Registry No. **1a**, 420-12-2; **1b**, 7117-41-1; **1c**, 1782-89-4; **2a**, 287-27-4; **2b**, 13153-11-2; **2c**, 5687-92-3; **3a**, 110-01-0; **3b**, 1600-44-8; **3c**, 126-33-0; **4a**, 1613-51-0; **4b**, 4988-34-5; **4c**, 4988-33-4; **5a**, 4753-80-4; **5b**, 6251-34-9; **5c**, 6251-33-8; **6a**, 6572-99-2; **6b**, 696-73-1; **6c**, 3142-87-8; **7a**, 408-32-2; **7c**, 75299-21-7; **8** (X = S), 6013-95-2; *cis*-**8** (X = SO), 15953-81-8; *trans*-**8** (X = SO), 15953-82-9; **8** (X = SO_2), 15953-83-0; **9** (X = S), 66810-25-1; *cis*-**9** (X = SO), 66809-92-5; *trans*-**9** (X = SO), 66810-23-9; **9** (X = SO_2), 66809-99-2; *cis*-**9** (X = SNTs), 66810-14-8; *trans*-**9** (X = S(O)NTs), 66809-97-0; **10** (X = S), 287-53-6; **10** (X = SO), 58816-63-0; **10** (X = SO_2), 60743-07-9; **11**, 74045-82-2; **12** (X = SO_2), 75299-22-8; **13** (X = SO_2), 22524-35-2; dimethyl sulfone, 67-71-0; bis(chloromethyl) sulfone, 37557-97-4; di-*n*-butyl sulfone, 598-04-9; diphenyl sulfone, 127-63-9; 3,3-dimethylthietane 1,1-dioxide, 27832-56-0; dimethyl sulfoxide, 67-68-5; 2,2,4,4-tetramethylthietane 1,1-dioxide, 75299-23-9; 2,2,4,4-tetramethylthietane, 75299-24-0.

Eric Block,* Ali A. Bazzi

Department of Chemistry
University of Missouri—St. Louis
St. Louis, Missouri 63121

Joseph B. Lambert, Steven M. Wharry

Department of Chemistry
Northwestern University
Evanston, Illinois 60201

Kenneth K. Andersen

Department of Chemistry
University of New Hampshire
Durham, New Hampshire 03824

Donald C. Dittmer, Bhalchandra H. Patwardhan

Department of Chemistry
Syracuse University
Syracuse, New York 13210

David J. H. Smith

Department of Chemistry
University of Leicester
Leicester, England LE1 7RH

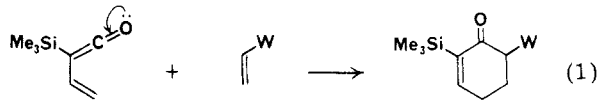
Received June 2, 1980

(Trimethylsilyl)vinylketene: A Stable Vinylketene and Reactive Enophile in [4 + 2] Cycloadditions

Summary: (Trimethylsilyl)vinylketene has been prepared by dehydrohalogenation of (*Z*)-2-(trimethylsilyl)-2-butenoyl chloride and shown to be a relatively stable compound which participates in Diels–Alder reactions as a reactive diene.

Sir: The recent extension of the Diels–Alder reaction to include highly functionalized dienes has greatly expanded the utility of this important synthetic method.[1] An objective of continuing interest in this area has been the development of vinylketene equivalents capable of participating as diene components in Diels–Alder reactions.[2] The tendency of vinylketenes to form only [2 + 2] cycloadducts with olefins[3] and the intrinsic instability of these substances[4] precludes their direct use as [4 + 2] enophiles. The availability of a generally effective synthon of this type would greatly facilitate the synthesis of cyclohexenone derivatives and phenolic compounds and could provide a new approach to the synthesis of anthracyclinone antitumor agents.

In this communication we describe a particularly simple enophilic vinylketene equivalent, (trimethylsilyl)vinylketene (**1**).[5] Our investigation of this compound was founded on the hypothesis that it would be a *relatively stable substance, inert to [2 + 2] cycloadditions,*[6] *and would participate in Diels–Alder reactions as a reactive diene.* It was further anticipated that the directing effect of the carbonyl group would dominate in controlling the regiochemical course of cycloadditions involving this diene (eq 1, where W is an electron-withdrawing group).[7]

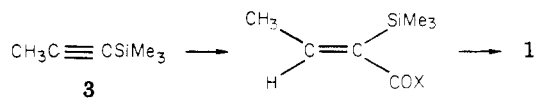


(1)

1 **2**

(Trimethylsilyl)vinylketene (**1**) was conveniently prepared as outlined in Scheme I. Treatment of 1-(trimethylsilyl)propyne (**3**)[8] with 1.1 equiv of diisobutylaluminum hydride (25 °C, 21 h) and 1.1 equiv of methyllithium (0 °C, 0.5 h) in ether–hexane,[9] followed by reaction of the resulting vinyl alanate with anhydrous

Scheme I



4, X = OH
5, X = O^-K^+
6, X = Cl

(1) For examples, see: (a) Danishefsky, S.; Kitahara, T.; Yan, C. F.; Morris, J. *J. Am. Chem. Soc.* **1979**, *101*, 6996; (b) Trost, B. M.; Vladuchick, W. C.; Bridges, A. J. *Ibid.* **1980**, *102*, 3554.

(2) (a) Carey, F. A.; Court, A. S. *J. Org. Chem.* **1972**, *37*, 4474. (b) Sonveaux, E.; Ghosez, L. *J. Am. Chem. Soc.* **1973**, *95*, 5417. (c) Corey, E. J.; Kozikowski, A. P. *Tetrahedron Lett.* **1975**, 2389. (d) Danishefsky, S.; McKee, R.; Singh, R. K. *J. Org. Chem.* **1976**, *41*, 2934. (e) Banville, J.; Brassard, P. *J. Chem. Soc., Perkin Trans. 1* **1976**, 1852. (f) Danishefsky, S.; Singh, R. K.; Gammill, R. B. *J. Org. Chem.* **1978**, *43*, 379. (g) Yamamoto, K.; Suzuki, S.; Tsuji, J. *Chem. Lett.* **1978**, 649. (h) Gillard, M.; T'Kint, C.; Sonveaux, E.; Ghosez, L. *J. Am. Chem. Soc.* **1979**, *101*, 5837.

(3) Payne, G. B. *J. Org. Chem.* **1966**, *31*, 718. Rey, M.; Dunkelblum, E.; Allain, R.; Dreiding, A. S. *Helv. Chim. Acta* **1970**, *53*, 2159. Holder, R. W.; Freiman, H. S.; Stefanchik, M. F. *J. Org. Chem.* **1976**, *41*, 3303.

(4) For the isolation and characterization of a sterically shielded *s-trans*-vinylketene, see: Wuest, J. D.; Madonik, A. M.; Gordon, D. C. *J. Org. Chem.* **1977**, *42*, 2111.

(5) While this investigation was in progress a report appeared on the preparation of a mixture of tricarbonyl[4-methoxy-4-phenyl-2,3-bis(trimethylsilyl)-1,3-butadienone]chromium and its metal-free derivative. Spectral analysis revealed an orthogonal arrangement of the vinyl and ketene moieties in these compounds: Dötz, K. H. *Angew. Chem., Int. Ed. Engl.* **1979**, *18*, 954.

(6) (Trimethylsilyl)ketene itself is a remarkably stable liquid which does not react in [2 + 2] cycloadditions with olefins and 1,3-dienes, presumably as a consequence of the hyperconjugative influence of the trimethylsilyl substituent: Shchukovskaya, L. L.; Pal'chik, R. I.; Lazarev, A. N. *Dokl. Akad. Nauk. SSSR* **1965**, *164*, 357; Ruden, R. A. *J. Org. Chem.* **1974**, *39*, 3607; Brady, W. T.; Cheng, T. C. *Ibid.* **1977**, *42*, 732.

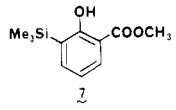
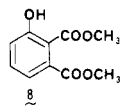
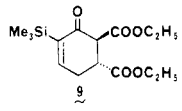
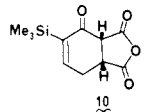
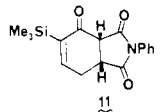
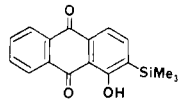
(7) The trimethylsilyl substituent exerts only a weak directing effect on the Diels–Alder reactions of 1- and 2-(trimethylsilyl) 1,3-dienes: Fleming, I.; Percival, A. *J. Chem. Soc., Chem. Commun.* **1976**, 681. Fleming, I.; Percival, A. *Ibid.* **1978**, 178; Batt, D. G.; Ganem, B. *Tetrahedron Lett.* **1978**, 3323; Jung, M. E.; Gaede, B. *Tetrahedron* **1979**, *35*, 621.

(8) Available from the Farchan Division of Story Chemical Corp.

(9) Eisch, J. J.; Damasevitz, G. A. *J. Org. Chem.* **1976**, *41*, 2214. Uchida, K.; Utimoto, K.; Nozaki, H. *Ibid.* **1976**, *41*, 2215.

0022-3263/80/1945-4810$01.00/0

Table I. Diels-Alder Reactions of (Trimethylsilyl)vinylketene

dienophile	equiv of 1	conditions	adduct	mp, °C	% yield
methyl propiolate	3.7	toluene, 95 °C, 63 h	 7		45
dimethyl acetylenedicarboxylate	1.3	chloroform, 40 °C, 25 h	 8		60[a]
diethyl fumarate	2.2	toluene, 95 °C, 38 h	 9	80-81.5	62
maleic anhydride	1.3	chloroform, 25 °C, 12 h	 10	95-100	89[b]
N-phenylmaleimide	2.0	chloroform, 40 °C, 24 h	 11	146.5-147.5	74
naphthoquinone	2.5	chloroform, 60 °C, 41 h	 12	153	28[c]

[a] Obtained after treatment of the initial adduct with CF_3CO_2H in chloroform at 55 °C for 23 h. The position of the trimethylsilyl group in the cycloadduct could not be determined with certainty by NMR. [b] Yield determined by NMR. Analytically pure material could not be obtained without partial decomposition. [c] The crude product was exposed to air in 5% KOH-EtOH (25 °C, 1 h) prior to isolation.

carbon dioxide,[10] furnished (*Z*)-2-(trimethylsilyl)-2-butenoic acid (**4**): mp 64–65 °C; 68% yield.[11,12] Exposure of the potassium salt of this acid (**5**) to 1.1 equiv of oxalyl chloride in pentane containing a catalytic amount of dimethylformamide (0–25 °C, 1.5 h) then produced a mixture of the acid chloride **6** and its geometric isomer which was dehydrohalogenated without further purification. A solution of **6** in pentane was added dropwise over 1–2 h to a solution of 0.9 equiv of triethylamine in pentane at 25 °C, and the resulting mixture was heated at reflux for 15–24 h and then filtered with the aid of pentane. Solvent was evaporated at −50 °C (0.5 mm), and the residue was distilled at 25 °C (1 mm) and then again at 5 mm into a receiver cooled at −78 °C. In this manner a yellow-green liquid was obtained in 39–50% overall yield (from **4**) which exhibited spectral characteristics consistent with those expected for (trimethylsilyl)vinylketene (**1**): IR ($CDCl_3$) 2085, 1610 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.25 (s, 9 H), 4.82 (dd, 1 H, J = 1, 10 Hz), 4.88 (dd, 1 H, J = 1, 17 Hz), 5.92 (dd, 1 H, J = 10, 17 Hz); ^{13}C NMR ($CDCl_3$) δ −1.0 (q), 22.3 (s), 111.6 (t), 125.1 (d), 183.7 (s); UV (isooctane) λ_{max} 233 nm (ϵ 9000). The purified vinylketene can be stored in solution at 0 °C without appreciable decomposition for 1–2 weeks.

(Trimethylsilyl)vinylketene undergoes Diels–Alder reactions with a variety of olefinic and acetylenic dienophiles (Table I).[12] The reactivity of this enophile compares favorably with previously reported vinylketene equivalents.[2,13] Reaction of **1** with methyl propiolate produced a single cycloadduct (**7**) with the expected regiochemical orientation.[14] Protodesilylation of this adduct with trifluoroacetic acid in chloroform (25 °C, 24 h) afforded methyl salicylate in 78% yield. Dimethyl acetylenedicarboxylate was converted to dimethyl 3-hydroxyphthalate (**8**)[15] in a similar fashion. Diels–Alder addition of **1** to olefinic dienophiles furnishes cyclohexenone derivatives (products **9**–**11**).[16] Addition of **1** to naphthoquinone afforded a mixture of several cycloadducts which could be oxidized to a single anthraquinone (**12**).

The presence of the trimethylsilyl group in the Diels–Alder adducts should facilitate further synthetic elaboration of these compounds. For example, regiospecific electrophilic substitution of arylsilanes permits the for-

(10) Zweifel, G.; Steele, R. B. *J. Am. Chem. Soc.* **1967**, *89*, 2754.

(11) Conditions for this transformation were developed with the assistance of Gary W. Ashley.

(12) Isolated yields of purified products. Infrared, 250-MHz ^1H NMR, ^{13}C NMR, and mass spectral data were fully consistent with the assigned structures. High-resolution mass spectra or combustion analyses were obtained for all new compounds.

(13) Significant decomposition of **1** occurs above 120 °C, preventing successful cycloaddition to less reactive dienophiles. Diels–Alder reaction of **1** with ethyl acrylate and α-chloroacrylonitrile could not be achieved.

(14) The isomeric cycloadduct could not be detected in the crude reaction product by NMR. The structure of **7** was established by NMR (250 MHz, $CDCl_3$) [δ 7.86 (dd, 1 H, J = 2.0, 7.9 Hz), 7.57 (dd, 1 H, J = 2.0, 6.9 Hz), 6.88 (dd, 1 H, J = 6.9, 7.9 Hz), 3.95 (s, 3 H), and 0.34 (s, 9 H)] and by its conversion to methyl salicylate.

(15) Gladysz, J. A.; Lee, S. J.; Tomasello, J. A. V.; Yu, Y. S. *J. Org. Chem.* **1977**, *42*, 4170.

(16) Cycloadducts **10** and **11** are assumed to possess cis ring fusions. For **10**: ^1H NMR (250 MHz, $CDCl_3$) δ 7.18 (dd, 1 H, J = 2.6, 5.5 Hz), 4.00 (d, 1 H, J = 9.6 Hz), 3.79 (ddd, 1 H, J = 2.2, 8.5, 9.6 Hz), 3.05 (ddd, 1 H, J = 2.2, 5.5, 19.5 Hz), 2.73 (ddd, 1 H, J = 2.6, 8.5, 19.5 Hz), 0.15 (s, 9 H). For **11**: δ 7.34–7.48 (m, 3 H), 7.18–7.22 (m, 2 H), 7.12 (dd, 1 H, J = 2.6, 5.9 Hz), 3.92 (d, 1 H, J = 8.6 Hz), 3.58 (ddd, 1 H, J = 1.8, 8.3, 8.6 Hz), 3.07 (ddd, 1 H, J = 1.8, 5.9, 18.8 Hz), 2.63 (ddd, 1 H, J = 2.6, 8.3, 18.8 Hz), 0.14 (s, 9 H).

mation of new carbon–carbon and carbon–heteroatom bonds at the site of the silicon substituent.[17] The chemistry of the α-(trimethylsilyl)cyclohexenone system and the application of this methodology in natural product synthesis are currently under investigation in our laboratory.[18]

Registry No. 1, 75232-81-4; 3, 6224-91-5; 4, 75232-82-5; 5, 75232-83-6; 6, 75232-84-7; 7, 75232-85-8; 8, 36669-02-0; 9, 75232-86-9; 10, 75232-87-0; 11, 75232-88-1; 12, 75232-89-2; methyl salicylate, 119-36-8; methyl propiolate, 554-12-1; dimethyl acetylenedicarboxylate, 762-42-5; diethyl fumarate, 623-91-6; maleic anhydride, 123-33-1; *N*-phenylmaleimide, 941-69-5; naphthoquinone, 130-15-4.

(17) Chan, T. H.; Fleming, I. *Synthesis* **1979**, 761.

(18) Support of this work by the National Institutes of Health is gratefully acknowledged.

Rick L. Danheiser,* Howard Sard

Department of Chemistry
Massachusetts Institute of Technology
Cambridge, Massachusetts 02139

Received September 24, 1980