Reactions of Ketals and Acetals with $(CO)_5MnSi(CH_3)_3$. A New Vinyl Ether Synthesis

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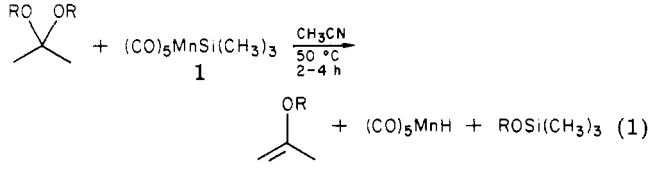
Received April 14, 1982

The reaction of $(CO)_5MnSi(CH_3)_3$ (1; 1.0–2.4 equiv, 2–4 h, 50 °C, acetonitrile) with ten different methyl ketals (Table I) gives methyl enol ethers in 56% to >95% yields. Easily removed byproducts $CH_3OSi(CH_3)_3$ and $(CO)_5MnH$ (or $Mn_2(CO)_9(CH_3CN)/Mn_2(CO)_{10}$) also form. When regio- and/or geometric isomers are possible, thermodynamic mixtures are obtained. The reaction of 1 with acetals is more complex, but when conducted under 200 psi of CO, manganese acyls $(CO)_5MnCOCH(OR)R'$ (derived from alkyl intermediates) can be isolated. A general mechanism is proposed in which a ketal or acetal oxygen is initially silylated by 1. Also, 1 rapidly converts cyclohexanone ethylene glycol ketal to $(CH_3)_3SiOCH_2CH_2OC{=}CHCH_2CH_2CH_2CH_2$ (7) and slowly transforms cyclohexanone diallyl ketal to 1-cyclohexenyl allyl ether. Ortho ester $CH_3C(OCH_3)_3$ and 1 react to give principally $CH_3CO_2CH_3$ and $CH_3OSi(CH_3)_3$.

Introduction

Reactions of transition-metal trialkylsilanes such as $(CO)_5MnSi(CH_3)_3$ (1)[2] and *cis*-$(CO)_4Fe[Si(CH_3)_3]_2$[3] with oxygen-containing organic molecules have been the subject of intensive study in our laboratory.[4-7] Two broad classes of useful transformations have been found: (1) new metal–carbon bond forming reactions which give isolable organometallic products[4,5] and (2) organic functional group transformations.[4,6,7]

Previously, we noted that $(CO)_5MnSi(CH_3)_3$ (1) cleanly converts ketones with α-hydrogens to their trimethylsilyl enol ethers.[4] In contrast to conventional silyl enol ether syntheses, no acid or base was required. The byproduct was the mildly acidic $(CO)_5MnH$ ($pK_a \simeq 7$).[8] Mechanistic considerations led us to predict that 1 might similarly transform ketals to enol ethers according to eq 1. Enol ethers are conventionally synthesized by the reaction of ketals and acetals with protic acids at temperatures in the 100–200 °C range.[9-11] Since such conditions are not compatible with thermally labile and acid sensitive groups, eq 1 appeared to offer distinct advantages over existing methodology. In this paper, we report (a) reactions of 1 with a variety of dimethyl ketals which give methyl vinyl ethers in good to excellent yields, (b) the high yield conversion of cyclohexanone ethylene glycol ketal to a ring-opened, silylated vinyl ether, (c) related, more complex reactions of 1 with acetals, cyclohexanone diallyl ketal, and ortho esters, and (d) mechanistic data on these transformations, including the use of CO to trap manganese alkyl intermediates. A portion of this study has been communicated.[7]



Results

The methyl ketals listed in Table I were treated with 1.0–2.4 equiv of 1 in CH_3CN (or CD_3CN) for 2–4 h at 50 ± 2 °C (eq 1). Methyl enol ethers formed in 56 to >95% yields, as determined by GLC and ^1H NMR spectroscopy. In three representative cases (entries 6–8), yields of isolated, distilled products were obtained. Identities of the enol ethers in Table I were confirmed by comparison with independently prepared authentic samples. Volatile byproduct $CH_3OSi(CH_3)_3$ formed in all reactions.

Hydride $(CO)_5MnH$ was the initial inorganic product of eq 1, as evidenced by a δ −7.9 ^1H NMR resonance.[12] However, $(CO)_5MnH$ decomposed during the reaction to $Mn_2(CO)_9(CH_3CN)$ (IR (cm^{-1}, hexane) 2094 (w), 2026 (s), 2005 (s), 1996 (vs), 1974 (m), 1954 (m))[13] and small amounts of $Mn_2(CO)_{10}$. Side reactions of some products with $(CO)_5MnH$ were observed, so an excess of 1 was utilized with the less reactive dimethyl ketals to increase the rate of initial reaction (Experimental Section). The GLC yield of α-methoxystyrene (entry 8) reached a maximum (93%) at ≥1.6:1.0 1:acetophenone dimethyl ketal ratios.

The trapping of byproduct $(CO)_5MnH$ was attempted. Reactions conducted in the presence of 1.0 equiv of PPh_3 or $Ph_2PCH_2CH_2PPh_2$ gave phosphine-substituted man-

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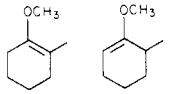
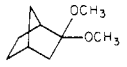
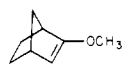
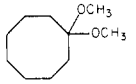
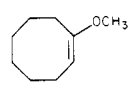
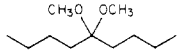
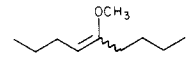
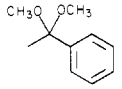
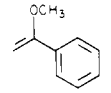
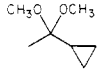
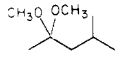
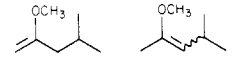
Table I. Vinyl Ethers Synthesized from Dimethyl Ketals and 1[a]

entry	starting ketal	product	yield data[b] % GLC	NMR	isol
1			97	95	
2		 38 62	98	98	
3			93	98	
4			56	60	
5			78	77	
6			85	95	79
7		 25(*E*):75(*Z*)[a]	88	95	74
8			93	97	81
9			78	84	
10		 2 (71) 3 (4(*Z*):25(*E*)[a]	97	93	

[a] See Experimental Section for reaction conditions and geometric isomer assignments. [b] Yields are based upon ketal and are estimated to be accurate within ± 5%.

ganese hydrides, as evidenced by ^{31}P-coupled ^1H NMR resonances (δ −7.4 (d, $J_{^1H-^{31}P}$ = 33 Hz) and −7.9 (t, $J_{^1H-^{31}P}$ = 46 Hz)). These hydrides were more stable than $(CO)_5MnH$ to the reaction conditions, but higher yields of enol ether products were not obtained. Base additives (n-$C_4H_9)_3N$, 2,6-di-*tert*-butylpyridine, DBU, 4-(dimethylamino)pyridine, and 2,2,6,6-tetramethylpiperidine either reacted with starting 1[2a] or failed to deprotonate $(CO)_5MnH$.

The disappearance of $(CO)_5MnH$ during the course of eq 1 was probed. No reaction occurred when equivalent amounts of 1 and $(CO)_5MnH$ were heated at 50 °C in CD_3CN for 24 h. Similarly, $(CO)_5MnH$ was unreactive toward 5-nonanone dimethyl ketal and acetophenone dimethyl ketal (2 h, 50 °C, CD_3CN). However, $(CO)_5MnH$ slowly converted α-methoxystyrene and 5-methoxy-4-nonene to the corresponding saturated ethers (GLC identified); $Mn_2(CO)_9(CH_3CN)$ formed concurrently.

The regio- and stereoselectivity of eq 1 was investigated. Reaction of 1 with 2-methylcyclohexanone gave regioisomeric enol ethers 1-methoxy-2-methylcyclohexene and 2-methoxy-3-methylcyclohexene (Table I, entry 2). At 50% conversion (30 min), the product ratio was (40 ± 2):(60 ± 2). At completion of the reaction, the product ratio was a (38 ± 2):(62 ± 2) thermodynamic mixture.[14] Treatment of 4-methyl-2-pentanone dimethyl ketal with 1 gave regioisomeric enol ethers (Table I, entry 10) **2** and **3** (mixture of Z/E isomers). After 1 hr, the ratio of **2**:**3** was (81 ± 2):(19 ± 2). After 24 h, the ratio of **2**:**3** was (71 ± 2):(29 ± 2) thermodynamic mixture.[14] A thermodynamic mixture of *geometric* isomers was obtained from 1 and 5-nonanone dimethyl ketal (Table I, entry 7).

The possible influence of $(CO)_5MnH$ upon reaction regiochemistry was examined. A (17 ± 2):(86 ± 2) mixture of 1-methoxy-2-methylcyclohexene and 2-methoxy-3-methylcyclohexene was treated with $(CO)_5MnH$ (0.32 equiv) at 50 °C in CH_3CN. After 0.4 h, the regioisomer ratio was (24 ± 2):(76 ± 2). At 1.5 and 3.5 h, ratios were (29 ± 2):(71 ± 2) and (35 ± 2):(65 ± 2), respectively.

Reactions of 1 with certain functionalized dimethyl ketals were not as clean as those in Table I. Ketal ether 1,3,3-trimethoxybutane and 1 (1.86 equiv) gave only ca. 25% of 2,4-dimethoxybutene, as determined by ^1H NMR and GLC coinjection. Traces of 3,3-dimethoxy-1-butene were present, but 2-methoxy-1,3-butadiene was absent. Similarly, ketal olefin 3,3-dimethoxy-1-butene and 1 (1.90 equiv) gave only a ca. 30% yield of 2-methoxy-1,3-butadiene. After 0.75 h, all of 1 had been consumed, but half of the starting material remained.

Reactions of 1 with acetals were complex and gave poor yields of enol ethers. Cyclic acetal 2-methoxytetrahydropyran and 1 reacted (eq 2) to give, among other products, olefins **4** (1(*Z*):1(*E*) mixture) and **5** and dihydropyran. The major product, **4**, formed in 10% yield. However, when this reaction was conducted under 200 psi of CO, manganese acyl **6** (eq 2) was isolated in 65% yield. Reaction of

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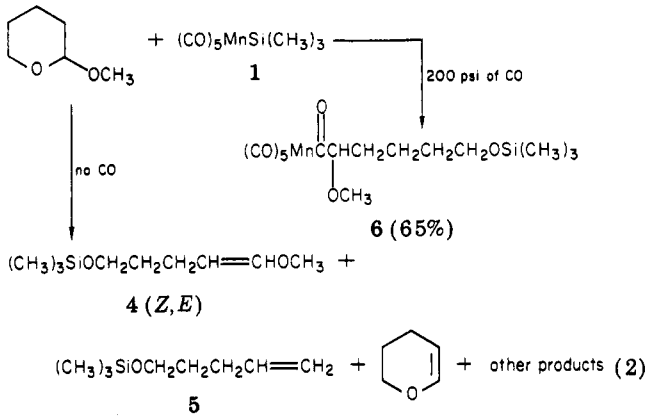
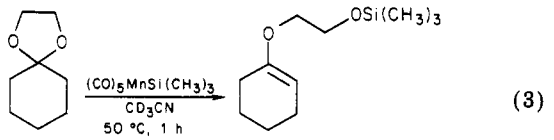
1 with hydrocinnamaldehyde dimethyl acetal gave only a 1–5% yield of vinyl ether 1-methoxy-3-phenylpropene, as assayed by (partial) preparative GLC purification and observation of characteristic $RHC{=}CHOCH_3$ ^1H NMR resonances. However, under 200 psi of CO, the labile acyl $(CO)_5MnCOCH(OCH_3)CH_2CH_2C_6H_5$ was obtained. Manganese acyls did not form when dimethyl ketals and 1 were reacted under CO.



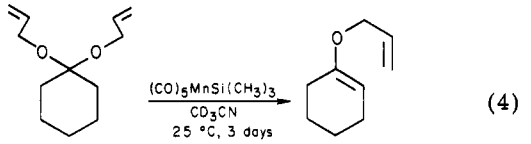
Since glycol-derived ketals are a common class of compounds, the reaction of 1 (1.16 equiv) with cyclohexanone ethylene glycol ketal was examined. As shown in eq 3, rapid conversion to functionalized enol ether 7 occurred (94% by ^1H NMR; 92% by GLC). Solvent removal and distillation gave pure 7 in 87% isolated yield.



(3)

7 (87% isolated)

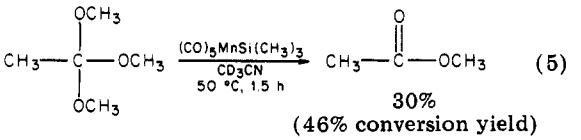
The diallyl ketal of cyclohexanone was treated with 3.55 equiv of 1 at 25 °C (eq 4). Slow conversion to 1-cyclohexenyl allyl ether (and $H_2C{=}CHCH_2OSi(CH_3)_3$) occurred. After 3 days, product and starting material were present in 42% and 58% yields, respectively; starting 1 had been consumed. No Claisen rearrangement product, 2-allylcyclohexanone, formed, but in reactions at 50 °C it became a significant byproduct.



(4)

42%
(100% conversion yield)

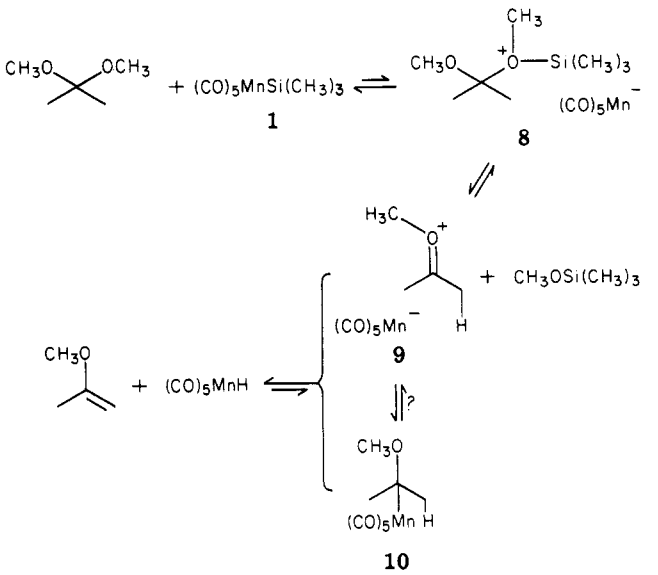
Reaction of the ortho ester $CH_3C(OCH_3)_3$ with 1 (1.35 equiv, 50 °C) gave, after 1.5 h, $CH_3CO_2CH_3$ (30%) and $CH_3OSi(CH_3)_3$ (60%) as the major organic products (eq 5). At this point, starting 1 had been consumed and 35% of the ortho ester remained. Traces of $(CO)_5MnCH_3$ were detected by IR, ^1H NMR, and TLC, but the major manganese-containing product was $Mn_2(CO)_9(CH_3CN)$. A similar reaction of 1 with $CH_3C(OCH_2CH_3)_3$ gave $CH_3CO_2CH_2CH_3$ (32%) and $CH_3CH_2OSi(CH_3)_3$ (40%) as the major organic products; 8% of the starting ortho ester remained.



(5)

30%
(46% conversion yield)

Scheme I. Proposed Mechanism of Methyl Enol Ether Formation



Discussion

The yields of methyl enol ethers from the simple monofunctional dimethyl ketals in Table I are uniformly good. However, entries 2, 7, and 10 show that when regioisomers and/or geometric isomers are possible, equilibrium mixtures can be expected. Only in the case of the cyclopropyl ketal (entry 9) was a mechanistically accessible,[11] thermodynamically more favored product (ring opened $H_2C{=}CHCH{=}C(OCH_3)CH_3$) *not* observed.

Since we had previously shown that $(CO)_5MnH$ slowly catalyzes the interconversion of trimethylsilyl enol ether regioisomers,[4b] we were not surprised to observe a similar $(CO)_5MnH$-promoted equillibrium of 2-methoxy-3-methylcyclohexene and 1-methoxy-2-methylcyclohexene. However, since the product ratios in entries 2 and 10 of Table I do not vary substantially with % conversion, we conclude that the kinetic isomer distribution is close to the thermodynamic one.

Conditions in Table I have been optimized for certain substrates to avoid C=C hydrogenation by $(CO)_5MnH$. Halpern has observed that $(CO)_5MnH$ converts α-methylstyrene to isopropylbenzene at conveniently measured rates at 40–75 °C ($\Delta H^{\ddagger} = 21.4 \pm 0.3$ kcal/mol; $\Delta S^{\ddagger} = -12 \pm 1$ eu).[15,16] This reaction has been shown to proceed via the geminate radical pair $\overline{(CO)_5Mn \cdot C_6H_5(CH_3)_2C\cdot}$. Vinyl ether α-methoxystyrene should be more reactive than α-methylstyrene toward $(CO)_5MnH$, since the more highly stabilized $C_6H_5(CH_3)(CH_3O)C\cdot$ radical would result. Current estimates for $D((CO)_5Mn - H)$ are only ca. 60 kcal/mol,[17] so $(CO)_5MnH$ is expected to be a good hydrogen atom donor.[15-18]

When 1 and $(CH_3)_3N$ are reacted, trimethylsilyl group transfer to give the isolable ion pair $(CH_3)_3N^+Si(CH_3)_3$ $(CO)_5Mn^-$ occurs.[2a] Hence we propose that the initial step of eq 1 is the silylation of a ketal oxygen to give the ion pair 8, as shown in Scheme I. As would be expected of a transformation involving neutral reactants and charged intermediates, the substitution of less polar solvents such as CH_2Cl_2 and benzene for acetonitrile slows eq 1 dramatically.

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(16) Halpern, J. *Pure Appl. Chem.* **1979**, *51*, 2171.
(17) Rathke, J. W.; Feder, H. M. *J. Am. Chem. Soc.* **1978**, *100*, 3623.
(18) Nappa, M. J.; Santi, R.; Diefenbach, S. P.; Halpern, J. *J. Am. Chem. Soc.* **1982**, *104*, 619.

We suggest that **8** subsequently extrudes the observed byproduct $CH_3OSi(CH_3)_3$ to give the new ion pair **9**. The most direct pathway to enol ether would then involve H^+ transfer from carbon to $(CO)_5Mn^-$. However, **9** might also collapse to the organometallic intermediate **10** (Scheme I), which could go on to products via a classical β-hydride elimination mechanism. These possibilities, and variants involving electron transfer steps, are not easily distinguished by experiment. Our ability to isolate manganese acyls from the reaction of **1** with acetals under CO indicates that manganese alkyls do form under the conditions of Scheme I.[19] Unfortunately, this trapping does not provide any information on the identity of the immediate precursor to the enol ether product. Our inability to isolate manganese acyls from the reaction of **1** with ketals under CO *may* be due in part to the fact that the Mn–C σ bond in **10** would be weaker and hence less likely to form. This parallels our previous observations with carbonyl compounds: aldehydes and **1** react under CO to give acyls $(CO)_5MnCOCHROSi(CH_3)_3$, but ketones (with α hydrogens) yield only silyl enol ethers.[4b,5b]

Reactions of ketals with several $(CH_3)_3Si$-X reagents have been studied, resulting in interesting variations on the chemistry in Scheme I. Jung has found that $(CH_3)_3SiI$ and dimethyl ketals react to give ketones, $CH_3OSi(CH_3)_3$, and CH_3I in high yields.[20] Oxonium ions analogous to **8** and **9** likely form but with I^- as the anion. Internal attack of I^- upon the methyl group of **9** would then afford the observed products. If $(CO)_5Mn^-$ (a strong nucleophile)[21] behaved similarly, two mutually inert products, $(CO)_5MnCH_3$ and ketone, would result. These species were not detected in any of the reactions in Table I.

An important article by Miller and McKean appeared while this study was in progress.[11] These authors found that methyl enol ethers could be isolated in high yield by treating dimethyl ketals with $(CH_3)_3SiI$ in the presence of $[(CH_3)_3Si]_2NH$ base. This reaction also likely involves the oxonium ion **9** (I^- anion), but now added base plays the role of $(CO)_5Mn^-$ and enol ether forms. The Miller/McKean procedure is distinctly better than ours at converting *acetals* to enol ethers. Otherwise, comparable yields are obtained for the substrates in entries 2, 6, 7, and 8 of Table I. However, the $(CH_3)_3SiI/[(CH_3)_3Si]_2NH$ recipe converts cyclopropyl ketals to ring-opened products, whereas with **1** the cyclopropane remains intact (entry 9, Table I).

In the presence of a catalytic amount of $SnCl_2$, dimethyl ketals and $(CH_3)_3SiCN$ react to give α-methoxy cyanides and $CH_3OSi(CH_3)_3$.[22] Since ^-CN is a poor base but makes a very strong (~120 kcal/mol)[23] bond to carbon, the replacement of $(CO)_5Mn^-$ by ^-CN in oxonium ion **9** would be expected to give C–CN bonded products. Noyori has found numerous reactions in which a catalytic amount of $(CH_3)_3SiOSO_2CF_3$ promotes nucleophilic attack upon dimethyl ketal carbon.[24] Oxonium ions analogous to **9** are presumed to be intermediates.

Reactions of $(CH_3)_3Si$–X reagents with ethylene glycol ketals have not to our knowledge been previously reported. Equation 3 provides a facile means of differentiating the two ends of the glycol moiety. The rate acceleration relative to entry 1 of Table I may be due to diminished steric hinderance in the initial oxonium ion forming step (Scheme I).

Allyl vinyl ethers are an important and often difficultly accessible class of compounds.[10c,d,25,26] Hence we hoped that they might be generally available from **1** and diallyl ketal precursors. However, diallyl ketals are distinctly less reactive than dimethyl ketals toward **1**, and (as shown in eq 4) long reaction times are required when temperatures are kept low enough to avoid Claisen rearrangement byproducts. This problem might be circumvented by using transition-metal silanes $L_nMSi(CH_3)_3$ in which the L_nM^- moiety is a better leaving group and poorer nucleophile than $(CO)_5Mn^-$ (e.g., $(CO)_3(L)CoSi(CH_3)_3$, L = phosphine, CO). These should be "hotter" silylating agents than **1** and will be utilized in future reactivity studies in our laboratory.

Another potential application for a more relative silylating agent than **1** would be in eq 5. Ortho esters are easily synthesized from nitriles,[27] and we had hoped for their ready conversion to difficultly accessible (but synthetically very useful)[28] ketene acetals. This would entail a mechanism similar to Scheme I. However, presumed intermediate $CH_3C^+(OCH_3)_2(CO)_5Mn^-$ apparently undergoes methyl transfer to give $CH_3CO_2CH_3$ in preference to H^+ transfer to give $H_2C{=}C(OCH_3)_2$. Since $(CO)_5MnCH_3$ is detected only in trace quantities in eq 5, we suspect that it undergoes decomposition, perhaps via an acyl.[18] In both eq 4 and 5, **1** was consumed at a significantly greater rate than the organic substrate. We are at present unable to account for this observation.

Reactions of **1** with acetals are seemingly complicated by several side reactions (homolysis, hydrogenation, hydrogenolysis). With 2-methoxytetrahydropyran (Eq 2), organic products derived from the silylation of both oxygens are obtained. Under CO, the manganese acyl derived from ring-oxygen silylation predominates. While the low yields of enol ethers from these substrates, as well as from functionalized ketals 1,3,3-trimethoxybutane and 3,3-dimethoxy-1-butene, apparently represent intrinsic limitations in the reagent **1**, some improvement may yet be possible by careful optimization of reaction conditions.

In summary, this study has resulted in a practical, low-temperature synthesis of methyl enol ethers from dimethyl ketals. Reagent **1** does not noticeably deteriorate over several hours in dry air, and functional groups which can be tolerated include arenes, nitriles, unactivated halides and olefins, and to some extent ethers[5] and esters. This investigation has also provided new fundamental data on transition-metal trialkylsilane/organic molecule reactivity. Additional applications of metal silane reagents in organic and organometallic chemistry will be the subject of future reports from our laboratory.

Experimental Section

Starting Chemicals. 5-Nonanone, 4-methyl-2-pentanone, cyclopentanone, cyclohexanone, 2-methylcyclohexanone, cyclooctanone, 2-norboranone, acetophenone, methyl vinyl ketone, hydrocinnamaldehyde, 2,2-dimethoxypropane, cyclopropyl methyl

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ketone, trimethyl orthoacetate, and triethyl orthoacetate were obtained from Aldrich or Eastman and were distilled prior to use. 2-Methoxypropene, $HC(OCH_3)_3$, PPh_3, and $Ph_2PCH_2CH_2PPh_2$ were obtained from Aldrich and used without purification. Other starting reagents were obtained from common commercial sources and used without purification.

Solvents CH_3CN and CD_3CN were distilled over P_2O_5 and freeze–pump–thaw degassed before use. Hexane was distilled from potassium under N_2. CO was obtained from Air Products and used without purification. $(CO)_5MnSi(CH_3)_3$ was synthesized by Malisch's route[2b,c] using $K^+(CO)_5Mn^-$ and stored under N_2.[29]

Instruments. ^1H and ^{13}C NMR spectra were recorded on Varian T-60, JEOL FX90Q, and Bruker WP-200 spectrometers. IR and mass spectra were obtained on Perkin-Elmer 521 and AEI-MS9 spectrometers, respectively. GLC analyses were performed on Varian Aerograph 90P (preparative) and Hewlett-Packard 5720A flame ionization (analytical) chromatographs.

Syntheses of Organic Substrates and Product Authentic Samples. Methyl ketals and acetals were synthesized by a method similar to that of House.[9e] To CH_3OH solvent was added 1.0 equiv of ketone or aldehyde, 1.3 equiv of $HC(OCH_3)_3$, and a catalytic amount of p-$CH_3C_6H_5SO_3H{\cdot}H_2O$. This solution was allowed to sit for 48 h and was then neutralized with an excess of Na_2CO_3 and filtered. Solvent was removed from the filtrate by rotary evaporation, and the residue was vacuum distilled to give 60–70% of pure ketal or acetal.

Cyclohexanone diallyl ketal,[30] 1,3,3-trimethoxybutane,[31] 2-methoxybutadiene,[9f] 3,3-dimethoxy-1-butene,[9f] α-methoxystyrene,[32] **2** and **3**,[14] $(CH_3)_3SiOCH_2CH_2CH_2CH{=}CH_2$,[33] 2-methoxytetrahydropyran,[34a] and cyclohexanone ethylene glycol ketal[34b] were prepared by literature methods.

Authentic samples of methyl enol ethers other than those noted above were prepared by heating the neat dimethyl ketal precursor to 100–200 °C in the presence of p-$CH_3C_6H_4SO_3H{\cdot}H_2O$ and subsequent distillation through a Vigreaux column.[9b] The distillate was washed with H_2O, dried over Na_2CO_3, and redistilled or preparatively gas chromatographed to give pure methyl enol ether. Product identities were verified by the comparison of spectral and physical properties with published data.[9b]

Organic Product Analysis. GLC yields of NMR tube reactions were obtained as follows: 1.0 μL aliquots of the reaction mixture (containing a standard) were chromatographed on $^1/_8$ in. diameter columns packed with UCW98 on Chrom W-HP (20 in. or 6 ft) or 15% Carbowax on Chromosorb W (6 ft). Peak areas were measured with a Hewlett-Packard 3380A integrator. Yields were corrected for detector response factors and were the average of at least three injections. Accuracy was estimated to be ±5%. All yields were based upon the limiting reactant. Methyl vinyl ether NMR yields were (unless noted) calculated by comparing the integral of the product $-OCH_3$ (δ 3.4–3.6) with that for the entire $-Si(CH_3)_3$ (δ 0.0–0.5) region.

Reaction of Cyclohexanone Dimethyl Ketal with 1. To a 5-mm NMR tube was added 71 mg (0.265 mmol, 0.98 equiv) of **1**. The tube was taken into a drybox, and 0.40 mL of CD_3CN was syringed in. The tube was capped with a latex septum, removed from the box, and weighed. Ketal (32 μL, 39.0 mg, 0.271 mmol) was then added, and the tube was reweighed and placed in a 50 ± 2 °C oil bath for 2 h. NMR analysis as described above gave the datum in entry 1, Table I.

A similar experiment was conducted with 60 mg (0.224 mmol, 1.24 equiv) of **1**, 26.1 mg (27 μL, 0.181 mmol) of ketal, and 20.5 mg of $C_6H_5CH_2CN$ (20 μL, 0.175 mmol) standard in CH_3CN. GLC analysis as described above gave the datum in entry 1, Table I.

Reaction of 2-Methylcyclohexanone Dimethyl Ketal with 1. A reaction was conducted at 50 °C in a 5-mm NMR tube with 92 mg (0.343 mmol, 1.93 equiv) of **1**, 28.1 mg of ketal (31 μL, 0.178 mmol), and 0.40 mL of CD_3CN as described above for cyclohexanone dimethyl ketal. After NMR analysis (2 h), 16.6 mg (0.157 mmol) of ethylbenzene was added as a standard for GLC analysis. Data: entry 2, Table I. A second experiment was run on an identical scale in CH_3CN but with the ethylbenzene added at t_0; the regioisomer ratios were GLC monitored from 0.5 to 24 h.

Reaction of Cyclopentanone Dimethyl Ketal with 1. A reaction was conducted at 50 °C in a 5-mm NMR tube with 65 mg (0.245 mmol, 1.19 equiv) of **1**, 26.8 mg (23 μL, 0.206 mmol) of ketal, and 0.40 mL of CD_3CN for 2 h as described above for cyclohexanone dimethyl ketal. A GLC yield experiment (3 h) was similarly conducted on a 0.270-mmol scale with 19.4 mg (0.166 mmol) of $C_6H_5CH_2CN$ standard. Data: entry 3, Table I.

Reaction of 2-Norbornanone Dimethyl Ketal with 1. A reaction was conducted at 50 °C in a 5-mm NMR tube with 62 mg (0.231 mmol, 1.00 equiv) of **1**, 36.0 mg of ketal (37 μL, 0.231 mmol), and 0.30 mL of CD_3CN as described above for cyclohexanone dimethyl ketal. Subsequent NMR analysis (2.5 h) showed 1 to be consumed and a 60% yield of enol ether.

A similar experiment was conducted with 74 mg (0.276 mmol, 1.93 equiv) of **1**, 22.3 mg (22 μL, 0.143 mmol) of ketal, and 12.0 mg of $C_6H_5CH_2Si(CH_3)_3$ (0.073 mmol) standard in CH_3CN. GLC analysis after 3.5 h at 50 °C gave the datum in entry 4, Table I.

Reaction of Acetone Dimethyl Ketal with 1. A reaction was conducted at 50 °C in a 5-mm NMR tube with 115 mg (0.429 mmol, 2.11 equiv) of **1** and 21.1 mg (25 μL, 0.203 mmol) of ketal, and 0.40 mL of CD_3CN as described above for cyclohexanone dimethyl ketal. After NMR analysis (1.1 h), 19.1 mg (0.116 mmol) of $C_6H_5CH_2Si(CH_3)_3$ was added as a standard for GLC analysis. Data: entry 5, Table I.

Reaction of Cyclooctanone Dimethyl Ketal with 1. A reaction was conducted at 50 °C in a 5-mm NMR tube with 97 mg (0.362 mmol, 1.29 equiv) of **1**, 48.2 mg (50 μL, 0.280 mmol) of ketal, and 0.30 mL of CD_3CN as described above for cyclohexanone dimethyl ketal. After 3 h, NMR analysis as described above gave the datum in entry 6, Table I.

A similar experiment was conducted with 89 mg (0.332 mmol, 1.27 equiv) of **1**, 45 mg (44 μL, 0.262 mmol) of ketal, and 15.1 mg (0.142 mmol) of ethylbenzene in CH_3CN. After 2 h at 50 °C GLC analysis as described above gave the datum in entry 6, Table I.

A preparative reaction was conducted with 750 mg (2.79 mmol, 1.31 equiv) of **1** and 368 mg (2.13 mmol) of ketal in 2 mL of CH_3CN at 50 °C. After 2 h the volatiles were removed by rotary evaporation, and the residue was distilled on a molecular still to give 235 mg (1.68 mmol, 79%) of 1-methoxy-1-cyclooctene which was >97% pure by GLC analysis.

Reaction of 5-Nonanone Dimethyl Ketal with 1. A reaction was conducted at 50 °C in a 5-mm NMR tube with 98 mg (0.366 mmol, 2.04 equiv) of **1**, 33.6 mg (37 μL, 0.179 mmol) of ketal, and (t, mL of CD_3CN, as described above for cyclohexanone dimethyl ketal. After 2.5 h, NMR analysis indicated a 95% yield of a 25(*E*):75(*Z*) mixture (*E*, δ 4.47 (t, J = 7 Hz, 1 H), 3.49 (s, 3 H); *Z*, δ 4.31 (t, J = 7 Hz, 1 H), 3.44 (s, 3 H)) of 5-methoxy-4-nonene.[35]

An experiment identical with the previous one was conducted in CH_3CN with $C_6H_5CH_2Si(CH_3)_3$ (16.3 mg, 0.099 mmol) standard. GLC analysis indicated an 88% combined yield of enol ether *Z*/*E* isomers.

A preparative reaction was conducted with 680 mg (2.54 mmol, 2.01 equiv) of **1** and 237 mg (1.26 mmol) of ketal in 2 mL of CH_3CN at 50 °C. After 3 h the volatiles were removed by rotary evaporation, and the residue was distilled on a molecular still to

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(35) There is some disagreement amongst the references cited in this paper on enol ether *Z*/*E* assignments. Isomers of 5-methoxy-4-nonene are assigned on the basis of vinyl proton ^1H NMR shielding constants[36] which have proven to be applicable to sterically unexceptional trisubstituted alkyl enol ethers.[37] Similar trends have been noted in trisubstituted trimethylsilyl enol ethers.[38] The isomer ratio in entry 7 of Table I was accidentially reversed in our communication.[7]
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give 145 mg (0.93 mmol, 74%) of 5-methoxy-4-nonene which was >97% pure by GLC analysis.

Reaction of Acetophenone Dimethyl Ketal with 1. A reaction was conducted at 50 °C in a 5-mm NMR tube with 111 mg (0.414 mmol, 1.75 equiv) of 1, 39.2 mg (40 μL, 0.236 mmol) of ketal, and 0.30 mL of CD_3CN, as described above for cyclohexanone dimethyl ketal. After NMR analysis (2.5 h), 16.8 mg (0.102 mmol) of $C_6H_5CH_2Si(CH_3)_3$ was added as a standard for GLC analysis. Data: entry 8, Table I.

A preparative reaction was conducted with 811 mg (3.03 mmol, 2.07 equiv) of 1 and 242 mg (1.46 mmol) of ketal in 3 mL of CH_3CN at 50 °C. After 4.5 h, the volatiles were removed by rotary evaporation, and the residue was distilled on a molecular still to give 158 mg (1.19 mmol, 81%) of α-methoxystyrene which was >97% pure by GLC analysis.

Reaction of Cyclopropyl Methyl Ketone Dimethyl Ketal with 1. A reaction was conducted at 50 °C in a 5-mm NMR tube with 99 mg (0.369 mmol, 1.69 equiv) of 1, 28.4 mg (29 μL, 0.218 mmol) of ketal, and 0.35 mL of CD_3CN as described above for cyclohexanone dimethyl ketal. After 1 h, NMR analysis was conducted by comparing the $=CH_2$ integral (δ 3.74 (d) and 3.80 (d, J = 2.2 Hz)) with that of the $-OSi(CH_3)_3$ region (δ 0.0–0.3). No RC*H*=CROR resonances (δ ~4.4) were present. Then 15.3 mg (15 μL, 0.093 mmol) of $C_6H_5CH_2Si(CH_3)_3$ was added for GLC analysis. Data: entry 9, Table I.

Reaction of 4-Methyl-2-pentanone Dimethyl Ketal with 1. A reaction was conducted at 50 °C in a 5-mm NMR tube with 60 mg (0.225 mmol, 1.24 equiv) of 1, 26.0 mg (24 μL, 0.178 mmol) of ketal, and 0.40 mL of CD_3CN as described above for cyclohexanone dimethyl ketal. The 2:3 ratio was obtained by NMR analysis (2 h). Then 16.9 mg (0.103 mmol) of $C_6H_5CH_2Si(CH_3)_3$ standard was added, and the 2:(*Z*)-3:(*E*)-3 ratio was determined by GLC analysis. Data: entry 10, Table I.[39] Isomer ratios were also determined by GLC after 1 and 24 h.

α-Methoxystyrene Yield Optimization Experiments. The reaction of 1 (69 mg, 0.258 mmol, 1.02 equiv) and acetophenone dimethyl ketal (42.1 mg, 43 μL, 0.254 mmol) was conducted as described above in 0.40 mL of CD_3CN. Under these conditions, only a 63% NMR yield of α-methoxystyrene was obtained (3.5 h). Identical experiments in the presence of PPh_3 (1.06 equiv, 0.238-mmol scale) and $Ph_2PCH_2CH_2PPh_2$ (1.03 equiv, 0.239-mmol scale) gave 69% and 44% yields of α-methoxystyrene, respectively.

Reaction of 1,3,3-Trimethoxybutane with 1. A reaction was conducted at 50 °C in a 5-mm NMR tube with 98 mg (0.366 mmol, 1.84 equiv) of 1, 29.4 mg (30 μL, 0.199 mmol) of ketal, and 0.40 mL of CD_3CN, as described above for cyclohexanone dimethyl ketal. After 3 h, NMR and qualitative GLC analyses were conducted. Data: see text.

Reaction of 3,3-Dimethoxy-1-butene with 1. A reaction was conducted at 50 °C in a 5-mm NMR tube with 83 mg (0.310 mmol, 1.90 equiv) of 1, 18.9 mg (20 μL, 0.163 mmol) of ketal, and 0.40 mL of CD_3CN, as described above for cyclohexanone dimethyl ketal. After 3 h, NMR and qualitative GLC analyses were conducted. Data: see text.

Reaction of 2-Methoxytetrahydropyran with 1. In a drybox, 1 (600 mg, 2.24 mmol, 1.10 equiv) and CH_3CN (3.0 mL) were added to a 5-mL round-bottom flask. The flask was sealed with a rubber septum, removed from the box, and 236 mg (2.03 mmol) of 2-methoxytetrahydropyran was syringed in. The reaction was heated at 50 °C for 1 h, after which the solvent and organic products were vacuum distilled away from the manganese-containing products. Starting material, dihydropyran, and $(CH_3)_3SiOCH_2CH_2CH_2CH{=}CH_2$ (**5**, eq 2) were identified by GLC coinjection with authentic samples. The major product (10% GLC yield), $(CH_3)_3SiOCH_2CH_2CH_2CH{=}CHOCH_3$ (**4**, 50(*E*):50(*Z*) mixture), was separated by preparative GLC into pure *E*- and *Z*-enriched fractions and characterized as follows. *E* isomer: ^1H NMR (δ, $CDCl_3$, 200 MHz) 6.26 (d of t, $J_{H-H'}$ = 12.7, 1.0 Hz, $=CHOCH_3$), 4.70 (d of t, J = 12.7, 6.8 Hz, RCH=C), 3.56 (t, J = 6.5 Hz, 2 H), 3.48 (s, 3 H), 1.96 (pseudoquartet, J = 7 Hz, 2 H), 1.55 (m, 2 H), 0.09 (s, 9 H); ^{13}C NMR (ppm, $CDCl_3$, 22.5 MHz) 147.3, 102.5 (*C*=C), 61.9, 55.9 (O–C), 33.6 (*C*C=C), 24.0 (CH_2-CH_2CH_2), –0.5 (SiC). *Z* isomer: ^1H NMR (δ, $CDCl_3$, 200 MHz) 5.85 (br d, J = 6.2 Hz, $=CHOCH_3$) 4.31 (pseudoquartet, J = 6.5 Hz, RCH=C) 3.56 (t, J = 6.7 Hz, 2 H), 3.45 (s, 3 H), 1.95 (pseudoquartet J = 7 Hz), 1.58 (m, 2 H), 0.08 (s, 9 H); ^{13}C NMR (ppm, $CDCl_3$, 22.5 MHz) 146.3, 106.2 (*C*=C), 62.3, 59.4 (O–C), 32.8 (*C*C=C), 20.2 ($CH_2CH_2CH_2$), –0.5 (SiC); mass spectrum (*m*/*e* (relative intensity), 16 eV, *Z*/*E* mixture): 188 (M^+, 6), 173 ($M^+ - CH_3$, 14), 98 (100), 89 (60); high-resolution data on M^+ ion, calcd for $C_9H_{20}O_2Si$ 188.1233, found 188.1232. The *E*/*Z* assignments are based upon the RC*H*=CHOCH$_3$ ^1H NMR chemical shifts,[35] coupling constants, and allylic carbon ^{13}C NMR chemical shifts.[38,39]

Reaction of 2-Methoxytetrahydropyran with 1 under CO. A Fischer-Porter bottle was charged with 200 mg (0.75 mmol, 1.56 equiv) of 1, 56 mg (57 μL, 0.48 mmol) of acetal, 0.40 mL of CH_3CN, and a micro magnetic stir bar. The bottle was purged with CO and then pressurized to 200 psi. The reaction was stirred for 3.5 h and then vented. The solvent was removed under vacuum, and the resulting yellow oil was dissolved in hexane. An IR spectrum showed the presence of a manganese acyl ($\nu_{C=O}$ 2117 (m), 2049 (m), 2017 (s), 2006 (s, sh), $\nu_{C=O}$, 1641 (w) cm^{-1}) and some $Mn(CO)_9(CH_3CN)$.[13] Flash chromatography[41] in a 5:95 ethyl acetate/hexane mixture gave pure $(CO)_5MnCOCH(OCH_3)CH_2CH_2CH_2CH_2OSi(CH_3)_3$ (**6**) as a colorless liquid (128 mg, 0.312 mmol, 65%) which solidified upon cooling to –78 °C: ^1H NMR (δ, $CDCl_3$, 200 MHz) 3.47 (t, $J_{H-H'}$ = 6.0 Hz, 2 H), 3.38 (s, 3 H), 3.00 (t, J = 5.4 Hz, 1 H), 1.26–1.51 (m, 6 H), 0.01 (s, 9 H); ^{13}C NMR (ppm, C_6D_6/Cr(acac)$_3$, 22.5 MHz) 264.3 (acyl), 210.2 (MnCO), 96.6, 62.3, 57.4 (C–O), 33.1, 30.1, 21.3 (other CH_2), –0.4 (CSi); mass spectrum (*m*/*e* (relative intensity), 16 eV) 223 ($Mn(CO)_6^+$, 31), 89 (35), 85 (72), 75 (100), 73 ($Si(CH_3)_3^+$, 73), 71 (36), 55 (42), 43 (32), 41 (40). Since neat samples of **6** showed significant decomposition after 24 h at 25 °C, freshly purified compound was hand carried at –78 °C to Elek Microanalytical Laboratories, Torrance, CA. Anal. Calcd for $C_{15}H_{21}O_8MnSi$: C, 43.69; H, 5.13. Found: C, 43.96; H, 4.94.

Reaction of Hydrocinnamaldehyde Dimethyl Acetal with 1 and CO. A Fischer-Porter bottle was charged with 334 mg (1.25 mmol, 1.32 equiv) of 1, 170 mg (0.94 mmol) of acetal, 0.40 mL of CH_3CN, and a micro magnetic stir bar. The bottle was purged with CO and then pressurized to 200 psi. The reaction was stirred for 3 h and then vented. The solvent was removed under vacuum, and the resulting yellow oil was flash chromatographed[41] in a 5:95 ethyl acetate/hexane mixture. Solvent was stripped from the eluent, and the labile acyl$(CO)_5MnCOCH(OCH_3)CH_2CH_2C_6H_5$ was vacuum sublimed: IR (cm^{-1}, hexane) $\nu_{C=O}$ 2119 (w), 2052 (w), 2019 (s), 2008 (s, sh), $\nu_{C=O}$ 1625 (m); ^1H NMR (δ, $CDCl_3$, 200 MHz) 7.25 (m, 5 H), 3.51 (s, 3 H), 3.17 (t, $J_{H-H'}$ = 6 Hz, 1 H), 2.73 (t, J = 6 Hz, 2 H), 2.00 (m, 2 H).

Reaction of Cyclohexanone Ethylene Glycol Ketal with 1. A reaction was conducted at 50 °C in a 5-mm NMR tube with 70 mg (0.261 mmol, 1.16 equiv) of 1, 32.0 mg (33 μL, 0.225 mmol) of ketal, and 0.30 mL of CD_3CN as described above for cyclohexanone dimethyl ketal. After 1 h, ^1H NMR analysis (relative integrals of the δ 4.56 vinyl resonance and the $-OCH_2$ region, δ 3.4–4.1) showed that **7** (eq 3) had formed in 94% yield. Then 17 mg of $C_6H_5CH_2Si(CH_3)_3$ standard was added for GLC analysis. A 92% yield of **7** was thus calculated.

A preparative reaction was conducted at 50 °C with 260 mg (0.970 mmol, 1.06 equiv) of 1 and 130 mg (0.915 mmol) of ketal in 0.1 mL of CD_3CN. After 1 h, ^1H NMR indicated the reaction to be complete. The solvent and $(CO)_5MnH$ were removed by rotary evaporation, and the residue was distilled on a molecular still to give 172 mg (0.804 mmol, 87%) of **7** which was >97% pure by GLC analysis. Data on **7**: ^1H NMR (δ, $CDCl_3$, 200 MHz) 4.56 (br s, =CHR), 3.79 (t, $J_{H-H'}$ = 4.9 Hz, OCH_2), 3.69 (t, J = 4.9 Hz, OCH_2), 2.10–1.90 (m, 4 H), 1.75–1.40 (m, 4 H), 0.10 (s, 9 H); ^{13}C NMR (ppm, $CDCl_3$, 50 MHz) 154.5, 93.9 (C=C), 67.4, 61.5 (OC), 27.8, 23.5, 22.9, 22.7 (CH_2), –0.4 (SiC); mass spectrum (*m*/*e* (relative intensity), 16 eV) 214 (M^+, 24), 199 ($M^+ - CH_3$, 14), 171 (69), 117 (29), 116 (100), 101 (31), 73 (35).

Reaction of Cyclohexanone Diallyl Ketal with 1. A reaction was conducted at 25 °C in a 5-mm NMR tube with 160 mg (0.597

(39) The *Z*/*E* assignement for **3** is supported by allylic carbon ^{13}C NMR chemical shifts.[40] This appears to be the most general method for distinguishing enol ether geometric isomers.[38]

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mmol, 3.55 equiv) of 1, 32.9 mg (0.168 mmol) of ketal, 10.7 mg (0.065 mmol) of $(C_6H_5)_2CH_2$ standard, and 0.30 mL of CD_3CN, as described above for cyclohexanone dimethyl ketal. After 3 days, ^1H NMR analysis showed 1 to be consumed. GLC analysis showed starting ketal (58%), 1-cyclohexenyl allyl ether (42%), and $H_2C{=}CHCH_2OSi(CH_3)_3$ (48%).

Reaction of Trimethyl Orthoacetate with 1. A reaction was conducted at 50 °C in a 5-mm NMR tube with 70 mg (0.261 mmol, 1.35 equiv) of 1, 23.2 mg (0.193 mmol) of orthoacetate, 14.0 mg (0.085 mmol) of $C_6H_5CH_2Si(CH_3)_3$, and 0.30 mL of CD_3CN as described above for cyclohexanone dimethyl ketal. After 1.5 h, ^1H NMR analysis showed 1 to be consumed and a trace of $(CO)_5MnCH_3$ (δ −0.15). GLC analysis indicated 30%, 60%, and 35% yields of $CH_3CO_2CH_3$, $CH_3OSi(CH_3)_3$, and starting material, respectively. An IR spectrum of an aliquot showed weak absorbances (2090, 2000, 1972 cm^{-1}) attributable to $(CO)_5MnCH_3$.[42]

Reaction of Triethyl Orthoacetate with 1. A reaction was conducted at 50 °C in a 5-mm NMR tube with 70 mg (0.261 mmol, 1.48 equiv) of 1, 28.4 mg (0.176 mmol) of orthoacetate, 9.6 mg (0.060 mmol) of $C_6H_5CH_2Si(CH_3)_3$, and 0.30 mL of CD_3CN as described above for trimethyl orthoacetate. After 1.5 h, ^1H NMR analysis showed 1 to be consumed. GLC analysis indicated 32%, 40%, and 8% yields of $CH_3CO_2CH_2CH_3$, $CH_3CH_2OSi(CH_3)_3$, and starting material, respectively.

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Acknowledgment. We thank the National Science Foundation for support. FT NMR spectrometers utilized in this study wre provided by NSF Departmental instrumentation grants.

Registry No. 1, 26500-16-3; 2, 53119-71-4; (*Z*)-3, 53119-73-6; (*E*)-3, 53119-72-5; (*E*)-4, 82996-09-6; (*Z*)-4, 82996-10-9; 5, 14031-96-0; 6, 83024-95-7; 7, 82996-11-0; cyclohexanone dimethyl ketal, 933-40-4; 2-methylcyclohexanone dimethyl ketal, 38574-09-3; cyclopentanone dimethyl ketal, 931-94-2; 2-norbornanone dimethyl ketal, 10395-51-4; acetone dimethyl ketal, 77-76-9; cyclooctanone dimethyl ketal, 25632-03-5; 5-nonanone dimethyl ketal, 69470-13-9; acetophenone dimethyl ketal, 4316-35-2; cyclopropyl methyl ketone dimethyl ketal, 52829-97-7; 4-methyl-2-pentanone dimethyl ketal, 1112-78-3; 1-methoxycyclohexene, 931-57-7; 1-methoxy-2-methylcyclohexene, 1728-38-7; 1-methoxy-6-methylcyclohexene, 1728-37-6; 1-methoxycyclopentene, 1072-59-9; 2-methoxy-2-norbornene, 17190-90-8; 2-methoxypropene, 116-11-0; 1-methoxycyclooctene, 50438-51-2; (*E*)-5-methoxy-4-nonene, 82215-72-3; (*Z*)-5-methoxy-4-nonene, 82215-71-2; 1-(methoxyethenyl)benzene, 4747-13-1; 1-(methoxyethenyl)-cyclopropane, 66031-87-6; 1,3,3-trimethoxybutane, 6607-66-5; 2,4-dimethoxybutene, 52128-62-8; 3,3-dimethoxy-1-butene, 72757-52-9; 2-methoxy-1,3-butadiene, 3588-30-5; 2-methoxytetrahydropyran, 6581-66-4; hydrocinnamaldehyde dimethyl acetal, 30076-98-3; cyclohexanone ethylene glycol ketal, 177-10-6; cyclohexanone diallyl ketal, 53608-84-7; 1-cyclohexenyl allyl ether, 79643-88-2; trimethyl orthoacetate, 1445-45-0; triethyl orthoacetate, 78-39-7; $(CO)_5MnCOCH(OCH_3)CH_2CH_2C_6H_5$, 83005-51-0.

Palladium-Catalyzed Formation of 1,4-Disilacyclohexa-2,5-dienes from 1-Silacyclopropenes

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Received June 3, 1982

When 3-(trimethylsilyl)-, 3-(ethyldimethylsilyl)-, 3-(*tert*-butyldimethylsilyl)-, or 3-(phenyldimethylsilyl)-1,1-dimethyl-2-phenyl-1-silacyclopropene was heated with a catalytic amount of dichlorobis(triethylphosphine)palladium(II) in a sealed glass tube at 120 °C, the respective 1,4-disilacyclohexa-2,5-diene was produced with high regioselectivity. Under identical conditions, 1-methyl-1,2-diphenyl-3-(trimethylsilyl)-1-silacyclopropene afforded *trans*-1,4-dimethyl-1,2,4,5-tetraphenyl-3,6-bis(trimethylsilyl)-1,4-disilacyclohexa-2,5-diene (**10**) as the sole product. Similar reaction of 1,1,2-triphenyl-3-(trimethylsilyl)-1-silacyclopropene gave 1,1,2,4,4,5-hexaphenyl-3,6-bis(trimethylsilyl)-1,4-disilacyclohexa-2,5-diene. Treatment of 1,2-dimethyl-1-phenyl-3-(trimethylsilyl)-1-silacyclopropene with the same catalyst in hexane gave *trans*-1,2,4,5,-tetramethyl-1,4-diphenyl-3,6-bis(trimethylsilyl)-1,4-disilacyclohexa-2,5-diene. The crystal structure of **10** has been determined. Compound **10** crystallizes in the orthorhombic space group *Pbca* with cell dimensions a = 20.771 (4) Å, b = 18.842 (3) Å, c = 9.201 (1) Å; V = 3600.7 (1) Å^3; D_{calcd} = 1.087 (Z = 4) Mg m^{-3}.

Introduction

Although considerable attention has been devoted to investigations of silacyclopropenes,[2] much less interest has been shown in the reaction of these compounds with transition-metal complexes.[3-6] Recently, we have reported that the nickel-catalyzed reaction of the silacyclopropenes prepared by the photolysis of (phenylethynyl)disilanes in the presence of phenylsilylacetylenes affords 1-silacyclopenta-2,4-dienes arising from two-atom insertion of the acetylene into a silicon–carbon bond in the silacyclopropene ring in excellent yields.[7] However, the palladium-catalyzed reaction of the silacyclopropenes led to the

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