Amination of Bis(trimethylsilyl)-1,2-bisketene to Ketenyl Amides, Succinamides, and Polyamides: Preparative and Kinetic Studies

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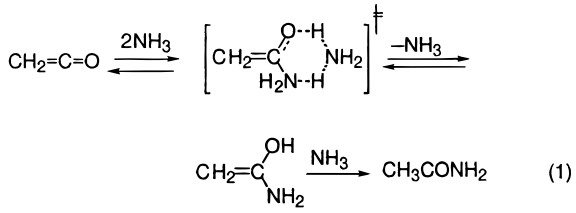
The reaction of the bisketene $(Me_3SiC{=}C{=}O)_2$ (**1**) with amines is facile and proceeds by two distinct steps forming first ketenylcarboxamides **3** and then succinamides **5**. Successive reaction of **1** with two different amines gives mixed succinamides, while phenylhydrazine gives succinimide **7**. The reactions of 1.8 equiv of **1** with 1,4-$(H_2NCH_2)_2C_6H_4$ gives α,ω-bisketenyldiamide **13**, while equivalent amounts of **1** and diamines gave polymeric amides. Mixed ester amides **8** are formed by sequential reaction of **1** with an alcohol, followed by an amine, or *vice versa*. Kinetic studies of the amination reaction of **1** with excess amines in CH_3CN gave rate constants k_{obs} for the formation of ketenylcarboxamides that were fit by the relationship $k_{obs} = k_a[\text{amine}]^2 + k_b[\text{amine}]^3$. Further reaction of the *n*-butyl ketenylcarboxamide **3b** with *n*-$BuNH_2$ to give the succinamide **5b** was first order in [*n*-$BuNH_2$], while the further reaction of the CF_3CH_2 ketenylcarboxyamide **3c** with $CF_3CH_2NH_2$ to form **5c** was fit by the equation $k_{obs} = k_c[\text{amine}]^2/(k_d[\text{amine}] + 1)$. The reaction of **3b** with CH_3OH to form the ester amide **8a** is strongly accelerated compared to CH_3OH addition to the corresponding ketenyl ester and gives significant stereoselectivity for formation of *erythro* product, and both these effects, as well as the absence of higher order kinetic terms in the reaction of **3b** with *n*-$BuNH_2$, may arise from coordination by the carboxamido group to the nucleophile.

The reactions of 1,2-bisketenes[1] with oxygen nucleophiles (H_2O[1a,b,f] and alcohols[1a,c,g]), electrophiles,[1b,d] diazoalkanes,[1e] alkenes,[1e] and alkynes[1e] have been studied in our laboratory and give a diverse chemistry. The reaction with amines is a prototypical reaction of ketenes[2] and has recently been the subject of theoretical[2b,c] and mechanistic study.[2d−j] In agreement with our criticism[3a] of earlier interpretations[3b,c] these theoretical studies[2b,c] for the reaction of $CH_2{=}C{=}O$ with NH_3 support a mechanism involving initial attack at the C=O bond with formation of an intermediate amide enol which then isomerizes to the product amide (eq 1). A pathway for addition to the C=O bond involving two molecules of amine (eq 1) was favored over pathways involving direct addition to the C=C bond.[3b,c]



(1)

Experimental studies[2j] of the amination of $PhMe_2SiCH{=}C{=}O$ and *t*-Bu(*i*-Pr)C=C=O in CH_3CN showed higher than first-order dependences of the observed rate constants on the [amine], whereas more reactive ketenes in CH_3CN[2e,i] or H_2O[2d] showed only a first-order dependence of k_{obs} on [amine]. This difference was interpreted[2j] to result from irreversibility of reaction of the reactive ketenes with a single amine molecule, whereas for less reactive ketenes the initial reaction was reversible and later steps involving further amine molecules as in eq 1 are kinetically significant.

The reaction of 1,2-bisketenes with amines has not been previously studied but is an attractive subject because such reactions provide potential routes to a variety of useful products. In particular, reactions with diamines offer the potential of a novel route for the formation of polyamides, including cyclic derivatives. We now report an examination of some of these processes.

Results and Discussion

The stable bis(trimethylsilyl)-1,2-bisketene **1**,[1a] formed from the corresponding cyclobutenedione **2**, exists preferentially in a twisted conformation.[4] The products from reaction of **1** with amines are summarized in Scheme 1.

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(2) (a) Tidwell, T. T. *Ketenes*; Wiley: New York, 1995. (b) Sung, K.; Tidwell, T. T. *J. Am. Chem. Soc.* **1998**, *120*, 3043−3048. (c) Raspoet, G.; Nguyen, M. T.; Kelly, S.; Hegarty, A. F. *J. Org. Chem.* **1998**, *63*, 9669−9677. (d) Andraos, J.; Kresge, A. J. *J. Am. Chem. Soc.* **1992**, *114*, 5643−5646. (e) Wagner, B. D.; Arnold, B. R.; Brown, G. W.; Lusztyk, J. *J. Am. Chem. Soc.* **1998**, *120*, 1827−1834. (f) Frey, J.; Rappoport, Z. *J. Am. Chem. Soc.* **1996**, *118*, 3994−3995. (g) Barton, D. H. R.; Chung, S. K.; Kwon, T. W. *Tetrahedron Lett.* **1996**, *37*, 3631−3634. (h) Birney, D. M.; Xu, X.; Ham, S.; Huang, X. *J. Org. Chem.* **1997**, *62*, 7114−7120. (i) Liu, R. Y.-c.; Lusztyk, J.; McAllister, M. A.; Tidwell, T. T.; Wagner, B. D. *J. Am. Chem. Soc.* **1998**, *120*, 6247−6251. (j) Allen, A. D.; Tidwell, T. T. *J. Org. Chem.* **1999**, *64*, 266−271.

(3) (a) Seikaly, H. R.; Tidwell, T. T. *Tetrahedron* **1986**, *42*, 2587−2613. (b) Lillford, P. J.; Satchell, D. P. N. *J. Chem. Soc. B* **1967**, 360−365. (c) Lillford, P. J.; Satchell, D. P. N. *J. Chem. Soc. B* **1970**, 1016−1019.

(4) (a) Allen, A. D.; Ma, J.; McAllister, M. A.; Tidwell, T. T.; Zhao, D.-c.; *Acc. Chem. Res.* **1995**, *28*, 265−271. (b) Allen, A. D.; Tidwell, T. T. *Chem. Commun.* **1996**, 2171−2172.

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Scheme 1

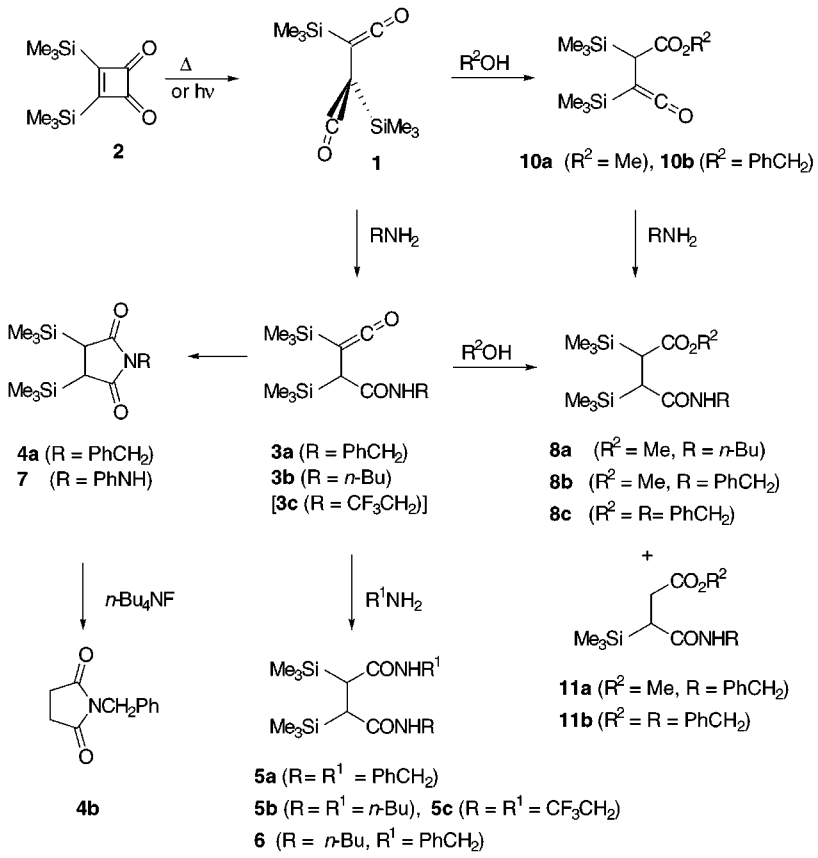


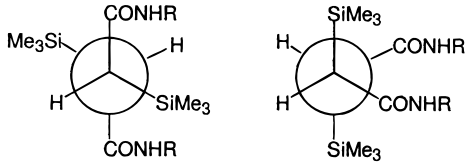
Table 1. Identifying Analytical Features of Ketenyl Amides

	IR (cm^{-1})		^{13}C NMR δ (C_β=C_α=O)	
ketenes	C=C=O	CONH	C_β	C_α
3a	2081	1653	2.0	179.6
3b	2077	1653	10.7	179.8
13	2085	1649	10.7	179.6

Reactions of **1** with 1 equiv of $PhCH_2NH_2$ or *n*-$BuNH_2$ in CH_2Cl_2 proceed efficiently to give ketenyl amides **3a**,**b**, respectively, as the only observable products, as established by their spectral properties, especially the distinctive IR and ^{13}C NMR absorptions of the C=C=O group (Table 1).

After 8 days at 0 °C in CH_2Cl_2 **3a** reacted completely as shown by ^1H NMR and IR to give a product tentatively identified as a mixture of the succinimide **4a** and desilylated products, and for characterization this mixture was converted by *n*-Bu_4NF in THF to benzyl succinimide **4b**.[5a] The reaction of **1** with 1 equiv of $CF_3CH_2NH_2$ proceeded slowly and after 3 h on the basis of the ^1H NMR spectrum gave 40% unreacted **1**, 35% of ketenylamide **3c**, and 25% of a product analogous to **4a**.

Reaction of **1** with 2 equiv of $PhCH_2NH_2$ or *n*-$BuNH_2$, or 6 equiv of $CF_3CH_2NH_2$, in CH_2Cl_2 at room temperature gave complete conversion to almost equal amounts of the diastereomeric *meso*- and *dl*-succinamides **5**, evidently through the ketenyl amides **3**. Chromatography of **5a** caused significant amounts of desilylation, but the *meso* and *d,l* isomers were separated in a total yield of 30%. Partial separation of *meso*- and *d,l*-**5c** was effected by recrystallization. Analogously to our examination[1c] of the formation of succinates from the reaction of **1** with alcohols, the identity of the separated diastereomers of **5a** were ascertained from the chemical shifts and from the vicinal coupling constants of the protons on C_2 and C_3 obtained from the natural abundance ^{13}C satellites in the ^1H NMR,[5b] with the *meso* and *d,l* diastereomers in the favored conformations shown. Comparable results had been obtained for the corresponding succinate esters,[1c] for which the structural and conformational assignments were confirmed by X-ray crystallography.[1c]

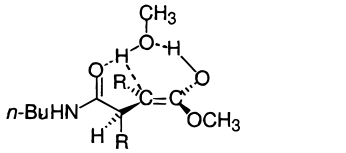


Reaction of **1** in CH_2Cl_2 with 1 equiv of $PhCH_2NH_2$ followed by addition of 1 equiv of *n*-$BuNH_2$ and evaporation of the solvent gave the mixed diamides **6** in 95% crude yield and 94% purity by ^1H NMR analysis, as a 2/1 mixture of the *erythro* and *threo* diastereomers. These were separated by chromatography and identified by their characteristic ^1H coupling constants.[5b]

Reaction of **1** with phenylhydrazine in CH_2Cl_2 gave complete conversion to succinimide **7** with a 90% preference for one stereoisomer, which was separated in 95% purity by chromatography. The structures of the analogous *cis*- and *trans*-succinic anhydrides were established by X-ray crystallography,[1a] but even with this comparison the stereochemistry of **7** is not certain.[5b]

(5) (a) Puertas, S.; Rebolledo, F.; Gotor, V. *Tetrahedron* **1995**, *51*, 1495−1502. (b) See the Experimental Section and the summary in Table 3 (Supporting Information).

The reaction of **3b** with CH_3OH gave a > 9/1 preference for formation of the *erythro* mixed ester amide **8a** with a conformation analogous to that shown for *meso*-**5** on the basis of the large vicinal H,H coupling constant of 11.5 Hz. The product-forming step in ketene esterification involves protonation at C_β of an intermediate ester enol, and a model (**9**) is shown for the observed selectivity with assistance by the amide oxygen in proton transfer by CH_3OH. This structure minimizes the interaction between the bulky Me_3Si groups in the transition state.



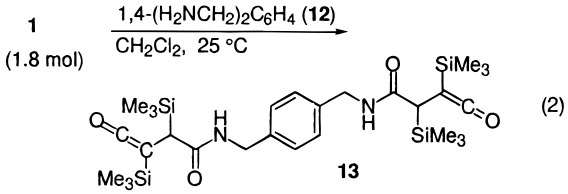
9 R = Me_3Si

Exposure of **1** to neat MeOH followed by rapid removal of the excess MeOH gave complete conversion to the ketenyl ester **10a**, as reported previously.[1a] Reaction of **10a** with 1 equiv of $PhCH_2NH_2$ in CH_2Cl_2 led to the succinyl ester amide **8b** as a mixture assigned as the *erythro* and *threo* diastereomers[5b] together with the desilylated product **11a** in a ratio of 63:27:10, respectively. The regioselectivity for formation of **11a** arises from a greater lability of groups α to the ester as opposed to amide groupings and was confirmed by the coupled ^{13}C NMR spectrum which showed that the carbon adjacent to the ester bears 2 protons. In other similar experiments, much less of the desilylated product **11a** was observed in the initial product, which contained *erythro*- and *threo*-**8b** in a 2:1 ratio. Upon chromatographic separation, extensive desilylation occurred, and the maximum yields of purified *erythro*- and *threo*-**8b** and **11a**, were 20, 25, and 15%, respectively.

Reaction of **1** with 0.95 equiv of benzyl alcohol catalyzed by Et_3N led to the ketenyl ester **10b**, which was identified by the ^1H NMR spectrum of the reaction mixture. The use of Et_3N to catalyze alcohol addition to **1** has not been reported previously and greatly accelerates the process. Addition of $PhCH_2NH_2$ to **10b** gave the *erythro* and *threo* ester amides **8c**, along with the desilylated product **11b** in a ratio of 62:22:16, respectively as determined by ^1H NMR. Upon chromatography, *erythro*-**8c** and **11b** were isolated in pure form and fully characterized.

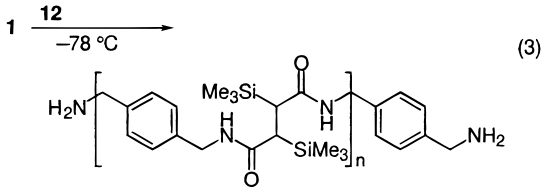
We have also recently utilized the methodology of reacting bisketene **1** with methyl poly(ethylene glycol) (MPEGOH) to form a soluble polymer-supported ketenyl ester analogous to **10** (R^2 = MPEGO) which reacted with amines to form polymer-supported ester amides analogous to **8**.[6] These were desilylated and cleaved from the polymer support to give either succinimides or ester amides.[6]

Reaction of 1,4-di(aminomethyl)benzene (**12**) with **1** in a 1/1.8 molar ratio in CH_2Cl_2 at room temperature for 10 min followed by evaporation of the solvent gave a white solid product that by ^1H NMR was identified as the bisketene **13** (eq 2) containing 8% of succinamide products, with the latter identified by the characteristic ^1H NMR signals at δ 2.03 and 2.33 typical of succinamides. The bisketene **13** was too sensitive for purification but was identified by its spectral characteristics (Table 1).



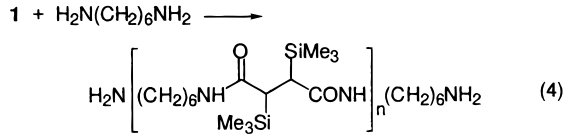
13 (2)

Reaction of **1** with 1.2 equiv of **12** at −78 °C in CH_2Cl_2 followed by warming to 25 °C and evaporation of the solvent gave a white solid which by ^1H NMR in CD_3OD has the structure **14** (eq 3), with a 4/1 preference for the *erythro* configuration of the vicinal succinic α-protons (δ 2.15) over the *meso* configuration (δ 2.45). Integration showed the benzylamino (s, δ 3.8, CH_2NH_2) and benzylamido (m, δ 4.2, CH_2NHCO) protons in a 1/8 ratio consistent with a value for *n* of 8 (eq 3).



14 (3)

Reaction of **1** with an equimolar amount of 1,6-hexanediamine led to a product with spectra attributable to the oligomeric amide **15** (eq 4). The IR spectrum showed the absence of ketenyl absorption near 2100 cm^{-1} and the presence of amide absorption at 1650 and 1499 cm^{-1}, and the ^1H NMR spectrum showed signals at δ 3.15 due to the CH_2 group adjacent to amido nitrogen $CONHCH_2$ and δ 5.9 for the CH_2 group next to amino nitrogen H_2NCH_2 in a 4/1 ratio, as well as the other signals expected for **15** with $n = 4$.



15 (4)

Kinetic Investigations

The kinetics of the reaction of **1** with excess *n*-$BuNH_2$ (0.188×10^{-2} to 4.02×10^{-2} M) and with $CF_3CH_2NH_2$ (0.0213 to 0.256 M) in CH_3CN to form ketenyl amides **3b** and **3c** (Scheme 1), respectively, were measured by observing the decrease in absorption near 386 nm using stopped-flow or conventional UV spectroscopy, and the derived first-order rate constants are reported in Table 4 (Supporting Information). With [*n*-$BuNH_2$] from 0.02 to 0.25 M and [$CF_3CH_2NH_2$] from 0.341 to 2.10 M and longer time scales, the pseudo-first-order rate constants for reaction of the intermediate ketenyl amides **3b** and **3c** to form the bisamides **5b** and **5c** were measured at 331 nm, as reported in Table 5 (Supporting Information).

Ketenyl amide **3b** was also generated in a preparative reaction (Scheme 1), and its UV spectrum showed the same λ_{max} at 332 nm observed in the kinetic experiments.

(6) Rafai Far, A.; Tidwell, T. T. *J. Org. Chem.* **1998**, *63*, 8636−8637.

Table 2. Summary of Rate Constants at 25 °C for Reactions of Bisketene 1 and Ketenyl Amides 3 with Nucleophiles in CH_3CN and Comparison to $PhMe_2SiCH{=}C{=}O$ (16)

ketene	nucleophile	k_a (M^{-2} s^{-1})	k_b (M^{-3} s^{-1})	k_a(**1**)/k_a(**16**)	k_b(**1**)/k_b(**16**)
1	*n*-$BuNH_2$	$(1.73 \pm 0.10) \times 10^6$	$(2.39 \pm 0.58) \times 10^7$	7.6	6.3
	$CF_3CH_2NH_2$	(5.37 ± 0.18)	(2.03 ± 0.89)	18	9.2
			k_{obs}(**1**)/k_{obs}(**3**)	k_{obs}(**16**)/k_{obs} (**3**)	
3b	*n*-$BuNH_2$	$k_{obs} = (2.11 \pm 0.03)$ M^{-1} s^{-1}	$(2.4-3.7) \times 10^4$ [a]	1.4×10^4 [b]	
	CH_3OH	$k_{obs} = 1.56 \times 10^{-2}$ s^{-1}	0.59[c]		
3c	$CF_3CH_2NH_2$	$k_c = (6.66 \pm 0.39) \times 10^{-4}$ M^{-2} s^{-1}	9.3×10^3 [d]	5.4×10^2 [d]	
		$k_d = 0.148 \pm 0.044$ M^{-1}			

[a] 2.4×10^4 and 3.8×10^4 at [*n*-$BuNH_2$] = 0.040 and 0.020 M, respectively. [b] [*n*-$BuNH_2$] = 0.050 M. [c] In neat CH_3OH. [d] [$CF_3CH_2NH_2$] = 0.256 M.

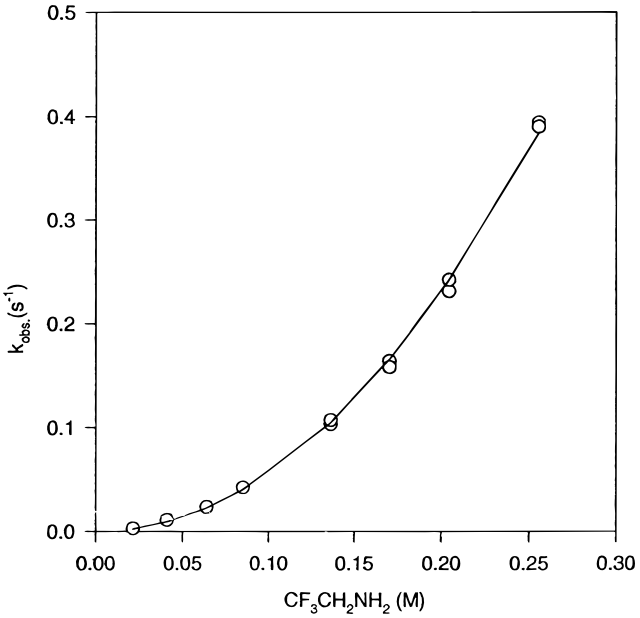


Figure 1. Fit of k_{obs} versus [$CF_3CH_2NH_2$] for monoamination of $(Me_3SiC{=}C{=}O)_2$ (**1**) by eq 5.

Reaction of **3b** from the preparative reaction with 0.0200 M *n*-$BuNH_2$ to form **5b** gave $k_{obs} = 2.66 \times 10^{-2}$ s^{-1}, in satisfactory agreement with the value 2.34×10^{-2} s^{-1} obtained in the kinetic experiments beginning with **1**.

The dependence of the measured rate constants for the amination of bisketene **1** to form **3b** and **3c** are fit by eq 5, as summarized in Table 2 and illustrated in Figure 1 for reaction with $CF_3CH_2NH_2$. Previously[2j] we found that rate data for the monoketene $PhMe_2SiCH{=}C{=}O$ (**16**) with amines were also fit by eq 5, and this rate expression was derived from the reaction scheme in eqs 6 and 7, which involves a complex of the ketene with two amine molecules.

$$k_{obs} = k_a[\text{amine}]^2 + k_b[\text{amine}]^3 \quad (5)$$

$$\text{ketene} + 2\ \text{amine} \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} \text{complex} \xrightarrow{k_2} \text{product} \quad (6)$$

$$\text{complex} + \text{amine} \xrightarrow{k_3} \text{product} \quad (7)$$

The sizable rate constant ratios k(**1**)/k(**16**) in Table 2 show that just as in hydration and esterification bisketene **1** is more reactive than less hindered monoketenes. For **1** the very large rate constant ratios $k_{n\text{-}BuNH_2}/k_{CF_3CH_2NH_2}$ (Table 2) are comparable to those found for $PhMe_2SiCH{=}C{=}O$ (**16**),[2j] confirming the strong dependence of ketene reactivity on amine basicity.

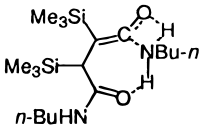
The further reaction of the ketenyl amide **3b** to form the bisamide **5b** gave a linear correlation of k_{obs} with [*n*-$BuNH_2$] (Figure 2), while the reaction of **3c** with $CF_3CH_2NH_2$ to form **5c** was fit by eq 8 (Figure 3, Supporting Information), with a second-order but no third-order term in [amine] (Table 2). Previously[2j] this latter behavior was found for reaction of the monoketene *t*-BuC(Pr-*i*)=C=O with *n*-$BuNH_2$, and the rate expression of eq 8 was derived from the reaction scheme in eq 9, with $k_c = k_2k_1/k_{-1}$ and $k_d = k_2/k_{-1}$.

$$k_{obs} = k_c[\text{amine}]^2/(k_d[\text{amine}] + 1) \quad (8)$$

$$\text{ketene} + \text{amine} \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} \text{complex} \xrightarrow[\text{amine}]{k_2} \text{product} \quad (9)$$

In the reaction of **3b** with *n*-$BuNH_2$ the initial step is evidently irreversible. This behavior has been found for reactive ketenes[2d,e] but is unusual for **3b** which is rather unreactive and is less reactive than $PhMe_2SiCH{=}C{=}O$ by a factor of 1.4×10^4 (Table 2).

Previously[2j] we suggested that for more reactive ketenes the instability of the reactant meant that further reaction of the initial ketene−amine adduct was faster than reformation of the reactant, and so the initial step was irreversible. However, as noted, **3b** is quite unreactive compared to **1**. As shown in eq 1, the function of the second amine molecule is to provide assistance in formation of an amide enol intermediate, and for **3b** the amide present in the molecule may assume this role, as depicted in **17**. A significant rate enhancement for the addition of CH_3OH to **3b** is also suggested to involve assistance by the carboxamido group (vide infra).



17

In the addition of $CF_3CH_2NH_2$ to **3c**, the poorly nucleophilic amine has a strong tendency to leave and reversibly reform the starting material, and a second amine molecule is needed to stabilize a transition structure analogous to that shown in eq 1. Just as in the reaction of *t*-BuC(Pr-*i*)=C=O with *n*-$BuNH_2$, which also is fit by eq 8,[2j] the reaction of **3c** with a second amine is a slow process with a crowded substrate and so leads irreversibly to product.

Because of the different rate expressions for the first and second reactions of **1** with amines, the rate ratio of bisketene **1** relative to ketenyl amide **3** depends on [amine] and varies from $(9.3-37) \times 10^3$ (Table 2). These large ratios for amines of widely different reactivity show

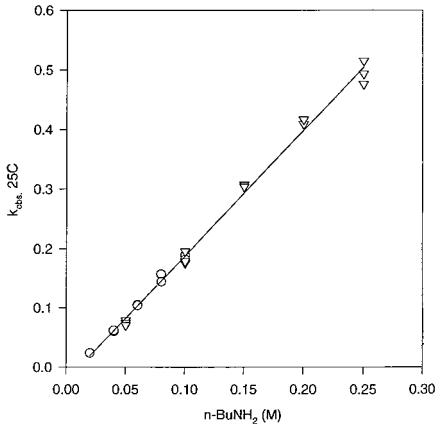
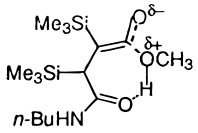


Figure 2. Plot of k_{obs} versus [*n*-BuNH$_2$] for amination of carboxamide ketene **3b**.

why preparative selective monoamination is feasible. The rate constant ratios k(**1**)/k(**16**) of 6.3−18 illustrate that even though the bisketene **1** is more crowded than PhMe$_2$SiCH=C=O, the former is significantly more reactive. Previously we have pointed out that 1,2-bisketenes, in which the adjacent β-carbons of the ketenyl groups both bear substantial negative charge, suffer from ground-state destabilization due to repulsive interactions between the two ketenyl groups.[4a] This effect, rather than any stabilization of a conjugated intermediate from reaction of a bisketene, was assigned as the cause of the relatively high reactivity of bisketenes. For comparison, the rate of hydration of **1** is similar to that of **16**,[1f] and hydration of **1** produces an intermediate ketenyl carboxylic acid, which cyclizes to a succinic anhydride with a rate constant 2.2 times less than the initial hydration.[1b]

The amination rate constants of the monoketene PhMe$_2$SiCH=C=O (**16**)[2j] are greater than the corresponding values for the ketenyl amides **3** by factors 5.4 × 10^2 and 1.4 × 10^4 (Table 2), reflecting the steric crowding in **3**. The rate ratio k(*n*-BuNH$_2$)/k(H$_2$O) for the bisketene **1** is concentration dependent, and at the lowest [H$_2$O] studied,[1a] 11.1 M, the value of $k_2 = k_{obs}$[H$_2$O]$^{-1}$ is 2.7 × 10^{-4} M^{-1} s^{-1}, and this value is 2.9 × 10^6 less than k_2 for reaction with *n*-BuNH$_2$ found here. This is somewhat larger than the ratio k(*n*-BuNH$_2$)/k(H$_2$O) = 7.1 × 10^4 estimated[2j] for Ph$_2$C=C=O in H$_2$O.

The rate constant for reaction of the amide-substituted ketene **3b** in neat CH$_3$OH forming ester amide **8a** was determined as 1.56 × 10^{-2} s^{-1} at 25 °C (Table 2), and this is the first measurement of the rate constant for such a reaction. Surprisingly this rate constant exceeds that of 9.21 × 10^{-3} s^{-1} found[1a] for the reaction of bisketene **1** with CH$_3$OH, and the rate ratio k(**1**)/k(**3b**) with CH$_3$OH is 0.59, much less than the ratio k(**1**)/k(**3b**) with *n*-BuNH$_2$ of (2.4 to 3.7) × 10^4 (Table 2). The further reaction with CH$_3$OH of the ester-substituted ketene **10a** from **1** was also clearly slower than the first reaction of **1** by a significant factor, estimated to be at least 10.[1a] This suggests a significant accelerating effect of CH$_3$OH addition by hydrogen-bonding assistance provided by the amido group as shown in **18**. A similar assistance by the carboxamido group in stabilizing the *n*-BuNH$_2$ adduct of **3b** is represented by **17** (vide supra). As discussed above, there is also a significant selectivity for forming *erythro*-**8a** and model **9** involving carboxamide assistance of proton transfer to C$_\beta$ in an intermediate ester enol was suggested to explain the stereoselectivity of the process.



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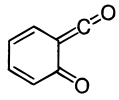
For the monoketene PhMe$_2$SiCH=C=O (**16**), the ratio k(*n*-BuNH$_2$)/k(H$_2$O) is estimated[2j] at a [nucleophile] of 11.1 M to be as high as 10^{13}, and this is significantly greater than for **1**, which was estimated as 2.9 × 10^6 (vide supra). In another comparison,[2i] the measured rate ratio k(Et$_2$NH)/k(H$_2$O) in CH$_3$CN is 73 for the highly reactive oxoketene **19**, and both reactions are first order in [nucleophile]. Although these substrates react by different mechanisms with different rate laws, it is nevertheless apparent that there are enormous differences in the selectivities of different ketenes for different nucleophiles.



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In summary, amination reactions of 1,2-bisketene **1** are facile and proceed in discrete steps to give ketenyl amides and then succinamides. Mixed succinamides and ester amides may also be prepared, and the reactions of diamides lead to new bisketenes and to polyamides. The rate constants for reaction of **1** with amines depend on both [amine]^2 and [amine]^3, but the rate laws for the further reaction of the resulting ketenyl amides **3** depend on the particular amine. The reaction of ketenyl amide **3b** with MeOH shows a selectivity for *erythro* product stereochemistry and a large rate acceleration consistent with specific interactions of the carboxamido group with MeOH as shown in **9** and **18**, respectively. The rate law for reaction of **3b** with *n*-BuNH$_2$ also suggests carboxamido assistance as shown by **17**.

Experimental Section

Infrared (IR) spectra were recorded on a Perkin-Elmer FTIR 1000 spectrometer. ^{1}H NMR spectra were recorded on Varian VXR-200 or Varian Unity-400 instruments referenced to residual CHCl$_3$ (7.26 ppm). ^{13}C NMR spectra are referenced to the center line of CDCl$_3$ (77.00 ppm). Reactions were carried out in flame- or oven-dried glassware under an atmosphere of N$_2$ or Ar.

***N*-Benzyl-2,3-bis(trimethylsilyl)-4-oxobut-3-enamide (3a).** Bisketene **1** (200 mg, 0.886 mmol) in 3 mL of CH$_2$Cl$_2$ was added in one portion to a stirred solution of PhCH$_2$NH$_2$ (96 μL, 71 mg, 0.98 mmol) in 3 mL of CH$_2$Cl$_2$ at room temperature. After 5 min the solution was stored at −70 °C, a 0.5 mL aliquot was removed, and the solvent was evaporated at room temperature. Analysis by ^{1}H NMR showed the monoketene as the only identifiable product, in 95% purity by ^{1}H NMR analysis: ^{1}H NMR (CDCl$_3$) δ 0.132 (s, 9, Me$_3$Si), 0.155 (s, 9, Me$_3$Si), 1.92 (s, 1, CHCO), 4.42 and 4.44 (ea s, PhCH$_2$), 6.09 (m, 1, NH), 7.29 (m, 5, Ph);^{13}C NMR (CDCl$_3$) δ −1.9, −1.0, 2.0, 10.8, 44.0, 127.3, 127.8, 128.5, 138.3, 173.1, 179.6; IR (CDCl$_3$) 3343 (w) NH, 2081 (C=C=O), 1653 (CON) cm^{-1}; EIMS *m*/*z* 333 (M$^+$, 34), 242 (M$^+$ − PhCH$_2$, 61), 91 (C$_7$H$_7^+$, 70), 73 (Me$_3$Si$^+$, 100); HRMS *m*/*z* calcd for C$_{17}$H$_{27}$NO$_2$Si$_2$ 333.1580, found 333.1577.

Cyclization of 3a. A solution of **3a** (0.50 mmol) prepared as above in 4.5 mL of CH$_2$Cl$_2$ was left at 0 °C for 8 day, and upon evaporation of the solvent no remaining **3a** was visible in the IR or ^{1}H NMR spectra, but ^{1}H NMR multiplets in the

region δ 2.3−3.3 were suggestive of the presence of succinimide **4a** and desilylation products. The product mixture was stirred with *n*-Bu_4NF (1.5 mL, 1.0 M in THF) in 3 mL of THF for 10 min and then diluted with 10 mL of H_2O and extracted with 5 mL of ether. The organic extract was dried and evaporated to give **4b**[5] as the major product by ^{1}H NMR, and this was purified by chromatography (2% MeOH in CH_2Cl_2) and identified by ^{1}H NMR ($CDCl_3$) peaks at δ 2.71 (s, 4, CH_2CH_2), 4.66 (s, 2, CH_2), and 7.3−7.4 (m, 5, Ph).

***N*-*n*-Butyl-2,3-bis(trimethylsilyl)-4-oxobut-3-enamide (3b).** To bisketene **1** (265 mg, 1.17 mmol) in 4 mL of CH_2Cl_2 stirred at 25 °C was added *n*-$BuNH_2$ (114 μL, 84.4 mg, 1.15 mmol) in 3 mL of CH_2Cl_2. After the exothermic reaction, the solution was stirred 5 min and then cooled to −70 °C for storage. A 1 mL aliquot was evaporated to give **3b** as a white solid, mp 73−77 °C: ^{1}H NMR ($CDCl_3$) δ 0.148 (s, 9, Me_3Si), 0.155 (s, 9, Me_3Si), 0.91 (t, 3, J = 7.3 Hz, CH_3), 1.3−1.6 (m, 4, CH_2CH_2), 1.85 (s, 1, CH), 3.2−3.3 (m, 2, NCH_2); ^{13}C NMR ($CDCl_3$) δ −2.09, −1.06, 10.7, 13.6, 20.1, 31.9, 32.1, 39.5, 173.1, 179.8; IR (CH_2Cl_2) 3443, 2077, 1653, 1509 cm^{-1}; UV $\lambda_{max}^{CH_3CN}$ 332 nm, ϵ = 40; EIMS *m*/*z* 299 (M^+, 21), 198 ($M^+ - CONH_2$-Bu-*n*, 100), 73 (Me_3Si^+, 67); HRMS *m*/*z* calcd for $C_{14}H_{29}NO_2Si_2$ 299.1737, found 299.1738.

***N*,*N*′-Dibenzyl-2,3-bis(trimethylsilyl)succinamide (*meso*- and *d*,*l*-5a).** Bisketene **1** (206 mg, 0.912 mmol) in 3 mL of CH_2Cl_2 was added in one portion to a stirred solution of benzylamine (198 μL, 1.81 mmol) in 3 mL of CH_2Cl_2 at room temperature, with transient generation of a pink color. After 2 min of stirring, the solvent was evaporated, giving crude **5a** (0.37 mg, 0.84 mmol, 92%) which by ^{1}H NMR analysis consisted of *meso*- and *d*,*l*-**5a** in a 1.0/1.0 ratio, with about 4% of an impurity tentatively identified as a desilylated product. Radial chromatography on silica gel (2% Et_3N in CH_2Cl_2) separated the diastereomeric products: *meso*-**5a** (89 mg, 0.20 mmol, 22%) mp 149−152 °C; ^{1}H NMR ($CDCl_3$) δ 0.06 (s, 18, Me_3Si), 2.39 (s, 2, $J_{C,H}$ = 125 Hz, $J_{H,H}$ = 11.1 Hz, C*H*$SiMe_3$), 4.31 (d, 4, CH_2Ph), 5.89 (t, 2, NH), 7.3 (m, 10, Ph); ^{13}C NMR ($CDCl_3$) δ −1.2, 37.2, 44.0, 127.4, 128.3, 128.5, 138.0, 173.6; IR ($CDCl_3$) 3446, 1649, 1499 cm^{-1}; EIMS *m*/*z* 440 (M^+, 14), 349 (M^+ − Bn, 26), 91 ($PhCH_2^+$, 100), 73 (Me_3Si^+, 54); HRMS *m*/*z* calcd for $C_{24}H_{36}N_2O_2Si_2$ 440.2315, found 440.2309. *d*,*l*-**5a** (32 mg, 0.073 mmol, 8%) mp 146−148 °C;^{1}H NMR ($CDCl_3$) 0.07 (s, 18, Me_3Si), 2.05 (s, 2, $J_{C,H}$ = 119 Hz, $J_{H,H}$ = 5.1 Hz), 4.35 (m, 4, CH_2Ph), 7.3 (m, 10, Ph), 7.82 (bs, 2, NH); ^{13}C NMR ($CDCl_3$) δ −1.3, 38.4, 44.0, 127.2, 128.1, 128.5, 138.4, 174.3; IR ($CDCl_3$) 3447, 1649, 1503 cm^{-1}; EIMS *m*/*z* 440 (M^+, 10), 349 (M^+ − $PhCH_2$, 21), 91 ($C_7H_7^+$, 100), 73 (Me_3Si^+, 40); HRMS *m*/*z* calcd for $C_{24}H_{36}N_2O_2Si_2$ 440.2315, found 440.2319.

***N*,*N*′-Di-*n*-butyl-2,3-bis(trimethylsilyl)succinamide (*meso*- and *d*,*l*-5b).** Bisketene **1** (182 mg, 0.804 mmol) in 3 mL of CH_2Cl_2 was added in one portion to *n*-$BuNH_2$ (158 μL, 1.60 mmol) as in the preparation of **5a**. The solid product was obtained in 85% crude yield and 89% purity by ^{1}H NMR, with a *meso*/*dl* ratio of 3/2: *meso*-**5b** ^{1}H NMR ($CDCl_3$) δ 0.06 (s, 18, Me_3Si), 0.92 (t, 6, CH_3), 1.4 (m, 8, $MeCH_2CH_2$), 2.28 (s, 2, $CHSiMe_3$), 3.32 (m, 4, CH_2N), 5.4 (t, 2, NH); *d*,*l*-**5b** ^{1}H NMR ($CDCl_3$) δ 0.10 (s, 18, Me_3Si), 0.92 (t, 6, CH_3), 1.4 (m, 8, $MeCH_2CH_2$), 1.96 (s, 2, $CHSiMe_3$), 3.32 (m, 4, CH_2N), 7.4 (t, 2, NH); IR ($CDCl_3$) 3447, 1651, 1508 cm^{-1}.

***N*,*N*′-Bis(trifluoroethyl)-2,3-bis(trimethylsilyl)succinamide (*meso*- and *d*,*l*-5c).** To a stirred solution of bisketene **1** (131 mg, 0.58 mmol) in 3 mL of CH_2Cl_2 was added $CF_3CH_2NH_2$ (0.280 mL, 3.52 mmol) at room temperature, and the solution was stirred for 3 h. The ^{1}H NMR showed 10% residual **1**; therefore, 0.050 mL of additional $CF_3CH_2NH_2$ was added, the solution was stirred for 1.5 h, and the solvent was evaporated to give a pale yellow solid that was not completely soluble in $CDCl_3$ and by ^{1}H NMR contained *meso*- and *d*,*l*-**5c** in a 1.2/1.0 ratio. The solid product was fractionated by partial dissolution in 4/1 pentane/CH_2Cl_2 to give a soluble fraction from which a solid rich in *meso*-**5c** crystallized on cooling and an insoluble fraction rich in *d*,*l*-**5c** was obtained: *meso*-**5c** ^{1}H NMR ($CDCl_3$) 0.079 (s, 18, Me_3Si), 2.45 (s, 2, $CHSiMe_3$), 3.9−4.05 (m, 4, CH_2CF_3), 5.78 (bs, 2, NH); ^{13}C NMR ($CDCl_3$) δ −1.59, 37.5, 40.6 ($^2J_{CF}$ = 34.4 Hz), 124.1 ($^1J_{CF}$ = 279 Hz), 174.1; *d*,*l*-**5c** ^{1}H NMR ($CDCl_3$) δ 0.11 (s, 18, Me_3Si), 2.11 (s, 2, $CHSiMe_3$), 3.75−3.95 (m, 4, CH_2CF_3), 7.75 (bs, 2, NH); ^{13}C NMR ($CDCl_3$) δ −1.75, 38.5, 40.7 (q, $^2J_{CF}$ = 34.4 Hz), 124.2 (q, $^1J_{CF}$ = 279 Hz), 175.0; **5c** IR ($CDCl_3$) 3452, 1670, 1508 cm^{-1}; EIMS *m*/*z* 424 (46, M^+), 73 (100, Me_3Si^+); HRMS *m*/*z* calcd for $C_{14}H_{26}F_6N_2O_2Si_2$ 424.1437, found 424.1453.

Reaction of **1** (7.7 mg, 0.034 mmol) in 0.7 mL of CD_2Cl_2 with $CF_3CH_2NH_2$ (2.7 μL, 0.034 mmol) in an NMR tube gave after 3 h a product tentatively assigned by the ^{1}H NMR spectrum to contain 35% **3c**: ^{1}H NMR ($CDCl_3$) 0.17 (s, 9, Me_3Si), 2.10 (s, 1, $CHSiMe_3$), 3.8−4.1 (m, 2, CH_2CF_3), 6.12 (s, 1, NH).

***N*-Benzyl-*N*′-*n*-butyl 2,3-bis(trimethylsilyl)butanediamide (6).** To a solution of **3a** (0.71 mmol, generated *in situ* from 0.71 mmol of **1** and 0.71 mmol of $PhCH_2NH_2$) in 8 mL of CH_2Cl_2 at room temperature was added *n*-$BuNH_2$ (70 μL, 0.71 mmol) in one portion. After 3 min of stirring, the solvent was evaporated, giving **6** as a 2/1 mixture of *erythro*/*threo* diastereomers in 95% crude yield and 94% purity by ^{1}H NMR. Chromatography (2% MeOH in CH_2Cl_2) gave the purified isomers. *erythro*-**6** (78 mg, 0.19 mmol, 27%), mp 141−144 °C: ^{1}H NMR ($CDCl_3$) δ 0.051 (s, 9, Me_3Si), 0.055 (s, 9, Me_3Si), 0.90 (t, 3, CH_3), 1.3 (m, 2, CH_2Me), 1.4 (m, 2, CH_2Et), 2.32 (d, 1, J = 11.2 Hz, CHCO), 2.36 (d, 1, J = 11.2 Hz, CHCO), 3.16 (m, 2, NCH_2Pr-*n*), 4.33 (dd, 2, CH_2Ph), 5.55 (t, 1, NH), 5.90 (t, 1, NH), 7.31 (m, 5, Ph); ^{13}C NMR ($CDCl_3$) δ −1.34, −1.30, 13.8, 20.2, 31.7, 37.2, 37.3, 39.3, 44.0, 127.4 128.3, 128.6, 138.1, 173.6, 173.7; IR ($CDCl)_3$ 3445, 3330, 1664, 1628 cm^{-1}; EIMS *m*/*z* 406, (M^+, 22), 391 (M^+ − CH_3, 22), 315 (M^+ − C_7H_7, 40), 200 (29), 147 (24), 91 ($C_7H_7^+$, 100), 73 (Me_3Si^+, 77); HRMS *m*/*z* calcd for $C_{21}H_{38}N_2O_2Si_2$ 406.2472, found 406.2484. *threo*-**6** (26 mg, 0.064 mmol, 9%) mp 126−128 °C: ^{1}H NMR ($CDCl_3$) δ 0.079 (s, 9, Me_3Si), 0.83 (s, 9, Me_3Si), 0.92 (t, 3, CH_3), 1.37 (m, 2, CH_2Me), 1.50 (m, 2, CH_2Et), 1.98 (d, 1, J = 5.2 Hz, CHCO), 2.02 (d, 1, J = 5.2 Hz, CHO), 3.2 (m, 2, CH_2Pr-*n*), 4.4 (m, 2, CH_2Ph), 7.3 (m, 5, Ph); 7.36 (s, 1, NH); 7.87 (s, 1, NH). ^{13}C NMR ($CDCl_3$) δ −1.37, −1.30, 13.8, 20.3, 31.7, 38.4, 38.5, 39.6, 43.9, 127.2, 128.1, 128.5, 138.5, 174.3, 174.4; IR ($CDCl_3$) δ 3445, 3257, 1656, 1621 cm^{-1}; EIMS *m*/*z* 406 (M^+, 31), 315 (M^+ − C_7H_7, 70), 91 ($C_7H_7^+$, 100); 73 (Me_3Si^+, 87); HRMS *m*/*z* calcd for $C_{21}H_{38}N_2O_2Si_2$ 406.2472, found 406.2470.

***N*-Phenylimino-3,4-bis(trimethylsilyl)succinimide (7).** To a stirred solution of **1** (173 mg, 0.763 mmol) in 3 mL of CH_2Cl_2 at room temperature was added phenylhydrazine (75 μL, 0.76 mmol) in CH_2Cl_2. After 10 min of stirring, the solvent was evaporated and ^{1}H NMR analysis showed that one stereoisomer of **7** was formed to the extent of 90%. Upon chromatography (10% EtOAc in hexanes, silica gel) the major stereoisomer was isolated in 95% purity, as a yellow solid, mp 144−158 °C (decomp): ^{1}H NMR ($CDCl_3$) δ 0.16 (s, 18, Me_3Si), 2.34 (s, 2, CHCO), 6.08 (s, 1, NH), 6.8−7.2 (m, 5, Ph); ^{13}C NMR ($CDCl_3$) δ −3.1, 33.4, 115.6, 122.7, 129.1, 132.1, 176.9; IR (CCl_4) 3344 (w), 1703 cm^{-1}; EIMS *m*/*z* 334 (M^+, 42), 242 (M^+ − NHPh, 52), 150 (32), 91 (19), 73 (Me_3Si^+, 100); HRMS *m*/*z* calcd for $C_{16}H_{26}N_2O_2Si_2$ 334.1533, found 334.1525.

***erythro*-*N*-*n*-Butyl 2,3-bis(trimethylsilyl)-4-methoxy-4-oxobutanamide (8a).** Methanol (2 mL) was added to solid **3b** (25 mg, 0.084 mmol) at room temperature, and after 5 min the resulting solution was evaporated to give a pale yellow solid which by ^{1}H NMR consisted of *erythro*-**8a** with less than 10% of any impurities or isomeric byproducts. This was recrystallized from pentane to give *erythro*-**8a**, mp 102−105 °C: ^{1}H NMR ($CDCl_3$) δ 0.045 (s, 9, Me_3Si), 0.064 (s, 9, Me_3Si), 0.91 (t, 3, J = 7.3 Hz, CH_3), 1.33 (sextet, 2, J = 7.4 Hz, CH_2), 1.47 (quintet, 2, J = 7.1 Hz, CH_2), 2.45 (d, 2, J = 11.5 Hz, CH), 2.66 (d, 2, J = 11.5 Hz, CH), 3.18 (q, 2, J = 7.1 Hz, CH_2N), 3.59 (s, 3, OCH_3), 5.28 (bs, 1, NH); ^{13}C NMR ($CDCl_3$) δ −1.80, −1.46, 13.7, 20.2, 31.7, 35.4, 37.3, 39.3, 50.9, 173.1, 175.6; IR ($CDCl_3$) 3450, 1707, 1656, 1505 cm^{-1}; EIMS *m*/*z* 331 (M^+, 13), 258 (M^+ − $SiMe_3$, 41), 73 (Me_3Si^+, 75); HRMS *m*/*z* calcd for $C_{15}H_{33}NO_3Si_2$ 331.1999, found 331.2005.

***N*-Benzyl-2,3-bis(trimethylsilyl)-4-methoxy-4-oxobutanamide (8b).** Bisketene **1** (259 mg, 1.14 mmol) was slowly added via syringe to 13 mL of CH_3OH at 0 °C, and after 7 min of stirring, the CH_3OH was evaporated at 25 °C to give ketenyl ester **10a**, which was dissolved in 3 mL of CH_2Cl_2. To the

stirred solution of **10a** was added $PhCH_2NH_2$ (1.12 mg, 1.05 mmol) in 4 mL of CH_2Cl_2 at 25 °C, and after 15 min of stirring, the solvent was evaporated to give crude **8b** (375 mg, 1.025 mmol, 98%), which by ^1H NMR analysis contained *erythro*- and *threo*-**8b** in a 2/1 ratio. Chromatography on silica gel (10% EtOAc/hexane) resulted in significant desilylation of **8b** to form **11a**, and in several experiments the highest purified yields of the isomers of **8b** were obtained using 33% EtOAc in hexane containing 2% Et_3N. *erythro*-**8b** (mp 59 °C, 11%):^1H NMR ($CDCl_3$) δ 0.043 (s, 9, Me_3Si), 0.063 (s, 9, Me_3Si), 2.29 (d, 1, J = 11.3 Hz, $CHSiMe_3$), 2.69 (d, 1, J = 11.7 Hz, $CHSiMe_3$), 3.59 (s, 3, OCH_3), 4.36 and 4.37 (each d, 1, J = 3.3 Hz, $PhCH_2$), 5.52 (bs, 1, NH), 7.3 (m, 5, Ph); ^{13}C NMR ($CDCl_3$) δ −1.75, −1.44, 35.3, 37.2, 44.1, 51.0, 127.6, 128.4, 128.7, 138.1, 173.0, 175.6; IR ($CDCl_3$) 3445, 1708, 1657, 1497 cm^{-1}; EIMS *m/z* 365 (M^+, 8), 350 ($M^+ - CH_3$, 38), 292 (M^+ − TMS, 14), 91 ($C_7H_7^+$, 100), 73 (Me_3Si^+, 54); HRMS *m/z* calcd for $C_{13}H_{31}NO_3Si_2$ 365.1843, found 365.1854. *threo*-**8b** (oil, 12%): ^1H 0.068 (s, 9, Me_3Si), 0.083 (s, 9, Me_3Si), 2.13 (d, 1, J = 5.2 Hz, $CHSiMe_3$), 2.36 (d, 1, J = 5.5 Hz, $CHSiMe_3$), 3.64 (s, 3, OCH_3), 4.22 (dd, 1, J = 14.7, 4.7 Hz, PhCH), 4.59 (dd, 1, J = 14.3, 6.3 Hz, PhCH), 7.32 (m, 5, Ph), 8.51 (bs, 1, NH); ^{13}C NMR ($CDCl_3$) δ −1.55, −1.47, 35.5, 38.2, 43.9, 51.7, 127.1, 128.2, 128.4, 138.8, 173.3, 178.2; IR ($CDCl_3$) 2957, 1699, 1633 cm^{-1}; EIMS *m/z* 365 (M^+, 6), 91 ($C_7H_7^+$, 100), 73 (Me_3Si^+, 60); HRMS *m/z* calcd for $C_{18}H_{31}NO_3Si_2$ 365.1843, found 365.1845.

***N*-Benzyl-2-trimethylsilyl-4-methoxy-4-oxobutanamide 11a** (white solid, mp 68−69 °C, 69 mg, 21%): ^1H NMR ($CDCl_3$) δ 0.068 (s, 9, Me_3Si), 2.18 (dd, 1, J = 11.5, 3.0 Hz, C*H*CO_2CH_3), 2.34 (dd, 1, J = 17.3, 3.0 Hz, C*H*CO_2CH_3), 2.99 (dd, 1, J = 17.3, 11.6 Hz, C*H*CONH), 3.64 (s, 3, OCH_3), 4.43 (d, 2, J = 5.7 Hz, $PhCH_2$), 5.70 (bs, 1, NH), 7.3 (m, 5, Ph); ^{13}C NMR ($CDCl_3$) −2.82, 31.2 (t, J_{CH} = 132.6 Hz), 34.5 (d, J_{CH} = 125.2 Hz), 43.6, 51.7, 127.2, 127.8, 128.5, 138.6, 173.5, 174.0; IR ($CDCl_3$) 2931, 1731, 1660, 1503 cm^{-1}; EIMS *m/z* 293 (M^+, 26), 91 ($C_7H_7^+$, 100), 73 (Me_3Si^+, 58); HRMS *m/z* calcd for $C_{15}H_{23}NO_3Si$ 293.1447, found 293.1453.

***N*-Benzyl-2,3-bis(trimethylsilyl)-4-benzyloxy-4-oxobutanamide (8c).** Benzyl alcohol (60.6 mg, 0.561 mmol) and 1 mL of Et_3N in 2 mL of pentane were added to bisketene **1** (138 mg, 0.611 mmol) in 3 mL of pentane, and the solution was stirred for 20 min at 25 °C. The solvent was evaporated, and the spectral properties of the intermediate ketenyl ester **benzyl 2,3-(bistrimethylsilyl)-4-oxobut-3-enoate (10b)** were recorded: ^1H NMR ($CDCl_3$) δ 0.093 (s, 9, Me_3Si), 0.131 (s, 9, Me_3Si), 2.01 (s, 1, $CHSiMe_3$), 5.14 (s, 2, $PhCH_2$), 7.35 (m, 5, Ph); ^{13}C NMR $CDCl_3$) δ −2.35, −1.03, 30.0, 46.0, 66.7, 128.1, 128.4, 128.5, 135.9, 174.8, 180.8; IR ($CDCl_3$) 2959, 2085, 1716 cm^{-1}. Then 2 mL of CH_2Cl_2 and $PhCH_2NH_2$ (66 mg, 0.617 mmol) in 2 mL of CH_2Cl_2 were added, and the solution was stirred for 15 min and concentrated at reduced pressure. Analysis by ^1H NMR revealed the presence of *erythro*- and *threo*-**8c** in a 5/1 ratio, together with traces of **11b**. Chromatography (3% Et_3N, 33% CH_2Cl_2/hexane) gave pure *erythro*-**8c** and **11b**, but only some of the spectral properties of *threo*-**8c** were obtained from a mixture containing the *erythro* isomer. *erythro*-**8c**:^1H NMR ($CDCl_3$) δ 0.033 (s, 9, Me_3Si), 0.056 (s, 9, Me_3Si), 2.30 and 2.73 (each d, 1, J = 11.5 Hz, $CHSiMe_3$), 4.36 and 4.37 (each d, 1, J = 3.4 Hz, CH_2N), 4.94 and 5.10 (each d, 1, J = 12.3 Hz, CH_2O), 5.50 (bs, 1, NH), 7.4 (m, 10, Ph); ^{13}C NMR ($CDCl_3$) δ −1.66, −1.35, 35.5, 37.3, 44.1, 66.2, 127.6, 128.2, 128.4, 128.5, 128.7, 135.7, 138.1, 173.0, 174.9; IR ($CDCl_3$) 1705, 1656, 1498 cm^{-1}; EIMS *m/z* 441 (M^+, 9), 350 ($M^+ - C_7H_7$, 47), 91 ($C_7H_7^+$, 100), 73 (Me_3Si^+, 42); HRMS *m/z* calcd for $C_{24}H_{35}NO_3Si_2$ 441.2156, found 441.2152. *threo*-**8c**: ^1H NMR ($CDCl_3$) δ 0.043 (s, 9, Me_3Si), 0.064 (s, 9, Me_3Si), 2.12 and 2.39 (each d, 1, J = 5.2 Hz, $CHSiMe_3$).

***N*-Benzyl-2-trimethylsilyl-4-benzyloxy-4-oxobutanamide (11b):** ^1H NMR ($CDCl_3$) δ 0.072 (s, 9, Me_3Si), 2.18 (dd, 1, J = 11.7, 3.0 Hz, $CHCO_2$), 2.40 (dd, 1, J = 17.6, 3.0 Hz, CHCO), 3.07 (dd, 1, J = 17.6, 11.7 Hz, CHCON), 4.42 (dq, 2, J = 15.4, 5.5 Hz, CH_2N), 5.07 and 5.13 (each d, 1, J = 12.4 Hz, $PhCH_2O$), 5.57 (bs, 1, NH), 7.3 (m, 10, Ph); ^{13}C NMR ($CDCl_3$) δ −2.72, 31.9, 35.7, 43.8, 66.6, 127.4, 128.0, 128.21, 128.24, 128.5, 128.6, 135.8, 138.6, 173.3, 178.4; IR ($CDCl_3$) 3446, 1730, 1655 cm^{-1}; EIMS *m/z* 369 (M^+, 12), 91 ($C_7H_7^+$, 100) 73 (Me_3Si^+, 34); HRMS *m/z* calcd for $C_{21}H_{27}NO_3Si$ 369.1760, found 369.1767.

***N,N′*-Bis[1′,4′-dioxo-2′,3′-bis(trimethylsilyl)-1′-but-3′-enyl]-1,4-bis(aminomethyl)benzene (13).** To a stirred solution of 1,4-bis(aminomethyl)benzene (**12**) (61 mg, 0.45 mmol) in 3 mL of CH_2Cl_2 at 25 °C was added in one portion bisketene **1** (187 mg, 0.825 mmol) in 3 mL of CH_2Cl_2. After 10 min, the solvent was evaporated, giving a white solid identified by ^1H NMR as **13** containing 8% succinamides with ^1H NMR signals at δ 2.03 and 2.33. **13**: ^1H NMR ($CDCl_3$) δ 0.122 (s, 18, Me_3Si), 0.138 (s, 18, Me_3Si), 1.91 (s, 2, CHSi), 4.39 (d, 4, $PhCH_2$, J = 5.6 Hz), 6.15 (s, 2, NH, J = 5.7 Hz), 7.22 (s, 4, Ar); ^{13}C NMR ($CDCl_3$) δ −2.0, −1.0, 10.7, 32.1, 43.5, 128.2, 137.8, 173.2, 179.6; IR ($CDCl_3$) 3444, 2085, 1649, 1503 cm^{-1}; EIMS *m/z* 588 (M^+, 24), 73 (Me_3Si^+, 100); HRMS *m/z* calcd for $C_{28}H_{48}N_2O_4Si_4$ 588.2691, found 588.2710.

Reaction of Bisketene 1 with 1.2 Equiv of 1,4-Bis(aminomethyl)benzene. To a stirred solution of **12** (128 mg, 0.940 mmol) in 4 mL of CH_2Cl_2 at −78 °C was added in one portion bisketene **1** (184 mg, 0.814 mmol) in 2 mL of CH_2Cl_2. After 10 min, the solution was allowed to warm to 25 °C over 20 min and was evaporated, giving a white solid which by ^1H NMR was consistent with the formation of **14** without the presence of other products. **14**: ^1H NMR (CD_3OD) δ −0.01 (s, Me_3Si), 0.04 (s, Me_3Si), 2.15 (s, rel area 1, CHSi), 2.45 (s, rel area 4, CHSi), 3.8 (s, rel area 1, CH_2NH_2), 4.25 (m, rel area 8, CH_2NHCO), 7.3 (m, rel area 9, Ar).

Reaction of 1,6-Diaminohexane with Bisketene 1. A solution of bisketene **1** (0.5 mmol) in CH_2Cl_2 at −78 °C was added to 1,6-diaminohexane (55.8 mg, 0.480 mmol) in 3 mL of CH_2Cl_2 cooled to −78 °C, and a pink color developed which persisted. The solution was stirred 30 min at −78 °C and warmed to room temperature as the pink color disappeared and a solid formed. The ^1H NMR spectrum of the soluble portion of the solid was consistent with structure **15**: ^1H NMR ($CDCl_3$) δ 0.07, 0.11 (each s, 9, Me_3Si), 1.35 (b, CH_2CH_2CH_2-NH), 1.5 (b, CH_2CH_2NH), 2.35 (b, CHTMS), 2.7 (b, NH_2), 3.15 (b, CH_2NH), 5.9 and 7.8 (b, NH); IR ($CDCl_3$) 1650, 1499 cm^{-1}.

Kinetics. Kinetic measurements were carried out by either conventional UV spectroscopy or by stopped flow techniques as reported previously.[2j] The program SigmaPlot was used to fit the kinetics, using a statistical error weighted fitting, which was shown before[2j] to give the best fit for ketene aminations.

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Supporting Information Available: Kinetic data and NMR spectra. This material is available free of charge via the Internet at http://pubs.acs.org.

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