Synthesis of Polysubstituted Cyclopentenones via [4+1] Reactions of TIPS-Vinylketenes

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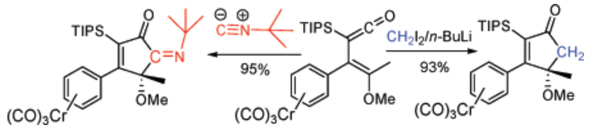


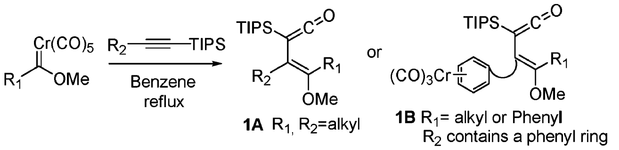
An efficient method for preparing a series of polysubstituted cyclopentenones from TIPS-vinylketenes and Köbrich reagent has been developed in this paper. Additionally, highly substituted cyclopentenones can be prepared via [4+1] reaction of TIPS-vinylketenes with *tert*-butyl isocyanide and there is a remarkable preference for formation of products with an exocyclic (*Z*)-imine moiety.

Cyclopentenones are common structural units in bioactive natural products and useful building blocks.[1] While various approaches such as the Nazarov,[2] Pauson−Khand,[3] [3+2],[4] Rautenstrauch rearrangement,[5] and Intramolecular Hydroacylation reaction[6] have been developed for construction of this important ring system, only a few [4+1] reactions to these five-membered carbocycles have been reported to date.[7]

Silyl vinylketenes have recently been used as versatile "1,4-dipole" equivalents[7a,b,d] and the stabilizing influence of the silyl group suppresses the dimerization process typical of ketenes.[8] With Köbrich reagent as a 1,1-dipole equivalent, we decided to use silyl vinylketene as the activated diene part to carry out research on the [4+1] reaction as people have done before.[7a,d] Since Köbrich reagents are highly unstable and have to be generated from alkyl dihalides by RLi in the presence of substrates at low temperature, the difficult subject is that the ketene group will suffer from direct nucleophilc attack of RLi because of its known electrophilic property.[8b]

Bearing a formally divalent carbon, isocyanides are highly reactive toward cations, anions, and radicals. But most of the reactions reported thus far require a promoter to proceed efficiently. In this paper, we found isocyanide could serve as a 1,1-dipole equivalent to undergo [4+1] reaction[9a] with silyl vinylketenes without any promoter. To date, however, all reported reactions between ketenes and isocyanides only afforded imino lactone-type products[9b] or l-imino-2,4-cyclopentanediones.[9c]

The classical synthetic route to silyl vinylketenes contained two steps, the silylation of α-diazo ketones and the photochemical Wolff rearrangement of α-silyl-α-diazo ketones. Recently, Moser has discovered an efficient method for preparing C4 oxygenated triisopropylsilyl (TIPS) vinylketenes **1A** from the thermal reaction of Fischer carbene complexes with TIPS-substituted acetylenes.[10] It was found that the aromatic ring of R_2 on TIPS-vinylketenes **1B** was usually complexed with $Cr(CO)_3$ even if R_1 was a phenyl group (eq 1). [4+1] reaction of such ketenes with diazoalkanes and sulfur ylides[10b] by Danheiser's protocol[7a] afforded cyclopentenones bearing an oxygenated quaternary center on C4, an important structural moiety found in many bioactive natural products.[11] The $Cr(CO)_3$ moiety in the [4+1] products[10b] could provide a handle for further synthetic manipulations based on the significant ways in which the $Cr(CO)_3$ fragment alters reactivity on the arene ring itself,



(1)

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(1) For reviews, see: (a) Roberts, S. M.; Santoro, M. G., Sickle, E. S. *J. Chem. Soc., Perkin Trans. 1* **2002**, 1735. (b) Proksch, P.; Edrada, R.; Ebel, R.; Bohnenstengel, F. I.; Nugroho, B. W. *Curr. Org. Chem.* **2001**, *5*, 923.

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(9) (a) Rigby's pioneering work revealed that isocynides could undergo [4+1] reaction with vinyl isocyanates to form nitrogen heterocycles. See: Rigby, J. H.; Qabar, M. *J. Am. Chem. Soc.* **1991**, *113*, 8975. (b) Ugi, I.; Rosendahl, K. *Chem. Ber.* **1961**, *94*, 2233. (c) Moore, H. W.; Yu, C.-C. *J. Org. Chem.* **1981**, *46*, 4935.

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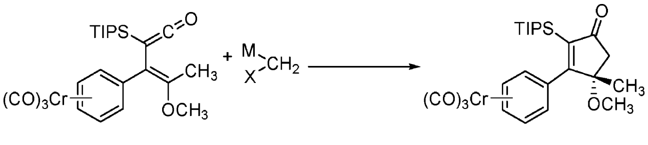
TABLE 1. Reactions of TIPS-Vinylketene 1a with Carbenoid Reagents



1a **2** **3a**

entry	carbenoid reagent	solvent	yield of **3a**[a] [%]
1	CH_2I_2/Zn−Cu	Et_2O	0
2	CH_2I_2/*i*-PrMgCl	THF	0
3	CH_2Cl_2/*n*-BuLi	THF	27
4	CH_2Br_2/*n*-BuLi	THF	60
5	CH_2I_2/*n*-BuLi	THF	62
6	CH_2I_2/*n*-BuLi	DME	20
7	CH_2I_2/*n*-BuLi	Toluene	5
8	CH_2I_2/*n*-BuLi	Hexane	10
9	CH_2I_2/*n*-BuLi	cyclohexane/Et_2O = 1:1	12
10	CH_2I_2/*n*-BuLi	Et_2O	93

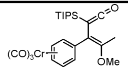
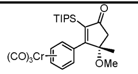
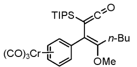
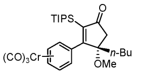
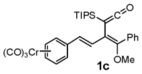
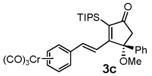
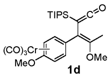
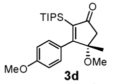
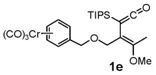
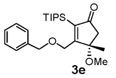
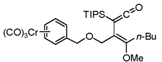
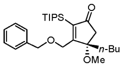
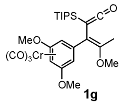
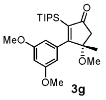
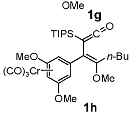
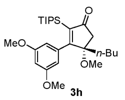
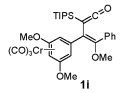
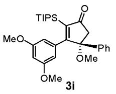
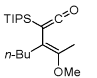
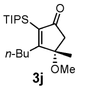
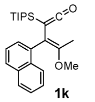
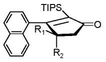
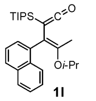
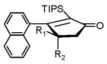
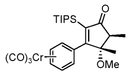
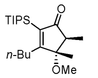
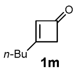
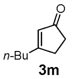
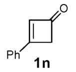
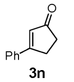
[a] Isolated yield.

as well as on the vicinal functionality.[12] All silyl vinylketenes in this paper were prepared by this protocol (see the Supporting Information).[13]

As shown in Table 1, TIPS-vinylketene **1a** was selected as a model substrate and a variety of reaction conditions were screened. Attempts by the employment of carbenoids prepared from CH_2I_2/Zn−Cu, CH_2I_2/*i*-PrMgCl, and CH_2I_2/Et_2Zn were unsuccessful; in each case no significant reaction occurred and **1a** was recovered. We assumed that these carbenoids were not active to fulfill this transformation.[14a] We were pleased to find that Li/Cl carbenoid generated from CH_2Cl_2 by *n*-BuLi in THF did afford the desired cyclopentenone **3a**, however, in only 27% yield. Switching to the Li/I carbenoid significantly improved the yield. Examination of the effect of solvent revealed that Et_2O produced the desired adduct with a marked improvement in yield. The reaction was easily performed by slow addition of *n*-BuLi to an ether solvent of **1a** and CH_2I_2 at −78 °C and no byproduct formed by addition of *n*-BuLi to the ketene group of **1a** was observed. All attempts to employ carbenoids generated from dibromoalkenes[14b] with *n*-BuLi were unsuccessful.

With optimized reaction conditions in hand, we set out to synthesize polysubstituted cyclopentenones via this [4+1] reaction. The reaction is tolerant of substituents at the C3 position of TIPS-vinylketenes. Specifically, C3 chromium complexed aryl- (entries 1, 2, 4, 7, 8, and 9, Table 2), alkyl- (entries 5, 6, and 10, Table 2), and alken- (entry 3, Table 2) substituted TIPS-vinylketenes participated in the [4+1] reaction. The [4+1] reaction also proceeded smoothly with substrates such as C4 aryl- (entries 3 and 9, Table 2) and alkyl-substituted TIPS-vinylketenes. Methoxy substituents on the C3 chromium complexed phenyl ring have little effect on product yield (entries 4 and 7−9, Table 2). The $Cr(CO)_3$ in annulation products could be removed quantitatively by exposure of the crude product to air with the aid of silica gel (entries 4−6, Table 2).

TABLE 2. Reactions with Köbrich Reagents[a]

Entry	Substrate	Product	Yield [%]
1	 **1a**	 **3a**	93
2	 **1b**	 **3b**	98
3	 **1c**	 **3c**	94
4	 **1d**	 **3d**	72[b]
5	 **1e**	 **3e**	64[b]
6	 **1f**	 **3f**	84[b]
7	 **1g**	 **3g**	85[c]
8	 **1h**	 **3h**	80[c]
9	 **1i**	 **3i**	62[c]
10	 **1j**	 **3j**	55
11	 **1k**	 **3ka** R_1=Me, R_2= OMe **3kb** R_1=OMe, R_2=Me	61 **3ka**/**3kb** = 3/5
12	 **1l**	 **3la** R_1=Me, R_2= O*i*-Pr **3lb** R_1=O*i*-Pr, R_2=Me	40 **3la**/**3lb** = 4/3
13	**1a**	 **3a'**	93[d]
14	**1j**	 **3j'**	67[d]
15	 **1m**	 **3m**	60
16	 **1n**	 **3n**	40

[a] All products in this table are racemic. [b] The removal of chromium fragment could be achieved quantitatively by the exposure of the crude product to air with the aid of silica gel. [c] The chromium fragment was decomposed in the reaction. [d] Köbrich reagent was generated from Br_2CHCH_3 instead of CH_2I_2.

Interestingly, two diastereoisomers **3ka** and **3kb** were isolated in 61% yield with a 3 to 5 ratio in entry 11. Diastereoisomers

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(12) (a) Schmalz, H. G.; Siegel, S.; Bats, J. W. *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 2383. (b) Lin, H.; Yang, L.; Li, C. *Organometallics* **2002**, *21*, 3848. (c) Merlic, C. A.; Miller, M. M.; Hietbrink, B. N.; Houk, K. N. *J. Am. Chem. Soc.* **2001**, *123*, 4904. (d) Lin, C.; Chen, Q.; Cao, L.; Yang, L.; Wu, Y.-D.; Li, C. *J. Org. Chem.* **2006**, *71*, 3328.

(13) In the preparation of **1k**, product with $Cr(CO)_3$ complexed C3 naphthyl ring was not found probably because $Cr(CO)_3$ was easily decomposed in refluxing benzene. In the case of **1*l***, the TIPS-vinylketene with $Cr(CO)_3$ complexed C3 naphthyl ring was found to be very unstable as expected, so **1*l*** was formed by photolysis of crude product.

(14) (a) Nakamura, M.; Hirai, A.; Nakamura, E. *J. Am. Chem. Soc.* **2003**, *125*, 2341. (b) For a review, see: Braun, M. *Angew. Chem., Int. Ed.* **1998**, *37*, 430.

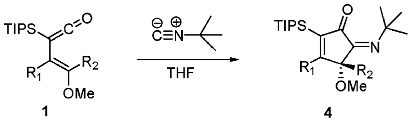
3ka and **3kb** were formed by a rotation-restricted 1-naphthyl group on the C3 of the cyclopentenone ring. In entry 12, the C4 substituent of TIPS-vinylketene **1*l*** was shifted to isopropoxyl, the reverse diastereoselectivity of **1*l*** in the [4+1] reaction was observed, and **3la** and **3lb** were separated in 40% yield with a ratio of 4 to 3.

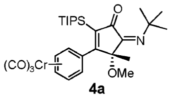
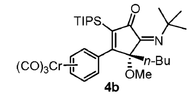
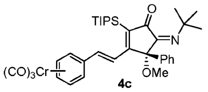
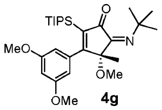
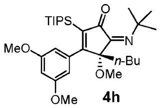
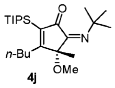
We were also pleased to find that Köbrich reagents generated from 1,1-dibromoethane serve as suitable reagents in [4 + 1] annulations with the silyl vinylketenes (entries 13 and 14, Table 2). Notably, the cyclopentenone products **3a′** and **3j′** contain two contiguous stereogenic centers, and in both cases only a single diastereomer could be observed by ^{1}H NMR spectroscopy of the crude reaction mixtures. NOE experiment of cyclopentenone **3a′** established the cis relationship between the two methyl substituents on the cyclopentenone ring.

In entries 15 and 16, the ring expansion reaction of cyclobutenones **1m** and **1n** with Li/I carbenoid proceeded smoothly to afford **3m** and **3n**, respectively. The mechanism of this reaction may be similar to the reaction of cyclobutanone with diazomethane.[15] Despite a number of reports on one-carbon insertion to cyclobutanones, only a few[16] on cyclobutenone have been reported. Since this one-carbon insertion preferentially takes place between C1 and C4 of cyclobutenones, it could avoid regiochemical difficulties found in the reaction of cyclobutanones with carbene reagents.[15,17]

More recently, aminocyclopentitols have been recognized as important bioactive compounds in their role as glycosidase inhibitors.[18] Several groups[19] have reported that isocyanides could be used in place of CO in the intramolecular Pauson−Khand-type transformation of enynes to iminocyclopentenes or cyclopentenones, but the use of a transition metal promoter was necessary. Successful [4+1] reaction of TIPS-vinylketenes with isocyanide will lead to cyclopentenone products with C5 imine groups, which could serve as precursors for the synthesis of aminocyclopentitols. As indicated in Table 3, reactions of TIPS-vinylketenes (entries 1, 2) with *tert*-butyl isocyanide in THF at room temperature afforded cyclopentenone products with C5 imine groups in excellent yield without any promoter. In entries 3−6, elevated temperature was required to complete cyclizations and desired products could also be separated in good yield. A notable feature of these [4+1] annulations is that exocyclic C5 imine groups in all products are *Z* configuration.

TABLE 3. [4+1] Reactions of TIPS-Vinylketenes with *tert*-Butyl Isocyanide[a]



Entry	Silyl Vinylketene	Product	Yield [%]
1	**1a**	 **4a**	95[b]
2	**1b**	 **4b**	91[b]
3	**1c**	 **4c**	73[c]
4	**1g**	 **4g**	98[c, d]
5	**1h**	 **4h**	76[c, d]
6	**1j**	 **4j**	98[c]

[a] All products in this table are racemic. [b] Stirred at room temperature for 48 h. [c] Refluxed in THF for 4 h. [d] The chromium fragment was decomposed in the reaction.

A mechanistic hypothesis that accounts for the [4+1] reaction of TIPS-vinylketenes with Köbrich reagents or isocyanide is shown in Scheme 1 (**1j** was selected as the model). Because of the allenic bonding in a ketene, the nucleophile is required to approach the π-orbital of the carbonyl group in ketenes in the same plane as that containing the ketene substituent.[8b,20a] Thus Li/Br carbenoid will attack the ketene group from the side of the vinyl substitute of the ketene group of **1j** to avoid steric hindrance with the bulky TIPS group, and the *Z*-bromo enolate **5** is formed stereoselectively. The following S_N1 loss of bromide[20b] from the bromo enolate **5** leads to the oxidopentadienylic cation **6** containing a C1 external methyl group. Obviously, **6** is more stable than its stereoisomer with a C1 internal methyl group that will suffer steric hindrance with the C5 internal methyl.[20c] A similar S_N1 loss of bromide from the bromo enolate is proposed in the mechanism of formation of cyclopropanone from α,α'-dibromoketone with PPN^{+}Cr(CO)$_4$NO^{-}.[20b] Since oxidopentadienylic cation could be regarded as a vinyl-stabilized oxyallyl,[21] the S_N1 loss of bromide from **5** should be more favorable than that from simple bromo enolate.[20b] The oxidopentadienylic cation **6** undergoes conrotatory 4π-electrocyclic closure to afford the cyclopentenone product **3j′** with two cis methyl groups. Since the C3 or C5 electron of the dienolate system in **5** is not suitably situated for direct backside S_N2 displacement of bromide because of its planar structure, formation of cyclopentenone product **3j′** or a vinyl cyclopropanone from **5** by intramolecular S_N2 reaction should be difficult. Sorensen's recent work[20b] may support that oxidopentadienylic cations are involved in the reaction pathway of the [4+1] reaction of TIPS-vinylketenes with Köbrich reagents. In his research, an oxyallyl structure is proposed as

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(18) For reviews, see: (a) Bereubar, A.; Grandjean, C.; Siriwardena, A. *Chem. Rev.* **1999**, *99*, 779. (b) Acar, E. A.; Glarner, F.; Burger, U. *Helv. Chim. Acta* **1998**, *81*, 1095.

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(20) (a) Sorensen, T. S.; Sun, F. *J. Am. Chem. Soc.* **1997**, *119*, 11327. (b) Sorensen, T. S.; Sun, F. *J. Am. Chem. Soc.* **1995**, *117*, 5592. (c) Frontier, A. J.; Collison, C. *Tetrahedron* **2005**, *61*, 7577.

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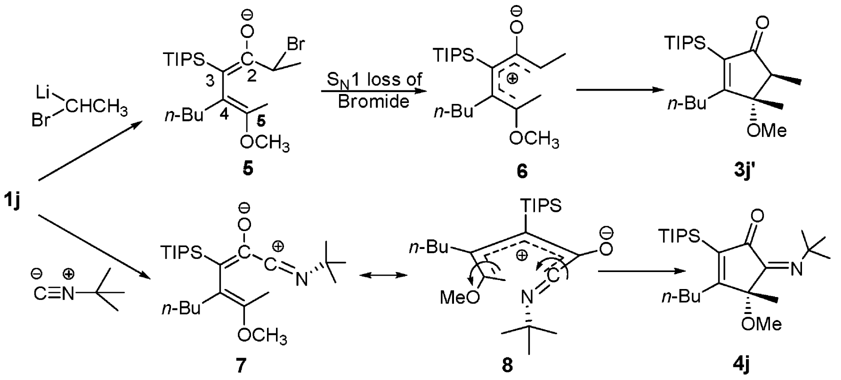
SCHEME 1. Proposed Mechanism for [4+1] of 1j



the key intermediate in the reaction of ketenes with diazoalkanes to form cyclopropanones.[22]

The formation of **4j** with exocyclic (*Z*)-imine moiety involves the initial formation of zwitterion **7**[23] by the attack of isocyanide to the ketene group as Moore suggested.[9c] The oxidopentadienylic cation **8** is another resonance form of the zwitterion **7**. The following step is conrotatory 4π-electrocyclic closure of **8** to **4j**. Although conrotation in both the clockwise and the counterclockwise sense of **8** is allowed, for steric reasons, **8** will preferentially undergo counterclockwise conrotation. In this way, the bulky *tert*-butyl group moves away from the methyl group on C5. The proposed transition **8** resembles the intermediate in the cyclization of oxyallenones, which lead to cyclopentenones with an exocyclic (*Z*)-double bond.[24]

In summary, we have developed an efficient method for preparing polysubstituted cyclopentenones from TIPS-vinylketenes and Köbrich reagents. Additionally, highly substituted cyclopentenones can be prepared via [4+1] reaction of TIPS-vinylketenes with *tert*-butyl isocyanide without any promoter. Ongoing studies on the application of the [4+1] reaction in the synthesis of natural products will be reported in due course.

Experimental Section

General Procedure for the [4+1] Annulation of Silyl Vinylketenes with Köbrich Reagents in Et$_2$O. A solution of the silyl vinylketene (0.5 mmol, 1.0 equiv) and CH_2I_2 or Br_2CHCH_3 (0.75 mmol, 1.5 equiv) in 5 mL of Et_2O was cooled to −78 °C. *n*-BuLi (2.2 M, 0.36 mL, 0.75 mmol, 1.5 equiv) was added within 10 min by syringe. After stirring at −78 °C for 1 h, the solution was allowed to warm to room temperature and stirred overnight. The resulting solution was diluted with 30 mL of Et_2O and extracted with saturated NaCl (3 × 10 mL). The aqueous layer was back-extracted with Et_2O (3 × 10 mL). The combined organic layer was dried over anhydrous Na_2SO_4. After filtration, the solvent was removed under reduced pressure and the residue was purified via flash chromatography (SiO_2) to afford the cyclopentenone compound.

Cyclopentenone 3c: mp 106−107 °C. IR (neat) υ 2944, 2863, 1968, 1900, 1692, 1610, 1186, 1076, 1020 cm^{-1}. 500 MHz ^{1}H NMR ($CDCl_3$) δ 7.37−7.30 (m, 4H), 7.25−7.21 (m, 1H), 7.01 (d, J = 16.0 Hz, 1H), 6.70 (d, J = 16.0 Hz, 1H), 5.32−5.23 (m, 5H), 3.29 (s, 3H), 3.01 (d, J = 19.0 Hz, 1H), 2.55 (d, J = 19.0 Hz, 1H), 1.68−1.62 (m, 3H), 1.17−1.02 (m, 18H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 232.1, 209.3, 175.6, 145.9, 145.0, 137.9, 128.8, 127.3, 124.5, 123.3, 101.9, 93.1, 92.5, 91.6, 91.5, 91.1, 87.0, 50.6, 49.7, 19.2, 19.1, 12.4. HRMS (FAB) *m*/*z* calcd for $C_{32}H_{38}CrO_5Si$ 582.1894, found 582.1890.

General Procedure for the [4+1] Annulation of Silyl Vinylketenes with Isocyanide in THF. A solution of the silyl vinylketene (0.33 mmol, 1.0 equiv) and *tert*-butyl isocyanide (42 mg, 0.50 mmol, 1.5 equiv) in 10 mL of THF was stirred at room temperature or 66 °C until the TLC analysis revealed that the reaction was complete. The solvent was removed under reduced pressure and the residue was purified via flash chromatography (SiO_2) to afford the cyclopentenone compound.

Cyclopentenone 4a: mp 146−147 °C. IR (neat) υ 3085, 2946, 2866, 1975, 1885, 1700, 1552, 1454, 1388, 1361, 1228, 1117, 1068, 1018 cm^{-1}. ^{1}H NMR (500 MHz, $CDCl_3$) δ 5.90 (d, J = 6.5 Hz, 1H), 5.63 (t, J = 6.0 Hz, 1H), 5.57 (d, J = 6.0 Hz, 1H), 5.13 (t, J = 6.0 Hz, 1H), 5.08 (t, J = 6.5 Hz, 1H), 3.24 (s, 3H), 1.71 (s, 3H), 1.44 (s, 9H), 1.26 (sept, J = 7.0 Hz, 3H), 1.00 (d, J = 7.0 Hz, 9H), 0.97 (d, J = 7.0 Hz, 9H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 231.6, 191.3, 175.3, 161.2, 153.1, 102.2, 97.5, 96.3, 95.6, 86.0, 85.2, 80.7, 57.9, 51.5, 29.8, 24.1, 19.3, 19.2, 11.9. HRMS (FAB) *m*/*z* calcd for $[C_{29}H_{41}CrNO_5Si + H]^+$ 564.2232, found 564.2229.

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Note Added after ASAP Publication. There was an error in Scheme 1 in the version published ASAP on November 16, 2007; the corrected version was published November 19, 2007.

Supporting Information Available: Detailed experimental procedures and characterization data for all cyclopentenone products and new silyl vinylketenes. This material is available free of charge via the Internet at http://pubs.acs.org.

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[23] The formation of **7** is proposed to involve rehybridization and a geometry change at nitrogen to sp^2, with the plus charge on carbon. An sp geometry may also be reasonable, as this would maintain conjugation of all the electrons on nitrogen, with plus charge on N.

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