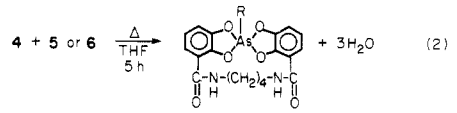
Again, as with **11**, we presume cis stereochemistry for the major isomer. Compound **3**, a benzo-substituted catechol, reacted with **5** or with **6** to give the five-coordinate organoarsenic compounds **14** and **15**, respectively. While no stereochemistry is involved in the formation of either **14** or **15**, it is important to note that substitution on the naphthyl ring is certainly possible for future attachment of this type of compound to a polymeric backbone. The pertinent ^{1}H NMR data (250 MHz, Me_2SO-d_6, Me_4Si) provided an upfield shift, as with the NMR spectra of compounds **7–13**, for the catechol ring protons of **14** and **15** when compared to **3**. Thus, **14** had the catechol protons (singlet) at 7.09 ppm, **15** catechol protons at 7.10 ppm, and **3** catechol protons at 7.12 ppm, indicative of the arsenic atoms influence on shifting, to higher fields, protons on catechol rings. A similar NMR result was obtained by Raymond et al.[8] for some gallium and rhodium catecholate complexes.

Our final ligand of interest, **4**,[9] was important to study, since it represented a model for a recently reported polymer of potential use for our future applications.[10] We chose **4** (4-LICAM) after making Dreiding models that clearly showed the central cavity being able to accommodate an arsenic atom (~3.58–3.63 Å, see Figure 1). Reaction of **4** with either **5** or **6** provided the intramolecular five-coordinate organoarsenic derivatives **16** and **17** (eq 2).



16 R = CH_3
17 R = Ph

The 250-MHz ^{1}H NMR and 70-ev MS (solid probe) data were consistent with the structures assigned. Notably, the mass spectra provided the parent ion and an ion resulting from a loss of the catechol group with a carbonyl attached. This was followed by a fragmentation of the $-CH_2CH_2NH$ groupings. For example, with **17** the MS ions of interest were the following: m/e 508 (M^+), 373 ($M - C_7H_{13}N_2O_3$), 331 ($M - C_9H_8NO_3$), and 287 ($M - C_{11}H_{13}N_2O_3$).

A typical procedure for the preparation of a five-coordinate organoarsenic catecholate derivative is described as follows for **9**.

In a 50-mL flask, equipped with condenser, drying tube, and Dean-Stark trap for water removal, was placed 1.05 g (5.21 mmol) of phenylarsonic acid and 1.29 g (10.42 mmol) of 3-methylcatechol (freshly sublimed) in 30 mL of benzene. The reaction mixture was refluxed for 5 h. The benzene was removed on a rotary evaporator and the compound recrystallized from carbon tetrachloride/methanol and dried under vacuum to give 1.88 g (91% yield) of **9**: mp 134–135 °C; EIMS (70 eV, solid probe) m/e 396 (M^+), 274, 197, 151, 106.[11] Anal. Calcd for $C_{20}H_{17}O_4As$: C, 60.6; H, 4.3. Found: C, 60.39; H, 4.46.

In future experiments, we hope to place several of our catechol derivatives in polymeric backbones to see if their reactivity remains in reactions with organoarsonic acids.

Acknowledgment. We wish to thank Drs. F. L. Weitl and K. N. Raymond for several samples of LICAM derivatives for evaluation and helpful suggestions during the initial stages of this subject. Helpful discussions with Drs. K. Irgolic and R. Zingaro are also acknowledged. We wish to thank Drs. F. E. Brinckman and R. B. Johannesen, of the National Bureau of Standards, for obtaining the 400-MHz ^{1}H NMR spectrum of **9**. The crystal structure analysis for **9** was performed by Dr. F. J. Hollander at U.C. Berkeley X-ray Crystallographic Facility (CHEXRAY). The work was supported by the Assistant Secretaries for Fossil Energy and Oil, Gas and Shale Technology, and the Bartlesville Energy Technology Center (project manager, Dexter Sutterfield) of the U.S. Department of Energy under Contract No. DE-AC03-76SF00098.

Registry No. **1**, 488-17-5; **2**, 2150-43-8; **3**, 92-44-4; **4**, 71636-73-2; **5**, 124-58-3; **6**, 98-05-5; **7**, 82338-03-2; **8**, 82398-38-7; **9**, 82338-04-3; **10**, 82398-39-8; **16**, 82338-05-4; **17**, 82338-06-5.

Supplementary Material Available: A listing of observed and calculated structure factors including tables of positional and thermal parameters, temperature factors, thermal vibrations, and bond lengths and angles (14 pages). Ordering information is given on any current masthead page.

(8) Mcardle, J. V.; Sofen, S. R.; Cooper, S. R.; Raymond, K. N. *Inorg. Chem.* **1978**, *17*, 3075.

(9) The series of LICAM derivatives of increasing methylene chain, 2–6, were prepared according to the procedures of Dr. F. L. Weitl (cf. Weitl, F. L.; Raymond, K. N. *J. Am. Chem. Soc.* **1980**, *102*, 2289).

(10) Dawson, M. I.; Chan, R. L.-S.; Clousdale, I. S.; Harris, W. R. *Tetrahedron Lett.* **1981**, *22*, 2739.

(11) We have used this procedure to derivatize both methyl and phenylarsonic acid, **5** and **6**, that had been isolated from a Green River oil shale kerogen by extraction with methanol. Since **7** and **9** can be chromatographed on a 30-m fused silica capillary column (OV101), the use of GC–MS will enhance the utility of these organoarsonic acid derivatives for other applications. Fish, R. H.; Tannous, R. S.; Weiss, C. S.; Brinckman, F. E., in preparation.

Silicon in Synthesis. 19. 1-(Trimethylsilyl)-1-(phenylthio)ethylene and 1-(Trimethylsilyl)-2-(phenylthio)ethylene: Reagents for Thiophenyl-Functionalized Cyclopentenone Annulations

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Summary: 1-(Trimethylsilyl)-1-(phenylthio)ethylene and 1-(trimethylsilyl)-2-(phenylthio)ethylene on treatment with cyclopentene-1-carbonyl chloride, in the presence of a Lewis acid, gave 4-(phenylthio)- and 1-(phenylthio)bicyclo[3.3.0]oct-3-en-2-one, respectively.

Vinylsilanes are one of the more useful functionalized organosilicon reagents, since they undergo regiospecific electrophilic substitution reactions.[1] This is a direct manifestation of the so-called β effect, where the buildup of electrophilic character β to the C–Si bond is stabilized, provided the developing electrophilic $2p_z$ orbital is the same plane as the C–Si σ bond.[2]

[†] Part of this work was carried out at the Ohio State University, Columbus, Ohio 43210.

(1) For leading references to the electrophilic substitution reactions of vinylsilanes see: Chan, T. H.; Fleming, I. *Synthesis* **1979**, 761. Magnus, P. *Aldrichimica Acta* **1980**, *13*, 41.

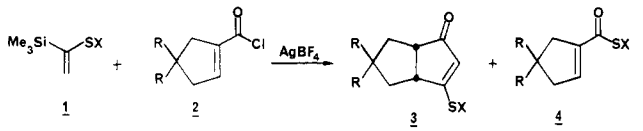
(2) Jarvie, A. W. P. *Organomet. Chem. Rev., Sect. A* **1970**, *6*, 153. Cooke, M. A.; Faborn, C.; Walton, D. R. M. *J. Organomet. Chem.* **1970**, *24*, 301. Traylor, T. G.; Berwin, H. J.; Jetkunica, J.; Hall, M. L. *Pure Appl. Chem.* **1972**, *30*, 599.

0276-7333/82/2301-1240$01.25/0

Another class of heterosubstituted alkenes which have engendered much recent interest in synthesis are aryl (or alkyl) thioalkenes.[3] The polarization of thioalkenes directs electrophiles β to the sulfur, opposite to the situation for vinyltrialkylsilanes.

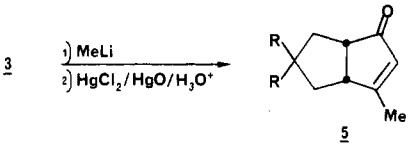
Combining both vinylsilane and vinyl sulfide functional groups, with their opposed polarization, would produce somewhat unpredictable and interesting electrophilic chemistry.[4] Here we report some acylations of trimethylsilyl-substituted thioalkenes, directed toward synthesizing functionalized cyclopentenones that eventually might be viable reactions for convergent syntheses of cyclopentenoid natural products.

Cyclopentene-1-carbonyl chloride (**2**, R = H) in $CH_2Cl_2/ClCH_2CH_2Cl$ was treated with $AgBF_4$, at −60 °C, followed by 1-(trimethylsilyl)-1-(phenylthio)ethylene (**1**, X = Ph)[5] for 1 h. Warming the above mixture to 20 °C



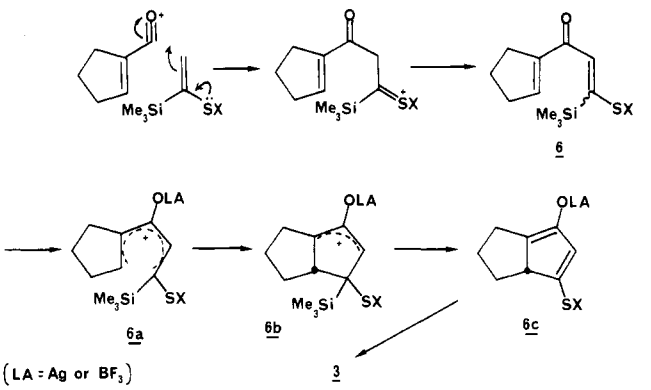
gave, after 14 h, 4-(phenylthio)bicyclo[3.3.0]oct-3-en-2-one (**3**, R = H, X = Ph) in 35–45% yield.[6] Using other Lewis acids such as $SnCl_4$, $TiCl_4$, BF_3·OEt, and $AlCl_3$ gave none of the desired product **3** but only the thioester **4** (R = H, X = Ph). The blank reaction using the same conditions that gave **3**, except **1** (X = Ph) was replaced by phenyl vinyl sulfide, gave none of the bicyclic enone **3**, thus demonstrating the necessity for the trimethylsilyl substituent. The structure of **3** (R = H, X = Ph) was confirmed by treatment with MeLi, followed by a mercuric ion assisted hydrolysis ($HgCl_2/HgO/THF/H_3O^+$) to give 4-methylbicyclo[3.3.0]oct-3-en-2-one (**5**, R = H) in 90% yield.[7]

Similarly **1** (X = Ph), on treatment with **2** (R = Me) in the presence of $AgBF_4$, gave **3** (R = Me, X = Ph) in 38% yield on a 2-g scale.[8] Treatment of **3** (R = Me, X = Ph)



with MeLi/Et_2O at −78 °C, followed by hydrolysis, gave the bicyclic enone **5** (R=Me) in 93.5% yield. The enone **5** (R = Me) has found extensive use in the synthesis of cyclopentenoid natural products but was only available by lengthy routine procedures.[9]

Scheme I



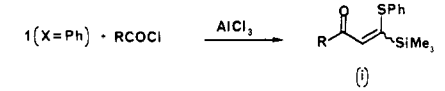
While this is a very direct and convergent method of annulating a functionalized cyclopentenone ring onto an α,β-unsaturated acid chloride, the yields are only moderate, although fairly typical of Nazarov electrocyclic-type processes.[10] In an effort to improve the yields we examined other derivatives of **1**. While the (methylthio)- and (*tert*-butylthio)-1-(trimethylsilyl)ethylenes (**1**, X = Me and *t*-Bu, respectively) gave no useful results, we concluded that a substituent attached to sulfur that would decrease the availability of electron density on sulfur and consequently suppress the formation of thioester byproducts was needed. To test this hypothesis, the reagent 1-(trimethylsilyl)-1-(2,4-dinitrophenyl)thio)ethylene [**1**, X = C_6H_3-2,4-$(NO_2)_2$][5] was treated with **2** (R = H) with use of the same conditions ($AgBF_4/CH_2Cl_2/ClCH_2CH_2Cl$) to give **3** [R = H, X = C_6H_3-2,4-$(NO_2)_2$] in 58% yield.[11] Unfortunately we were unable to add MeLi, MeMgBr, or Me_2CuLi to **3** [R = H, X = C_6H_4-2,4-$(NO_2)_2$] or carry out any mercuric ion assisted hydrolysis to give β-diketones. The reagent 1-(trimethylsilyl)-1-((4-chlorophenyl)thio)-ethylene (**1**, X = C_6H_4-4-Cl) gave **3** (X = C_6H_4-4-Cl) in only 15% yield. A plausible mechanistic interpretation of these annulations is outlined in Scheme I.

The first phase of the reaction is dominated by the nucleophilicity of the thio–enol ether functionality, leading to the dienone **6**.[4] Conrotatory cyclization (Nazarov reaction)[10] via the pentadienyl cation **6a** to the oxyallyl cation **6b** places the trimethylsilyl group in the same plane as the empty $2p_z$ orbital. Consequently the oxyallyl cation **6b** is stabilized by the trimethylsilyl group (β effect) and subsequently eliminates the $SiMe_3$ group to give the diene **6c**, which on protonation gives the cis-fused 4-(arylthio)-cyclopentenones **3**.

In terms of stabilization of cationic character, the trimethylsilyl group and the thioaryl group in the reagents

(3) Trost, B. M.; Tanigawa, Y. *J. Am. Chem. Soc.* **1979**, *101*, 4743. Trost, B. M.; Tanigawa, Y. *Ibid.* **1979**, *101*, 4413 and references cited therein.

(4) Dr. David Ager (University of Liverpool) is thanked for sending us a preprint concerning the acylation chemistry of **1** (X = Ph), in which



the adducts (**i**) are formed, in keeping with Scheme I, proceeding via **6**: *Tetrahedron Lett.*, **1982**, *23*, 1945. See also: Hase, T. A.; Lahtinen, L. *Ibid.* **1981**, *22*, 3285.

(5) The reagents **1** (X = Ph etc.) were described by: Cooke, F.; Moerck, R.; Schwindeman, J.; Magnus, P. *J. Org. Chem.* **1980**, *45*, 1046. For a recent example of a silicon-directed Nazarov cyclization see: Denmark, S. E.; Jones, T. K. *J. Am. Chem. Soc.* **1982**, *104*, 2642.

(6) Anal. Calcd for $C_{14}H_{14}OS$: C, 73.04; H, 6.09. Found: C, 72.79; H, 6.16. NMR ($CDCl_3$): δ 1.0–1.9 (6 H, m), 2.3–2.7 (1 H, m), 2.8–3.3 (1 H, m), 5.10 (1 H, s), 7.0–7.5 (5 H, m).

(7) NMR (CCl_4): δ 1.0–1.9 (6 H, m), 1.90 (3 H, s), 2.25–2.60 (1 H, m), 2.65–3.00 (1 H, m), 5.60 (1 H, b s). MS: $C_9H_{12}O$ requires *m/e* 136.088; found *m/e* 136.089.

(8) Anal. Calcd for $C_{16}H_{18}OS$: C, 74.42; H, 6.98. Found: C, 74.73; H, 7.27. NMR ($CDCl_3$): δ 0.86 (3 H, s), 0.90 (3 H, s), 1.0–1.85 (4 H, m), 2.70–3.10 (1 H, m), 3.20–3.50 (1 H, m), 5.17 (1 H, s), 7.1–7.5 (5 H, m).

(9) Fex, T.; Froberg, J.; Magnusson, G.; Thorên, S. *J. Org. Chem.* **1976**, *41*, 3518. Ohfune, Y.; Shirahama, H.; Matsumoto, T. *Tetrahedron Lett.* **1975**, 4377. Miyano, K.; Ohfune, Y.; Azuma, S.; Matsumoto, T. *Ibid.* **1974**, 1545. Paquette, L. A.; Farkas, E.; Galemmo, R. *J. Org. Chem.* **1981**, *46*, 5434.

(10) Nazarov, N. I.; Zaretskaya, I. I. *Zh. Obshch. Khim.* **1957**, *27*, 693. See also ref 5.

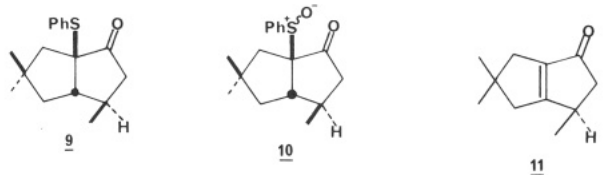
(11) Melting point: 124–125 °C (from benzene/hexane). Anal. Calcd for $C_{14}H_{12}N_2O_5S$: C, 52.50; H, 3.75. Found: C, 52.80; H, 3.87. NMR ($CDCl_3$): δ 1.8 (6 H, b m), 2.92 (1 H, b m), 3.45 (1 H, b m), 5.83 (1 H, s), 7.88 (1 H, d, *J* = 9 Hz), 8.40 (1 H, q, *J* = 9 and 3 Hz), 8.82 (1 H, *d*, *J* = 3 Hz).

Figure 1. ORTEP drawing.

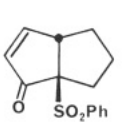
1 are opposed to one another and are not in electronic concert. Consequently a reagent based upon Si and S substituents that work together (both stabilize the buildup of electrophilic character) should accomplish the above annulation reaction.

(Trimethylsilyl)acetylene and thiophenol (1:1) were irradiated to give 1-(trimethylsilyl)-2-(phenylthio)ethylene (**7**) in 98.8% yield.[12] Treatment of **2** (R = H) with **7** in

the presence of $AlCl_3/ClCH_2CH_2Cl$ at 50 °C gave 1-(phenylthio)bicyclo[3.3.0]oct-3-en-2-one (**8**, R = H) in 55% yield.[13] Similarly **7**, on treatment with **2** (R = Me) in the presence of $AlCl_3$ at 20 °C gave the bicyclic enone **8** (R = Me) in the 40% yield.[14] Treatment of **8** with Me_2CuLi gave **9** (78%) which was oxidized (MCPBA) to the diastereomeric sulfoxides **10**. Thermolysis (100 °C) of **10** cleanly gave the enone **11**, isomeric with, but different from **5** (R = Me).

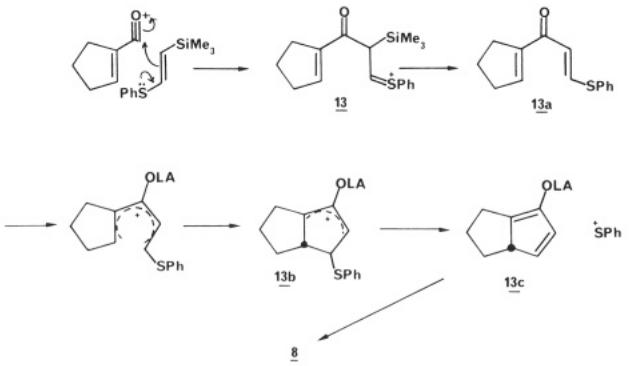


While structure **8** (R = Me or H) indicates that the phenylthio group is attached to the ring fusion position, it is not conclusive that this group is adjacent to the carbonyl group. The ^1H and ^{13}C NMR data are in keeping with the assigned structures, but not diagnostic. Oxidation of **8** (R = H; 2 equiv of MCPBA) gave the crystalline sulfone **12**. Diffusion crystallization from diethyl ether gave suitable crystals for single-crystal X-ray crystallography (Figure 1).[15]



12

Scheme II



The mechanism of the formation of **8** (Scheme II) is similar to Scheme I, in that the nucleophilicity of the phenylthio enol–ether functionality dominates the first acylation step to give **13**. Since the trimethylsilyl group is β to a sulfonium ion, it can be lost at this stage to give the dienone **13a**. Conrotatory cyclization of **13a** leads to the oxyallyl cation **13b**, which can lose PhS^+ to give the kinetic enol **13c**. Sulfenylation of **13c** using the in situ generated PhS^+ gives **8**.[16]

In summary, the described annulations provide a one step reaction for the synthesis of (phenylthio)cyclopentenones, albeit in moderate yield. The reagent **2** on treatment with the α,β-unsaturated acid chlorides in the presence of $AlCl_3$ results in an unprecedented rearrangement to give **8**. In the following paper an application of the annulation reaction **1** to **3** is described for the total synthesis of (±)-hirsutene.

Acknowledgment. The National Science Foundation is gratefully thanked for their support of this work.

Registry No. (trimethylsilyl)acetylene, 1066-54-2; thiophenol, 108-98-5; $AgBF_4$, 14104-20-2; $SnCl_4$, 7646-78-8; $TiCl_4$, 7550-45-0; BF_3·OEt, 109-63-7; ACl_3, 7446-70-0; **1** (X = Ph), 62762-20-3; **1** (X = C_6H_3-2,4-$(NO_2)_2$), 82494-84-6; **1** (X = C_6H_4-4-Cl), 72622-67-4; **2** (R = H), 59253-90-6; **2** (R = Me), 78064-83-2; (±)-**3** (R = H, X = Ph), 82494-85-7; (±)-**3** (R = Me, X = Ph), 82494-86-8; (±)-**3** (R = H, X = C_6H_3-2,4-$(NO_2)_2$), 82494-87-9; (±)-**3** (R = H, X = C_6H_4-4-Cl), 82494-88-0; **4** (R = H, X = Ph), 82494-89-1; (±)-**5** (R = H), 82494-90-4; (±)-**5** (R = Me), 60064-71-3; **7**, 82494-8]-5; (±)-**8** (R = H), 82494-92-6; (±)-**8** (R = Me), 82494-93-7; (±)-**9**, 82494-94-8; (±)-**10** isomer 1, 82494-95-9; (±)-**10** isomer 2, 82494-96-0; (±)-**11**, 82494-97-1; (±)-**12**, 82494-98-2.

Supplementary Material Available: fractional coordinates and thermal parameters (6 pages). Ordering information is given on any current masthead page.

(12) Komarov, N. V.; Yorosh, O. G. *Izv. Akad. Nauk SSSR, Ser. Khim.* **1967** (3), 690.

(13) NMR (CCl_4) δ 1.1–2.3 (6 H, m), 3.26 (1 H, m), 5.97 (1 H, dd, J = 2 and 7 Hz), 7.12–7.58 (6 H, m). MS: $C_{14}H_{14}OS$ requires m/e 230.077, found m/e 230.076.

(14) NMR (CCl_4): δ 0.87 (3 h, s), 1.13 (3 H, s), 1.85 (2 H, m), 2.40 (2 H, m), 3.30 (1 H, m), 5.85 (1 H, dd, J = 2 and 7 Hz), 7.08–7.45 (6 H, m).

(15) The sulfone **12** has a melting point of 155–157 °C (from ether). Anal. Calcd for $C_{14}H_{14}O_3S$: C, 64.12; H, 5.34. Found: C, 64.32; H, 5.17. A Single crystal of **12**, obtained by slow recrystallization from ether, was subjected to a single-crystal structural analysis at −165 °C. The Picker goniostat, low-temperature equipment, and general procedures have been described previously [Huffman, J. C.; Lewis, L. N.; Caulton, K. G. *Inorg. Chem.* **1980**, *19*, 2755]. The compound crystallizes in the triclinic space group $P\bar{1}$, although the packing is pseudomonoclinic ($P2_1/n$). Crystal data are as follows: a = 10.358 (3) Å, b = 12.981 (5) Å, c = 9.323 (3) Å, α = 89.41 (2)°, β = 100.55 (2)°, γ = 90.03 (2)°, D(calcd) = 1.409 g/cm^3 for Z = 4. The structure was solved by direct methods assuming the monoclinic symmetry and transformed to the triclinic lattice. Two independent molecules were located, with one molecule being slightly disordered. Full-matrix refinement converged to R = 0.077 and R_w = 0.069 for the 2893 reflections with $I \geq 2.33\sigma(I)$, based on counting statistics.

(16) For references describing the so-called thioallylic rearrangement see: Gerber, U.; Widmer, U.; Schmid, R.; Schmid, H. *Helv. Chim. Acta* **1978**, *83*, 61. Kozikowski, A. P.; Huie, E.; Springer, J. P. *J. Am. Chem. Soc.* **1982**, *104*, 2059 and references cited therein. Brownbridge, P.; Warren, S. *J. Chem. Soc., Perkin Trans 1* **1976**, 2125.