2 H, $J = 12$, $\nu_{AB} = 27.0$), 4.51 (AB, 2 H, $J = 12$, $\nu_{AB} = 44.1$), 4.67 (d, 1 H, $J = 10$), 4.80 (s, 1 H), 7.27 (m, 10 H).

Diesters 40a,b. These compounds were prepared by the method already described for (±)-**36**.

From faster eluting ester: $[\alpha]^{20}{}_{D}$ −22.4° (*c*, 0.020 in $CHCl_3$); IR ($CHCl_3$) 1740 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.05 (d, 3 H, $J = 7$), 1.13 (s, 3 H), 1.18 (s, 3 H), 1.20 (d, 3 H, $J = 7$), 1.32 (s, 3 H), 1.63 (m, 1 H), 2.62 (m, 1 H), 3.40 (s, 3 H), 3.67 (s, 3 H), 3.68 (br s, 1 H), 3.75 (m, 1 H), 4.34 (AB, 2 H, $J = 12$, $\nu_{AB} = 38.8$), 4.56 (AB, 2 H, $J = 12$, $\nu_{AB} = 45.9$), 4.78 (s, 1 H), 7.2–7.4 (m, 10 H).

From slower eluting ester: $[\alpha]^{20}{}_{D}$ −12.8° (*c*, 0.018 in $CHCl_3$); IR ($CHCl_3$) 1740 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.04 (d, 3 H, $J = 7$), 1.09 (3 H, s), 1.21 (d, 3 H, $J = 7$), 1.38 (s, 3 H), 1.40 (s, 3 H), 1.62 (m, 1 H), 2.61 (m, 1 H), 3.40 (s, 3 H), 3.66 (s, 3 H), 3.69 (br s, 1 H), 3.74 (m, 1 H), 4.34 (AB, 2 H, $J = 12$, $\nu_{AB} = 22.8$), 4.48 (AB, 2 H, $J = 12$, $\nu_{AB} = 53.9$), 4.75 (1 H, s), 7.2–7.4 (m, 10 H).

Ester Aldehyde 1. The same procedure was used as was used to prepare (±)-1.

From the diester 40 with $[\alpha]^{20}{}_{D}$ −22.4°: (−)-**1**; $[\alpha]^{20}{}_{D}$ −27.0° (*c*, 0.022, in $CHCl_3$).

From the diester 40 with $[\alpha]^{20}{}_{D}$ −12.8°: (+)-**1**; $[\alpha]^{20}{}_{D}$ +27.0° (*c*, 0.020 in $CHCl_3$).

Acknowledgment. This work was supported by a research grant from the United States Public Health Service (AI15027). R. Pilli thanks the Brazilian National Science Foundation (CNPq) and U. Badertscher thanks the Swiss National Science Foundation for fellowship support. Single-crystal X-ray analysis of compounds **27c** and **32** were carried out by Dr. Frederick Hollander and Mr. Greg Michelson, of the Berkeley College of Chemistry X-ray facility.

Registry No. (±)-**1**, 95513-72-7; 1 (enantiomer 1), 95587-20-5; 1 (enantiomer 2), 95587-21-6; **2**, 79027-28-4; **3**, 92817-88-4; **4**, 95513-73-8; **5**, 72507-50-7; **6a**, 95513-74-9; **6b**, 95513-75-0; **6c**, 95513-76-1; **7a**, 95513-77-2; **7b**, 95513-78-3; **7c**, 95513-79-4; **8**, 94942-09-3; **8** triol, 94842-97-4; **9**, 86654-54-8; **9** triol, 95671-21-9; **10**, 71885-51-3; (*E*)-**11**, 95513-80-7; (*Z*)-**11**, 95513-81-8; **12**, 92817-93-1; **13**, 72507-39-2; **14**, 95513-82-9; **15**, 95587-22-7; **16**, 95513-83-0; **17**, 95587-23-8; **18**, 95513-84-1; **19** (isomer 1), 95513-85-2; **19** (isomer 2), 95587-24-9; **20**, 95513-86-3; **21**, 95587-25-0; **22a**, 92817-41-9; **22b**, 92817-42-0; **22c**, 92817-43-1; **25a**, 95513-87-4; **25b**, 95513-88-5; **25c**, 95513-89-6; **26a**, 95587-26-1; **26b**, 95587-27-2; **26c**, 95587-28-3; **27a**, 95513-90-9; **27b**, 95588-26-4; **27c**, 95587-29-4; **28a**, 95587-30-7; **28b**, 95513-91-0; **28c**, 95587-31-8; **29**, 95513-92-1; **30**, 95587-32-9; **31**, 95513-93-2; **32**, 95513-94-3; **33**, 95513-95-4; **34**, 95531-28-5; **35**, 95513-96-5; **36**, 95513-97-6; **36** free acid, 95513-98-7; **37**, 95513-99-8; **39** (isomer 1), 95514-00-4; **39** (isomer 2), 95587-33-0; **40** (isomer 1), 95514-01-5; **40** (isomer 2), 95587-34-1; (*S*)-(+)-3-hydroxy-2-methylpropanoic acid, 26543-05-5; (*R*)-1-(benzyloxy)-2-methyl-3-propanol, 63930-49-4; (*S*)-3-[(*tert*-butyldiphenylsilyl)oxy]-2-methylpropanoic acid, 95514-02-6; methyl (*S*)-3-[(*tert*-butyldiphenylsilyl)oxy]-2-methylpropanoate, 95514-03-7; (*S*)-3-[(*tert*-butyldiphenylsilyl)oxy]-2-methylpropanol, 95514-04-8; 2-methylpropane-1,3-diol, 2163-42-0; 2-methylpropane-1,3-diol diacetate, 55289-53-7; (*RS*)-3-acetoxy-2-methylpropanol, 95514-05-9; mesityl oxide, 141-79-7; 2,4-dimethylpent-2-enal, 623-36-9; (*R*)-(−)-*O*-methylmandelic acid acyl chloride, 34713-98-9; erythronolide A, 26754-37-0.

Generation, Alkylation, and Silylation of Directed Enolates Formed by Reaction of Ketenes and Organolithium Reagents[1]

Lynn M. Baigrie, Dieter Lenoir, Hani R. Seikaly, and Thomas T. Tidwell*

Department of Chemistry, University of Toronto, Toronto, Ontario, Canada M5S 1A1

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Symmetrical ketenes $R_2C{=}C{=}O$ [R_2 = *t*-Bu_2 (**1**), Et_2 (**2**), $(CH_2)_4$ (**3**), $(CH_2)_5$ (**4**)] were reacted with organolithium reagents R′Li to give directed enolates $R_2C{=}C(OLi)R'$ which were alkylated with MeI or silylated with Me_3SiCl. The silylation results for **2**–**4** were compared to those for reaction of ketones R_2CHCO-*n*-Bu (**16**–**18**) with Me_3SiCl and either *i*-Pr_2NLi, KH, or Et_3N. These latter conditions usually favored different regioisomers from the ketene route. Reaction of **1** with *t*-BuLi gave the previously inaccessible enolate *t*-$Bu_2C{=}C(OLi)$-*t*-Bu (**25**), which on reaction with MeI gave a mixture of the O-methylation product **27** along with some C-methylation product and with Me_3SiCl gave the silyl enol ether **26**. The vinyl ethers **26** and **27** are among the first substituted tri-*tert*-butylethylenes which have been reported.

The generation of ketone enolates,[2] and their alkylation, silylation,[3] and acylation continue among the most important of synthetic organic transformations. One of the most extensively studied problems in this area concerns the selective generation of specific regioisomeric enolates. In some cases conditions of kinetic or equilibrium control have been found under which there is a significant preference for a particular enolate, and sometimes mixtures of enol acetates or silyl ethers have been prepared and separated into the individual regioisomers as precursors for specific enolates.[2,3]

The reactivity of ketenes has been the object of recent interest in this laboratory,[4] and we were attracted to the possibility that these intermediates might be useful in the generation of specific enolates, particularly species not readily available by other methods.

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Table I. Yields of Anilides Obtained (Equation 5)

R_2	T, °C[a]	yield, % ketene distilled	 in situ	mp, °C
Et	40	62	82	120–125
$(CH_2)_4$	−10	35	87	159–160
$(CH_2)_5$	20	66	90	143–146

[a] Temperature of the reaction with zinc.

Ketenes have long been studied[5,6] but it appeared to us that the reactions of ketenes with organolithium reagents to give enolates (eq 1) ought to be a more widely utilized procedure than has hitherto been the case. There have been scattered reports of such reactions, including the addition of phenyllithium to diphenylketene to give the enolate which was trapped as the enol benzoate by benzoyl chloride (eq 2).[7a] Other examples include the reaction of PhLi with di-*tert*-butylketene (**1**) (eq 3),[7b] the reaction of bis(trimethylsilyl)ketene with *n*-BuLi (eq 4),[7c,d] and the corresponding reaction of bis(trimethylgermyl)ketene.[7d]

$$R_2C{=}C{=}O + R'Li \rightarrow R_2C{=}C(OLi)R' \qquad (1)$$

$$Ph_2C{=}C{=}O \xrightarrow[(2)\ PhCOCl]{(1)\ PhLi} Ph_2C{=}C(O_2CPh)Ph \qquad (2)$$

$$\underset{\mathbf{1}}{t\text{-}Bu_2C{=}C{=}O} \xrightarrow[(2)\ H_2O]{(1)\ PhLi} t\text{-}Bu_2CHC({=}O)Ph \qquad (3)$$

$$(Me_3Si)_2C{=}C{=}O \xrightarrow[(2)\ H_2O]{(1)\ n\text{-}BuLi} (Me_3Si)_2CHC({=}O)\text{-}n\text{-}Bu \qquad (4)$$

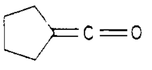
The goal of the present study was to test if reactions of symmetrically substituted ketenes with organolithium reagents could be utilized for the preparation of intermediates not available by other routes.

Results and Discussion

The ketenes **1**–**4** were chosen for initial study. Ketene **1**[8] has the advantage of being a persistent species even in the presence of air and can be distilled, purified by gas chromatography, and is slow to react with water.[8]

$Et_2C{=}C{=}O$

2



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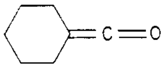
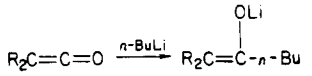


4

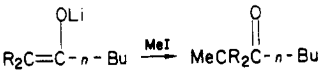
In our experience[9] the most convenient of the known[5,10,11] preparative methods for simple aliphatic ketenes such as **2**–**4** has been the reaction of α-bromoacyl bromides with activated zinc in THF.[11] The ketenes can be codistilled with THF at reduced pressure and stored in THF solution at −78 °C, but the yields of ketenes from this procedure as determined by trapping with aniline (eq 5)[11a] were improved when the ketene solution obtained was filtered to remove the zinc salts and the distillation was omitted (Table I).

$$R_2CBrCOBr \xrightarrow[THF]{Zn} R_2C{=}C{=}O \xrightarrow{PhNH_2} R_2CHCONHPh \qquad (5)$$

Ketenes **2**–**4** generated by debromination of α-bromoacyl bromides were added to 4 equiv of *n*-BuLi in THF at −78 °C to give enolates (eq 6) which were trapped with MeI to give the methyl ketones **5**–**7** or with Me_3SiCl to give silyl ethers **8**–**10** (eq 7 and 8) (yields based on starting dibromide).



$$R_2C{=}C{=}O \xrightarrow{n\text{-}BuLi} R_2C{=}C(OLi)\text{-}n\text{-}Bu \qquad (6)$$



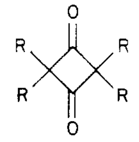
$$R_2C{=}C(OLi)\text{-}n\text{-}Bu \xrightarrow{MeI} MeCR_2C({=}O)\text{-}n\text{-}Bu \qquad (7)$$

5, $R_2 = Et_2$, 35%; **6**, $R_2 = (CH_2)_4$, 28%, **7**, $R_2 = (CH_2)_5$, 30%

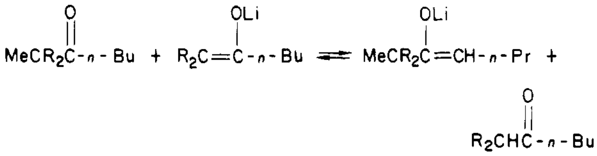
$$R_2C{=}C(OLi)\text{-}n\text{-}Bu \xrightarrow{Me_3SiCl} R_2C{=}C(OSiMe_3)\text{-}n\text{-}Bu \qquad (8)$$

8, $R_2 = Et_2$, 58%; **9**, $R_2 = (CH_2)_4$, 38%; **10**, $R_2 = (CH_2)_5$, 60%

The ketene dimers **11**–**13** were also formed as byproducts with both MeI and Me_3SiCl trapping, with the yields shown determined for the latter reaction. In the MeI trapping other products were formed that while not fully characterized appeared to be dimethylated ketones and di-*n*-butylcarbinols. These latter materials could result from equilibration of the monoalkylated ketones with unreacted enolate (eq 9) and further reaction of the resulting enolate and ketone with MeI and *n*-BuLi, respectively, whereas the dimers arise from thermal reactions. Enolate addition to ketenes is another known[12] reaction that could contribute to the rather low yields of **5**–**10**.



11, R = Et, 40%
12, R, R = $(CH_2)_4$, 50%
13, R, R = $(CH_2)_5$, 22%



$$MeCR_2C({=}O)\text{-}n\text{-}Bu + R_2C{=}C(OLi)\text{-}n\text{-}Bu \rightleftharpoons MeCR_2C(OLi){=}CH\text{-}n\text{-}Pr + R_2CHC({=}O)\text{-}n\text{-}Bu \qquad (9)$$

Ketene **4** was also reacted with MeLi and with PhLi, and the product enolates were trapped with Me_3SiCl to give

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(9) The treatment of substituted malonic acids with trifluoroacetic anhydride followed by pyrolysis (ref 10) is limited to volatile ketenes and dehydrohalogenation of unhindered aliphatic acyl chlorides usually does not proceed to completion.

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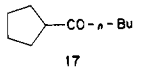
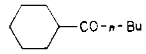
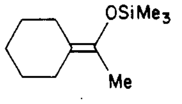
Table II. Silyl Ethers Obtained from Reaction of Ketones with Base and Me_3SiCl

		relative yield of silyl ethers	
ketone	base[a]	**8–10**	**19–21**
Et_2CHCO-*n*-Bu **16**	*i*-Pr_2NLi	0 (**8**)	80/20 (**19**)
	KH	18	32/50
	Et_3N	18	41/41
 17	*i*-Pr_2NLi	10 (**9**)[c]	45/45 (**20**)[d]
	KH	60	30/10
	Et_3N	20	35/35
 18	*i*-Pr_2NLi	0 (**10**)	40/60 (**21**)
	KH	0	75/25
	Et_3N	0	80/20

[a] Conditions: *i*-Pr_2NLi in DME at −78 °C; KH in THF at 25 °C; Et_3N in DMF at reflux. [b] *E* and *Z* stereochemistry assigned to the isomers with the lower and higher field vinyl ^1H NMR absorption, respectively, as in ref 13b,c, and Heathcock, C. H.; Buse, C. T.; Kleischick, W. A.; Pirrung, M. C.; Sohn, J. E.; Lampe, J. *J. Org. Chem.* **1980**, *45*, 1066–1081. [c] **9** and **20***E* had identical retention times on all columns tested, analyzed by ^1H NMR. [d] Vinyl hydrogen absorptions identical, structures tentatively assigned by comparison of VPC retention times to **21** *E*/*Z* (*Z* has shorter retention time on all columns tested).

the silyl ethers **14** and **15** in 52 and 42% distilled yields, respectively, based on α-bromoacyl bromides.



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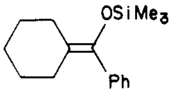
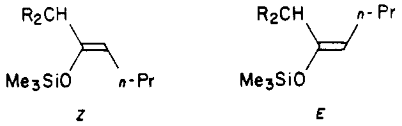


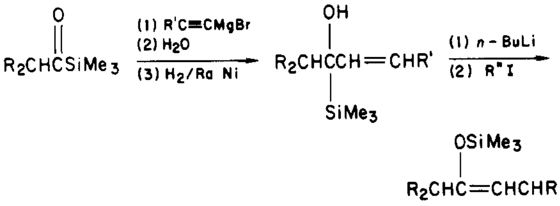
15

The yields of these reactions are modest but they do provide specific routes for the generation of silyl ethers and ketones derived from regiochemically defined enolates. For comparison reaction of the ketones **16–18** by standard enolization conditions[13a,b] were compared, as shown in Table II. These procedures gave the less substituted silyl enol ethers **19–21** as the major regioisomer in every case but one, whereas generation of the enolates from the ketenes gave exclusively the more substituted regioisomer in every case.

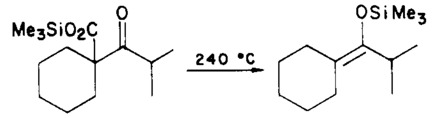


19, $R_2 = Et$
20, $R_2 = (CH_2)_4$
21, $R_2 = (CH_2)_5$

A recent example of a synthetic sequence for regioselective generation of enol silyl ethers is shown in eq 10.[14a] Preparation of a silyl ether with an exocyclic double bond has been reported in one case by the sequence of eq 11,[14b] and acid-catalyzed acetylation did give an exocyclic enol acetate in 47% yield (eq 12).[14c] However the general utility of these procedures for the selective preparation of specific regioisomers comparable to the ketene reactions has not been established.



$$R_2CHC(=O)SiMe_3 \xrightarrow[(3)\ H_2/Ra\ Ni]{(1)\ R'C\equiv CMgBr,\ (2)\ H_2O} R_2CHC(OH)(SiMe_3)CH{=}CHR' \xrightarrow[(2)\ R''I]{(1)\ n\text{-}BuLi} R_2CHC(OSiMe_3){=}CHCHR''R' \quad (10)$$



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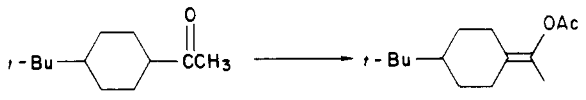
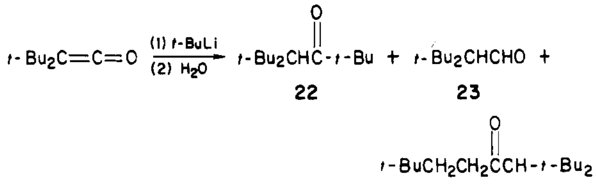


(12)

Reaction of di-*tert*-butylketene (**1**) with *tert*-butyllithium in THF did not occur at −70 °C but at 25 °C in this solvent the products **22–24** were obtained as 7, 46, and 30% of the volatile product, respectively (eq 13). The ketone **24** evidently arises from the known[15] reaction of THF with *t*-BuLi forming $CH_2{=}CH_2$ which adds to *t*-BuLi to give neohexyllithium which reacts with **1**.



$$t\text{-}Bu_2C{=}C{=}O \xrightarrow[(2)\ H_2O]{(1)\ t\text{-}BuLi} \underset{\mathbf{22}}{t\text{-}Bu_2CHC(=O)\text{-}t\text{-}Bu} + \underset{\mathbf{23}}{t\text{-}Bu_2CHCHO} + \underset{\mathbf{24}}{t\text{-}BuCH_2CH_2C(=O)CH\text{-}t\text{-}Bu_2} \quad (13)$$

When the reaction of **1** and *t*-BuLi was conducted in hexane solvent the ketone **22**[16] comprised 73% of the product, along with 17% **23** and 10% unreacted **1**.

When Me_3SiCl was added to the reaction product of **1** and *t*-BuLi in hexane only **22** and **23** were isolated after hydrolysis, with no evidence of any silylated derivatives. However when the hexane was evaporated from the solution of the preformed enolate **25** and THF was added then reaction with Me_3SiCl gave the silyl ether **26** in 70% yield (eq 14).

$$\underset{\mathbf{25}}{t\text{-}Bu_2C{=}C(OLi)\text{-}t\text{-}Bu} \xrightarrow{Me_3SiCl} \underset{\mathbf{26}}{t\text{-}Bu_2C{=}C(OSiMe_3)\text{-}t\text{-}Bu} \quad (14)$$

This reaction of **1** with *t*-BuLi is the only known route to enolate **25**. Thus reaction of ketone **22** with either KH or *i*-Pr_2NLi followed by Me_3SiCl gave only unreacted **22**, and earlier efforts to enolize **22** with *t*-BuOK/*t*-BuOD[17a] were also unsuccessful. Attempts to enolize *t*-Bu_2CHCO_2Et with either *i*-Pr_2NLi or KH, or *t*-$Bu_2CHCO_2CEt_3$ using KNH_2, also failed.[17b,c]

Reaction of **25** in THF with methyl iodide gave a mixture of the products **27** and **28** resulting from O- and C-alkylation, in yields of 20 and 16%, respectively (eq 15). The tendency of **25** for O-alkylation is remarkable and evidently reflects the greater steric retardation of C-alkylation relative to O-alkylation in this highly crowded enolate. When HMPA was added to the reaction mixture

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the formation of **28** was surpressed entirely and only **27** was formed.

$$\mathbf{25} \xrightarrow{\text{MeI}} \underset{\mathbf{27}}{t\text{-Bu}_2\text{C}{=}\text{C(OMe)-}t\text{-Bu}} + \underset{\mathbf{28}}{\text{Me-}t\text{-Bu}_2\text{CC}({=}\text{O})\text{-}t\text{-Bu}} \quad (15)$$

The reaction of **1** with n-BuLi followed by Me_3SiCl also produced the silyl ether **29**. When **1** was reacted with MeLi followed by hydrolysis **30** was obtained as the only product.

$$\underset{\mathbf{29}}{t\text{-Bu}_2\text{C}{=}\text{C(OSiMe}_3\text{)-}n\text{-Bu}} \qquad \underset{\mathbf{30}}{t\text{-Bu}_2\text{CHCOCH}_3}$$

In summary the reactions of ketenes with organolithiums have proved to be of value for a number of different purposes. These include the convenient preparation of **22** by the route of eq 13, and the formation of the hitherto inaccessible **26**, **27**, and **28**. There is continuing interest in the study of such crowded compounds[16c,18] and ketenes promise to be of further utility in this area.

The reactions of the less crowded ketenes **2**–**4** do not proceed in excellent yields, evidently because of competing dimerization and oligomerization. However procedures have been devised for the one pot formation and further reaction of directed enolates in reasonable yields and complete regiochemical selectivity, and these enolates are usually not the isomer favored from direct ketone enolization under either kinetic or equilibrium control. The ketene route also offers advantages over an analogous alkylation of ketenimines to give ketones,[19] as this requires first preparing precursor dihydro-1,3-oxazines, and also precludes trapping of intermediate enolates as they are not intermediates in the reaction.

Experimental Section[20]

All reactions were carried out in flame- or oven-dried glassware under a nitrogen atmosphere. Solutions were transferred with syringes or double-tipped needles by using a positive pressure of nitrogen; transfer of KH was carried out in a glove bag. THF was distilled from the sodium ketyl of benzophenone. α-Bromoacyl bromides were obtained from the corresponding commercially available acids (Aldrich) by reaction with Br_2/P as has been reported.[11] Me_3SiCl was distilled from CaH_2 under N_2 and Et_3N was distilled from $LiAlH_4$. n-BuLi in THF was obtained by evaporating the hexane from Aldrich n-BuLi in hexane at −78 °C and adding THF. Ketones **16**–**18** were obtained by reaction of n-BuLi with the appropriate carboxylic acid.[21]

Zinc Debromination of α-Bromoacyl Bromides. In a typical procedure α-bromocyclohexanecarbonyl bromide (3.7 g, 14 mmol) was added dropwise to a stirred suspension of 2 g (0.03 mol) of Zn dust (activated by HCl) at 0 °C. After 0.5 h stirring at 0 °C the IR of the crude solution showed an intense band at 2100 cm^{-1} (C=C=O) and a weak band at 1800 cm^{-1} attributed to the dimer **13**. The green solution was cooled to −78 °C and the precipitated $ZnBr_2$ was allowed to settle. The solution was transferred slowly by N_2 pressure via a double-tipped needle to a flask containing a stirred solution of 54 mmol of n-BuLi in 34 mL of hexane and 100 mL of THF at −78 °C. After 0.5-h stirring a solution of Me_3SiCl (7.5 g, 70 mmol) and Et_3N (7 g, 70 mmol) in 5 mL of THF was added through a filter tube by N_2 pressure and the reaction mixture warmed to 25 °C and stirred 2 h. The solvent was then evaporated, 25 mL of pentane was added, the mixture was filtered through a fine sintered glass tube, and the solvent was again evaporated to leave 2.31 g of an oil from which was distilled (85 °C, 1 torr) **10** (1.8 g, 7.5 mmol, 55%) pure by VPC.

The preparations of **2** and **3** and the reactions of these ketenes with n-BuLi, and of **4** with MeLi and PhLi, were carried out by analogous procedures. For the alkylation experiments neat MeI (6 equiv) was substituted for the Me_3SiCl solution. Physical properties of the products are listed separately.

Enolate Generation with KH. In a typical procedure a suspension of KH in THF was added to a solution of cyclopentyl n-butyl ketone (**17**, 0.58 g, 3.7 mmol) in THF with stirring at 25 °C until gas evolution ceased. The yellow enolate solution was then treated with a solution of 5 mmol of Me_3SiCl and 5 mmol of Et_3N in 10 mL of THF added through a fritted glass filter tube. Aqueous THF was added to the resulting mixture which was then poured into water and extracted with pentane, and the pentane layer was dried over $MgSO_4$ and evaporated. VPC separation (SE-30) of the resulting oil showed the presence of starting ketone **17** as 10% of the volatile material, a single peak for **9** and **20*E***, and a peak for **20*Z***. The ratio of **9** (60%) and **20*E*** (30%) was determined from the relative intensity of the ^{1}H NMR signal of **20*E*** at δ 4.37.

Enolate Generation with *i*-Pr$_2$NLi. To a magnetically stirred solution of 20 mL of DME and 5 mg of Ph_3CH was added 7 mL of 1.1 M MeLi (8 mmol) in Et_2O at 0 °C. To the resulting red solution was successively added via a syringe 0.8 g (8 mmol) of i-Pr_2NH and 1.09 g (7 mmol) of cyclopentyl n-butyl ketone (**17**) until the red color was discharged. The yellow enolate solution was stirred at 0 °C for 15 min and then a mixture of Me_3SiCl (1.08 g, 10 mmol) and Et_3N (1.01 g, 10 mmol) in 5 mL of DME was added via a filter tube. After 15-min stirring the solution was washed with cold $NaHCO_3$, dried, and analyzed by VPC as described in the KH procedure.

For reaction of **16** and **18** i-Pr_2Li was generated from n-BuLi in hexane and THF without Ph_3CH, and the reagents were added in THF at −78 °C, followed by 2 h stirring at 25 °C.

Silylation with Et$_3$N/Me$_3$SiCl. To a solution of 10 mmol of Me_3SiCl and 20 mmol of Et_3N in 10 mL of DMF was added **17** (1.0 g, 7 mmol) and the mixture was refluxed 72 h. After cooling to 25 °C the solution was diluted with 15 mL of pentane and washed with cold $NaHCO_3$ solution, cold 0.5 N HCl solution, and then cold $NaHCO_3$ again. The solution was then dried over Drierite, evaporated, and analyzed as described in the KH procedure and reported in Table II.

Ketene Dimers. The products from treatment of α-bromoacyl bromides with zinc followed by Me_3SiCl and workup as described above were fractionated by distilling off material at 1 torr and 80 °C. The residue was mainly the known[22] dimers as analyzed by the IR band at 1755 cm^{-1} and the ^{1}H NMR spectra. On dissolving the oily residues in pentane the crystalline dimers **12** [mp 68–70 °C (lit.[22a] mp 70–70.5 °C)] and **13** [mp 160–164 °C (lit.[22c,d] mp 164–165 °C)] were obtained. Dimer **11**[22b] is a liquid at 25 °C: IR (CCl_4) 1750 cm^{-1} (C=O); ^{1}H NMR (CCl_4) δ 0.95 (t, 12, J = 7 Hz, 4 Me), 1.68 (q, 8, J = 7 Hz, 4 CH_2).

Di-*tert*-butylketene (**1**)[8] (0.50 g, 3.2 mmol) in 10 mL of pentane was added to a solution of t-BuLi (6.4 mmol) in 4 mL of pentane stirred at 0 °C. The mixture was stirred at 25 °C for 12 h and then 2 mL of water was added. The pentane layer was separated, dried, evaporated, and analyzed by VPC (SE-30, 160 °C) to contain unreacted **1** (10%), ketone **22**[16c] (73%), and di-*tert*-butylacetaldehyde (**23**,[8] 17%).

Addition of **1** (0.350 g, 2.27 mmol) to t-BuLi (3.40 mmol) as above was followed by 24-h reflux, removal of the pentane at 1 torr, and addition of 15 mL of THF to the solid residue cooled

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(20) ^{1}H and ^{13}C NMR spectra were run on Varian T-60 and CFT-20 instruments, respectively. IR spectra were measured using a Nicolet 5DX FT instrument. Elemental analyses were by Galbraith or the Stanford Microanalysis Laboratory.

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with an ice bath. Then Me_3SiCl (0.85 g, 7.8 mmol) was added and the solution stirred 2 h, evaporated, and 10 mL of pentane added. After filtration through a fine sintered glass tube the pentane was evaporated to give 0.76 g of an oil that was analyzed by VPC (OV-101 column, 150 °C, bicyclohexyl as internal standard) to consist of **26** (1.5, mmol, 70%). A similar reaction of **1** with *n*-BuLi gave **29** in 84% yield.

To a solution of **1** (0.50 g, 3.2 mmol) in 10 mL of pentane at 0 °C was added *t*-BuLi (3.2 mmol) in 2 mL of pentane and the solution was stirred 1 h at 0 °C and then overnight at 25 °C. The pentane was evaporated and the residual yellow solid was cooled to 0 °C. THF (15 mL) containing HMPA (1.16 g, 6.48 mmol) was added followed by MeI (9.6 mmol) and the solution was stirred overnight at 25 °C, poured into water, extracted with pentane, dried over Drierite, and evaporated. Purification by VPC (OV-101 column, 100 °C) gave **27** (0.29 g, 39%). When the HMPA was omitted in this procedure the separated product (Carbowax 20 M, 150 °C) consisted of **27** (0.16 g, 20%) and **28** (0.12 g, 16%).

Dropwise addition of *t*-BuLi (20 mmol in 10 mL of pentane) to **1** (2.0 g, 13 mmol) in 20 mL of THF at 0 °C was followed by 2-h stirring at 25 °C, addition of 10 mL of saturated NH_4Cl solution, and extraction with ether which was dried and evaporated. Separation by VPC (SE-30 column, 160 °C) indicated the presence of **22**, **23**, and **24** as 7, 46, and 30% of the volatile product, respectively.

Characterization of Products.[23] **5**: IR (CCl_4) 1720 cm^{-1} (C=O); ^{1}H NMR (CCl_4) δ 0.85 (broad t, 9, J = 7 Hz, 3 Me), 0.6–1.0 (m, 2, $CH_2\mathit{CH_2}CH_3$), 1.10 (s, 3, quaternary Me), 1.2–1.8 (m, 6, 3CH_2 δ to C=O), 2.30 (t, 2, J = 7 Hz, CH_2CO). Anal. Calcd for $C_{11}H_{22}O$ (170.29): C, 77.58; H, 13.02. Found: C, 76.69; H, 13.42. Mass spectrum 170 (M^+).

6: IR (CCl_4) 1706 cm^{-1} (C=O); ^{1}H NMR (CCl_4) δ 0.6–2.0 (m, 15), 1.20 (s, 3, quaternary Me), 2.40 (t, 2, J = 7 Hz, CH_2CO). Anal. Calcd for $C_{11}H_{20}O$ (168.20): C, 78.51; H, 11.98. Found: C, 78.19; H, 12.16.

7: IR (film) 1710 cm^{-1} (C=O); ^{1}H NMR (CCl_4) δ 0.9–1.8 (m, 17), 1.00 (s, 3, quaternary Me), 2.40 (t, 2, J = 7 Hz, CH_2CO). Anal. Calcd for $C_{12}H_{22}O$ (182.31): C, 79.05; H, 12.16. Found: C, 78.25; H, 12.07. Mass spectrum M^+ 182.1676, calcd 182.1669.

8: IR (film) 1670 cm^{-1} (C=C); ^{1}H NMR (CCl_4) δ 0.12 (s, 9, $OSiMe_3$), 0.9–2.0 (m, 19). Anal. Calcd for $C_{13}H_{28}OSi$ (228.44): C, 68.35; H, 12.35. Found: C, 68.54; H, 12.12.

9: IR (film) 1670 cm^{-1} (C=C); ^{1}H NMR (CCl_4) δ 0.12 (s, 9, $OSiMe_3$), 0.6–2.0 (m, 17); mass spectrum M^+ 226.1768, $C_{13}H_{26}OSi$ requires 226.1753.

10: IR (film) 1670 cm^{-1} (C=C); ^{1}H NMR (CCl_4) δ 0.15 ($OSiMe_3$), 0.91 (t, 3, J = 7 Hz, Me), 1.1–1.6 (m, 10, 5 CH_2), 1.8–2.2 (m, 6, 3CH_2C=C); mass spectrum M^+ 240.1926, $C_{14}H_{28}OSi$ requires 240.1908. Anal. Calcd: C, 69.92; H, 11.73. Found: C, 69.70; H, 11.78.

14: IR (CCl_4) 1670 cm^{-1} (C=C); ^{1}H NMR (CCl_4) δ 0.11 (s, 9, $OSiMe_3$), 1.3–1.6 (m, 6, $(CH_2)_3$), 1.68 (s, 3, Me), 1.8–2.2 (m, 4, $(CH_2)_2$ C=C); ^{13}C NMR ($CDCl_3$) δ 0.38, 17.82, 26.76, 27.14, 27.78, 29.38, 117.82, 137.36; mass spectrum M^+ 198.1432, $C_{11}H_{22}OSi$ requires 198.1438.

15: IR (CCl_4) 1670 cm^{-1} (C=C); ^{1}H NMR (CCl_4) δ −0.09 (s, 9, $OSiMe_3$), 1.3–1.7 (m, 6, $(CH_2)_3$), 2.0–2.4 (m, 4, $(CH_2)_2$ C=C), 7.22 (s, 5, Ph); ^{13}C NMR ($CDCl_3$) δ 0.21, 26.78, 27.36, 27.67, 28.08, 29.76, 101.67, 120.72, 127.02, 127.57, 129.15, 138.80; mass spectrum M^+ 260.1598, $C_{16}H_{24}OSi$ requires 260.1596.

19(*E*): IR (film) 1656 cm^{-1} (C=C); ^{1}H NMR (CCl_4) δ 0.14 (s, 9, $OSiMe_3$), 0.8–1.0 (m, 9, 3 Me), 1.0–1.6 (m, 6, 3$C\mathit{H_2}Me$), 1.7–2.2 (m, 3, $C\mathit{H_2}C$=$CC\mathit{H}$), 4.49 (t, 1, J = 7 Hz, C=CH); mass spectrum M^+ 228.1908, $C_{13}H_{28}OSi$ requires 228.1909. Anal. Calcd (M_r 228.44): C, 68.35; H, 12.35. Found: C, 68.68; H, 12.23.

19(*Z*): IR (film) 1672 cm^{-1} (C=C); ^{1}H NMR (CCl_4) δ 0.14 (s, 9, $OSiMe_3$), 0.8–1.0 (m, 9, 3Me), 1.0–1.6 (m, 6, 3$C\mathit{H_2}Me$), 1.7–2.2 (m, 3, C=CCH), and 4.30 (t, 1, J = 7 Hz, C=CH). Anal. Found: C, 68.56; H, 12.17.

20(*E*): ^{1}H NMR (CCl_4) δ 0.14 (s, 9, $OSiMe_3$), 0.8–1.1 (m, 5, Et), 1.4–1.7 (m, 8, $(CH_2)_4$), 1.8–2.2 (m, 3, $C\mathit{H_2}C$=$C\mathit{H}$), 4.37 (t, 1, J = 7 Hz, C=CH); mass spectrum (obtained on an *E*/*Z* mixture) M^+ 226.1716, $C_{13}H_{26}OSi$ requires 226.1753.

20(*Z*): ^{1}H NMR (CCl_4) δ 0.15 (s, 9, $OSiMe_3$), 0.8–1.1 (m, 5, Et), 1.4–1.7 (m, 8, $(CH_2)_4$), 1.8–2.2 (m, 3, $C\mathit{H_2}C$=$C\mathit{H}$), 4.34 (t, 1, J = 7 Hz, C=C*H*); mass spectrum, see **20**(*E*).

21(*E*): ^{1}H NMR (CCl_4) δ 0.12 (s, 9, $OSiMe_3$), 0.8–2.1 (m, 20), 4.34 (t, 1, J = 7 Hz, C=CH); mass spectrum (obtained on an *E*/*Z* mixture) M^+ 240.1918, $C_{14}H_{28}OSi$ requires 240.1908.

21(*Z*): ^{1}H NMR (CCl_4) δ 0.12 (s, 9, $OSiMe_3$), 0.8–2.2 (m, 20), 4.27 (t, J = 7 Hz, C=CH); mass spectrum, see **21**(*E*).

24: IR (CCl_4) 1710 cm^{-1} (C=O); ^{1}H NMR (CCl_4) δ 0.86 (s, 9, *t*-*Bu*CH_2), 1.02 (s, 18, *t*-*Bu*$_2$CH), 1.2–1.5 (m, 2, t-Bu$C\mathit{H_2}$), 2.1–2.5 (m, 3, $C\mathit{H}COC\mathit{H_2}$); ^{13}C NMR ($CDCl_3$) δ 28.0, 33.4, 38.2, 39.1, 46.7, 69.8 (CO not observed); mass spectrum 169 (M^+ − *t*-BuCH_2).

26: IR (CCl_4) 1687 cm^{-1} (weak, C=C); ^{1}H NMR (CCl_4) δ 0.25 (s, 9, $OSiMe_3$), 1.23, 1.28, 1.32 (each s, 9, *t*-Bu); ^{13}C NMR ($CDCl_3$) 4.9, 34.3, 36.4, 37.7, 38.0, 41.2, 42.4, 138.5, 159.8; mass spectrum 195 (M^+ − Me_3SiO).

27: IR ($CDCl_3$) 1685 cm^{-1} (weak, C=C); ^{1}H NMR ($CDCl_3$) δ 1.16, 1.28, 1.32 (each s, 9, *t*-Bu), 3.50 (s, 3, OMe); ^{13}C NMR ($CDCl_3$) δ 29.53, 31.91, 32.83, 35.63, 38.64, 39.95, 64.47, 107.35, 139.27; mass spectrum 226 (M^+). Anal. Calcd for $C_{15}H_{30}O$ (226.40): C, 79.58; H, 13.36. Found: C, 79.90; H, 13.24.

28: IR ($CDCl_3$) 1669 cm^{-1} (C=O); ^{1}H NMR ($CDCl_3$) δ 1.03 (s, 18, *t*-Bu), 1.17 (s, 9, *t*-BuCO), 1.40 (s, 3, Me); ^{13}C NMR ($CDCl_3$) δ 18.31, 29.97, 30.56, 35.70, 40.82, 62.8 (no signal observed for C=O); CI mass spectrum 171 (M^+ − C_4H_7).

29: ^{1}H NMR (CCl_4) δ 0.16 (s, 9, $OSiMe_3$), 0.8–1.7 (m, 7, n-Pr), 1.26 (s, 9, *t*-Bu trans to $OSiMe_3$),[24] 1.30 (s, 9, *t*-Bu cis to $OSiMe_3$),[24] 2.1–2.4 (m, 2, C=CCH_2); ^{13}C NMR ($CDCl_3$) δ −3.91, 11.21, 22.54, 30.98, 33.39, 34.27, 37.91, 45.98, 148.95; mass spectrum M^+ 284.2529, $C_{17}H_{36}OSi$ requires 284.2535.

30:[19c] ^{1}H NMR (CCl_4) δ 1.05 (s, 18, *t*-Bu$_2$), 2.11 (s, 3, MeCO), 2.37 (s, 1, C*H*CO).

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Registry No. **1**, 19824-34-1; **2**, 24264-08-2; **3**, 29713-50-6; **4**, 22589-13-5; **5**, 74326-61-7; **6**, 32524-97-3; **7**, 95999-27-2; **8**, 74326-62-8; **9**, 95999-28-3; **10**, 95999-29-4; **11**, 3898-61-1; **12**, 5011-61-0; **13**, 950-21-0; **14**, 64639-28-7; **15**, 95999-30-7; **16**, 19781-29-4; **17**, 6636-80-2; **18**, 5445-35-2; (*E*)-**19**, 74326-63-9; (*Z*)-**19**, 74326-64-0; (*E*)-**20**, 95999-31-8; (*Z*)-**20**, 95999-35-2; (*E*)-**21**, 95999-32-9; (*Z*)-**21**, 95999-36-3; **22**, 24534-83-6; **23**, 2987-13-5; **24**, 85576-53-0; **25**, 85576-54-1; **26**, 85576-55-2; **27**, 95999-33-0; **28**, 81931-83-1; **29**, 95999-34-1; **30**, 35378-08-6; $Et_2CBrCOBr$, 26074-53-3; $(CH_2)_4CBrCOBr$, 95999-37-4; *i*-Pr_2NLi, 4111-54-0; KH, 7693-26-7; Et_3N, 121-44-8; Et_2C=C(OLi)*n*-Bu, 95999-39-6; $(CH_2)_4C$=C(OLi)*n*-Bu, 95999-40-9; $(CH_2)_5C$=C(OLi)*n*-Bu, 95999-41-0; $Et_2CHCONHPh$, 6832-96-8; $(CH_2)_4CHCONHPh$, 3400-41-7; $(CH_2)_5CHCONHPh$, 2719-26-8; $(CH_2)_5C$=C(OLi)Me, 95999-42-1; $(CH_2)_5C$=C(OLi)Ph, 95999-43-2; *i*-Pr_2NH, 108-18-9; $(CH_2)_5CBrCOBr$, 95999-38-5.

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(23) The trimethylsilyl enol ethers tended to decompose after a few days in glass containers and usually did not give satisfactory elemental analysis if mailed to the analyst, so were characterized by mass spectrometry. The branched ketones **5–7** and **28** gave consistently low values for carbon, even on repeated analysis.

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