$$R\overset{\beta}{C}{\equiv}\overset{\alpha}{C}{-}OSi \leftrightarrow RC^{-}{=}C{=}O^{+}Si$$
19

$$R\overset{\beta}{C}{\equiv}\overset{\alpha}{C}{-}OTs \leftrightarrow RC^{-}{=}C{=}O^{+}Ts$$
17

$$R\overset{\beta}{C}{\equiv}\overset{\alpha}{C}OR' \leftrightarrow RC^{-}{=}C{=}O^{+}R'$$
26

Likewise, ketenes **21** and **22** show characteristic, very strong IR absorptions at 2050–2070 cm^{-1} due to the ketene vibrations. Their mass spectra show respectable molecular ions and appropriate fragmentation patterns. Proton and ^{13}C NMR are in concert with the proposed structures and the C=C=O signals at 16–23 and 175–181 ppm are particularly characteristic for ketenes.

Hence, there is no doubt about the identity of these stable, readily isolable siloxyalkynes and ketene derivatives. Therefore, alkynolates, like enolates, can react via O-alkylation (silylation) or C-alkylation,[5-7] although at the moment we neither understand nor can we control the exact site of reaction. In analogy with enolate chemistry we expect that the counterion, solvent, complexing agents, etc. play a crucial role in the control of site selection and these factors as well as the rich chemistry we expect from alkynolates are under investigation.

In summary, we have developed a simple, general means of alkynolate generation from readily available alkynyl tosylates. Reaction with t-BuMe$_2$SiCl results in little-known[12] stable, novel siloxyalkynes, whereas trapping with R$_3$GeCl or R$_3$SnCl gives C-alkylation and stable ketenes as products. The full scope of alkynolate chemistry will be the subject of future reports.

Acknowledgment. Financial support by the National Cancer Institute of the NIH (CA16903) is gratefully acknowledged.

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(13) Levy, G. T.; Lighter, R. L.; Nelson, G. L. *Carbon-13 Nuclear Magnetic Resonance Spectroscopy*, 2nd ed.; Wiley: New York, 1980; pp 90–95.

Ynol Silyl Ethers via O-Silylation of Ester-Derived Ynolate Anions

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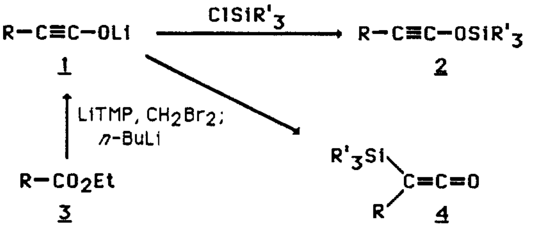
Received July 14, 1986

Herein we report that lithium ynolate anions **1**, derived from esters **3** using our previously described homologation method,[2] react with chlorotrialkylsilanes on oxygen to afford silyl ynol ethers **2**. This represents the first silylation of ynolate anions on oxygen,[3] in contrast to literature reports[4] in which reactions with chlorotrimethylsilane resulted in formation of only the corresponding ketenes (**4**). In our hands, chlorotrimethylsilane treatment of ynolate anion **1** (R = CH$_2$CH$_2$Ph) in THF/hexane at −78 °C, followed by warming to room temperature, similarly afforded ketene **4** (R = CH$_2$CH$_2$Ph, R′ = SiMe$_3$; IR 2080 cm^{-1}); however, when a solution of the same ynolate was treated with chlorotrimethylsilane at −78 °C, but then diluted with pentane at −78 °C, and quenched into aqueous bicarbonate without warming, silyl ynol ether **2** (R = CH$_2$CH$_2$Ph, R′ = SiMe$_3$; IR 2280 cm^{-1}) was obtained along with ketene **4** (in a ratio of about 2:1). It appears that silylation by ClSiMe$_3$ had occurred kinetically on oxygen to afford ynol ether **2**, but upon warming the reaction mixture in the first case, isomerization to the more stable ketene **4** had occurred. Previous workers apparently observed only the thermodynamic (ketene) products from ynolate anion silylation.



Unfortunately, our attempts to purify the very sensitive trimethylsilyl ynol ether **2** (R = CH$_2$CH$_2$Ph) were unsuccessful. It seemed to us that more bulky silylating reagents might also react kinetically with ynolate anions on oxygen but without subsequent rearrangement to ketene products. The literature had recently shown that ynol silyl ethers **2** were indeed thermally stable when a triisopropylsilyl or *tert*-butyldimethylsilyl group was attached[5] (in contrast to the triethylsilyl derivatives[5a]). It was gratifying to find, therefore, that quenching solutions of ynolate anion **1** (R = CH$_2$CH$_2$Ph) with either chlorotriisopropylsilane or chloro-*tert*-butyldimethylsilane afforded exclusively the ynol silyl ether products **2**, and, moreover, if excess chlorosilane was removed in vacuo from the crude product after workup, the ynol ethers could be purified by rapid flash chromatography on silica gel to afford the triisopropylsilyl and *tert*-butyldimethylsilyl ynol ethers (R = CH$_2$CH$_2$Ph) in 66% and 53% yield, respectively.

Triisopropylsilyl ynol ethers are expected to be less sensitive than the *tert*-butyldimethylsilyl analogues.[6] Since we sought a stable class of silyl ynols as reagents for subsequent studies, the triisopropylsilyl compounds were selected as targets for testing the generality of this new synthetic approach. Several ynolate anions, prepared from esters, were therefore treated with chlorotriisopropylsilane to afford ynol ethers as indicated in Table I.

The method[7] proved successful for preparing ynols **2** having R groups attached at primary, secondary, tertiary, alkenyl, and aryl carbon centers, as well as for functionalized R groups derived from lactone starting materials. While the yields were moderate (50–74%), the directness of this "one-pot" conversion of esters into triisopropylsilyl ynol ethers (i.e., **3** → **1** → **2**), coupled with its generality, should serve to make it an important method for

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(1) Smith Kline & French Postdoctoral Research Scientist (a) 1985–1986, (b) 1983–1985.

(2) Kowalski, C. J.; Haque, M. S.; Fields, K. W. *J. Am. Chem. Soc.* **1985**, *107*, 1429–1430.

(3) Near the conclusion of this work, we learned from Professor Peter Stang that he and his co-workers had independently observed silylation of ynolate anions on oxygen. His results are reported in the preceding paper in this issue. We thank Professor Stang for sharing this information prior to publication.

(4) (a) Hoppe, I.; Schollkopf, U. *Justus Liebigs Ann. Chem.* **1979**, 219–226. (b) Woodburgy, R. P.; Long, N. L.; Rathke, M. W. *J. Org. Chem.* **1978**, *43*, 376.

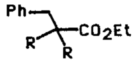
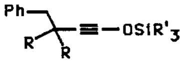
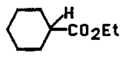
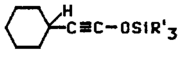
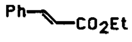
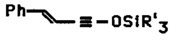
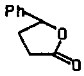
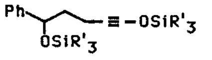
(5) (a) Maas, G.; Bruckmann, R. *J. Org. Chem.* **1985**, *50*, 2801–2802. (b) Dr. Michael Pirrung has informed us that his previously reported preparation of some ynol silyl ethers was in error. For that report see: Pirrung, M. C.; Hwu, J. R. *Tetrahedron Lett.* **1983**, *24*, 565–568.

(6) Cunico, R. F.; Bedell, L. *J. Org. Chem.* **1980**, *45*, 4797–4798.

(7) In a typical procedure, performed under N$_2$, 4.4 mmol of 2.5 M n-butyllithium solution in hexane was added dropwise to a stirred solution of 4.8 mmol of 2,2,6,6-tetramethylpiperidine in 6 mL of THF with ice bath cooling. This mixture was then cooled with a −78 °C (dry ice/acetone) bath and added dropwise via syringe to a solution of 4.4 mmol of dibromomethane in 6 mL of THF, cooled with a −78 °C bath. After 5 min, a solution of 2.0 mmol of starting ester **3** in 5 mL of THF was added dropwise, and 10 min later a solution of 10 mmol of 2.5 M n-butyllithium in hexane was added dropwise. The −78 °C bath was replaced with a 30 °C water bath for 30 min and then returned, after which 10 mmol of chlorotriisopropylsilane was added. The temperature was raised to 0 °C (room temperature for **5b** and **13**) and stirring was continued for 1.5–24 h (see Table I). The mixture was diluted with 200 mL of petroleum ether and then washed with three 50-mL portions of aqueous sodium bicarbonate solution and two 50-mL portions of water. After drying over MgSO$_4$, removal of the solvent in vacuo, and removal of remaining chlorosilane under high vacuum, the residue was passed through a silica gel (15 g/g) flash column and eluted with 0.5% ether in petroleum ether (<5 min residence time). Evaporation of solvent in vacuo then afforded pure product. Some modifications of the reagent amounts were required for certain esters as previously discussed for simple homologation.[2]

0002-7863/86/1508-7127$01.50/0

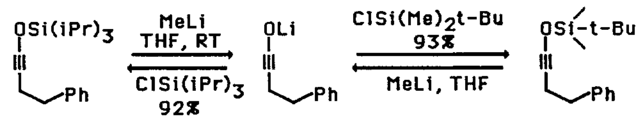
Table I.

Starting Ester	Silyl Ynol Ether (time/yield)[a,b]
 5a (R=H) 5b (R=Me)	 6a (1.5 hr/66%) 6b (18 hr/71%)
 7	 8 (3.5 hr/68%)
 9	 10 (1.5 hr/50%)
$Ph{-}CO_2Et$ 11	$Ph{-}C{\equiv}C{-}OSiR'_3$ 12[5a] (1.5 hr/63%)
 13	 14 (24 hr/74%)

[a] R' = *i*-Pr. [b] Silylation time/yield of purified material after flash chromatography; satisfactory analytical and spectral data for all products is presented in the supplementary material.

the synthesis of these little-studied intermediates.

Along with the fact that silyl ynol ethers can now be easily prepared, we would also like to report that they can be cleaved by methyllithium to afford clean solutions of lithium ynolate anions. Both the triisopropylsilyl ynol **6a** and the *tert*-butyldimethylsilyl ynol **16** afforded the ynolate **15** with methyllithium in THF at room temperature. As expected, **6a** was cleaved more slowly than **16** (3.5 h vs. 30 min), but both afforded high yields of ynolate **15** as evidenced by silylation to the other silyl ynol ether (i.e., **6a** afforded **16** in 93% yield while **16** afforded **6a** in 92% yield). Silyl ynol **6a** was shown to be unchanged after a period of 2 weeks in hexane solution, and so these ethers effectively offer a means of "storing" ynolate anions, much as silyl enol ethers can be used to "store" ketone enolate anions. This ability to interconvert ynol silyl ethers and ynolate anions, coupled with their direct synthesis from simple ester precursors, now makes the study and utilization of these materials a much easier task. We are continuing to pursue the chemistry of ynolate anions and silyl ynol ethers in our labs.



6a 15 16

Acknowledgment. We thank Walter Johnson, of Analytical, Physical and Structural Chemistry at SK&F, for high-resolution mass spectra.

Supplementary Material Available: IR, NMR, and high-resolution mass spectral data for **6a,b**, **8**, **10**, **12**, **14**, and **16** (1 page). Ordering information is given on any current masthead page.

Reactions of Gas-Phase Dipositive Titanium Ions with Alkanes

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Received June 25, 1986

The chemical reactions of gas-phase atomic metal cations M^+,[1] metal cluster ions M_n^+,[2] mixed-metal cluster ions such as $FeCo^+$,[3] atomic metal anions M^-,[4] and metal anion complexes[5] are remarkable in their diversity. Here we report the first reactivity studies of a *dipositive* transition-metal ion, namely, Ti^{2+}. This is a highly energetic, open-shell species whose second ionization energy of 13.58 eV[6] exceeds the first ionization energy of most organic neutrals. The chemistry of Ti^{2+} with small alkanes in 0.4 torr of He is remarkably selective. The dominant reaction paths are completely different for CH_4 (collisional stabilization of dipositive adduct ions), C_2H_6 (hydride ion abstraction), and C_3H_8 (electron transfer).

The experiments are carried out in a fast flow reactor[7] equipped with a laser vaporization source of metal ions upstream; neutral reagent inlets for addition of small, calibrated flows of reactant gas midstream; and a quadrupole mass spectrometer which samples the flow through a 1-mm pinhole in a Mo disk downstream. For He buffer gas pressures below about 0.5 torr, we find that a Ti metal target produces Ti^{2+} ions almost exclusively, while at higher pressure Ti^+ becomes the dominant ion.[8] No Ti^{n+}, $n \geq 3$, is observed; if such species are created, they can charge transfer with He. Product ion mass spectra were obtained at alkane flows sufficiently small that the branching of the primary Ti^{2+} reaction is not perturbed by secondary reactions. The detection is about 5 times more sensitive to +2 ions than to +1 ions, so that total detected signal diminishes in reactions leading to +1 ions. Reaction rate constants were obtained from the logarithmic decay of the Ti^{2+} signal vs. calibrated alkane flow at fixed reaction length of 42 cm.[7]

Figure 1 shows the Ti^{2+} + alkane product ion mass spectra. All exothermic product channels form at least one Ti-containing ion whose charge and mass are directly determined.[9] The corresponding neutral and hydrocarbon ion products are inferred. Interference from alkane reactions with He^+, He_2^+, and metastable He^* (2^3S, 2^1S) created in the source produces large hydrocarbon ion signals which preclude direct determination of hydrocarbon ion products from the Ti^{2+} reactions. The only Ti^{2+} + CH_4 primary product definitely observed is the collisionally stabilized adduct ion $TiCH_4^{2+}$. Experiments at lower CH_4 pressure than used in Figure 1 show that ≥80% of the primary product is the adduct ion; small Ti^+ or TiH^+ signals (≤20%) could be obscured by higher cluster ions at m/q = 48 and 49. Additional sequential reactions form larger dipositive adduct ions $Ti(CH_4)_n^{2+}$, $n \leq 4$. The $n = 4$ species is relatively inert to further CH_4 addition. Impurity H_2O can readily substitute for at least one CH_4 unit in all of the adducts. The Ti^{2+} + C_2H_6 reaction yields the H^-

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(1) See, for example: Allison, J.; Ridge, D. P. *J. Am. Chem. Soc.*1979, *101*, 4998. Peake, D. A.; Gross, M. L.; Ridge, D. P. *J. Am. Chem. Soc.* **1984**, *106*, 4307. Mandich, M. L.; Halle, L. F.; Beauchamp, J. L. *J. Am. Chem. Soc.* **1984**, *106*, 4403. Elkind, J. L.; Armentrout, P. B. *J. Phys. Chem.* **1985**, *89*, 5626. Jacobson, D. B.; Freiser, B. S. *J. Am. Chem. Soc.* **1983**, *105*, 7484. Jones, R. W.; Staley, R. H. *J. Am. Chem. Soc.* **1982**, *104*, 1235 and references therein.

(2) Hanley, L.; Anderson, S. L. *Chem. Phys. Lett.* **1985**, *122*, 410. Ervin, K.; Loh, S. K.; Aristov, N.; Armentrout, P. B. *J. Phys. Chem.* **1983**, *87*, 3593.

(3) Jacobson, D. B.; Freiser, B. S. *J. Am. Chem. Soc.* **1984**, *106*, 5351; **1985**, *107*, 1581.

(4) Sallans, L.; Lane, K.; Squires, R. R.; Freiser, B. S. *J. Am. Chem. Soc.* **1983**, *105*, 6352. Sallans, L.; Lane, K. R.; Squires, R. R.; Freiser, B. S. *J. Am. Chem. Soc.* **1985**, *107*, 4379.

(5) Lane, K. R.; Squires, R. R. *J. Am. Chem. Soc.* **1985**, *107*, 6402. McDonald, R. N.; Chowkhury, A. K.; Jones, M. T. *J. Am. Chem. Soc.* **1986**, *108*, 3105.

(6) Moore, C. E. *Atomic Energy Levels*; N.B.S. Circular No. 467: Washington, DC, 1949.

(7) Tonkyn, R.; Weisshaar, J. C. *J. Phys. Chem.* **1986**, *90*, 2305. Tonkyn, R.; Weisshaar, J. C., unpublished results.

(8) It appears that the target produces predominantly Ti^{2+} when embedded in He, perhaps because the metastable He^* (2^1S) state at 20.6 eV and He^+ at 24.6 eV both have sufficient energy to *doubly* ionize Ti. The sum of the first two ionization energies of Ti is 20.4 eV. We suggest that above 0.5 torr, the ablated material is confined to sufficiently small volume that $Ti^{2+} + Ti \rightarrow 2Ti^+$ is efficient, whereas below 0.5 torr the Ti^{2+} ions escape the source region without colliding with a neutral Ti atom. There is some evidence that Ti^+ is lost more rapidly by diffusion than is Ti^{2+}.

(9) The stable Ti isotopes (natural abundances) are m/q = 46 (7.9%), 47 (7.3%), 48 (73.9%), 49 (5.5%), and 50 (5.3%). We typically do not entirely resolve the 2+ ion pattern centered at m/q = 24. The isotope pattern precludes the remote possibility of contamination of Mg^+ ions at m/q = 24.

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