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THE REGIOCHEMICAL COURSE OF [2+2] CYCLOADDITIONS OF DICHLOROKETENE WITH VINYL- AND ALKYNYLSILANES

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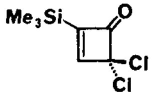
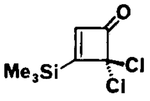
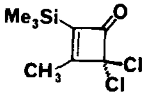
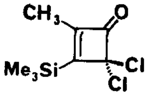
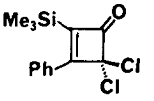
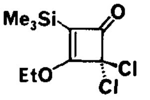
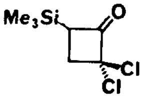
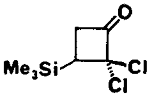
Summary: Alkynylsilanes undergo regioselective [2+2] cycloadditions with dichloroketene in good yield; the regiochemical course of these reactions is in accord with frontier molecular orbital predictions.

Cycloaddition reactions of vinyl- and alkynylsilanes have been employed in expeditious routes to a variety of silicon-substituted carbocyclic and heterocyclic compounds. Recent investigations have explored the synthetic potential of Diels-Alder reactions involving silicon-substituted dienes[2,3] and dienophiles,[3c,4] [2+2] cycloadditions of silylketenes,[5] photocycloadditions using silyl derivatives,[6] and the application of organosilane dipolarophiles in 1,3-dipolar cycloaddition reactions.[7] In addition to their synthetic utility, regiochemical features of these cycloadditions have attracted considerable interest. Silyl substituents have the capacity to function as both σ-donors and π-acceptors, and their effect in controlling the regiochemical course of cycloadditions is often not easily predicted.

In this communication we describe the successful [2+2] cycloaddition of dichloroketene with several alkynylsilanes, as well as the unexpectedly high regioselectivity observed in the reaction of (trimethylsilyl)acetylene itself. This investigation was carried out in connection with our interest in 2-(trimethylsilyl)cyclobutenone derivatives as precursors to (trimethylsilyl)vinylketenes. The application of the latter compounds as reactive dienes in Diels-Alder reactions is currently under study in our laboratory.[2]

Relatively few examples of the addition of dichloroketene to alkynes have previously been reported. These reactions generally proceed in poor yield when the ketene is generated via the dehydrohalogenation of dichloroacetyl chloride[8] or by thermal decomposition of sodium trichloroacetate.[8a] In this study we prepared dichloroketene by the zinc-promoted reductive dechlorination of trichloroacetyl chloride, as recently recommended by Hassner[9] and Brady[10] for cycloadditions employing relatively unreactive ketenophiles. Table I presents our results. In a typical reaction, a solution of 2.0 mmol of trichloroacetyl chloride in 25 mL of diethyl ether was added dropwise over 3 h to a mixture of 1.0 mmol of alkynylsilane and 6.0-6.6 equiv of activated zinc[10] in 15 mL of ether at reflux. The resulting mixture was heated at reflux for 16-18 h (only 1 h in the case of

Table I. [2+2] Cycloadditions of Dichloroketene and Vinyl- and Alkynylsilanes

Ketenophile	Cycloadducts		Ratio	%Yield
$Me_3SiC\equiv CH$	 1	 2	1:99	67
$Me_3SiC\equiv CCH_3$	 3	 4	64:36	74
$Me_3SiC\equiv CPh$[18]	 5	(mp 77-78°C)		93
$Me_3SiC\equiv COEt$[19]	 6	(mp 56-57°C)		86
$Me_3SiCH{=}CH_2$	 7	 8	18:82	37

ethoxy(trimethylsilyl)acetylene), cooled to room temperature, and filtered with the aid of ether. The filtrate was washed with $NaHCO_3$ solution, water, and saturated NaCl solution, dried over anhydrous Na_2SO_4, filtered, and concentrated. Ratios of regioisomeric cycloadducts were determined by 250 MHz ^1H NMR analysis of the crude reaction products; yields refer to material purified by column chromatography on silica gel.[11]

Remarkably, reaction of dichloroketene with (trimethylsilyl)acetylene leads almost exclusively to a single cycloadduct (2). The two regioisomeric products were easily distinguished by the ^1H NMR chemical shifts of their vinyl protons (δ 8.45 in 1, 6.68 in 2). The high regioselectivity exhibited in this [2+2] cycloaddition is notable in view of the modest regiocontrol exerted by silicon substituents in Diels-Alder reactions.[3c,g-i,k]

Methyl, phenyl, and ethoxy are more powerful directing groups than trimethylsilyl in controlling the regiochemical course of these [2+2] cycloadditions (see Table I). In the latter two cases only a single cyclobutenone could be detected in the crude reaction product. Finally, addition of dichloroketene to vinyltrimethylsilane resulted in the formation of two cycloadducts in a ratio of 82:18.[12] This reaction is reported to fail when the ketene is generated by dehydrohalogenation.[13] Column chromatography on silica gel furnished the major product 8 in 37% yield, while the minor isomer (7) underwent decomposition as would be expected for an α-silylcyclobutanone derivative.[14a] The identity of 8 was established unambiguously by its conversion to 3-(trimethylsilyl)cyclobutanone[14] upon dechlorination with tri-*n*-butyltin hydride (cat. AIBN, cyclohexane, 80°C, 6 h; 79% yield).

Electrophilic reagents attack alkynylsilanes exclusively at the silicon-bearing carbon.[15] The regiospecificity of these electrophilic substitution reactions is generally attributed to the preferential formation of an intermediate vinyl cation stabilized by the silicon "β-effect."[15b] However, the reaction of (trimethylsilyl)acetylene and dichloroketene occurs via attack of the electrophilic ketene carbonyl at C_2 of the alkynylsilane. The regiochemical course of this concerted [2+2] cycloaddition is best understood employing frontier molecular orbital considerations.[16] FMO theory predicts that the most important interaction in these cycloadditions involves the ketene LUMO and ketenophile HOMO. The regiochemistry of the reaction is then determined by bonding between the ketene carbonyl and the ketenophile carbon with the largest coefficient in the HOMO. STO-3G ab initio calculations indicate that the largest coefficient in the HOMO of $H_3SiC\equiv CH$ appears at C_2,[17] implying that the cyclobutenone 2 should be the predominant product in the reaction of dichloroketene with (trimethylsilyl)acetylene, as is in fact observed. However, it should be noted that the influence of the silyl group can be overwhelmed by powerful directing substituents such as phenyl and alkoxy.

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References and Notes

1. Alfred P. Sloan Research Fellow, 1981-1983.
2. R.L. Danheiser and H. Sard, *J. Org. Chem.*, 45, 4810 (1980).
3. (a) M. Petrzilka and J.I. Grayson, *Synthesis*, 753 (1981); (b) S.I. Sadykh-Zade and A.D. Petrov, *Zh. Obshch. Khim.*, 28, 1542 (1958); (c) C.S. Kraihanzel and M.L. Losee, *J. Am. Chem. Soc.*, 90, 4701 (1968); (d) A.J. Ashe, *Ibid.*, 92, 1233 (1970); (e) Y.A. Ustynyuk, A.V. Kisin, I.M. Pribytkova, A.A. Zenkin, and N.D. Antonova, *J. Organomet. Chem.*, 42, 47 (1972); (f) A.R. Chamberlin, J.E. Stemke, and F.T. Bond, *J. Org. Chem.*, 43, 147 (1978); (g) I. Fleming and J.P. Michael, *J. Chem. Soc., Chem. Commun.*, 245 (1978); (h) D.G. Batt and B. Ganem, *Tetrahedron Lett.*, 3323 (1978); (i) M.E. Jung and B. Gaede, *Tetrahedron*, 35, 621 (1979); (j) W. Oppolzer, S.C. Burford, F. Marazza, *Helv. Chim. Acta*, 63, 555 (1980); (k) M.J. Carter, I. Fleming, and A. Percival, *J. Chem. Soc., Perkin Trans. I*, 2415 (1981); and references cited therein.

4. (a) H.G. Kuivila and C.R. Warner, J. Org. Chem., 29, 2845 (1964); (b) R.F. Cunico, Ibid., 36, 929 (1971); (c) D.Seyferth and D.L. White, J. Organomet. Chem., 34, 119 (1972); (d) L. Birkofer and R. Stilke, Ibid., 74, C1 (1974); (e) M.G. Voronkov, T.D. Burnashova, O.G. Yarosh, N.V. Komarov, Izv. Akad. Nauk SSSR, Ser. Khim., 2621 (1974); (f) T.H. Chan and D. Massuda, J. Am. Chem. Soc., 99, 936 (1977); (g) L.A. Paquette and R.V. Williams, Tetrahedron Lett., 4643 (1981); (h) K. Tamao, J.-I. Yoshida, M. Akita, Y. Sugihara, T. Iwahara, and M. Kumada, Bull. Chem. Soc. Jpn., 255 (1982); and references cited therein.
5. (a) G.S. Zaitseva, Y.I. Baukov, V.V. Mal'tsev, and I.P. Lutsenko, Zh. Obshch. Khim., 44, 1415 (1974); (b) G.S. Zaitseva, N.G. Vinokurova, and Y.I. Baukov, Zh. Obshch. Khim., 45, 1398 (1975); (c) W.T. Brady and R.A. Owens, Tetrahedron Lett., 1553 (1976).
6. (a) L. Birkofer and D. Eichstädt, J. Organomet. Chem., 145, C29 (1978); (b) C. Shih, E.L. Fritzen, and J.S. Swenton, J. Org. Chem., 45, 4462 (1980).
7. (a) L. Birkofer in "Organometallic Chemistry Reviews", Vol. 9 , D. Seyferth, Ed., Elsevier, Amsterdam, 1980, p. 295-326, and references cited therein; (b) I.G. Kolokoltseva, V.N. Chistokletov, and A.A. Petrov, Zh. Obshch. Khim., 40, 2612 (1970); (c) R.F. Cunico and H.M. Lee, J. Am. Chem. Soc., 99, 7613 (1977); (d) A.R. Bassindale, A.G. Brook, P.F. Jones, and J.A.G. Stewart, J. Organomet. Chem., 152, C25 (1978); (e) A. Padwa and J.G. MacDonald, Tetrahedron Lett., 3219 (1982).
8. (a) E.V. Dehmlow, Chem. Ber., 100, 3829 (1967); (b) H. Knoche, Justus Liebigs Ann. Chem., 722, 232 (1969); (c) A. Krebs and H. Kimling, Ibid., 2074 (1974); (d) N. Morita, T. Asao, and Y. Kithara, Chem. Lett., 927 (1972); (e) H.N.C. Wong, F. Sondheimer, R. Goodin, and R. Breslow, Tetrahedron Lett., 2715 (1976).
9. L.R. Krepski and A. Hassner, J. Org. Chem., 43, 2879 (1978). This method has also been successfully applied to cycloadditions involving simple alkynes: A. Hassner and J. Dillon, Synthesis, 689 (1979).
10. D.A. Bak and W.T. Brady, J. Org. Chem., 44, 107 (1979).
11. Infrared, ^{1}H and ^{13}C NMR, and mass spectral data were fully consistent with the assigned structures. Representative spectral data: 2: IR (tf) 3080,2960, 2900,1790,1250,1080,1045,1000,840, and 755 cm^{-1}; ^{1}H NMR (270 MHz, CDCl$_3$) δ 6.68 (s, 1 H) and 0.38 (s, 9 H); ^{13}C NMR (22.5 MHz, CDCl$_3$) δ 191.3,180.0, 148.7,95.0, and -1.9; 3: ^{1}H NMR δ 2.34 (s, 3 H) and 0.23 (s, 9 H); ^{13}C NMR δ 186.8, 182.7,154.9,93.6,12.0, and -2.1; 4: ^{1}H NMR δ 1.93 (s, 3 H) and 0.41 (s, 9 H); ^{13}C NMR δ 183.7,182.6,160.8,94.3,10.4, and -1.4; 5: ^{1}H NMR δ 7.94-7.98 (m, 2 H), 7.61-7.63 (m, 3 H), and 0.42 (s, 9 H); ^{13}C NMR δ 182.9,180.5, 150.7,133.1,130.1,129.2,128.1,91.2, and -1.6; 6: IR (CDCl$_3$) 2950,1765,1575, 1460,1370, and 1340 cm^{-1}; ^{1}H NMR δ 4.63 (q, 2 H, J=7.1), 1.50 (t, 3 H, J= 7.1), and 0.18 (s, 9 H); ^{13}C NMR δ 184.9,180.6,127.6,87.5,70.2,14.9, and -1.7; 8: IR (tf) 2955,1810 cm^{-1}; ^{1}H NMR δ 3.45 (dd, 1 H, J=12.1, 17.3), 3.16 (dd, 1 H, J=9.9,17.3), 2.37 (dd, 1 H, J=9.9, 12.1), and 0.20 (s, 9 H); ^{13}C NMR δ 192.5, 89.3, 44.6, 37.5, and -2.2; 7: ca. 3.45 (1 H, obscured by 8), 2.93 (dd, 1 H, J=11.7, 13.2), 2.62 (dd, 1 H, J=8.3, 13.2), and 0.11 (s, 9 H).
12. The possibility that the labile α-silyl ketone 7 partially decomposed during the reaction cannot be excluded with certainty.
13. W.T. Brady and T.C. Cheng, J. Org. Chem., 42, 732 (1977).
14. (a) W.T. Brady and T.C. Cheng, J. Organomet. Chem., 137, 287 (1977); (b) G.S. Zaitseva, G.S. Bogdanova, Y.I. Baukov, and I.F. Lutsenko, Zh. Obshch. Khim., 48, 131 (1978)
15. (a) T.H. Chan and I. Fleming, Synthesis, 761 (1979); (b) E. Colvin, "Silicon in Organic Synthesis", Butterworths, London, 1981.
16. (a) R. Sustmann, A. Ansmann, and F. Vahrenholt, J. Am. Chem. Soc., 94, 8099 (1972); (b) N.D. Epiotis, Ibid., 94, 1924 (1972); (c) K.N. Houk, R.W. Strozier, and J.A. Hall, Tetrahedron Lett., 897 (1974); (d) K.N. Houk, Acc. Chem. Res., 8, 361 (1975); see also (e) I. Fleming, "Frontier Orbitals and Organic Chemical Reactions", Wiley, N.Y., 1976, p.143-7.
17. We are grateful to Prof. K.N. Houk and Dr. Nelson G. Rondan (Univ. of Pittsburgh) for carrying out these calculations.
18. Prepared by the method of R.A. Benkeser and R.A. Hickner, J. Am. Chem. Soc., 80, 5298 (1958).
19. Prepared according to the procedure of R.A. Ruden, J. Org. Chem., 39, 3607 (1974).

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