lished.[25] There was no absorption at 720 $cm^{-1}$, at which point the cis isomer absorbs strongly.

After reduction of the analytical run, only 55% of Hg was isolated. Addition of acid to the aqueous layer produced evolution of gas (presumably $H_2$) so that incomplete reduction was not due to insufficient hydride. During the preparative run, Hg was observed to emerge from the separated THF layer during work-up.

(25) B. Heilmann, G. de Gaudemaris, and P. Arnaud, *Bull. Soc. Chim. Fr.*, 123 (1957).

**Registry No.**—**1**, 34386-60-2; **2**, 34386-61-3; **4**, 17264-01-6; **7**, 2004-67-3; **12**, 18625-77-9; **13**, 34386-65-7; **14**, 34386-66-8; **15**, 138-86-3; **16**, 100-40-3; **17**, 592-57-4; **18**, 513-81-5; **19**, 78-79-5; **20**, 2004-70-8; mercuric acetate, 1600-27-7; 1,4-pentadiene, 591-93-5; 1,7-octadiene, 3710-30-3; 1,11-dodecadiene, 5876-87-9; mercuric trifluoroacetate, 13257-51-7; 11-methyl-11-dodecen-2-ol, 34386-69-1.

# Hydroxypropylation

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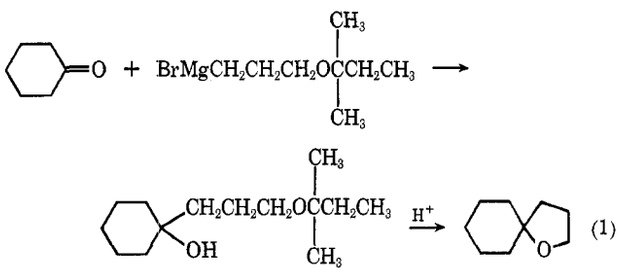
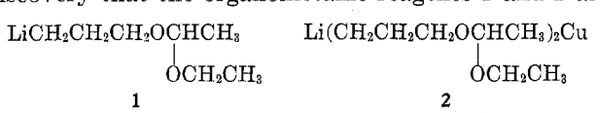
Organometallic reagents (**1**, **2**) useful in Grignard-type addition reactions are readily prepared from ethyl 3-bromopropyl acetaldehyde acetal (**3**). These reagents provide convenient means for the introduction of the hydroxypropyl group and the propionic acid chain.

We recently faced the problem of finding a convenient method for the introduction of the hydroxypropyl group, $-CH_2CH_2CH_2OH$, *via* organometallic-type reactions. Surprisingly, little in the literature is applicable to this problem. Grignard reagents from methyl,[1] ethyl,[2] and *tert*-amyl[3] ethers of 3-bromopropanol have been used in reactions with carbonyl compounds, but subsequent liberation of the primary hydroxyl group from its protecting ether mask cannot be accomplished readily without complication (*e.g.*, eq 1).[3]

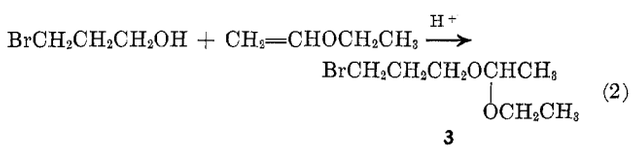


(1)

We report now our simple but exceedingly useful discovery that the organometallic reagents **1** and **2** are



completely satisfactory carriers of the hydroxypropyl group. The parent of these reagents is ethyl 3-bromopropyl acetaldehyde acetal (**3**, alternate name, 1-ethoxyethyl 3-bromopropyl ether). This masked 3-bromopropanol is prepared by acid-catalyzed addition of the bromo alcohol to ethyl vinyl ether (eq 2). Ethyl



(2)

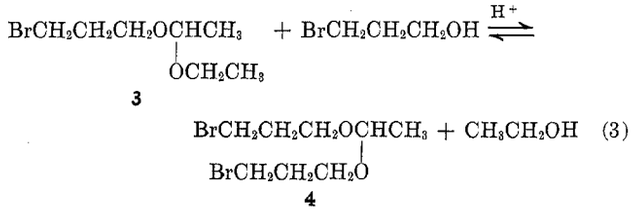
(1) H. Erlenmeyer and R. Marbet, *Helv. Chim. Acta*, **29**, 1946 (1946). See also M. S. Kharasch and O. Reinmuth, "Grignard Reactions of Nonmetallic Substances," Prentice-Hall, Englewood Cliffs, N. J., 1954, p 36, and references cited therein.

(2) L. I. Smith and J. A. Sprung, U. S. Patent 2,421,090; *cf. Chem. Abstr.*, **41**, 5543 (1947).

(3) W. R. Renfrow, D. Oakes, C. Laver, and T. A. Walter, *J. Org. Chem.*, **26**, 935 (1961).

vinyl ether was chosen for protection of the hydroxyl group rather than the more common reagent dihydropyran as (1) ethoxyethyl ethers are more readily removed by hydrolysis than the corresponding tetrahydropyranyl ethers,[4] and (2) the hydrolysis of an ethoxyethyl ether gives ethanol and acetaldehyde, both volatile and easily removed, whereas a tetrahydropyranyl ether gives the less convenient by-product 5-hydroxypentanal.

The reaction of 3-bromopropanol with ethyl vinyl ether is nearly quantitative and can be carried out readily on multimole scale if suitable care is exercised in the choice and use of the acid catalyst. Initially we used small amounts of methanesulfonic acid, but on too many occasions this led to explosive polymerization of the vinyl ether or, less disastrously, to production of the symmetrical acetal **4** *via* the exchange reaction shown in eq 3. We now employ dichloroacetic acid as the catalyst and avoid both these problems.



(3)

The lithium reagent **1** can be prepared on mole scale in ethyl ether as easily as a simple Grignard. The reaction of **3** with lithium wire (1% sodium) initiates spontaneously at room temperatures and continues rapidly below 0°.[5] One-molar solutions of **1** in ether are stable for months at −30°. Such solutions can be worked with unhurriedly at room temperature, but slow decomposition does occur to cyclopropane, among other things.

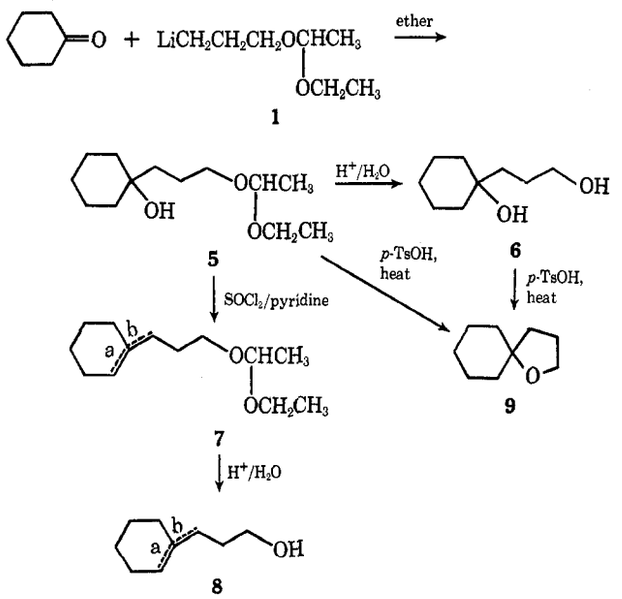
Addition of the lithium reagent **1** to a simple ketone is straightforward and proceeds in excellent yield. The product can be hydrolyzed to the primary alcohol *without* disturbing the nearby tertiary hydroxyl group, or

(4) S. Chladek and J. Smrt, *Chem. Ind.* (London), 1719 (1964).

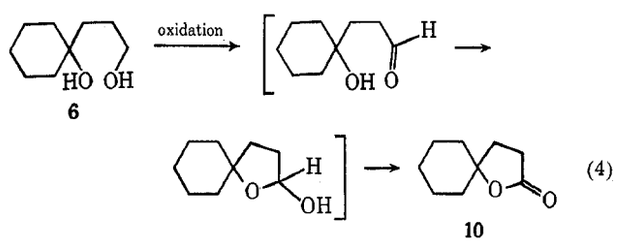
(5) Oddly, the corresponding reaction with magnesium turnings does not proceed at all well in ether solvent. The Grignard can, however, be prepared in tetrahydrofuran. It is less useful than **1**.

if desired, taken to the corresponding unsaturated primary alcohol (protected or free), or cyclized to the tetrahydrofuran (Scheme I).

SCHEME I



Oxidation of the diol produced on hydrolysis of the adduct of 1 with a ketone leads in excellent yield to the γ-lactone, as in eq 4. The oxidation presumably proceeds by way of the corresponding aldehyde and its hemiacetal[6] and is brought about by a large number of oxidizing systems, including chromium trioxide in aqueous acid and the chromium trioxide–pyridine complex in dichloromethane.



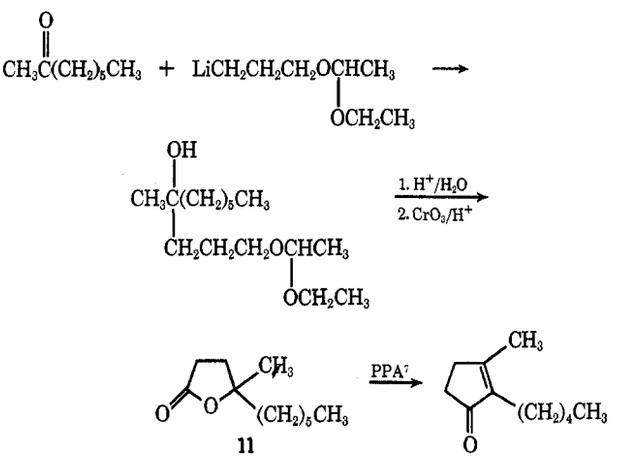
(4)

The γ-lactones very readily available by the reactions outlined here are useful precursors of substituted cyclopentenones.[7] Hydrolysis and oxidation of the adduct of the lithium reagent 1 to 2-octanone as in Scheme II provides, for example, an alternate approach to the lactone 11 used in the synthesis of dihydrojasmone.[7] We have made good use of equivalent reactions with more complex systems in the synthesis of peristylane as reported elsewhere.[8]

Reaction at −60° of the lithium reagent 1 with 0.5 equiv of cuprous iodide suspended in ether gives the lithium organocuprate 2.[9] We have not taken this organometallic over the full gamut of possible reactions, as this is outside our purpose. Instead, we have shown only that the reagent provides for the conjugate addition of the hydroxypropyl group to 2-cyclopentenone

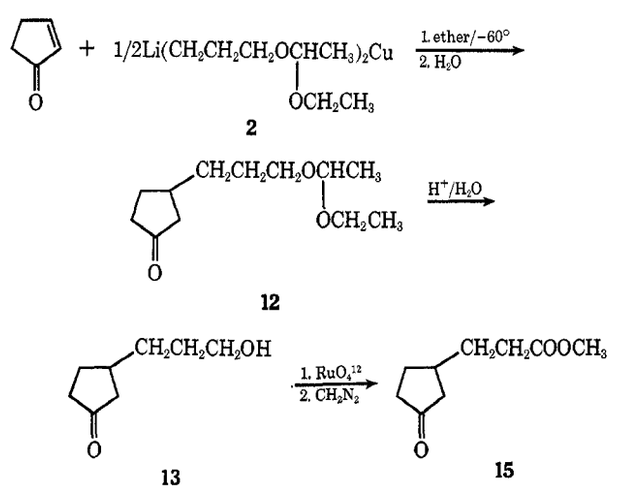
(6) W. A. Mosher and D. M. Preiss, *J. Amer. Chem. Soc.*, **75**, 5605 (1953).
(7) C. Rai and S. Dev, *J. Indian Chem. Soc.*, **34**, 178 (1957), and references cited therein.
(8) P. E. Eaton and R. H. Mueller, *J. Amer. Chem. Soc.*, **94**, 1014 (1972).
(9) This convenient designation represents only the stoichiometry of the reaction; see E. J. Corey and G. H. Posner, *ibid.*, **90**, 5615 (1968), footnote 7.

SCHEME II



(Scheme III).[10] Oxidation of the keto alcohol from hydrolysis of this adduct and subsequent esterification gives the keto ester 15, a key material in our synthesis of peristylane,[8] and previously available only by lower yield, longer synthetic schemes.[11]

SCHEME III



The hydroxypropyl group can, of course, be oxidized easily to the corresponding acid, as in eq 4 and Schemes II and III. With this small extension, use of the organometallics 1 and 2 offers by far the most convenient way of introducing the propionic acid side chain.[13] The overall scheme should be regarded as

(10) H. O. House, W. L. Respess, and G. M. Whitesides, *J. Org. Chem.*, **31**, 3128 (1966), and references cited therein give other examples using different systems.
(11) H. Stetter, I. Krüger-Hansen, and M. Rizk, *Chem. Ber.*, **94**, 2702 (1961).
(12) We thank Dr. B. W. Roberts for calling this oxidation method to our attention.
(13) No Grignard-type carrier of a simply protected (*i.e.*, same oxidation state) propionic acid chain is known. Attempts to prepare such a reagent from 3-bromopropionic acid ortho esters were thwarted by lack of a ready route to these derivatives of this particular acid.[14] Our single attempt to prepare a dihydro-1,3-oxazine[15,16] concealing a 3-bromopropionic acid led to elimination of the halogen; further work here is called for. The Grignard from 3-bromopropionaldehyde ethylene acetal (note oxidation state) is a useful reagent,[17] but it cannot be made in ether nor, as its thermal stability is poor, can it be prepared in quantity in tetrahydrofuran.
(14) J. P. Schroeder, D. C. Schroeder, J. Hardin, and J. K. Marshall, *J. Org. Chem.*, **34**, 3332 (1969).
(15) A. I. Meyers, I. R. Politzer, B. K. Bandlish, and G. R. Malone, *J. Amer. Chem. Soc.*, **91**, 5886 (1969).
(16) J. J. Ritter and E.-J. Tillmans, *J. Org. Chem.*, **22**, 839 (1957).
(17) G. Büchi and H. Wüest, *ibid.*, **34**, 1122 (1969).

cousin to the Reformatsky reaction, so useful in the introduction of the shorter acetic acid side chain.

## Experimental Section

**Ethyl 3-Bromopropyl Acetaldehyde Acetal (3).**—Commercial 3-bromopropanol (1600 g, Eastman), containing water, hydrogen bromide, and organic impurities, was diluted with an equal volume of dichloromethane. The solution was washed in succession once with 200 ml of water, twice with 200-ml portions of saturated aqueous sodium bicarbonate, and once with 200 ml of saturated aqueous sodium chloride, and then dried over sodium sulfate. The solvent was removed *in vacuo*. The residue was neutral to pH paper and was distilled (in four separate batches) to give 3-bromopropanol, bp 60–64° (5 mm), 1250 g, reasonably pure, but acidic to pH paper. The distilled product was stirred over powdered sodium carbonate until the pH was above 5 (*ca.* 6 hr) and then stored until used at −30° over sodium carbonate.

Ethyl vinyl ether (289 ml, 220 g, 3.06 mol) was added to purified, nonacidic 3-bromopropanol (272 g, 1.96 mol) in a 1-l., three-necked flask equipped with a magnetic stirring bar, thermometer, and condenser with drying tube. At first only a small amount of the ether was added to check that there would be no violent reaction. Dichloroacetic acid (2.75 ml) was added. The temperature rose gradually to 50° over 1 hr. An hour later 1 ml more of acid was added and again after an additional 4 hr. The mixture was stirred overnight. In the morning, 8 g of powdered sodium carbonate was added, and the mixture was stirred for several hours. Filtration, removal of excess ethyl vinyl ether *in vacuo*, and vacuum distillation from sodium carbonate gave the required bromo acetal **3** as a colorless liquid, bp 49–51° (1 mm), 379 g, 92% yield. The acetal was stored over powdered sodium carbonate at −30°: nmr ($CCl_4$) $\delta$ 4.63 (1 H, quartet, $J$ = 5.5 Hz), 3.8–3.2 (4 H, complex), 3.48 (2 H, triplet, $J$ = 7 Hz), 2.03 (2 H, pentuplet, $J$ = 6 Hz), 1.23 (3 H, doublet, $J$ = 5.5 Hz), 1.14 ppm (3 H, triplet, $J$ = 7 Hz).

**Organolithium 1.**—Generation of **1** was accomplished most conveniently using a jacketed, 2-l., three-necked flask with a drain tube at the bottom carrying a glass stopcock and terminating in a male ⅌ joint. The flask was equipped with a mechanical stirrer, low-temperature thermometer, and pressure-equalizing addition funnel topped with a gas inlet and bubbler. The entire apparatus was carefully dried and purged with argon. The flask was charged with 1 l. of dry ether and 18.1 g (2.62 g-atoms) of 0.5-in. lengths of lithium wire (1% sodium). About 25 ml of bromo acetal **3** was added to the stirred mixture. Soon, shiny spots appeared on the lithium wire, and the solution became cloudy. At this point, coolant was pumped from a refrigerated bath through the flask jacket. The temperature of the reaction solution was lowered to −5° and maintained between −5 and −15° as the remaining bromo acetal (total 244 g, 1.15 mol) was added dropwise over 1 hr. The chilled mixture was stirred after the addition was complete until the surface of the residual lithium metal tarnished (about 2 hr). The solution was then drained into a vessel suitable for whatever reaction was next.[18] If desired, the cloudy solution of **1** could be pressure-filtered through a medium porosity frit to give a crystal-clear solution of the organolithium stable for months at −30°. In either case, solutions of **1** prepared by this recipe were regarded as being 1 *M* in organolithium. This underestimates the actual concentration somewhat but provides a convenient guide.

**Addition of 1 to Cyclohexanone.**—About 70 ml of the ether solution of **1** prepared as just described was run from the preparation flask into a flame-dried, 250-ml, round-bottomed flask equipped for magnetic stirring and flushed with nitrogen. The flask was cooled in an ice bath as a solution of dry cyclohexanone (4.9 g, 0.05 mol) in 20 ml of ether was added dropwise with stirring. The mixture was stirred for 1 hr and then poured into 100 ml of half-saturated aqueous ammonium sulfate solution. After the usual work-up (ether),[19] distillation gave 10.3 g (90%) of colorless adduct **5**, bp 94–95° (0.07 mm).

*Anal.* Calcd for $C_{13}H_{26}O_3$: C, 67.78; H, 11.38. Found: C, 67.83; H, 11.18.

(18) Many simple addition reactions can just as well be run without bothering with this transfer (see addition of **1** to 2-octanone). Excess lithium metal does not interfere.

(19) "Usual work-up" is shorthand for extraction with the named solvent, drying the extract with sodium sulfate, filtration, and concentration under vacuum on a rotary evaporator.

**1-(3-Hydroxypropyl)cyclohexanol (6).**—A sample of adduct **5** (24 g), prepared as above but in a larger run, was stirred into 100 ml of a 60:40 mixture of water and ethanol and 4 ml of concentrated hydrochloric acid. After 15 min the homogeneous solution was neutralized by addition of solid potassium carbonate. The mixture was reduced to a small volume under vacuum on a rotary evaporator. The organic material in the residue was taken up in chloroform, and this solution was concentrated under vacuum. Molecular distillation at 100° (0.04 mm) of the residue gave 15.8 g (96%) of the diol **6** as a colorless, extremely viscous oil contaminated (nmr) with traces of chloroform and ethanol. No attempt was made to push the purification process further.

*Anal.* Calcd for $C_9H_{18}O_2$: C, 68.31; H, 11.47. Found: C, 67.88; H, 11.68.

**Dehydration of 5. Formation of 7a,b.**—The adduct **5** (27.9 g, 0.121 mol) and anhydrous pyridine (150 ml) were mixed together in a 500 ml, three-necked, round-bottomed flask equipped with an addition funnel, drying tube, thermometer, and magnetic stirrer. The solution was cooled to 2° using an ice–water bath. Thionyl chloride (25 ml, 0.346 mol)[20] was added dropwise. The solution was held at 10° by cooling (the reaction is quite exothermic). After the addition was complete, the mixture was stirred for 30 min and then poured onto 200 g of ice. The work-up procedure (ether) was standard except for the addition of three quick washes with 5% hydrochloric acid to remove excess pyridine and a final wash with saturated aqueous sodium bicarbonate solution. Distillation gave 21.3 g (83%) of **7**, bp 61–68° (0.1 mm), containing about 90% **7a** (nmr, vinyl hydrogen $\delta$ 5.35 ppm, broadened singlet, no $J > 2$ Hz) and 10% **7b** ($\delta$ 5.00 ppm, broadened triplet, $J \sim 8$ Hz).

*Anal.* Calcd for $C_{13}H_{24}O_2$: C, 73.54; H, 11.39. Found: C, 73.35; H, 11.61.

**Formation of the Olefin-Alcohols 8a and 8b.**—The sequence just described was repeated starting with 18.9 g of adduct **5**. The distillation was omitted; crude **7** was hydrolyzed as described for the conversion of **5** to **6**. Simple distillation of the product gave 10.4 g (90%) of a mixture, bp 60–65° (1 mm), approximately 9:1 in the olefins **8a** and **8b**, respectively, as determined by nmr.

*Anal.* Calcd for $C_9H_{16}O$: C, 77.09; H, 11.50. Found: C, 77.11; H, 11.58.

**1-Oxaspiro[4.5]decane (9).**—An 11.1-g sample of distilled adduct **5** was mixed with 70 mg of *p*-toluenesulfonic acid in a 25-ml, round-bottomed flask provided with a magnetic stirring bar. The flask was topped with a 25-cm Vigreux column connected to a simple distilling head with receiver immersed in a Dry Ice bath. The system pressure was reduced to 25 mm (aspirator), and the reaction mixture was heated quickly to 150–200°. The distillate (collected over about 1 hr) was dried and redistilled to give 5.5 g (81%) of the known ether **9**, bp 72–75° (19 mm) [lit.[3] bp 182° (742 mm)], identified spectroscopically.

**Formation of Lactone 10.**—A small sample of **6** (~1 g) was added slowly with 10 ml of water to a stirred solution of 2 g of chromium trioxide in a mixture of 20 g of water and 20 g of concentrated sulfuric acid. The temperature was held at 5–15°. The crude lactone **10** obtained by a standard work-up (chloroform) was purified by molecular distillation at 50° (0.05 mm), ir (neat) 5.65 $\mu$.

*Anal.* Calcd for $C_9H_{14}O_2$: C, 70.10; H, 9.15. Found: C, 70.18; H, 9.38.

**Formation of 4-Methyl-4-hydroxydecanoic Acid Lactone (11).**—A solution of the lithium reagent **1** was prepared as described earlier using 91.0 g (0.432 mol) of the bromo acetal **3**, 6.9 g (1.0 g-atom) of lithium wire, and 300 ml of ether. A solution of 42.6 g (0.33 mol) of distilled 2-octanone in 100 ml of ether was added dropwise over 30 min to this solution of **1** held at 0°. The reaction mixture was stirred for 1 hr after the addition was complete and then processed as described under the preparation of **5**. The crude adduct was not distilled but was hydrolyzed directly to the corresponding diol as described in the hydrolysis of **5** to **6**. The crude diol was added dropwise to a stirred (Vibromixer) solution of 70.5 g of chromium trioxide and 2 g of manganous sulfate in 500 ml of water and 580 g of concentrated sulfuric acid in a jacketed, 2-l. reaction kettle. Chilled water was passed through the jacket to hold the flask contents below 22°. The crude diol was added as rapidly as consistent with temperature control. After the addition was

(20) This large excess of thionyl chloride is probably not needed.

complete, the mixture was agitated for 1 hr. Standard work-up (chloroform) followed by distillation through a 40-cm spinning band column gave 44.2 g (71%) of pure lactone **11**, bp 75° (0.07 mm) [lit.[7] bp 159–160° (18 mm)].

*Anal.* Calcd for $C_{11}H_{20}O_2$: C, 71.70; H, 10.94. Found: C, 71.58; H, 10.96.

**Preparation of Methyl β-(3-Oxocyclopentyl)propionate (15).**

**A. Addition of 2 to 2-Cyclopentenone.**—The entire apparatus as described earlier for the preparation of the organolithium reagent **1** was assembled atop a jacketed, four-necked, 3-l. reaction kettle. The connection between the two flasks being made *via* the male ⅌ joint terminating the drain tube at the bottom of the upper flask. The lower pot was equipped in addition with a mechanical stirrer, a low-temperature thermometer, and a pressure-equalizing addition funnel topped with a nitrogen inlet and bubbler. Provision was made to cool this flask by forced circulation of acetone through the flask jacket and a heat exchanger (copper coils) immersed in a Dry Ice bath. Care was taken to dry the entire apparatus. A solution of the lithium reagent **1** in ether was prepared under argon in the upper flask exactly as described in the second experiment. This solution was added dropwise to a well-stirred slurry in the lower flask of purified[21] cuprous iodide (136.5 g, 0.72 mol)[22] in 700 ml of dry ether maintained at −60 to −70° throughout the addition. The addition required about 1 hr. Another 1 hr was let pass to ensure complete formation of the lithium cuprate **2**. After this time, a solution of 82.8 g (1.02 mol) of pure, dry 2-cyclopentenone in 100 ml of ether was added dropwise. The reaction mixture was held below −60° throughout this addition, which required about 1.5 hr. (Color changes during the addition varied considerably from run to run. In some runs only a light green or yellow color developed, whereas in others the mixture became brick red and later orange. No obvious correlation with ultimate yield could be made.) After the addition of cyclopentenone had been completed, the mixture was stirred for 1 hr at −65° and then allowed to warm over 30 min to −35°. At this point the reaction was quenched by transferring the mixture by suction through $^3/_{16}$-in.-i.d. polyethylene tubing into a 5-l. flask already containing a well-stirred (Vibromixer) solution of 250 g of ammonium sulfate in 600 ml of water. The main reaction flask was rinsed with 400 ml of ether. The mixture in the quenching flask was agitated for 30 min. The insoluble salts were then removed by filtration. The ether portion of the filtrate was separated; the blue, aqueous layer was extracted with ether (2 × 300 ml). The combined ether solution was washed with saturated aqueous ammonium sulfate solution, dried over sodium sulfate, and concentrated *in vacuo* to give 238 g of crude adduct **12**.

**B. Removal of the Protecting Group.**—The entire sample of crude adduct **12** was stirred into a solution of 1.5 g of dichloroacetic acid[23] in 750 ml of water contained in a 2-l., single-necked, round-bottomed flask. The mixture went essentially homogeneous after about 1 hr. At this point, the solution was neutralized by addition of solid potassium carbonate. The flask was then attached to a rotary evaporator, and the easily volatile materials (ethanol, acetaldehyde) were removed under vacuum. The residue was saturated with ammonium sulfate. The organic phase was separated, and the aqueous layer was extracted with chloroform (3 × 350 ml). The organic material was combined and concentrated under vacuum to leave 155 g of crude 3-(3-hydroxypropyl)cyclopentanone (**13**). A small sample from this crude product was purified by column chromatography on silica gel followed by molecular distillation at 50° (0.02 mm).

*Anal.* Calcd for $C_8H_{14}O_2$: C, 67.57; H, 9.92. Found: C, 67.67; H, 9.90.

**C. Oxidation.**[12]—A suspension of 616 g (2.68 mol) of potassium metaperiodate and 0.75 g of ruthenium dioxide in 2 l. of water and 1 l. of acetone was made up in a 5-l., jacketed kettle equipped with thermometer, addition funnel, and Vibromixer stirrer. The crude hydroxy ketone **13** was dissolved in 200 ml of acetone, and this solution was added dropwise over 30 min to the well-agitated oxidizing mixture. The reaction is mildly exothermic and was moderated by passing cold water through the kettle jacket. The temperature of the reaction mixture was not allowed to exceed 45°. The progress of the reaction was monitored by nmr analysis of small aliquots, following the signals in the region δ 3.5–3.9 ppm due to starting material. These signals were barely visible after the reaction had run for 2–5 hr. At this point, the insoluble salts were removed by filtration, and the filtrate was concentrated *in vacuo* to remove most of the acetone. The concentrate was saturated with ammonium sulfate, and this was extracted with chloroform (3 × 500 ml). The extract was concentrated *in vacuo*. The residue (which sometimes crystallizes) was mixed with 600 ml of water and titrated with 40% aqueous sodium hydroxide solution to the phenolphthalein end point. The basic solution was extracted twice with chloroform and then acidified with 6 *N* sulfuric acid. Thorough extraction of the acid solution with chloroform followed by evaporation of the solvent under vacuum gave 110 g of crude solid acid. A small part of this was purified by crystallization successively from ethyl ether, *n*-butyl ether, and ethyl ether–pentane to give pure acid **14** as a white, crystalline solid, mp 51–53°.

*Anal.* Calcd for $C_8H_{12}O_3$: C, 61.52; H, 7.74. Found: C, 61.55; H, 7.86.

**D. Esterification.**—The main part of the crude acid was dissolved in ether (the little that did not dissolve readily was discarded) and converted to the methyl ester **15** by reaction with ethereal diazomethane in the usual way. The ester was purified by distillation, bp 78° (0.005 mm); 85.5 g of pure **15** was obtained, a 50% yield overall from cyclopentenone.

*Anal.* Calcd for $C_9H_{14}O_3$: C, 63.51; H, 8.29. Found: C, 63.47; H, 8.23.

**Registry No.**—**3**, 34399-67-2; **5**, 34399-68-3; **6**, 6963-45-7; **7a**, 34399-70-7; **7b**, 34399-71-8; **8a**, 22516-18-3; **8b**, 4361-24-4; **10**, 699-61-6; **11**, 7011-83-8; **13**, 34399-76-3; **14**, 34399-77-4; **15**, 34399-78-5.

**Acknowledgment.**—We are grateful to the National Science Foundation for support of this work. R. H. M. thanks the National Institutes of Health for a predoctoral fellowship.

(21) G. B. Kauffman and L. A. Teter, *Inorg. Syn.*, **7**, 9 (1963). The purified cuprous iodide should be finely powdered before use.

(22) Neither the course nor stoichiometry of the addition reaction to cyclopentenone is changed by varying the ratio of cuprous iodide to organolithium from 0.5:1 to 1:1.

(23) The use of stronger acids, *e.g.*, HCl or $H_2SO_4$, leads to this case to resinification of the product.