(1S,2R)-(-)-indene epoxide, 85354-35-4; (1S,2R)-(-)-3,4-dihydronaphthalene epoxide, 24825-01-2; indan, 496-11-7; 2-ethylnaphthalene, 939-27-5; 1-ethylnaphthalene, 1127-76-0; (R)-(+)-(1-hydroxyethyl)benzene, 1517-69-7; (R)-(+)-4-methoxy-1-(1-hydroxyethyl)benzene, 1517-70-0; (R)-(+)-1-phenylpropanol, 1565-74-8; (R)-(+)-1-indanol, 697-64-3; (R)-(-)-1,2-dihydro-1-naphthalenol, 123849-23-0; (R)-(+)-2-(1-hydroxyethyl)-naphthalene, 52193-85-8; (R)-(+)-1-(1-hydroxyethyl)naphthalene, 42177-25-3; 1-(1-naphthalenyl)ethanone, 941-98-0; [1(R)-[(2-(R)-phenylpropionyl)oxy]ethyl]benzene, 79121-13-4; 4-methoxy-1-[1(R)-[(2(R)-phenylpropionyl)oxy]ethyl]benzene, 126218-77-7; 1(R)-phenyl-1-[(2(R)-phenylpropionyl)oxy]propane, 126218-78-8; 1(R)-[(2(R)-phenylpropionyl)oxy]indan, 126218-79-9; 1(R)-[(2-(R)-phenylpropionyl)oxy]-1,2-dihydronaphthalene, 126218-80-2; 2-[1-[(2(R)-phenylpropionyl)oxy]ethyl]naphthalene, 126218-81-3; 1-[1-[(2(R)-phenylpropionyl)oxy]ethyl]naphthalene, 126218-82-4; ethylbenzene, 100-41-4; 4-methoxyethylbenzene, 1515-95-3; 1-phenylpropane, 103-65-1; 2,3-dihydro-4H-1-benzothiopyran-4-one, 3528-17-4; (+)-2,3-dihydro-4H-1-benzothiopyran-4-one 1-oxide, 126218-84-6.

Nucleophilic Additions to Ketenes by (Trimethylsilyl)lithium and by Enolates[1]

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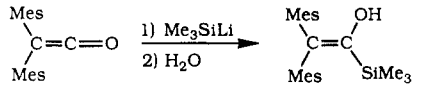
Reaction of t-$Bu_2C{=}C{=}O$ (**5**) with Me_3SiLi at -78 °C followed by trapping of the intermediate enolate with Ac_2O gave t-$Bu_2C{=}C(OAc)SiMe_3$ (**9**). Other ketenes gave similar products. Reaction of ketenes $PhCR{=}C{=}O$ (R = Me, **13**; R = Et, **3**) with enolates $CH_2{=}C(OLi)R^1$ (R^1 = H, Me, t-Bu, Ph) at -78 °C followed by warming to 25 °C and hydrolysis gave vinyl esters $PhCHRCO_2C(R^1){=}CH_2$, along with 10% $PhCHMeCOCH_2COPh$ for R = Me, R^1 = Ph. Under the same conditions the ketenes $PhCR{=}C{=}O$ with enolates $CH_2{=}C(OK)R^1$ (R^1 = Me, t-Bu, Ph) gave only 1,3-diketones $PhCHRCOCH_2COR^1$, but vinyl esters were the major products if the reactions were quenched at -78 °C. It is proposed that enolates undergo preferential O-acylation by ketenes in a kinetically favored process, but that these intermediates can revert to thermodynamically more stable C-acylated products.

Nucleophilic additions to ketenes[2] have been the subject of synthetic,[1,3] mechanistic,[4] and theoretical[5] studies in our laboratory. We now report results on the addition of (trimethylsilyl)lithium (Me_3SiLi) and enolates to ketenes.

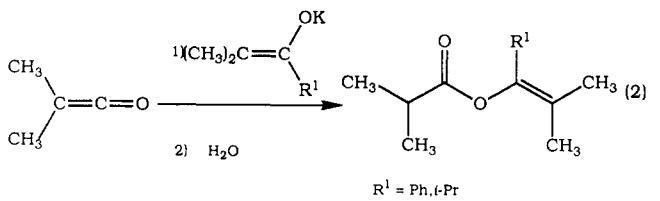
One previous example of the addition of Me_3SiLi to a ketene has been reported, namely to dimesitylketene (**1**, eq 1).[6] The product of addition to the carbonyl carbon was obtained in 49% yield and exists as the enol tautomer **2**. Such reactions appear promising for the preparation of silyl derivatives, and we have accordingly examined several other examples.



(1)

1 (Mes = 2,4,6-$(CH_3)_3C_6H_2$) **2**

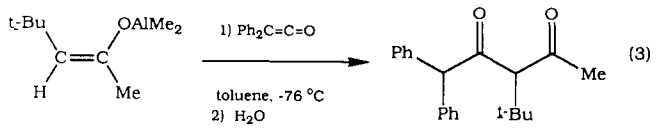
There have been a few previous studies of the reactions of enolates with ketenes.[7] Interestingly, these have shown that enolates reacted with ketenes mainly by O-acylation in relatively polar solvents. Thus, Yoshida et al. have reported[7a] that the reaction of dimethylketene with the potassium enolates of isobutyrophenone and diisopropyl ketone in dimethyl ether resulted in the formation of the O-acylation products exclusively, at -30 °C (eq 2). Similarly, the reaction of ketene itself with the sodium enolate of propiophenone afforded the alkenyl ester in 23-28% yield.[7b]



(2)

R^1 = Ph, t-Pr

However, the Z isomer of dimethylaluminum 4,4-dimethylpent-2-en-2-olate underwent C-acylation on reaction with diphenylketene in toluene. It has been suggested that this was due to the covalent nature of the Al-O bond (eq 3).[7c]



(3)

(57%)

Because of the synthetic potential and theoretical interest of the addition of Me_3SiLi and of enolates to ketenes, we have undertaken further study of both reactions.

Results and Discussion

Silylations. The reactions of Me_3SiLi with ketenes **3-5** gave the enol acetates **6-9** as shown in eqs 4-6 on trapping

(1) Presented in part in a preliminary communication: Baigrie, L. M.; Leung Toung, R.; Tidwell, T. T. *Tetrahedron Lett.* **1988**, *29*, 1673-1676.
(2) For a review, see: Seikaly, H. R.; Tidwell, T. T. *Tetrahedron* **1986**, *42*, 2587-2613.
(3) (a) Baigrie, L. M.; Lenoir, D.; Seikaly, H. R.; Tidwell, T. T. *J. Org. Chem.* **1985**, *50*, 2105-2109. (b) Baigrie, L. M.; Seikaly, H. R.; Tidwell, T. T. *J. Am. Chem. Soc.* **1985**, *107*, 5391-5396.
(4) (a) Allen, A. D.; Stevenson, A.; Tidwell, T. T. *J. Org. Chem.* **1989**, *54*, 2843-2848. (b) Allen, A. D.; Tidwell, T. T. *J. Am. Chem. Soc.* **1987**, *109*, 2774-2780. (c) Allen, A. D.; Kresge, A. J.; Schepp, N. P.; Tidwell, T. T. *Can. J. Chem.* **1987**, *65*, 1719-1723.
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(6) Nadler, E. B.; Rappoport, Z.; Arad, D.; Apeloig, Y. *J. Am. Chem. Soc.* **1987**, *109*, 7873-7875.
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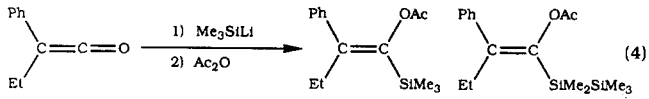
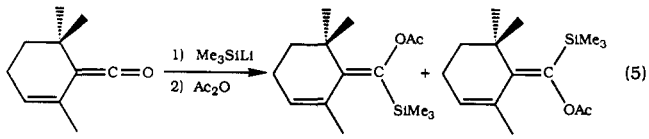
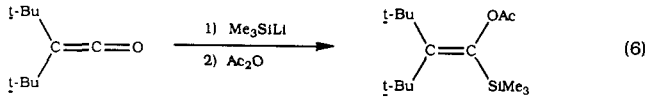
of the intermediates with acetic anhydride. The reaction of $(Me_3Si)_2C{=}C{=}O$ with Me_3SiLi was also examined but gave no identifiable products.



(4)



(5)

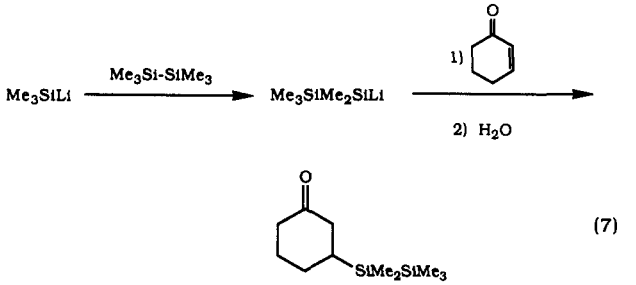


(6)

The structure and the *E* stereochemistry of **6** follow from the spectral properties and previous work[3b] which established that nucleophilic additions to **3** occurred with a strong preference for approach from the less hindered side of the ketene syn to the ethyl group. No sign of **6***Z* was detected, and it is estimated to constitute less than 3% of the total product.

The structural assignment of **7***E* follows from the spectral properties, which resemble those for **6***E* except that whereas **6** has a nine-proton singlet in the ^1H NMR spectrum at δ 0.23, **7***E* has singlets at δ 0.10 and 0.16 corresponding to nine and six protons, respectively. The IR spectra of **6***E* and **7***E* were practically identical, including an acetyl carbonyl in each. In the mass spectra **6** showed the presence of the parent ion at m/z 262 while **7***E* showed no M^+ but an intense peak at 247 assigned to $M^+ - Me_3Si$.

Precedent for the formation of the disilyl compound **7** comes from the work of Hudrlik and co-workers,[8] who also observed the formation of a disilyl side product in the reaction with cyclohexenone. They suggested[8b] that Me_3SiLi, generated from hexamethyldisilane, reacted with excess hexamethyldisilane to give the disilyllithium reagent which reacted with cyclohexenone to afford the disilyl compound as a side product (eq 7).



(7)

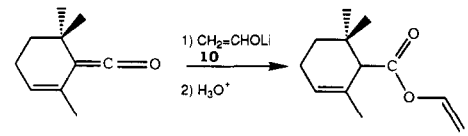
The reaction of the cyclohexenylidene ketene **4** with Me_3SiLi followed by acetylation with Ac_2O furnished a mixture of *E* and *Z* regioisomers **8** in a 7:3 ratio in 69% yield (eq 5). The major product has been tentatively assigned as **8***E* by analogy with the results of NOE experiments of Naef and Decorzant.[9] They reported that the reaction of allylmagnesium chloride with **4** followed by silylation with Me_3SiCl gave a mixture of isomers in a ratio of 9/1 and assigned the predominant product as arising from approach of the nucleophile anti to the geminal dimethyls in **4**.

Attempts to separate the two isomers **8***E* and *-Z* by chromatographic methods (flash chromatography on silica gel with hexane–ethyl acetate or preparative gas chromatography) failed. However, the two isomers were clearly distinguishable from the ^1H NMR (200 MHz) spectrum, and the product ratio was determined from the 7:3 ratio of the Me_3Si peaks. Analytical GC (OV-101) showed two closely spaced peaks in a 7:3 ratio.

The sterically crowded di-*tert*-butylketene (**5**) afforded **9** in 57% yield, and the structure is readily established from the spectral properties. No disilyl products analogous to **7***E* were detected in the reactions of **4** and **5** with Me_3SiLi.

At present we are unable to make a priori predictions of the preference for syn vs anti attack of various nucleophiles on unsymmetrical ketenes such as **4**, but experimental and computational approaches to this problem are under investigation.

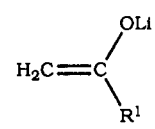
Enolate Acylations. Reaction of the cyclohexenylidene ketene **4** with acetaldehyde lithium enolate ($CH_2{=}CHOLi$, **10**)[10a] followed by hydrolysis gave the product **11** of O-acylation of **10** by the ketene as well as the corresponding *n*-butyl ester **12** in a 3.6/1 ratio. The formation of **12** is attributed to reaction of **4** with *n*-BuOLi formed by oxidation of the *n*-BuLi.



(8)

The formation of the O-acylated product **11** was unexpected. We had reasoned that the observation of O-acylation by ketenes[7a,b] (eq 2) was primarily due to the relatively loose coordination of the Na and K cations to oxygen, rendering this center open to attack, while the substituents on the enolate carbon hindered C-acylation. For $CH_2{=}CHOLi$ tighter coordination of the cation to oxygen[10b] and an unencumbered carbon were expected to promote C-acylation, but none was observed.

In view of this unexpected development, and our interest in exploring the synthetic utility of the reaction of organolithium reagents with ketenes, a more detailed study of the reaction of methylphenylketene **13** and ethylphenylketene **3** with the lithium enolates **10** and **14–16** was undertaken.



R^1 =	
H	**10**
CH_3	**14**
t-Bu	**15**
Ph	**16**

Lithium Enolates. The reaction of the ketenes with the lithium enolates followed by hydrolysis led to the formation of the vinyl esters **17–24** (eq 9) as reported in Table I, with the given yields based on precursor acid chlorides.[3] Dilute solutions of the ketenes were added dropwise to stirred solutions of 2 equiv of the lithium

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(9) Naef, F.; Decorzant, R. *Tetrahedron* **1986**, *42*, 3245–3250.

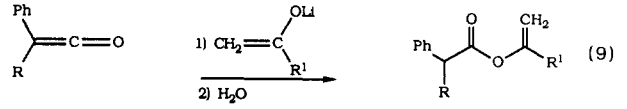
(10) (a) Jung, M. E.; Blum, R. B. *Tetrahedron Lett.* **1977**, *18*, 3791–3794. (b) House, H. O. *Modern Synthetic Reactions*, 2nd ed.; Benjamin: Menlo Park, 1972; pp 734–816.

Table I. Acylation of Lithium Enolates by Ketenes

ketene	lithium enolate	product	yield[a]
13	10	$PhCHMeCO_2CH{=}CH_2$, 17	40
13	14	$PhCHMeCO_2C(Me){=}CH_2$, 18	50
13	15	$PhCHMeCO_2C(t\text{-}Bu){=}CH_2$, 19	87
13	16	$PhCHMeCO_2C(Ph){=}CH_2$, 20	60[b]
3	10	$PhCHEtCO_2CH{=}CH_2$, 21	47
3	14	$PhCHEtCO_2C(Me){=}CH_2$, 22	40
3	15	$PhCHEtCO_2C(t\text{-}Bu){=}CH_2$, 23	57
3	16	$PhCHEtCO_2C(Ph){=}CH_2$, 24	60

[a] Percentage yield determined by GC or product isolation. [b] $PhCHMeCOCH_2COPh$ (25, 10%) also isolated.

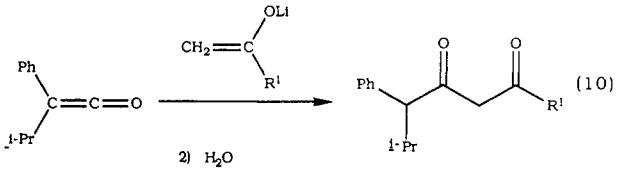
enolates at −78 °C, and the resultant solutions were stirred for 2 h while warming to 25 °C before hydration.



(9)

R = Me,Et; R^1 = H,CH_3,t-Bu,Ph 17–24

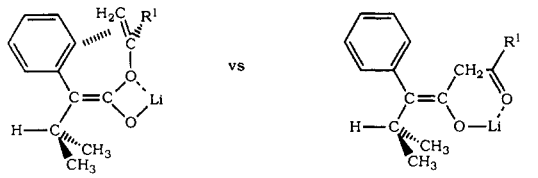
The vinyl esters (17–24) were readily separated by preparative GC (OV-17 or OV-101 columns) after filtering the crude reaction mixtures through silica gel with 9/1 hexane–ethyl acetate solvent mixture. C-Acylation was observed in only one case, namely the C-acylation product **25** was obtained in 10% yield in the reaction of methylphenylketene (**13**) with the lithium enolate of acetophenone (**16**) followed by hydration. However, Baigrie-Boyd[1,11] observed only the C-acylation products **27** and **28** from addition of isopropylphenylketene (**26**) to the lithium enolates **14** and **16**.



(10)

26 R^1 = Me, **27** (54%); Ph, **28**, (48%)

Evidently, C-acylation is favored relative to O-acylation because of the larger steric requirements of the substituents of ketene **26**. The possible greater steric interaction in the enolate intermediate of O-acylation (**29**) as compared to that of C-acylation (**30**) is illustrated.



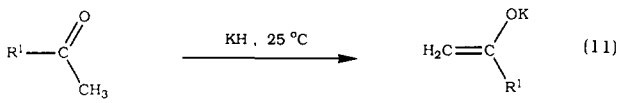
29 **30**

In the reactions of methylphenylketene (**13**) with the lithium enolates **10** and **14–16**, methyl 2-phenylpropanoate (9–16%) and *n*-butyl 2-phenylpropanoate (10–20%) were obtained as side products. When ethylphenylketene (**3**) was employed, the side products isolated were *n*-butyl 2-phenylbutanoate (16–29%) and propiophenone (**31**, 6–12%).

Propiophenone could arise from the autooxidation of ethylphenylketene (**3**). Staudinger et al.[12] have reported the autooxidation of diphenylketene to benzophenone by molecular oxygen. The *n*-butyl alkanoates resulted from the competing reaction of *n*-BuOLi with ketenes **3** and **13** as suggested earlier for ketene **4**. Several experiments were repeated under strictly air-free conditions, and several new bottles of *n*-BuLi (1.6 M in hexane) were used after titration with diphenylacetic acid,[13] and no indication of the presence of *n*-BuOLi was found. Nevertheless, the amount of side products were not notably reduced. Some unidentified source of methoxide evidently led to the methyl esters.

The additions of lithium alkoxides to ketenes have been reported before by Hegarty et al.[14] Thus reaction of lithium methoxide and lithium *tert*-butoxide with bis(pentamethylphenyl)ketene afforded ketene acetals after trapping with dimethyl sulfate and Me_3SiCl, respectively.

Potassium Enolates. In order to study the effect of the metal counterion on the competition between O- and C-acylation, the potassium enolates **32–34**[15] were examined (eq 11). These also have the advantage of the absence of



(11)

R^1 = CH_3 **32**; t-Bu **33**; Ph **34**

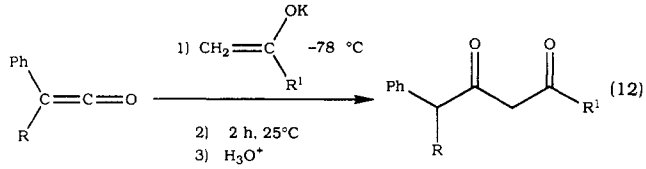
troublesome alkoxides.

The dilute ketene solutions were added dropwise to 2 equiv of stirred solutions of the potassium enolates at −78 °C, and the resultant solutions were stirred for 2 h before hydration. Potassium enolates often favor O-acylation, but surprisingly, the reactions of ketenes **13** and **3** with the potassium enolates **32–34** furnished the C-acylated β-diketone products **25** and **35–39** under these conditions, after hydrolytic workup (eq. 12). The yields of C-acylation products given are based on the precursor acid chlorides (Table II).

Table II. Acylation of Potassium Enolates 32–34 by Ketenes 3 and 13

ketene	potassium enolate	product	yield[a]	e/k[b]
13	32	$PhCHMeCOCH_2COMe$, 35	63	9/2
13	33	$PhCHMeCOCH_2CO$-t-Bu, 36	78	5/1
13	34	$PhCHMeCOCH_2COPh$, 25	74	10/1
3	32	$PhCHEtCOCH_2COMe$, 37	71	5/1
3	33	$PhCHEtCOCH_2CO$-t-Bu, 38	76	7/1
3	34	$PhChEtCOCH_2COPh$, 39	75	12/1

[a] Percentage yield determined by GC or product isolation. [b] Enol/ketone ratio obtained from 200-MHz ^1H NMR spectroscopy.



(12)

R = Me (**13**), Et (**3**); R^1 = CH_3, t-Bu, Ph. **25**,**35-39**

The C-acylation products were readily separated from the reaction mixture by flash chromatography[16] on silica gel with 9/1 hexane–ethyl acetate, and further purified by preparative GC (OV-101 or OV-17 columns). The products **25** and **35–39** were found to exist predominantly as the enol tautomers, and the enol/keto ratios were easily determined

(11) Baigrie-Boyd, L. M., unpublished results in this laboratory.
(12) Staudinger, H.; Dycherhoff, K.; Klever, H. W.; Ruzicka, L. *Chem. Ber.* **1925**, *58*, 1079–1087.
(13) Kofron, W. G.; Baclawski, L. M. *J. Org. Chem.* **1976**, *41*, 1879–1880.
(14) (a) O'Neill, P.; Hegarty, A. F. *J. Org. Chem.* **1987**, *52*, 2113–2114. (b) O'Neill, P.; Hegarty, A. F. *J. Chem. Soc., Chem. Commun.* **1987**, 744–745.
(15) Brown, C. A. *J. Org. Chem.* **1974**, *39*, 3913–3918.
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Table III. C/O Product Ratio Dependence on Reactant Ratio and Reaction Time

reaction	enolate ratio	time, h (temp, °C)[a]	product ratio (C/O)[b]
PhEtC=C=O (**3**) + CH_2=C(*t*-Bu)OLi (**15**)	2	2 (25)	0/100
3 + **15**	2	16 (25)	50/50
3 + CH_2=C(*t*-Bu)OK (**33**)	2	2 (25)	100/0
3 + **33**	0.9	2 (25)	100/0
3 + CH_2=C(Me)OK (**32**)	1	0.1 (−78)	15/85[c]
3 + **32**	1	2 (25)	100/0
PhCHMeCO$_2$C(Me)=CH_2 + **32**	2	1.5 (25)	100/0
PhCHMeCOCl (**40**) + CH_2=C(Ph)OLi (**16**)	1.5	2 (25)	30/70

[a] Initial reaction at −78 °C. [b] Determined by GC using authentic materials for comparison. [c] Unchanged after 2 h at −78 °C.

from the relatively intensities of the C=CH band near δ 5.5 and the $COCH_2CO$ band near δ 3.5 in the ^1H NMR spectrum.[17]

Several experiments were carried out to determine the C/O product ratio dependence on the reactant ratio and the reaction time (Table III), and these reveal not only that the initial O-acylated lithium salts are converted to C-acylated products on prolonged standing at 25 °C, but also that the potassium enolates also undergo predominant O-acylation at −78 °C.

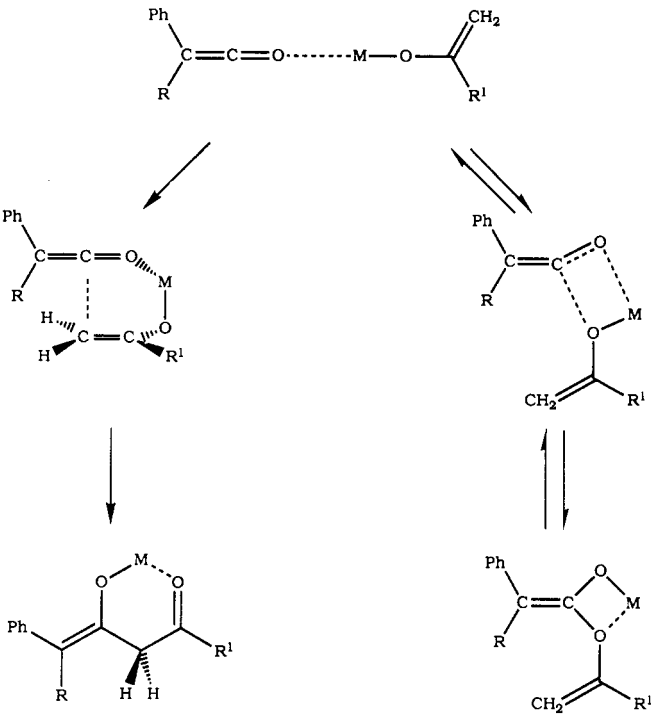
Ketene **3** reacted with CH_2=C(*t*-Bu)OLi (**15**) at −78 °C to afford the O-acylation product **23** exclusively when the reaction was stopped after warming to 25 °C over 2 h (Table I). When the reaction time was increased to 16 h, a 1/1 mixture of O- and C-acylation products **23** and **38** was obtained (Table III). Reaction of **3** with either 0.9 or 2 equiv of CH_2=C(*t*-Bu)OK (**33**) led to the formation of the C-acylation product **38** exclusively at 25 °C (Table III), but when **3** was reacted with CH_2=C(Me)OK (**32**) at −78 °C and the reaction mixture was quenched at this temperature O-acylation was favored and no change in the product ratio was detected on reaction times of 0.1–2 h. However, when the reaction product was warmed to 25 °C only C-acylation was observed.

A possible reaction pathway to rationalize the results obtained is illustrated in Scheme I. C-Acylation of enolates by ketenes leads to the thermodynamically more stable product irreversibly, but O-acylation is often the kinetically favored process for both lithium and potassium enolates. Reversal of O-acylation and formation of the C-acylated product occurs for both cations but is more facile for potassium salts, perhaps because of weaker coordination of the metal to oxygen lowering the barrier for dissociation. Steric crowding in the product favors C-acylation. The true kinetic C/O acylation ratios are not known, but in most cases (Tables I–III) either the C- or O-acylation products can be obtained preparatively as desired.

As shown in Scheme I O-acylation of enolates occurs in the plane of the enolate for stereoelectronic reasons, whereas C-acylation occurs in the plane that is perpendicular to the plane of the enolate. For similar reasons, as stated earlier, nucleophiles approach in the plane of the ketene.[4] O-Acylation of enolates by ketenes involves a planar four-centered transition state, whereas C-acylation occurs through a six-membered transition state.

Molecular orbital calculations for the reaction of the lithium enolate of acetaldehyde with ketene support the

Scheme I. Reversible O-Acylation of Enolates by Ketenes



path of Scheme I.[5b] There is also experimental[18] and theoretical[19] evidence for the formation of initial complexes in the reaction of lithium reagents with carbonyl compounds.

The reversion of the O-acylated ketene adduct to ketene and enolate is well precedented. Thus the E1cB mechanism of ester hydrolysis[20] involves formation of ester enolates which cleave to alkoxides and ketenes, and the latter have been directly observed.[20d]

The cleavage of ester enolates as a preparative route to form ketenes has been reported in a few examples. Seebach et al.[21] have shown that above −20 °C solutions of 2,6-di-*tert*-butyl-4-methylphenyl (BHT) ester enolates cleave to ketenes which react in situ with organolithium reagents. Similarly, cyclohexenylidene ketene **4**[22] and bis(trimethylsilyl)ketene[23] have been prepared by similar routes.

Summary

The reactions of ethylphenylketene (**3**) and the cyclohexenylidene ketene **4** with trimethylsilyllithium at −78 °C followed by acetylation with acetic anhydride afforded the corresponding α-silyl enol acetates. These unsymmetrical ketenes afforded enolates stereoselectively as already noted in the reactions of these ketenes with alkyllithiums.[3b,9] The crowded di-*tert*-butylketene (**5**) reacted with the silyllithium reagent to give a highly crowded

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tetrasubstituted enolate, which was trapped with Ac_2O, forming **9**.

O-Acylation of either lithium or potassium enolates by ketenes is often kinetically favored at −78 °C, but at 25 °C the initial adducts isomerize to the thermodynamically more stable C-acylation products. The formation of C-acylated products is more facile with potassium salts and is also favored for crowded ketenes. For ethylphenylketene (**3**) and methylphenylketene (**13**) the choice of reaction conditions permits the formation of either O- or C-acylation products as desired.

Experimental Section

Materials. Glassware was dried in an oven at 250 °C and cooled in a dessicator before use. Sensitive reactions were carried out under a nitrogen atmosphere. Solutions were transferred via glass syringes under a positive N_2 pressure. Unless otherwise indicated, materials were obtained from commercial suppliers and used without further purification. Hexamethyldisilane and hexamethylphosphoramide were from Aldrich. Tetrahydrofuran (THF) was distilled from sodium and benzophenone ketyl under argon. Triethylamine (Et_3N) was dried over KOH pellets and then distilled, and diisopropylamine (i-Pr_2NH) was distilled from CaH_2 under argon. Potassium hydride (KH, 35% in dispersion oil) was washed with pentane in a nitrogen glovebag prior to use. Acetone was diluted and stored over activated 4-Å molecular sieves. n-Butyllithium (n-BuLi) was standardized[13] by titration with a solution of diphenylacetic acid in THF of known concentration at 0 °C under N_2. Di-*tert*-butylketene[24] was available from previous studies. Methylphenylketene,[25a] and ethylphenylketene,[25b] were prepared from 2-phenylpropanoyl chloride and 2-phenylbutanoyl chloride, respectively, by treatment with Et_3N as described.[3b] Ketene **4**[26a] was prepared similarly as described,[26] and details are given in the supplementary material.

^1H NMR spectra were run at 60 or 400 MHz and ^{13}C NMR spectra were measured at 50 or 100 MHz. Gas chromatographic (GC) analyses were conducted on 3% OV-101 (Chrom G, HP 80/100 × 2 mm) or OV-17 (Chrom W, HP 80/100 × 2 mm) columns and are reported as relative peak areas without correction for detector response. Chromatographic separations were performed using flash chromatography[16] on silica gel and preparative GC (10% OV-101 and OV-17 columns). All new compounds were purified by GC and judged to be >95% pure by this criterion. Elemental analyses were by Galbraith.

(Trimethylsilyl)lithium (Me_3SiLi).[27] In a typical procedure, to a mixture of 10 mL of HMPA and hexamethyldisilane (3.10 mL, 15 mmol) previously cooled to 0 °C was added MeLi (1.25 M in Et_2O, LiBr, 12 mL, 15 mmol). The resultant brick red solution was stirred for 5 min at 0 °C. Then 40 mL of THF (previously cooled to 0 °C) was quickly added, and the dark red solution was chilled to −78 °C and used immediately.

(*E*)-1-(Trimethylsilyl)-2-phenylbut-1-enyl Acetate (6). To 15 mmol of Me_3SiLi in THF–HMPA (4/1) at −78 °C was added a solution of ethylphenylketene (**3**) (5 mmol) in 15 mL of THF. There was an immediate discharge of the red color, and the resultant solution was stirred for 1.5 h. Acetic anhydride (Ac_2O, 5 mL, 45 mmol) in 10 mL of THF was then added, and the mixture was left stirring overnight. The solution was poured over 50 mL of aqueous 10% HCl and extracted with pentane. The organic layer was washed with saturated $NaHCO_3$ solution, water, and brine. After drying over $MgSO_4$, the organic solution was concentrated to furnish 1.67 g of a yellow oil. Analysis by GC (OV-17, 150 °C, 34 mL/min) indicated the formation of **6*E*** and **7*E*** in a 2.7/1 ratio, with retention times of 5 and 13 min, respectively. Preparative GC (OV-17) afforded **6*E*** (0.67 g, 2.6 mmol, 54%): IR (CCl_4) 1736 cm^{-1} (C=O); ^1H NMR ($CDCl_3$) δ 0.23 (s, 9, $SiMe_3$), 0.88 (t, 3, J = 7.4, CH_3CH_2), 1.77 (s, 3, COMe), 2.44 (q, 2, J = 7.4, CH_3CH_2), 7.07–7.34 (m, 5, Ph); ^{13}C NMR ($CDCl_3$) δ −0.6, 13.0, 20.4, 26.7, 126.8, 127.8, 127.9, 138.7, 146.2, 148.6, 170.3; mass spectrum, m/z (relative intensity) 262 (8, M^+), 247 (19, $M^+ - CH_3$), 220 (67, $M^+ - C_2H_2O$), 205 (14, $M^+ - C_2H_2O, CH_3$), 176 (18), 161 (33), 117 (57), 103 (3), 91 (19, $C_7H_7^+$), 77 (7, Ph^+), 73 (100, Me_3Si^+); high-resolution mass spectrum M^+ 262.1384 ($C_{15}H_{22}O_2Si$ requires 262.1389). Anal. Calcd: C, 68.65; H, 8.45. Found: C, 68.33; H, 8.46.

7*E*: IR (CCl_4) 1734 cm^{-1}; ^1H NMR (CCl_4) δ 0.10 (s, 9), 0.16 (s, 6), 0.82 (t, 3, J = 7.2), 1.61 (s, 3), 2.31 (q, 2, J = 7.2), 6.70–7.20 (m, 5); mass spectrum, m/z (relative intensity) 247 (37), 202 (6), 175 (20), 159 (10), 147 (12), 131 (12), 117 (100), 105 (16), 91 (19), 77 (15), 73 (67, Me_3Si^+).

Reaction of Cyclohexenylidene Ketene 4 with Me_3SiLi/Ac_2O. Using the same procedure as for the reaction of **3**, the reaction of cyclohexenylidene ketene **4** (0.60 g, 4 mmol) with Me_3SiLi (10 mmol) followed by acetylation with Ac_2O (5 mL, 45 mmol) afforded 1.50 g of a light yellow oil after hydrolytic workup. Analytical GC (OV-101, 150 °C, 34 mL/min) indicated the formation of 1′-(trimethylsilyl)-1′-acetoxy-2,6,6-trimethylcyclohexen-2-en-1-ylidene as a mixture of two isomers **8*Z*** and **-*E***, in a 1/2.2 ratio with retention times of 6.7 and 7.3 min, respectively. Attempts to separate the two products by chromatographic methods (preparative GC, flash chromatography on silica gel with hexane/ethyl acetate) failed. The 200-MHz ^1H NMR spectrum of the purified mixture (0.71 g, 2.7 mmol, 69%) permitted assignment of the signals due to **8*Z*** and **-*E*** and from the relative intensities of the Me_3Si peaks the Z/E ratio was determined to be 7:3.

8*E*/*Z*: IR (neat) 1741 cm^{-1} (C=O); mass spectrum, m/z (relative intensity) 266 (5, M^+), 251 (6, $M^+ - CH_3$), 207 (20, $M^+ - C_2H_3O_2$), 150 (6, $C_{10}H_{14}O^+$), 135 (13, $C_9H_{11}O^+$), 117 (7), 107 (100, $C_8H_{11}^+$), 91 (16, $C_7H_7^+$), 79 (55, $C_6H_7^+$), 73 (80, Me_3Si^+). Anal. Calcd: C, 67.61; H, 9.84. Found: C, 67.49; H, 9.81.

8*E*: ^1H NMR ($CDCl_3$) δ 0.24 (s, 9, $SiMe_3$), 1.17 (s, 6, Me_2), 1.21 (m, 2, CH_2), 1.57 (m, 2, CH_2), 1.89 (m, 3, HC=C*Me*), 2.06 (s, 3, COMe), 5.54 (m, 1, *H*C=CMe).

8*Z*: ^1H NMR ($CDCl_3$) δ 0.17 (s, 9, $SiMe_3$), 1.16 (s, 6, Me_2), 1.21 (m, 2, CH_2), 1.57 (m, 2, CH_2), 1.97 (m, 3, HC=C*Me*), 2.11 (s, 3, COMe), 5.80 (m, 1, *H*C=CMe).

1-Acetoxy-1-(trimethylsilyl)-2-*tert*-butyl-3,3-dimethylbut-1-ene (9). To the dark red solution of Me_3SiLi (12 mmol) was added di-*tert*-butylketene (**5**) (0.62 g, 4 mmol) in 10 mL of THF, followed by acetylation with Ac_2O (5 mL, 45 mmol) after 1 h. Following usual workup as described for **6**, 1.56 g of a yellow oil was obtained. Analysis by GC (OV-17, 150 °C, 34 mL/min) indicated the presence of unreacted **5** and **9** in a 1/8 ratio, with retention times of 0.9 and 2.3 min, respectively. Preparative GC (OV-17, 190 °C) afforded **9** (0.63 g, 2.3 mmol, 57%).

5: IR (CCl_4) 2086 cm^{-1} (C=C=O).

9: IR (CCl_4) 1734 cm^{-1} (C=O); ^1H NMR ($CDCl_3$) δ 0.20 (s, 9, $SiMe_3$), 1.27 (s, 9, *t*-Bu), 1.31 (s, 9, *t*-Bu), 2.07 (s, 3, $COCH_3$); ^{13}C NMR ($CDCl_3$) δ 3.3, 21.9, 32.7, 33.1, 37.9, 39.4, 153.7, 160.4; mass spectrum, m/z (relative intensity) 270 (1, M^+), 213 (100, M^+ – *t*-Bu), 157 (18), 156 (5, $M^+ - 2t$-Bu), 117 (46), 73 (97, Me_3Si^+), 57 (58, *t*-Bu^+).

Reaction of Cyclohexenylidene Ketene 4 with Acetaldehyde Lithium Enolate (10). The lithium enolate **10** was generated according to the procedure reported by Jung.[10a] Thus n-BuLi (1.6 M in hexane, 5.8 mL, 9 mmol) was stirred in 30 mL THF at room temperature for 16 h. The resultant white slurry was then cooled to −78 °C before adding cyclohexenylidene ketene **4** (0.5 g, 3.3 mmol) in 10 mL of THF. After 2 h, the reaction mixture was poured over 25 mL of aqueous 10% HCl followed by extraction with ether. The ether extract was washed with water, saturated $NaHCO_3$ solution and brine. After evaporation of the solvent, the residue (1.52 g) was analyzed by GC (OV-17, 105 °C, 30 mL/min) and found to contain vinyl 2,6,6-trimethylcyclohexen-2-enoate carboxylate (**11**) and n-butyl 2,6,6-trimethylcyclohex-2-enoate carboxylate (**12**) in a 3.6/1 ratio, with retention times of 3.1 and 7.5 min, respectively. The products were separated by preparative GC (OV-17, 130 °C).

11: IR (CCl_4) 1752 cm^{-1} (C=O); ^1H NMR (CCl_4) δ 0.98 (s, 6,

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Me_2), 1.20 (m, 2, CH_2), 1.66 (br s, 3, HC=C*Me*), 2.00 (m, 2, CH_2), 2.55 (s, 1, HCCO), 4.60 (two d of d, 2, HC=C*H*$_2$), 5.50 (m, 1, *H*C=CMe), 7.25 (q, 1, *H*C=CH_2); mass spectrum, *m/z* (relative intensity) 194 (2, M^+), 167 (20, $M^+ - C_2H_3$), 151 (6, $M^+ - C_2H_3O$), 137 (58, $MH^+ - C_2H_3O$, CH_3), 123 (100, $C_9H_{15}^+$), 121 (80), 107 (73, $C_8H_{11}^+$), 91 (22, $C_7H_7^+$), 83 (30), 79 (22, $C_6H_7^+$), 73 (4), 69 (23).

12: IR (CCl_4) 1733 cm^{-1} (C=O); ^1H NMR (CCl_4) δ 0.85 (s, 6, Me_2), 0.90 (t, 3, CH_2CO), 1.20–2.20 (m, 8), 1.50 (br s, 3, HC=C*Me*), 2.40 (s, 1, HCCO), 3.95 (t, 2, $COCH_2$), 5.40 (m, 1, *H*C=CMe); mass spectrum, *m/z* (relative intensity) 224 (16, M^+), 167 (20, $M^+ - C_4H_9$), 153 (6, $MH^+ - C_4H_9$, CH_3), 150 (4, $C_{10}H_{14}O^+$), 135 (20, $C_9H_{11}O^+$), 123 (100, $C_9H_{15}^+$), 122 (67, $C_9H_{14}^+$), 107 (35, $C_8H_{11}^+$), 91 (9, $C_7H_7^+$), 81 (23), 79 (6, $C_6H_7^+$), 69 (15).

Lithium Enolate of Acetone (14), Pinacolone (15), and Acetophenone (16).[28] A solution of LDA (6 mmol) was prepared as 0 °C from an equimolar amount of *i*-Pr_2NH and *n*-BuLi (1.6 M in hexane) in THF. After the solution was stirred for 5 min at −78 °C, acetone (0.4 mL, 6 mmol) in 10 mL of THF was added, and the resulting lithium enolate solution **14** was stirred for 2 h at −78 °C prior to use. The lithium enolates of 3,3-dimethylbutanone (pinacolone) (**15**) and acetophenone (**16**) were prepared by the same procedure.

1-Methylvinyl 2-Phenylpropanoate (18). To a solution of the lithium enolate of acetone (**14**) (6 mmol) was added methylphenylketene (**13**) (3 mmol) in 25 mL of THF at −78 °C. After being warmed to 25 °C over a period of 2 h, the reaction mixture was poured over 50 mL of aqueous 10% HCl and extracted with ether. The ethereal layer was washed successively with saturated $NaHCO_3$ solution, water, and brine and then dried ($MgSO_4$). Evaporation of the solvent gave 0.87 g of an oil that on analysis by GC (OV-101, 150 °C, 34 mL/min) was found to consist of methyl 2-phenylpropanoate (**41**), 1-methylvinyl 2-phenyl-propanoate (**18**), and *n*-butyl 2-phenylpropanoate (**42**) in 1.0:3.1:1.1 ratios, with retention times of 1.7, 2.5, and 5.2 min, respectively. The crude product was chromatographed on silica gel with hexane–ethyl acetate (9/1) and further purified by preparative GC (OV-101, 190 °C) to afford **18** (0.29 g, 1.5 mmol, 50%).

18: IR (CCl_4) 1751 (C=O), 1672 (C=C) cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.44 (d, 3, J = 7.2, PhC*H*MeCH), 1.75 (br s, 3, *Me*C=CH_2), 3.70 (q, 1, J = 7.2, CH), 4.53–4.59 (m, 2, MeC=C*H*$_2$), 7.24 (s, 5, Ph); ^{13}C NMR ($CDCl_3$) δ 18.5, 19.2, 45.5, 101.9, 127.2, 127.4, 128.7, 140.2, 153.0, 172.6; mass spectrum, *m/z* (relative intensity) 190 (1, M^+), 133 (11, $M^+ - C_3H_5O$), 105 (100, $C_8H_9^+$), 77 (10, Ph^+); high-resolution mass spectrum M^+ 190.1001 ($C_{12}H_{14}O_2$ requires 190.0990).

41: IR (CCl_4) 1736 cm^{-1} (C=O); ^1H NMR (CCl_4) δ 1.50 (d, 3, J = 7.4, PhC*H*MeCH), 3.62 (q, 1, J = 7.4, PHMeC*H*), 3.60 (s, 3, OMe), 7.20 (s, 5, Ph); mass spectrum, *m/z* (relative intensity) 164 (21, M^+), 105 (100, $C_8H_9^+$), 77 (10, Ph^+), 59 (1).

42: IR (CCl_4) 1736 cm^{-1} (C=O); ^1H NMR (CCl_4) δ 0.85 (t, J = 7, 3, $(CH_2)_3CH_3$), 1.10–1.65 (m, 4), 1.50 (d, 3, J = 7.2, PhC*H*MeCH), 3.50 (q, 1, J = 7.2, PhMeC*H*), 3.90 (t, 2, $COCH_2$), 7.10 (s, 5, Ph); mass spectrum, *m/z* (relative intensity) 206 (7, M^+), 150 (8, PhCHMeCOOH), 106 (10), 105 (100, $C_8H_9^+$), 77 (7, Ph^+), 57 (13, $C_4H_9^+$).

The reaction of methylphenylketene **13** with the lithium enolates **10**, **15**, and **16** to afford **17**, **19**, and **20**, respectively, were carried out analogously and the vinyl ester yields are given in Table I. Product characterizations of **17**, **19**, and **20** are given in the supplementary material.

1-*tert*-Butylvinyl 2-Phenylbutanoate (23). Ethylphenylketene (**3**) (4.68 mmol) in 25 mL of THF was added to a solution of the lithium enolate of pinacolone (**15**) (9.36 mmol) at −78 °C. After being warmed to 25 °C in 2 h, the reaction mixture was worked up as described for **18**, and 1.02 g of an oil was obtained. Analytical GC (OV-101, 150 °C, 34 mL/min) indicated the formation of propiophenone, *n*-butyl 2-phenylbutanoate (**43**), and 1-*tert*-butylvinyl 2-phenylbutanoate (**23**) in 1.0:2.2:4.8 ratios, with retention times of 1.4, 6.4, and 10.5 min, respectively. The products were separated by preparative GC (OV-101, 190 °C). The spectral data of propiophenone were similar to the authentic material available commercially (Aldrich).

23: IR (CCl_4) 1755 (C=O), 1655 (C=C) cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.95 (t, 3, J = 7.4, Me), 0.95 (s, 9, *t*-Bu), 1.79–2.25 (m, 2, CH_2), 3.55 (t, 1, J = 7.7, CH_2CHCO), 4.70 (dd, 2, AB, C=CH_2), 7.30 (s, 5, Ph); ^{13}C NMR ($CDCl_3$) δ 12.1, 26.1, 27.5, 36.0, 53.8, 98.7, 127.2, 128.0, 128.5, 138.7, 162.5, 172.0; mass spectrum, *m/z* (relative intensity) 246 (1, M^+), 177 (15), 164 (1, $PhEtCHCO_2H$), 147 (32, $M^+ - C_6H_{11}O$), 119 (76, $C_9H_{11}^+$), 91 (100, $C_7H_7^+$), 77 (7, Ph^+); high-resolution mass spectrum M^+ 246.1624 ($C_{16}H_{22}O_2$ requires 246.1614).

43: IR (CCl_4) 1735 (C=O) cm^{-1}; ^1H NMR (CCl_4) δ 0.90 (br t, J = 7, 6, two Me), 1.20–1.60 (m, 4, $(CH_2)_2$), 1.60–2.05 (m, 2, CH_3CH_2CH), 3.25 (t, J = 7, 1, CH_2CHCO), 3.95 (t, J = 7, 2, $COCH_2$), 7.03 (s, 5, Ph); mass spectrum, *m/z* (relative intensity) 220 (11, M^+), 164 (16, $PhCHEtCOOH^+$), 119 (95, $C_9H_{11}^+$), 91 (100, $C_7H_7^+$), 77 (5, Ph^+), 57 (18, $C_4H_9^+$).

Similarly, ethylphenylketene (**3**) was reacted with the lithium enolates **10**, **14**, and **16** to afford **21**, **22**, and **24**. The vinyl ester yields are shown in Table I, and product characterizations are given in the supplementary material.

Potassium Enolates of Acetone (32), Pinacolone (33), and Acetophenone (34).[15] In a typical procedure, a solution of acetone (0.4 mL, 5.6 mmol) in 10 mL of THF was added to a slight excess of potassium hydride (KH, 0.25 g, 6.3 mmol, prewashed with pentane) in THF with vigorous stirring at 25 °C. The potassium enolate **32** was stirred for 15 min and then cooled to −78 °C prior to use. The potassium enolates of pinacolone (**33**) and acetophenone (**34**) were prepared similarly.

Reaction of Methylphenylketene (13) with the Potassium Enolate 32. To 5.2 mmol of the potassium enolate of acetone (**32**) at −78 °C was added a solution of methylphenylketene (**13**) (2.6 mmol) in 25 mL of THF. The reaction mixture was left to warm to 25 °C over 2 h. Ethanol (10 mL) was added dropwise to destroy excess KH, and the resultant solution was acidified with a 10% HCl solution and extracted with ether. The ethereal layer was washed with saturated $NaHCO_3$ solution followed by brine and dried ($MgSO_4$). Evaporation of the solvent gave an oil, which was chromatographed on silica gel with hexane–ethyl acetate (9/1) to afford 5-phenylhexane-2,4-dione (**35**) (0.31 g, 1.7 mmol, 63%) as a colorless oil. Preparative GC (OV-101, 210 °C) gave pure **35**, which exists predominantly as the enol tautomer as evidenced in the ^1H NMR spectrum. The reaction was repeated, but this time 0.9 instead of 2 equiv of the potassium enolate **32** was employed. After workup, the crude product was found to contain mainly **35** by GC analysis.

Similarly, methylphenylketene (**13**) was reacted with the potassium enolates **33** and **34**, and ethylphenylketene (**3**) with **32–34**, as indicated in Table II. Characterizations of the products **35–39** are given in the supplementary material.

Reaction of 2-Phenylpropanoyl Chloride (40) with the Lithium Enolate of Acetophenone (16). To a stirred solution of **16** (6 mmol) at −78 °C was added **40** (4 mmol) in 10 mL of THF. After being stirred for 2 h, the reaction mixture was poured over a solution of 10% HCl and extracted with ether. The ether layer was washed with saturated $NaHCO_3$ solution and then with water followed by brine and dried over $MgSO_4$. After evaporation of the solvent, spectral data and analytical GC of the crude product were obtained and compared to those of authentic products obtained previously. Analysis by GC (OV-101, 210 °C, 42 mL/min) thus indicated the formation of 1-phenylvinyl 2-phenylpropanoate (**20**) and 1,4-diphenylpentane-1,3-dione (**25**) in a 2.5/1 ratio.

Reaction of 1-Methylvinyl 2-Phenylpropanoate (18) with the Potassium Enolate 32. Vinyl ester **18** (0.12 g, 0.63 mmol), obtained as reported above, in 5 mL of THF was added to the potassium enolate **32** (1.30 mmol) at −78 °C. After being stirred for 2 h, the mixture was worked up as described for the reaction of **13** with **32**. Analysis by GC (OV-101, 150 °C, 34 mL/min) of the crude product showed the formation of 5-phenylhexane-2,4-dione (**35**) and the absence of vinyl ester **18**.

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Supplementary Material Available: Preparation of **4** and spectral characterization of **17**, **19**, **20–22**, **24**, **25**, and **35–39** (9 pages). Ordering information is given on any current masthead page.

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