Alkoxide-Induced Succinate Ester Formation from Alcohols and Bis(trimethylsilyl) 1,2-Bisketene

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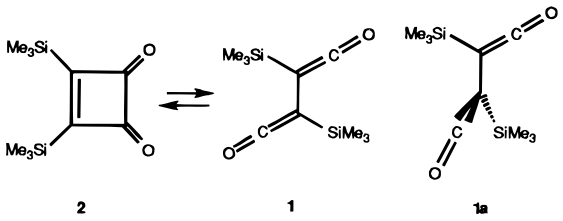
Reaction of the 1,2-bisketene $(Me_3SiC{=}C{=}O)_2$ (**1**) with alcohols (ROH) catalyzed by LiOR gives rapid and efficient conversion to mixtures of the *meso* and *dl* succinates $(Me_3SiCHCO_2R)_2$ (**4**). There is a change in selectivity with the *dl*/*meso* ratio varying from 18/82 with MeOH to 92/8 for *t*-BuOH. This procedure occurs with minimal desilylation, which is the predominant path in the uncatalyzed reaction. Preferential attack of lithium alkoxides on the carbonyl carbon of ketenes induced by lithium coordination to the ketenyl oxygen is proposed to account for the low extent of desilylation. The stereochemical assignments of the *meso* and *dl* configurations are based upon vicinal H,H coupling constants both from a mixed succinate ester and also from $^{13}C,^{1}H$ satellite spectra and are confirmed by X-ray structure determinations. Reaction of **1** with catechols **10**−**12** catalyzed by *n*-BuLi leads to *ortho* esters **15**−**18**, while reaction with the perhalo catechols **13** and **14** gives isolable hydroxaryl ketenyl esters **19** and **20**.

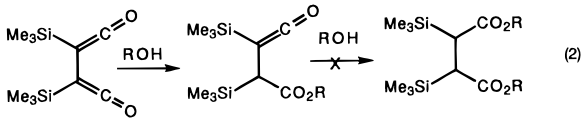
We have reported that the bis(trimethylsilyl) 1,2-bisketene (**1**) is formed from thermolysis or photolysis of cyclobut-3-ene-1,2-dione (**2**)[1,2] and is stable indefinitely in the absence of O_2, H_2O, electrophiles, or other reactive materials.[1a,b] Several mono(trimethylsilyl) 1,2-bisketenes have also been prepared and studied.[1c,d] Calculations,[1e,f]



(1)

as well as experimental photoelectron and dipole moment studies[1f] and an X-ray structure,[1g] indicate that the favored geometry of 1,2-bisketenes is not a planar form but rather a twisted almost perpendicular structure as indicated by **1a**. This preference is not primarily due to steric effects, as even for the unsubstituted derivative $(CH{=}C{=}O)_2$ the twisted form is calculated to be 2.4 kcal/mol more stable.[1e] This effect is understandable because of the unfavorable interactions between the two strong ketenyl dipoles in the coplanar conformations, the repulsion of the π electrons at C_β of the two ketenyl units, and the absence of any favorable conjugation between the dienyl units.[1a]

The reaction of bisketene **1** with alcohols leads to the isolable monoketenyl esters **3** (eq 2),[1b] but further reactions of the ketenyl esters **3** with alcohols are rather sluggish, as the ketenyl group in **3** is not so reactive as those in the bisketene **1**, and this has been attributed to electronic destabilization of **1** as well as steric crowding in **3**.[1b] Furthermore the reaction of **3** with alcohols does not lead to efficient formation of succinate esters **4**, as there is instead a competing reaction of desilylation forming mono(trialkylsilyl)succinate esters **5**. This could occur by nucleophilic attack by the alcohol on the α-trialkylsilyl ester moiety in **3** (eq 3).



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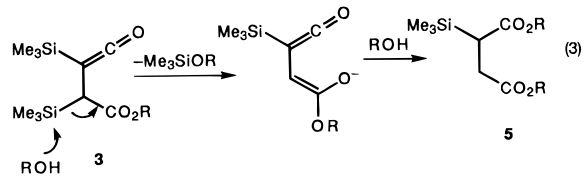

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There has been an interest in developing suitable catalysts for the esterification of $Me_3SiCH{=}C{=}O$, and BF_3[3a] and $ZnCl_2$[3b] have been used for the addition of alcohols and ZnI_2[3b] for the addition of phenols. There is an interesting report that a small amount of lithium alkoxide is an effective catalyst for the addition of tertiary alcohols to $PhN{=}C{=}O$.[3c]

To our knowledge there are no previous reports of 2,3-bis(trimethylsilyl) succinates such as **4**, although an 8% yield of $(Me_3SiCHCO_2H)_2$ from electrochemical alkyne dicarboxylation has been reported,[4a] without details of the product characterization, and the hydrosilylation of

[⊗] Abstract published in *Advance ACS Abstracts,* December 1, 1996.

(1) (a) Allen, A. D.; Ma, J.; McAllister, M. A.; Tidwell, T. T.; Zhao, D.-c. *Acc. Chem. Res.* **1995**, *28*, 265−271. (b) Zhao, D.-c.; Allen, A. D.; Tidwell, T. T. *J. Am. Chem. Soc.* **1993**, *115*, 10097−10103. (c) Allen, A. D.; Lai, W.-Y.; Ma, J.; Tidwell, T. T. *J. Am. Chem. Soc.* **1994**, *116*, 2625−2626. (d) Allen, A. D.; Ji, R.; Lai, W.-Y.; Ma, J.; Tidwell, T. T. *Heteroatom. Chem.* **1994**, *5*, 235−244. (e) McAllister, M. A.; Tidwell, T. T. *J. Am. Chem Soc.* **1994**, *116*, 7233−7238. (f) Werstiuk, N. H.; Ma, J.; McAllister, M. A.; Tidwell, T. T.; Zhao, D.-c. *J. Chem. Soc., Faraday Trans.* **1994**, *90*, 3383−3390. (g) Allen, A. D.; Lough, A.; Tidwell, T. T. *J. Chem. Soc., Chem. Commun.* **1996**, 2171−2172. (h) Allen, A. D.; Ma, J.; McAllister, M. A.; Tidwell, T. T.; Zhao, D.-c. *J. Chem. Soc., Perkin Trans. 2* **1995**, 847−851. (i) Liu, R.; Tidwell, T. T. *Can. J. Chem.* **1995**, *73*, 1818−1822.

(2) Tidwell, T. T. *Ketenes*; Wiley: New York, 1995.

(3) (a) Ruden, R. A. *J. Org. Chem.* **1974**, *39*, 3607−3608. (b) Kita, Y.; Sekihachi, J.; Hayashi, Y.; Da, Y.; Yamamoto, M.; Akai, S. *J. Org. Chem.* **1990**, *55*, 1108−1112. (c) Bailey, W. J.; Griffith, J. R. *J. Org. Chem.* **1978**, *43*, 2690−2692.

(4) (a) Dunach, E.; Derien, S.; Perichon, J. *J. Organomet. Chem.* **1989**, *364*, C33−C36. (b) Kopping, B.; Chatgilialoglu, C.; Zehnder, M.; Geise, B. *J. Org. Chem.* **1992**, *57*, 3994−4000.

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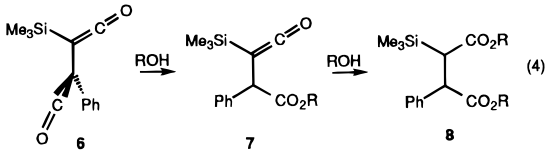
Table 1. Formation of 2,3-Bis(trimethylsilyl)succinates 4 from Bisketene 1 and Lithium Alkoxides and Alcohols (ROLi/ROH) at 22 °C (Unless Noted)

R	solvent	time	yield[a]	dl[b]	meso[b]	desilylation[b]	monoketene
Me	pentane	1 min		3(7)[c]	7(11)[c]	5(9)[c]	85(73)[c]
		2 min		9(12)[c]	23(23)[c]	10(24)[c]	58(41)[c]
		10 min		19(21)[c]	60(48)[c]	12(26)[c]	9(5)[c]
		75 min	60	15(20)[c]	70(58)[c]	15(22)[c]	0(0)[c]
Et	pentane	1 min		54	44	2	
		2 min	65	51	47	2	
		1 h		28	46	25	
	THF	2 h		19	15	64	
		24 h		19	17	64	
i-Pr	pentane	1 min	65	57	43	0	
		20 min	65	57	43	0	
		48 h		35	47	18	
	THF	5 min		50	20	30	
		11 days		17	22	61	
	THF[d]	25 min		0	0	50	50
		5 h		0	0	80	20
t-Bu	pentane	20 min		92	8	0	
		160 min	72	91	9	0	
		70 h		90	10	0	
	THF	5 min		95	5	0	
		70 h		74	11	15	
$(CF_3)_2CH$	pentane	90 h	45	58	39	0	3

[a] Isolated yield (%) succinate. [b] Relative yield (%). [c] 0 °C.

diethyl methylfumarate to give a monosilylated succinate has been reported.[4b]

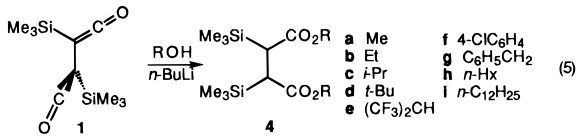
In the case of 2-(trimethylsilyl)-3-phenyl bisketene **6**, reaction with alcohols is much faster on the nonstabilized phenyl-substituted ketenyl group, and the resulting monoketenyl esters **7** are not subject to the desilylation reaction shown in eq 3 and may be isolated, purified, and converted to succinate esters **8** on further treatment with alcohol (eq 4).[1c,d] Similar results were obtained for the 2-(trimethylsilyl)-3-methyl bisketene.



Desilylation is also circumvented by the use of bulky silyl groups such as *t*-BuMe$_2$Si,[1b] but it was desirable to find methods to achieve formation of 2,3-bis(trimethylsilyl)succinate esters **4** without extensive desilylation. We now report success in meeting this goal.

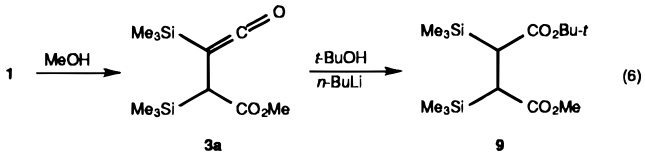
Results

Addition of 2,3-bis(trimethylsilyl) bisketene (**1**) in pentane to an excess of alcohol in pentane containing 0.1 equiv of *n*-BuLi at room temperature leads to a product which by ^{1}H NMR analysis consists of a mixture of *meso* and *dl* succinate esters **4**, isolated in 50−70% yields (eq 5). In the case of MeOH addition 15% desilylated product



was observed after completion of the reaction (75 min), but in the other cases the reactions were completed with little or no desilylation. The diastereomeric esters **4a**−**i** were separated by preparative radial thin layer chromatography or gas chromatography, and with the exception of **4d**−**f** both isomers of each pair were isolated. The isomers were identified as described below. The yields of separated esters were, however, rather low, due to losses of these sensitive materials on chromatography. Experiments to determine the effect of substituting THF for pentane in the solvent, and for varying the reaction time, are reported in Table 1. Desilylation was much more prevalent in THF solvent, and the reaction with MeOH was faster at 0 °C than at 22 °C.

Preparation of an unsymmetrical ester was effected by first reacting bisketene **1** with MeOH to form the monoketenyl ester **3a**, which on further reaction with *tert*-butyl alcohol and a catalytic amount of *n*-BuLi gave **9**, which was separated by radial chromatography into the *erythro* and *threo* stereoisomers (eq 6).



The structures of the separated succinate esters **4** were clearly established by their ^{1}H NMR spectra, as each showed a Me$_3$Si peak between δ 0.0 and 0.3, a Me$_3$SiC*H* signal between δ 2.1 and 2.95, signals for the alkoxy groups, an ester IR band at 1707−1743 cm^{-1}, and consistent mass spectral and ^{13}C NMR data. In each case the ^{1}H NMR signal of the Me$_3$SiC*H* proton of one diastereomer was at 0.31−0.38 ppm higher field than for the other diastereomer.

Convincing evidence for the stereochemical assignment of the diastereomers of **4** comes from the ^{1}H NMR spectra of the mixed esters **9**. Thus for one isomer the two tertiary Me$_3$SiC*H* protons appeared with different chemical shifts, at δ 2.519 and 2.594, respectively, with $J_{^1H,^1H}$ of 11.6 Hz, while for the other isomer these protons were at δ 2.178 and 2.224, respectively, with $J_{^1H,^1H}$ of 6.1 Hz. The nonequivalence of these protons in each isomer evidently results from a perturbation due to the adjacent carbonyl groups, which are affected differently by the presence of a *t*-BuO or MeO substituent. Based on these coupling constants, the former structure is assigned as the *erythro* isomer with the *anti* conformation shown,

Table 2. Coupling Constants (Hz) Determined from $^{13}C,^{1}H$ Satellites of Dialkyl Succinates 4, $(Me_3SiCHCO_2R)_2$

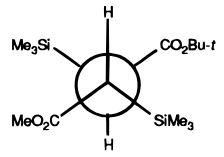
R	$^3J_{HH}$ (*meso*)	$^1J_{CH}$ (*meso*)	$^3J_{HH}$ (*dl*)	$^1J_{CH}$ (*dl*)
Me	11.9	129	6.6	122
Et	11.9	129	6.2	122
i-Pr	11.6	130	5.8	121
t-Bu			5.5	119
$(CF_3)_2CH$			6.5	127
$PhCH_2$	11.9	130		
n-Hex			6.0	121
n-$C_{12}H_{25}$	11.9	130		

Table 3. Relative Energies (kcal/mol) for Succinate Esters Calculated by MM$^+$

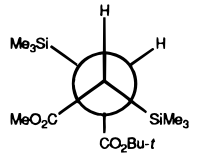
R	compd	anti-dl	syn-dl	gauche-dl	anti-meso	gauche-meso
Me	**4a**	2.8	0.4	6.4	0.0	4.8
Et	**4b**	2.6	0.6	6.4	0.0	4.5
i-Pr	**4c**	2.5	0.3	6.8	0.0	4.4
t-Bu	**4d**	2.5	0.0	6.1	3.2	7.2
$(CF_3)_2CH$	**4e**	3.0	1.0	7.3	0.0	6.1
Me	**8**	0.0[a]	2.6[b]	3.6[c]	0.8[d]	1.9, 4.3[e]

[a] *Anti-threo.* [b] *Syn-threo.* [c] *Gauche-threo.* [d] *Anti-erythro.* [e] Syn-erythro.

while the latter is the *threo* isomer with the *syn* conformation shown, which avoids a *gauche* Me_3Si/Me_3Si interaction and displays a *gauche* $^1H,^1H$ coupling. By analogy the diastereomers of **4** with the lower field (δ 2.47−2.95) Me_3SiCH proton are assigned as the *meso* isomers corresponding to *erythro*-**9**, and those at higher field (δ 2.09−2.61) are assigned as the *dl* isomers corresponding to *threo*-**9**.



erythro - **9**



threo - **9**

Further evidence for the stereochemical assignments of the succinates **4** came from the natural abundance ^{13}C satellites[5] of the Me_3SiCH protons. As these satellites arise from succinates containing only one ^{13}C, the degeneracy of the protons is lifted and the vicinal $^1H,^1H$ coupling constants can be observed, as collected in Table 2, along with the $^{13}C,^1H$ coupling constants. As can be seen the coupling constants for the diastereomers assigned the *meso* and *dl* configurations range from 11.6 to 11.9 Hz and from 5.5 to 6.6 Hz, respectively. Thus these values are consistent with the structural assignments already made, with the *meso* isomers preferring conformations analogous to that for *erythro*-**9**, with *anti* protons, while the *dl* isomers prefer conformations analogous to that for *threo*-**9**, with a *gauche* arrangement of the protons.

In final confirmation the molecular structures of the *dl*-di-*tert*-butyl ester **4d** and the *meso*-4-chlorophenyl ester **4f** were obtained by X-ray crystallography (Figures 1 and 2)[6] and agree with the assignments already made.

(5) (a) Erickson, L. E. *J. Am. Chem. Soc.* **1965**, *87*, 1867−1875. (b) Hawkes, G. E.; Lewis, D. *J. Chem. Soc., Perkin Trans. 2* **1984**, 2073−2078. (c) Lit, E. S.; Mallon, F. K.; Tsai, H. Y.; Roberts, J. D. *J. Am. Chem. Soc.* **1993**, *115*, 9563−9567.

(6) The authors have deposited atomic coordinates for this structure with the Cambridge Crystallographic Data Centre. The coordinates can be obtained, on request, from the Director, Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, U.K.

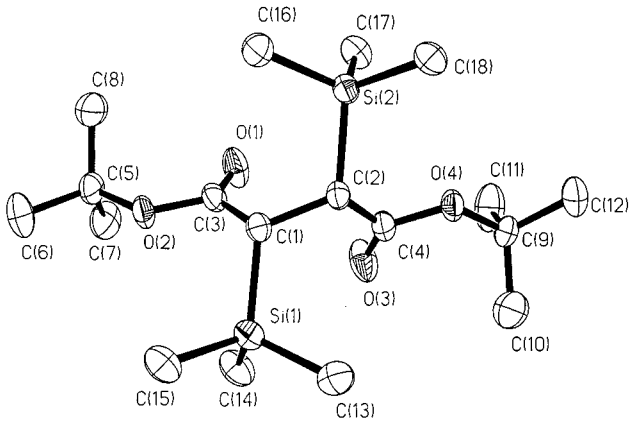
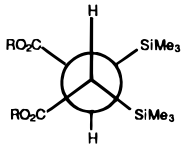
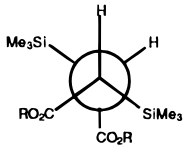


Figure 1. Molecular structure of *dl*-$(Me_3SiCHCO_2$-*t*-$Bu)_2$ (**4d**) determined by X-ray crystallography.

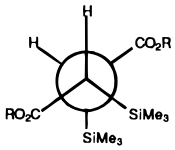
As a further guide to the assignment of these conformations, MM$^+$ molecular mechanics calculations[7] of the structures and energies for five conformations of **4a**−**e**, as well as the ester **8**, were carried out, and the relative energies are given in Table 3.



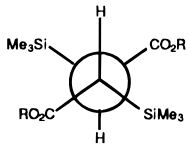
anti-dl – **4**



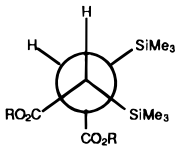
syn-dl – **4**



gauche-dl – **4**

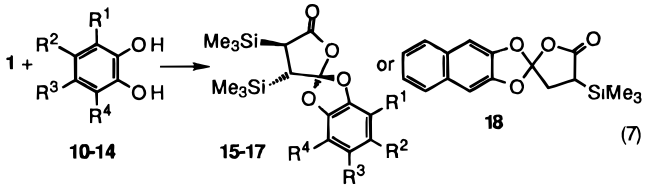


anti-meso – **4**

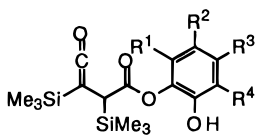


syn-meso – **4**

To further examine the scope of this acylation, **1** was reacted with 1,2-dihydroxybenzene derivatives **10**−**14**, and the reactions with **10**−**12** gave the *ortho* esters **15**−**18** in 64%, 50%, 29%, and 26% purified yields, respectively, while **13** and **14** gave ketenyl esters **19** and **20**, in 91% and 59% purified yields, respectively (eq 7). The



10, 15 $R^1 = R^2 = R^3 = R^4 = H$
11, 16 $R^1 = R^3 = t$-Bu, $R^2 = R^4 = H$
12, 17 $R^1 = R^2 = H$, R_2, R_4 = CH=CHCH=CH



13, 19 $R^1 = R^2 = R^3 = R^4 = Cl$
14, 20 $R^1 = R^2 = R^3 = R^4 = Br$

structure of **16** was established by X-ray crystallography

(7) (a) Hyperchem package of programs available from Hypercube Inc., Waterloo, Ontario, Canada. (b) Allinger, N. L. *J. Am. Chem. Soc.* **1977**, *99*, 8127−8134.

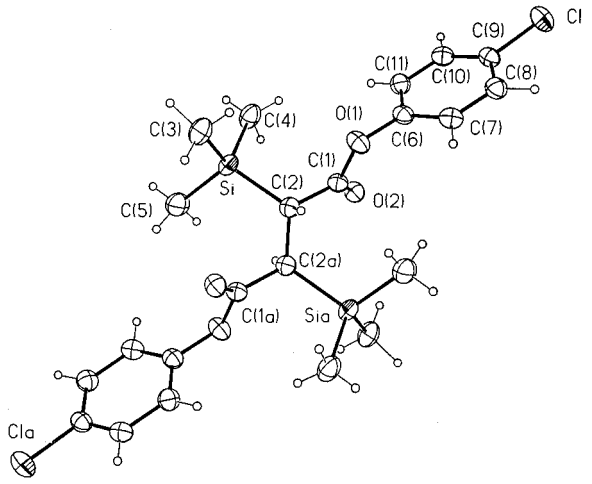


Figure 2. Molecular structure of *meso*-$(Me_3SiCHCO_2C_6H_4$-4-Cl$)_2$ (**4f**) determined by X-ray crystallography.

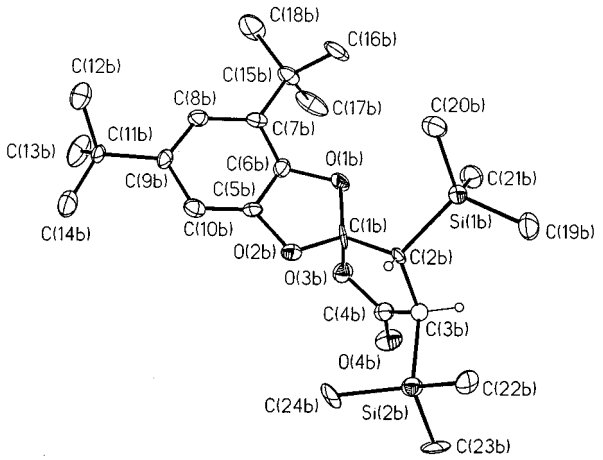
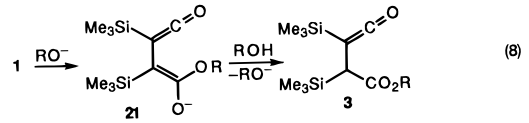


Figure 3. Molecular structure of *ortho* ester **16** determined by X-ray crystallography.

(Figure 3)[6] and supported by its spectroscopic properties, while **15** and **17** displayed analogous and consistent spectral properties, and the structures of **19** and **20** followed from their distinctive spectral properties, especially the ketenyl, ester, and OH peaks in their IR spectra, and the characteristic ^{13}C NMR ketenyl signals.

Discussion

A proposed mechanism for the *n*-BuLi-catalyzed formation of the succinate esters **4** from **1** is shown in eqs 8 and 9. The rationale of the effect of *n*-BuLi catalyst is that this generates the alkoxide of the alcohol, which adds rapidly to the bisketene **1** to generate enolate **21**, which is protonated by the alcohol forming the monoketene **3** and alkoxide, which react together to form enolate **22**, which is protonated to yield succinate **4**. Desilylation is proposed to occur by reaction of alcohol with **3** on silicon as shown in eq 3, but alkoxide preferentially reacts on carbon as shown in eq 9.



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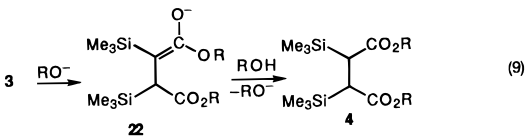
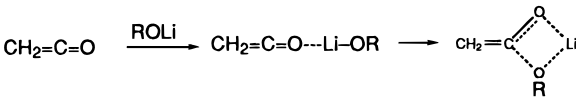


(9)

The reason for the preference for attack of the lithium alkoxide at the carbonyl carbon of the ketenyl moiety as opposed to attack at silicon may be found from previous calculations from this laboratory regarding the reaction of acetaldehyde lithium enolate with ketene.[8a] These studies showed the initial step of this reaction was complexation of the lithium cation to the ketene oxygen followed by conversion to the transition state for bond formation involving 4-center coordination, with the lithium complexed to both oxygens. Experimental studies supported this interpretation.[8b] The analogous process for alkoxide addition to ketene is shown in eq 10.



(10)

Thus the coordination of the lithium cation to both oxygens favors attack of alkoxide at the carbonyl carbon of ketenes. For the addition of alcohols such coordination is not so favorable, and attack of the alcohol at silicon with desilylation (eq 3) is more prevalent. The much greater extent of desilylation observed in THF solvent (Table 1) is consistent with strong coordination of lithium to the solvent and concomitant diminished coordination to the ketenyl oxgyen, permitting greater alkoxide attack on silicon. The lesser extent of desilyation in the reactions with catechols, even though these reactions were carried out in THF, may result from bidentate coordination involving the *ortho* hydroxy group.

The reactions in pentane are complete after 1 min for EtOH and *i*-PrOH, but 15−75 min are required for MeOH (Table 1). There is a steady change in the ratio of *dl*/*meso* products from 18/82 (MeOH), 55/45 (EtOH), 57/43 (*i*-PrOH), to 92/8 (*t*-BuOH). The reaction of MeOH forms diesters roughly 2 times as fast at 0 °C compared to room temperature (22 °C) and, in contrast to the other alcohols, causes appreciable amounts of desilylation, reaching 15% after completion of the reaction at 22 °C. The decrease in the ratio of *dl*/*meso* products with increasing extent of desilylation suggests selective desilylation of the *dl* esters.

The cause of the lower reactivity of MeOLi/MeOH compared to EtOH, *i*-PrOH, and *t*-BuOH cannot be specified based on the information available, but factors to be considered include a lower nucleophilicity of MeOLi, as the conjugate base of a more acidic alcohol, or possible different states of aggregation of the different alkoxides, which are not completely soluble in pentane.

The variable selectivity for formation of the *dl* and *meso* esters could arise from a varying preference for proton transfer via the conformation **23a** which is favored by the more bulky alcohols and leads to *dl* product, and conformation **23b**, which is favored for MeOH and leads to the *meso* isomer. The preference would be affected by the size of the proton donor ROH and the group R in the ester and possibly also by coordination of the ester

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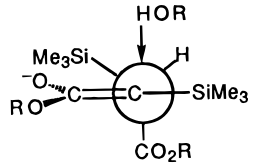
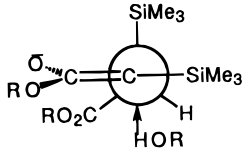
enolate to the proton donor. Product formation by hydrogen atom transfer to a succinate radical in a conformation analogous to **23a** with formation of *threo* product has been proposed.[4b]



23a

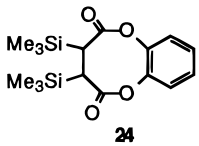


23b

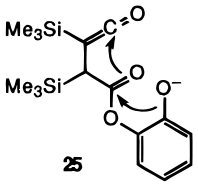
The MM^+ calculated energies (Table 3) of the different staggered conformations of *dl*- and *meso*-**4a**−**e** confirm that the *syn* and *anti* conformations respectively, are always predicted to be the most stable in agreement with the conclusion reached from the ^1H NMR satellite spectra (Table 2). Similarly the calculations also predict (Table 3) that the *anti-erythro* and *anti-threo* conformations of **8**, analogous to the *anti-meso* and *anti-dl* conformations of **4**, respectively, are the most stable, as had been assigned based on the observed vicinal $J_{H,H}$ values.[1d]

The MM^+ calculations also predict that for all of **4a**−**e** the *anti* conformer of *meso*-**4** is more stable than the most stable *syn* conformer of *dl*-**4** by 0.3−1.0 kcal/mol, with the exception of the *tert*-butyl ester **4d**, in which there is an abrupt change to a preference for the *syn-dl* conformer by 3.2 kcal/mol. This is also the isomer favored experimentally and the conformer seen in the X-ray structure (Figure 1). As may be seen in the crystal structure (Figure 1), there are no major steric interactions apparent from having the two *tert*-butyl ester groups in the *gauche* arrangement in this conformation. The preference for formation of the *meso* isomer by MeOH evidently reflects a kinetic effect and not the product stability, as there is little difference in the calculated relative stabilities of the *meso* and *dl* isomers for the Me, Et, and *i*-Pr esters.

The formation of the *ortho* esters **15**−**18** in the reaction of **1** with 1,2-dihydroxyarenes instead of conceivable isomeric 8-membered ring bislactones **24** demonstrates not only the difficulty of forming the latter structures but also the propensity of bisketene **1** to react with difunctional reagents by formation of 5-membered ring lactones. The former effect was noted as long ago as 1930 by Carothers and Dorough,[9a] who found no 8-membered rings from reaction of succinic acid derivatives with ethylene glycol, although some 16-membered ring product was obtained. There has, however, been some success in the formation of 8-membered bislactone derivatives of succinic acid and catechol,[9b,c] although "pseudo-esters" analogous to **15**−**18** are also obtained.[9b] The formation of 5-membered lactones has been observed in many cycloaddition and dimerization reactions of bisketenes,[10] including the reaction with C_{60}.[10f] In the case of the reaction of **1** with catechol, this reaction is best explained by the process shown in **25**. The failure of ring closure to occur in the isolable ketenes **19** and **20** probably reflects the decrease in nucleophilicity of these halogenated aryl groups and steric crowding in the cyclized forms.



24



25

In summary this base-catalyzed reaction provides a simple and efficient method for the formation of succinate esters $(Me_3SiCHCO_2R)_2$ (**4**) with a variable *dl*/*meso* selectivity. The stereochemistry and conformations of these esters have been deduced by spectroscopic analysis and confirmed by X-ray structure determinations. The reactions of **1** with catechols lead to *ortho* esters **15**−**18** or novel ketenyl hydroxyphenyl esters **19** and **20**.

Experimental Section

All reactions were carried out under an atmosphere of nitrogen or argon in oven-dried glassware. Reagents were generally the best quality commercial grade and used without further purification unless indicated otherwise. Tetrahydrofuran (THF) and diethyl ether (Et_2O) were freshly distilled from sodium benzophenone ketyl. Pentane was distilled from sodium and stored over sodium. Deuteriochloroform ($CDCl_3$) when used as a reaction solvent was successively dried over 4-Å molecular sieves. Ethanol was distilled from magnesium and stored over 3-Å molecular sieves. *tert*-Butyl alcohol was distilled from calcium hydride. 2,3-Bis(trimethylsilyl)buta-1,3-diene-1,4-dione (**1**) (bisketene)[1b] was prepared by injecting a sample of 3,4-bis(trimethylsilyl)cyclobut-3-ene-1,2-dione (**2**) into a preparative gas chromatograph (OV-17, column temperature 120 °C, injector temperature 200 °C). The X-ray crystallographic measurements were performed by Dr. Alan Lough[6] and mass spectra by Dr. Alex Young.

General Procedures for Reaction of 1 with ROLi. To a pentane or hexane solution of the alcohol was added *n*-butyllithium (0.1 equiv, 2 M solution in pentane) followed by addition of a pentane solution of bisketene **1** (the molar ratio of alcohol to bisketene was 2:1 or greater). After an appropriate interval the reaction mixture was diluted with pentane, and water was added. The organic layer was separated, dried, and evaporated to give the corresponding dialkyl succinate as a solid or oil as a mixture of *meso* and *dl* isomers, as indicated by NMR analysis.

Dimethyl 2,3-Bis(trimethylsilyl)succinate (4a). To 1.5 mL of pentane containing anhydrous methanol (0.083 mL, 2.1 mmol) was added at 0 °C *n*-BuLi (128 μL, 1.6 M in hexane, 0.21 mmol). The solution was warmed to 22 °C, and bisketene **1** (114 mg, 0.50 mmol) in 1.5 mL of dry pentane was added. After 75 min water was added, the mixture was extracted twice with hexanes, and the combined hexane layers were dried and concentrated. Analysis by ^1H NMR showed a mixture of the **4a** diastereomers along with the desilylated product **5** (as identified by the Me_3Si peak in the ^1H NMR at δ 0.096)[1b] in the ratio 15/70/15 for *dl*-**4a**/*meso*-**4a**/**5**, respectively. The stereoisomeric **4a** was separated by column chromatography on silica gel with 4% EtOAc in hexanes. *meso*-**4a** (28%): mp 44.0−44.5 °C; ^1H NMR ($CDCl_3$) δ 0.05 (s, 18), 2.63 (s, 2), 3.61 (s, 6); ^{13}C NMR ($CDCl_3$) δ −1.76, 35.3, 51.0, 175.0; IR (CCl_4) 1715 (s), 1435 (s) cm^{-1}; EIMS *m*/*z* 290 (M^+, 6), 275 ($M^+ - CH_3$, 40), 186 (54), 171 (69), 73 (100); HRMS calcd for $C_{12}H_{26}O_4Si_2$ 290.1370, found 290.1382. *dl*-**4a** (colorless liquid, 10%): ^1H NMR ($CDCl_3$) δ 0.12 (s, 18), 2.30 (s, 2), 3.64 (s, 6); ^{13}C NMR (CCl_4) δ −0.97, 34.7, 51.2, 175.2; IR ($CDCl_3$) 1729 cm^{-1}; EIMS *m*/*z* 290 (M^+, 4), 275 ($M^+ - CH_3$, 28), 186 (44), 171 (52), 73 (100); HRMS calcd for $C_{12}H_{26}O_4Si_2$ 290. 1370, found 290.1385.

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Diethyl 2,3-Bis(trimethylsilyl)succinate (4b). To 5 mL of pentane containing anhydrous ethanol (0.114 mL, 89.2 mg, 1.94 mmol) was added at 0 °C *n*-BuLi (121 μL, 0.194 mmol, 1.6 M in hexane). The solution was warmed to 22 °C, bisketene **1** (200 mg, 0.88 mmol) in 1 mL of dry pentane was added, and the mixture was stirred for 2 min. Hexane (2 mL) and water (0.5 mL) were added, and the organic layer was washed twice with H_2O, dried over $MgSO_4$, and evaporated to yield 185 mg of yellow liquid which by ^{1}H NMR contained *dl*- and *meso*-**4b** along with diethyl 2-(trimethylsilyl)succinate (**5b**) in the ratio 52/46/2, respectively. Radial chromatography (4% EtOAc/hexanes) on silica gel afforded the stereoisomers as clear colorless liquids. *meso*-**4b** (R_f 0.2, 56 mg, 20%): ^{1}H NMR δ 0.077 (s, 18), 1.26 (t, 6, J = 7.2 Hz), 2.61 (s, 2), 4.04 (dq, 2, J = 10.8, 7.2 Hz), 4.11 (dq, 2, J = 10.8, 7.2 Hz); ^{13}C NMR δ −1.64, 14.3, 35.4, 59.9, 174.7; IR (neat) 1715 cm^{-1}; EIMS m/z 318 (M^+, 2), 303 ($M^+ - CH_3$, 2), 289 ($M^+ - C_2H_5$, 37), 275 (16), 245 ($M^+ - C_2H_5 - CO_2$, 18), 171 (66), 127 (51), 73 (100, Me_3Si^+); HRMS m/z calcd for $C_{14}H_{30}O_4Si_2$ 318.1682, found 318.1669. *dl*-**4b** (R_f 0.15, 40 mg, 14%): ^{1}H NMR δ 0.14 (s, 18), 1.25 (t, 6, J = 7.2 Hz), 2.27 (s, 2), 4.09 (q, 4, J = 7.2 Hz); ^{13}C NMR δ −0.85, 14.3, 34.7, 59.9, 174.6; IR ($CDCl_3$) 1715 cm^{-1}; EIMS m/z 318 (M^+, 2), 303 ($M^+ - CH_3$, 4), 289 (M^+ -C_2H_5, 36), 275 (12), 245 ($M^+ - C_2H_5 - CO_2$, 18), 171 (63), 73 (100); HRMS m/z calcd for $C_{14}H_{30}O_4Si_2$ 318.1682, found 318.1679. The ^{1}H NMR of **5b** is consistent with that reported previously.[1b]

Diisopropyl 2,3-Bis(trimethylsilyl)succinate (4c). To 5 mL of pentane containing 2-propanol (0.585 mL, 7.6 mmol) at 0 °C was added *n*-BuLi (1.4 M solution in hexane, 0.535 mL, 0.76 mmol). The mixture was warmed to 22 °C, and bisketene **1** (442 mg, 1.96 mmol) in 2 mL of pentane was added dropwise over 1 min. After 20 min 5 mL of hexane and 0.5 mL of water were added, the organic layer was washed twice with water was dried over $MgSO_4$, and the solvent was evaporated to yield crude product (410 mg), as a 1.3:1 mixture of *dl*- and *meso*-**4c**. Separation of the residue by VPC (OV-17 column, 130 °C, injector temperature 150 °C) gave *dl*- and *meso*-**4c** (retention times 80 and 116 min, respectively, each >95% pure by ^{1}H NMR), free of their respective stereoisomer but contaminated with a small amount of diisopropyl 2-(trimethylsilyl)succinate (**5c**). This was confirmed by isolating **5c** by collecting the fraction eluting before *dl*- or *meso*-**4c**. Further purification was achieved for *dl*-**4c** by radial chromatography (5% EtOAC/hexanes on silica gel) and *meso*-**4c** by sublimation (2 mmHg/47 °C) to yield the pure compounds. *dl*-**4c** (clear colorless liquid, 48 mg, 7%): ^{1}H NMR δ 0.143 (s, 18), 1.21 (d, 6, J = 6.3 Hz), 1.23 (d, 6, J = 6.2 Hz), 2.195 (s, 2), 4.98 (sept, 2, J = 6.3 Hz); ^{13}C NMR δ −0.69, 22.0, 22.1, 34.8, 67.3, 174.1; IR ($CDCl_3$) 1722 cm^{-1}; EIMS m/z 347 (MH^+, 3), 346 (M^+, 2), 331 (M^+ − Me, 6), 303 ($M^+ - C_3H_7$, 12), 287 ($M^+ - OC_3H_7$, 18), 261 (69), 245 (70), 171 (70), 147 (80), 73 (100); HRMS m/z calcd for $C_{13}H_{26}O_4Si$ ($M^+ - CH_3$) 331.1760, found 331.1760. *meso*-**4c** (white solid, 50 mg, 7%): mp 61.5−62 °C; ^{1}H NMR δ 0.090 (s, 18), 1.24 (d, 6, J = 6.3 Hz), 1.25 (d, 6, J = 6.3 Hz), 2.56 (s, 2), 4.93 (sept, 2, J = 6.3 Hz); ^{13}C NMR δ −1.32, 22.0, 22.1, 35.5, 67.5, 174.4; IR (KBr) 1708 cm^{-1}; EIMS m/z 346 (M^+, 2), 331 ($M^+ - CH_3$, 5), 303 ($M^+ - C_3H_7$, 7), 287 ($M^+ - C_3H_7O$, 6), 261 (58), 245 (57), 171 (68), 73 (100); HRMS calcd for $C_{16}H_{34}O_4Si_2$ m/z 346.1995, found 346.2000. **5c**: ^{1}H NMR δ 0.098 (s, 9), 1.218 (d, 6, J = 6.3 Hz), 1.231 (d, 3, J = 6.3 Hz), 1.241 (d, 3, J = 6.3 Hz), 2.297 (dd, 1, J = 16.5, 3.4 Hz), 2.432 (dd, 1, J = 11.4, 3.4 Hz), 2.792 (dd, 1, J = 16.5, 11.4 Hz), 4.996 (sept, 1, J = 6.3 Hz), 5.01 (sept, 1, J = 6.3 Hz); ^{13}C NMR δ −2.66, 21.8, 21.83, 22.0, 22.1, 31.7, 33.1, 67.3, 68.0, 172.5, 173.9; IR (neat) 1736 cm^{-1}; CIMS m/z 275 (MH^+, 2), 215 (MH^+ − *i*-PrOH, 39), 190 (17), 187 (MH^+ − *i*-PrOH − CO, 6), 173 (72), 129 (40), 100 (33), 73 (100); HRMS m/z calcd for $C_{12}H_{23}O_4Si$ ($MH^+ - CH_3$) 259.1365, found 259.1363.

Di-*tert*-butyl 2,3-Bis(trimethylsilyl)succinate (4d). To 3 mL of pentane containing *t*-BuOH (0.516 mL, 5.2 mmol) was added *n*-BuLi (0.346 mL, 0.52 mmol, 1.5 M in hexanes) at 0 °C. After warming to 25 °C, **1** (310 mg, 1.37 mmol) in 1 mL of pentane was added and the solution was stirred for 160 min. Pentane (5 mL) and 0.5 mL of water were added, the organic layer was separated, washed twice with water, and dried over $MgSO_4$, and the solvent was evaporated to yield 367 mg of an off-white solid, which by ^{1}H NMR was shown to contain a 10:1 mixture of *dl*- and *meso*-**4d**, respectively. The crude product was purified by VPC (OV-17 column, 127 °C, injector temperature 150 °C) to yield 65 mg of *dl*-**4d** (>98% pure by ^{1}H NMR). Further purification by sublimation at 1 mmHg/55 °C and recrystallization from pentane yielded *dl*-**4d** (50 mg, 10%) as colorless needles suitable for X-ray structure determination: mp 73−73.5 °C; ^{1}H NMR δ 0.146 (s, 18), 1.45 (s, 18), 2.09 (s, 2); ^{13}C NMR δ −0.44, 28.3, 35.4, 79.6, 173.6; IR (KBr) 1722 cm^{-1}; CIMS m/z 375 (MH^+, 28), 319 ($MH^+ - C_4H_8$, 40), 263 ($MH^+ - 2C_4H_8$, 100). Pure *meso*-**4d** was not isolated: ^{1}H NMR δ 0.13 (s, 18, Me_3Si), 1.45 (s, 18, *t*-Bu, degenerate with *dl*-**4d**), 2.47 (s, 2, CH). Di-*tert*-butyl 2-(trimethylsilyl)succinate **(5d)**, which was observed in fractions eluted off the VPC (2−5%), was not isolated but assigned in analogy to **5b**,**c**: ^{1}H NMR δ 0.00 (s), 1.44 (s), 2.21 (dd, J = 16.4, 3.3 Hz), 2.35 (dd, J = 11.4, 3.3 Hz), 2.68 (dd, J = 16.4, 11.4 Hz).

Bis(1,1,1,3,3,3-hexafluoro-2-propyl) 2,3-Bis(trimethylsilyl)succinate (4e). To 5 mL of pentane containing HFIP (405 μL, 3.85 mmoL) was added with stirring *n*-BuLi (513 μL, 0.77 mmol of a 1.5 M solution in hexane) at 0 °C. After warming to 25 °C, bisketene **1** (325 mg, 1.44 mmol) in 1 mL of pentane was added and the reaction monitored by periodic analysis by ^{1}H NMR. After 90 min more *n*-BuLi (250 μL, 0.375 mmol) was added and analysis continued. After 90 h Et_2O (5 mL) and water were added, and the organic layer was washed twice with water, dried over $MgSO_4$, and evaporated to yield 376 mg of a pale yellow solid. ^{1}H NMR showed a 5.1:1 mixture of *meso*- and *dl*-**4e** (>97%) and **3e** (<3%). Separation by VPC (OV-17 column, 90 °C, injector temperature 165 °C) afforded *meso*-**4e** (65 mg, >97% pure by ^{1}H NMR), and sublimation of this sample at 62−63 °C/1.5 mmHg yielded pure *meso*-**4e** (30 mg, 4%): mp 82−83 °C; ^{1}H NMR δ 0.170 (s, 18), 2.79 (s, 2), 5.74 (sept, 2, J = 6.1 Hz); ^{13}C NMR −1.08, 35.6, 66.7 (sept, J = 34.4 Hz), 120.4 (q, J = 282 Hz), 120.5 (q, J = 281 Hz), 171.4; IR (KBr) 1743 cm^{-1}; EIMS m/z 562 (M^+, 2), 519 (10), 411 ($M^+ - CH(CF_3)_2$, 9), 367 ($M^+ - CO_2CH(CF_3)_2$, 6), 97 (18), 73 (Me_3Si^+, 100); HRMS m/z calcd for $C_{16}H_{22}O_4Si_2F_{12}$ 562.0865, found 562.0862. Pure *dl*-**4e** was not isolated: ^{1}H NMR δ 0.186 (s, 18), 2.42 (s, 2), 5.77 (sept, 2, J = 6.1 Hz); ^{13}C NMR δ −1.24, 34.3, 66.4 (sept, J = 34.1 Hz), 120.39 and 120.42 (each q, J = 282 Hz), 170.6; GC/EIMS m/z 562 (M^+, 3), 519 (10), 411 ($M^+ - CH(CF_3)_2$, 17), 367 ($M^+ - CH(CF_3)_2 - CO_2$, 11), 249 (16), 73 (100). The identity of **3e** was confirmed by its independent preparation.

3-Carbo-(1,1,1,3,3,3-hexafluoro-2-propoxy)-2,3-bis(trimethylsilyl)prop-1-en-1-one (3e). Bisketene **1** (113 mg, 0.5 mmol) was added to neat HFIP (500 μL, 4.75 mmol) and stirred at 25 °C for 20 h. Following evaporation of the excess HFIP, analysis by ^{1}H NMR showed the monoketene **3e**, diester *dl*-**4e**, bisketene **1**, and (*Z*)-2,3-bis(trimethylsilyl)succinic anhydride[1b] in the ratio 78/12/5/5, respectively. The crude product (130 mg) was purified by VPC (OV-17 column, 100 °C, injector temperature 175 °C), and **3e** was collected as a white solid (21 mg, 0.053 mmol, 11%): mp <5 °C; ^{1}H NMR δ 0.156 (s, 9), 0.189 (s, 9), 2.13 (s, 1), 5.79 (sept, 1, J = 6.2 Hz); ^{13}C NMR δ −2.45, −1.21, 10.5, 29.8, 66.8 (sept, $^3J_{CF}$ = 34.5 Hz), 120.5 (q, $^1J_{CF}$ = 282 Hz), 172.2, 180.1; IR ($CDCl_3$) 2095, 1764 cm^{-1}; EIMS m/z 394 (M^+, 15), 351 (10), 243 ($M^+ - CH(CF_3)_2$, 31), 215 ($M^+ - CH(CF_3)_2 - CO_2$, 2), 73 (Me_3Si^+, 100); HRMS m/z calcd for $C_{13}H_{20}F_6O_3Si_2F_6$ 394.0855, found 394.0865.

Bis(4-chlorophenyl) 2,3-Bis(trimethylsilyl)succinate (4f). To 4-ClC_6H_4OH (104 mg, 0.811 mmol) in 1.5 mL of pentane was added *n*-BuLi (20 μL, 0.032 mmol, 1.6 M solution in hexanes). After 15 min a solution of bisketene **1** (30 mg, 0.132 mmol) in 1.5 mL of pentane was added. After 2 h the reaction mixture was poured into pentane/water, and the organic layer was washed three times with water and once with brine, dried over $MgSO_4$, and evaporated to give 50 mg of a colorless solid, which was shown by ^{1}H NMR to be a 9:2 mixture of *meso*- and *dl*-**4f**, respectively. Recrystallization from pentane yielded pure *meso*-**4f** (29.1 mg, 45%): mp 111.6−112.3 °C; IR (KBr) 1743 cm^{-1}; ^{1}H NMR δ 0.25 (s, 18), 2.95 (s, 2), 7.1−7.4 (m, 8, Ar); ^{13}C NMR δ −0.91, 35.7, 122.8, 129.4, 131.0, 149.1, 172.7; EIMS m/z 482 (M^+, 9), 439 (21), 355 (23), 327 (100), 282 (16), 267 (15), 239 (19), 200 (41), 185 (46), 127

(80), 99 (18), 73 (Me_3Si^+, 87); HRMS *m*/*z* calcd for 482.0903, found 482.0905. Anal. Calcd for $C_{22}H_{28}Cl_2O_4Si_2$: C, 54.64; H, 5.84; Cl, 14.66. Found: C, 54.26; H, 5.99; Cl, 14.88. Crystals of *meso*-**4f** suitable for X-ray analysis were obtained form slow evaporation of a pentane solution. Pure *dl*-**4e** was not isolated: ^{1}H NMR δ 0.28 (s, 18), 2.61 (s, 2), 6.7−7.2 (m, 8, Ar).

Dibenzyl Succinate (4g). To benzyl alcohol (50 μL, 0.483 mmol) in 1 mL of diethyl ether and *n*-BuLi (250 μL, 0.400 mmol, 1.6 M in hexane) was added bisketene **1** (46.7 mg, 0.207 mmol) in 1 mL of diethyl ether dropwise with stirring, and the solution was stirred for 17 h at 25 °C. Then 3 mL of diethyl ether was added, and the mixture was washed with water, dried over anhydrous $MgSO_4$, and evaporated to give 41.3 mg of pale yellow crystals shown by ^{1}H NMR to be a 3.5:1 mixture of the *meso*- and *dl*-**4g** diastereomers, respectively, which were separated by radial chromatography (4% EtOAc in hexane) as colorless crystals. *meso*-**4g**: ^{1}H NMR ($CDCl_3$) δ 0.020 (s, 18), 2.68 (s, 2), 4.93 (d, 2, J = 12.2 Hz), 5.08 (d, 2, J = 12.2 Hz), 7.4 (m, 10, Ph); ^{13}C NMR ($CDCl_3$) δ −1.62, 35.4, 66.2, 128.2, 128.5, 128.7, 135.7, 174.4; IR (CCl_4) 1713 cm^{-1}; CIMS *m*/*z* 443 (MH^+), 425, 397, 377, 335 ($M^+ - C_7H_7O$), 307 ($M^+ - C_7H_7O - CO$), 279 ($M^+ - C_7H_7O - 2CO$), 245, 91 ($C_7H_7^+$), 73 (Me_3Si^+, 100); HRMS *m*/*z* calcd for $C_{23}H_{31}O_4Si_2$ ($M^+ - CH_3$) 427.1761, found 427.1777. *dl*-**4g**: ^{1}H NMR ($CDCl_3$) δ 0.088 (s, 18, Me_3Si), 2.37 (s, 2, CHCO), 4.99 (d, 2, J = 11.7 Hz), 5.07 (d, 2, J = 11.7 Hz), 7.34 (m, 10); IR (CCl_4) 1726 cm^{-1}; EIMS *m*/*z* 427 ($M^+ - CH_3$), 397, 367, 351 ($M^+ - C_7H_7$), 321, 307 ($M^+ - C_7H_7O - CO$), 277, 233, 91 (C_7H_7), 73 (Me_3Si).

Di-*n*-hexyl Succinate (4h). To *n*-hexanol (52 μL, 42.3 mg, 0.415 mmol) in 2 mL of hexane was added *n*-BuLi (130 μL, 0.208 mmol, 1.6 m in hexane) with stirring. Bisketene **1** (46.2 mg, 0.204 mmol) in 1 mL of hexane was added dropwise, and the solution was stirred for 30 min at 25 °C. Then 5 mL of hexane was added, and the mixture was washed twice with H_2O, dried over anhydrous $MgSO_4$, and evaporated to give 44.9 mg of yellow liquid, which was shown by ^{1}H NMR to be a 5:3:3.4 mixture of the monoketene **3h** and *meso*- and *dl*-**4h** which were separated as colorless liquids by radial chromatography (4% EtOAc in hexane). **3h**: IR (film) 2087 (C═C═O), 1721 cm^{-1} (CO_2Me); ^{1}H NMR ($CDCl_3$) δ 0.14 (s, 9), 0.15 (s, 9), 0.9 (m, 3), 1.3 (m, 6), 1.6 (m, 2), 1.96 (s, 1), 4.07 (m, 2); ^{13}C NMR ($CDCl_3$) δ −2.25, −0.91, 10.9, 14.0, 22.5, 25.6, 28.7, 30.2, 31.4, 65.1, 175.1, 181.1; EIMS *m*/*z* 328 (M^+, 15), 243 ($M^+ - C_6H_{13}$, 40), 154 ($M^+ - C_6H_{13}O - Me_3Si$, 32), 147 (36), 73 ($Me_3Si^+$, 100); HRMS *m*/*z* calcd for $C_{16}H_{32}O_3Si_2$ 328.1890, found 328.1888. *meso*-**4h**: IR (CCl_4) 1712 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 0.07 (s, 18), 0.9 (m, 6), 1.3 (m, 12), 1.6 (m, 4), 2.61 (s, 2), 3.98 (m, 4); ^{13}C NMR ($CDCl_3$) δ −1.62, 14.0, 22.5, 25.7, 28.6, 31.4, 35.4, 64.3, 174.8; EIMS *m*/*z* 430 (M^+, 7), 415 ($M^+ - CH_3$, 5), 402 ($M^+ - CO$), 387 ($M^+ - CH_3$, CO, 14), 345 ($M^+ - C_6H_{13}$, 14), 329 ($M^+ - C_6H_{13}O$, 7), 301 ($M^+ - C_6H_{13}O - CO$, 24), 245 ($M^+ - CH_3 - 2C_6H_{13}$, 76), 201 (32), 171 ($M^+ - 2C_6H_{13}O - Me_2Si$, 90), 73 ($Me_3Si^+$, 100); HRMS *m*/*z* calcd for $C_{22}H_{46}O_4Si_2$ 430.2935, found 430.2925. *dl*-**4h**: IR (CCl_4) 1725 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 0.14 (s, 18), 0.9 (m, 6), 1.3 (m, 12), 1.6 (m, 4), 2.26 (s, 2), 4.02 (m, 4); ^{13}C NMR ($CDCl_3$) δ −0.75, 14.0, 22.6, 25.7, 28.7, 31.5, 34.8, 64.3, 174.7; EIMS *m*/*z* 430 (M^+, 9), 415 ($M^+ - CH_3$, 11), 402 ($M^+ - CO$), 387 ($M^+ - CH_3 - CO$, 13), 345 ($M^+ - C_6H_{13}$, 20), 329 ($M^+ - C_6H_{13}O$, 18), 301 ($M^+ - CO_2C_6H_{13}$, 29), 245 ($M^+ - CH_3 - 2C_6H_{13}$, 92), 201 (25), 171 (97), 147 (60), 129 (27), 99, 73 (Me_3Si^+, 100); HRMS *m*/*z* calcd for $C_{22}H_{46}O_4Si_2$ 430.2935, found 430.2916.

Di-*n*-dodecyl Succinates (4i). To 1-dodecanol (0.0430 g, 0.230 mmol) in 3 mL of hexane in a 5 mL flask under argon was added *n*-BuLi (72 μL, 0.115 mmol, 1.6 M in hexane) with stirring. Bisketene **1** (26.1 mg, 0.115 mmol) in 1 mL of hexane was added dropwise, and the solution was stirred for 30 min at 25 °C. Then 5 mL of hexane was added, and the mixture was washed twice with water, dried over anhydrous $MgSO_4$, and evaporated to give 48.4 mg of yellow liquid, which was shown by ^{1}H NMR to be a 1:3:2 mixture of trimethylsilyl *n*-dodecyl ether (**26**) and the stereoisomeric esters **4i**, which were separated by radial chromatography (4% EtOAc). **26**: ^{1}H NMR ($CDCl_3$) δ 0.11 (s, 9), 0.9 (m, 3), 1.3 (m), 1.6 (m), 3.57 (t, 2); EIMS *m*/*z* 258 (M^+), 243 ($M^+ - CH_3$, 100), 103 (27), 97 (37), 89 (Me_3SiO^+, 17), 73 (Me_3Si^+, 36); HRMS *m*/*z* calcd for $C_{14}H_{31}OSi$ ($M^+ - CH_3$) 243.2144, found 243.2143. *meso*-**4i**: IR (CCl_4) 1711 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 0.07 (s, 18), 0.9 (m), 1.3 (m), 1.6 (m), 2.61 (s, 2), 4.0 (m, 4); ^{13}C NMR ($CDCl_3$) δ −1.60, 14.1, 22.7, 26.1, 28.6, 29.2, 29.3, 29.5, 29.6, 31.9, 35.4, 64.3, 174.8 (peaks overlap between 29.2 and 29.6); EIMS *m*/*z* 598 (M^+, 33), 429 ($M^+ - C_{12}H_{25}$, 22), 385 ($M^+ - C_{12}H_{25}O - CO$, 26), 340 ($M^+ - Me_3Si - C_{12}H_{25}O$, 24), 261 (92), 245 (87), 171 (89), 147 (34), 73 (Me_3Si^+, 100); HRMS *m*/*z* calcd for $C_{34}H_{70}O_4Si_2$ 598.4813, found 598.4788. *dl*-**4i**: IR (CCl_4) 1725 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 0.14 (s, 18), 0.9 (m), 1.3 (m), 1.6 (m), 2.26 (s, 2), 4.0 (m, 4); ^{13}C NMR ($CDCl_3$) δ −0.81, 14.1, 22.7, 26.0, 28.7, 29.2, 29.3, 29.5, 29.6, 31.9, 34.8, 64.3, 174.7 (peaks overlap between δ 29.3 and 29.6); EIMS *m*/*z* 598 (M^+, 7), 429 ($M^+ - C_{12}H_{25}$, 5), 385 ($M^+ - C_{12}H_{25}O - CO$, 7), 340 ($M^+ - Me_3Si - C_{12}H_{25}O$, 7), 261 (53), 245 (58), 171 (70), 147 (30), 85 (24), 73 (100).

***erythro*- and *threo*-Methyl *tert*-Butyl Succinates (9).** To bisketene **1** (21.9 mg, 0.097 mmol) in a 10 mL flask cooled in an ice bath was added cold MeOH (1.5 mL, 37 mmol, dried with 3-Å molecular sieves). After 7 min the solvent was removed under reduced pressure to give monoketene **3a** (20.5 mg) as a yellowish oil, identified by comparison to its reported[1b] spectral properties.

A sample of **3a** (44.3 mg) in 1.5 mL of hexane was added dropwise with stirring to *t*-BuOH (1 mL, 0.011 mol) in 4 mL of hexane and *n*-BuLi (0.4 mL, 0.026 mol, 1.6 M in hexane), and the solution was stirred for 67 h at 25 °C. Then 10 mL of water was added, and the mixture was extracted with hexane, dried over anhydrous $MgSO_4$, and evaporated to give 34.2 mg of colorless liquid. Radial chromatography (4% EtOAc in hexane) gave the stereoisomeric esters **9** as colorless liquids. *erythro*-**9** (R_f = 0.3): ^{1}H NMR ($CDCl_3$) δ 0.081 (s, 9), 0.099 (s, 9), 1.46 (s, 9), 2.52 and 2.59 (each d, 1, J = 11.6 Hz), 3.60 (s, 3); ^{13}C NMR ($CDCl_3$) δ −1.54, −1.12, 28.4, 35.1, 36.6, 50.9, 80.2, 173.9, 175.3; IR (film) 1710 cm^{-1}; EIMS *m*/*z* 332 (M^+), 317 ($M^+ - CH_3$), 302, 289 ($M^+ - CH_3 - CO$), 275 ($M^+ - t$-Bu), 171, 73; HRMS *m*/*z* calcd for $C_{15}H_{32}O_4Si_2$ 332.1839, found 332.1849. *threo*-**9**: ^{1}H NMR ($CDCl_3$) δ 0.132 (s, 9), 0.144 (s, 9), 1.44 (s, 9), 2.18 and 2.22 (each d, 1, J = 6.1 Hz), 3.64 (s, 3); ^{13}C NMR ($CDCl_3$) δ −0.82, −0.76, 28.2, 34.8, 35.6, 51.2, 79.9, 173.7, 175.2; IR (film) 1721 cm^{-1}; EIMS *m*/*z* 332 (M^+), 317 ($M^+ - CH_3$), 302, 289 ($M^+ - CH_3 - CO$), 275 ($M^+ - t$-Bu), 171, 73.

General Procedure for the Reaction of 1 with 1,2-Dihydroxyarenes. To a solution of the 1,2-dihydroxyarene (ca. 0.25 mmol) in THF (40 mL) was added *n*-BuLi (15 μL of a 1.6 M solution in hexanes, 0.024 mmol). After 5 min a solution of **1** (1.0 equiv) in THF (20 mL) was added dropwise over 1 h, the mixture was stirred for 1 h, and the solvent was evaporated. The residue was dissolved in ether, washed 3 times with water and three times with brine, dried over $MgSO_4$, and evaporated to yield the crude products **15**−**20**.

***Ortho* ester 15:** isolated in 64% yield by radial chromatography (10% EtOAc in hexanes) as a colorless oil: R_f 0.26; IR (CCl_4) 1806, 1715 cm^{-1}; ^{1}H NMR δ 0.14 (s, 9), 0.27 (s, 9), 2.23 (d, 1, J = 3.7 Hz), 2.38 (d, 1, J = 3.7 Hz), 6.92 (m, 4); ^{13}C NMR δ −2.62, −2.34, 33.8, 35.4, 108.7, 108.8, 122.2, 122.4, 131.9, 144.7, 144.9, 174.1; EIMS *m*/*z* 336 (M^+, 33), 174 (54), 146 (62), 73 (Me_3Si^+, 100); HRMS *m*/*z* calcd 336.1213, found 336.1206.

***Ortho* ester 16:** isolated in 50% yield by recrystallization from pentane as a colorless solid; mp 185.0−186.2 °C; IR (KBr) 1757 cm^{-1}; ^{1}H NMR δ 0.18 (s, 9), 0.27 (s, 9), 1.29 (s, 9), 1.36 (s, 9), 2.24 (d, 1, J = 3.7 Hz), 2.39 (d, 1, J = 3.7 Hz), 6.83 (d, 1, J = 1.8 Hz), 6.88 (d, 1, J = 1.9 Hz); ^{13}C NMR δ −2.51, −2.27, 29.8, 29.9, 31.6, 33.0, 34.0, 34.9, 104.4, 116.2, 131.4, 132.3, 140.3, 144.7, 145.6, 174.5; EIMS *m*/*z* 448 (M^+, 98), 286 (31), 258 (100), 243 (22), 147 (28), 73 (Me_3Si^+, 97); HRMS *m*/*z* calcd 448.2465, found 448.2450. Anal. Calcd for $C_{24}H_{40}O_4Si_2$: C, 64.23; H, 8.98. Found: C, 64.01; H, 9.31. Crystals of **16** suitable for X-ray analysis were grown by slow evaporation of a pentane solution.

***Ortho* Esters 17 and 18.** These were isolated by radial chromatography using 10% EtOAc in hexanes followed by recrystallization from pentane. **17** (29%): colorless needles; mp 105.5−107.2 °C; R_f 0.27; IR (KBr), 1764 cm^{-1}; ^{1}H NMR δ 0.16 (s, 9), 0.30 (s, 9), 2.42 (d, 1, J = 4.2 Hz), 2.29 (d, 1, J =

3.6 Hz), 7.26 (s, 2), 7.38 (dd, 2, J = 3.4, 6.11 Hz), 7.73 (dd, 2, J = 3.30, 5.98 Hz); ^{13}C NMR δ −2.64, −2.34, 33.8, 35.4, 104.3, 124.7, 127.3, 130.2, 130.4, 132.2, 144.7, 145.0, 174.0; EIMS m/z 386 (M^+, 39), 343 (8), 269 (23), 224 (32), 196 (46), 73 (Me_3Si^+, 100); HRMS m/z calcd 386.1370, found 386.1387. Anal. Calcd for $C_{20}H_{26}O_4Si_2$: C, 62.13; H, 6.78. Found: C, 61.18; H, 6.77. **18** was obtained in 26% yield as colorless prisms: mp 150.1−151.9 °C; R_f 0.17; IR (KBr) 1813 cm^{-1}; ^{1}H NMR δ 0.11 (s, 9), 2.42 (collapsed dd, 1, J = 10.4, 10.5 Hz), 2.70 (dd, 1, J = 10.40, 18.1 Hz), 2.95 (dd, 1, J = 10.4, 18.1 Hz), 7.24 (s, 1), 7.26 (s, 1), 7.3−7.7 (m, 4, Ar); ^{13}C NMR δ −2.60, 31.7, 31.8, 104.7, 104.9, 124.9, 125.0, 127.3, 127.4, 130.3, 130.4, 132.6, 144.8, 144.9, 171.9; EIMS m/z 314 (32), 259 (30), 197 (100), 127 (37), 73 (47), 55 (50); HRMS m/z calcd 314.0974, found 314.0970.

Monoketene 19: isolated in 91% yield after recrystallization from pentane as a colorless , amorphous powder; mp 147.5−149.1 °C; IR (KBr) 2094, 1736 cm^{-1}; ^{1}H NMR δ 0.22 (s, 9), 0.29 (s, 9), 2.28 (s, 1), 5.78 (s, 1, exchangeable); ^{13}C NMR δ −2.07, −1.03, 10.8, 30.1, 119.76, 135.5, 144.6, 171.6, 180.5; EIMS m/z 474 (M^+, 3), 305 (6), 199 (36), 171 (20), 154 (29), 73 (Me_3Si^+, 100); HRMS m/z calcd 471.9654, found 471.9669. Anal. Calcd for $C_{16}H_{20}Cl_4O_4Si_2$: C, 40.51; H, 4.25; Cl, 29.90. Found: C, 40.39; H, 4.29; Cl, 30.83.

Monoketene 20: isolated in 59% yield after recrystallization from pentane as a colorless, amorphous powder; mp 141.7−145.2 °C; IR (KBr) 2080, 1736 cm^{-1}; ^{1}H NMR δ 0.22 (s, 9), 0.29 (s, 9), 2.28 (s, 1), 5.77 (s, 1, exchangeable); ^{13}C NMR δ −1.88, −0.67, 10.9, 30.2, 114.2, 119.2, 121.5, 124.6, 136.9, 145.8, 171.4, 180.5; EIMS m/z 652 (M^+, 7), 482 (16), 404 (8), 226 (22), 199 (37), 155 (58), 73 (Me_3Si^+, 100); HRMS m/z calcd 651.7593, found 651.7594. Anal. Calcd for $C_{16}H_{20}Br_4O_4Si_2$: C, 29.47; H, 3.09; Br, 49.01. Found: C, 29.19; H, 3.13; Br, 48.19.

Molecular mechanics calculations were carried out using the Hyperchem[7a] package of programs utilizing the MM$^+$ (a version of the MM2 force field[7b]) method. All comformations were fully optimized using the Polak-Ribiere conjugate gradient method, setting the gradient at 0.01 kcal/mol/Å. A single-point energy calculation was then carried out.

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Supporting Information Available: Copies of ^{1}H NMR spectra (26 pages). This material is contained in libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.

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