Reactions of $(CO)_5MnSi(CH_3)_3$ with α-Bromo Carbonyl and Related Organic Compounds. Facile Reductive Silylation

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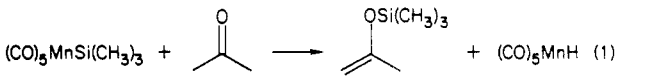
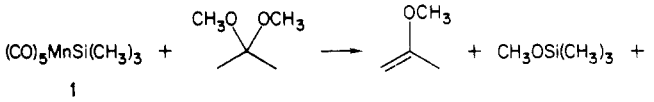
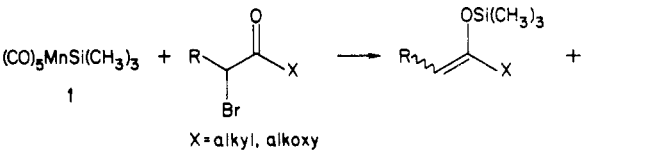
Reactions of $(CO)_5MnSi(CH_3)_3$ (1, 1.0–3.0 equiv, 25–50 °C) with α-bromo carbonyl compounds, α-(diphenylphosphino)isobutyraldehyde, and α-bromo dimethyl acetals and ketals are examined. The α-bromo carbonyl compounds are reductively silylated to trimethylsilyl enol ethers in fair to excellent yields. The initial inorganic product is $(CO)_5MnBr$. A mechanism is proposed in which 1 initially silylates the carbonyl oxygen and $(CO)_5Mn^-$ subsequently abstracts bromine. The phosphino aldehyde is similarly reduced, and the acetals and ketals are converted to methyl enol ethers and $CH_3OSi(CH_3)_3$. The synthetic utility of these transformations is discussed.

Our research group has been engaged in a systematic study of the reactions of transition metal trialkylsilane complexes with organic molecules.[3] We have reported that the readily available manganese complex $(CO)_5MnSi(CH_3)_3$ (1)[4] and aliphatic ketones and aldehydes react under mild conditions to give trimethylsilyl enol ethers and $(CO)_5MnH$ (eq 1).[5] Similarly, 1 and dimethyl ketals react to give methyl enol ethers, $CH_3OSi(CH_3)_3$, and $(CO)_5MnH$ (eq 2).[6] Equations 1 and 2 differ from conventional methodologies for these functional group transformations in that no added acid or base is required.





In this paper, we describe a study of the reactions of 1 with α-bromo carbonyl and related organic compounds. We were prompted to undertake this investigation for two reasons. First was the issue of chemoselectivity. Would α-hydrogen abstraction (giving $(CO)_5MnH$) or α-bromine abstraction (giving $(CO)_5MnBr$) be the dominant reaction pathway? Second was the possibility that synthetically useful transformations might be realized. For instance, although there exist many methods for the reductive dehalogenation of α-halo ketones,[7,8] few if any proceed under aprotic, neutral conditions and in the absence of a metal (0) reductant. As is depicted in the generalized eq 3, 1 proves to be an effective reagent for the reductive silylation of α-bromo carbonyl and related compounds.



Results

(1) Reactions of α-Halo Ketones and α-Halo Aldehydes. Reaction of α-bromocyclohexanone with 1.0 equiv of 1 for 3 h in acetonitrile at room temperature gave, as assayed by GLC, debrominated products cyclohexanone trimethylsilyl enol ether and cyclohexanone in a 81:19 ratio and a combined yield of >96% (entry 1, Table I).[9] A preparative reaction was conducted without solvent for 2 days at 50 °C (1.5 equiv of 1). Cyclohexanone trimethylsilyl enol ether of >95% purity was subsequently isolated in 88% yield. Careful drying of solvents, or addition of pyridine (0.5 equiv) to the reaction, failed to eliminate the cyclohexanone byproduct.

The reaction of α-bromocyclohexanone with 1 in acetonitrile gave $(CO)_5MnBr$ as the initial organic product, as assayed by IR spectroscopy. However, by the time the organic substrate was consumed, other manganese carbonyls could be detected. Column chromatography yielded $(CO)_5MnBr$ (53% of theory), $Mn_2(CO)_{10}$ (14% of theory), $Mn_2(CO)_9(CH_3CN)$ (3% of theory), and $[(CO)_4MnBr]_2$ (9% of theory). In experiments with less reactive organic substrates (vide infra), $Mn_2(CO)_{10}$ and $Mn_2(CO)_9(CH_3CN)$ became the major products, and $(CH_3)_3SiBr$ was observed by ^1H NMR spectroscopy (δ 0.57) and GLC. To test one possible origin for these products, equimolar amounts of 1 and $(CO)_5MnBr$ were reacted in acetonitrile (eq 4). Over the course of 12–46 h, $Mn_2(CO)_{10}$ and $(CH_3)_3SiBr$, and lesser amounts of $Mn_2(CO)_9(CH_3CN)$ and $[(CO)_4MnBr]_2$, formed. Hence, an excess of 1 was employed in most subsequent experiments.

$$(CO)_5MnSi(CH_3)_3 + (CO)_5MnBr \xrightarrow[12\ h]{CH_3CN} Mn_2(CO)_{10} + (CH_3)_3SiBr \quad (4)$$

Entry 1 of Table I was repeated in the presence of 0.1 equiv of $(CO)_5Mn^-K^+$. No change in the rate of formation

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(3) Gladysz, J. A. *Acc. Chem. Res.* **1984**, *17*, 326.
(4) (a) Berry, A. D.; MacDiarmid, A. G. *Inorg. Nucl. Chem. Lett.* **1969**, *5*, 601. (b) Malisch, W.; Kuhn, M. *Chem. Ber.* **1974**, *107*, 979. (c) Gladysz, J. A.; Williams, G. M.; Tam, W.; Johnson, D. L.; Parker, D. W.; Selover, J. C. *Inorg. Chem.* **1979**, *18*, 553.
(5) Johnson, D. L.; Gladysz, J. A. *Inorg. Chem.* **1981**, *20*, 2508.
(6) Marsi, M.; Gladysz, J. A. *Organometallics* **1982**, *1*, 1467.
(7) Noyori, R.; Hayakawa, Y. *Org. React.* **1983**, *29*, 163; see especially Table III.
(8) See, inter alia: (a) Rubottom, G. M.; Mott, R. C.; Krueger, D. S. *Synth. Commun.* **1977**, *7*, 327. (b) Olah, G. A.; Arvanaghi, M.; Vankar, Y. D. *J. Org. Chem.* **1980**, *45*, 3531. (c) Clive, D. L. J.; Beaulieu, P. L. *Ibid.* **1982**, *47*, 1124. (d) Engman, L.; Cava, M. P. *Ibid.* **1982**, *47*, 3946. (e) Urata, H.; Suzuki, H.; Moro-oka, Y.; Ikawa, T. *J. Organomet. Chem.* **1982**, *234*, 367. (f) Osuka, A.; Suzuki, H. *Chem. Lett.* **1983**, 119. (g) Dubois, J.-E.; Lion, C.; Dugast, J.-Y. *Tetrahedron Lett.* **1983**, *24*, 4207.

(9) All products from reactions of 1 were identified by chromatographic and spectroscopic comparisons to commercial or independently prepared authentic samples, unless noted. Yields were based upon the limiting reagent.

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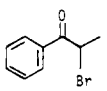
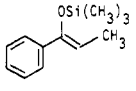
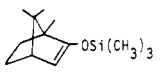
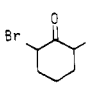
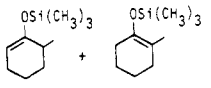
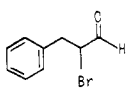
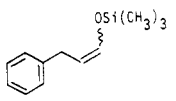
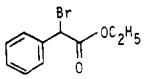
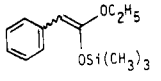
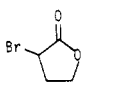
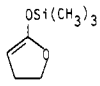
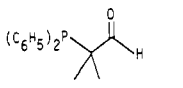
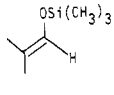
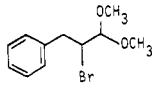
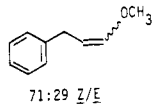
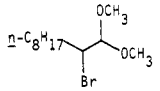
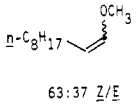
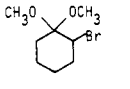
Table I. Summary of Reactions of $(CO)_5MnSi(CH_3)_3$ (1) with α-Bromo Carbonyl and Related Compounds[a]

entry	starting material	product	yield data %[b] NMR	GLC	isol
1			–	79	88
2			98	85	–
3			97	–	–
4		 82:18[d]	85[c]	–	–
5		2 + 3 1-2:99-98[d]	–	75	–
6		 72:28 Z/E	56	–	–
7			92	94	90
8			45[d]	–	–
9			84	84	–
10		 71:29 Z/E	92	–	62
11		 63:37 Z/E	83	–	51
12			78	–	–

[a] See Experimental Section for reaction conditions and isomer assignments. [b] Yields are based upon the organic substrate (limiting reagent) and are estimated to be accurate within ±5%. [c] Yield of isomer **2** only. [d] Data from reaction conducted in the presence of $(C_2H_5)_3N$.

of organic products, and their final yields, was observed.

Reactions of **1** (2 equiv, acetonitrile, 25–45 °C) with α-bromopropiophenone and α-bromocamphor (entries 2 and 3, Table I) also gave good yields of trimethylsilyl enol ethers. The product from the former reaction was >95% isomerically pure and assigned as the *Z* geometric isomer by comparison to NMR data of Heathcock.[10] In side-by-side reactions (CD_3CN, 25 °C), α-bromocamphor and camphor were treated with **1** (1.5 equiv). After 110 min, camphor trimethylsilyl enol ether was present in 86% yield in the former reaction, but only 21% yield in the latter. The organic substrate was consumed in the former reaction, but remained in the latter.

Reactions of **1** with 2-bromo-6-methylcyclohexanone and 2-bromo-2-methylcyclohexanone in acetonitrile were investigated next (entries 4 and 5, Table I). In initial experiments, poor regioselectivity was observed. For example, **1** (1.5 equiv) and 2-bromo-6-methylcyclohexanone reacted over the course of 65 min at 25 °C to give a 62:38 mixture of isomeric trimethylsilyl enol ethers **2** and **3** (see structures, Table I). Analysis by ^1H NMR showed **2** to be present in 63% yield. After an additional 24 h, the ratio of **2**/**3** was 43:57.

A similar reaction of **1** (1.7 equiv) and 2-bromo-6-methylcyclohexanone was conducted in the presence of $(C_2H_5)_3N$ (0.45 equiv). A 82:18 mixture of **2** and **3** formed. Analysis by ^1H NMR showed **2** to be present in 85% yield. The product composition did not change over the course of 24 h. A comparable reaction of **1** (1.5 equiv) and 2-bromo-2-methylcyclohexanone gave, after 25 min at 25 °C, a 1–2:99–98 mixture of **2** and **3** in a combined yield of ca. 75% (entry 5, Table I). GLC analysis also showed the presence of 2-methylcyclohexanone (16%) and some starting bromo ketone. After an additional 75 min all ketones had been consumed, and **2** and **3** were present in a 4:96 ratio and a 99% combined yield.

The reaction of **1** (1.3 equiv, acetonitrile) with 2-chloro-2-methylcyclohexanone was qualitatively investigated. After 5 days at 25 °C, starting chloro ketone was >95% consumed. However, the anticipated product **3** was absent. Two major products—2-methylcyclohexanone and a species provisionally assigned as 3-chloro-3-methyl-2-[(trimethylsilyl)oxy]cyclohexene (δ 5.12)—had formed. Poor ^1H NMR resolution precluded obtaining quantitative yield data.

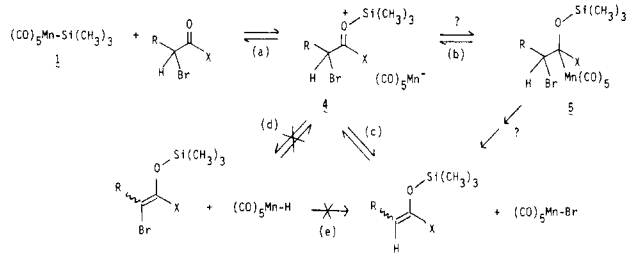
To probe a possible route for the generation of dehalogenated ketones noted in some of the above reactions, 2-bromo-6-methylcyclohexanone was treated with $(CO)_5MnH$ (1.2 equiv) in CH_3CN. Analysis by GLC after 15 min showed that 2-methylcyclohexanone had formed in >99% yield. Reaction of 2-chloro-2-methylcyclohexanone with $(CO)_5MnH$ (1.0 equiv) in CH_3CN gave, over the course of 2 days at 25 °C, an 83% yield of 2-methylcyclohexanone.

Attempts were also made to identify species which might equilibrate **2** and **3** in reactions of bromo-2-methylcyclohexanones with **1**. It was found that $(CO)_5MnH$ (0.3 equiv) converted a 98:2 mixture of **2** and **3** in acetonitrile to a 85:15 mixture over the course of 24 h at 25 °C. An identical 98:2 mixture of **2** and **3** was unaffected by $(CH_3)_3SiBr$ (1 equiv, 2 days, 25 °C). However, a combination of approximately 1 equiv each of $(CO)_5MnH$, $(CO)_5MnBr$, and **1** isomerized (19 h, 25 °C) the 98:2 **2**/**3** mixture to a 43:57 mixture.

Reactions of **1** with α-bromo aldehydes gave somewhat lower yields of trimethylsilyl enol ethers, as shown for α-bromodihydrocinnamaldehyde in entry 6 of Table I. Product dihydrocinnamaldehyde trimethylsilyl enol ether was obtained as a 72:28 mixture of *Z*/*E* isomers, as assigned from vinyl proton ^1H NMR chemical shifts and coupling constants previously reported by Hassner.[11]

(10) Heathcock, C. H.; Buse, C. T.; Kleschick, W. A.; Pirrung, M. C.; Sohn, J. E.; Lampe, J. E. *J. Org. Chem.* **1980**, *45*, 1066.
(11) Rasmussen, J. K.; Hassner, A. *J. Org. Chem.* **1974**, *39*, 2558.

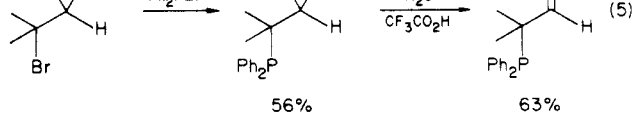
Scheme I. Proposed Mechanism for the Reaction of 1 and α-Bromo Carbonyl Compounds



Finally, as a control experiment, $(CO)_5MnH$ (1.0 equiv) and the brominated trimethylsilyl enol ether $H_3C(Br)C{=}CHOSi(CH_3)_3$[12] were mixed in CD_3CN. No reaction, as assayed by ^1H NMR, occurred over the course of 24 h at 25 °C.

(2) Reactions of Other Substrates. As shown in entry 7 of Table I, 1 (1.0 equiv) efficiently converted ethyl phenylbromoacetate (acetonitrile, 1.5–3.0 h, 25 °C) to phenylketene trimethylsilyl ethyl acetal. This material appeared isomerically pure by GLC and ^1H NMR. Inorganic products $(CO)_5MnBr$ (76%) and $Mn_2(CO)_{10}$ (10%) were isolated from a preparative reaction. A much lower yield of ketene acetal was obtained from 1 and α-bromo-γ-butyrolactone (entry 8). The product was not stable to the reaction conditions, as observed by ^1H NMR monitoring.

In connection with another project,[13] we prepared α-(diphenylphosphino)isobutyraldehyde as shown in eq 5 and treated it with 1 (1.1 equiv, acetonitrile, 2 h, 25 °C). To our suprise, the diphenylphosphino group was abstracted and isobutyraldehyde trimethylsilyl enol ether was obtained in 84% yield (entry 9, Table I).



(5)

As shown in entries 10–12 of Table I, α-bromo dimethyl acetals and ketals were converted to methyl enol ethers by 1 (1.5–3.0 equiv, acetonitrile). These substrates were somewhat less reactive, so temperatures of 45–50 °C were employed. The *Z*/*E* product assignments in entries 10[14] and 11 were made on the basis of ^1H NMR chemical shifts and coupling constants of the vinyl protons.[15]

Discussion

The reactions summarized in Table I establish that 1 preferentially abstracts bromine from α-bromo carbonyl substrates. Based upon our earlier mechanistic studies of the reactions of 1 with non-halogenated ketones,[5,16] we propose the initial silylation step shown in step a of Scheme I. The resulting ion pair **4** could possibly collapse to the metal–carbon σ-bonded complex **5** (step b, Scheme I). It is also possible that 4 is in equilibrium with a bromonium ion. However, the most direct route to product would entail α-bromine abstraction by anion $(CO)_5Mn^-$ from the cationic portion of ion pair 4 (step c). Any of these steps, as well as the corresponding steps in reactions of other types of substrates with 1, could plausibly involve initial electron transfer.

Although an α-bromo substituent should diminish the basicity of a carbonyl oxygen and hence the rate of step a of Scheme I, α-bromo substituents in fact enhance the reactivity of carbonyl compounds toward 1. For example, ethyl acetate does not react with 1 in CD_3CN,[5] but α-bromo esters do (entries 7 and 8, Table I). Similarly, α-bromocamphor is much more reactive toward 1 than camphor. This suggests that the rate-determining step in Scheme I (and in the analogous mechanism for eq 1)[5] occurs *subsequent* to step a. Finally, the fact that the rates of these reactions are not accelerated by added $(CO)_5Mn^-$ eliminates a possible anionic chain mechanism involving enolate intermediates.

An important question is whether α-bromine abstraction is kinetically preferred over α-hydrogen abstraction. For instance, it is a priori conceivable that $(CO)_5Mn^-$ could reversibly abstract *hydrogen* from the cationic portion of ion pair 4 as shown in step d of Scheme I. Furthermore, in view of the ready dehalogenation of 2-bromocyclohexanone by $(CO)_5MnH$ (see above), reaction of the resulting bromo trimethylsilyl enol ether with $(CO)_5MnH$ (step e) might directly lead to product. Both of these possibilities are excluded by the lack of reaction of $H_3C(Br)C{=}CHOSi(CH_3)_3$ with $(CO)_5MnH$. Also, the substrates 2-bromo-2-methylcyclohexanone (entry 5, Table I) and α-(diphenylphosphino)isobutyraldehyde (entry 9) show that an α-hydrogen is not required for reaction with 1.

The preference for α-bromine abstraction is likely principally due to the fact that sp^3 carbon–bromine bonds are generally ca. 30 kcal/mol weaker than sp^3 carbon–hydrogen bonds.[17] Also, the Mn–Br bond of $(CO)_5MnBr$ appears slightly stronger (58–62 kcal/mol) than the Mn–H bond of $(CO)_5MnH$ (51–55 kcal/mol).[18] However, we do not observe α-chlorine abstraction from 2-methyl-2-chlorocyclohexanone, even though sp^3 carbon–chlorine bonds are typically ca. 16 kcal/mol weaker than sp^3 carbon–hydrogen bonds.[17] The Mn–Cl bond strength of $(CO)_5MnCl$ is 70–73 kcal/mol.[18]

However, there is evidence that some α-hydrogen abstraction or other side reaction yielding $(CO)_5MnH$ may occur in reactions of 1 with α-bromo carbonyl substrates. For example, some cyclohexanone and 2-methylcyclohexanone were observed in the reactions given in entries 1 and 5 of Table I. Control experiments show that $(CO)_5MnH$ rapidly dehalogenates α-bromo ketones under the reaction conditions. Similar reduction of alkyl chlorides and bromides by $(L)(CO)_4MnH$ (L = phosphines, phosphites) have been previously reported.[19] Also, $(CO)_5MnH$ may be in part responsible for the equilibration of 2 and 3. However, since control experiments show this to be a slow reaction, we believe that HBr (possibly formed from $(CO)_5MnH$ and $(CO)_5MnBr$) is a more likely catalyst. In any event, $(C_2H_5)_3N$ proves effective in suppressing the equilibration.

By analogy to our earlier mechanistic studies of the reactions of 1 with non-halogenated methyl ketals and acetals,[5] we propose the mechanism shown in Scheme II for entries 10–12 of Table I. An ion pair **6**, analogous to 4 in Scheme I, is formed by loss of $CH_3OSi(CH_3)_3$ (step

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b). Abstraction of a bromine from the cation by $(CO)_5Mn^-$ (step c) then gives products. Alternatively, ion pair **6** could collapse to a metal alkyl (step d) and undergo a subsequent net β-bromide elimination. Interestingly, α-bromo methyl acetals give much cleaner reactions with **1** than nonhalogenated methyl acetals.

Several studies of other reseachers are of particular relevance to our data. First, Olah has found that $(CH_3)_3SiCl/NaI$ converts, after an aqueous workup, a wide variety of α-bromo and α-chloro ketones to ketones.[8b] Initial carbonyl group silylation, analogous to step a of Scheme I, is likely. Similar results have been obtained by Ho with $(CH_3)_3SiI$.[20] Second, Miller and McKean found that $(CH_3)_3SiI/HN(Si(CH_3)_3)_2$ transforms α-chloro ketones to chlorinated trimethylsilyl enol ethers.[21] In this case, hydrogen abstraction analogous to step d of Scheme I, with $HN(Si(CH_3)_3)_2$ as the base, is likely occurring.

Other methods for the reductive silylation of α-halo ketones include $Zn/(CH_3)_3SiCl/TMEDA$,[8a] $Li^+{}^-N(i\text{-}C_3H_7)_2/(CH_3)_3SiCl$,[8g] and iron graphite/$(CH_3)_3SiCl$.[22] The former recipe has been successfully used to prepare **3** free from regioisomer **2**. This is difficult to accomplish from the parent ketone.[23]

We are not aware of any literature precedent for the reductive conversion of α-bromo dimethyl acetals and ketals to methyl enol ethers (entries 10–12, Table I), or the reductive silylation of α-phosphino carbonyl compounds (entry 9). We note in passing that the first step in the preparation of α-(diphenylphosphino)isobutyraldehyde (eq 5) is likely an electron-transfer chain-substitution ($S_{RN}1$) reaction.[24]

In conclusion, we have identified a new mode of reactivity of **1** which enables the reductive silylation of α-bromo carbonyl and related organic compounds under very mild conditions. Reagent **1** does not noticeably deteriorate over several hours in dry air and can tolerate functional groups such as arenes, nitriles, unactivated halides and olefins, esters, and to some extent[16] ethers. Hence, we anticipate that the new reactions described above will prove of use in synthesis.

Experimental Section

General Methods. Instrumentation, general procedures, preparations of $(CO)_5MnX$ reagents, and solvent purifications utilized were identical with those described in previous publications[6,16,25] unless noted.

Organic Substrates and Authentic Product Samples. The following compounds were purchased from Aldrich or Eastman and were distilled prior to use: cyclohexanone, 2-methylcyclohexanone, α-bromopropiophenone, α-bromo-γ-butyrolactone, decanal, dihydrocinnamaldehyde, $(CH_3)_3SiCl$, $(C_6H_5)_2PCl$, and *p*-di-*tert*-butylbenzene. α-Bromocamphor and $HC(OCH_3)_3$ were used as received from Aldrich. Standards *sec*-butylbenzene (MCB) and $C_6H_5CH_2Si(CH_3)_3$ (Petrach) were purified by vacuum distillation; Ph_3CH (MCB) was used as received. Other starting materials were obtained from common commercial sources and were used as received.

Trimethylsilyl enol ethers of cyclohexanone, propiophenone,[10] dihydrocinnamaldehyde,[11] and decanal[11] were prepared from $(CH_3)_3SiCl$ and $(CH_3CH_2)_3N$ in DMF as described by House.[26] A 12:88 mixture of **2**/**3** was similarly prepared from 2-methylcyclohexanone.[26] Camphor trimethylsilyl enol ether[8a,22] was prepared from camphor, $(CH_3)_3SiCl$, and $Li^+{}^-N(i\text{-}C_3H_7)_2$ as described by House.[26] A 98:2 mixture of **2**/**3** was similarly prepared from 2-methylcyclohexanone.[26] Isobutyraldehyde and propionaldehyde trimethylsilyl enol ethers were prepared by the routes of Stang[27] and Olofson,[28] respectively. Ethyl trimethylsilyl phenylketene acetal was synthesized from ethyl phenylacetate, $Li^+{}^-N(i\text{-}C_3H_7)_2$, and $(CH_3)_3SiCl$.[29]

Bromides 2-bromocyclohexanone, α-bromodihydrocinnamaldehyde, and α-bromodecanal were prepared from the corresponding trimethylsilyl enol ethers by the method of Hassner.[30] 2-Bromo-6-methylcyclohexanone was prepared by Hassner's procedure with NBS. 2-Bromo-2-methylcyclohexanone[31] was prepared from 2-methylcyclohexanone and Br_2 in CCl_4 at 0 °C. Ethyl bromophenylacetate[32] and $H_3CC(Br)=CHOSi(CH_3)_3$[12] were synthesized by literature procedures. 2-Chloro-2-methylcyclohexanone was prepared from 2-methylcyclohexanone and SO_2Cl_2 in CCl_4.[33]

α-Bromodihydrocinnamaldehyde dimethyl acetal, α-bromodecanal dimethyl acetal,[34] and α-bromocyclohexanone dimethyl ketal[35] were synthesized from the corresponding carbonyl compounds and 1.3 equiv of $HC(OCH_3)_3$ in CH_3OH with a catalytic amount of $p\text{-}CH_3C_6H_4SO_3H\cdot H_2O$.[36] After 2 days, the solution was neutralized with Na_2CO_3 and filtered. The solution was concentrated in vacuo and the product was vacuum distilled. Data on α-bromodecanal dimethyl acetal:[34] ^1H NMR (δ, toluene-d_8, 300 MHz) 4.25 (d, J_{HH} = 5.8 Hz, 1 H), 3.89 (m, 1 H), 3.14 (s, 3 H), 3.13 (s, 3 H), 1.93 (m, 1 H), 1.73 (dt, J_{HH} = 5, 15 Hz, 1 H), 1.58 (m, 1 H), 1.19 (m, 11 H), 0.88 (t, J_{HH} = 7.5 Hz, 3 H). Anal. Calcd for $C_{12}H_{25}BrO_2$: C, 51.25; H, 8.96. Found: C, 51.43; H, 9.03. An authentic sample of 1-methoxycyclohexene was prepared as described previously.[6]

Product Analysis. Procedures for the GLC analysis of organic products have been previously descried.[5,6,16] Experiments where yields are determined by ^1H NMR were conducted with a Varian EM-390 spectrometer. Manganese carbonyls were identified from both chromatographic comparisons to authentic samples and IR spectra. Typically observed $\nu_{C\equiv O}$ (cm^{-1}): $Mn_2(CO)_{10}$ (hexanes) 2046 m, 2015 s, 1984 m (lit.[37] 2045.8, 2014.7, 1983.8); $Mn_2(CO)_9(CD_3CN)$ (hexane) 2092 w, 2025 s, 2005 s, 1989 vs, 1965 s, 1948 m (lit.[38] 2094, 2026, 2005, 1990–1988, 1964, 1947); $(CO)_5MnBr$ (CCl_4) 2136 w, 2052 s, 2002 m (lit. (cyclohexane)[39] 2133, 2049, 2004); $[(CO)_4MnBr]_2$ (CCl_4) 2100 w, 2044 s, 2013 m, 1978 m (lit.[40] 2099, 2042, 2011, 1975).

Reaction of α-Bromocyclohexanone with 1. A. A 5-mm NMR tube was charged with **1** (54.8 mg, 0.204 mmol, 1.00 equiv), α-bromocyclohexanone (35.9 mg, 0.203 mmol), and Ph_3CH (28.0 mg, 0.115 mmol) internal standard. A second tube was charged with **1** (55.1 mg, 0.206 mmol, 1.02 equiv), $(CO)_5Mn^-K^+$ (4.7 mg, 0.020 mmol), α-bromocyclohexanone (35.6 mg, 0.203 mmol), and Ph_3CH (28.6 mg, 0.117 mmol). Both tubes were simultaneously injected with CD_3CN (0.5 mL) and capped with septa. The tubes were kept at room temperature for 20 min, and then cooled to 0 °C (to retard reaction) for GLC analysis. The same amount of starting bromo ketone (ca. 20%) was present in each tube. After a total of 3 h at room temperature, GLC analysis showed cyclohexanone trimethylsilyl enol ether and cyclohexanone to be

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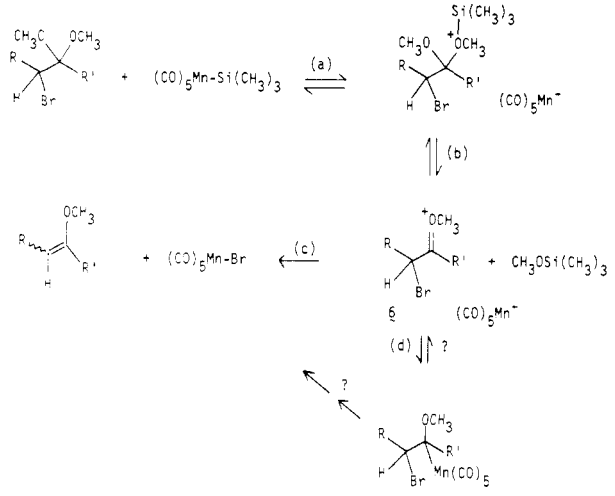
Scheme II. Proposed Mechanism for the Reaction of 1 and α-Bromo Acetals and Ketals



present in a 81:19 ratio and a combined yield of 96%. The manganese containing products of the first tube were isolated by silica gel chromatography with hexane, then CH_2Cl_2/hexane, and then CH_2Cl_2. Thus eluted were $(CO)_5MnBr$ (29.9 mg, 0.109 mmol), $Mn_2(CO)_{10}$ (5.5 mg, 0.014 mmol), $Mn_2(CO)_9(CD_3CN)$ (1.1 mg, 0.003 mmol), and $[(CO)_4MnBr]_2$ (4.2 mg, 0.009 mmol). **B.** A 5-mm NMR tube was charged with 1 (201 mg, 0.75 mmol, 1.50 equiv) and α-bromocyclohexanone (88 mg, 0.50 mmol) under an argon atmosphere. The reaction was kept at 50 °C for 2 days. Subsequent vacuum distillation gave 75 mg (0.44 mmol, 88%) of cyclohexanone trimethylsilyl enol ether which was >95% pure as assayed by ^1H NMR spectroscopy.

Reaction of α-Bromopropiophenone with 1. A 5-mm NMR tube was charged with 1 (92.0 mg, 0.343 mmol, 2.07 equiv) and capped with a septum. The tube was evacuated/refilled with argon four times and then CD_3CN (0.4 mL) followed by α-bromopropiophenone (35.4 mg, 0.166 mmol) and $C_6H_5CH_2Si(CH_3)_3$ (18.0 mg, 0.107 mmol) were added via syringe. After 45 min, ^1H NMR analysis showed that the reaction had gone to completion. Integration of the vinyl region (δ 5.2–5.8) vs. the trimethylsilyl region (δ 0.0–0.6) indicated propiophenone trimethylsilyl enol ether to be present in 98% yield. A substantial amount of $(CH_3)_3SiBr$ (δ 0.57) was also present. An IR spectrum showed $(CO)_5MnBr$, $Mn_2(CO)_{10}$, and $Mn_2(CO)_9(CH_3CN)$. An identical reaction was subjected to GLC analysis with $C_6H_5CH_2Si(CH_3)_3$ as the internal standard. Propiophenone trimethylsilyl enol ether of ≥96% isomeric purity was present in 85% yield.

Reaction of α-Bromocamphor with 1. A 5-mm NMR tube was charged with 1 (60.0 mg, 0.224 mmol, 2.0 equiv), α-bromocamphor (25.6 mg, 0.111 mmol), and Ph_3CH (20.8 mg, 0.085 mmol) internal standard. Then CD_3CN (0.4 mL) was added and the tightly septumed tube was kept at 45 °C for 40 min. Subsequent ^1H NMR analysis showed 0.108 mmol (97%) of camphor trimethylsilyl enol ether, as assayed by integration of the vinyl proton resonance (δ 4.71, d, J_{HH} = 4 Hz) vs. the standard. Product identity was confirmed by GLC comparison to an authentic sample.

Reaction of 2-Bromo-6-methylcyclohexanone with 1 and $(C_2H_5)_3N$. A 5-mm septum capped NMR tube was charged with 1 (70 mg, 0.261 mmol, 1.74 equiv), 2-bromo-6-methylcyclohexanone (28.7 mg, 0.150 mol) of 98% isomeric purity, $(C_2H_5)_3N$ (6.85 mg, 0.068 mmol, 0.45 equiv), and Ph_3CH (26.1 mg, 0.107 mmol) internal standard. Then CD_3CN (0.4 mL) was added and the reaction was kept at room temperature. After 45 min, ^1H NMR analysis showed 0.111 mmol (85%) of **2**, as assayed by the vinyl proton resonance (δ 4.83, t, J_{HH} = 4 Hz). Analysis by GLC indicated a 82:18 ratio of **2/3**. The amount of the minor isomer was not sufficient to be quantified by ^1H NMR. The **2/3** ratio remained unchanged for an additional 24 h.

Reaction of 2-Bromo-2-methylcyclohexanone with 1 and $(C_2H_5)_3N$. A 1-mL septum-capped culture tube was charged with 1 (41 mg, 0.153 mmol, 1.49 equiv), 2-bromo-2-methylcyclohexanone (19.7 mg, 0.103 mmol) of 96.3% isomeric purity, $(C_2H_5)_3N$ (4.8 mg, 0.047 mmol, 0.46 equiv), and *sec*-butylbenzene (8.0 mg, 0.060 mmol) internal standard. Then CH_3CN (0.4 mL) was added and the reaction was kept at room temperature. After 25 min, GLC analysis showed **2/3** in a combined yield of 75% and a 1.4:98.6 isomer ratio. Also present were 2-methylcyclohexanone (16%) and a small amount of starting material. After an additional 75 min **2/3** were present in a combined yield of 99% (0.102 mmol) and a 3.9:96.1 isomer ratio.

Reaction of 2-Bromo-6-methylcyclohexanone with $(CO)_5MnH$. A septum-capped 1-mL culture tube was charged with $(CO)_5MnH$ (18.3 mg, 0.093 mmol, 1.21 equiv), 2-bromo-6-methylcyclohexanone (14.7 mg, 0.077 mmol), and *sec*-butylbenzene (4.7 mg, 0.035 mmol) internal standard. Then CH_3CN (0.4 mL) was added and the reaction was kept at room temperature. After 15 min, GLC analysis indicated 2-methylcyclohexanone to be present in >99% (0.077 mmol) yield.

Reaction of α-Bromodihydrocinnamaldehyde with 1. A 5-mm NMR tube was charged with 1 (56.0 mg, 0.21 mmol, 2.0 equiv), α-bromodihydrocinnamaldehyde (22.4 mg, 0.105 mmol), and Ph_3CH (21.8 mg, 0.089 mmol) internal standard and was capped with a septum. Then CD_3CN (0.4 mL) was added and the reaction was kept at room temperature for 3 h. Subsequent ^1H NMR analysis showed 0.059 mmol (56%) of dihydrocinnamaldehyde trimethylsilyl enol ether, as assayed by integration of the methylene protons (*Z* δ 3.41 (d of m, J_{HH} = 7 Hz), *E* δ 3.23 (d of m, J_{HH} = 8 Hz)) vs. the standard. GLC analysis indicated a 72:28 *Z*/*E* ratio. In a separate experiment, α-bromodihydrocinnamaldehyde was similarly treated with 1.2 equiv of 1 in CD_3CN at 5 °C. Identical ^1H NMR and GLC analysis indicated a 51% yield of enol ether, *Z*/*E* 76:24.

Reaction of Ethyl Phenylbromoacetate with 1. A. A 5-mm NMR tube was charged with 1 (60 mg, 0.22 mmol, 1.01 equiv) and CD_3CN (0.3 mL). The tube was capped with a septum and ethyl phenylbromoacetate (55 mg, 0.22 mmol) was added via syringe. The reaction was kept at room temperature for 2.5 h. Subsequent ^1H NMR analysis showed 1 to be consumed and a 92% yield of phenylketene trimethylsilyl ethyl acetal, as assayed by integration of the vinyl region vs. the trimethylsilyl region. **B.** An identical reaction was conducted with 60 mg (0.22 mmol, 1.03 equiv) of 1, 53 mg (0.22 mmol) of ethyl phenylbromoacetate, and 0.3 mL of CH_3CN, except that after 3 h $C_6H_5CH_2Si(CH_3)_3$ was added as a standard. Subsequent GLC analysis indicated a 94% yield of product of ≥96% isomeric purity. **C.** A Schlenk flask was charged with 1 (660 mg, 2.46 mmol, 1.03 equiv), ethyl phenylbromoacetate (579 mg, 2.38 mmol), CH_3CN (3 mL), and a stir bar. The reaction was stirred for 1.5 h. The CH_3CN solution was decanted away from material which had precipitated, and was concentrated to an oil. The oil was extracted with petroleum ether, and solvent was removed from the extract under reduced pressure to give 505 mg (2.14 mmol, 90%) of product as a colorless oil which was >95% pure by GLC and ^1H NMR. The insoluble materials from above were extensively washed with hexanes and these extracts chromatographed (silica gel) to give $Mn_2(CO)_{10}$ (48 mg, 0.12 mmol, 10%). The remaining material was identified as $(CO)_5MnBr$ (515 mg, 1.87 mmol, 76%) by its IR spectrum.

Reaction of α-Bromo-γ-butyrolactone with 1. A 5-mm septum-capped NMR tube was charged with α-bromo-γ-butyrolactone (22.4 mg, 0.136 mmol), Ph_3CH (24.1 mg , 0.099 mmol) standard, $(C_2H_5)_3N$ (7.3 mg, 0.072 mmol, 0.53 equiv), 1 (55 mg, 0.205 mmol, 1.51 equiv), and CD_3CN (0.4 mL). The tube was placed in a NMR probe (ca. 35 °C). After 25 min, ^1H NMR analysis indicated γ-butyrolactone trimethylsilyl ketene acetal to be present in 45% yield (0.061 mmol): δ 4.25 (t, J_{HH} = 9 Hz, 2 H), 3.71 (t, J_{HH} = 2.3 Hz, 1 H), 2.68 (dt, J_{HH} = 2.3, 9 Hz, 2 H), 0.26 (s, 9 H) (lit (δ, $CDCl_3$)[11] 4.32 (t, *J* = 9 Hz), 3.70 (t, *J* = 2 Hz), 2.62 (dt, *J* = 2, 9 Hz), 0.27 (s)). The sample was kept for 13 h at 25 °C, after which time this material had disappeared.

Preparation of α-(Diphenylphosphino)isobutyraldehyde. A 250-mL Schlenk flask was charged with THF (90 mL) and Li wire (ca. 0.5 g). Then Ph_2PCl (4.0 mL, 22 mmol) was added and the reaction was stirred for 12 h. The remaining Li wire was removed with forceps and the Ph_2PLi solution was cooled to −78 °C. Then 5.174 g (26.3 mmol) of $BrC(CH_3)_2CH(OCH_3)_2$[41] was

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added. The reaction was stirred at −78 °C for 0.5 h, after which the cooling bath was removed. After an additional 2.5 h, THF was removed in vacuo and hexanes was added to the residue. This solution was filtered through a 30-mL M frit funnel containing flame activated silica gel. The silica gel was further eluted with ca. 200 mL of hexanes. Solvent was removed from the filtrate by rotary evaporation. The residue was distilled at 10^{-5} torr and 157–158 °C to give 3.76 g (12.4 mmol, 56%) of $Ph_2PC(CH_3)_2CH(OCH_3)_2$ as a colorless liquid. ^1H NMR (δ, $CDCl_3$, 300 MHz) 7.67–7.62 (m, 4 H), 7.34–7.13 (m, 6 H), 3.94 (d, J_{HP} = 3.6 Hz, 1 H), 3.37 (s, 6 H), 1.15 (d, J_{HP} = 10.6 Hz, 6 H); $^{31}P\{^1H\}$ NMR (ppm, $CDCl_3$, 121 MHz) 13.8.

This portion of the synthesis must be done under a N_2 atmosphere. A Schlenk flask was charged with $Ph_2PC(CH_3)_2CH(OCH_3)_2$ (1.805 g, 5.97 mmol), acetone (30 mL), H_2O (6 mL), and CF_3CO_2H (0.1 mL). This mixture was refluxed for 4 h. The solvents were then removed in vacuo. The residue was taken up in a minimum of acetone and applied to the top of a 3 × 41 cm silica gel column which had been packed in 85:15 (v/v) hexanes/ethyl acetate. Elution with hexanes/ethyl acetate gave, after solvent removal in vacuo, 0.972 g (3.79 mmol, 63%) of α-(diphenylphosphino)isobutyraldehyde as a colorless liquid. This sublimed as a sticky white solid onto an ice-cooled probe at 10^{-5} torr and 50 °C. Two attempts to obtain good C,H analyses for this extremely air sensitive material were unsuccessful. ^1H NMR (δ, $CDCl_3$, 300 MHz) 9.36 (s, 1 H), 7.55–7.18 (m, 10 H), 1.32 (d, J_{HP} = 14.8 Hz, 6 H); ^{13}C NMR (ppm, $CDCl_3$, 75 MHz) 204.5 (s, C=O); C_6H_5 at 135.0 (d, J_{CP} = 19.7 Hz), 133.7 (d, J_{CP} = 17.2 Hz), 129.9 (s), 128.9 (d, J_{CP} = 7.3 Hz), 45.2 (d, J_{CP} = 22.0 Hz, $PC(CH_3)_2$), 20.8 (d, J_{CP} = 19.6 Hz, CH_3); $^{31}P\{^1H\}$ NMR (ppm, $CDCl_3$, 121 MHz) 11.8; IR (cm^{-1}, $CHCl_3$) ν_{C-H} 2823 w, 2726 w; $\nu_{C=O}$ 1719 ms, sh, 1698 s.

Reaction of α-(Diphenylphosphino)isobutyraldehyde with 1. A 5-mm septum-capped NMR tube was charged with α-(diphenylphosphino)isobutyraldehyde (11.0 mg, 0.043 mmol), toluene (8.3 mg, 0.090 mmol) standard, 1 (1.14 equiv, 13.2 mg, 0.049 mmol), and CD_3CN (0.4 mL). The reaction was kept at room temperature for 2 h. Subsequent ^1H NMR analysis indicated the aldehyde proton to have disappeared. After an additional hour, the areas of the methyl groups of the isobutyraldehyde trimethylsilyl enol ether (δ 1.72, br s) were integrated vs. the standard. This indicated an 84% yield of product. An identical yield was obtained by GLC analysis.

Reaction of α-Bromodihydrocinnamaldehyde Dimethyl Acetal with 1. A. A 5-mm NMR tube was charged (in a glove box) with 1 (61 mg, 0.228 mmol, 1.48 equiv) and CD_3CN. The tube was capped with a septum, removed from the box, and α-bromodihydrocinnamaldehyde dimethyl acetal (39.1 mg, 0.154 mmol) was added via syringe. The tube was placed in a 50 °C oil bath for 2 h. Subsequent ^1H NMR analysis indicated 1 to be consumed and a 92% yield of 1-methoxy-3-phenylpropene,[14] as assayed by integration of the vinyl region vs. the trimethylsilyl region. **B.** In a similar, preparative, reaction 1 (390 mg, 1.46 mmol, 2.1 equiv) and α-bromodihydrocinnamaldehyde (176 mg, 0.69 mmol) were reacted in 0.4 mL of CH_3CN at 50 °C. The reaction was then concentrated under vacuum (removing $(CH_3)_3SiBr$) and stored overnight at 0 °C, whereupon manganese containing byproducts precipitated. Product 1-methoxy-3-phenylpropene (64 mg, 0.43 mmol, 62%) was isolated from the supernatant by preparative GLC, E/Z 71:29.

Reaction of 2-Bromodecanal Dimethyl Acetal with 1. A. A 5-mm septum-capped NMR tube was charged with 2-bromodecanal dimethyl acetal (28.0 mg, 0.100 mmol), Ph_3CH (20.5 mg, 0.084 mmol) standard, 1 (54 mg, 0.201 mmol, 2 equiv), and CD_3CN (0.4 mL). The reaction was kept at 45 °C for 90 min. Subsequent ^1H NMR analysis indicated 0.083 mmol (83%) of 1-methoxy-1-decene, Z/E 63:37. **B.** A 5-mm septum-capped NMR tube was charged with 2-bromodecanal dimethyl acetal (500 mg, 1.78 mmol), 1 (955 mg, 3.56 mmol, 2.0 equiv), and CD_3CN (1.0 mL). The tube was warmed to 45 °C and was connected via a syringe to a bubbler to relieve CO pressure. After 3 h, the reaction was transferred to a round-bottom flask and the volatile components were removed under aspirator vacuum. The residue was taken up in 20 mL of petroleum ether (bp 30–60 °C) and was subsequently cooled (−78 °C, 0.5 h) to precipitate the inorganic products. This mixture was filtered cold and the filtrate was concentrated under aspirator vacuum and chromatographed on alumina with petroleum ether. This gave a total of 154.4 mg (0.91 mmol, 51%) of (*Z*)- and (*E*)-1-methoxy-1-decene. Earlier fractions contained pure *Z* isomer, and later fractions contained pure *E* isomer. Anal. Calcd for $C_{11}H_{22}O$: C, 77.58; H, 13.02. Found: C, 77.69; H, 12.98. Spectral data. *Z*: IR (cm^{-1}, thin film) $\nu_{C=C}$ 1666; ^1H NMR (δ, C_6D_6, 300 MHz) 5.70 (d, J_{HH} = 5.8 Hz, 1 H), 4.36 (q, J_{HH} = 7.0 Hz, 1 H), 3.16 (s, 3 H), 2.23 (q, J_{HH} = 7.3 Hz, 2 H), 1.22 (m, 12 H), 0.86 (m, 3 H); ^{13}C NMR (ppm, C_6D_6, 20 MHz) 146.5 (=*C*-H-OCH_3), 107.0 (=*C*HC), 58.9 (OCH_3), CH_2 at 32.3, 36.3, 29.9, 29.8 (2C), 24.4, 23.0, CH_3 at 14.3. *E*: IR (cm^{-1}, thin film) $\nu_{C=C}$ 1656; ^1H NMR (δ, C_6D_6, 300 MHz) 6.32 (d, J_{HH} = 12.6 Hz, 1 H), 4.66 (d of t, J_{HH} = 7.3, 12.6 Hz, 1 H), 3.19 (s, 3 H), 1.88 (q, J_{HH} = 6.6 Hz, 2 H), 1.25 (m, 12 H), 0.89 (t, J_{HH} = 6.6 Hz, 3 H); ^{13}C NMR (ppm, C_6D_6, 20 MHz) 147.8 (=*C*$HOCH_3$), 102.8 (=*C*HC), 55.3 (OCH_3), CH_2 at 32.3, 31.4, 29.9, 29.8, 29.5, 28.2, 23.1, CH_3 at 14.3.

Reaction of α-Bromocyclohexanone Dimethyl Ketal with 1. A 5-mm septum-capped NMR tube was charged with α-bromocyclohexanone dimethyl ketal (26.8 mg, 0.120 mmol), Ph_3CH (20.2 mg, 0.083 mmol) standard, 1 (96 mg, 0.358 mmol, 3 equiv), and CD_3CN (0.5 mL). The tube was kept at 45 °C and shaken occasionally. The disappearance of starting material (δ 4.43, t, J = 4 Hz) and the appearance of 1-methoxycyclohexene (δ 4.66, t, J = 3 Hz) was monitored by ^1H NMR. After 48 h, 0.094 mmol (78%) of product was present and 0.020 mmol (17%) of starting bromide remained. All 1 had been consumed.

Reaction of $(CO)_5MnBr$ with 1. A 5-mm NMR tube was charged with 1 (55.6 mg, 0.207 mmol, 1.00 equiv), $(CO)_5MnBr$ (57.2 mg, 0.208 mmol), *p*-di-*tert*-butylbenzene (19.0 mg, 0.100 mmol) internal standard, and CD_3CN (0.5 mL). The tube was capped with a septum and kept at 25 °C for 46 h. Subsequent ^1H NMR analysis showed $(CH_3)_3SiBr$ (δ 0.57, 0.178 mmol, 86%) and $(CH_3)_3SiOSi(CH_3)_3$ (δ 0.07, 0.011 mmol, 11% of theory). These assignments were verified by GLC (including coinjection). Silica gel column chromatography (hexanes, CH_2Cl_2/hexanes, CH_2Cl_2) gave $Mn_2(CO)_{10}$ (46.8 mg, 0.120 mmol, 58% of theory), $Mn_2(CO)_9(CD_3CN)$ (19.8 mg, 0.047 mmol, 23% of theory), and $[(CO)_4MnBr]_2$ (3.8 mg, 0.008 mmol, 4% of theory), as identified by IR.

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Registry No. 1, 26500-16-3; 2, 19980-33-7; 3, 19980-35-9; $C_6H_5COCHBrCH_3$, 2114-00-3; (*Z*)-$C_6H_5C(OSi(CH_3)_3)$=$CHCH_3$, 66323-99-7; $C_6H_5CH_2CHBrCHO$, 51075-28-6; (*Z*)-$C_6H_5CH_2CH$=$CHOSi(CH_3)_3$, 51425-56-0; (*E*)-$C_6H_5CH_2CH$=$CHOSi(CH_3)_3$, 51425-55-9; $C_6H_5CHBrCOOC_2H_5$, 2882-19-1; C_6H_5CH=$C(OC_2H_5)OSi(CH_3)_3$, 31491-20-0; $(C_6H_5)_2PC(CH_3)_2CHO$, 97294-88-7; $(CH_3)_2C$=$CHOSi(CH_3)_3$, 6651-34-9; $C_6H_5CH_2CHBrCH(OCH_3)_2$, 97294-89-8; (*Z*)-$C_6H_5CH_2CH$=$CHOCH_3$, 60053-39-6; (*E*)-$C_6H_5CH_2CH$=$CHOCH_3$, 60053-38-5; *n*-$C_8H_{17}CHBrCH(OCH_3)_2$, 18207-21-1; (*Z*)-*n*-$C_8H_{17}CH$=$CHOCH_3$, 93775-03-2; (*E*)-*n*-$C_8H_{17}CH$=$CHOCH_3$, 93222-35-6; $(CH_3)_2CBrCH(OCH_3)_2$, 36365-21-6; Ph_2PCl, 1079-66-9; Ph_2PLi, 4541-02-0; $Ph_2PC(CH_3)_2CH(OCH_3)_2$, 97294-87-6; $(CO)_5Mn^-K^+$, 15693-51-3; $(CO)_5MnBr$, 14516-54-2; $Mn_2(CO)_{10}$, 10170-69-1; $Mn_2(CO)_9(CO_3CN)$, 97315-01-0; $[(CO)_4MnBr]_2$, 18535-44-9; $(CH_3)_3SiBr$, 2857-97-8; $(CO)_5MnH$, 16972-33-1; $[(CH_3)_3Si]_2O$, 107-46-0; cyclohexanone, 108-94-1; α-bromocyclohexanone, 822-85-5; cyclohexanone trimethylsilyl enol ether, 6651-36-1; camphor, 76-22-2; α-bromocamphor, 76-29-9; camphor trimethylsilyl enol ether, 56613-17-3; 2-bromo-6-methylcyclohexanone, 36504-12-8; 2-bromo-2-methylcyclohexanone, 10409-47-9; 2-chloro-2-methylcyclohexanone, 10409-46-8; 2-methylcyclohexanone, 583-60-8; 3-chloro-3-methyl-2-[(trimethylsilyl)oxy]cyclohexene, 97294-90-1; α-bromo-γ-butyrolactone, 5061-21-2; γ-butyrolactone trimethylsilyl ketene acetal, 51425-66-2; α-bromocyclohexanone dimethyl ketal, 1728-17-2; cyclohexanone methyl enol ether, 931-57-7.