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Synthesis and Reactivity of Silyl Vinylketenes: A Formal Interrupted Dötz Benzannulation with Unexpected Silyl Migration

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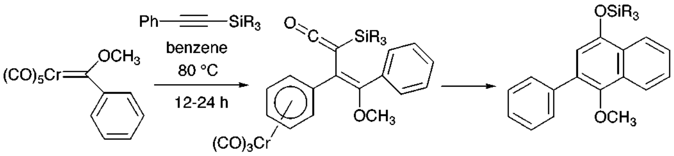
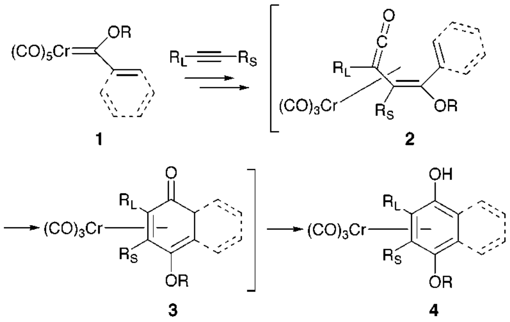
ABSTRACT



An efficient method for the generation of silyl vinylketenes from the thermal reaction of Fischer carbene complexes with silyl-substituted phenylacetylenes is described. Although the silyl vinylketene products are highly stable, conditions have been identified to induce a benzannulation/silyl migration process, providing aromatic silyl ethers.

Scheme 1. Dötz Benzannulation Reaction



The thermal benzannulation of Fischer carbene complexes with alkynes, commonly known as the Dötz reaction, represents one of the most widely utilized methods to generate substituted aromatic ring systems from nonaromatic precursors.[1] It is believed that the penultimate intermediate in this compelling transformation is the chromium η^4-vinylketene **2**, which can undergo electrocyclic ring closure and tautomerization to afford the $Cr(CO)_3$-complexed benzannulation product **4** (Scheme 1). Steric considerations dictate that incorporation of the alkyne favorably occurs to place the larger alkyne substituent (R_L) *ortho* to the phenolic group. Several isolated cases have been reported in which attempted benzannulation reactions involving silyl-substituted alkynes resulted in the formation of silyl vinylketenes related to purported intermediate **2** rather than the expected aromatic products.[2] The ability of the silyl group to electronically stabilize ketenes[3] and the steric congestion introduced by

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(1) For reviews of the Dötz benzannulation, see: (a) Dötz, K. H.; Tomuschat, P. *Chem. Soc. Rev.* **1999**, *28*, 187. (b) Wulff, W. D. In *Comprehensive Organometallic Chemistry II*; Abel, A. W., Stone, F. G. A., Wilkinson, G., Eds.; Pergamon: Oxford, 1995; Vol. 12. (c) Hegedus, L. S. In *Comprehensive Organometallic Chemistry II*; Abel, A. W., Stone, F. G. A., Wilkinson, G., Eds.; Pergamon: Oxford, 1995; Vol. 12. (d) Harvey, D. F.; Sigano, D. M. *Chem. Rev.* **1996**, *96*, 271.

(2) (a) Dötz, K. H. *Angew. Chem., Int. Ed. Engl.* **1979**, *18*, 954. (b) Dötz, K. H.; Fügen-Köster, B. *Chem. Ber.* **1980**, *113*, 1449. (c) Wulff, W. D.; Tang, P.-C. *J. Am. Chem. Soc.* **1984**, *106*, 1132. (d) Wulff, W. D.; Xu, Y.-C. *J. Org. Chem.* **1987**, *52*, 3263.

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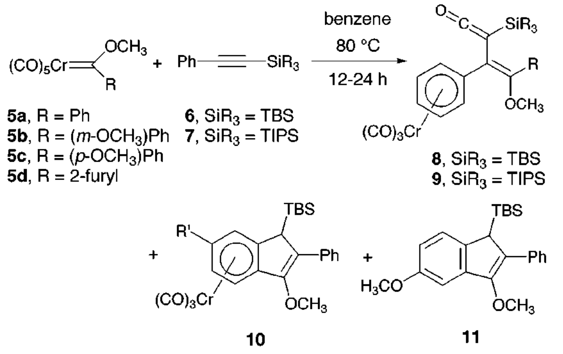
the bulky silyl group have been suggested as the key factors impeding the final electrocyclic ring closure.

In addition to mechanistic interest, the isolation of silyl vinylketenes carries synthetic implications. The stabilizing influence of the silyl group suppresses the dimerization process typical of ketenes and has allowed silyl vinylketenes obtained by other methods to be utilized in a number of profitable bond-forming reactions.[4] In contrast, the chemical reactivity of silyl vinylketenes bearing the substitution patterns unique to the Dötz reaction have remained virtually unexplored.[5] Significantly, we were unable to locate any studies reporting the participation of isolable silyl vinylketenes in 6π electrocyclic reactions.

On the basis of our interest in the Dötz reaction and the potential synthetic utility of silyl vinylketenes derived from this process, we have undertaken an investigation of the synthesis and subsequent reactivity of these intriguing compounds. A primary question that we wished to answer was whether silyl vinylketenes prepared by this route are capable of participating in the electrocyclic ring closures closely associated with the Dötz reaction.

Initial studies involved the thermal reaction of aryl methoxy and furyl methoxy chromium carbene complexes **5** with *tert*-butyldimethylsilyl (TBS)-substituted phenylacetylene **6**. As indicated in Table 1, heating benzene solutions of **5** and **6** at reflux under argon atmosphere for 12−24 h afforded the yellow crystalline silyl vinylketenes **8** as the major products in fair to good yields. Trials with aryl carbene complexes **5a**−**c** (entries 1−3) also afforded minor amounts of indenes **10** or **11**, which are believed to arise via cyclization without insertion of a carbonyl ligand. X-ray crystallographic analysis of **8a**[6] verified the proposed structure and demonstrates the exclusive formation of the (*E*) alkene isomer in this process.[7] Switching to the triisopropylsilyl (TIPS)-substituted phenylacetylene **7** under identical conditions significantly improved the yields of the silyl vinylketenes and suppressed the formation of indenes (entries 5−8).

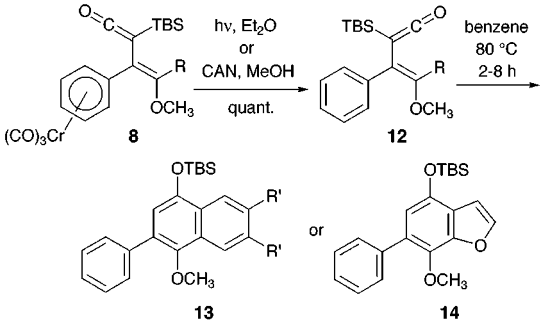
Table 1. Synthesis of Silyl Vinylketenes



entry	carbene complex	alkyne	products (% yield)
1	**5a**	**6**	**8a**, R = Ph (55) + **10**, R′ = H (19)
2	**5b**	**6**	**8b**, R = (m-OCH$_3$)Ph (57) + **11** (12)
3	**5c**	**6**	**8c**, R = (p-OCH$_3$)Ph (53) + **10**, R′ = OCH$_3$ (18)
4	**5d**	**6**	**8d**, R = 2-furyl (36)
5	**5a**	**7**	**9a**, R = Ph (88)
6	**5b**	**7**	**9b**, R = (m-OCH$_3$)Ph (84)
7	**5c**	**7**	**9c**, R = (p-OCH$_3$)Ph (87)
8	**5d**	**7**	**9d**, R = 2-furyl (62)

Silyl vinylketenes **8** and **9** contain a conjugated 6πe^- system and the (*E*) alkene geometry required for electrocyclic ring closure; however, these compounds were unchanged upon heating over extended periods of time in refluxing toluene. Photolytic or oxidative removal of the chromium moiety from compounds **8**, however, quantitatively afforded the corresponding silyl vinylketenes **12**, whose chemical reactivity was quite different (Table 2).

Table 2. Ring Closures of Free Silyl Vinylketenes



entry	substrate	product (% yield)
1	**8a**, R = Ph	**13a**, R′ = R″ = H (96)
2	**8b**, R = (m-OCH$_3$)Ph	**13b**, R′ = H, R″ = OCH$_3$ (92)
3	**8c**, R = (p-OCH$_3$)Ph	**13c**, R′ = OCH$_3$, R″ = H (94)
4	**8d**, R = 2-furyl	**14** (89)

Although the free silyl vinylketenes **12** were stable at room temperature and could be stored at −20 °C for several weeks without noticeable decomposition, they smoothly underwent 6π electrocyclic ring closure over several hours when heated at reflux in benzene. To our surprise, however, the lack of an alcohol absorbance in the IR spectra indicated that the products were not the expected phenols. Rather, careful analysis of all spectral data revealed that the silyl ethers **13** or **14** were the sole products that had been formed.

Attempts to repeat this benzannulation protocol with the TIPS-substituted vinylketenes were initially unsuccessful. Following oxidative or photolytic removal of the chromium

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

(4) (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. (c) Loebach, J. L.; Bennett, D. M.; Danheiser, R. L. *J. Am. Chem. Soc.* **1998**, *120*, 9690. (d) Bennett, D. M.; Okamoto, I.; Danheiser, R. L. *Org. Lett.* **1999**, *1*, 641.

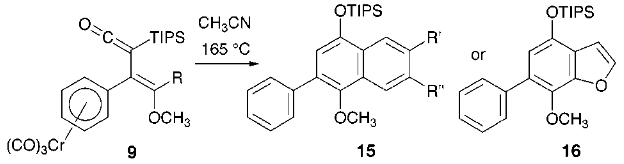
(5) Dötz, K. H.; Mühlemeier, J.; Trenkle, B. *J. Organomet. Chem.* **1985**, *289*, 257.

(6) Crystallographic data can be found in the Supporting Information.

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

fragment from **9a**−**d** as in the TBS series, the resultant free silyl vinylketenes were isolated as interconverting (*E*) and (*Z*) isomers.[8] Heating the isomeric mixtures in refluxing benzene did not induce any benzannulation; at higher temperatures, some benzannulation was observed but was always accompanied by significant decomposition. Following these initial trials, we discovered that benzannulation and removal of the chromium fragment could be efficiently accomplished in one step by heating degassed acetonitrile solutions of the complexes **9** at 165 °C in a sealed tube. The rapid isomerization of the free silyl vinylketenes that takes place at room temperature suggests that electrocyclic ring closure precedes loss of the chromium fragment under these conditions, although further study will be necessary to confirm this hypothesis. By utilizing this protocol, the benzannulation products **15** or **16**, again in which silyl migration had occurred, could be obtained in essentially quantitative yields (Table 3).

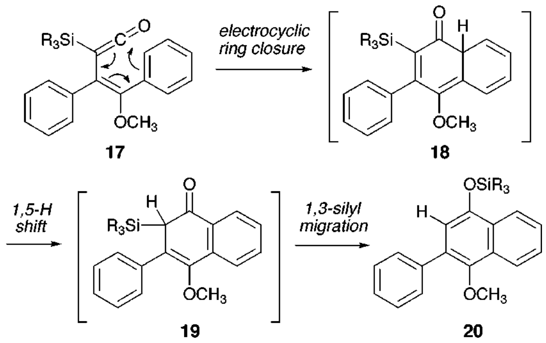
Table 3. High-Temperature Benzannulations



entry	substrate	product (% yield)
1	**9a**, R = Ph	**15a**, R′ = R″ = H (96)
2	**9b**, R = (*m*-OCH$_3$)Ph	**15b**, R′ = H, R″ = OCH$_3$ (96)
3	**9c**, R = (*p*-OCH$_3$)Ph	**15c**, R′ = OCH$_3$, R″ = H (86)
4	**9d**, R = 2-furyl	**16** (96)

Our proposed mechanism to explain the formation of silyl ethers **13**−**16** is depicted for generic silyl vinylketene **17** in Scheme 2. Initial 6π electrocyclic ring closure of **17** to cyclohexadienone **18** is followed by a 1,5-H shift to **19** and subsequent 1,3-silyl migration to **20**. The relief of steric strain may provide the driving force for the unexpected 1,5-H shift, as the resultant conversion of the silyl-bearing carbon from sp^2 to sp^3 hybridization in **19** provides an increase in conformational flexibility in the newly generated ring system. The subsequent 1,3-silyl migration is precedented,[4b] including related examples observed in Dötz benzannulation reactions.[9]

Scheme 2. Proposed Benzannulation Mechanism



In summary, we have developed an expedient protocol for the generation of silyl vinylketenes from the thermal reaction of Fischer carbene complexes and silyl substituted phenylacetylenes and demonstrated their ability to participate in 6π electrocyclic ring closures. The initial chromium-complexed silyl vinylketene products obtained by this route are highly stable, but the benzannulation process can be induced either by removal of the chromium fragment or by heating at elevated temperatures in acetonitrile. With either protocol, the electrocyclic ring closure is accompanied by 1,3-silyl migration, affording aromatic products bearing substitution patterns otherwise unattainable through the Dötz reaction.

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Supporting Information Available: Experimental procedures and complete spectral characterization data for compounds **8**−**16** and crystal structure data for **8a**. This material is available free of charge via the Internet at http://pubs.acs.org.

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(8) Isomerizations of this type are well documented for bis-silyl ketenes and silyl allenylketenes and by analogy are presumed to take place through a reversible 4π electrocyclic ring closure. Further details of this process will be reported elsewhere.

(9) a) Chamberlin, S.; Wulff, W. D. *J. Org. Chem.* **1994**, *59*, 3047. (b) Fogel, L.; Hsung, R. P.; Wulff, W. D.; Sommer, R. D.; Rheingold, A. L. *J. Am. Chem. Soc.* **2001**, *123*, 5580.