C=O) cm^{-1}; MS, *m/e* 246 ($M^+ + 1$), 214 ($M^+ - CH_2OH$), 172 ($M^+ - CO_2CH_2CH_3$); TLC, R_f 0.50 (EtOAc).

Preparation of 6b and 2b: 5(*S*)-(Hydroxymethyl)-2-(*R*)-carboxypyrrolidine and *N*-Carbobenzoxy-5(*S*)-(hydroxymethyl)-2(*R*)-carbomethoxypyrrolidine. 6a (880 mg, 3.59 mmol) was dissolved in 12 mL of 4 N NaOH and stirred at room temperature. After 17 h 10 mL of concentrated HCl was carefully added, and the resulting solution was brought to reflux. After 5 h reflux was stopped, and KOH pellets were added to bring the pH to 12. The solution was chilled to 0 °C and 0.80 mL (5.6 mmol, 1.5 equiv) of carbobenzoxy chloride dissolved in 15 mL of dioxane and 15 mL of H_2O was added. The reaction stirred at 0 °C for 1 h, then at room temperature. After 20 h the solution was poured into a separating funnel and washed three times with Et_2O. The aqueous layer was acidified to pH 2 with concentrated HCl and extracted four times with EtOAc. The combined EtOAc extracts were dried ($MgSO_4$), filtered, and evaporated. A crude oil remained, 416 mg (41%). This oil was dissolved in 5 mL of THF and treated with excess CH_2N_2 in ether. The excess CH_2N_2 was quenched with excess AcOH, and the solvent was evaporated to an oil from which **2b** was obtained pure by flash chromatography (4:1 EtOAc/hexane); 308 mg (29% from **6a**) of a clear oil was obtained: $[\alpha]^{22}_D$ +9.6° (*c* 0.27, CH_2Cl_2); ^1H NMR ($CDCl_3$) δ 7.45–7.25 (5 H, m), 5.25–5.05 (2 H, m), 4.55 -4.40 (1 H, m), 4.20–3.95 (2 H, m), 3.90–3.20 (2 H, m), 3.80, 3.65 (3 H, 2 s), 2.30–1.85 (4 H, m), 1.65 (1 H, br s); IR ($CHCl_3$) 3560 (OH), 1735 (ester C=O), 1700 (urethane C=O) cm^{-1}; TLC, R_f 0.63 (EtOAc); MS, *m/e* 294 ($M^+ + 1$), 293 (M^+), 262 ($M^+ - OCH_3$), 234 ($M^+ - CO_2CH_3$).

Anal. Calcd for $C_{15}H_{19}NO_5$: C, 61.42; H, 6.43; N, 4.78. Found: C, 61.67; H, 6.58; N, 5.00. HRMS calcd for $C_{15}H_{19}NO_5$ 293.1263, found, 293.1262.

***cis*-*N*-Carbobenzoxy-2,5-dicarbomethoxypyrrolidine. 2b** (84.5 mg, 0.288 mmol) was dissolved in 5 mL of acetone and treated with 0.60 mL of 8 N chromic acid (4.8 mmol, 16.6 equiv). After the mixture was stirred for 1 h at room temperature 1.0 mL of isopropyl alcohol was added. After an additional hour at room temperature, the chromium salts were removed by filtration. The filtrate was evaporated to a green oil, which was dissolved in 15 mL of Et_2O and washed with 3 × 5 mL of brine. The Et_2O was dried ($MgSO_4$), filtered, and evaporated to a clear oil. This oil was dissolved in 4 mL of THF and treated with excess CH_2N_2. Excess AcOH was added to quench the excess CH_2N_2. The solvent was evaporated. The oil that remained was dissolved in 15 mL of Et_2O and washed with 3 × 5 mL of saturated $NaHCO_3$ and 1 × 5 mL of brine. The Et_2O was evaporated, leaving a crude oil. Flash chromatography (1:1 EtOAc/hexane) yielded one compound, a clear oil, 6.14 mg (66%): $[\alpha]^{22}_D$ 0.0° (*c* 1.54, CH_2Cl_2); ^1H NMR ($CDCl_3$) δ 7.34 (5 H, s with shoulders), 5.19, 5.14 (2 H, 2 d, *J* = 12 Hz), 4.53–4.48 (1 H, t, *J* = 4 Hz), 4.46–4.40 (1 H, t, *J* = 5 Hz), 3.78 (3 H, s), 3.65 (3 H, s), 2.30–2.10 (4 H, m); TLC, R_f 0.54 (1:1 EtOAc/hexane); MS, m/e 321 (M^+), 262 ($M^+ - CO_2CH_3$).

Preparation of 8: 5,5-Dicarbethoxytetrahydro-1*H*-pyrrolo[1,2-*c*]oxazol-3-one.[7] Racemic **6a** (560 mg, 2.28 mmol) and 1.53 g (9.44 mmol) of 1,1'-carbonyldiimidazole were dissolved in 20 mL of anhydrous benzene under N_2, and the solution was brought to reflux. After 15.5 h the benzene was cooled and evaporated. The tan oil that remained was dissolved in 50 mL of EtOAc and washed: 3 × 10 mL of 1 N HCl, 1 × 10 mL of saturated $NaHCO_3$, and 1 × 10 mL of brine. The EtOAc was dried ($MgSO_4$), filtered, and evaporated. **8** (479 mg, 78%) was obtained as a clear oil: ^1H NMR ($CDCl_3$) δ 4.60–4.54 (1 H, t, *J* = 7.5 Hz), 4.35–4.17 (6 H, m), 2.72–2.54 (2 H, m), 2.17–2.07 (1 H, m), 2.03–1.90 (1 H, m), 1.37–1.25 (6 H, m); IR ($CHCl_3$) 1770 (urethane C=O), 1750 (ester C=O) cm^{-1}; TLC, R_f 0.65 (EtOAc); MS, *m/e* 271 (M^+), 227 ($M^+ - CO_2$), 198 ($M^+ - CO_2CH_2CH_3$).

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Registry No. 2a, 102208-90-2; **2b**, 102108-00-9; **2b** (R = H), 102108-01-0; **4**, 102107-97-1; **6a**, 102107-98-2; (±)-**6a**, 102208-91-3; **8**, 102107-99-3; diethyl (*N*-carbobenzoxyamino)malonate, 3005-66-1; (*R*)-4-iodo-1,2-epoxybutane, 76282-42-3; carbobenzoxy chloride, 501-53-1; *N*-carbobenzoxy-2(*R*)-carbomethoxy-5(*S*)-carboxypyrrolidine, 102108-02-1; diethyl (*N*-carbobenzoxyamino)malonate sodium salt, 102108-03-2; *cis*-*N*-carbobenzoxy-2,5-dicarbomethoxypyrrolidine, 22328-84-3.

Lithium Diphenylphosphide as a Reagent for the Dehydroxylation of α-Hydroxy Ketones

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As a result of our interest in the utility of a number of phosphorus-containing materials as intermediates in synthesis, we have developed a unique method for the dehydroxylation of α-hydroxy ketones. This new reaction allows facile access to α-methylene ketones of the type RC(O)CH_2R by reduction of the corresponding α-hydroxy ketones. The latter are, in turn, available in good yields by chlorotrimethylsilyl-mediated acyloin condensations[1] of the appropriate esters. To date, the two most commonly employed reagent combinations for dehydroxylation of α-hydroxy ketones are red phosphorus/iodine[2] or trimethylsilyl iodide/sodium thiosulfate.[3] In this paper we would like to report the successful application of a readily available phosphorus-derived reagent to accomplish the same transformation. Thus, lithium diphenylphosphide (LDP) has been used to reduce a wide variety of α-hydroxy ketones to their analogous α-methylene ketones (Scheme I).

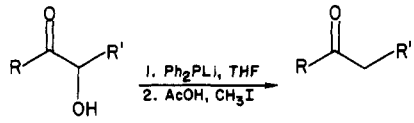
The utility of LDP as a reagent for the epoxide-mediated inversion of olefin stereochemistry has been reported previously.[4] This reaction proceeds via stereospecific epoxide ring-opening by LDP. The intermediate formed is treated with methyl iodide thereby effecting quarternization of phosphorus to give a betaine. Subsequent fragmentation of the betaine, usually at room temperature, produces an olefin and methyldiphenylphosphine oxide. This methodology has been employed to isomerize a variety of olefins via their epoxide derivatives, most notably, the conversion of *cis*- to *trans*-cyclooctene in >90% yield with >99.5% isomeric purity[5] (Scheme II).

We have investigated the effect of similar reaction conditions on α-hydroxy ketones with the thought that a similar mechanism could result in their dehydroxylation. Indeed, treatment of benzoin with 2 equiv of LDP at room temperature followed by quenching with methyl iodide and acetic acid gave desoxybenzoin in 76% yield after chromatography over silica gel. This reaction is not limited in its scope to benzoin-like molecules, but can be extended to include aliphatic, cyclic, and heteroaromatic systems as well. Good yields were obtained in all cases studied (Table I).

(1) For a review of the Me_3SiCl method, see: Ruchlmann, K. *Synthesis* **1971**, 236–253.
(2) Ho, T. L.; Wong, C. M. *Synthesis* **1975**, 161.
(3) Ho, T. L. *Synth. Commun.* **1979**, *9*, 665–668.
(4) Bridges, A. J.; Whitham, G. H. *Chem. Commun.* **1974**, 142. Vedejs, E.; Fuchs, P. L. *J. Am. Chem. Soc.* **1971**, *93*, 4070–4072. Vedejs, E.; Fuchs, P. L. *J. Am. Chem. Soc.* **1973**, *95*, 822–825.
(5) Vedejs, E.; Snoble, K. A. J.; Fuchs, P. L. *J. Org. Chem.* **1973**, *38*, 1178–1183.

0022-3263/86/1951-2378$01.50/0

Scheme I



Scheme II

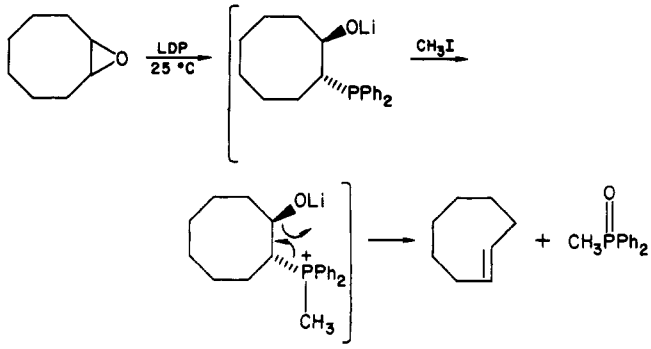
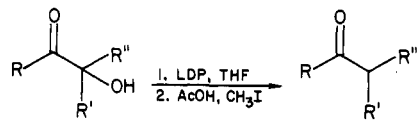


Table I. Dehydroxylation of α-Hydroxy Ketones with Lithium Diphenylphosphide (LDP)



R	R′	R″	% yield product
Ph	Ph	H	76[a]
anisoyl	anisoyl	H	86[a]
Me	Me	Me	60[b]
$(CH_2)_{10}$		H	72[a]
n-Pr	*n*-Pr	H	52[a]
furyl	furyl	H	81[a]

[a] Isolated yield. [b] GC yield.

A reasonable mechanism can be envisioned that considers initial deprotonation of the α-hydroxyl group by the first equivalent of LDP, followed by nucleophilic attachment of the second equivalent on the ketone carbonyl. Methyl iodide then reacts with the dianion formed to give the betaine intermediate **2**, which undergoes elimination of methyldiphenylphosphine oxide through standard Wittig-type fragmentation. Quenching of the reaction with acetic acid gives the observed α-methylene ketone product (Scheme III) via the enolate **2**. The intermediacy of the enolate **2** is substantiated by treatment of the reaction mixture with excess methyl iodide to obtain the expected α-methyl ketone as the only product. This information and the analogy of this mechanism to that proposed by Vedejs and Fuchs[5] for the isomerization of the *cis*-cyclooctene support our proposal for a mechanism.

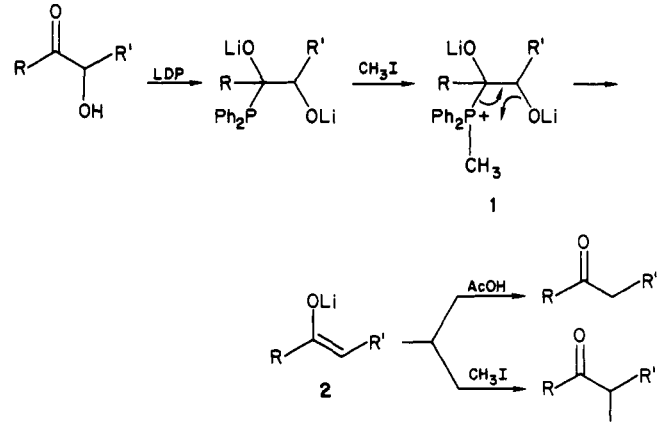
In addition to providing support for our proposed mechanism, this trapping experiment expands the utility of our reaction. By variation of the workup conditions, we are able to effect either simple hydroxyl reduction or alkylative hydroxyl replacement. Workup of the crude reaction mixture with excess methyl iodide gives the α-methylated ketone product through overall replacement of the hydroxyl function by an alkyl group in one synthetic step. Similarly, aqueous workup gives the dehydroxylated methylene ketone product.

Thus, we have developed a novel reaction in the field of organophosphorus chemistry, which should be a useful tool for the synthetic chemist.

Experimental Section

All reactions were conducted under a nitrogen atmosphere. In each case, the reaction products were characterized by comparison

Scheme III



to authentic samples and found to be identical. The term MPLC refers to medium-pressure liquid chromatography on a prepacked lobar column size C at 20 psi. Although we chose to prepare LDP from lithium and diphenylphosphinous chloride, this reagent may also be made by treatment of diphenylphosphine with *n*-butyllithium.[6] The following experimental procedure is representative of the dehydroxylation of α-hydroxy ketones by use of lithium diphenylphosphide.

Dehydroxylation of Benzoin. Diphenylphosphinous chloride (5.0 g, 22.6 mmol) was added dropwise to a suspension of lithium shot (237 mg, 28.3 mmol) in THF (10 mL) at room temperature. After about 2 h most of the lithium had dissolved. The orange LDP solution was separated from the unreacted lithium, and a solution of benzoin (2.4 g, 11.3 mmol) in THF (25 mL) was added to it dropwise. The clear yellow reaction mixture was stirred overnight at room temperature. Acetic acid (678 mg, 11.2 mmol) was then added, followed by methyl iodide (1.6 g, 11.3 mmol). After stirring for an additional 30 min, the reaction mixture was poured into water (100 mL) and extracted with ethyl acetate. The combined organic extracts were dried over magnesium sulfate and concentrated in vacuo, giving a yellow oil. MPLC purification on silica gel (eluting solvent, ethyl acetate) gave desoxybenzoin (1.7 g, 76%) as a white crystalline solid.

Registry No. PhCOCH(OH)Ph, 119-53-9; $CH_3OC_6H_4COCH(OH)C_6H_4OCH_3$, 30587-18-9; $CH_3COC(CH_3)_2OH$, 115-22-0; $CH_3(CH_2)_2COCH(OH)(CH_2)_2CH_3$, 496-77-5; $CH_3OC_6H_4COCH_2C_6H_4OCH_3$, 97981-16-3; $CH_3COCH(CH_3)_2$, 563-80-4; $CH_3(CH_2)_2CO(CH_2)_3CH_3$, 589-63-9; $PhCOCH_2Ph$, 451-40-1; Li, 7439-93-2; LDP, 4541-02-0; 2-hydroxydodecanone, 19025-38-8; 1,2-difurylhydroxyacetaldehyde, 552-86-3; cyclododecanone, 830-13-7; 1,2-difurylacetaldehyde, 51490-07-4; diphenylphosphinous chloride, 1079-66-9.

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An Unusual Synthesis of 5-Methoxy-7,12-dimethylbenz[*a*]anthracene[1]

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In an attempt to work out an improved synthesis of 1,4-dimethoxy-7,12-dimethylbenz[*a*]anthracene the con-

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