

phenylphosphorane is unaffected by this treatment.

The results delineated in Table I suggest that the phosphorane 1 should prove useful in organic synthesis, particularly in carbohydrate-based synthesis and in the "chain extension" approaches of Kishi⁷ and Sharpless/Masamune.⁸ The preparation of 1 is detailed below.

Experimental Section

Preparation of Phosphorane 1. A solution of 13.93 g of recrystallized bromoacetic acid, 9.65 mL (1.3 eq) of ethanethiol,⁹ and 1.22 g (0.1 equiv) of 4-(dimethylamino)pyridine in 450 mL of CH₂Cl₂ was cooled to 0 °C with stirring under an atmosphere of nitrogen. Dicyclohexylcarbodiimide (21.71 g, 1.05 equiv) was added in three portions, and the solution slowly warmed to room temperature overnight. The solution was then filtered through Celite, and the cake was washed several times with CH₂Cl₂. The filtrate was then washed with saturated aqueous NaHCO₃ solution, water, and brine, then dried over Na₂SO₄, and concentrated in vacuo to give 17.50 g (95%) of a light yellow oil. This oil was allowed to stand with 26.3 g of triphenylphosphine in 150 mL of benzene at room temperature for 2 days¹⁰ to yield 35.54 g (83.5%) of colorless saltlike crystals after filtering and washing with toluene. The crystals were dissolved in 150 mL of CH₂Cl₂ and vigorously stirred with 100 mL of 10% aqueous Na₂CO₃ solution for 30 min. The layers were separated and the aqueous layer was extracted twice with CH₂Cl₂. The combined organic phases were partially concentrated in vacuo and then diluted with pentane to yield 25.2 g of saltlike crystals (mp 82-83 °C). A second crop was similarly isolated (3.16 g, mp 79-83 °C) to give a combined yield of 98% (78% overall).

General Procedure for Reaction of 1 with Aldehydes. A solution of approximately 0.20 g of aldehyde and 1.3 equiv of ylide 1 in 15-20 mL of reagent grade HCCl₃ was heated at reflux for 12-18 h. The solution was concentrated in vacuo and chromatographed on a 25 cm × 1.2 cm silica gel column (slurry packed in hexane), eluting with hexane and then with 10% ether in hexane. Characteristic spectral data that is indicative of the formation of a trans α,β -unsaturated thiol ester (e.g., from 3) is as follows: IR 1670 and 1630 cm⁻¹; NMR (CDCl₃, 90 MHz) δ 6.83 (dd, J = 6, 16, 1 H), 6.02 (dd, J = 16, 2, 1 H), 2.90 (q, J = 8, 2 H).

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Registry No. 1, 32443-51-9; 2, 2605-67-6; 3, 2043-61-0; 4, 14371-10-9; 5, 73814-73-0; 6, 89869-02-3; 7, 94498-98-3; (E,E)-PhCH=CHCH=CHC(O)SEt, 94498-99-4; (Z,E)-PhCH=CHCH=CHC(O)SEt, 94499-00-0; (E)-PhCH₂OCH₂CH(CH₃)CH=CHC(O)SEt, 94499-01-1; (Z)-PhCH₂OCH₂CH(CH₃)CH=CHC(O)SEt, 94499-02-2; BrCH₂C(O)SEt, 60277-18-1; Ph₃P, 603-35-0; *t*-BuSH, 75-66-1; *S*-ethyl (E)-3-cyclohexyl-2-propene-thioate, 94499-03-3; *S*-ethyl (Z)-3-cyclohexyl-2-propene-thioate, 94499-04-4; (S)-ethyl (E)-4-(benzyloxy)-4-cyclohexyl-2-butenethioate, 94499-05-5; *S*-ethyl (Z)-4-(benzyloxy)-4-cyclohexyl-2-butenethioate, 94499-06-6; 4(S)-[3-(ethylthio)-3-oxo-1(E)-propenyl]-5(R)-[2(R)-hydroxypropyl]-2,2-dimethyldioxolane, 94499-07-7; 4(S)-[3-(ethylthio)-3-oxo-1(Z)-propenyl]-5(R)-[2(R)-hydroxypropyl]-2,2-dimethyldioxolane, 94595-41-2.

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(9) The use of *tert*-butyl mercaptan was also examined. However, the derived phosphorane could not be obtained in crystalline form, and also reacted only very sluggishly with substrate 7.

(10) (a) Choice of temperature is important here. At benzene reflux, the phosphonium salt decomposes with formation of methyltriphenylphosphonium bromide. (b) The mixture should not be stirred, as this results in the formation of poor quality crystals.

Intramolecular Photoreduction of α -Keto Esters. Total Synthesis of (\pm)-Isoretronecanol¹

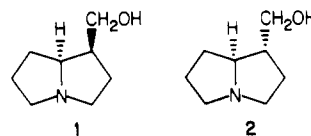
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There is much interest in pyrrolizidine alkaloids² and their derivatives because of their wide range of physiological properties.³

The two simplest members of this group are the diastereoisomers of 1-(hydroxymethyl)pyrrolizidine: isoretronecanol (1) and trachelanthamidine (2). Many syntheses of 1 and 2 have been reported.⁴ We now describe a new, short, and efficient synthesis of isoretronecanol (1).



In this approach, the second ring is created in a key photochemical step based on the intramolecular photoreduction of an α -keto ester. We already reported that the hydrogen α to the nitrogen of an amide function was easily abstracted by the n,π^* excited triplet state of an aryl ketone.⁵ The coupling of the two radicals resulting from this process created a carbon-carbon bond α to a nitrogen atom. The intramolecular version of this reaction should be an efficient method to generate heterobicyclic systems with a nitrogen in a bridgehead position: irradiation of aryl ketones such as 3 leads via the diradical 4 to 1-azabicyclo[*x*.3.0]alkanes 5.⁶ In the absence of hydrogen in the γ position, the hydrogen in the δ position is efficiently abstracted to lead to a five-membered ring (Scheme I).

However, the applicability of this reaction is limited by the difficulty in transforming the aromatic ring (Scheme II). The most useful function is the α -keto ester group which is easily photoreduced by various hydrogen donors.⁷

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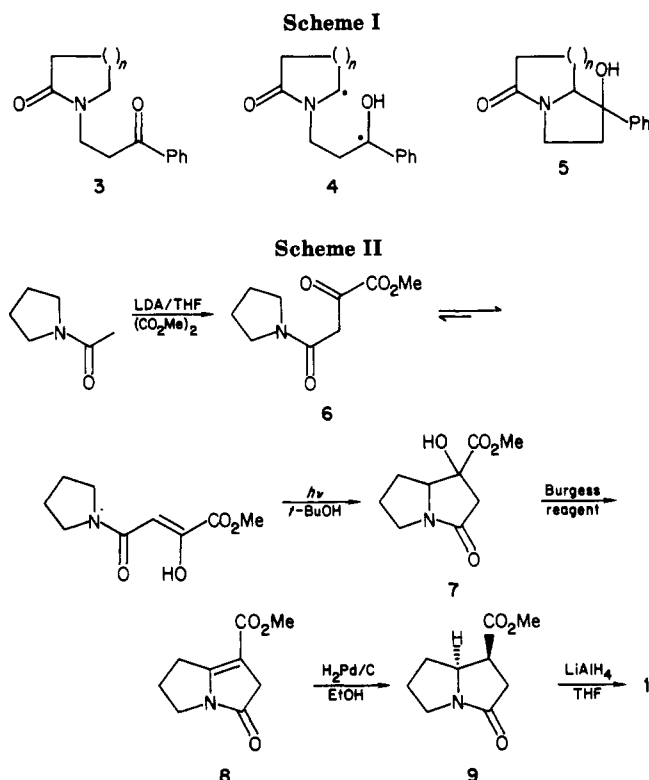
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The α -keto ester **6** is obtained in 80% yield by addition of the anion of *N*-acetylpyrrolidine (LDA, THF) on methyl oxalate (THF, HMPA). ^1H and ^{13}C NMR spectra show that **6** is completely enolized in solution. The enol form of **6** is obviously not photoreducible and constitutes an internal filter during irradiation ($\epsilon = 3400$, EtOH). This is confirmed by the failure of irradiation in acetonitrile and benzene.

On the other hand, irradiation (medium pressure mercury lamp, Pyrex) of **6** in *tert*-butyl alcohol, which destabilizes the enol form, leads to **7** in 70% yield as a mixture of two diastereoisomers in a 1 to 1 ratio. The dehydration step may be performed on the mixture of these isomers either by treatment with Burgess reagent⁸ in refluxing benzene leading to **8** in 63% yield or in a two-step procedure where the mesylate of **7** was treated with tetrabutylammonium bromide in THF⁹ leading to **8** in 64% yield.

The ethyl ester analogous to **8** has been recently obtained by Pinnick et al.^{4b} and its transformation into isoretronecanol in 61% yield has been described. The yield can be improved by using the Danishefsky procedure¹⁰ in the LAH reduction step. The catalytic hydrogenation of **8** (H_2 , Pd/C, EtOH) leads to a single product **9** in 96% yield with a *cis* stereochemistry (cf. ref 4b). The reduction of both ester and amide groups by LAH in THF¹¹ leads to isoretronecanol in 92% yield. (Picrate mp 188–189 °C; lit.¹¹ mp 188–189 °C).

Thus, isoretronecanol (**1**) has been obtained in a five-step synthesis in a 32% overall yield from very simple precursors (namely, *N*-acetylpyrrolidine and methyl oxalate). Moreover, this sequence constitutes a formal synthesis of trachelanthamide (**2**) as the transformation of

the ethyl ester analogous to **9** into **2** was recently reported by Pinnick et al.^{4b}

Experimental Section

Proton nuclear magnetic resonance spectra were recorded on a JEOL C60H instrument (relative to internal Me_4Si). Carbon-13 nuclear magnetic resonance spectra were recorded on a JEOL FX60 spectrometer. A Perkin-Elmer 377 spectrometer was used to determine IR spectra. Low-resolution (70 eV) and high-resolution mass spectroscopy spectra were recorded on a Varian CH5 spectrometer. Elemental analyses were performed by the Microanalysis Central Service of the CNRS in Lyon. Reagent grade THF was distilled from sodium benzophenone prior to use. Other anhydrous solvents were distilled from CaH_2 and stored over 4-Å molecular sieves until use. Analytical samples were obtained by flash chromatography on Merck 40–63- μm silica gel. Irradiation was performed in a Pyrex glass vessel using a medium pressure mercury lamp (Philips 400 W). The reaction mixture was flushed with a stream of dry nitrogen to remove oxygen.

Preparation of α -Keto Ester **6.** To a solution of lithium diisopropylamide (LDA) (10 mmol) in dry THF (40 mL) at -40 °C under an argon atmosphere was added a solution of *N*-acetylpyrrolidine (1.13 g, 10 mmol) in dry THF (10 mL). The mixture was stirred for 1 h at -40 °C before HMPA (20 mmol) was added and then the mixture was rapidly poured into a solution of methyl oxalate (5.9 g, 50 mmol) in dry THF (40 mL). The reaction mixture was heated at 40 °C for 42 h and then treated with water (1 mL), evaporated to dryness, and leached with CH_2Cl_2 . The solution was dried (MgSO_4) and evaporation of solvent afforded crude product. Purification by flash chromatography eluting with ethyl acetate gave **6** (1.6 g, 80%) mp 76 °C; IR γ_{max} (CCl_4) 1735 (CO_2CH_3), 1635 ($\text{NC}=\text{O}$) cm^{-1} ; ^1H NMR (CDCl_3) δ 14.4 (1 H, s, exchangeable with D_2O , OH), 6.08 (1 H, s, $\text{CH}=\text{C}$), 3.85 (3 H, s, CO_2CH_3), 3.52 (4 H, m, CH_2N), 1.98 (4 H, m, CH_2CH_2); ^{13}C NMR (CDCl_3) δ 169.1 ($\text{NC}=\text{O}$), 163.4 ($\text{C}-\text{O}_2\text{CH}_3$), 159.0 ($=\text{COH}$), 95.5 ($\text{CH}=\text{C}$), 52.8 (OCH_3), 46.6 and 45.5 (CH_2NCH_2), 25.7 and 24.4 (CH_2CH_2). Anal. Calcd for $\text{C}_9\text{H}_{13}\text{NO}_4$: C, 54.26; H, 6.58; N, 7.03. Found: C, 54.30; H, 6.64; N, 6.88.

Photocyclization of α -Keto Ester **6.** A solution of **6** (1 g, 10 mmol) in *tert*-butyl alcohol (200 mL) was irradiated under nitrogen for 48 h. Solvent was distilled thoroughly and purification by flash chromatography afforded **7** (0.7 g, 70%): IR γ_{max} (CCl_4) 3540 (OH), 1740 (CO_2CH_3), 1710 ($\text{NC}=\text{O}$) cm^{-1} ; ^1H NMR (CDCl_3) δ 4.0 (1 H, s, exchangeable with D_2O , OH), 3.77 (3 H, s, CO_2CH_3), 3.78 (3 H, s, CO_2CH_3), 2.94 (2 H, s, $\text{CH}_2\text{C}=\text{O}$), 2.0 (4 H, m); ^{13}C NMR (CDCl_3) δ 173.2 ($\text{NC}=\text{O}$), 172.1 and 171.9 (CO_2CH_3), 78.5 (C_1), 70.9 and 68.3 (C_8), 53.0 and 52.6 (CH_3CO_2), 47.8 and 46.1 (C_5), 41.8 (C_2), 26.6 and 26.0 (C_7), 22.7 (C_6); exact mass calcd for $\text{C}_9\text{H}_{13}\text{NO}_4$ 199.0845, found 199.0846 (M^+).

Preparation of the Olefinic Ester **8. Method A.** To a solution of the alcohol **7** (0.4 g, 2 mmol) in dry THF (10 mL) containing triethylamine (0.22 g, 2.2 mmol) under nitrogen was added dropwise a solution of methanesulfonyl chloride (0.25 g, 2.2 mmol) in THF (10 mL). The mixture was stirred at 0 °C for 15 min and then tetrabutylammonium bromide (0.78 g, 2.4 mmol) was added. The reaction mixture was heated at 40 °C under nitrogen for 24 h, then hydrolyzed, and extracted with CH_2Cl_2 . Purification by chromatography on alumina eluting with CHCl_3 -ether (1–1) afforded **8** (0.23 g, 64%).

Method B. To a solution of the alcohol **7** (0.3 g, 1.55 mmol) in anhydrous benzene (2 mL) was added at room temperature under nitrogen a solution of Burgess reagent^{8a} (0.4 g, 1.7 mmol) in anhydrous benzene (3 mL). The resulting solution was stirred at room temperature for 1.5 h and then in refluxing benzene for 3 h. Water (1 mL) was added, the mixture was decanted, the aqueous phase was extracted with CH_2Cl_2 , and the organic extracts were combined and dried (MgSO_4). Purification by chromatography on alumina afforded **8** (0.17 g, 63%): IR γ_{max} (CCl_4) 1730 (CO_2CH_3), 1700 ($\text{NC}=\text{O}$), 1650 ($\text{C}=\text{C}$) cm^{-1} (lit. IR γ_{max} (CHCl_3) 1712, 1672, 1660 cm^{-1}); ^1H NMR (CDCl_3) δ 3.75 (3 H, s, CO_2CH_3), 3.5–3.7 (2 H, m, $\text{CH}_2\text{C}=\text{O}$), 1.8–3.1 (6 H, m).

Catalytic Hydrogenation of **8.** Lactam **8** (0.16 g, 0.9 mmol) was dissolved in absolute ethanol (10 mL) and a catalytic amount of 10% Pd/C was added. This was maintained under hydrogen at 3 atm and room temperature overnight (18 h) and filtered

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through Celite and the filtrate was concentrated to give the lactam **9** (0.16 g, 96%): IR γ_{\max} (CCl₄) 1745 (CO₂CH₃), 1710 (NC=O) cm⁻¹; ¹H NMR (CDCl₃) δ 4.2 (1 H, m, NCH), 3.7 (3 H, s, CO₂CH₃), 2.8 (2 H, unsym d, *J* = 6 Hz, CH₂C=O); ¹³C NMR (CDCl₃) δ 174.25, 172.37, 62.89, 52.04, 41.78, 40.02, 36.25, 27.48, 26.12; exact mass calcd for C₉H₁₃NO₃ 183.0892, found 183.0895 (M⁺).

Reduction of Lactam Ester 9. To a solution of **9** (0.1 g, 0.55 mmol) in anhydrous THF (5 mL) was added lithium aluminium hydride (0.06 g, 1.5 mmol), and the system was heated under reflux for 18 h. Then, we added successively, water (60 μ L), 15% aqueous sodium hydroxide (60 μ L), and water (180 μ L). Evaporation of volatiles left a residue which was leached with ether and the resulting solution was dried (MgSO₄). Evaporation and purification on alumina gave **1** (0.07 g, 92%) as a yellow oil: picrate mp 188–189 °C (lit.¹¹ mp 188–189 °C).

Registry No. (\pm)-**1**, 18929-90-3; **6**, 94500-38-6; (\pm)-**7** (isomer 1), 94500-39-7; (\pm)-**7** (isomer 2), 94500-40-0; **8**, 56783-09-6; (\pm)-**9**, 93264-55-2; *N*-acetylpyrrolidine, 4030-18-6; methyl oxalate, 553-90-2.

Model Reactions for Sterically Controlled Syntheses of Cyclohex-2-enones with 4,4- or 5,5-Quaternary Centers: A Direct Chiral Synthesis of 4-Allyl-4-cyanocyclohex-2-enone from the Anion of (+)-Tricarbonyl(5-cyano-2-methoxycyclohexa-1,3-diene)iron

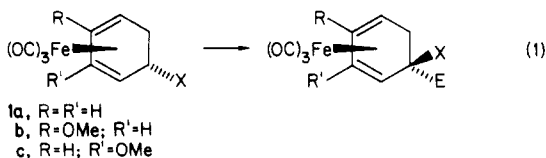
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The temporary π -attachment of complexed transition metals to olefinic double bonds results in forms of activation and steric control (lateral control) in organic synthesis differing from those achievable by classical functional groups attached by σ -bonds to the skeleton of a molecule (endogenous control). In particular, steric¹ and chiral² formations of new bonds can be directed.

A new type of synthetic capability provided here is the stereospecific protonation of some (cyclohexadienyl)Fe(CO)₃ anions or alkylation of these to produce a quaternary center. In these derivatives formation of the carbanion is permitted in the classical manner by endogenous activation due to CN, SO₂Ar, or CO₂Me (eq 1).^{3,4} The steric

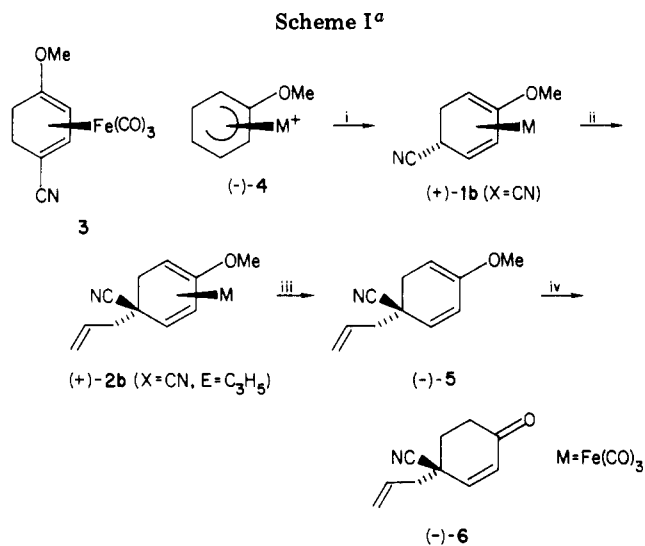


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(3) An entirely different set of processes operate when the complex without the activating group (e.g., **1a**, X = H) is treated with lithium bases, see: M. F. Semmelhack, M. F.; Harndon, J. W. *J. Organomet. Chem.* 1984, 265, C15 and references therein.

(4) A case can be made for relating this process to the phosphonium salt analogue reported by Lewis (e.g., **1a**, X = Ph₃P⁺). However, the products of the reaction are structurally different and also the Wittig procedure described is limited to aldehydes. Hackett, P.; Johnson, B. F. G.; Lewis, J.; Jaouen, G. *J. Chem. Soc., Dalton Trans.* 1982, 1247.



^a (i) KCN; (ii) LDA, C₃H₅Br; (iii) Me₃NO, (Me)₂NCOMe, 70 °C, 0.5 h; (iv) Amberlyst (H⁺) Resin, Et₂O, 45 min.

effect of a bulky complexing group such as Fe(CO)₃ on one face of the molecule is similar to that already demonstrated for the reduction of a carbonyl^{1,5} and for the reactions of related cyclohexadienyl cations.¹ A new feature is that regioselective electrophilic attack is achieved (Table I) in the same situation as that defined by the position of initial nucleophilic attack of cyanide on the substituted cation complex.

The expected⁶ α (exo) direction of attack for carbon electrophiles is supported in this series by the identity of the product of methylation of **1a** (X = CO₂Me) with the known⁷ compound **2a** (E = Me, X = CO₂Me, entry 6). The kinetic products of α (exo) protonation or deuteration of the anions correspondingly have the CN β (endo) to the Fe(CO)₃, as supported by NMR spectra⁸ and nonidentity with the α -isomer. This is a novel method of forming these β -isomers in steric purity following initial 5- β (endo) hydrogen removal from the 5 α -CN precursor.

In the 2-OMe series (b; X = CN, entries 8 and 9) partial isomerization occurs to form the more stable complex **3**, which itself is resistant to proton loss under the conditions of reaction. Nevertheless, the process remains a useful one, producing in this series, as shown below, 4,4-disubstituted cyclohex-2-enones. The isomerization side reaction is apparently restricted to the 2-OMe derivatives since no similar reaction is observed in the related 3-OMe structures (compare entries 8 and 11).

It is significant that when the anion derived from **1b** (X = CN) is reacted at -70 °C with benzaldehyde, an immediate color change from red to yellow is seen and the

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(6) The direction of attack was expected to be the same as that observed in the related cyclohexadienyl cation series (ref 1). There is some evidence to suggest that electrophiles approach the cycloheptatrienyl cation from the exo direction (Moll, M.; Wurstl, P.; Behrens, H.; Merbach, P. *Z. Naturforsch.* 1978, 33B, 1304), while tricarbonylcyclohexadienylmanganese anion reacts with methyl iodide to give endo-methylated derivatives (Lamanna, W.; Brookhart, M. *J. Am. Chem. Soc.* 1981, 103, 989). In the present series α -attack of the electrophile is supported by correlation with a known compound (ref 7) and by comparison of physical and spectral properties of **2b** (E = Me, X = CN) with its reported C-5 epimer (Pearson, A. J. *J. Chem. Soc., Chem. Commun.* 1977, 339).

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