Amination of Bis(trimethylsilyl)-1,2-bisketene with Secondary Amines: Formation of Aminodihydrofuranones

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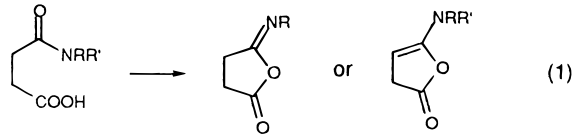
Received April 4, 2000

The bisketene $(Me_3SiC{=}C{=}O)_2$ (**3**) reacts rapidly with 1 equiv of secondary amines to form aminodihydrofuranones **11** as the only observable products. This is in contrast to previous studies (*J. Org. Chem.* **1999**, *64*, 4690) of the reactions of **3** with primary amines in which **3** with 1 equiv of amine gives ketenyl amides **4**, which slowly cyclize to succinimides **7**. The kinetics of the reaction of **3** with morpholine obeyed a rate law with the term [morpholine]^2, consistent with rate-limiting formation of the enol amide **14** with catalysis by a second amine molecule. The subsequent formation of **11** is attributed to hindrance of ketonization of intermediate enol amides **14**. The furanones **11** react with Me_3SiOTf to form silyloxyfurans **16**, and these react with diethyl diazodicarboxylate, forming maleamide derivatives **17**.

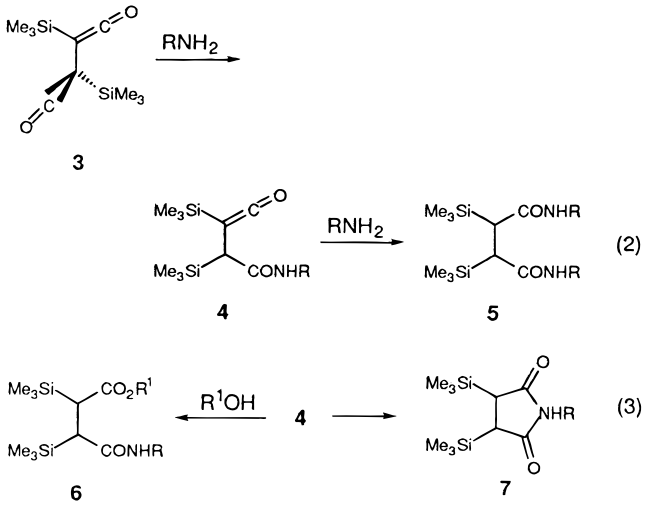
The dehydration of the monoamides of dicarboxylic acids (amic acids **1**) is a process which has been known for over a century to give either imides or cyclic isoimides (**2**, eq 1).[1] These latter compounds are versatile substances that react with both nucleophiles and electrophiles, and the isoimide of phthalic acid has been proposed as a more transient alternative to phthalimides in the protection of amines.[1e]



1 **2a** (R' = H) **2b** (1)

The reactions of ketenes with amines have been of recent interest,[2] and for 1,2-bisketene **3** (which has been demonstrated to have a twisted conformation as shown) with amines it was found[2f] that the reaction with 1 equiv of a primary amine gave complete conversion to isolable ketenyl amide **4**, which reacted with a second equivalent of amine to give bisamide **5** (eq 2), while reaction of **4** with alcohols gave mixed ester amides **6** (eq 3).[2] Upon standing, the ketenyl amides **4** cyclized to succinamides **7**, and no evidence for isoimides analogous to **2** was observed.[2f]

The kinetics of the reaction of **3** with *n*-$BuNH_2$ and $CF_3CH_2NH_2$,[2f] as well as the reactions of $PhSiMe_2CH{=}C{=}O$ with amines,[2e] were fit by the rate law of eq 4, derived from the mechanism of eqs 5 and 6.[2e,f] The formation of the enol amide was in accord with theoretical calculations[2a,b] and direct observation by time-resolved IR.[2d]



$$k_{obs} = k_a[\text{amine}]^2 + k_b[\text{amine}]^3 \quad (4)$$

$$\text{ketene} + 2\ \text{amine} \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} \text{enol amide} \xrightarrow{k_2} \text{product} \quad (5)$$

$$\text{enol amide} + \text{amine} \xrightarrow{k_3} \text{product} \quad (6)$$

However, for the reaction of **4** (R = CF_3CH_2) with $CF_3CH_2NH_2$,[2f] and for the reaction of *t*-Bu(*i*-Pr)C=C=O with *n*-$BuNH_2$,[2e] the kinetics were fit better by eq 7, derived from the mechanism of eq 8.

$$k_{obs} = k_d[\text{amine}]^2/(k_d[\text{amine}] + 1) \quad (7)$$

$$\text{ketene} + \text{amine} \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} \text{complex} \xrightarrow[\text{amine}]{k_2} \text{product} \quad (8)$$

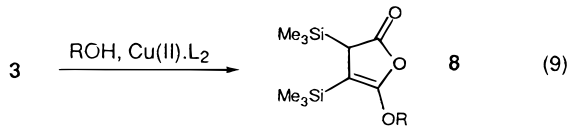
Cyclization has, however, been reported for reaction of bisketene **3** with alcohols catalyzed by chelated Cu(II)

(1) (a) Roderick, W. R.; Bhatia, P. L. *J. Org. Chem.* **1963**, *28*, 2018−2024. (b) Boyd, G. V.; Monteil, R. L. *J. Chem. Soc., Perkin Trans. 1* **1978**, 1338−1350. (c) Boyd, G. V.; Monteil, R. L.; Lindley, P. F.; Mahmoud, M. M. *J. Chem. Soc., Perkin Trans. 1* **1978**, 1351−1360. (d) Baydar, A. E.; Boyd, G. V. *J. Chem. Soc., Perkin Trans. 1* **1978**, 1360−1366. (e) Kukolja, S.; Lammert, S. R. *J. Am. Chem. Soc.* **1975**, *97*, 5582−5583.

(2) (a) Sung, K.; Tidwell, T. T. *J. Am. Chem. Soc.* **1998**, *120*, 3043−3048. (b) Raspoet, G.; Nguyen, M. T.; Kelly, S.; Hegarty, A. F. *J. Org. Chem.* **1998**, *63*, 9669−9677. (c) Andraos, J.; Kresge, A. J. *J. Am. Chem. Soc.* **1992**, *114*, 5643−5646. (d) Wagner, B. D.; Arnold, B. R.; Brown, G. W.; Lusztyk, J. *J. Am. Chem. Soc.* **1998**, *120*, 1827−1834. (e) Allen, A. D.; Tidwell, T. T. *J. Org. Chem.* **1999**, *64*, 266−271. (f) Allen, A. D.; Moore, P. A.; Missiha, A. Tidwell, T. T. *J. Org. Chem.* **1999**, *64*, 4690−4696. (g) Huang, W.-w.; Moore, P. A.; Rafai Far, A.; Tidwell, T. T. *J. Org. Chem.* **2000**, *65*, 3877−3879.

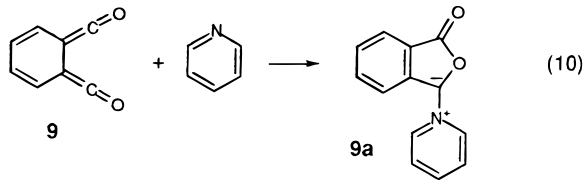
10.1021/jo000508k CCC: $19.00
Published on Web 08/15/2000

catalysts, giving efficient conversion to 5-alkoxydihydrofuranones **8** (eq 9).[3a,b] Some precedent for cyclization in



(9)

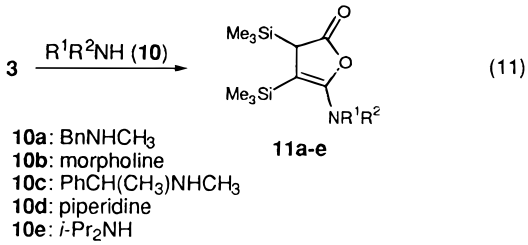
a bisketene reaction with an amine was obtained from the reaction of ketene **9** with pyridine (eq 10).[3c] The UV and IR bands due to **9** disappeared, and a new UV absorption at 590 nm appeared which was ascribed to the ylide **9a**,[3c] but no IR absorption assigned to **9a** was observed, so this assignment is not secure. We now report the unexpected finding that reaction of **3** with secondary amines proceeds with efficient cyclization to isoimides.



(10)

Results and Discussion

Reaction of **3** with 1 equiv of secondary amines **10a**−**d** at room temperature for 30 min gave the 5-amino-3,4-bis(trimethylsilyl)dihydrofuran-2-ones **11** in 97−99% yields (eq 11). These products were clearly identified from their



(11)

spectral properties, but unlike the alkoxyfuranones **8**[3a,b] they were rather sensitive and decomposed upon standing. Reaction of **3** with 1 equiv of *i*-Pr_2NH (**10e**) was much slower than for the other amines, and the product **11e** was quite unstable and could only be observed in solution.

The reaction of **3** with 2 equiv of Et_2NH led to the partially desilylated succinamide **12** (eq 12). Such α-silylated carbonyl compounds are sensitive to desilylation. This evidently arose from attack of the amine on the carbonyl of the intermediate lactone **11**, as the reaction of the furanone **11a** with benzylamine led to ring opening with formation of a partially desilyated succinamide, characterized as **13** after desilylation (eq 13).

Kinetic studies of the reaction of **3** with morpholine in CH_3CN at 25 °C were carried out and showed a higher than first-order dependence of the rate constants on [morpholine]. Similar behavior was observed previously in the reactions of primary amines with monoketenes[2e] and with **3**,[2f] and a number of different rate laws were tested to ascertain the best fit of the data.[2e,f] As noted above, the particular rate law followed, such as those shown in eqs 4 and 7, depended on the particular ketene

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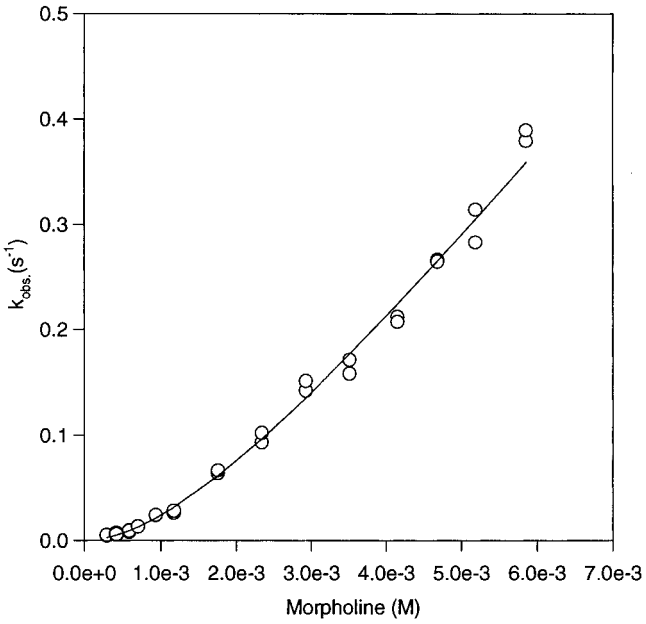
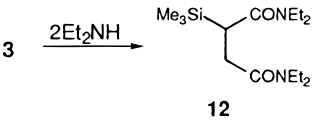


Figure 1. Rate constants for reaction of **3** versus [morpholine] and fit by eq 7.



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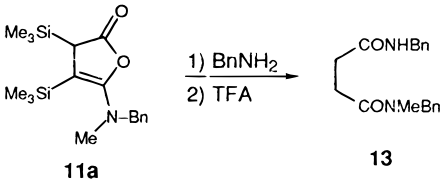


(13)

studied, and these rate laws could be derived from reasonable mechanisms (eqs 5, 8) that are consistent with theoretical studies.[2a,b]

For the reaction of **3** with morpholine, the most satisfactory fit (Figure 1) of the data was found with the rate law of eq 7, with values of $k_c = (3.21 \pm 0.23) \times 10^4$ and $k_d = (3.53 \pm 0.44) \times 10^2$ M^{-1} s^{-1}. An almost superimposable fit (Figure 2) was obtained with the rate law of eq 14, which is derived for the mechanism of eq 8 with the additional step of eq 15 with values $k_e = (2.35 \pm 0.40) \times 10^4$, $k_f = (5.50 \pm 2.53)$, and $k_g = (2.22 \pm 0.63) \times 10^2$ M^{-1} s^{-1}. The rate law of eq 7 is deemed more satisfactory because of its greater simplicity and smaller standard errors, but the latter cannot be completely ruled out. The full rate data are given in the Supporting Information.

$$k_{obs} = (k_e[\text{amine}]^2 + k_f[\text{amine}])/(k_g[\text{amine}] + 1) \quad (14)$$

$$\text{complex} \xrightarrow{k_3} \text{product} \quad (15)$$

Because of the change in rate law of **3** for morpholine compared to that of primary amines,[2f] the ratio $k_{n-BuNH_2}/k_{morpholine}$ for k_{obs} is 1/50 at [amine] = 4×10^{-3} M whereas for $PhMe_2SiCH{=}C{=}O$ which reacts with both amines with the rate law of eq 4 the ratio $k_{n-BuNH_2}/k_{morpholine}$ for k_{obs} is 7.4 at [amine] = 4.0×10^{-3} M.[2e] The explanation for the absence of observable ketenyl amides, and for the

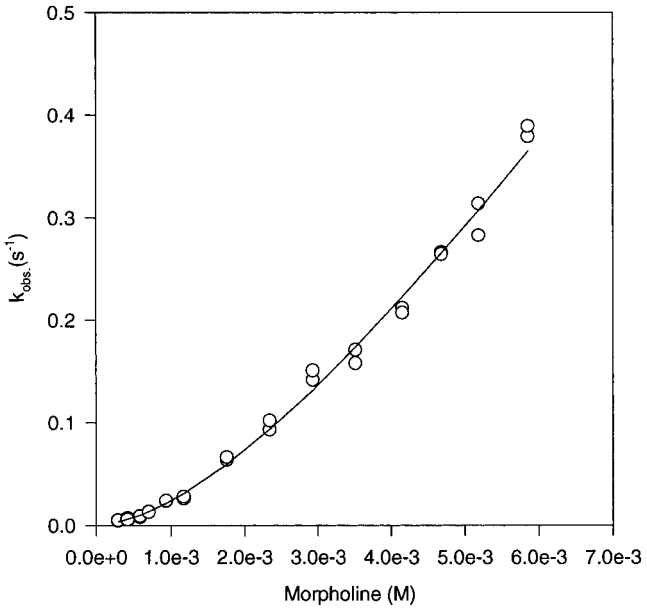
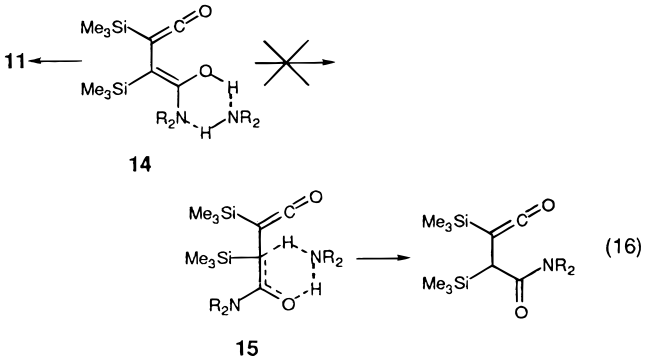


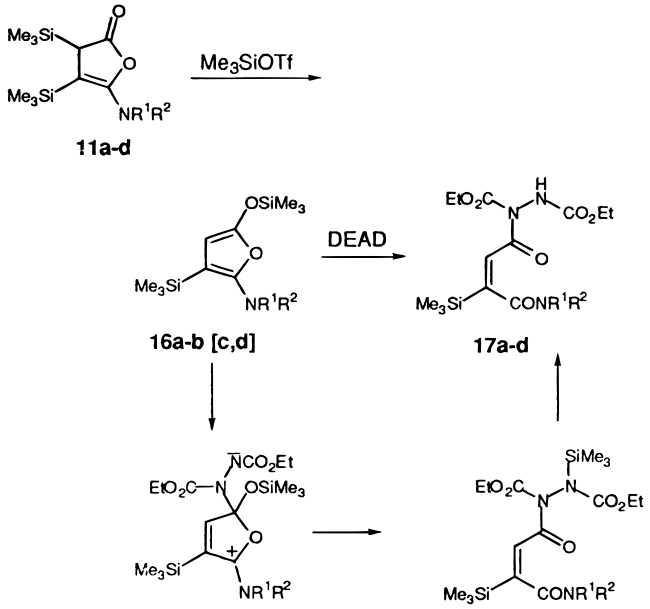
Figure 2. Rate constants for reaction of **3** versus [morpholine] and fit by eq 14.

occurrence of cyclization to isoimides (eq 11), may be found from the mechanistic details of the amination of ketenes and bisketenes. The kinetic data lead to the preferred mechanism of eq 8, in which a second molecule of amine is involved in the rate-limiting step. For the reaction of **3** with morpholine, formation of the amine-complexed enol amide **14** is thus indicated to be rate limiting, and this is then converted to the isoimide **11** (eq 16). Thus, the mechanism of eq 8 involves formation



of an initial hydrogen-bonded complex which reacts with a second amine, forming **14** in the rate-limiting step, and this forms **11** (eq 16). Formation of a ketenyl amide would also proceed through the formation of enol amide **14**, but this would require catalysis by another amine molecule to undergo ketonization to the amide. The involvement of enol amides in ketene amination is supported by both theoretical studies[2a,b] and direct observation,[2d] and further conversion to the amide is amine catalyzed.[2d] In the reaction of **3** with a secondary amine, this would involve the conversion of complexed enol amide **14** to transition structure **15**, which would involve significant steric crowding (eq 16). Evidently cyclization of enol amide **14** to isoimide **11** becomes competitive when the ketonization is slow. An alternative pathway for the formation of **11** would be rapid conversion of an unobserved ketenyl amide analogous to **4** from the secondary amine, but we see no apparent reason that cyclization to the isoimide would be enhanced in a ketenyl amide formed from a secondary amine. Another alternative involving direct cyclization of **3** to **11** upon amination involving two amine molecules would appear to be disfavored by more sterically demanding secondary amines.

Scheme 1



The recent application[4] of 2-silyloxyfurans in vinylogous aldol and Mannich-type reactions suggested that the furanones **11** could be converted to analogous derivatives. The conversion of α-silylated carbonyl compounds to the corresponding silyl enol ethers may be effected by the addition of a catalytic amount of Me_3SiOTf,[5] and this procedure gave rapid and quantitative conversion of **11a**,**b** to the furans **16a**,**b**, as monitored by ^1H NMR (Scheme 1). These products were too sensitive for isolation but upon reaction with diethyl diazodicarboxylate (DEAD) gave conversion to the ring-opened products **17a**,**b**. The one-pot conversions of **11c**,**d** to **17c**,**d** were also carried out. The structure of product **17a** was confirmed by an X-ray determination. The reactions may be envisaged as involving electrophilic attack at the Me_3-SiO-substituted position of the furan followed by ring opening (Scheme 1). Initial formation of a [4 + 2] cycloadduct of **16** and DEAD followed by rearrangement was not observed but cannot be excluded.

In summary, the reactions of bisketene **3** with 1 equiv of secondary amines form isoimides **11** (eq 11), in contrast to the reaction of primary amines, which leads to ketenyl amides **4** (eq 2).[2f] A mechanism (eqs 8, 16) consistent with the theoretical,[2a,b] product, and kinetic studies is presented. The conversion of the isoimides **11** to furans **16** and their reaction with diethyl azodicarboxylate is demonstrated.

Experimental Section

Dichloromethane was dried over 4 Å molecular sieves 24 h prior to use. $CDCl_3$ was dried over anhydrous potassium

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carbonate overnight. Trimethylsilyl triflate was freshly distilled from calcium hydride. Morpholine, piperidine, and diisopropylamine were distilled from calcium hydride. Bisketene **3** was made by injection of a solution of 3,4-bis(trimethylsilyl)cyclobutenedione in pentane (approximately 300 μL per 200 mg) through a gas chromatograph with an injector temperature of 200 °C and an OV-17 column heated at 120 °C. All other reagents were used directly from commercially available sources. All the reactions were performed under a positive pressure of argon.

Reaction of Bisketene 3 with Secondary Amines. To a solution of bisketene (100 mg, 0.44 mmol) in 2 mL of CH_2Cl_2 or $CDCl_3$ at 25 °C was added 0.44 mmol of the amine. After 30 min, the solvent was removed in vacuo to give the product as an oil. The products **11a**−**d** were obtained in 97−99% crude yields but are rather sensitive, and except for **11c** they were not purified and were characterized as described. The product **11e** formed slowly and was quite unstable, so the same reaction as above was performed in $CDCl_3$ for 6 h and the product was not isolated but was analyzed by NMR directly.

11a: ^{1}H NMR ($CDCl_3$) δ 0.16 (s, 9), 0.164 (s, 9), 2.67 (s, 3), 3.04 (s, 1), 4.06 (d, 1, J = 14.3 Hz), 4.27 (d, 1, J = 14.3 Hz), 7.24−7.36 (m, 5); ^{13}C NMR ($CDCl_3$) δ −2.6, 0.5, 39.1, 44.9, 57.6, 91.3, 127.4, 128.4, 128.4, 137.2, 160.4, 178.6; IR (neat) 1762, 1618 cm^{-1}; EIMS m/z 347 (M^+, 70), 256 (100), 73 (89); HRMS m/z calcd for $C_{18}H_{29}NO_2Si_2$ 347.1737, found 347.1751.

11b: ^{1}H NMR ($CDCl_3$) δ 0.15 (s, 9), 0.17 (s, 9), 2.98 (m, 5), 3.62 (m, 4). ^{13}C NMR ($CDCl_3$) δ −2.6, 0.0, 44.7, 50.6, 66.5, 99.7, 159.8, 178.6; EIMS m/z 313 (M^+, 61), 73 (100); HRMS m/z calcd for $C_{14}H_{27}NO_3Si_2$ 313.1530, found 313.1529; IR ($CDCl_3$) 1748, 1638 (broad and strong) cm^{-1}.

11c: **Reaction of Bisketene 3 with (*R*)-(+)-*N*,α-Dimethylbenzylamine (10c)**. To bisketene **3** (0.133 g, 0.59 mmol) in 10 mL of CH_2Cl_2 stirred at −78 °C was added amine **10c** (0.080 g, 0.58 mmol) in 2 mL of CH_2Cl_2. The solution was stirred for 1 h at −78 °C, and then the solvent was evaporated, giving crude **11c** as an oil (99%) which by ^{1}H NMR consisted of two diastereomers in a 3/1 ratio. The major isomer was obtained by recrystallation of the crude product from ether at −20 °C as a white crystalline solid: ^{1}H NMR ($CDCl_3$) δ 0.12 (s, 9), 0.14 (s, 9), 1.36 (d, 3, J = 6.8 Hz, CH_3), 2.42 (s, 3), 2.98 (s, 1), 4.22 (q, 1, J = 6.8 Hz), 7.20−7.34 (m, 5); ^{13}C NMR ($CDCl_3$) δ −1.9, 0.4, 20.4, 38.3, 44.7, 60.3, 98.1, 127.2, 128.4, 142.8, 159.8, 179.2 (one phenyl carbon not seen); IR ($CDCl_3$) 1746, 1637, 1607 cm^{-1}; EIMS m/z 361 (M^+, 14), 73 (100); HRMS m/z calcd for $C_{19}H_{31}NO_2Si_2$ 361.1893, found 361.1876.

11d: ^{1}H NMR ($CDCl_3$) δ 0.14 (s, 9), 0.15 (s, 9), 1.55 (m, 6), 2.93 (m, 5); ^{13}C NMR ($CDCl_3$) δ −2.6, −0.1, 23.5, 25.6, 44.6, 51.5, 97.2, 161.3, 179.1; EIMS m/z 311 (M^+, 100), 73 (83); HRMS m/z calcd for $C_{15}H_{29}NO_2Si_2$ 311.1737, found 311.1730; IR ($CDCl_3$) 1750, 1637 cm^{-1}.

11e: ^{1}H NMR ($CDCl_3$) δ 0.18 (s, 9), 0.20 (s, 9), 1.10 [m made of 1.10 (d, J = 7.3 Hz, 6) and 1.11 (d, J = 6.6 Hz, 6)], 2.98 (s, 1), 3.34 (septet, J = 6.6 Hz, 2); ^{13}C NMR ($CDCl_3$) δ −2.4, −0.2, 21.4, 21.5, 33.2, 51.8, 84.9, 173.0 (one carbon missing); IR ($CDCl_3$) 1782, 1634 cm^{-1}.

Reaction of 11a with Benzylamine. To a solution of **11a** (151 mg, 0.43 mmol) in 2 mL of CH_2Cl_2 was added 48 μL (47 mg, 0.44 mmol) of benzylamine. The mixture was stirred at room temperature for 1 h. The solvents were removed in vacuo, the residue was taken up in 2 mL of methanol, and 200 μL of TFA were added. After 30 min, the volatiles were removed in vacuo, and the residue was purified by chromatography (2/8 methanol/CH_2Cl_2), to give **13** (103 mg, 0.33 mmol, 76%): ^{1}H NMR 2.60 (m, 2), 2.73 (broad t, J = 6.2 Hz, 2), 2.89 (s, 51% of 3), 2.91 (s, 49% of 3), 4.41 (m, 2), 4.53 (d, J = 6.2 Hz, 2), 6.73 (broad s, 42% of 1), 6.81 (broad s, 58% of 1), 7.24 (m, 10); ^{13}C NMR δ 28.7, 29.1, 31.4, 34.0, 34.7, 43.5, 51.0, 53.2, 126.4, 127.2, 127.4, 127.60, 127.61, 127.64, 127.8, 128.5, 128.6, 128.9, 137.0, 138.4, 172.6 (broad); EIMS m/z 310 (M^+, 21), 91 (100); HRMS m/z calcd for $C_{19}H_{22}N_2O_2$ 310.1681, found 310.1670; IR ($CDCl_3$) 1631 cm^{-1}.

Preparation of Furans. To a solution of bisketene **3** (100 mg, 0.44 mmol) in 2 mL of CH_2Cl_2 or $CDCl_3$ was added 0.44 mmol of a secondary amine. After stirring for 30 min, 10 μL (0.05 mmol) of trimethylsilyl triflate was added, giving a purple solution. The reactions with $BnNHCH_3$ and morpholine were checked by ^{1}H NMR and were complete after 15 min. The furans thus prepared were then used directly in the next step.

16a: ^{1}H NMR δ 0.18 (s, 9), 0.32 (s, 9), 2.60 (s, 3), 4.04 (s, 2), 4.87 (s, 1), 7.32 (m, 5); ^{13}C NMR δ −0.6, −0.2, 41.8, 60.7, 86.2, 107.9, 127.0, 129.2, 128.2, 128.4, 128.5, 128.8, 138.5, 152.2, 153.7.

16b: ^{1}H NMR δ 0.17 (s, 9), 0.28 (s, 9), 2.94 (t, J = 4.7 Hz, 4), 3.73 (t, J = 4.6 Hz, 4), 4.84 (s, 1).

Reaction of Furans with DEAD. To the furan solutions prepared from 100 mg of bisketene **3** was added dropwise 69 μL (0.44 mmol) of DEAD. The resulting light brown solutions were stirred for 15 min, 2 mL of methanol was added, and the mixtures were stirred for 30 min. The solvents were then removed in vacuo, and the resulting products were purified by flash chromatography on silica gel, using the indicated eluent and giving the yields shown. In the ^{1}H NMR spectra the vinylic proton could not be detected.

17a: eluent EtOAc (75%); mp 106−108 °C; ^{1}H NMR δ 0.23 (s, 9), 1.27 (m, 3), 1.31 (t, J = 7.1 Hz, 3), 2.72 (s, 3), 4.23 (m, 6), 7.01 (broad s, 1), 7.27 (m, 5); ^{13}C NMR δ −1.9, 14.1, 14.3, 34.6, 49.7, 53.9, 62.3, 64.0, 127.2, 127.4, 128.4, 128.5, 137.0, 153.0, 155.4, 157.6, 164.2, 171.5; EIMS m/z 450 (MH^+, <1), 91 (100), 73 (29); HRMS m/z calcd for $C_{21}H_{32}N_3O_6Si$ (MH^+) 450.2060, found 450.2067; IR ($CDCl_3$) 1748 (broad but strong) 1616 cm^{-1}.

17b: eluent 1/4 hexanes/EtOAc (70%); ^{1}H NMR ($CDCl_3$) δ 0.23 (s, 9), 1.28 (m, 3), 1.32 (t, J = 7.1 Hz, 3), 3.64 (broad m, 8), 4.20 (q, J = 7.1 Hz, 2), 4.30 (q, J = 7.1 Hz, 2), 7.05 (broad s, 1); ^{13}C NMR ($CDCl_3$) δ −1.9, 14.1, 14.4, 41.4, 46.4, 62.5, 64.1, 66.3, 66.5, 128.4, 153.0, 155.4, 157.8, 164.1, 170.3; EIMS m/z 415 (M^+, <1%), 240 (100), 73 (44); HRMS m/z calcd for $C_{17}H_{30}N_3O_7Si$ (MH^+) 416.1853, found 416.1837; IR ($CDCl_3$) 1752 (broad but strong), 1616 cm^{-1}.

17c: eluent 1/1 hexanes/EtOAc (51%); ^{1}H NMR ($CDCl_3$) δ 0.24 (s, 9), 1.29 (m, 3), 1.31 (t, J = 7.1 Hz, 3), 1.51 (d, J = 7.0 Hz, 3), 2.47 (s, 3), 4.19 (m, 3), 4.29 (q, J = 7.1 Hz, 2), 7.00 (broad s, 1), 7.25 (m, 5); ^{13}C NMR ($CDCl_3$) δ −1.8, 14.1, 14.2, 29.5, 49.7, 62.4, 63.9, 122.8, 127.1, 127.7, 128.2, 150.4, 153.1, 155.5, 164.1, 171.2; EIMS m/z 464 (MH^+, 57), 134 (100), 73 (30); HRMS m/z calcd for $C_{22}H_{34}N_3O_6Si$ (MH^+) 464.2217, found 464.2207; IR ($CDCl_3$) 1744 (broad but strong), 1616 cm^{-1}.

17d: eluent 1/1 hexanes/EtOAc (51%); ^{1}H NMR ($CDCl_3$) δ 0.22 (s, 9), 1.27 (m, 3), 1.32 (t, J = 7.2 Hz, 3), 1.59 (broad m, 6), 3.23 (broad t, J = 4.8 Hz, 4), 4.19 (q, J = 7.2 Hz, 2), 4.30 (q, J = 7.2 Hz, 2), 6.96 (broad s, 1); ^{13}C NMR ($CDCl_3$) δ −1.8, 14.1, 14.3, 24.5, 25.2, 25.6, 41.8. 46.9, 62.4, 64.0, 127.6, 153.0, 155.4, 164.3, 169.9, 179.3; EIMS m/z 414 (MH^+, 37), 238 (100), 73 (15); HRMS m/z calcd for $C_{18}H_{32}N_3O_6Si$ (MH^+) 414.2060, found 414.2044; IR ($CDCl_3$) 1748 (broad but strong), 1616 cm^{-1}.

Kinetic Procedure. Rate constants were obtained by injecting aliquots of freshly prepared solutions of **3** (0.229 or 0.257 M) in CH_3CN into 2 mL solutions of morpholine [(0.293 to 5.85) × 10^{-3} M] in CH_3CN in a UV cell equipped with a magnetic stirrer and observing the decrease in the ketene absorption at 385 nm using a Perkin-Elmer Lambda 12 instrument. Initial concentrations of **3** ranged from 6.41 × 10^{-4} to 0.286 × 10^{-4} M. The program SigmaPlot was used to fit the kinetics, using a statistical error weighting program. A weighting of $1/k_{obs}$ gave the best fit of the data. A variety of other rate laws were tested, as we have done previously.[2e]

Acknowledgment. Financial support by the Natural Sciences and Engineering Research Council of Canada is gratefully acknowledged.

Supporting Information Available: Kinetic data, ^{1}H NMR spectra, and an X-ray crystallographic file on **17a** in CIF format. This material is available free of charge via the Internet at http://pubs.acs.org.

JO000508K