera, J.; Nozaki, H. *Tetrahedron Lett.* **1990**, *31*, 1581.

(5) Lambert, J. B.; McConnell, J. A.; Schilf, W.; Schultz, W. J., Jr. *J. Chem. Soc., Chem. Commun.* **1988**, 455.

(6) The more substituted ketene silyl acetals were preferentially consumed in every crossover experiment of β,β-disubstituted, β-substituted, and unsubstituted ones. Use of mesityl oxide in place of **1** also resulted in the same selectivity (see the supplementary material).

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