at 0 °C for 1 h and analysis showed that potassium diisopinocampheylborohydride had formed in quantitative yield; ^{11}B NMR δ -4.84 (t, J = 69 Hz).

F. Reaction of Monoisopinocampheylborane with Potassium Hydride. The N,N,N',N'-tetramethylethylenediamine (TMED) adduct of $IPCBH_2$ (10 mmol) was prepared as described previously[9] and was dissolved in THF so as to give a 1 M solution. To this, BMS (~10 M), 1 mL, was added with constant stirring. After 1 h, the solid TMED·$2BH_3$ was centrifuged and the supernatant liquid was transferred to a vial containing potassium hydride (oil free, 10 mmol) and stirred for 10 min at 25 °C to remove any traces of BMS in the reaction mixture. Pure $IPCBH_2$ solution in THF was then removed from potassium hydride by centrifugation and its concentration was adjusted to 0.5 M by dilution with THF. This solution was used for the reaction with potassium hydride (15 mmol) and the reaction was complete in 0.5 H; ^{11}B NMR δ -21.2 (q, J = 72 Hz).

Stoichiometry. A. Ratio of Li^+:B:H^- in Lithium 9-Boratabicyclo[3.3.1]nonane. In a typical experiment, a 1.0-mL aliquot of the clear solution of lithium 9-boratarabicyclo[3.3.1]nonane, ~0.5 M, was hydrolyzed in a THF–water–glycerine mixture (1:1:1) and the hydrogen evolved (24.7 mL) was measured. This indicated the hydride concentration to be 0.96 M. In another experiment, 10 mL (~5 mmol) of Li-9-BBNH was quenched with methanol and oxidized with NaOH–H_2O_2. The oxidation product was analyzed by GLC as described previously. From the amount of cyclooctanediol, the concentration of boron was calculated to be 0.5 M.

The above borohydride solution (3 mL) was quenched with water and titrated with 0.4985 N hydrochloric acid to a phenolphthalein endpoint. It required 2.77 mL of the standard acid, indicating the concentration of the lithium ion to be 0.46 M. The ratio of Li^+:B:H^- is thus 1.00:1.09:2.08.

B. Ratio of Na^+:B:H^- in Sodium Thexylborohydride. Upon hydrolysis, a 1.0-mL aliquot of a solution of sodium thexylborohydride gave 37.9 mL of hydrogen, indicating the hydride concentration to be 1.47 M. Oxidation of 10 mL (5 mmol) of this solution produced 5.0 mmol of thexyl alcohol, indicating a 0.5 M concentration of boron. Sodium thexylborohydride solution (3 mL) was quenched with water and titrated with 0.4985 N hydrochloric acid to a phenolphthalein endpoint. It required 3.05 mL of the acid, revealing the concentration of the sodium ion to be 0.5 M. Hence, the ratio of Na^+:B:H^- is 1.00:1.00:2.94.

C. Ratio of K^+:B:H^- in Potassium Thexylborohydride. The hydrolysis of 1.0 mL of an approximately 0.5 M solution liberated 38.7 mL of hydrogen, corresponding to a hydride concentration of 1.5 M. The oxidation of 10 mL of the hydride solution using alkaline hydrogen peroxide, followed by GLC analysis, using n-dodecane as an internal standard, revealed 5.0 mmol of thexyl alcohol. This indicates the boron concentration to be 0.5 M. Potassium was estimated by hydrolyzing 3 mL of the hydride solution, followed by titration with standard acid (0.4985 N); 3.05 mL of the acid was required, indicating a concentration of 0.5 M in potassium.

Stability of Alkali Metal Alkylborohydrides. Solutions of alkali metal mono- and dialkylborohydrides were stored at 25 °C under dry nitrogen and analyzed for the active hydride concentration periodically. The stability of these solutions was also monitored by determining their ^{11}B NMR spectra periodically. The results clearly indicated that, under dry nitrogen, these are stable at least for 90 days without any detectable hydride loss, isomerization, or redistribution.

Regeneration of Mono- and Dialkylboranes from Their Alkali Metal Borohydrides. The following procedure for the liberation of free 9-BBN from K-9-BBNH in THF is representative. To a solution of 5 mmol of K-9-BBNH in 10 mL of THF was added 7.5 mmol (50% excess) of CH_3I with stirring at 25 °C. A heavy white solid precipitated immediately with evolution of methane (5 mmol) gas. Stirring was continued for 15 min and then the solid centrifuged down. The supernatant solution was decanted and ^{11}B NMR revealed the presence of pure 9-BBN dimer in equilibrium with its monomer–THF complex; ^{11}B NMR δ +27.8 (s), +13.9 (d, J = 61 Hz).

Registry No. Lithium 9-boratobicyclo[3.3.1]nonane, 76448-08-3; sodium 9-boratobicyclo[3.3.1]nonane, 76448-07-2; potassium 9-boratobicyclo[3.3.1]nonane, 76448-06-1; lithium dicyclohexylborohydride, 67813-27-8; sodium dicyclohexylborohydride, 76430-43-8; potassium dicyclohexylborohydride, 76430-44-9; lithium disiamylborohydride, 67813-43-8; sodium disiamylborohydride, 76430-45-0; potassium disiamylborohydride, 76430-46-1; lithium diisopinocamphenylborohydride, 76430-47-2; sodium diisopinocamphenylborohydride, 76496-36-1; potassium diisopinocamphenylborohydride, 76496-37-2; lithium thexylborohydride, 76430-48-3; sodium thexylborohydride, 76430-49-4; potassium thexylborohydride, 76430-50-7; sodium monoisopinocamphenylborohydride, 76430-51-8; potassium monoisopinocamphenylborohydride, 76496-38-3; cyclohexanol, 108-93-0; 3-methyl-2-butanol, 598-75-4; isopinocamphenol, 27779-29-9; cyclohexene, 110-83-8; 2-methyl-2-butene, 513-35-9; 2-pinene, 80-56-8; tricyclohexylboron, 1088-01-3; tris(3-methyl-2-butyl)boron, 32327-52-9; lithium cyclohexylborohydride, 76430-52-9; lithium (3-methyl-2-butyl)borohydride, 76430-53-0; 9-BBN, 280-64-8; $(CChx)_2BH$, 1568-65-6; Sia_2BH, 1069-54-1; IPC_2BH, 24041-59-6; $ThxBH_2$, 3688-24-2; $IPCBH_2$, 28875-08-3; LiH, 7580-67-8; NaH, 7646-69-7; KH, 7693-26-7.

Reaction of Enol Silyl Ethers with Silver Carboxylate–Iodine. Synthesis of α-Acyloxy Carbonyl Compounds

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The sequential treatment of enol silyl ethers with silver carboxylate–iodine (2:1) and then fluoride affords high yields of the corresponding α-acyloxy carbonyl compounds. Thus a wide range of variation is now possible for the acyloxy portion of the molecule. The oxidation is most successful when used with five- and six-membered-ring enol silyl ethers. When applied to larger ring sizes, the formation of α-iodo carbonyl compounds occurs as an important side reaction. The oxidation is regiospecific with respect to double bond placement in the enol silyl ethers.

The oxidation of enol silyl ethers **1** with m-chloroperbenzoic acid (MCPBA)[1,2] or lead(IV) carboxylates[3] affords ready access to a variety of useful α-oxygenated carbonyl systems **2** and **3**. Continuing interest in the use of these

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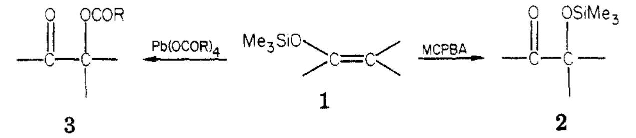
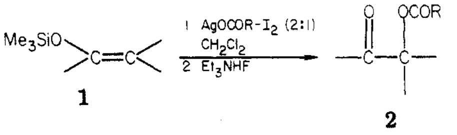
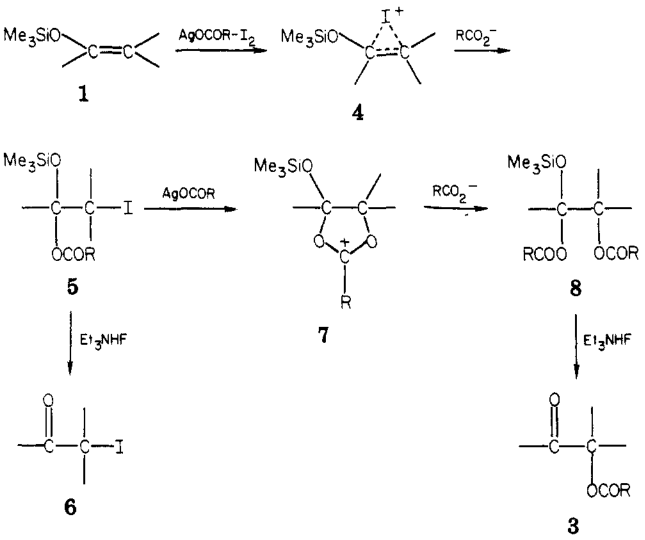


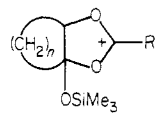
classes of protected compounds in synthesis[4] has prompted us to seek new and efficient methods for the introduction of oxygen on carbon which is adjacent to a carbonyl group. In line with this approach we would like to report a new oxidative method wherein the reaction of **1** with silver carboxylate–iodine in a ratio of 1:2:1 allows the identity of the α-acyloxy functionality to be varied with ease in the resulting product **3**. A number of examples of the procedure are noted in Table I. In terms of the yields of **3**, the variety of α-acyloxy groups, and the ease of preparation of **3**, the method seems to have wide applicability. Formation of **3j** and **3k** indicates that the reaction also proceeds in a regiospecific manner as well. The mechanism of the formation of **3** is believed to proceed as outlined in the Scheme I. Reaction of **1** with AgOCOR–I$_2$ gives **4** and then **5**. In the absence of a second molar equivalent of AgOCOR, **5** upon treatment with Et$_3$NHF gives high yields of the corresponding α-iodo ketone **6**.[5] However, when a second molar equivalent of AgOCOR is present **5** is diverted to cation **7** and hence **8**. Finally, the reaction of **8** with Et$_3$NHF affords the observed α-acyloxy ketone **3**. The success of the reaction depends on the ability of **5** to be transformed into the cation **7**. This key step will be hindered if **5** is not reasonably stable or if the actual formation of **7** is not favored. When the enol silyl ethers of either cyclopentanone or cyclohexanone are used the reaction proceeds smoothly and **3** is produced in high yield (Table I). However, attempts to extend the current procedure to include enol silyl ethers of cycloheptanone, cyclooctanone, and cyclododecanone lead to the production of varying amounts of **6** along with **3**. The results of these experiments are given in Table II.



Scheme I



The appearance of **6** can be rationalized by invoking the decomposition of **5** (Scheme I) directly to **6** before **7** can form. The fact that **6** is not on the pathway leading to **3** was determined by reacting α-iodo ketone **6d** with AgOAc for 20 h. After this period of time, the NMR spectrum of the crude reaction mixture showed no evidence of the appearance of α-acetoxycyclododecanone, **3q**. Further, when **1g** was treated with AgOAc–I$_2$ (2:1) for 3 h and the crude product was examined by NMR prior to treatment with Et$_3$NHF, the major component of the mixture was α-iodo ketone **6c**. These data would seem to show that conversion of **5** to **6** competes favorably with the transformation of **5** into **7** in these cases. The reticence of **5** to form **7** when the cation is fused to a 7-, 8-, or 12-membered ring as in **9** can be roughly correlated to the inherent ring strain associated with these systems.[6] We have found this to be a general phenomenon in the reactions of cyclic enol silyl ethers with lead(IV) carboxylates as well as with silver carboxylates in concert with iodine. This aspect of our studies will be presented in a separate account. It should be noted too that **1e** gives a 55% isolated yield of **6a** when treated with AgOAc–I$_2$ (2:1). In this case, it is likely that the formation of **7** is hindered by steric factors. Despite the limitations noted above for the method, it is hoped that the flexibility and mildness of the procedure will prove to make it of use for functionalizing cyclopentanones and cyclohexanones. We are continuing in our studies of the synthetic potential of enol silyl ethers **1**.



9, n = 5, 6, 10

Experimental Section

General Procedures. Melting points were determined with a Thomas-Hoover capillary melting point apparatus and are uncorrected. Proton magnetic resonance (NMR) spectra were recorded at 60 MHz on a Varian Anaspect EM 360 spectrometer, using either carbon tetrachloride or chloroform-d as solvent with tetramethylsilane as internal standard. Infrared (IR) spectra were obtained on a Perkin-Elmer 621 grating infrared spectrometer. Low-resolution mass spectra were obtained with a Perkin-Elmer RMU 6E instrument at 15eV and are recorded as m/e with relative abundance in parentheses. Elemental microanalyses were determined with a Perkin-Elmer 240 elemental analyzer. For column chromatography, silica gel, Woelm, 0.032–0.063 mm (ICN Pharmaceuticals GmbH & Co.), was used. Triethylammonium fluoride was prepared according to the procedure of Hunig.[7] Anhydrous magnesium sulfate served as drying agent.

Preparation of Silver Carboxylates. The procedure of Newman and Beal[8] was used to prepare the silver carboxylates. A solution of 7.20 g (0.050 mol) of sodium benzoate was dissolved in 50 mL of water and stirred into a solution of 8.50 g (0.050 mol) of silver nitrate. The resulting voluminous white precipitate was collected by filtration, washed successively with water, ethanol,

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(4) See, for example: Boeckman, R. K., Jr.; Ramaiah, M. *J. Org. Chem.* **1977**, *42*, 1581.

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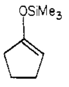
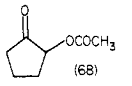
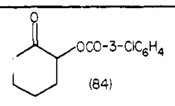
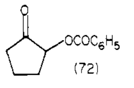
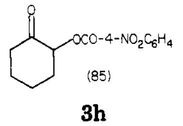
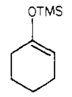
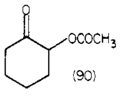
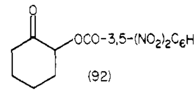
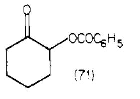
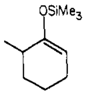
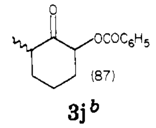
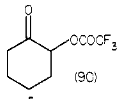
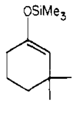
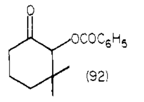
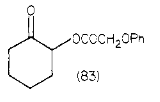
Table I. Reaction of Enol Silyl Ethers 1 with AgOCOR-I_2 (2:1)

1^a	AgOCOR, R =	isolated 3 (% yield)	1^a	AgOCOR, R =	isolated 3 (% yield)
 1a	CH_3	 3a	1b	3-ClC_6H_4	 3g
1a	C_6H_5	 3b	1b	$4\text{-NO}_2C_6H_4$	 3h
 1b	CH_3	 3c	1b	$3,5\text{-(NO}_2)_2C_6H_3$	 3i
1b	C_6H_5	 3d	 1c	C_6H_5	 $3j^b$
1b	CF_3	 3e	 1d	C_6H_5	 3k
1b	CH_2OPh	 3f			

[a] See Experimental Section. [b] 2:1 mixture of *cis-trans*-3j (NMR analysis).

and ether, and dried in vacuo. The silver benzoate was used without further purification. The silver salts of phenoxyacetic, 3-chlorobenzoic, 4-nitrobenzoic, and 3,5-dinitrobenzoic acids were prepared in an analogous manner. Silver acetate (Fisher Scientific) and silver trifluoroacetate (Aldrich) were used without purification.

Preparation of Enol Silyl Ethers 1. Compounds **1a–c,f–h** were prepared by procedure A outlined by House.[9] Physical properties for **1a–c,1g**, and **1h** are noted in ref 9 and 5.

1-(Trimethylsiloxy)cycloheptene, 1f: 75%; bp 78–81 °C (10.7 mm) [lit.[10] bp 94–95 °C (19 mm)]; $n^{24}{}_D$ 1.4504.

3,3-Dimethyl-1-(trimethylsiloxy)cyclohexene, 1d. Physical properties for **1d** are noted in ref 5.

2-Methyl-1-(trimethylsiloxy)cyclohexene, 1e, was prepared by the method of Rubottom.[11]

Reaction of Silver Carboxylates and Iodine with Enol Silyl Ethers 1a–h. General Procedure. A mixture of 4.4 mmol of silver carboxylate and 0.508 g (2 mmol) of iodine was stirred in 50 mL of dry methylene chloride under 1 atm of N_2 until the iodine had reacted completely. A solution of 2 mmol of enol silyl ether 1 in 3 mL of dry methylene chloride was then rapidly added with vigorous stirring. After 2 h, the mixture was filtered into a flask containing 0.480 g (4 mmol) of triethylamine hydrofluoride and the solution stirred for 2 h under 1 atm of N_2. The solution was washed with 1 25-mL portion of water, 1 25-mL portion of saturated sodium bicarbonate, and 1 25-mL portion of water and dried, and the solvent removed in vacuo. The crude reaction product was purified by recrystallization, molecular distillation, or chromatography to afford the pure products.

Reaction of Silver Acetate and Iodine with 1a. Starting materials were 0.735 g of silver acetate and 0.312 g of **1a**; purification of the crude reaction product by column chromatography ($CHCl_3$) afforded 0.193 g (68%) of pure 2-acetoxycyclopentanone, **3a**: $n^{23}{}_D$ 1.4528 (lit.[12] $n^{20}{}_D$ 1.456); IR (neat) 1755, 1735 cm^{-1}; NMR ($CDCl_3$) δ 1.56–2.66 (m, 6 H), 2.18 (s, 3 H), 5.13 (t, 1 H, J = 9 Hz); mass spectrum, m/e 142 (M^+, 30), 100 (19), 99 (100), 86 (13), 72 (25), 43 (81), metastable 70.4.

Reaction of Silver Benzoate and Iodine with 1a. Starting materials were 1.010 g of silver benzoate and 0.312 g of **1a**; purification of the crude reaction product by recrystallization from ether afforded 0.294 g (72%) of pure 2-(benzoyloxy)cyclopentanone, **3b**: mp 88–91 °C (lit.[13] mp 90–91 °C); IR (KBr) 1757, 1712 cm^{-1}; NMR ($CDCl_3$) δ 1.70–2.73 (m, 6 H), 5.27 (t, 1 H, J = 8 Hz), 7.25–8.25 (m, 5 H); mass spectrum, m/e 204 (M^+, 10), 105 (100), metastable 54.0.

Reaction of Silver Acetate and Iodine with 1b. Starting materials were 0.735 g of silver acetate and 0.340 g of **1b**; purification of the crude reaction product by recrystallization from pentane afforded 0.280 g (90%) of pure 2-acetoxycyclohexanone, **3c**: mp 38–40 °C (lit.[14] mp 41–42 °C); IR (KBr) 1735, 1718 cm^{-1}; NMR (CCl_4) δ 1.25–2.62 (m, 8 H), 2.08 (s, 3 H), 4.80–5.23 (m, 1 H); mass spectrum, m/e 156 (M^+, 37), 114 (42), 113 (100), 96 (18), 85 (21), 68 (12), 67 (25), 58 (10), 43 (58).

Reaction of Silver Benzoate and Iodine with 1b. Starting materials were 1.010 g of silver benzoate and 0.340 g of **1b**; purification of the crude reaction product by recrystallization from ether and pentane afforded 0.308 g (71%) of pure 2-(benzoyloxy)cyclohexanone, **3d**: mp 85–85.5 °C (lit.[13] mp 85–86 °C); IR (KBr) 1719, 1705 cm^{-1}; NMR ($CDCl_3$) δ 1.33–2.80 (m, 8 H), 5.10–5.66 (m, 1 H), 7.30–8.43 (m, 5 H); mass spectrum, m/e 218 (M^+, 22) 113 (11), 105 (100).

Reaction of Silver Trifluoroacetate and Iodine with 1b. Starting materials were 0.974 g of silver trifluoroacetate and 0.340 g of **1b**; purification of the crude reaction product by molecular distillation afforded 0.377 g (90%) of pure 2-(trifluoroacetoxy)cyclohexanone, **3e**: molecular distillation 61 °C (8.3 mm); mp 36–37 °C; IR (neat) 1780, 1725 cm^{-1}; NMR (CCl_4) δ 1.37–2.67 (m, 8 H), 5.06–5.47 (m, 1 H); mass spectrum, m/e 210 (M^+, 76), 166 (71), 96 (24), 84 (16), 69 (13), 68 (49), 55 (100), metastable 43.9. Anal. Calcd for $C_8H_9O_3F_3$: C, 45.75; H, 4.32. Found: C, 46.04; H, 4.14.

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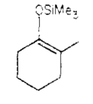
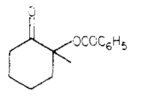
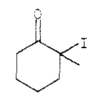
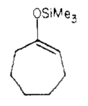
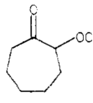
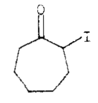
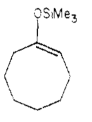
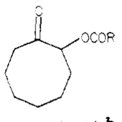
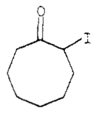
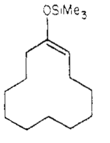
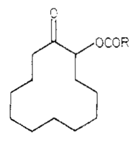
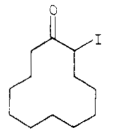
Table II. Reaction of Enol Silyl Ethers 1 with AgOCOR-I_2 (2:1)

1^a	AgOCOR, R =	isolated 3 (% yield)	isolated 6 (% yield)
 **1e**	C_6H_5	 **3l** (12)	 **6a** (55)
 **1f**	CH_3 C_6H_5	 **3m**, R = CH_3 (36) **3n**, R = C_6H_5 (48)	 **6b** (51) **6b** (44)
 **1g**	CH_3 C_6H_5	 **3o** $(11)^b$ $\mathbf{3p}^c$	 **6c** (72) **6c** (71)
 **1h** (*E*/*Z* mixture)	CH_3 C_6H_5	 **3q**, R = CH_3 (15) **3r**, R = C_6H_5 (33)	 **6d** (49) **6d** (40)

^{a} See Experimental Section. ^{b} NMR analysis on crude product, no isolation attempted. ^{c} No analysis attempted.

Reaction of Silver Phenoxyacetate and Iodine with 1b. Starting materials were 1.206 g of silver phenoxyacetate and 0.340 g of **1b**; purification of the crude reaction product by recrystallization from ethyl acetate and hexane afforded 0.413 g (83%) of pure 2-(phenoxyacetoxy)cyclohexanone, **3f**: mp 96–97 °C; IR (KBr) 1765, 1718 cm^{-1}; NMR ($CDCl_3$) δ 1.17–2.75 (m, 8 H), 4.80 (s, 2 H), 5.10–5.50 (m, 1 H), 6.77–7.60 (m, 5 H); mass spectrum, *m/e* 248 (M^+, 100), 127 (13), 113 (15), 107 (15), 97 (10), 94 (15). Anal. Calcd for $C_{14}N_{16}O_4$: C, 67.72; H, 6.50. Found: C, 67.51; H, 6.25.

Reaction of Silver 3-Chlorobenzoate and Iodine with 1b. Starting materials were 1.180 g of silver 3-chlorobenzoate and 0.340 g of **1b**; purification of the crude reaction product recrystallization from ether and hexane afforded 0.423 g (84%) of pure 2-[(3-chlorobenzoyl)oxy]cyclohexanone, **3g**: mp 62–63 °C (lit.[1] mp 62–63 °C); IR (KBr) 1730, 1710 cm^{-1}; NMR ($CDCl_3$) δ 1.27–2.76 (m, 8 H), 5.38 (m, 1 H), 7.16–8.15 (m, 5 H); mass spectrum, *m/e* 254 (25), 252 (M^+, 75), 141 (34), 140 (10), 139 (100), 113 (88), 96 (16).

Reaction of Silver 4-Nitrobenzoate and Iodine with 1b. Starting materials were 1.206 g of silver 4-nitrobenzoate and 0.340 g of **1b**; purification of the crude reaction product by recrystallization from ethyl acetate and hexane afforded 0.447 g (85%) of pure 2-[(4-nitrobenzoyl)oxy]cyclohexanone, **3h**: mp 124–125 °C (lit.[15] mp 125–125.5 °C); IR (KBr) 1730, 1712 cm^{-1}; NMR ($CDCl_3$) δ 1.50–2.73 (m, 8 H), 5.30–5.71 (m, 1 H), 8.36 (s, 4 H); mass spectrum, *m/e* 263 (M^+, 60), 233 (12), 151 (90), 150 (67), 134 (24), 120 (14), 113 (100), 96 (74), 85 (12), 68 (21), 67 (17), metastables 86.7, 35.0.

Reaction of Silver 3,5-Dinitrobenzoate and Iodine with 1b. Starting materials were 1.405 g of silver 3,5-dinitrobenzoate and 0.340 g of **1b**; purification of the crude reaction product by recrystallization from ethyl acetate and hexane afforded 0.568 g (92%) of pure 2-[(3,5-dinitrobenzoyl)oxy]cyclohexanone, **3i**: mp 145–146 °C; IR (KBr) 1720, 1698 cm^{-1}; NMR ($CDCl_3$) δ 1.45–2.82 (m, 8 H), 5.30–5.73 (m, 1 H), 9.26 (s, 3 H); mass spectrum, *m/e* 308 (M^+, 55), 290 (12), 278 (36), 264 (67), 196 (26), 195 (36), 165 (21), 149 (19), 109 (10), 108 (100), 107 (21), 97 (12), 96 (95), 95 (12), 85 (21), 83 (21), 74 (17), 68 (95), 67 (26), 59 (17), 55 (17). Anal. Calcd for $C_{13}H_{12}N_2O_7$: C, 50.65; H, 3.93; N, 9.09. Found: C, 50.58; H, 3.86; N, 8.87.

Reaction of Silver Benzoate and Iodine with 1c. Starting materials were 1.010 g of silver benzoate and 0.368 g of **1c** which afforded a 2:1 mixture of *cis*- and *trans*-2-(benzoyloxy)-6-methylcyclohexanone, **3j** (NMR): 0.404 g (87%); IR (KBr) 1725, 1710 cm^{-1} (lit.[3b] IR 1725, 1710 cm^{-1}); NMR ($CDCl_3$) δ 1.05 (d, 3 H, *J* = 6 Hz, cis), 1.18 (d, 3 H, *J* = 7 Hz, trans), 1.22–3.15 (m, 7 H), 5.20–5.40 (m, 1 H, cis), 5.40–5.55 (m, 1 H, trans, 7.20–8.20 (m, 5 H); mass spectrum, *m/e* 232 (M^+, 45), 127 (20), 110 (10), 106 (10), 105 (100), 82 (11).

Reaction of Silver Benzoate and Iodine with 1d. Starting materials were 1.010 g of silver benzoate and 0.396 g of **1d**; purification of the crude reaction product by recrystallization from ether and pentane afforded 0.451 g (92%) of pure 2-(benzoyloxy)-3,3-dimethylcyclohexanone, **3k**: mp 108.5–109.5 °C; IR (KBr) 1715 cm^{-1}; NMR ($CDCl_3$) δ 1.07 (s, 3 H), 1.18 (s, 3 H), 5.23 (s, 1 H), 7.33–8.32 (m, 5 H); mass spectrum, *m/e* 246 (M^+, 31), 141 (28), 105 (100), metastable 44.8. Anal. Calcd for $C_{15}H_{18}O_3$: C, 73.15; H, 7.37. Found: C, 73.31; H, 7.49.

Reaction of Silver Benzoate and Iodine with 1e. Starting with 1.010 g of silver benzoate and 0.368 g of **1e** afforded a 1:3.3 mixture (NMR) of **3l** and **6a**. Preparative layer chromatography ($CHCl_3$) of the mixture afforded pure 2-(benzoyloxy)-2-methylcyclohexanone, **3l**, and 2-iodo-2-methylcyclohexanone, **6a**.

2-(Benzoyloxy)-2-methylcyclohexanone, 3l: 0.057 g (12%); IR (neat) 1720 cm^{-1}; NMR ($CDCl_3$) δ 1.46 (s, 3 H), 1.35–2.82 (m, 8 H), 7.20–8.20 (m, 5 H); mass spectrum, *m/e* 232 (M^+, 15), 127 (75), 110 (43), 106 (11), 105 (100). Anal. Calcd for $C_{14}H_{16}O_3$: C, 72.39; H, 6.94. Found: C, 72.16; H, 7.00.

2-Iodo-2-methylcyclohexanone, 6a: 0.263 g (55%); molecular distillation 55 °C (1 mm); $n^{32.5}_{\mathrm{D}}$ 1.5380; IR (neat) 1705 cm^{-1}; NMR (CCl_4) δ 1.13–2.60 (m, 5 H), 2.07 (s, 3 H), 3.03–3.85 (m, 1 H); mass spectrum, *m/e* 238 (M^+, 36), 112 (26), 111 (100), 110 (68), 84 (11), 83 (37), 82 (41), 69 (21), 68 (24), 51 (10), 50 (37), metastables 62.1, 51.7, 36.4. Anal. Calcd for $C_7H_{11}OI$: C, 35.31; H, 4.66. Found: C, 35.62; H, 4.72.

Reaction of Silver Acetate and Iodine with 1f. Starting with 0.735 g of silver acetate and 0.368 g of **1f** afforded a 2:3 mixture (NMR) of **3m** and **6b**. Preparative layer chromatography ($CHCl_3$) of the mixture afforded pure 2-acetoxycycloheptanone, **3m**, and 2-iodocycloheptanone, **6b**.

2-Acetoxycycloheptanone, 3m: 0.123 g (36%); $n^{29.5}_{\mathrm{D}}$ 1.4716 (lit.[16] n^{22}_{D} 1.4648); IR (neat) 1710 cm^{-1}; NMR (CCl_4) δ 0.97–2.63 (m, 10 H), 2.07 (s, 3 H), 5.00–5.30 (m, 1 H); mass spectrum, *m/e* 170 (M^+, 6) 128 (13), 127 (100), 110 (52), 99 (19), 84 (12), 82 (11), 81 (45), 43 (39), metastables 77.2, 66.3, 51.7.

2-Iodocycloheptanone, 6b: 0.241 g (51%); molecular distillation 51 °C (2 mm); n^{17}_{D} 1.5640; IR (neat) 1698 cm^{-1}; NMR (CCl_4) δ 1.00–3.20 (m, 10 H), 4.46 (dd, 1 H, *J* = 10, 6 Hz); mass spectrum, *m/e* 238 (M^+, 100), 112 (35), 111 (65), 93 (10), 84 (22), 83 (38), 69 (23), 68 (40), 67 (12), 56 (17), 55 (92), 41 (20), metastables 62.0, 52.2, 36.4. Anal. Calcd for $C_7H_{11}IO$: C, 35.31; H, 4.66. Found: C, 35.20; H, 4.58.

Reaction of Silver Benzoate and Iodine with 1f. Starting with 1.010 g of silver benzoate and 0.368 g of **1f** afforded a 1:1 mixture (NMR) of **3n** and **6b**. Preparative layer chromatography ($CHCl_3$) of the mixture afforded pure 2-(benzoyloxy)cycloheptanone, **3n**, and 2-iodocycloheptanone, **6b**.

2-(Benzoyloxy)cycloheptanone, 3n: 0.221 g (58%); mp 57–57.5 °C; IR (KBr) 1720, 1705 cm^{-1}; NMR ($CDCl_3$) δ 1.20–2.80 (m, 10 H), 5.33–5.63 (m, 1 H), 7.30–8.23 (m, 5 H); mass spectrum, *m/e* 232 (M^+, 51), 127 (31), 110 (22), 106 (10), 105 (100), metastables 179.4, 52.2, 47.5. Anal. Calcd for $C_{14}H_{16}O_3$: C, 72.39; H, 6.94. Found: C, 72.41; H, 7.02.

2-Iodocycloheptanone, 6b: 0.208 g (44%); identical (IR, NMR, TLC) with **6b** obtained from treatment of **1f** with silver acetate and iodine (see above).

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Reaction of Silver Acetate and Iodine with 1g. Starting materials were 0.735 g of silver acetate and 0.396 g of **1g**; purification of the crude reaction product by preparative layer chromatography ($CHCl_3$) afforded 0.360 g (72%) of pure 2-iodocyclooctanone, **6c**: molecular distillation 45 °C (2 mm) [lit.[5] 45 °C (1.75 mm)]; n^{25}_{D} 1.5490 (lit.[5] n^{23}_{D} 1.5494); IR (neat) 1700 cm^{-1}.

Reaction of Silver Benzoate and Iodine with 1g. Starting materials were 1.010 g of silver benzoate and 0.396 g of **1g**; purification of the crude reaction product by preparative layer chromatography ($CHCl_3$) afforded 0.356 g (71%) of pure **6c**: molecular distillation 45 °C (2 mm) [lit.[5] 45 °C (1.75 mm)]; IR (neat) 1700 cm^{-1}.

Reaction of Silver Acetate and Iodine with 1h. Starting with 0.735 g of silver acetate and 0.508 g of **1h** afforded a 1:4 mixture (NMR) of **3q** and **6d**. Preparative layer chromatography ($CHCl_3$) of the mixture afforded pure 2-acetoxycyclododecanone, **3q**, and 2-iodocyclododecanone, **6d**.

2-Acetoxycyclododecanone, 3q: 0.072 g (15%); mp 83–84 °C IR (KBr) 1745, 1715 cm^{-1}; NMR (CCl_4) δ 1.00–2.70 (m, 20 H), 2.08 (s, 3 H), 5.00 (dd, 1 H, J = 5.5, 4 Hz); mass spectrum, *m/e* 240 (M^+, 7), 198 (21), 197 (100), metastables 163.4, 161.7. Anal. Calcd for $C_{14}H_{24}O_3$: C, 69.96; H, 10.07. Found: C, 69.75; H, 9.79.

2-Iodocyclododecanone, 6d: 0.300 g (49%); mp 52–52.5 °C (lit.[5] mp 52–52.5 °C); IR (KBr) 1695 cm^{-1}.

Reaction of Silver Benzoate and Iodine with 1h. Starting with 1.010 g of silver benzoate and 0.508 g of **1h** afforded a 2:3 mixture (NMR) of **3r** and **6d**. Preparative layer chromatography ($CHCl_3$) of the mixture afforded pure 2-(benzoyloxy)cyclododecanone, **3r**, and 2-iodododecanone, **6d**.

2-(Benzoyloxy)cyclododecanone, 3r: 0.201 g (33%); mp 96–97 °C; IR (KBr) 1725, 1715 cm^{-1}; NMR ($CDCl_3$) δ 1.03–2.93 (m, 20 H), 5.46 (dd, 1 H), J = 8, 6 Hz), 7.40–8.40 (m, 5 H); mass spectrum, *m/e* 302 (M^+, 27), 198 (15), 197 (100), 122 (11). Anal. Calcd for $C_{19}H_{26}O_3$: C, 75.46; H, 8.67. Found: C, 75.44; H, 8.56.

2-Iodocyclododecanone, 6d: 0.244 g (40%); mp 51.5–52.5 °C (lit.[5] mp 52–52.5 °C); IR (KBr) 1695 cm^{-1}.

Acknowledgment. We thank the Research Council of the University of Idaho and acknowledge the donors of the Petroleum Research Fund, administered by the American Chemical Society, for support of this research.

Registry No. 1a, 19980-43-9; **1b**, 6651-36-1; **1c**, 19980-33-7; **1d**, 61175-92-6; **1e**, 19980-35-9; **1f**, 22081-48-7; **1g**, 50338-42-6; (*E*)-**1h**, 55314-44-8; (*Z*)-**1h**, 55314-46-0; **3a**, 52789-75-0; **3b**, 59058-16-1; **3c**, 17472-04-7; **3d**, 7472-23-3; **3e**, 66197-69-1; **3f**, 77256-21-4; **3g**, 61543-83-7; **3h**, 66049-47-6; **3i**, 77256-22-5; *cis*-**3j**, 59058-21-8; *trans*-**3j**, 59058-25-2; **3k**, 77256-23-6; **3l**, 59058-22-9; **3m**, 19347-07-0; **3n**, 53429-51-9; **3o**, 23438-71-3; **3p**, 77256-24-7; **3q**, 26307-31-3; **3r**, 77269-99-9; **6a**, 77256-25-8; **6b**, 77256-26-9; **6c**, 63641-49-6; **6d**, 69381-33-5; silver acetate, 563-63-3; silver benzoate, 532-31-0; silver phenoxyacetate, 13126-87-9; silver 3-chlorobenzoate, 72247-97-3; silver 4-nitrobenzoate, 35363-49-6; silver 3,5-dinitrobenzoate, 57542-56-0; I_2, 7553-56-2; silver trifluoroacetate, 2966-50-9.

Direct and Regioselective Transformation of α-Chloro Carbonyl Compounds into Alkenes and Deuterioalkenes

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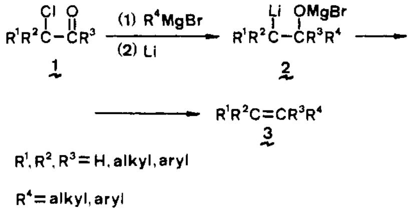
The successive treatment ethyl chloroacetate or chloroacetyl chloride with Grignard reagents and lithium powder leads to symmetrical terminal olefins in a regioselective manner. The best results are obtained with acid chlorides. The influence of the temperature and the reaction time on the overall yield of the process are studied; in general, yields are increased by working at low temperature (−60 °C). Internally substituted olefins are obtained from α-chloro acid chlorides through a similar process. The treatment of α-chloro aldehydes, ketones, and carboxylic acid derivatives (esters or acid chlorides) with lithium aluminium hydride or lithium aluminium hydride/aluminium chloride and lithium powder at low temperature (−60 °C) leads in a regioselective manner to olefins with the same carbon skeleton as the starting carbonyl compound. Reactions with lithium aluminium deuteride lead to incorporation of deuterium at predetermined positions in the alkene.

The key step of most of the methods for the synthesis of olefins is a β-elimination reaction which implies, as the main disadvantage, a loss of the regioselectivity.[1] However, in previous papers[2-4] we described the addition of Grignard reagents to α-chloro aldehydes or ketones **1** followed by metalation with lithium powder to give β-substituted organometallic compounds **2** which undergo a spontaneous β elimination to afford olefins **3** (see Scheme I).

Scheme I



$$R^1R^2\overset{\displaystyle Cl}{\overset{|}{C}}-\overset{\displaystyle O}{\overset{\|}{C}}R^3 \xrightarrow[(2)\ Li]{(1)\ R^4MgBr} R^1R^2\overset{\displaystyle Li}{\overset{|}{C}}-\overset{\displaystyle OMgBr}{\overset{|}{C}}R^3R^4 \longrightarrow R^1R^2C{=}CR^3R^4$$

1 2 3

R^1, R^2, R^3 = H, alkyl, aryl

R^4 = alkyl, aryl

Intermediate organometallics **2**[5] were recently prepared from organomercurials by transmetalation[6] under conditions in which they are stable species. Their application in the synthesis of bifunctional organic compounds[7] has been studied.

We report now the "one flask" regioselective transformation of carbonyl compounds (i.e., aldehydes, ketones, and carboxylic acid derivatives) into alkenes and deuter-

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