an excited species, which decomposes to silanone or hydroxysilylene (HSiOH),¹⁴ also observed in these experiments.¹² Photodecomposition ($\lambda > 400$ nm) of HSiOH gives H₂ and SiO, eq 3.^{12,14}

$$HSiOH + h\nu \rightarrow SiO + H_2 \tag{3}$$

Either silanone or hydroxysilylene can react with additional O atoms, eq 4, to give silanoic acid:

$$H_2SiO + O \text{ or } HSiOH + O \rightarrow (HO)HSiO$$
 (4)

Silicic acid most likely involves a concerted reaction with both ozone photoproducts, eq 5, probably involving the hydroxysilylene intermediate.

$$SiH_4 + O(^1D) + O_2 \rightarrow H_2 + [HSiOH]^* + O_2$$

$$\rightarrow H_2 + (HO)_2SiO \qquad (5)$$

Acknowledgment. We gratefully acknowledge support for this research from the National Science Foundation and calculations performed by D. A. Dixon.

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Zirconium-Promoted Bicyclization of Enynes¹

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We wish to report that the reaction of ω -vinyl-1-silyl-1-alkynes (1) with a $Zr^{II}Cp_2$ reagent, where Cp is η^5 -C₅H₅, produces in excellent yields zirconabicyclic derivatives 2, which can be treated in situ with CO (ca. 1 atm) to produce in good yields the corresponding α -silvlcyclopentenones 3 (eq 1). Since α -silvl enones



are known to readily undergo conjugate addition² and regiospecific [2 + 2] photocycloaddition,³ 3 can serve as valuable intermediates for the synthesis of complex cyclopentanoids.

Although formation of zirconacycles by the reaction of Zr^{II}Cp₂ complexes has been reported repeatedly over the past decades,⁴ its scope has been mostly limited to those cases where symmetrical zirconacyclopentanes or zirconacyclopentadienes are products.5 Even more limited is the current scope in the literature of conversion of zirconacycles into cyclic ketones. Bercaw⁶ reports a

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(5) Bercaw reports the formation of zirconacyclopentenes by the reaction of $(\pi^2-C_5Me_5)_2ZrH_2$ with propyne (McDade, C.; Bercaw, J. E. J. Organomet. Chem. 1985, 279, 281). (b) Erker has described the formation of zirconaindan derivatives by the reaction of Cp₂Zr^{1V}Ph₂ with alkenes (Erker, G.; Kropp, K. J. Am. Chem. Soc. 1979, 101, 3660) and their carbonylation (Erker, G. Acc. Chem. Res. 1984, 17, 103).

clean conversion of η^5 -(C₅Me₅)₂Zr(CH₂)₄ into cyclopentanone, while Erker^{5b} describes formation of mixtures of carbocyclic products in carbonylation of a zirconaindan derivative. It may therefore be stated that the utility of the cyclization-carbonylation sequence as a synthetic tool for preparing bicyclic and polycyclic cyclopentanoids has not been well delineated.7

The operational simplicity of the transformation shown in eq 1 is indicated by the following representative procedure. 7-(Trimethylsilyl)hept-1-en-6-yne (10 mmol) and Cl₂ZrCp₂ (10 mmol) were added at 0 °C under nitrogen to a mixture of HgCl₂ (10 mmol), Mg^{4e} (100 mequiv), and THF. After 12 h at 25 °C the yellow-brown supernatent liquid was siphoned into a separate flask and treated with CO (1.1 atm) for 1 h at 0 °C. Quenching with 3 N HCl and pentane followed by the standard workup provided 2-(trimethylsilyl)bicyclo[3.3.0]oct-1(2)-en-3-one⁸ (3a)



in 55-65% isolated yield (65-75% by GLC). Similarly, the corresponding bicyclo[4.3.0] nonenone derivative 3b⁸ was obtained in comparable yield.

The intermediacy of 2 has been demonstrated by the following isolation and characterization of 2a. The yellow-brown supernatent liquid obtained as described above was evaporated, extracted with hexane, filtered through Celite under nitrogen, and evaporated to provide 90–95% pure 2a in ca. 90% yield: ¹H NMR (toluene- d_8 , Me_4Si) δ 0.11 (s, 9 H), 0.9–2.4 (m, 9 H), 5.78 (s, 5 H), 5.82 (s, 5 H); ¹³C NMR (toluene- d_8 , Me₄Si) δ 1.75, 20.89, 33.63, 38.50, 41.51, 43.09, 109.31, 110.45, 152.10, 156.32. Furthermore, protonolysis of 2a yielded $4a^8$ in 63% yield, while its treatement



with 2.5 equiv of I_2 (-78 to 25 °C) gave a diiodo derivative $5a^8$ in 61% yield. Likewise, $4b^8$ and $5b^8$ were obtained in comparable yields. Both 4 and 5 were obtained as essentially single stereoisomers (by ${}^{13}C$ NMR). The anticipated E stereochemistry for 4 was established by comparing the spectral data for 4a with those of an authentic sample prepared by an independent method,9 while retention of the alkene geometry in iodinolysis was assumed in assigning the Z geometry to 5. Formation of 5 not only further supports the intermediacy of 2, but also provides a novel entry into bicyclic compounds containing cyclobutenylsilanes. For example, treatment of **5b** with 1 equiv of *n*-BuLi¹⁰ in ether at -78°C cleanly produced 8-(trimethylsilyl)bicyclo[4.2.0]oct-1(8)-ene⁸ (6) in 70% yield. The corresponding reaction of 5a also gave 7,



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Table I. Zirconium-Promoted Bicyclization of Enynes

enyne (CH ₂ =CHR ¹ C=CZ)		zircona- cyclopentene		cyclopentenone	
\mathbf{R}^1	Z	time,ª h	yield, %	time, ^b h	yield, ^c %
-(CH ₂) ₃ -	SiMe ₃	12	95 ^d	1	55-65 (65-75)
-Me ₂ C(CH ₂),-	SiMe,	18	е	4	62
-CH ₂ Me ₂ CCH ₂ -	SiMe ₃	18	е	4	50
-(CH ₂) ₄ -	SiMe,	12	90-100 ^d	3	60
12		18	е	2	55

^a At room temperature. ^b At 0 °C. ^c Isolated yield. The number in parentheses is a GLC yield. d Isolated yield. The corresponding figure was not observed.

but the product was extensively contaminated with a couple of byproducts one of which presumably is 8.

While the full scope of the cyclization-carbonylation sequence is yet to be delineated, the experimental data summarized in Table I indicate that the method shows considerable promise as a synthetic tool. It should be noted that the required acyclic precursors are readily available in most cases. For example, various alkyl-substituted 7-silylhept-1-en-6-ynes (9) required for preparing 10 can be conveniently prepared via the Sakurai conjugate allylation¹¹ and conversion of methyl ketones into silylalkynes¹² (eq 2).



In conjugation with our other projects directed toward highly selective syntheses of exocyclic alkenes of biological interest, we sought a convenient route to bicyclo[3.3.0]oct-1(2)-en-3-one derivatives containing a stereodefined exocyclic alkenyl group in the C-7 position, such as 11. To this end, we prepared the required precursor 12^8 as an isomerically >97% pure substance in 50% yield from 1-(trimethylsilyl)-1,4-pentadiyne¹³ via Zr-catalyzed allylalumination¹⁴ with allyldiisobutylalane-Cl₂ZrCp₂ and methylation. No difficulty was encountered in converting 12 into isomerically >97% pure 11^8 in 55% yield (eq 3). Retention of configuration during the conversion of 12 into 11 is assumed.



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The scope of the bicyclization reaction and utilization of α silvlcyclopentenones are being investigated in detail.

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Lewis Acid Assisted Condensations between a 5-Methoxyisoxazolidine and Silicon-Based Nucleophiles: γ -Amino Alcohol Building Block in the Synthesis of Agroclavine I

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The Lewis acid assisted reactions of various storable nucleophiles (e.g., enol silyl ethers, allyl- and vinylsilanes, and stannanes) with onium ion intermediates formed by the reaction of a metal salt with an appropriate substrate (e.g., aldehydes, ketones, acetals, hemithioacetals, hemiaminals, thioacetals, and hemithioaminals) constitute a selective method of C-C bond formation which continues to grow in both popularity and practicality.¹



In further developing approaches to the ergot alkaloids,² we envisioned that one could obtain appropriately substituted precursors to the tetracyclic members of this family by carrying out Lewis acid assisted condensation reactions between an appropriately constituted 5-methoxyisoxazolidine and an enol silyl ether. Of course, such an isoxazolidine derivative could react through either the cyclic oxonium ion intermediate A or the acyclic oxonium ion species B (Scheme I). The formation of such oxonium

Scheme I



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