H, $Si(CH_3)_2$); IR (neat) 1724 cm^{-1}; MS calcd for $C_{12}H_{23}O_4Si$ (m-H_2O), 259.1365 (found, 259.1355).

Anal. Calcd for $C_{13}H_{26}O_4Si$: C, 56.89; H, 9.55. Found: C, 56.73; H, 10.06.

***tert*-Butyldimethylsilyl *tert*-Butyldimethylsilyloxyacetate (6).** This was prepared from 10.0 g (130 mmol) of glycolic acid, 40.6 g (270 mmol) of *tert*-butyldimethylchlorosilane, and 36.3 g (530 mmol) of imidazole in 80 mL of DMF (25 °C, 18 h) to give after removal of solvent and drying under vacuum 39.2 g (98%) of **6** as a white solid: ^1H NMR δ_{Me_4Si} ($CDCl_3$) 4.14 (s, 2 H, OCH_2), 0.87 (s, 18 H, $C(CH_3)_3$), 0.22 (s, 6 H, Si $(CH_3)_2$), 0.04 (s, 6 H, Si $(CH_3)_2$); IR (KBr) 1748 cm^{-1}.

Anal. Calcd for $C_{14}H_{32}O_3Si_2$: C, 55.21; H, 10.59.

***tert*-Butyldimethylsilyl *m*-(*tert*-Butyldimethylsilyloxybenzoate) (7).** This was prepared from 10.0 g (72 mmol) of m-hydroxybenzoic acid, 22.9 g (152 mmol) of *tert*-butyldimethylchlorosilane, and 19.7 g (290 mmol) of imidazole (50–60°, 5 hr) to give after molecular distillation (bath temperature 170 °C (1.0 mm)) 25.5 g (98%)) of **7**: ^1H NMR δ_{Me_4Si} ($CDCl_3$) 7.44, 7.22, 7.00 (m's, 4 H, aromatic), 0.96 (s, 9 H, $C(CH_3)_3$), 0.93 (s, 9 H, $C(CH_3)_3$), 0.32 (s, 6 H, $Si(CH_3)_2$), 0.16 (s, 6 H, $Si(CH_3)_2$); IR (neat) 1703 cm^{-1}.

Anal. Calcd for $C_{19}H_{34}O_3Si_2$: C, 62.24; H, 9.35. Found: C, 62.11; H, 9.28.

General Procedure for the Reaction of *tert*-Butyldimethylsilyl Esters with Oxalyl Chloride–DMF: Ethyl Heptanoate (2). To a solution of 10.0 g (41 mmol) of **1** in 40 mL of CH_2Cl_2 containing 4 drops of DMF was added dropwise 4.5 mL (51 mmol) of oxalyl chloride at 0 °C. After stirring 1.5 h at 0 °C and 0.5 h at room temperature, the solvent was removed. To the residue was slowly added a mixture of 10 mL of ether, 10 mL of pyridine, and 10 mL of ethanol. After stirring 1 h, the mixture was diluted with ether and filtered. The solvents were removed and the residue was distilled twice to give 5.98 g (92%) of **2**: ^1H NMR δ_{Me_4Si} ($CDCl_3$) 4.12 (q, 2 H, OCH_2CH_3), 2.28 (t, 2 H, CH_2CO), 2.70–2.10 (m, 8 H, $-(CH_2)_4-$), 1.22 (t, 3 H, OCH_2CH_3), 0.87 (m, 3 H, terminal CH_3).

Anal. Calcd for $C_9H_{18}O_2$: C, 68.31; H, 11.46. Found: C, 68.00; H, 11.82.

Heptanoyl Chloride. The above reaction was repeated without the addition of ethanol–pyridine. The CH_2Cl_2 was removed and the residue was distilled under aspirator pressure giving a low-boiling fraction (40–43 °C) consisting of *tert*-butyldimethylchlorosilane and a higher boiling fraction (70–73 °C) consisting of 5.2 g (86%) of heptanoyl chloride. Both compounds were identified by comparison of their ^1H NMR spectrum with that of authentic samples.

Ethyl 2-Methyl-1,3-dioxolan-2-propionate (4). This was prepared from 5.1 g (19 mmol) of **3** and 2.72 g (21 mmol) of oxalyl chloride in 19 mL of CH_2Cl_2 containing 3 drops of DMF. After a 1.25-h reaction time, ethanol–pyridine quenching, and molecular distillation (bath temperature 90–110 °C (0.5 mm)), 3.3 g (95%) of **4** was obtained: ^1H NMR δ_{Me_4Si} ($CDCl_3$) 4.10 (q, 2 H, CH_2CH_3), 3.90 (s, 4 H, OCH_2CH_2O), 2.17 (m, 4 H, $(CH_2)_2CO$), 1.28 (s, 3 H, CH_3), 1.22 (t, 3 H, CH_2CH_3); IR (neat) 1740 cm^{-1}.

Anal. Calcd for $C_9H_{16}O_4$: C, 57.43; H, 8.57. Found: C, 57.68; H, 8.49.

Ethyl *tert*-Butyldimethylsilyloxyacetate (8). This was obtained from 15.0 g (49 mmol) of **6** and 7.2 g (57 mmol) of oxalyl chloride in 60 mL of CH_2Cl_2 containing 10 drops of DMF. After a reaction time of 3 h, ethanol–pyridine quenching, and molecular distillation (bath temperature 110–120 °C (25 mm)), 9.24 g (87%) of **8** was obtained: ^1H NMR δ_{Me_4Si} ($CDCl_3$) 4.17 (s, 2 H, OCH_2), 4.16 (q, 2 H, CH_2CH_3), 1.20 (t, 3 H, CH_2CH_3), 0.84 (s, 9 H, $SiC(CH_3)_3$), 0.03 (s, 6 H, $Si(CH_3)_2$); IR (neat) 1760 cm^{-1}.

Anal. Calcd for $C_{10}H_{22}O_3Si$: C, 55.00; H, 10.15. Found: C, 54.63; H, 10.42.

Ethyl *m*-(*tert*-Butyldimethylsilyloxy)benzoate (9). This was prepared from 6.0 g (16 mmol) of **8** and 2.0 mL (23 mmol) of oxalyl chloride in 13 mL of CH_2Cl_2 containing 6 drops of DMF. After a 40 h reaction time, quenching with ethanol–pyridine, and molecular distillation (bath temperature 115 °C (0.4 mm)), 4.51 g (98%) of **9** was obtained: ^1H NMR δ_{Me_4Si} ($CDCl_3$) 7.40, 7.16, 6.88 (m's, 4 H, aromatic), 4.26 (q, 2 H, CH_2CH_3), 1.28 (t, 3 H, CH_2CH_3), 0.90 (s, 9 H, $C(CH_3)_3$), 0.12 (s, 6 H, $Si(CH_3)_2$); IR (neat) 1724 cm^{-1}; MS calcd for $C_{15}H_{24}O_3Si$, 280.1494 (found, 280.1485).

Anal. Calcd for $C_{15}H_{24}O_3Si$: C, 64.24; H, 8.63. Found: C, 63.83; H, 8.54.

Reaction of 2-Methyl-1,3-dioxolan-2-propionic Acid (5) with Oxalyl Chloride–DMF. To a solution of 1.0 g (6.3 mmol) of **5**[4] in 4 mL of CH_2Cl_2 containing 2 drops of DMF was added 0.61 mL (7.0 mmol) of oxalyl chloride. The solution was stirred at room temperature for 1 h. The solvent was removed and a mixture of 1.3 mL of ethanol and 2.6 mL of pyridine was added. After stirring 15 min, the solution was poured into a saturated solution of $NaHCO_3$ and extracted with ether. The ether solution was dried over Na_2SO_4. The solvent was removed. The residue was distilled (bath temperature 90–110 °C (0.5 mm)) to give 0.28 g of distillate and 0.28 g of pot residue.

TLC ($CHCl_3$–ether, 19:1) of the distillate indicated that it consisted of **4** and three additional more polar components; the pot residue consists only of the more polar side products.

Acknowledgments. We wish to thank Mr. L. Brancone and staff for microanalyses and Messrs. W. Fulmor and G. Morton and Dr. R. T. Hargreaves and staff for spectral data.

Registry No.—5, 4388-57-2; heptanoic acid, 111-14-8; *tert*-butyldimethylchlorosilane, 18162-48-6; glycolic acid, 79-14-1; m-hydroxybenzoic acid, 99-06-9; oxalyl chloride, 79-37-8; dimethylformamide, 68-12-2; heptanoyl chloride, 2528-61-2.

References and Notes

(1) M. F. Ansell, "The Chemistry of Acyl Halides", S. Patai, Ed., Interscience, London, 1972, pp 35–68.
(2) (a) E. J. Corey and A. Venkateswarlu, *J. Am. Chem. Soc.*, **94,** 6190 (1972); (b) K. K. Oglivie and D. J. I. Iwacha, *Tetrahedron Lett.*, 317 (1973).
(3) J. Hausler and U. Schmidt, *Chem. Ber.*, **107,** 145 (1974).
(4) C. K. Warren and B. C. L. Weedon, *J. Chem. Soc.*, 3972 (1958).
(5) H. H. Bosshard, R. Mory, M. Schmid, and H. Zollinger, *Helv. Chim. Acta,* **42,** 1653 (1959).
(6) J. B. Lee, *J. Am. Chem. Soc.*, **88,** 3440 (1966).
(7) (a) R. Adams and L. H. Ulich, *J. Am. Chem. Soc.*, **42,** 599 (1920); (b) F. Reber, A. Lardon, and T. Reichstein, *Helv. Chem. Acta,* **37,** 45 (1954).

Synthesis of 2-Methyl-1-cyclopentene-1-carboxylate Esters. Reaction of Cuprates with β-Substituted Cyclopentenecarboxylates

Kenn E. Harding* and Chung-ye Tseng

Department of Chemistry, Texas A&M University, College Station, Texas 77843

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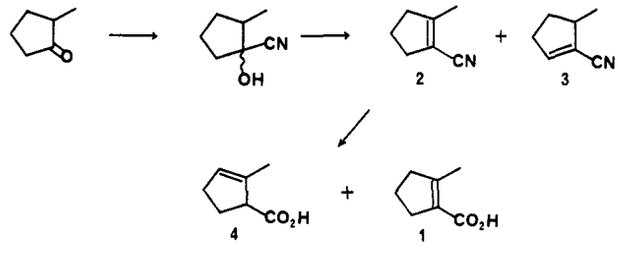
In connection with other synthetic work we had need for an efficient synthesis of 2-methyl-1-cyclopentene-1-carboxylic acid (**1**). The classical procedure[1] for preparation of this material (Scheme I) involves addition of cyanide to 2-methylcyclopentanone, dehydration of the resulting cyanohydrin, and hydrolysis to the acid. Recent studies[2] have shown that this procedure gives a mixture of acids, since dehydration of the cyanohydrin gives both unsaturated nitriles **2** and **3.** We found[3] that even after separation of pure nitrile **2,** hydrolysis gave a mixture of acid **1** and the nonconjugated isomer **4,**[4] from which acid **1** could be isolated by crystallization.[5]

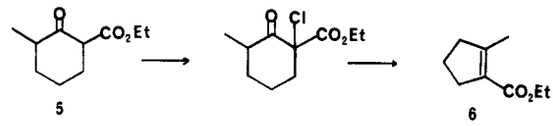
The inefficiency of the above procedure, which requires a somewhat expensive starting material, led us to investigate new methods for synthesis of acid **1.** Subsequent to the development of the methodology described below, another method for synthesis of the ethyl-2-methyl-1-cyclopentene-1-carboxylate (**6**) was described[6] (Scheme II) based upon methodology reported by Büchi. By this method, ester **6** can be prepared from keto ester **5** in 46% yield. Keto ester **5** was prepared from 2-methycyclohexanone in two steps in unreported yield.[8] The reports by Casey[9] that acyclic β-acyloxy

Scheme I

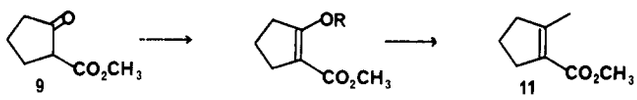


0022-3263/78/1943-3974$01.00/0

Scheme II



Scheme III



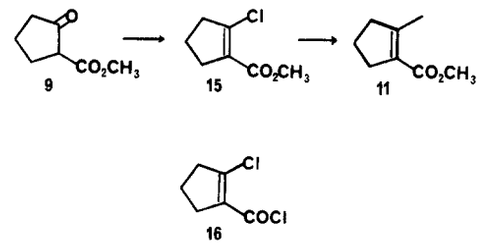
10a, R = $COCH_3$
10b, R = COPh
10c, R = $COPhOCH_3$
10d, R = CO_2Et
10e, R = $COPh(CH_3)_3$
10f, R = $COC(CH_3)_3$

α,β-unsaturated esters were readily converted to the corresponding β-methyl α,β-unsaturated esters (e.g., **7** → **8**) by treatment with lithium dialkylcuprates suggested a route to ester **11** involving a similar reaction with derivatives of the readily available 2-carbomethoxycyclopentanone (Scheme III).

2-Carbomethoxycyclopentanone (**9**) was converted in excellent yield into the enol acetate derivative **10a** by treatment with isopropenyl acetate in the presence of a catalytic amount of *p*-toluenesulfonic acid.[9] Treatment of **10a** with an excess of lithium dimethylcuprate according to Casey's procedure gave only cyclopentanone **9** as a product. This product was observed with either acidic workup or workup using methanol. The corresponding benzoate, **10b**, was prepared by treating ketone **9** with benzoyl chloride and triethylamine in HMPA at −5 °C.[9c] Reaction of this ester with lithium dimethylcuprate did give the desired β-methyl α,β-unsaturated ester **11** in 50% yield. Analysis of the crude product indicated the presence of acetophenone and methyl benzoate as major byproducts. The different results with **10a** and **10b** suggested the possibility that addition of the cuprate to these cyclic derivatives was slower than to the acyclic analogues resulting in significant attack on the enol ester either by the cuprate reagent or by the alkoxide always present to some extent in the methyllithium used to prepare the cuprate. We then investigated a series of enol ester derivatives (**10c–f**) to determine the effect of further changes in the enol ester functionality. Reaction of esters **10c** and **10d** with lithium dimethylcuprate gave the desired product in yields of 60 and 50%, respectively. The yield with ester **10e** was only 36%. In this case starting enol ester **10e** was recovered even after long reaction time. Thus, in this case, cleavage of the enol ester group was prevented, but the desired reaction appeared to be slowed also. The best enol ester derivative found for this conversion was ester **10f**. Reaction **10f** with 2 equiv of lithium dimethylcuprate gave ester **11** in 71% yield. The yield for the two-step conversion of **9** to **11** was 55%. Thus, the procedure outlined in Scheme III is reasonably effective, provided a suitable enol ester derivative is chosen.

The report by Clark and Heathcock[10] that lithium dimethylcuprate converted methyl 2-chloro-2-cyclohexene-1-carboxylate (**13**) into methyl 2-methyl-1-cyclohexene-1-carboxylate (**14**) in quantitative yield led us to investigate this type of procedure for preparation of ester **11**. The problem with this procedure is to find a method for obtaining the requisite chloro derivative. Heathcock[10] has shown that his oxalyl chloride procedure for β-dicarbonyl systems did not convert keto ester **12** to **13**. Other reagents such as phosphorus trichloride, phosphorus oxychloride, and thionyl chloride are also unsatisfactory for this conversion.

Scheme IV



In 1935, Rapson and Robinson[11] reported the synthesis of ethyl 2-chloro-1-cyclopentene-1-carboxylate in 45% yield by the treatment of 2-carbethoxycyclopentanone with phosphorus pentachloride in petroleum ether at 55 °C. Our attempts to apply this reaction to 2-carbomethoxycyclopentanone (**9**) gave the chloro derivative **15** in even lower yields. However, by a modification of this procedure, we have improved the yield significantly. Treatment of keto ester **9** with phosphorus pentachloride in anhydrous hexane or benzene for 2 h at 60–65 °C followed by addition of methanol to the cooled reaction mixture gave, after normal workup, chloro ester **15** in 80% yield. It is known that esters can be converted into acid chlorides by vigorous treatment with phosphorus pentachloride. Thus, the addition of methanol is necessary to convert any acid chloride **16** in the reaction mixture into the desired ester **15**. Reaction of chloro ester **15** with 1.1 equiv of lithium dimethylcuprate gave ester **11** in quantitative yield. Thus, the procedure of choice for synthesis of this cyclopentene ester is that shown in Scheme IV. Hydrolysis of ester **11** gave the carboxylic acid **1** in excellent yield.[12]

Experimental Section

General Procedures. Infrared spectra were determined on a Perkin-Elmer Model 327B or on a Beckman Instruments Model IR8 infrared spectrophotometer. Proton nuclear magnetic resonance (^1H NMR) spectra were determined on Varian Associates Model HA-100, T-60, or EM-360 spectrometers in the solvent indicated. Carbon-13 NMR spectra were obtained in $CDCl_3$ solution in the Fourier transform mode on a JEOL PFT-100 spectrometer system operating at 25.034 MHz (proton resonance frequency 99.539 MHz) and equipped with a Nicolet 1085 data system. Tetramethylsilane (Me_4Si) was used as the internal reference for all spectra except where stated otherwise. Chemical shifts are reported on the δ scale in parts per million downfield from Me_4Si for all spectra. High-resolution mass spectra were determined on a CEC Model 21-110B spectrometer under the supervision of Dr. R. Grigsby.

Vapor phase chromatographic (VPC) analyses were performed on a Hewlett-Packard Instrument, Model 700, equipped with a thermal conductivity detector with helium as the carrier gas, or on a Varian Aerograph Model 940 equipped with a flame ionization detector with nitrogen as the carrier gas. Column chromatography was performed using EM Reagents silica gel (60–200 mesh) or Grace silica gel (60–200 mesh).

Anhydrous ether was distilled from lithium aluminum hydride prior to use. Hexane and benzene were distilled from sodium–benzophenone.

"Bicarbonate" refers to a saturated aqueous solution of sodium bicarbonate. "Brine" refers to a saturated aqueous solution of sodium chloride. "Concentration" refers to the removal of solvent by rotary evaporation (Büchi Rotovapor) at 60 mmHg. "Evaporative distillation" refers to bulb-to-bulb (Kugelrohr) short-path distillation in which the bulb was heated in an air oven. The temperatures cited for

these distillations refer to the maximum temperature attained by the air chamber during the distillation.

Preparation of Enol Esters. Methyl 2-Acetoxy-1-cyclopentene-1-carboxylate (10a). A mixture of 2-carbomethoxycyclopentanone (**9**) (28.4 g, 0.2 mol), 75.0 g (0.75 mol) of isopropenyl acetate, and 1.0 g of *p*-toluenesulfonic acid monohydrate was heated at 110 °C for 12 h. The excess isopropenyl acetate and the acetone formed in the reaction were removed at reduced pressure, and the residue was distilled at 93 °C (1.7 mm) to give 33.54 g (91%) of enol acetate **10a:** IR (film) 1750, 1710, 1650 cm^{-1}; ^1H NMR (CCl_4) δ 3.62 (s, 3 H, CO_2CH_3), 2.45–2.75 (m, 4 H), 2.12 (s, 3 H, $OCCH_3$), 1.75–2.10 (m, 2 H).

General Procedure for Esters 10b–f. All other enol esters were prepared by the treatment of keto ester **9** with the appropriate acid chloride and triethylamine in hexamethylphosphoric triamide.[9c] Freshly distilled acid chloride (1.1 equiv) was added dropwise to a stirred solution of keto ester **9** (1.0 equiv) and triethylamine (1.1 equiv) in hexamethylphosphoric triamide at −5 °C. The reaction mixture was then brought to room temperature and stirred overnight. The reaction mixture was quenched with water (or bicarbonate) and ether and the separated aqueous layer was extracted with ether. The combined ether extracts were washed (water and brine), dried over $MgSO_4$, concentrated, and distilled at reduced pressure to give the enol ester. Each product was checked for purity by VPC analysis and characterized by a combination of spectral (IR, ^1H NMR, MS) and analytical data. Boiling points, yields, and ^1H NMR data are given below:

Methyl 2-Benzoyloxy-1-cyclopentene-1-carboxylate (10b): 124 °C (0.16 mm); 85% yield; ^1H NMR (CCl_4) δ 1.80–2.95 (m, 6 H), 3.60 (s, 3 H, CO_2CH_3), 7.20–7.60 (m, 3 H, aromatic H), and 7.90–8.20 (m, 2 H, aromatic H).

Methyl 2-Anisoyloxy-1-cyclopentene-1-carboxylate (10c): 140 °C (0.01 mm); mp 45–46 °C; 68% yield; ^1H NMR (CCl_4) δ 1.80–2.95 (m, 6 H), 3.60 (s, 3 H, CO_2CH_3), 3.80 (s, 3 H, $ArOCH_3$), 6.84 (2 H, aromatic H), and 7.98 (2 H, aromatic H).

Methyl 2-Ethoxycarbonyloxy-1-cyclopentene-1-carboxylate (10d): 74 °C (0.06 mm); 89% yield; ^1H MNR (CCl_4) δ 1.37 (t, J = 7 Hz, 3 H, CH_3CH_2), 1.65–2.80 (m, 6 H), 3.64 (s, 3 H, CO_2CH_3), 4.20 (q, J = 7 Hz, 2H, OCH_2CH_3).

Methyl 2-Mesitoyloxy-1-cyclopentene-1-carboxylate (10e): 140 °C (0.2 mm); 91% yield; ^1H NMR (CCl_4) δ 1.80–2.95 (m, 15 H), 3.66 (s, 3 H, CO_2CH_3), and 6.82 (bs, 2 H, aromatic H).

Methyl 2-Pivaloyloxy-1-cyclopentene-1-carboxylate (10f): 79 °C (0.6 mm); 78% yield; ^1H NMR (CCl_4) δ 1.27 (s, 9 H, $C(CH_3)_3$), 1.72–2.78 (m, 6 H), and 3.64 (s, 3 H, CO_2CH_3).

Reaction of Enol Esters with Lithium Dimethylcuprate. Lithium Dimethylcuprate.[13] To a cooled (−5 to 0 °C), stirred suspension of CuI (3.81 g, 20 mmol) in 60 mL of anhydrous ether under an atmosphere of nitrogen was added 20 mL of 2.0 M ethereal methyllithium (Aldrich, 40 mmol). Upon the addition of 1 equiv of methyllithium a bright yellow methylcopper solid was formed; the methylcopper dissolved when the second equivalent of methyllithium was added to give a colorless to pale pink solution of lithium dimethylcuprate (~20 mmol).

Reaction of Enol Benzoate 10b with Lithium Dimethylcuprate. To a cooled (−78 °C), stirred solution of lithium dimethylcuprate (20 mmol) was added 2.46 g (10 mmol) of enol benzoate **10b.** The reaction was maintained at −20 °C for 2.5 h, then quenched with 3 N HCl. The copper salt was filtered, and the aqueous layer was extracted twice with 50-mL portions of ether. The combined ethereal solution was washed (water, bicarbonate, and brine), dried over $MgSO_4$, and concentrated to give 1.20 g of crude product. The VPC analysis on 3% SE-30 showed the product contained the methylated ester **11**, β-keto ester **9**, acetophenone, and methyl benzoate. The crude product was chromatographed (silica gel) and evaporatively distilled at 55 °C (2.0 mm) to give 800 mg (54% yield) of ester **11:** IR (film) 1720 (C=O), 1650 (C=C) cm^{-1}; ^1H NMR δ 1.60–2.80 (m, 9 H) and 3.65 (s, 3 H, CO_2CH_3); ^{13}C NMR δ 16.2 (C-2 CH_3), 21.5 (C-4), 33.6 and 40.8 (C-3 and C-5), 50.8 (OCH_3), 127.1 (C-1), 156.0 (C-2), and 166.7 (CO_2R). Hydrolysis in methanolic KOH (see below) gave 2-methyl-1-cyclopentene-1-carboxylic acid (**1**) in 95% yield: mp 129–130 °C (lit.[11] 125 °C).

Reaction of Enol Anisoate 10c with Lithium Dimethylcuprate. To a cooled (−78 °C), stirred solution of lithium dimethylcuprate (20 mmol) was added 2.78 g (10 mmol) of enol anisoate **10c.** The reaction mixture was kept at −20 °C for 2.5 h, quenched with methanol at −20 °C, filtered to remove the copper salt, diluted with water, and extracted with ether. The ethereal extracts were washed (water and brine), dried over $MgSO_4$, and concentrated. The crude product was chromatographed and evaporatively distilled at 55 °C (2 mm) to give 850 mg (60% yield) of ester **11.**

Reaction of Enol Ethylcarbonate 10d with Lithium Dimethylcuprate. To a cooled (−78 °C), stirred solution of lithium dimethylcuprate (20 mmol) was added 2.14 g (10 mmol) of enol ethylcarbonate **10d.** The reaction mixture was kept at − 20 °C for 2.5 h, then quenched with methanol. Isolation as described for reaction with **10c** gave 635 mg (45%) of ester **11.**

Reaction of Enol Mesitoate 10e with Lithium Dimethylcuprate. To a cooled (−78 °C), stirred solution of lithium dimethylcuprate (20 mmol) was added 1.15 g (4 mmol) of enol mesitoate **10e.** The reaction mixture was maintained at −20 °C for 2.5 h, then quenched with methanol. Isolation as described for **10c** gave 200 mg (36% yield) of ester **11.**

Reaction of Enol Pivaloate 10f with Lithium Dimethylcuprate. To a cooled (−78 °C), stirred solution of lithium dimethylcuprate (40 mmol) was added 4.52 g (20 mmol) of enol pivaloate **10f.** The reaction mixture was stirred at that temperature for 30 min, then raised to room temperature and stirred for another 1.5 h. The reaction mixture was quenched with 3 N HCl at −20 °C, and the copper salt was filtered. Isolation as described for reaction with **10c** gave 2.0 g (71% yield) of ester **11.**

Methyl 2-Chloro-1-cyclopentene-1-carboxylate (15). To a cooled (0 °C), stirred suspension of PCl_5 (50 g, 0.24 mol) in 100 mL of anhydrous hexane was added dropwise 14.2 g (0.1 mol) of keto ester **9.** Reaction set in immediately with evolution of hydrogen chloride, and the reaction was completed by refluxing at 60 °C for 2 h, cooling with a dry-ice bath, and adding anhydrous methanol (10 mL). The methanol layer was extracted twice with 50-mL portions of hexane, and the hexane solution was washed (water, bicarbonate, and brine), dried over $MgSO_4$, and concentrated. The residue was distilled at 52 °C (0.5 mm) to give 12.80 g (80%) of chloro ester **15:** IR (film) 1720 (C=O), 1630 cm^{-1} (C=C); ^1H NMR (CCl_4) δ 3.66 (s, 3 H, CO_2CH_3), 1.65–2.84 (m, 6 H).

Reaction of Chloro Ester 15 with Lithium Dimethylcuprate. To a cooled (−78 °C), stirred solution of ethereal lithium dimethylcuprate (60 mmol) was added 6.85 g (42.6 mmol) of β-chloro ester **15** in 15 mL of anhydrous ether. After 1.5 h at −78 °C, the reaction mixture was quenched with 3 N HCl at −30 °C. The copper salt was filtered, and the aqueous layer was extracted twice with 100-mL portions of ether. The combined ethereal solution was washed (water, bicarbonate, and brine), dried over $MgSO_4$, and concentrated. The crude product was chromatographed and distilled at 55 °C (2 mm) to give 5.90 g (greater than 99% yield) of methyl ester **11.**

2-Methyl-1-cyclopentene-1-carboxylic acid (1). Methyl 2-methyl-1-cyclopentene-1-carboxylate (**11**) (800 mg, 5.71 mmol) was added to methanolic potassium hydroxide solution (1.0 g of KOH) at room temperature, and the mixture was refluxed overnight. The residue remaining after concentration was acidified with 3 M H_2SO_4. The liberated acid was extracted three times with 50-mL portions of ether, and the combined ethereal solution was washed (water and brine) and dried over $MgSO_4$. The solvent was removed at reduced pressure to give 750 mg of crude acid as a yellow solid, which upon recrystallization from hexane at 0 °C gave 700 mg (97% yield) of acid **1** as a white solid (mp 129–130 °C; lit.[11] mp 125 °C): ^{13}C NMR δ 16.5 (C-2 CH_3), 21.3 (C-4), 33.3 and 41.1 (C-3 and C-5), 126.8 (C-1), 159.3 (C-2), and 171.9 (C-6).

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Registry No.—**1,** 67209-77-2; **9,** 10472-24-9; **10a,** 55226-41-0; **10b,** 67209-78-3; **10c,** 67209-79-4; **10d,** 67209-80-7; **10e,** 67209-81-8; **10f,** 67209-82-9; **11,** 25662-30-0; **15,** 66839-38-1; isopropenyl acetate, 108-22-5; benzoyl chloride, 98-88-4; ethyl carbonochloridate, 541-41-3; *p*-methoxybenzoyl chloride, 100-07-2; 2,4,6-trimethylbenzoyl chloride, 938-18-1; 2,2-dimethylpropanoyl chloride, 3282-30-2; lithium dimethylcuprate, 15681-48-8.

References and Notes

(1) L. E. King and R. Robinson, *J. Chem. Soc.*, 465 (1941); O. H. Wheeler and I. Lerner, *J. Am. Chem. Soc.*, **78,** 63 (1956).
(2) (a) T. Holm, *Acta Chem. Scand.*, **18,** 1577 (1964); (b) S. J. Rhoads, J. K. Chattopadhyay, and E. E. Waali, *J. Org. Chem.*, **35,** 3352 (1970).
(3) This sequence of reactions was reinvestigated in our laboratories by Dr. J. M. Wilson.
(4) The isomer **4** was also observed by Rhoads[2b] from the hydrolysis of the nitrile mixture.
(5) The initial report[1] of only acid **1** from this reaction sequence undoubtedly resulted from the isolation of products by crystallization.

(6) A. Takeda, K. Shinhama, and S. Tsuboi, *Bull. Chem. Soc. Jpn.* **50**, 1831 (1977).
(7) G. Büchi and B. Egger, *J. Org. Chem.*, **36**, 2021 (1971).
(8) N. N. Chatterjee and A. Bose, *J. Indian Chem. Soc.*, **18**, 196 (1941); *Chem. Abstr.*, **36**, 762 (1942).
(9) (a) C. P. Casey, D. F. Marten, and R. A. Boggs, *Tetrahedron Lett.*, 2071 (1973); (b) C. P. Casey and D. F. Marten, *Synth. Commun.*, **3**, 321 (1973); (c) C. P. Casey and D. F. Marten, *Tetrahedron Lett.*, 925 (1974).
(10) R. D. Clark and C. H. Heathcock, *J. Org. Chem.*, **41**, 636 (1976), ref 24. The method used to prepare chloro ester **13** was not reported.
(11) W. S. Rapson and R. Robinson, *J. Chem. Soc.*, 1533 (1935).
(12) It should be noted that all attempts to prepare the cyclohexenyl ester **14** through enol ester derivatives in analogy with Scheme III failed. Likewise, the procedure for conversion of **9** into **15** gave low yields when applied to keto ester **12**. Conducting the phosphorus pentachloride reaction at room temperature did give **13** in usable yield.
(13) G. M. Whitesides, W. F. Fischer, Jr., J. S. Filippo, Jr., R. W. Bashe, and H. O. House, *J. Am. Chem. Soc.*, **91**, 4871 (1969). For a general discussion and review of cuprate preparation and reactions see: G. H. Posner, *Org. React.*, **19**, 1 (1975); and G. H. Posner, *ibid.*, **22**, 253 (1975).

Reduction by Tributyltin Hydride of Carbonyl Compounds Adsorbed on Silica Gel: Selective Reduction of Aldehydes

Norman Y. M. Fung, Paul de Mayo,* J. Herman Schauble,[1] and Alan C. Weedon

Department of Chemistry, University of Western Ontario, London N6A 5B7, Ontario, Canada

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Recently, we became interested in photochemically initiated reductions of adsorbed organic substrates by tributyltin hydride and were surprised to observe the rapid and efficient reduction of carbonyl groups adsorbed on dried silica gel, *but in the dark*.[2] This note describes investigations of these reactions and reveals the synthetic utility of tributyltin hydride reductions under these conditions.

Tributyltin hydride is one of the more readily available[3] and least reactive organotin hydrides.[4] In the absence of catalysts it will readily reduce strongly electrophilic species such as carbonium ions,[5] isocyanates,[6] isothiocyanates,[6] and carbonyl groups bearing powerful electron-withdrawing functions.[4] It also reacts spontaneously with alkyl iodides and bromides.[4] If radical initiators are present [e.g., ultraviolet light, azobis(isobutyryl)nitrile], then alkyl chlorides, aryl halides, esters, ketones, and other functional groups can also be reduced,[4,8-10] although elevated temperatures are often required. However, we found that in the presence of a cyclohexane slurry of dried silica gel, tributyltin hydride cleanly reduced aldehydes and ketones to give high yields of the corresponding alcohols (Table I). Sulfoxides, nitro groups, esters, arylnitriles, and alkyl, aryl, and benzylic chlorides were not effectively reduced. Attempted reduction of phenyl benzoate gave some phenol, but a blank reaction in the absence of tributyltin hydride gave the same result, indicating that the product arose from silicolysis of the ester on the silica gel. The fact that the silica gel had been activated to remove water and the failure to isolate any benzoic acid suggest that the phenol is displaced from the ester by hydroxyl end groups on the silica gel to give a benzoylated silica. Diphenylmethyl benzoate was also not reduced, and in this case no evidence for ester dissociation was observed.

Attempted reduction of an epoxide, that of *trans*-stilbene, led to the product of acid-catalyzed opening of the epoxide followed by pinacol rearrangement and reduction of the resulting carbonyl group. This was confirmed by a blank reaction where stilbene epoxide was treated with a cyclohexane slurry of dried silica gel; 2,2-diphenylacetaldehyde was isolated as the only major product.

With the exception of strained ketones such as norcamphor, the rate of reduction of carbonyl groups was found to be in the order aldehydes > dialkyl ketones > aralkyl ketones > diaryl ketones (Table I). When equimolar mixtures of aldehydes and ketones were treated with 1 equiv of tributyltin hydride in the presence of silica gel, selective aldehyde reduction was achieved (Table II).

Relatively few reagents are available for the selective reduction of aldehydes in the presence of ketones; tetrabutylammonium cyanoborohydride,[11] lithium aluminum tri-*tert*-butyloxyhydride,[12] sodium triacetoxyborohydride,[13] lithium di-*n*-butyl-9-borabicyclo[3.3.1]nonane,[14] diisopropylcarbinol on alumina,[15] and samarium diiodide[16] are ones which have been reported. Excluding the last of these reagents, a comparison has shown[15] that while all are capable of reducing an aldehyde in the presence of a *methyl* ketone, only diisopropylcarbinol on alumina has the ability to distinguish between a cyclohexanone and an aliphatic aldehyde. Tributyltin hydride in the presence of dried silica gel is superior to these reagents in its selectivity (Table II). Since this work was

Table I. Reduction of Organic Functional Groups by Excess Tributyltin Hydride on Dried Silica Gel at Room Temperature

substrate	product	isolated yield, %	minimum reaction time, h
norcamphor	norborneol (*exo* + *endo*)	69[a,b]	0.5
3-cholestanone	3-cholestanol (α + β)	89[a,c]	2
methyl naphthyl ketone	1-(β-naphthyl)ethanol	91[a,d]	4
benzophenone	diphenylmethanal	94[a]	6
benzaldehyde	benzyl alcohol	81[a]	1
octanal	1-octanol	90[a]	1
nitrobenzene	aniline	<5[a,e]	24
trans-stilbene epoxide	1,2-diphenylethanol	82[a]	6
phenyl benzoate	phenol	trace[e]	72
diphenylmethyl benzoate		0[e]	24
1-chloro-2-phenylethane		0[e]	48
diphenyl sulfoxide		0[e]	18
benzyl chloride		0[e]	24
phenyl bromide		0[e]	24
benzonitrile		0[e]	24

[a] Average of at least two determinations. [b] 92% endo by VPC (20% Carbowax 20M on Chromosorb W, 100 °C, 7 ft) and ^{1}H NMR assay (average of at least two determinations); reduction with $Bu_3SnH/ZnCl_2/Et_2O$ solution gave 89% endo. [c] 89% β, computed from isolated yields of α and β isomers after separation by TLC and crystallization (average of at least two experiments); reduction with $Bu_3SnH/ZnCl_2/Et_2O$ solution gave 85% β. [d] Reduction with $Bu_3SnH/ZnCl_2/Et_2O$ solution gave a 77% yield of the alcohol. [e] Starting material recovered unchanged.

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