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Stereoselective [4 + 1] Annulation Reactions with Silyl Vinylketenes Derived from Fischer Carbene Complexes

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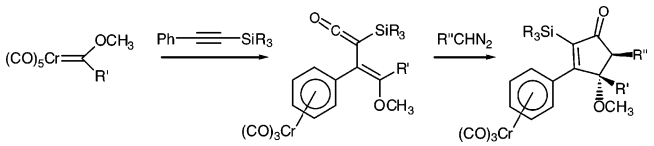

Stable silyl vinylketenes were prepared via the thermal reaction of Fischer carbene complexes with triisopropylsilyl- or *tert*-butyldimethylsilyl-substituted alkynes. The ability of these silyl vinylketenes to participate with carbenoid reagents in [4 + 1] annulation reactions was investigated. The best results were obtained with diazomethane and substituted diazomethane reagents, which provided cyclopentenone products in excellent yields and essentially complete stereoselectivity.

Introduction

Cyclopentenones are common structural units in natural products and useful synthons for the construction of more complex compounds. As a result, a wide variety of strategies for the synthesis of cyclopentenones have been developed.[1] A particularly appealing subset of these strategies consists of cycloaddition reactions, in which the cyclopentenone ring is formed in a single step from appropriate acyclic precursors. The most widely established method of this type is the Pauson−Khand reaction, involving a formal [2 + 2 + 1] cycloaddition that joins alkene, alkyne, and carbon monoxide moieties together (Figure 1, path a).[2] However, since regio- and stereochemical ambiguities exist with intermolecular versions of the Pauson−Khand reaction, motivation to develop complementary methods persists.

A [4 + 1] cycloaddition provides another attractive approach to the cyclopentenone ring system since regiochemical difficulties are avoided.[3] As depicted in Figure 1, path b, the combination of a vinylketene and a carbenoid unit would appear to represent a very direct approach to cyclopentenones. However, despite the ability of vinylketenes to serve as versatile four-carbon building blocks,[4] their use in [4 + 1] cycloaddition reactions is rendered difficult by their characteristic instability and a preference to undergo dimerization and/or [2 + 2] cycloaddition reactions instead.[5] In contrast, *silyl* vinylketenes

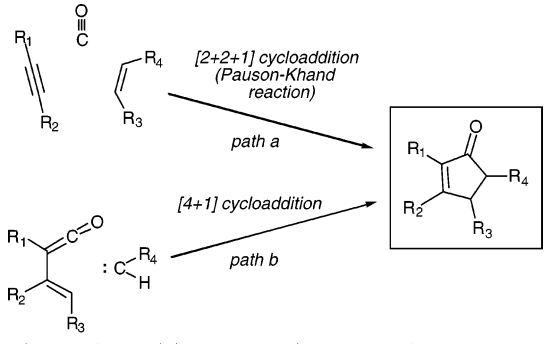

FIGURE 1. Cycloaddition strategies toward cyclopentenones.

(1) For reviews, see: (a) Gibson, S. E.; Lewis, S. E.; Mainolfi, N. *J. Organomet. Chem.* **2004**, *689*, 3873. (b) Tius, M. A. *Acc. Chem. Res.* **2003**, *36*, 284. (c) Mitsudo, T.; Kondo, T. *Synlett* **2001**, 309. (d) Mikolajczyk, M.; Mikina, M.; Zurawinski, R. *Pure Appl. Chem.* **1999**, *71*, 473. (e) Iwasawa, N. *Synlett* **1999**, 13. (f) Piancatelli, G.; D'Auria, M.; D'Onofrio, F. *Synthesis* **1994**, 867. (g) Hudlicky, T.; Price, J. D. *Chem. Rev.* **1989**, *89*, 1467. (h) Paquette, L. A. *Top. Curr. Chem.* **1984**, *119*, 1. (i) Ramaiah, M. *Synthesis* **1984**, 529.

(2) For recent reviews of the Pauson−Khand reaction, see: (a) Sugihara, T.; Yamaguchi, M.; Nishizawa, M. *Chem.−Eur. J.* **2001**, *7*, 1589. (b) Brummond, K. M.; Kent, J. L. *Tetrahedron* **2000**, *56*, 3263. (c) Keun Chung, Y. *Coord. Chem. Rev.* **1999**, *188*, 297. (d) Oliver, G.; Schmalz, H. *Angew. Chem., Int. Ed.* **1998**, *37*, 911. (e) Schore, N. E. *Org. React.* **1991**, *40*, 1.

(3) For a rhodium-catalyzed carbonylative [4 + 1] cycloaddition, see: Murakami, M.; Itami, K.; Ito, Y. *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 2691.

(4) For a review, see: Tidwell, T. T. *Ketenes*; Wiley: New York, 1991.

(5) Vinylketenes stabilized by transition metals have also been utilized as four-carbon synthons. See: Gibson, S. E. *Adv. Organomet. Chem.* **1999**, *44*, 275.

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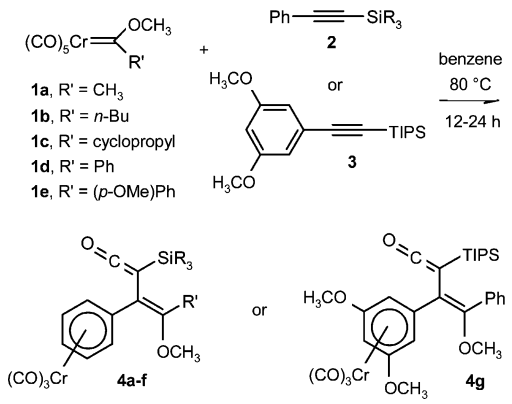
TABLE 1. Synthesis of Silyl Vinylketenes



entry	carbene complex	alkyne	SiR_3	products (% yield)
1	**1a**	**2**	TIPS	**4a**, R′ = CH_3 (58)
2	**1b**	**2**	TIPS	**4b**, R′ = *n*-Bu (65)
3	**1c**	**2**	TIPS	**4c**, R′ = *c*-C_3H_5 (32)
4	**1d**	**2**	TIPS	**4d**, R′ = Ph (88)
5	**1d**	**2**	TBS	**4e**, R′ = Ph (55)
6	**1e**	**2**	TIPS	**4f**, R′ = (*p*-OMe)Ph (87)
7	**1d**	**3**	TIPS	**4g** (76)

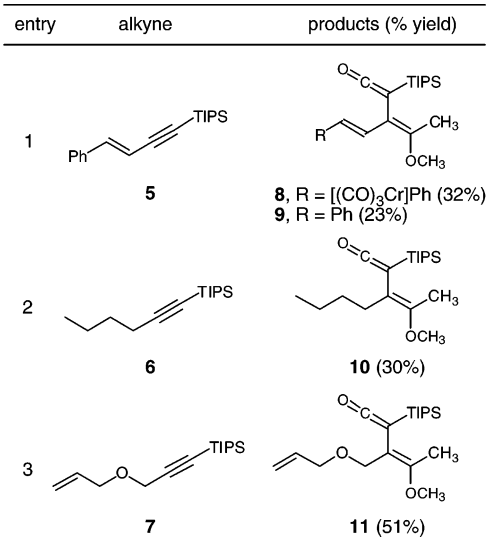
have been demonstrated as viable precursors to cyclopentenones[6] and other cycloadducts.[7] The silyl substituent provides significant stabilization to the ketene moiety and suppresses the dimerization pathway,[8] thereby facilitating their participation in [4 + 1] cycloaddition reactions with carbenoid reagents.

The development of silyl vinylketenes in [4 + 1] cycloadditions has entailed not only explorations of the scope of the transformation, but also the evolution of new methods to prepare the silyl vinylketene precursors themselves.[8,9] Previously we have established an efficient protocol for the construction of silyl vinylketenes from the thermal reaction of Fischer carbene complexes and silyl-substituted alkynes.[10] On the basis of the unique silyl vinylketene substitution pattern available from this method, we have chosen to further examine the process and investigate their utility in [4 + 1] cycloaddition reactions with carbenoid units. Herein we report a highly efficient and stereoselective construction of functionalized cyclopentenones that complements existing [4 + 1] strategies.

Results and Discussion

Silyl vinylketenes were prepared by our previously reported thermal reaction of Fischer carbene complexes **1a**−**e** with triisopropylsilyl (TIPS) or *tert*-butyldimethylsilyl (TBS) substituted alkynes.[10] As indicated in Table 1 (entries 1−6), heating benzene solutions of **1** and **2** at reflux under argon atmosphere for 12−24 h afforded the yellow crystalline silyl vinylketenes **4a**−**f** as the major products in good yields. The use of **3** to generate silyl vinylketene **4g** (entry 7) also demonstrates that substitution on the aromatic alkyne precursor is tolerated.

TABLE 2. Silyl Vinylketenes from 1a and Alkyl- or Alkenyl-Substituted Alkynes



Structural assignments of silyl vinylketenes **4**, which were readily purified by crystallization or flash chromatography on silica gel, were initially based on characteristic IR ketene absorbances (ca. 2085−2090 cm^{-1}) and ^{13}C NMR chemical shifts for the ketene carbonyl carbon and silyl-bearing carbon (ca. 179−180 ppm and 15−16 ppm, respectively).[11] As previously reported,[10] X-ray crystallographic analysis of **4e** verified the proposed structure and demonstrates the exclusive formation of the (*E*)-alkene isomer in this process when carbene complexes bearing aryl groups are employed. To verify the same stereochemical result for carbene complexes bearing sterically and electronically different alkyl groups, **4c** was subjected to X-ray crystallographic structure determination, and indeed the (*E*)-alkene isomer was observed in this case as well.[12] The exclusive formation of the (*E*)-alkene isomers in this process is consistent not only with previously reported examples, but also with the "trans effect" hypothesis suggested by the Wulff group.[13] In support of this stereoelectronic hypothesis, Wulff and co-workers demonstrated that formation of the corresponding (*Z*)-alkene isomers in related transformations required the use of alkynes bearing strongly electron-withdrawing substituents such as aryl or alkyl ketones.[13]

The use of the silyl-substituted phenylacetylenes is notable in that it promotes capture of the chromium fragment by the phenyl ring and affords access to the silyl vinylketenes as arene complexes that display excellent thermal stability.[10] However, we have also observed that arene complex formation is not a prerequisite for generation of silyl vinylketenes by this method. As shown in Table 2, treatment of Fischer carbene complex **1a** with the TIPS-substituted alkynes **5**−**7** under the same reaction conditions generates silyl vinylketenes **8**−**11**, which are all stable to purification via silica gel chromatography.

Our initial cycloaddition studies entailed the reaction of arene chromium tricarbonyl-containing silyl vinylketenes (**12**) with

(6) (a) Davie, C. P.; Danheiser, R. L. *Angew. Chem., Int. Ed.* **2005**, *44*, 5867. (b) Rigby, J. H.; Wang, Z. *Org. Lett.* **2003**, *5*, 263. (c) Dalton, A. M.; Zhang, Y.; Davie, C. P.; Danheiser, R. L. *Org. Lett.* **2002**, *4*, 2465. (d) Loebach, J. L.; Bennett, D. M.; Danheiser, R. L. *J. Am. Chem. Soc.* **1998**, *120*, 9690. (e) Colomvakos, J. D.; Egle, I.; Ma, J.; Pole, D. L.; Tidwell, T. T.; Warkentin, J. *J. Org. Chem.* **1996**, *61*, 9522.

(7) Bennett, D. M.; Okamoto, I.; Danheiser, R. L. *Org. Lett.* **1999**, *1*, 641.

(8) Huang, W.; Tidwell, T. T. *Synthesis* **2000**, 457 and references therein.

(9) (a) Pommier, A.; Kocienski, P.; Pons, J. *J. Chem. Soc., Perkin Trans. 1* **1998**, 2105. (b) Loebach, J. L.; Bennett, D. M.; Danheiser, R. L. *J. Org. Chem.* **1998**, *63*, 8380.

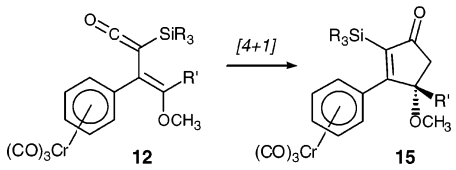
(10) Moser, W. H.; Sun, L.; Huffman, J. C. *Org. Lett.* **2001**, *3*, 3389.

(11) Dötz, K. H.; Fügen-Köster, B. *Chem. Ber.* **1980**, *113*, 1449.

(12) See the Supporting Information for X-ray crystallographic structures.

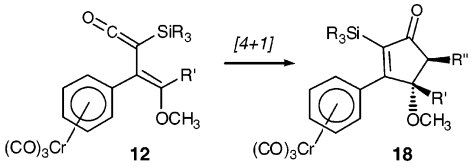
(13) Waters, M. L.; Brandvold, T. A.; Isaacs, L.; Wulff, W. D.; Rheingold, A. L. *Organometallics* **1998**, *17*, 4298.

TABLE 3. [4 + 1] Annulation Reactions



entry	SiR_3	R′	carbenoid reagent	products (% yield)
1	TIPS	CH_3	$Me_2\overset{+}{S}-\overset{-}{C}H_2$ **13**	**15a** (49)
2	TIPS	*n*-Bu	**13**	**15b** (27)
3	TIPS	CH_3	CH_2N_2 **14**	**15a** (84)
4	TIPS	*n*-Bu	**14**	**15b** (83)
5	TIPS	Ph	**14**	**15c** (72)
6	TBS	Ph	**14**	**15d** (70)

TABLE 4. Stereoselective [4 + 1] Annulation Reactions



entry	SiR_3	R′	carbenoid reagent	products (% yield)
1	TIPS	CH_3	$TMSCHN_2$ **16**	**18a**, R″ = TMS (93)
2	TIPS	*n*-Bu	**16**	**18b**, R″ = TMS (79)
3	TIPS	Ph	**16**	**18c**, R″ = TMS (62)
4	TBS	Ph	**16**	**18d**, R″ = TMS (86)
5	TIPS	CH_3	$PhCHN_2$ **17**	**18e**, R″ = Ph (80)
6	TIPS	*n*-Bu	**17**	**18f**, R″ = Ph (83)
7	TIPS	Ph	**17**	**18g**, R″ = Ph (73)
8	TIPS	(*p*-OMe)Ph	**17**	**18h**, R″ = Ph (77)
9	TBS	Ph	**17**	**18i**, R″ = Ph (76)

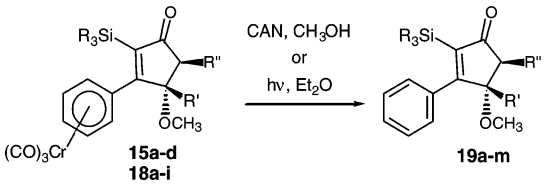
dimethylsulfonium methylide **13**, whose participation in [4 + 1] cycloadditions was previously established by Danheiser and co-workers.[6d] Addition of 1.1 equiv of **13** to a solution of the silyl vinylketenes **12** in 1:1 THF/DMSO at 0−25 °C for 1.5 h provided moderate yields of the desired cyclopentenone products **15a**,**b** after chromatographic purification, along with significant decomposition of the silyl vinylketene starting material (Table 3, entries 1 and 2). A notable improvement was observed upon switching to diazomethane as the carbenoid reagent, which cleanly provided the cyclopentenone products **15a**−**d** in good to excellent yields (Table 3, entries 3−6).[14]

We were also pleased to find that substituted diazomethane reagents serve as suitable reagents in [4 + 1] annulations with the silyl vinylketenes. Both phenyldiazomethane (**17**)[15] and commercially available (trimethylsilyl)diazomethane (**16**) provided the corresponding cyclopentenone products **18** in good to excellent yields (Table 4).[14] The cyclopentenone products could be purified by silica gel chromatography, although the trimethylsilyl group in cyclopentenones **18a**−**d** was found to be somewhat labile to these conditions.[6e] Alternatively, the desired products could be crystallized directly from the crude

(14) Silyl vinylketenes **8**−**11** were also suitable for [4 + 1] annulation reactions. Results with these substrates will be reported elsewhere.

(15) Creary, X. In *Organic Syntheses*; Wiley & Sons: New York, 1990; Collect. Vol. VII, pp 438−443.

TABLE 5. Removal of Chromium Fragment



entry	substrate	SiR_3	R′	R″	product
1	**15a**	TIPS	CH_3	H	**19a**
2	**15b**	TIPS	*n*-Bu	H	**19b**
3	**15c**	TIPS	Ph	H	**19c**
4	**15d**	TBS	Ph	H	**19d**
5	**18a**	TIPS	CH_3	TMS	**19e**
6	**18b**	TIPS	*n*-Bu	TMS	**19f**
7	**18c**	TIPS	Ph	TMS	**19g**
8	**18d**	TBS	Ph	TMS	**19h**
9	**18e**	TIPS	CH_3	Ph	**19i**
10	**18f**	TIPS	*n*-Bu	Ph	**19j**
11	**18g**	TIPS	Ph	Ph	**19k**
12	**18h**	TIPS	(*p*-OMe)Ph	Ph	**19l**
13	**18i**	TBS	Ph	Ph	**19m**

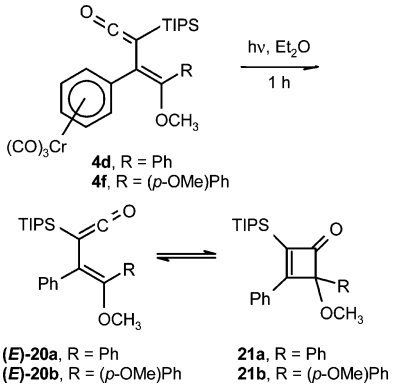
reaction mixtures. Notably, the cyclopentenone products **18** contain two contiguous stereogenic centers, and in all cases only a single diastereomer could be observed by ^1H NMR spectroscopy of the crude reaction mixtures. X-ray crystallographic analysis of cyclopentenone **18h** established the cis relationship between the two phenyl substituents, while the crystal structure of **18a** verifies that the same cis relationship is observed when (trimethylsilyl)diazomethane is utilized, even with the sterically smaller methyl group.[12]

In all cases, the chromium tricarbonyl group is readily removed from the [4 + 1] annulation products by treatment with ceric ammonium nitrate (CAN), providing cyclopentenones **19a**−**m** in essentially quantitative yields (Table 5). For substrates **15a**−**d** and **18a**−**d**, photolytic removal of the chromium fragment is also successful; however, similar irradiation of compounds **18e**−**i** results in rapid product decomposition. This decomposition may be due to a Norrish Type I cleavage of the cyclopentenone ring, which should be rendered more facile by the presence of the phenyl ring adjacent to the carbonyl moiety. The construction of the cyclopentenone products **19** can be considered a formal [2 + 1 + 1 + 1] annulation process in which the five carbons of the cyclopentenone products are derived from the two carbons of the alkyne, the carbene complex carbon, carbon monoxide, and the carbon of the carbenoid reagent. The wide range of substituents that can be incorporated by variation of these four components suggests that the method will provide broad access to cyclopentenone and/or cyclopentanoid products.

An important aspect of this [4 + 1] annulation reaction is the apparent preservation of the (*E*)-alkene geometry in the diastereoselective cyclopentenone formation. To further probe this observation, we sought to obtain the corresponding silyl vinylketenes bearing the (*Z*)-alkenyl geometry, with the hopes that they would provide stereoselective access to the alternate cyclopentenone diastereomers. It seemed feasible that isomerization of the (*E*)-alkenyl silyl vinylketenes may be possible through reversible thermal 4π electrocyclic ring closures, which have been documented for vinylketenes,[16] and silyl allenylketenes.[8,17] Silyl vinylketene **4d** bearing the chromium tricar-

(16) Moore, H. W.; Yerxa; B. R. *Adv. Strain Org. Chem.* **1995**, *4*, 81.

SCHEME 1. Equilibration of (*E*)-SVK and Cyclobutenone

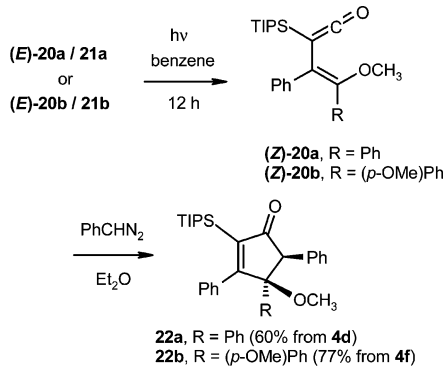


bonyl moiety did not display any propensity toward thermal isomerization upon heating at reflux in toluene over extended periods of time. In contrast, photolytic removal of the chromium moiety quantitatively afforded silyl vinylketene **(*E*)-20a**, which slowly converted to an equilibrium mixture of **(*E*)-20a** and cyclobutenone **21a** at room temperature (Scheme 1). Evidence for this transformation is provided by IR spectroscopy, as the initially generated silyl vinylketene **(*E*)-20a** displays a strong absorption at 2086 cm^{-1}, with subsequent emergence of a characteristic cyclobutenone absorption at 1745 cm^{-1} over several hours. This observation suggested that even when the cyclobutenone form is thermally accessible, torquoselective preference to have the electron-donating alkoxy group rotate outward would preclude thermal ring opening to the desired (*Z*)-silyl vinylketene isomer.[18] Thermal isomerization to the (*Z*)-silyl vinylketene was even unsuccessful with **(*E*)-20b**, in which the phenyl substituent at the terminal position was replaced by the more electron-rich *para*-methoxyphenyl substituent. Fortunately, it has also been established that this stereoelectronic effect can be overridden by photolytic ring opening of cyclobutenones.[19] Indeed, we were pleased to find that photolysis of the **(*E*)-20/21** mixtures in degassed benzene for 12 h resulted in complete conversion to silyl vinylketenes **(*Z*)-20a**,**b** (Scheme 2), as evidenced by a single carbonyl IR absorbance in the 2085−2090 cm^{-1} range and ^1H and ^{13}C NMR spectral data consistent with silyl vinylketenes but distinct from those obtained for **(*E*)-20a**,**b**. Importantly, the (*Z*)-silyl vinylketene isomers were found to be stable to silica gel chromatography and displayed no tendency to isomerize at room temperature.

Following their purification, we were gratified to find that exposure of silyl vinylketenes **(*Z*)-20a**,**b** to phenyldiazomethane provided cyclopentenones **22a**,**b** in good yield, with none of the original diastereomers **19k** or **19l** visible by ^1H NMR spectroscopy. (Scheme 2) These experiments not only provided further evidence that the geometry of the silyl vinylketene is conserved in a concerted ring-closure process, but also demonstrated that either diastereomer of the cyclopentenone products should be generally accessible through our approach.

Stereoselective silyl vinylketene/carbenoid [4 + 1] annulations have also been reported by the Danheiser group, who have proposed several alternative pathways to account for the

SCHEME 2. Isomerization to (*Z*)-SVK and Resultant [4 + 1] Annulation



mechanism of the transformation.[6a,c,d] One interpretation, as outlined in Figure 2, involves initial stereoselective addition of

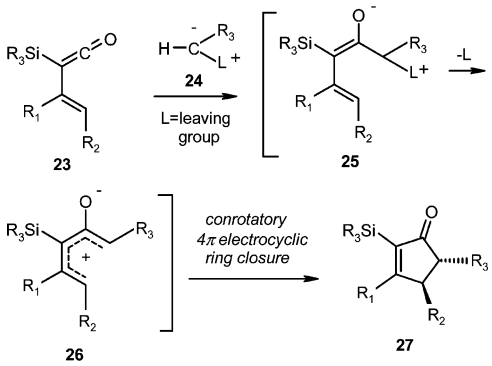


FIGURE 2. Possible annulation mechanism.

carbenoid reagents **24** to provide the (*Z*)-enolate **25**,[20] followed by ionization of the leaving group to generate 2-oxidopentadienyl cation **26** as the sterically favored intermediate. A concerted 4π electrocyclic ring closure would preserve the original alkene geometry and provide the observed diastereomer of the cyclopentenone. Although we cannot discount any of the other mechanisms suggested by Danheiser, we have observed rate differences that may lend credence to the mechanism in Figure 2. Specifically, the [4 + 1] annulation with substrates **4d** or **4f** bearing the chromium tricarbonyl fragment proceeded significantly faster than the identical reactions with the chromium-free silyl vinylketenes **20** (ca. 24 h vs 72 h, respectively). This rate difference would be consistent with the proposed mechanism, as the ability of the chromium fragment to stabilize developing charge character in the benzylic position[21] should accelerate the rate-determining cationic 4π electrocyclic ring closure.[22]

Conclusion

Thermal reaction of Fischer carbene complexes with silyl-substituted alkynes provides an efficient route to stable silyl

(17) Huang, W.; Fang, D.; Temple, K.; Tidwell, T. T. *J. Am. Chem. Soc.* **1997**, *119*, 2832.

(18) For a review on torquoselective electrocyclic reactions, see: Dolbier, W. R., Jr.; Koroniak, H.; Houk, K. N.; Sheu, C. *Acc. Chem. Res.* **1996**, *29*, 471.

(19) Foland, L. D.; Karlsson, J. O.; Perri, S. T.; Schwabe, R.; Xu, S. L.; Patil, S.; Moore, H. W. *J. Am. Chem. Soc.* **1989**, *111*, 975.

(20) (a) Tidwell, T. T. *Acc. Chem. Res.* **1990**, *23*, 273. (b) Baigrie, L. M.; Seikaly, H. R.; Tidwell, T. T. *J. Am. Chem.* Soc. **1985**, *107*, 5391.

(21) (a) Davies, S. G.; Dohohoe, T. J. *Synlett* **1993**, 323. (b) Davies, S. G.; Donohoe, T. J.; Williams, J. M. J. *Pure Appl. Chem.* **1992**, *64*, 379. (c) Uemura, M.; Minami, T.; Hayashi, Y. J. *Organomet. Chem.* **1986**, *299*, 119.

(22) Similar rate accelerations have been observed for Nazarov cyclizations, which are also proposed to proceed through electrocyclic ring closures of pentadienyl cations. See: Habermas, K. L.; Denmark, S. E. In *Organic Reactions*; Paquette, L. A., Ed.; Wiley: New York, 1994; Vol. 45, pp 1−158.

vinylketenes, with capture of the chromium fragment occurring in cases where the alkyne precursor contains a phenyl substituent. We have demonstrated that these silyl vinylketenes participate in [4 + 1] annulation reactions with carbenoid reagents to afford cyclopentenones in excellent yields. Annulations with substituted carbenoids and silyl vinylketenes bearing (*E*)- or (*Z*)-alkenes each proceed with essentially complete stereoselectivity to provide diastereomeric cyclopentenone products. Further studies of the scope and limitations of this transformation and application to the synthesis of natural products are ongoing.

Experimental Section

Representative Procedure for the Reaction of Fischer Carbene Complexes with Alkynes: Silyl Vinylketene 4a. A solution of carbene complex **1a** (500 mg, 2.00 mmol) and TIPS-substituted phenylacetylene (620 mg, 2.40 mmol) in benzene (20 mL) was degassed using several freeze−pump−thaw cycles. The solution was then heated at reflux for 12 h. Upon cooling to room temperature, the solvents were removed under reduced pressure, and the residue was purified via flash chromatography (SiO_2, 19/1 hexane/ethyl acetate), affording silyl vinylketene **4a** (560 mg, 58% yield) as a yellow solid. IR (neat): ν 2084, 1960, 1885 cm^{-1}. ^1H NMR ($CDCl_3$): δ 5.69 (d, $J = 5.9$ Hz, 2H), 5.30 (dd, $J = 6.6$, 5.9 Hz, 2H), 5.22 (t, $J = 5.9$ Hz, 1H), 3.72 (s, 3H), 2.19 (s, 3H), 1.02 (s, 21H). ^{13}C NMR ($CDCl_3$): δ 233.9, 179.3, 155.3, 110.1, 100.0, 96.5, 91.8, 91.2, 56.0, 18.5, 16.3, 14.0, 12.4. Anal. Calcd for $C_{24}H_{32}CrSiO_5$: C, 59.98; H, 6.71. Found: C, 60.06; H, 6.65.

Representative Procedure for [4 + 1] Annulation Reactions: Cyclopentenone 15a. Diazomethane, which was generated in a 125-mL Erlenmeyer flask by addition of an aqueous NaOH solution to a slurry of diazald (90 mg, 0.42 mmol) in EtOH, was bubbled into a solution of silyl vinylketene **12** (SiR_3 = TIPS, R′ = CH_3; 100 mg, 0.21 mmol) in Et_2O (20 mL). (Warning: diazomethane is an explosion hazard. Be sure that all glassware used in this procedure is flame-polished and contains no rough edges.) After 12 h, argon was bubbled through the solution for 15 min to remove any remaining diazomethane. The resultant solution was then concentrated under reduced pressure, and the crude product was purified by flash chromatography (SiO_2, 19/1 hexane/Et_2O), affording cyclopentenone **15a** (87 mg, 84% yield). IR (neat): ν 1971, 1892, 1704 cm^{-1}. ^1H NMR ($CDCl_3$): δ 5.87 (d, $J = 6.6$ Hz, 1H), 5.59 (dd, $J = 6.6$, 5.9 Hz, 1H), 5.52 (d, $J = 6.6$ Hz, 1H), 5.09 (dd, $J = 7.4$, 6.6 Hz, 1H), 5.04 (dd, $J = 6.6$, 5.9 Hz, 1H), 3.29 (s, 3H), 2.74 (d, 16.9 Hz, 1H), 2.47 (d, $J = 16.9$ Hz, 1H), 1.67 (s, 3H), 1.11 (sept, $J = 7.4$ Hz, 3H), 0.96 (d, $J = 7.4$ Hz, 9H), 0.91 (d, $J = 7.4$ Hz, 9H). ^{13}C NMR ($CDCl_3$): δ 232.2, 207.6, 179.4, 146.6, 103.5, 99.1, 96.7, 96.6, 85.9, 85.2, 83.8, 51.1, 48.9, 23.1, 19.2, 11.8. Anal. Calcd for $C_{25}H_{34}CrSiO_5$: C, 60.71; H, 6.93. Found: C, 60.76; H, 6.85.

Representative Procedure for Decomplexation of Cyclopentenones: Cyclopentenone 19a. Cerium ammonium(IV) nitrate (CAN, 439 mg, 0.800 mmol) was directly added to a 0 °C solution of cyclopentenone **15a** (198 mg, 0.400 mmol) in methanol (20 mL). After 15 min, the solution was diluted with H_2O and extracted with Et_2O. The combined organic layers were dried over $MgSO_4$, filtered, and concentrated under reduced pressure. The residue was purified via flash chromatography (SiO_2, hexane/Et_2O 19/1) to afford cyclopentenone **19a** (138 mg, 97% yield) as a clear, colorless oil. IR (neat): ν 1702 cm^{-1}. ^1H NMR ($CDCl_3$): δ 7.33−7.31 (m, 3H), 7.21−7.20 (m, 2H), 3.24 (s, 3H), 2.78 (d, $J = 18.4$ Hz, 1H), 2.37 (d, $J = 18.4$ Hz, 1H), 1.28 (s, 3H), 1.03 (sept, $J = 7.4$ Hz, 3H), 0.93 (d, $J = 7.4$ Hz, 9H), 0.88 (d, $J = 7.4$ Hz, 9H). ^{13}C NMR ($CDCl_3$): δ 209.8, 184.6, 141.8, 135.8, 128.4, 127.8, 127.3, 83.8, 51.0, 45.4, 25.0, 19.1, 11.3. HRMS calcd for $C_{19}H_{27}SiO_2$ ($M^+ - C_3H_7$), 315.1781; found, 315.1777.

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Supporting Information Available: Full experimental procedures for all new compounds, copies of ^1H NMR and ^{13}C NMR spectra for compounds **4**, **8**−**11**, **15**, **18**−**20**, and **22**, and crystal structure data for **4c**, **18a**, and **18h**. This material is available free of charge via the Internet at http://pubs.acs.org.

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