(van der Waals) energy change upon twisting (indeed, in the case of the germanium analogue, the relative Pc–Pc staggering angle changes upon partial oxidation, from 0° to 40 (4)°).[4b] The experimental staggering angle in B of 36.6° and in $\{[Si(Pc)O]I_{1.1}\}_n$ of 39 (3)° comes very near to maximizing the magnitude of the bandwidth; this is important if the stabilizing effect of the partly filled band in the conductive polymer is to be large. More important for present purposes, the high sensitivity of the bandwidth to changes in twist angle implies that this mechanism will effectively scatter the conduction electrons and lead to substantial contributions to the resistivity.

It is clear from the present study that experimental work which either raises the frequency of these two modes or reduces the sensitivity of bandwidth to them will reduce the resistivity. Such work is presently under way in our laboratory.

The success of the Wolfsberg–Helmholtz approximation for calculating H_{12} and the geometry dependence thereof has interesting consequences. It implies that future electronic structure studies need calculate only the monomeric subunit of any π-type conductive chain; the expansion of the HOMO in a Gaussian basis as in eq 1 and subsequent calculations using eq 2 and 3 should lead to accurate calculations of exchange integrals and, therefore, of the tight-binding bandwidths. This use of (far simpler) monomer calculations to replace either dimer studies or bandwidth calculations should greatly enhance the value of electronic structure calculations as a screening tool for characterizing and mechanistically understanding linear-chain conductors.

Acknowledgment. We are grateful to the Chemistry Division of the NSF and to the ONR for partial support of this work, which was also partially supported by the Materials Research Division of the NSF through the Northwestern MRL (NSF Grant No. DMR82-16972). We are grateful to K. Doris, P. Hale, N. S. Hush, and B. M. Hoffman for helpful remarks and to D. E. Ellis and F. Kutzler for advice in the use of the DVM method.

Registry No. $[Si(Pc)O]_n$, 39114-20-0; HOSi(Pc)OH, 19333-15-4.

Stereospecific Formation of Enolates from Reaction of Unsymmetrical Ketenes and Organolithium Reagents

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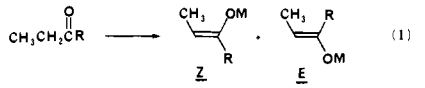
Abstract: Reaction of unsymmetrical ketenes RR′C=C=O (**4**, R, R′ = $CMe_2(CH_2)_4$; **8**, R = Ph, R′ = Me; **9**, R = Ph, R′ = Et; **10**, R = Me_3Si, R′ = Et; **11**, R = *t*-Bu, R′ = H) with organolithiums R″Li (R″ = *n*-Bu, Ph, *t*-Bu, CH_2=CH, HC≡C) followed by silylation with Me_3SiCl gave stereospecific formation of a single silyl enol ether in each case. This result is interpreted in terms of preferential attack by the organolithium reagent in the plane of the ketene from the side opposite the more sterically demanding group. Enolization/silylation of several ketones was carried out and was found to yield additional regio- and stereoisomeric enol ethers besides those formed from the ketenes. Thus the ketene route provides a stereospecific route to silylated enolates that are generally not formed with high selectivity by ketone silylation. Furthermore, a variety of different groups have been incorporated selectively at the different positions of the products. This methodology for stereoselective generation of highly substituted enolate derivatives offers significant advantages over others recently communicated. Hydrolysis of the product (*Z*)-Me_3SiCEt=C(OSiMe_3)-*n*-Bu (**15**) gave EtCH($SiMe_3$)CO-*n*-Bu (**29**), so the ketene methodology also is an attractive method for preparation of such α-silyl ketones.

The generation of enolates and silyl enol ethers of defined *E*/*Z* stereochemistry at the carbon–carbon double bond is of significant practical importance, as the geometry of these species plays an important role in determining the stereochemistry of the products formed from their aldol reactions under conditions of kinetic control.[1]

There have been a number of recent attempts to control the stereochemistry of enolates, or of silyl enol ethers that may be used to generate enolates. For example, enolization of 3-pentanone (**1**, R = Et) with $Me_3SiCH_2CO_2Et$ and *n*-Bu_4NF gives the *Z* enol silyl ether with more than 99% selectivity,[2] and the *Z*/*E* ratio of enolates from this ketone is 30/70, 2/98, and 100/0, using the bases *i*-Pr_2NLi, *t*-Bu(*t*-octyl)NLi, and $(Me_2PhSi)_2NLi$, respectively (eq 1).[3,4] When R in **1** is large (Ph, *t*-Bu), several bases



(1)

gave the *Z* enolate with 100% selectivity,[3] and in some cases enhanced selectivity for the *E* isomer occurred in the presence of Me_3SiCl to trap the initial enolate formed during the proton abstraction by amide bases.[4b] It was also found possible for particular cases to form *E* and *Z* boron enolates selectively.[5]

There has been considerable discussion[4b,6a,b] as to the origin of the preference for formation of *E* enolates in proton abstraction by bulky lithium dialkylamides in THF, and the model **2** originally proposed by Ireland and co-workers[6b] appears to be the most useful for this purpose.

(1) (a) Dubois, J. E.; Fellmann, P. *Tetrahedron Lett.* **1975**, *16*, 1225–1228. (b) Heathcock, C. H. *Science* **1981**, *214*, 395–400. (c) Brownbridge, P. *Synthesis* **1983**, 1–28. (d) Heathcock, C. H. In "Asymmetric Synthesis"; Morrison, J. D., Ed.; Academic Press: New York, 1983; Vol. 3. (e) Mukaiyama, T. *Org. React.* **1982**, *28*, 203–331. (f) Bartlett, P. A. *Tetrahedron* **1980**, *36*, 3–72. (g) Evans, D. A. *Top. Stereochem.* **1982**, *13*, 1–115. (h) Heathcock, C. H. In "Comprehensive Carbanion Chemistry: Part B. Selectivity in Carbon–Carbon Bond Forming Reactions"; Buncel, E., Durst, T., Eds.; Elsevier: New York, 1984.

(2) (a) Nakamura, E.; Hashimoto, K.; Kuwajima, I. *Tetrahedron Lett.* **1978**, *19*, 2079–2082. (b) Kato, M.; Mori, A.; Oshino, H.; Enda, J.; Kobayashi, K.; Kuwajima, I. *J. Am. Chem. Soc.* **1984**, *106*, 1773–1778. See also: Hudrlik, P. F.; Hudrlik, A. M.; Kulkarni, A. K. *Ibid.* **1985**, *107*, 4260–4264.

(3) Heathcock, C. H.; Buse, C. T.; Kleischick, W. A.; Pirrung, M. C.; Sohn, J. E.; Lampe, J. *J. Org. Chem.* **1980**, *45*, 1066–1081.

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(5) (a) Evans, D. A.; Nelson, J. V.; Vogel, E.; Taber, T. R. *J. Am. Chem. Soc.* **1981**, *103*, 3099–3111. (b) Van Horn, D. E.; Masamune, S. *Tetrahedron Lett.* **1979**, *20*, 2229–2232. (c) Hooz, J.; Oudenes, J. *Ibid.* **1983**, *24*, 5695–5698.

(6) (a) Narula, A. S. *Tetrahedron Lett.* **1981**, *22*, 4119–4122. (b) Ireland, R. E.; Mueller, R. H.; Willard, A. K. *J. Am. Chem. Soc.* **1976**, *98*, 2868–2877. (c) Tamaru, Y.; Hioki, T.; Kawamura, S.; Satomi, H.; Yoshida, Z. *Ibid.* **1984**, *106*, 3876–3877. For a recent discussion of stereoselection in enolate formation see: Moreland, D. W.; Dauben, W. G. *Ibid.* **1985**, *107*, 2264–2273.

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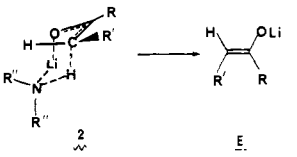
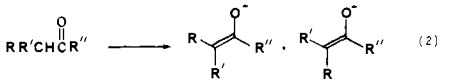
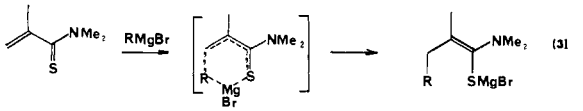


The R′ avoids the large coordinated oxygen so the H occupies the position shown near the bulky R″ group on the base and is consequently syn to the oxygen in the enolate. It has recently been shown by Corey and Gross[4b] that a decreased preference for formation of the *E* isomer (eq 1) in the presence of HMPA is due to equilibration of the initially formed enolate to favor the thermodynamically more stable *Z* isomer. Narula[6a] criticized model **2** because the base does not attack along the C–H axis in this structure, but his alternative model fails to account for the demonstrated[4,6a,b] effect of the bulk of the amide substituents R″. A somewhat flattened form of **2** would bring the base more nearly colinear with the C–H bond and would still preserve this important steric role of the groups R″.

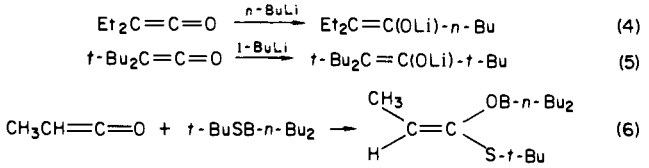
However, despite the effort which has been expended in these efforts, general procedures for the stereoselective generation of tetrasubstituted enolates or silyl enol ethers by proton abstraction from secondary carbons (eq 2) are not available, and the development of new strategies for the formation of such enolates and enol ethers is a desirable goal.



A different approach to the synthesis of more highly substituted enolates was reported very recently and involves addition of Grignard reagents to *N,N*-dimethyl-α-methacrylothioamide (eq 3).[6c] High stereoselectivity was observed and was ascribed to the intervention of a cyclic transition state to favor the *Z* isomers shown which then gave stereoselective aldol reactions. However, this approach does not satisfy the requirement of selectivity forming ketone enolates **3** with flexibility in the choice and stereochemistry of the three R groups.

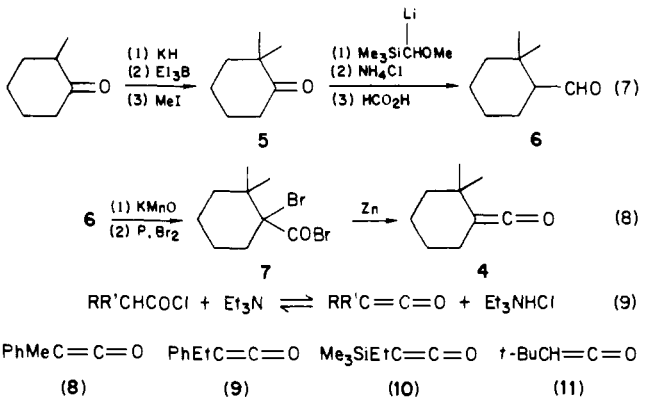


It has been found in previous work in this laboratory that the addition of alkyllithium reagents to ketenes provides a regioselective synthesis of enolates (eq 4) capturable as silyl enol ethers that are not the favored isomers formed from ketone enolization under either kinetic or thermodynamic conditions.[7a,d] Furthermore, in certain cases enolates can be formed from ketenes and alkyllithium reagents (eq 5) even though all attempts to form these enolates by proton abstraction form the corresponding ketones have so far been unsuccessful.[7b] Also an example has been recorded where stereospecific attack on methylketene by a sulfur nucleophile took place (eq 6).[7c] Therefore it appeared that the reactions of unsymmetrical ketenes with organolithiums could provide a novel and general method for the generation of ketone enolates of defined stereochemistry, and the present investigation was undertaken to explore this possibility.

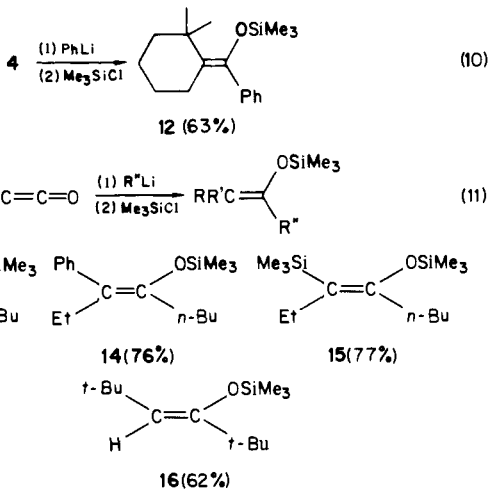


Results and Discussion

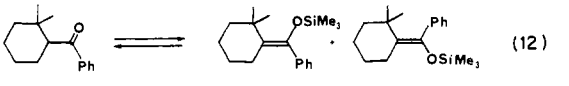
Ketene **4** was obtained by the sequence shown in eq 7 and 8, and methylphenylketne (**8**),[8] ethylphenylketene (**9**),[8,9] and ethyl(trimethylsilyl)ketene (**10**) were prepared from their acyl chlorides (eq 9) and *tert*-butylketene (**11**)[10] was also formed by Zn debromination. Ketenes **4** and **8–11** were reasonably stable at room temperature in the absence of air or water, but they showed varying degrees of decomposition on distillation so were usually filtered and then utilized for further reactions directly in the solutions in which they were formed.



Reaction of the ketenes with organolithium reagents followed by quenching with Me_3SiCl gave a single enol trimethylsilyl ether in each case (eq 10 and 11) with the stereochemistry of the products **12–16** assigned as shown with the indicated yields based on the precursor acyl halides.



For comparative purposes in the structure elucidation the ketone **17** was silylated under standard conditions (eq 12).[11] Thus reaction of **17** with KH in THF followed by Me_3SiCl gave the silyl ethers **12** and **18** in relative yields of 55 and 45%, respectively. These conditions have been proposed[11a] to correspond to the equilibrium mixture of the enolate precursors. However, reaction of **17** with *i*-Pr_2NLi in THF at −78 °C followed by Me_3SiCl gave only **18**; these conditions have been proposed[11b] to occur with kinetic control of the formation of enolate.



The assignment of stereochemistry for **12** and **18** is based on their spectral properties. Thus the structurally related 2-*tert*-

(7) (a) Tidwell, T. T. *Tetrahedron Lett.* **1979**, *20*, 4615–4618. (b) Lenoir, D.; Seikaly, H. R.; Tidwell, T. T. *Ibid.* **1982**, *23*, 4987–4990. (c) Hirama, M.; Masamune, S. *Ibid.* **1979**, *20*, 2225–2228. (d) Baigrie, L. M.; Lenoir, D.; Seikaly, H. R.; Tidwell, T. T. *J. Org. Chem.* **1985**, *50*, 2105–2109.

(8) Kresze, G.; Runge, E.; Ruch, E. *Justus Liebigs Ann. Chem.* **1972**, *756*, 112–127.

(9) Brady, W. T.; Dorsey, R. D.; Parry, F. H., III *J. Org. Chem.* **1969**, *34*, 2846–2848.

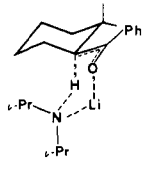
(10) Brady, W. T.; Ting, P. L. *J. Org. Chem.* **1976**, *41*, 2336–2339.

(11) (a) Brown, C. A. *J. Org. Chem.* **1974**, *39*, 3913–3918. (b) House, H. O.; Czuba, L. J.; Gall, M.; Olmstead, H. D. *J. Org. Chem.* **1969**, *34*, 2324–2336.

butylstyrenes *t*-BuCH=CHPh show a UV λ_{max} of 220 nm (ϵ 6400) for the *Z* isomer and 251 nm (ϵ 18 100) for the *E* isomer.[12] The corresponding values are 230 nm (ϵ 4500) for the isomer **18** and 245 nm (ϵ 24 000) for the isomer **12**. Evidently the presence of a bulky alkyl group cis to the phenyl group results in twisting of the phenyl group out of conjunction and causes a concomitant shift of the absorption maximum to shorter wavelength.

The ^{1}H NMR shifts of the methyls in **12** and **18** are δ 1.24 and 0.85, respectively, as compared to values of 1.09 and 0.95 for the *tert*-butyl groups in the (*E*)- and (*Z*)-2-*tert*-butylstyrenes, respectively.[12] The twisting of the phenyl ring in **18** and in (*Z*)-2-*tert*-butylstyrene places the methyl protons in the shielding region of the phenyl ring so they absorb at relatively high field. The downfield shift of the methyl protons in **12** is the normal effect for protons cis to the oxygen of a vinyl ether,[13] but comparison with reported[7b,14,15] values for some β-*tert*-butylvinyl ethers suggests the effect may be somewhat enhanced in **12** because bond rotation of the methyls away from the oxygen is precluded by the cyclic structure.

Some further confirmation of the stereochemistry of **12** and **18** comes from the observation that reaction of **17** with *i*-Pr_2NLi followed by silylation gives only **18**. In the reaction of ketones with lithium amide bases the enolate is formed under conditions of kinetic control and frequently gives a high selectivity for formation of one stereoisomer,[11b] as predicted by the transition-state model **2**.[4,6b] The chair transition-state models **19**, with axial proton removal, and **20** with equatorial proton removal analogous to **2**, would each lead to the enolate corresponding to **18**, and are dominated by the avoidance of the interaction of the isopropyl groups of the base and the ring methyls.



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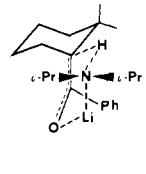
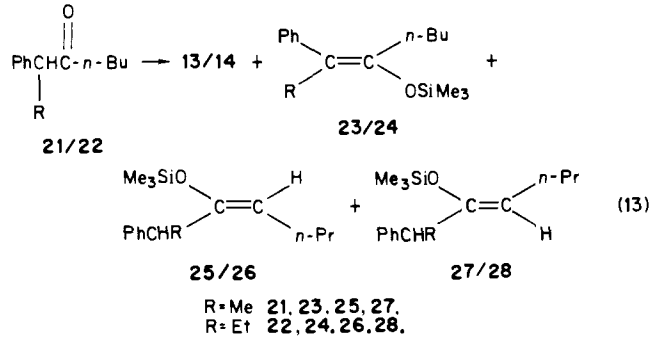


20

The preferential formation of **13** and **14** from the reaction of *n*-BuLi with the ketenes **8** and **9**, respectively, was anticipated on the basis that attack would occur preferentially anti to the larger phenyl group (vide infra). For comparative purposes the ketones **21** and **22** were silylated to give the silyl vinyl ethers **23–28** (eq 13) in addition to **13** and **14**.



(13)

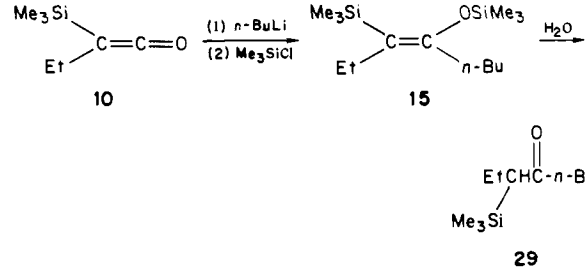
Reaction of **21** with KH/Me_3SiCl gave **13** and **23** in relative yields of 60 and 40%, respectively, and **22** gave **14** and **24** in relative yields of 85 and 15%, respectively. As expected these conditions of equilibrium control give the conjugated derivatives, and the preference for formation of the isomers with the phenyl group cis to the oxygen indicates either that these are the favored enolates or alternatively a failure to achieve true equilibrium.

Silylation of the ketone **21** with *i*-Pr_2NLi/Me_3SiCl at −78 °C gave a mixture of **23**, **25**, and **27** in 15, 35, and 50% relative yields, respectively. The preference for formation of **23** instead of **13** under these conditions is in accord with the transition-state **2** where the larger phenyl group avoids the bulky base, and the slight preference for **27** relative to **25** agrees with the known[3] selectivity for *Z* isomers (eq 1) with a relatively large group such as PhCHR. Similarly, silylation of **22** gave **24**, **26**, and **28** in 25, 30, and 45% relative yields, respectively. The formation of **25–28** as the predominant products in these reactions illustrates a high degree of kinetic control of these deprotonations so that only small amounts of the more stable conjugated isomers are formed.

The relative stereochemistry of **13**/**23** and of **14**/**24** was confirmed by the ^{1}H NMR chemical shifts of the Me_3Si groups, which in the *Z* isomers **13** and **14** were upfield of Me_4Si (δ −0.20 and −0.25, respectively) in contrast to the *E* isomers **23** and **24**, which absorbed at δ 0.25 and 0.12, respectively. Evidently in **13** and **14** the Me_3Si is in the region shielded by the aromatic ring and absorbs at higher field. A similar effect occurs in the stereoisomers of $PhCMe{=}CHOSiMe_3$,[16] although in this case the difference is not so great, presumably because of the greater flexibility of this less crowded substrate.

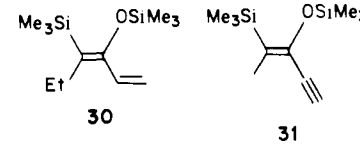
Assignment of the stereochemitry of the non-conjugated isomeric pairs **25**/**27** and **26**/**28** was made on the basis of the lower field absorption in the ^{1}H NMR of the vinyl protons cis to the oxygen in the *E* isomers **25** and **26**.[13]

Addition of *n*-BuLi to ketene **10** followed by Me_3SiCl gave a single silyl vinyl ether **15**, assigned to *Z* stereochemistry shown based on NMR comparisons and the expectation that attack to form this isomer would have less steric hindrance (vide infra). Hydrolysis of **15** gave the α-silyl ketone **29**, and this sequence of reactions (eq 14) provides a convenient route to this compound that may be compared to a recently reported method in which α-silyl esters were reacted with Grignard reagents.[17] In this latter procedure addition of 2 mol of Grignard reagent was a problem in several cases,[17] but this complication does not arise in addition to ketenes.



(14)

Ketene **10** was also reacted with vinyllithium and lithium acetylide to give after silylation the diene **30** and the enyne **31**, respectively, assigned the *Z* stereochemistry shown. We are now examining the reactivity of these products in Diels–Alder reactions as both 2-silyloxydienes[18a] and 1-silyldienes[18b] have recently found wide applications in such syntheses.



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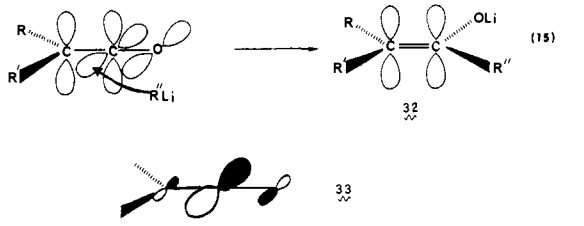
(13) Jackman, L. M.; Sternhell, S. "Applications of Nuclear Magnetic Resonance Spectroscopy in Organic Chemistry", 2nd ed.; Pergamon Press: New York, 1969; pp 185 and 225.
(14) Chiang, Y.; Kresge, A. J.; Tidwell, T. T.; Walsh, P. A. *Can. J. Chem.* **1980**, *58*, 2203–2206.
(15) Kirmse, W.; Urbach, H. *Chem. Ber.* **1972**, *105*, 840–849. The isomers of *t*-BuCH=CHOSiMe have been prepared but the NMR spectra were not reported: Dedier, J.; Gerval, P.; Frainnet, E. *J. Organomet. Chem.* **1980**, *185*, 183–197.
(16) (a) Stang, P. J.; Mangum, M. G.; Fox, D. P.; Haak, P. *J. Am. Chem. Soc.* **1974**, *96*, 4562–4569. (b) Rasmussen, J. K.; Hassner, A. *J. Org. Chem.* **1974**, *39*, 2558–2561.
(17) Larson, G. L.; de Lõpez-Cepero, I. M.; Torres, L. E. *Tetrahedron Lett.* **1984**, *25*, 1673–1676. See Corey and Rücker (Corey, E. J.; Rücker, C. *Ibid.* **1984**, *25*, 4345–4348) for another recent β-silyl ketone synthesis.
(18) (a) Danishefsky, S. *Acc. Chem. Res.* **1981**, *14*, 400–406. (b) Fleming, I.; Percival, A. *J. Chem. Soc., Chem. Commun.* **1978**, 178–180.

Table I. E_s, A, and υ Parameters

R	H	Me	Et	*i*-Pr	*t*-Bu	Ph	$SiMe_3$
E_s[22a]	0	−1.24	−1.31	−1.71	−2.78	−3.79	−3.36
A[22b]	0	−1.70	−1.75	−2.15	−5.4	−3.0	−3.41[22c]
υ[22d]	0	0.52	0.56	0.76	1.24	0.57–2.15	1.40

The NMR spectra are supportive that the Et group is cis to *n*-Bu, $CH{=}CH_2$, and C≡CH in **15**, **30**, and **31**, respectively. Thus in model compounds[19] the chemical shifts (see supplemental material) for both the ^{13}C and ^1H resonances of allylic CH_2 groups cis to these substituents are in the order C≡CH > $CH{=}CH_2$ > *n*-alkyl, and the same order is observed for **15**, **30**, and **31**. If the Et group were cis to Me_3SiO, no such trend would be expected.

Nucleophilic attack of an organolithium reagent on a ketene is expected to occur on the C=O π bond in the plane of the substituted ketene leading directly to the product enolate **32** (eq 15). Bond formation occurs between the HOMO of the organolithium and the LUMO **33** of the ketene.[20]



(15)

32

33

In the cases studied the steric interactions between the approaching organolithium and the substituents on the ketene are expected to determine the preferred direction of attack, and evidently these effects are quite significant as only a single isomeric product was observed in each addition. Furthermore, the product enolates formed need not be the thermodynamically more stable, as the repulsion between R′ and R″ in **32** is probably less than that in the transition state, whereas the repulsion between R and OLi is probably greater in the product than in the transition state and could be the dominant interaction in the product. There is experimental support for the conjecture, in that silylation of **21** and **22** under equilibrating conditions (KH/Me_3SiCl) gives 40% of **23** from **21** and 15% of **24** from **22**, although **23** and **24** were not detected at all from the ketene additions.

Evaluation of the steric crowding in the two alternative transition states for attack by the organolithium reagent on either side of the ketene could be compared by the methods of molecular mechanics.[21] However, the complexity of the molecular systems involved and the uncertainty of the actual structure of the transition state casts doubt as to whether the utility of this approach would justify the effort involved.

This reaction is likely to have an early transition state so a simpler approach to the prediction of the product stereochemistry is a comparison of steric parameters for the two groups R and R′ in the ketene. Examples of such parameters are the Taft E_s constants,[22a] the Winstein–Holness A values,[22b,c] and the Charton υ parameters,[22d] as summarized in Table I for some substituents relevant to this study.

These steric parameters are derived for quite different situations: the E_s values refer to the steric effect of the substituent R in hydrolysis of esters RCO_2X, A values refer to the difference in $\Delta G°$ for the equatorial and axial isomers of substituted cyclohexanes, and the υ values are derived from van der Waals radii, and have the further feature that different values are assigned to a group depending upon the direction of approach. It is not expected that the effective sizes of groups are invariant properties of the groups independent of the particular process used to measure the parameters. Nevertheless, the qualitative agreement between these measures of size as summarized in Table I suggests that these parameters are of general applicability, and can be used for the prediction of the preferred stereochemistry of enolate formation by nucleophilic addition to unsymmetrical ketenes. In particular, it may be noted that Me_3Si is quite large by any measure and that phenyl is evidently larger than methyl or ethyl. For some cases it may be anticipated that it will be difficult to predict the product stereochemitry in advance, but for the examples reported here the prediction of the product stereochemistry appears to be unambiguous, and is consistent with the observed stereochemistries deduced from spectral comparisons.

In conclusion, the reactions of unsymmetrical ketenes with organolithium reagents followed by silylation provide a stereospecific route to enol silyl ethers that are not generally formed with high selectivity by other routes. This tandem approach also involves formation of a new C–C bond, allows wide choice in the groups contained in the final product, and permits rational prediction of the final stereochemistry.

Experimental Section

Tetrahydrofuran (THF) was purified by distillation from sodium and benzophenone ketyl under nitrogen. Trimethylsilyl chloride (Me_3SiCl) was distilled from CaH_2. 2-Phenylpropionic acid, 2-phenylbutyric acid, and *tert*-butylacetic acid were obtained from Aldrich and converted to their acid chlorides with $SOCl_2$. Potassium hydride was obtained from Alpha and was washed with pentane prior to use.[11a]

Glassware was flame dried and cooled under N_2, and all reactions were conducted under a N_2 atmosphere. Solutions were transferred by using a positive pressure of N_2 and either glass syringes or double-tipped stainless steel needles.

^1H NMR spectra were run on a Varian T-60 instrument at 60 MHz with Me_4Si as an internal standard except as indicated. ^{13}C NMR spectra were measured on a Varian CFT-20 instrument. High-resolution mass spectrometry with an AEI MS-30 instrument was used for compositional analysis of trimethylsilyl vinyl ethers which tended to decompose prior to combustion analysis.

2-(Trimethylsilyl)butanoic acid was prepared as has been described[23] by the reaction of (trimethylsilyl)acetic acid with 2.2 equiv of *i*-Pr_2NLi followed by EtI and was converted to the acid chloride with oxalyl chloride in CCl_4.

2,2-Dimethylcyclohexanone (**5**) was prepared by the reaction of 2-methylcyclohexanone (8.97 g, 0.080 mol) with a suspension of KH (3.4 g, 0.084 mol) followed by the addition of triethylborane in THF (Aldrich, 100 mL, 0.10 mol).[5a] After 12 h of stirring at 25 °C MeI (34 g, 0.33 mol) was added to the resulting enol borate and stirred 10 h. The resulting solution was poured into 150 mL of saturated NH_4Cl and extracted twice with ether. After drying, the ether was evaporated and distillation (60 °C, 12 torr) to give **5** (7.90 g, 0.063 mol, 78%) which showed no trace of isomeric products by ^1H NMR.

Dropwise addition of **5** (6.7 g, 0.053 mol) to the reagent prepared from addition of *sec*-butyllithium (Aldrich, 0.068 mol in 52 mL cyclohexane) to Me_3SiCH_2OMe (7.5 g, 0.063 mol) (Aldrich)[24] at −78 °C was followed by 0.5 h of stirring at −23 °C (CCl_4/dry ice bath). The solution was stirred overnight at 25 °C, poured into NH_4Cl solution, and extracted twice with ether. The ether layers were dried with $MgSO_4$, the ether evaporated, and the residual ketone distilled from the product oil at 60 °C (12 torr). This oil was added carefully to 25 mL of 98% HCO_2H and stirred for 15 min followed by 2 h reflux. Water was added, and after cooling the solution was extracted with ether and the extract washed with $NaHCO_3$ and dried to give 2,2-dimethylcyclohexylcarboxaldehyde (**6**)[25]

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(5.11 g, 68% crude yield). The aldehyde was oxidized directly to 2,2-dimethylcyclohexanecarboxylic acid[26] with $KMnO_4$ and H_2SO_4 and was then converted to the α-bromo acid bromide **7** by reaction with phosphorous and Br_2.

Preparation of Ketenes. 2-Phenylbutanoyl chloride (6.75 g, 0.037 mol) was stirred with Et_3N (1.49 g, 0.148 mol) in 125 mL of THF at room temperature for 3 h.[9] The resulting solution was filtered by N_2 pressure through a sintered glass tube, leaving a solid residue of Et_3NHCl (4.95 g, 0.033 mol, 89%). Distillation of the filtrate gave ethylphenylketene (**8**)[8] (2.55 g, 0.017 mol, 48%): bp 70 °C (0.5 torr); IR (CCl_4) 2130 cm^{-1} (C=C=O); ^1H NMR (CCl_4) δ 0.95 (t, 3, J = 7 Hz, Me), 1.85 (q, 2, J = 7 Hz, CH_2), 7.0–7.5 (m, 5, phenyl).

2-Phenylpropanoyl chloride was reacted with Et_3N at 0 °C for 12 h as above to give an 84% yield of Et_3NHCl and on distillation at 50 °C (4 torr) gave a 25% yield of phenylmethylketene **7**:[8] IR (THF) 2135 cm^{-1} (C=C=O); ^1H NMR (CCl_4) δ 2.06 (s, 3, Me), 6.8–7.4 (5, m, Ph). There was considerable nonvolatile residue, so for reactions with organolithiums the product ketene solution in THF was usually used directly after filtration without distillation.

(Trimethylsilyl)butanoyl chloride (1.07 g, 6.2 mmol) was refluxed for 12 h with Et_3N (1.8 g, 18 mmol) in 50 mL of THF. Filtration of the solution gave Et_3NHCl (0.74 g, 5.4 mmol, 88%) and a THF solution of ethyl(trimethylsilyl)ketene (**11**): IR (ether) 2100 cm^{-1} (C=C=O). Evaporation of the solvent gave crude **10**: ^1H NMR (CCl_4) δ 0.10 (s, 9, $SiMe_3$), 1.10 (t, 3, J = 7 Hz, Me), 2.35 (q, 2, J = 7 Hz, CH_2).

A solution of **7** (1.7 g, 5.7 mmol) in 5 mL of THF was added over 30 min to a suspension of Zn (0.37 g, 5.7 mmol) in 50 mL of THF at 0 °C followed by 2 h of stirring. The greenish solution showed an IR band at 2100 cm^{-1} (C=C=O) and a weak band at 1750 cm^{-1} (attributed to ketene dimer). The solution was cooled to −78 °C and transferred via a double-tipped needle for reactions with organolithiums. Addition of excess aniline to a solution of 4 prepared in this way was followed by addition of water, and extraction with ether, washing with 1 N HCl, drying, and evaporation gave the anilide, mp 133–137 °C in 63% yield, which was taken as the yield in the conversion of **7** to **4**.

Reaction of *tert*-butylacetyl chloride with Et_3N to give *tert*-butylketene (**11**) as reported[10] gave only partial conversion to **11** so Zn debromination of the α-bromoacyl bromide was carried out. 2-Bromo-3,3-dimethylbutanoyl bromide (1.5 g, 7.0 mmol) was added dropwise to a stirring suspension of activated Zn dust (0.75 g, 11.4 mmol) in 40 mL of THF at 25 °C. After being stirred for 1 h the green solution showed a strong IR band at 2108 cm^{-1} (C=C=O) and weak bands at 1814 and 1738 cm^{-1} attributed to the dimer. This solution was used for reaction with *t*-BuLi without attempted purification.

Reaction of Ketenes with Alkyllithiums. Ethylphenylketene (**9**, from 0.022 mmol acyl chloride) in cold THF was transferred by means of a syringe to an addition funnel and was added dropwise over 1.5 h to a solution of *n*-BuLi (0.055 mol in 34 mL of hexane) and 150 mL of THF at −78 °C. After 1 h of stirring Me_3SiCl (7.1 g, 0.07 mol) was added in one portion and the solution allowed to warm to 25 °C while stirring overnight. The solvent was evaporated at reduced pressure at 25 °C, pentane was added, and the solution was removed from the residual white solid by filtration through a sintered glass tube under N_2. Evaporation of the solvent left an oil (4.86 g) which by VPC analysis (Carbowax 20 M, 200 °C) with bicyclohexyl as an internal standard contained 0.0133 mol (76% based on acyl chloride) of (*Z*)-3-phenyl-4-trimethylsilyloxy-3-octene (**14**) which was distilled at 150 °C and 0.5 torr: UV λ_{max} (cyclohexane) 249 nm (ε 19000); ^1H NMR (CCl_4) δ −0.25 (s, 9, $SiMe_3$), 0.7–1.1 (m, 6, 2 Me), 1.2–1.8 (m, 4, $(CH_2)_2$), 2.0–2.3 (m, 2, C=C$CH_2$$CH_2$), 2.30 (q, 2, J = 7 Hz, CH_2CH_2C=C), and 7.30 (s, 5 Ph); ^{13}C NMR ($CDCl_3$) δ 0.15, 13.92 (2 C), 22.47, 25.74, 29.79, 32.33, 121.86, 125.43, 127.43, 129.63, 141, and 146.45; mass spectrum M^+ 276.1904 ($C_{17}H_{28}OSi$ requires 276.1902).

Methylphenylketene (**8**, 0.020 mol) in 75 mL of THF was reacted as described for **9** with n-BuLi (0.05 mol in 50 mL of hexane) to yield 6.39 g of an oil analyzed by VPC as above to contain 0.010 mol (50%) of (*Z*)-2-phenyl-3-trimethylsilyloxy-2-heptene (**13**) which was distilled as above: ^1H NMR (CCl_4) −0.20 (s, 9, $SiMe_3$), 0.8–1.6 (m, 7, *n*-Pr), 1.94 (s, 3, C=CCH_3), 2.0–2.4 (m, 2, C=CCH_2), 7.20 (s, 5, Ph); ^{13}C NMR ($CDCl_3$) −2.14, 12.29, 16.90, 20.77, 27.79, 31.11, 112.70, 123.73, 125.87, 127.39, 141.06, and 145.71; mass spectrum M^+ 262.1766 ($C_{16}H_{26}OSi$ requires 262.1742).

Ketene 4 (obtained from 1.03 g, 3.4 mmol **7**) was added dropwise to a vigorously stirred suspension of phenyllithium (14 mmol in 10 mL of benzene, 5 mL of ether, and 50 mL of THF) at −78 °C, and after warming the solution to −30 °C, Me_3SiCl (2.5 g, 23 mmol) was added in one portion and the mixture allowed to warm to 25 °C overnight. The solution was evaporated, dissolved in 30 mL of pentane, filtered, and evaporated again to give 1.69 g of an oil found to contain 2.13 mmol (63%) of **12** by VPC analysis (3% OV-101, 150 °C with bicyclohexyl as an internal standard). Distillation (140 °C, 3 torr) gave **12** (0.54 g, 1.9 mmol, 56%): UV (pentane) λ_{max} 245 (ε 28000); ^1H NMR (CCl_4) δ −0.21 (s, 9, $SiMe_3$), 1.24 (s, 6, CMe_2), 1.3–1.5 (m, 6, $(CH_2)_3$), 1.8–2.0 (m, 2, C=CCH_2), 7.16 (s, 5, Ph); ^{13}C NMR ($CDCl_3$) δ 0.54, 21.55, 26.25, 27.30, 28.93, 35.99, 41.98, 123.44, 127.02, 127.29, 127.78, 129.69, 168.13; mass spectrum M^+ 288.1919 ($C_{18}H_{28}OSi$ requires 288.1902).

A solution of (trimethylsilyl)ethylketene (**10**) (obtained from 6.0 mmol of the acyl chloride) (6.0 mmol) in 25 mL of ether was added to *n*-BuLi (13.5 mmol) in 9 mL of hexane and 50 mL of ether at −78 °C, the mixture was stirred for 1 h at −78 °C, and then Me_3SiCl (1.62 g, 15 mmol) was added all at once and the mixture was allowed to warm to room temperature overnight. The solvent was evaporated, 30 mL of pentane added, and the solution filtered through a sintered glass tube. Evaporation of the solvent left 2.51 g of an oil analyzed by VPC as above with an OV-101 column (100 °C) to contain 4.2 mmol (78%) of (*Z*)-3-trimethylsilyl-4-trimethylsilyloxy-3-octene (**15**) which was distilled at a pot temperature of 80 °C (0.5 torr): IR (CCl_4) 1610 cm^{-1} (strong, C=C); 200-MHz ^1H NMR ($CDCl_3$) δ 0.052 (s, 9, $SiMe_3$), 0.177 (s, 9, $OSiMe_3$), 0.86 (t, 3, J = 7.5 Hz, CH_3CH_2C=C), 0.897 (t, 3, J = 6.9 Hz, Me), 1.20–1.53 (m, 4, $CH_3CH_2CH_2$), 1.934 (q, 2, J = 7.5 Hz, CH_3CH_2C=C), 2.153 (t, 2, J = 7.0 Hz, *n*-PrCH_2); ^{13}C NMR ($CDCl_3$) −1.58, −0.58, 12.53, 14.70, 21.17, 21.40, 29.09, 30.55, 114.24, 157.41; mass spectrum M^+ 272.1964 ($C_{14}H_{32}OSi_2$ requires 272.1983).

Similar reaction of **10** with vinyllithium (generated from vinyl bromide and *t*-BuLi) gave (*Z*)-3-trimethylsilyloxy-4-trimethylsilyl-1,3-hexadiene (**30**) in 73% yield: IR (CCl_4) 1561, 1596 cm^{-1} (C=CC=C); ^1H NMR (CCl_4) δ 0.12 (s, 9, $SiMe_3$), 0.20 (s, 9, $OSiMe_3$), 0.92 (t, 3, J = 6.5 Hz, Me), 2.09 (q, 2, J = 6.5 Hz, CH_2), 5.16 (dd, 1, J = 10 and 1.7 Hz, *Z*-H at C_1), 5.22 (dd, 1, J = 17 and 1.7 Hz, *E*-H at C_1), 6.42 (dd, 1, J = 17 and 10 Hz, C*H* = CH_2); ^{13}C NMR ($CDCl_3$) δ 0.00, 1.35, 16.03, 23.02, 116.46, 121.87, 131.81, 154.77; mass spectrum M^+ 242.1509 ($C_{12}H_{26}OSi_2$ requires 242.1515); UV (hexane) λ_{max} 257 nm (ε 9980).

Reaction of **10** with lithium acetylide (prepared from acetylene and *n*-BuLi) gave similarly (*Z*)-3-trimethylsilyloxy-4-trimethylsilyl-3-hexen-1-yne (**31**) in 43% yield: IR (CCl_4) 3300, 2100 cm^{-1} (C≡CH), 1580 cm^{-1} (C=C); ^1H NMR (CCl_4) δ 0.03 (s, 9, $SiMe_3$), 0.20 (s, 9, $OSiMe_3$), 0.87 (*t*, 3, J = 7 Hz, Me), 2.12 (q, 2, CH_2), 3.08 (s, 1, C*CH*); ^{13}C NMR ($CDCl_3$) δ 0.33, 0.62, 14.94, 24.50, 78.58, 80.89, 131.13, 137.65; mass spectrum M^+ 240.1373 ($C_{12}H_{24}OSi_2$ requires 240.1359); UV (hexane) λ_{max} 252 nm (ε 10700).

A solution of *tert*-butylketene (**11**) prepared from 7.0 mmol of the α-bromoacyl bromide in 40 mL of THF was transferred by a double-tipped needle to a solution of *tert*-butyllithium (21 mmol in 13 mL of hexane and 40 mL of THF) at −78 °C. After silylation with Me_3SiCl (1.52 g, 14 mmol) and workup as for **10** analysis by VPC (OV-101, 100 °C, bicyclohexyl internal standard) revealed a 4.3 mmol (62%) yield of **16**[27] which was isolated by VPC (OV-101): IR (CCl_4) 1647 cm^{-1} (strong, C=C); ^1H NMR (CCl_4) δ 0.28 (s, 9, Me_3Si), 1.01 (s, 9, *t*-Bu), 1.04 (s, 9, *t*-Bu), 4.40 (s, 1, C=CH); ^{13}C NMR ($CDCl_3$) δ 2.13, 29.17 (*Me*$_3$C), 30.33, 30.82 (*Me*$_3$C), 36.67, 114.06, 156.35.

Enolization of Ketones. 2,2-Dimethylcyclohexyl phenyl ketone (**17**) was prepared by addition of 2,2-dimethylcyclohexanecarbonyl chloride (1.27 g, 7.0 mmol) in 15 mL of benzene to a solution of diphenylcadmium prepared from PhBr (1.57 g, 10 mmol) and Mg (0.24 g, 10 mmol) in 15 mL of ether followed by evaporation of the ether and refluxing with 20 mL of benzene and anhydrous $CdCl_2$ (0.92 g, 7.0 mmol) to give **17** (0.685 g, 3.1 mmol, 45%) after chromatography (silica gel–hexane): bp 125 °C (3 torr); ^1H NMR (CCl_4) δ 0.85 (s, 3, Me), 1.05 (s, 3, Me), 1.20–2.0 (m, 8, $(CH_2)_4$), 3.10–3.40 (m, 1, *CH*CO–), 7.15–7.6 (m, 5, Ph); ^{13}C-NMR ($CDCl_3$) δ 21.35, 21.85, 25.27, 25.62, 31.42, 33.62, 41.50, 53.42, 128.03, 128.39, 132.31, 141.20, 211.22; mass spectrum M^+ 216.1518 ($C_{15}H_{20}O$ requires 216.1514).

Ketones **21** and **22** were obtained by the hydrolysis of the silyl enol ethers **13** and **14**, respectively. In a typical procedure a solution (0.642 g, 2.44 mmol) of **13** in 5 mL of THF was treated with 1 mL of 1 N HCl at 25 °C and the mixture stirred for 0.5 h and diluted with 5 mL of pentane and the organic layer separated, dried over $MgSO_4$ and concentrated to give the crude ketone which was purified by flash chromatography (silica gel/hexane–ethylacetate 4:1) to give pure **21** (0.371 g, 80%): ^1H NMR ($CDCl_3$) δ 0.75–1.85 (m, 7, *n*-Pr), 1.42 (d, 3, J = 7.5 Hz, Me), 2.32 (unsymmetrical t, 2, COCH_2-*n*-Pr), 3.72 (q, 1, J = 7.5 Hz, MePhC*H*CO), 7.25 (s, 5, Ph); mass spectrum M^+ 190.1365 ($C_{13}H_{18}O$ requires 190.1357).

For **22**: ^1H NMR (CCl_4) δ 0.65–2.15 (m, 12, Et and *n*-Pr), 2.15–2.50 (m, 2, COCH_2-*n*-Pr), 3.55 (t, 1, J = 7.5 Hz, Ph(Et)C*H*CO), 7.25 (s, 5,

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Ph); mass spectrum M^+ 204.1509 ($C_{14}H_{20}O$ requires 204.1514).

A solution of **17** (0.68 g, 3.1 mmol in 5 mL of THF) was added to 6.2 mmol of KH in 10 mL of THF at 25 °C and the solution refluxed for 30 min and filtered into a flask containing Me_3SiCl (0.93 g, 9 mmol) and Et_3N (0.6 g, 6 mmol) in 5 mL of THF at 25 °C. After stirring overnight wet THF and pentane were added and the solution was extracted with cold $NaHCO_3$ solution, dried over $CaSO_4$, and distilled at 140 °C (3 torr) to give a mixture of **12** and **18** (0.73 g, 81%) in the ratio of 55/45 as estimated from the relative intensities of the CMe_2 and the Me_3Si ^1H NMR resonances of the two isomers.

A solution of **17** (0.56 g, 2.6 mmol) in 2 mL of THF was added dropwise to a solution prepared from i-Pr_2NH (0.26 g, 2.6 mmol) in 20 mL of THF and 3.5 mmol of *n*-BuLi in 2 mL of hexane at 0 °C and then cooled to −78 °C. After 30 min of stirring Me_3SiCl (0.38 g, 3.5 mmol) was added and the solution allowed to warm to room temperature overnight. The solvent was evaporated to give crude **18** (0.72 g) which was separated by VPC (OV-101, 150 °C): IR (CCl_4) 1581 cm^{-1} (weak, C=C); UV λ_{max} ($CHCl_3$) 230 nm (ϵ 4500, sh, greater absorption at shorter λ); ^1H NMR (CCl_4) δ 0.22 (s, 9 $SiMe_3$), 0.85 (s, 6, CMe_2), 1.0–1.4 (m, 6, $(CH_2)_3$), 1.6–2.2 (m, 2, $C{=}CCH_2$), 7.25 (s, 5, Ph); mass spectrum $(M + 1)^+$ 289.1996 ($C_{18}H_{29}OSi$ requires 289.1980).

2-Phenyl-3-heptanone (**21**, 0.72 g, 3.8 mmol) in 3 mL of THF was added dropwise to a solution prepared from addition of *n*-BuLi (4 mmol in 2.5 mL of hexane) to i-Pr_2NH (0.404 g, 4.0 mmol) in 20 mL of THF at −78 °C. The solution was stirred for 1 h and Me_3SiCl (0.864 g, 8.0 mmol) was added in one portion. The solution was stirred for 2 h while warming to 25 °C, evaporated, and triturated with 20 mL of pentane which was filtered and evaporated again to give 0.77 g of an oil analyzed by VPC (3% OV-101, 150 °C) to contain **23**, **25**, and **27** in 15, 35, and 50% relative yields, respectively. These were separated on an OV-101 column. (*E*)-2-Phenyl-3-trimethylsilyloxy-2-heptene (**23**): ^1H NMR (CCl_4) δ 0.25 (s, 9, $SiMe_3$), 0.8–1.6 (m, 7, *n*-Pr), 1.87 (s, 3, $C{=}CCH_3$), 2.0–2.2 (m, 2, $C{=}CCH_2$), and 7.18 (s, 5, Ph). (*E*)-2-Phenyl-3-trimethylsilyloxy-3-heptene (**25**): ^1H NMR (CCl_4) δ 0.03 (s, 9, $OSiMe_3$), 1.06 (t, 3, J = 6 Hz, CH_3CH_2), 1.2–1.6 (m, 4, CH_2CH_2), 1.35 (d, 3, J = 7 Hz, CH_3CH), 3.40 (q, 1, J = 7 Hz, PhC*H*), 4.60 (t, 1, J = 7.5 Hz, C=CH), 7.20 (s, 5, Ph). (*Z*)-2-Phenyl-3-trimethylsilyloxy-3-heptene (**27**): ^1H NMR (CCl_4) δ 0.03 (s, 9, $OSiMe_3$), 1.06 (t, 3, J = 6 Hz, CH_3CH_2), 1.2–1.6 (m, 4, CH_2CH_2), 1.40 (d, 3, J = 7 Hz, CH_3CH), 3.90 (q, 1, J = 7 Hz) PhC*H*), 4.47 (t, 1, J = 7.5 Hz, C=CH), 7.20 (s, 5, Ph).

2-Phenyl-3-heptanone (**21**, 0.5 g, 2.6 mmol) in 3 mL of THF was added dropwise to a stirred suspension of KH (0.12 g, 3 mmol) in 10 mL of THF at 25 °C. After 30 min of stirring Me_3SiCl (0.59 g, 5.5 mmol) was added in one portion and after 1 h of stirring the solution was filtered through a filter stick, evaporated, diluted with 20 mL of pentane, filtered again, and concentrated to 0.80 g of an oil analyzed by VPC (3% OV-101, 150 °C) to show only one peak but which by ^1H NMR contained **13** and **23** in a ratio of 60 to 40.

3-Phenyl-4-octanone (**22**, 1.05 g, 5.0 mmol) was reacted with i-Pr_2NLi and Me_3SiCl as for **21** to give 1.04 g of an oil analyzed with the OV-101 column to contain **24**, **26**, and **28** in relative yields of 25, 30, and 45%, respectively. These were separated to give (*E*)-3-phenyl-4-trimethylsilyloxy-3-octene (**24**): ^1H NMR (CCl_4) δ 0.12 (s, 9, $SiMe_3$), 0.5–0.85 (m, 6, 2 CH_3), 1.0–1.5 (m, 4, CH_2CH_2), 1.9–2.4 (m, 4, $CH_2C{=}CCH_2$), 7.23 (s, 5, Ph); ^{13}C NMR ($CDCl_3$) 0.50, 13.75 (2 C), 22.18, 24.56, 29.67, 32.77, 122.94, 125.80, 127.79, 129.49, 141.70, 146.78. (*E*)-3-Phenyl-4-trimethylsilyloxy-4-octene (**26**): ^1H NMR (CCl_4) δ 0.02 (s, 9, $SiMe_3$), 0.8–1.1 (m, 6, 2 CH_3), 1.1–2.2 (m, 6, 3 CH_2), 3.04 (t, 1, J = 8 Hz, PhC*H*), 4.61 (t, 1, J = 7 Hz, C=CH), 7.22 (s, 5, Ph). (*Z*)-3-Phenyl-4-trimethylsilyloxy-4-octene (**28**): ^1H NMR (CCl_4) δ −0.01 (s, 9, $SiMe_3$), 0.66–1.05 (m, 6, 2 CH_3), 1.2–2.2 (m, 6, 3 CH_2), 3.53 (t, 1, J = 8 Hz, PhC*H*), 4.50 (t, 1, J = 7 Hz, C=CH), 7.18 (s, 5, Ph).

3-Phenyl-4-octanone (**22**) was reacted with KH followed by Me_3SiCl in a manner analogous to that for **21** to give the isomeric silyl vinyl ethers **14** and **24** in relative yields of 85 and 15%, respectively.

To a solution of **15** (1.0 g, 3.6 mmol) in 5 mL of pentane was added 1 mL of 1.5 N HCl, and the mixture was stirred 1 h at 25 °C. The pentane layer was separated, dried with $MgSO_4$, and evaporated to give 0.62 g (3.1 mmol, 86%) of crude 3-trimethylsilyl-4-octanone (**29**): IR ($CDCl_3$) 1681 cm^{-1} (C=O); ^1H NMR ($CDCl_3$) δ 0.10 (s, 9, SiMe), 0.8–1.9 (m, 12, Et and *n*-Pr), and 2.2–2.5 (m, 3, $CHCOCH_2$); mass spectrum M^+ 200.1592 ($C_{11}H_{24}OSi$ requires 200.1590). This material rearranged on distillation to give isomeric trimethylsilyl vinyl ethers.

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Supplementary Material Available: Comparative NMR spectra of compounds **15**, **30**, and **31** with model compounds (1 page). Ordering information is given on any current masthead page.

Regio- and Diastereoselective Preparation of Aldols from α-Branched Ketone Enolates Generated from BHT Ester Enolates and Organolithium Reagents—In Situ Generation and Trapping of Ketenes from Ester Enolates[1]

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Abstract: The thermally induced cleavage of the lithium enolates derived from α-branched 2,6-di-*tert*-butyl-4-methylphenyl (BHT) alkanoates and 3- to 6-membered ring carboxylates to ketenes and LiO–BHT in the presence of alkyllithium compounds, benzyllithium or phenyllithium, allows the generation of thermodynamically unstable tetrasubstituted ketone enolates. These enolates give, under the conditions chosen (no amide bases, dilute solution), the corresponding silyl enol ethers with trimethylchlorosilane and aldols with aldehydes. The aldols are produced regioselectively and, in the case of unsymmetrical ketenes, diastereoselectively. Almost two dozen examples are described, illustrating the use of BHT ester enolates as **nucleophilic** ketene precursors.

From X-ray crystal structure data of ester lithium enolates we could predict the trajectory of the incipient elimination of a leaving group from an sp^2-center with formation of a ketene[3-5] (see the black arrows in formula A of Figure 1). We could also make

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