recovery, the product was purified by chromatography (SiO_2 gel, 20 g, 2% acetone in C_6H_6) to give **11** as a colorless crystalline solid (0.55 g): mp 62–63 °C; $[\alpha]_D$ −23°; ^1H NMR δ 0.80 (d, J = 6 Hz, 2 CHCH_3), 1.75 (m, 2 CHCH$_3$), 2.50 (m, 2 ArCH_2), 3.83, 3.85 (2 s, 2 OCH_3), 5.90 (s, OCH$_2$O), 6.5–6.8 (m, 6 ArH). Anal. Calcd for $C_{21}H_{26}O_4$: C, 73.66; H, 7.66. Found: C, 73.65; H, 7.70.

Preparation of 12, 13, and 14. Compound **6** (1.7 g) was hydrolyzed with 1 N MeOH/HCl as given under **8**. After recovery and purification by chromatography, **12** was obtained as a colorless glass (0.72 g). Part of this sample (0.36 g) was converted to the acetate as described under **9**.. The acetate **13** was obtained as a colorless cyrstalline solid (0.38 g): mp 94–95 °C; ^1H NMR δ 0.80 (d, J = 6 Hz, 2 CHCH_3), 1.80 (m, 2 CHCH$_3$), 2.23 (s, 4 CH_3COO), 2.50 (m, 2 ArCH_2), 6.8–7.0 (m, 6 ArH). Anal. Calcd for $C_{26}H_{30}O_8$: C, 66.38; H, 6.43. Found: C, 66.28; H, 6.48.

Another part of **12** (0.36 g) was methylated using Me_2SO_4 (1.2 mL) and K_2CO_3 (3 g) in acetone (25 mL) as given under **10**. The product **14** was obtained as a colorless crystalline solid (0.4 g): mp 84–85 °C; $[\alpha]_D$ −26°; ^1H NMR δ 0.80 (d, 2 CHCH_3), 1.75 (m, 2 CHCH$_3$), 2.50 (m, 2 ArCH_2), 3.83, 3.86 (2 s, 4 OCH_3), 6.50–6.82 (m, 6 ArH). Anal. Calcd for $C_{22}H_{30}O_9$: C, 73.71; H, 8.44. Found: C, 73.52; H, 8.46.

Preparation of 1 from 6. A mixture of **6** (2.7 g), Me_2SO_4 (2.7 mL), and K_2CO_3 (5 g) in acetone (60 mL) was boiled under reflux for 6 h. The product recovered as given under **10** was hydrolyzed with 1 N MeOH/HCl as described earlier and chromatographed on SiO_2 (60 g) in benzene. Elution with 2% acetone in benzene and concentration of the appropriate fractions gave **1** as a crystalline solid (from hexane): yield, 1.3 g; mp 87–88 °C; $[\alpha]_D$ −27°; MS 330 ($M^{\bullet+}$, 18), 137 (100); ^1H NMR δ 0.80 (d, J = 6 Hz, 2 CHCH_3), 1.70 (m, 2 CHCH$_3$), 2.45 (m, 2 ArCH_2), 3.80, 3.85 (2 s, 2 OCH_3), 5.55 (br s, D_2O-exchangeable, 2 OH, 6.40–6.80 (m, 6 ArH).

***O*-Ethylvanillic Acid (7).** A sample of **1** (0.2 g) was ethylated using Et_2SO_4 (0.2 mL) and K_2CO_3 (1 g) in acetone (20 mL) by boiling under reflux for 4 h. The product, after recovery as described under **10**, was dissolved in 1:1 aqueous pyridine (10 mL) and boiled with $KMnO_4$ (1 g) for 1 h. After cooling, acidification (pH 2) with H_2SO_4, and treatment with $NaHSO_3$, the mixture was extracted two times with ether. The ether extract was washed two times with 5% aqueous $NaHCO_3$; the aqueous layer acidified and reextracted with ether two times. Concentration of the ether gave a crystalline solid, recrystallized from ether/hexane, yield 0.02 g, mp 188–90 °C, identical with an aunthentic sample prepared from vanillin by ethylation and oxidation.

Preparation of 15. A mixture of **6** (2.9 g), benzyl chloride (1 mL), and K_2CO_3 (3 g) in DMF (20 mL) was heated at 100 °C for 4 h. The cooled reaction mixture was diluted with water (50 mL) and extracted two times with benzene. The concentrated C_6H_6 extract was heated with 1 N MeOH/HCl (20 mL) for 1 h at reflux. The product was recovered by dilution with water (50 mL) and extraction with benzene. The concentrated bnezene extract was methylated using Me_2SO_4 (1 mL) and K_2CO_3 (2 g) in acetone (20 mL) by boiling under reflux for 4 h. The methyl ether was dissolved in ACOH containing 30% HBr and let stand at 20 °C for 2 h. After dilution with water, extraction with benzene, and washing of the C_6H_6 with aqueous $NaHCO_3$, followed by washing with 0.2 N aqueous NaOH, **15** was obtained in the aqueous hydroxide layer. It was recovered by acidification, extraction with ether, and concentration of the extract to give **15** as a colorless crystalline solid (from hexane): yield, 0.7 g; mp 92–95 °C; $[\alpha]_D$ −27°; IR 3560, 3520, 2970, 1590, 1510 cm^{-1}; ^1H NMR δ 0.80 (d, J = 6 Hz, 2 CHCH_3), 1.80 (m, 2 HCH$_3$), 2.5 (m, 2 ArCH_2), 3.93 (s, 2 OCH_3), 5.5 (s, D_2O-exchangeable, 2 OH), 6.45–6.83 (m, 6 ArH). Anal. Calcd for $C_{20}H_{26}O_4$: C, 72.70; H, 7.93. Found: C, 72.57; H, 7.93.

Alternatively, 30% H_2O_2 (15 mL) was added to a solution of **6** (1.35 g) in AcOH (30 mL), and the mixture was stirred at 50–55 °C for 18 h. After dilution with water, extraction with benzene, and washing of the C_6H_6 extract with aqueous $NaHCO_3$, the concentrated solvent extract was dissolved in MeOH (10 mL) and added to an effervescent mixture of Mg turnings (2 g) in MeOH (20 mL). The mixture was stirred with intermittent heating (60 °C) for 2 h. After concentration, addition of water, acidification, and extraction with benzene, the product was chromatographed on SiO_2 gel (25 g). The fractions from 2% acetone in benzene on concentration gave a colorless crystalline solid, mp 93–95 °C, identical with the sample described above.

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Registry No. **1**, 124649-78-1; **1** (acetate), 124649-79-2; **4**, 55890-23-8; **5**, 124605-67-0; **6**, 124605-68-1; **7**, 3535-30-6; **8**, 124605-69-2; **9**, 124605-70-5; **10**, 55890-24-9; **11**, 55731-00-5; **12**, 119584-40-6; **13**, 124649-80-5; **14**, 119182-23-9; **15**, 124605-71-6; *p*-thiocresol, 106-45-6.

New Heterodifunctional Ligands for Organotransiton-Metal Chemistry: $Ph_2P(CH_2)_nC_5Me_4H$ (n = 0, 2)

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The synthesis of two new heterodifunctional ligands for organotransition-metal chemistry, $Ph_2P(CH_2)_nC_5Me_4H$ (n = 0, 2), is described. Both compounds are derived from the same intermediate, lithium tetramethylcyclopentadienide. For n = 2 the ligand is obtained by a one-pot reaction including two successive nucleophilic substitutions.

The heterodifunctional ligands have been frequently used in recent years in organotransition-metal chemistry to build heterobimetallic complexes.[1]

Among them, those that incorporate both a phosphine and a cyclopentadienyl functionality[2] are suitable to link

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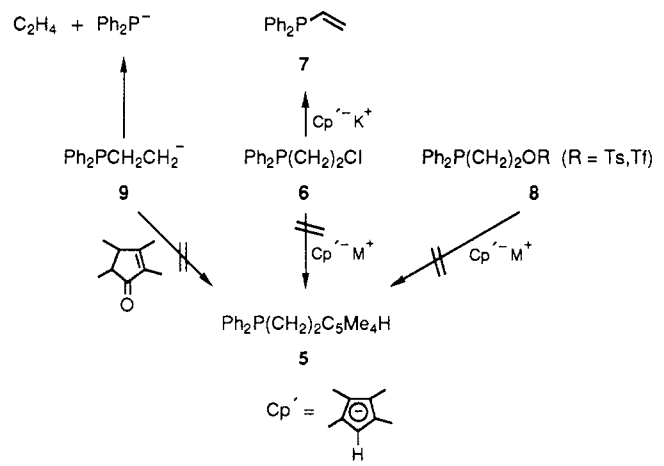
0022-3263/90/1955-1429$02.50/0

Scheme I



late and early transition-metal atoms.[3] On the other hand, owing to the electron-donating ability and steric bulk of the alkyl substituents of the cyclopentadienyl coordination unit, the resulting transition-metal complexes display increased stability and reactivity.[4]

Despite the interest in bidentate ligands, which incorporate both tetramethylcyclopentadienyl (Cp′) and diarylphosphine units, only three ligands have been reported.[5] Two of them display a one-[5a] and a three-carbon[5b]-atom chain with a diphenylphosphine terminal group. The third compound, which exhibits a direct bonding between the Cp′ and the phosphorus, belongs to the di-*p*-tolylphosphine series.[5c]

We were interested in the ligands in which zero or two carbon atoms separate the tetramethylcyclopentadienyl from the diphenylphosphine groups, namely, 1-(diphenylphosphino)-2,3,4,5-tetramethylcyclopentadiene (**3**) and 2-(tetramethylcyclopentadienyl)-1-(diphenylphosphino)ethane (**5**). In view of the distance between the P atom and the cyclopentadienyl ring **3** and **5** could represent two extreme cases of coordination capabilities. Compound **3** could be a precursor of heterobimetallic complexes, which have two different metal fragments held together not only through a bridging ligand but also through a direct metal–metal bond.[6] In the case of **5** the coordination sites may display chelating properties.[7]

We report here the first synthesis of **5**, of which several unsuccessful attempts have been made in our and other laboratories. In addition to that we mention the synthesis and characteristics of **3**, which can be obtained easily by a modification of the literature method.[2b,5c] The diphenylphosphine ligand series $Ph_2P(CH_2)_{n=0,4}C_5Me_4H$ has been completed in this way.

The strategy of the synthesis of **5** (vide infra) is based on the following negative results and comments (Scheme I): (i) Treatment of 2-chlorodiphenylphosphinoethane (**6**) with the tetramethylcyclopentadienyl anion **2** (Cp'^-) did not lead to the formation of C_2–Cp′ bond, contrary to the nonsubstituted Cp analogue;[2c] instead diphenylvinylphosphine (**7**) was obtained as an elimination product ($Me_4C_5^-K^+$, reflux in THF for 24 h). This result was in accord with the relatively poor nucleophilicity and the high basicity of the anion **2**,[8] compared to the nonsubstituted cyclopentadienide. (ii) The substitution reactions using 2-(diphenylphosphino)ethyl tosylates or triflates **8** led to a series of secondary reactions. (iii) The unstable anion **9**[9] could not be used as a nucleophilic reagent, to attack the cyclopentenone synthon.[10] (iv) The methodology applied by Bensley to synthesize 3-(tetramethylcyclopentadienyl)-1-(diphenylphosphino)propane was noted by these authors as unsuitable for the preparation of the two-carbon-chain analogue.[5b]

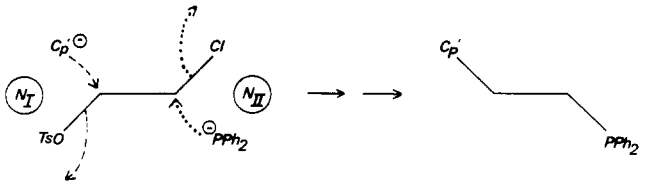
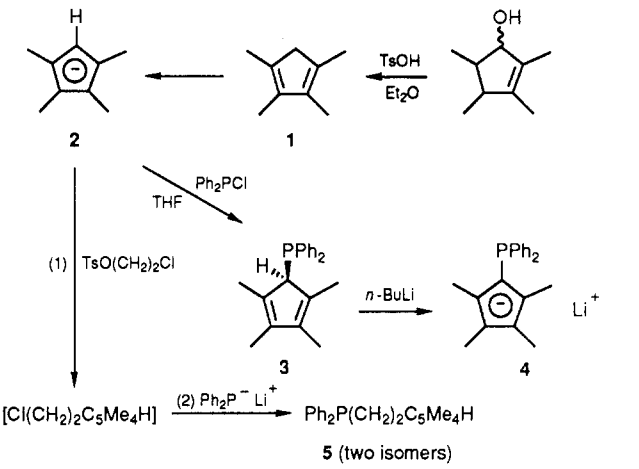


Figure 1. Synthesis strategy of the ligand **5**. The nucleophilic substitution N_I takes place before the N_{II} substitution.

Scheme II



The ligand **5** has been successfully obtained in a one-pot reaction (starting from **2**), including two successive nucleophilic substitutions N_I and N_{II} (Figure 1). In the N_I substitution Cp'^- is the attacking agent and TsO^- is the leaving group. In the N_{II} step Ph_2P^- is the nucleophile and the Cl^- the nucleofuge. Our strategy takes into account the two different nucleophilic characters: $Cp'^- < Ph_2P^-$. Indeed, as shown in Scheme I, Cp'^- does not substitute Cl^- in $Ph_2P(CH_2)_2Cl$ (**6**), whereas Ph_2P^- easily substitutes Cl^- in $Cl(CH_2)_2OLi$.[11] The choice of quite different leaving groups, $TsO^- \gg Cl^-$, is the consequence of the above-mentioned differentiation.

The proposed method gives a simple and rapid access to the ligand **5** (Scheme II). An easy dehydration of 2,3,4,5-tetramethylcyclopent-2-enol with *p*-toluenesulfonic acid in diethyl ether produced the diene **1**, which was immediately transformed into anion **2** (71% yield based

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on starting alcohol). The treatment of a suspension of **2** in THF with 2-chloroethyl tosylate led to the (chloroethyl)cyclopentadienyl derivative, which can be isolated and characterized (^{1}H NMR, IR). However such an isolation is not required. The direct addition of lithium diphenylphosphide to the reaction mixture followed by a careful workup under argon gave **5** in 68% yield as an extremely air-sensitive, pale yellow oil. Compound **5** can be converted to the corresponding oxide with air in pentane in a few minutes. Treatment of this phosphine oxide with $LiAlH_4$ in ether regenerated quantitatively the phosphine **5**.

The structure determination of **5** was based upon the results obtained from mass spectra and ^{1}H, ^{31}P, and ^{13}C NMR data. The mass spectrum has a molecular peak at m/e 334. The proton NMR spectrum shows different methyl groups (CH_3–C_{sp^2} and CH_3–C_{sp^3}). The analysis of ^{13}C and ^{31}P NMR spectra is in accordance with two isomeric structures with different Cp′ double-bond positions. Indeed, the ^{13}C NMR spectrum of **5** shows two methine resonances and two pairs of methylene resonances (α and β to P) coupled with phosphorus ($J_{^{31}P-^{13}C}$ = 18.1 and $J_{^{31}P-^{13}C}$ = 11.5 Hz). The ^{31}P NMR spectrum shows two resonances at −16.4 and −16.9 ppm; two signals are also observed at +27.9 and +28.3 ppm for the corresponding oxide.[12]

$Ph_2P(Me_4C_5H)$ (**3**) has been obtained from the key compound **2**,[13] by treatment with chlorodiphenylphosphine (Scheme II). This unstable material has been transformed in a straightforward manner to the solid lithium salt **4**, which can be kept at 0 °C for several months. The ^{1}H and ^{31}P NMR spectra of the phosphine **3** exhibit the presence of only one isomer.[14] The ^{1}H NMR spectrum shows only two Me resonances, and the methine proton resonance split into a multiplet by coupling both to the P atom and to the CH_3 groups. The ^{31}P NMR spectrum shows a major (>95%) peak at −0.1 ppm. Finally, the mass spectrum of the phosphine **3** oxide[15] reveals the molecular peak at m/e 322 as well as other characteristic fragments: 201, Ph_2PO; 121, Me_4C_5H; 92, Cp′ − $2CH_3$.

This work is in progress to test the utility of these new ligands for the synthesis of organometallic complexes.

Experimental Section

Except where indicated, all operations were carried out under argon using vacuum line and standard Schlenk techniques. The solvents used were distilled from sodium benzophenone ketyl under argon atmosphere. Ph_2PCl (Aldrich) was distilled and purged with Ar prior to use. Ph_2PH (Aldrich) was used as purchased. 2,3,4,5-Tetramethylcyclopent-2-enol, a starting material for the synthesis of cyclopentadienide **2**, was prepared according to the literature method.[16]

2-Chloro-1-(*p*-tolylsulfonyl)ethane obtained from 2-chloroethanol by treatment with tosyl chloride in pyridine has a correct ^{1}H NMR spectrum, and the bp of 159–160 °C/3 Torr is in agreement with the literature value.[17] IR spectra were obtained on a Perkin-Elmer 580B spectrometer. ^{1}H NMR spectra were recorded at 100 MHz on a JEOL FX100 instrument; ^{13}C and ^{31}P NMR spectra were recorded at 100.53 and 162.00 MHz, respectively, on a Brucker WM400 spectrometer. Spectra were measured at ambient temperature in C_6D_6 or $CDCl_3$ with residual solvent peaks as internal standard for ^{1}H and ^{13}C NMR. ^{31}P chemical shifts were reported relative to external 85% H_3PO_4, positive shifts representing deshielding. Mass spectra were measured on a Ribermag R 10-10 C instrument at 70 eV.

Lithium Tetramethylcyclopentadienide (2). a. Improved Preparation of 1,2,3,4-Tetramethylcyclopentadiene (1). *p*-Toluenesulfonic acid (1.03 g, 5.4 mmol) was added in one portion to an ethereal solution of 2,3,4,5-tetramethylcyclopent-2-enol (7.50 g, 53.6 mmol in 130 mL of Et_2O). The reaction mixture was then stirred at room temperature (under common atmosphere) for 20 min, in which time the mixture became cloudy and the reaction finished (TLC, hexane/ether = 8/2). After separation of the pink oil, the ethereal layer was washed with a 10-mL portion of saturated sodium bicarbonate and then with water until neutral. The organic layer was dried over anhydrous magnesium sulfate and filtered. A sample (1.5 mL) was taken, and the solvent was removed by evaporation, to give a pale yellow liquid (0.07 g), whose spectral properties (^{1}H NMR and IR) where in agreement with the reported data.[4d] The ethereal solution of **1** was then concentrated to about 50-mL volume, degassed, and purged with Ar. It was used directly in the next step.

b. Deprotonation of 1. A solution of MeLi in diethyl ether (69 mmol, 43 mL) was added dropwise to the ethereal solution of **1** (step a) at 0 °C. The reaction mixture was then stirred under argon at room temperature overnight to give a white precipitate. The precipitate was filtered by means of a jacketed frit under a vacuum–argon line. The product was washed several times with ether and dried under vacuum, yielding 5.32 g (71% based on starting alcohol) of white powder **2**. This highly oxygen and water sensitive material is of sufficient purity for further synthetic purposes, as could be seen from the ^{1}H NMR spectrum of its protonated product **1**.

1-(Diphenylphosphino)-2,3,4,5-tetramethylcyclopentadiene (3). Compound **3** was synthesized by a modification of the literature procedure.[2b,5c] A solution of freshly distilled chlorodiphenylphosphine (7.24 g, 32.8 mmol) in THF (15 mL) was added via syringe to a stirred suspension of **2** (4.20 g, 32.8 mmol) in 60 mL of THF at −75 °C. The mixture was allowed to warm gradually to room temperature (30 min). After 1 h at room temperature the solvent was removed under vacuum, and 50 mL of toluene was added to the residue. The white solid was removed by filtration through Celite, yielding a pale yellow solution. Removal of the solvent (vacuum line, room temperature) from a 0.5-mL sample gave a light yellow oil (0.08 g), which was reasonably pure by ^{1}H NMR and ^{31}P NMR spectroscopy. The main portion of **3** was concentrated to about 15 mL and was used immediately[18] to prepare the lithium derivative **4**; IR (neat) 3050 (m), 2965 (s), 2905 (s), 2855 (m), 1965 (w), 1900 (w), 1820 (w), 1715 (w), 1645 (w), 1620 (w), 1590 (w), 1480 (m), 1435 (vs), 1385 (m), 1330 (s), 1260 (w), 1185 (s), 1115 (s), 1070 (m), 1025 (m), 995 (w), 965 (w), 815 (s), 740 (s), 725 (s), 700 (vs) cm^{-1}; ^{1}H NMR (C_6D_6) δ 1.54 (s, CH_3), 1.79 (s, CH_3), 3.67 (br s, CHP), 7.02 (m, Ph-*m,p*), 7.47 (m, Ph-*o*); ^{31}P{^{1}H} NMR (C_6D_6) δ −0.1.

Lithium (Diphenylphosphino)tetramethylcyclopentadienide (4). *n*-BuLi (27.1 mL of 1.39 M solution in hexane, 37.7 mmol, 1.15 equiv based on starting Ph_2PCl and **2**) was added dropwise to a stirred, cold (0 °C) solution of **3** obtained in the previous step. Stirring was continued at room temperature for 30 min, giving rise to the formation of a yellow oil, which did not solidify after additional stirring (30 min). The mixture was then placed in a freezer (−20 °C) overnight and finally stirred for 5 min. The resulting yellow solid was collected by filtration and washed several times with pentane to give **4** as a pale yellow powder[19] (7.45 g, 74% yield based on starting Ph_2PCl and **3**). The ^{1}H NMR spectrum of the protonated product of **4** showed greater purity compared with the starting material **3**. Compound **4** can be stored under argon at 5 °C for several months; ^{1}H NMR (C_6D_6) δ 2.24 (s, CH_3), 2.33 (s, CH_3), 7.08 (m, Ph-*m,p*), 7.68 (m, Ph-*o*).

2-(Tetramethylcyclopentadienyl)-1-(diphenylphosphino)ethanes (5). A solution of 2-chloro-1-(*p*-tolylsulfonyl)ethane (3.39 g, 14.4 mmol) in THF (20 mL) was added

(12) It is noteworthy that the number of isomers is the same as for a two-carbon-chain nonsubstituted Cp analogue,[2c] whereas there are three isomers for the Me-substituted three-carbon-chain analogue.[5b]

(13) The cyclopentadienide **2** has been synthesized by the modified literature method.[16] Our procedure is superior to the previous one with respect to both yield and convenience.

(14) This isomer is different from the one observed for the unsubstituted analogue Ph_2PCp.[2a]

(15) Air-exposed **3** gives the corresponding oxide within few minutes.

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(18) Compound **3** decomposes at room temperature in 1–2 h.

(19) Compound **4** is extremely air sensitive; it becomes dark yellow immediately on contact with atmosphere.

slowly to a stirred suspension of **2** (2.04 g, 15.9 mmol) in 30 mL of THF at -10 °C. The mixture was stirred at room temperature for 1 h, during which time it became clear. The pale yellow solution was then cooled to -30 °C. Lithium diphenylphosphide[20] (3.03 g, 15.9 mmol) was added dropwise over a period of 30 min. The solution was allowed to warm gradually to room temperature, and then it was stirred for 5 h (TLC control). The solvent was removed under vacuum. The residue was taken up in pentane and fractionated rapidly (10 min) through 3 in. of degassed silica gel (Merck, 35-70mesh), with pentane/THF = 9/1 (200 mL), by means of a frit under vacuum-argon line. Removal of the solvent gave **5** (4.80 g, 68% yield) as a light yellow viscous oil. (The phosphine **5** is extremely sensitive to oxygen. The oxide precipitated by stirring **5** in pentane for a few minutes at room temperature in an open flask; mp 121-123 °C; $^{31}P\{^1H\}$ NMR δ +27.9, +28.3). A trace of the phosphine oxide may be eliminated from **5** by dissolving it in pentane; IR (neat) 3050 (s), 2960 (vs), 2910 (vs), 2850 (vs), 1950 (w), 1885 (w), 1810 (w), 1730 (m), 1650 (m), 1580 (m), 1475 (s), 1430 (vs), 1375 (m), 1315 (m), 1270 (m), 1180 (m), 1095 (s), 1065 (m), 1025 (s), 990 (m), 910 (w), 840 (m), 740 (vs), 695 (vs) cm^{-1}; ^1H NMR (C_6D_6) δ 0.99 (d, CH_3, 6.0 Hz), 1.49-1.55 (m, CH_2), 1.60 (s, CH_3), 1.65 (br s, CH_3), 1.74 (br s, CH_3), 1.80-1.90 (m, CH_2), 2.28 (m, CH), 7.13-7.22 (m, Ph-*m*,*p*), 7.36-7.53 (m, Ph-*o*); $^{13}C\{^1H\}$ NMR (C_6D_6) δ [11.5, 11.8, 13.0, 13.3, 14.7, 14.8] (CH_3), [23.3, 24.0] (CH_2 β to P, $J_{^{31}P-^{13}C}$ = 11.5 Hz), [32.0, 33.3] (CH_2 α to P, $J_{^{31}P-^{13}C}$ = 18.1 Hz), [56.1, 58.4] (CH), [128.4-149.0] (aromatic and olefinic carbons); $^{31}P\{^1H\}$ NMR (C_6D_6) δ -16.4, -16.9; MS, *m*/*e* (relative intensity) 334 (55, M^+), 319 (91), 213 (18), 183 (84), 149 (29), 121 (47), 77 (100).

Registry No. **1**, 4249-10-9; **2**, 87781-76-8; **3**, 125050-56-8; **4**, 125050-57-9; **5**, 125050-59-1; $TsO(CH_2)_2Cl$, 80-41-1; Ph_2PCl, 1079-66-9; $Ph_2P^-Li^+$, 4541-02-0; 2,3,4,5-tetramethylcyclopent-2-enol, 82061-20-9.

(20) Lithium diphenylphosphide was prepared by reaction of *n*-BuLi with diphenylphosphine in pentane.

Reactivites of Some Allylic Hydroperoxides toward Allylic Rearrangement and Related Reactions

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The allylic rearrangement has been studied of the hydroperoxides that are formed when singlet oxygen reacts with epicholesterol, $\Delta^{9,10}$-octahydronaphthalene, 2,3-dimethylbut-2-ene, cyclopentylidenecyclopentane, and cyclohexylidenecyclohexane. The reactivity in this sense decreases in the above sequence. 1-(Cyclopent-1-enyl)cyclopentyl hydroperoxide rearranges only slowly, but in the presence of triplet oxygen it reacts to give 1-(5-hydroperoxycyclopent-1-enyl)cyclopentyl hydroperoxide, and 1-(cyclohex-1-enyl)cyclohexyl hydroperoxide does not rearrange and shows only the reaction with oxygen to give 1-(6-hydroperoxycyclohex-1-enyl)cyclohexyl hydroperoxide. The various factors that affect the rates of these reactions are discussed. It is suggested that the reactivity and regioselectivity in the autoxidation which leads to the formation of dihydroperoxides implies that the reaction involves not the usual two-step propagation sequence, but a three-step sequence in which the chain carriers are a cycloalkenyl radical, a cycloalkenylperoxyl radical, and a cycloalkylperoxyl radical.

Introduction

Over three decades ago Schenck and co-workers demonstrated that 5α-hydroperoxycholest-6-en-3β-ol (**1**) formed in the reaction of singlet oxygen with cholesterol rearranges in a nonpolar solvent during about 1 day to give the corresponding Δ^5-7α-hydroperoxide (Scheme I).[2] Since this discovery, a dozen or so further examples of this phenomenon, in which an allyl hydroperoxide rearranges to its allylic isomer, have been identified.[3-5] Three others in particular that we have studied are the methyl- and ethyloctalin hydroperoxides[3] (**2**, **3**) and the hydroperoxide (**4**) derived from valencene.[4]

These rearrangement reactions are well established to proceed via the corresponding allylperoxyl radical.[2-6] In general, the product of singlet oxygenation rearranges to the product of triplet oxygenation. Under an atmosphere of $^{18}O_2$, the hydroperoxides **1** and **4**[4,6] and that derived from oleic acid[5] incorporate no labeled oxygen during the rearrangement. This, together with the observation that the reactions of the hydroperoxides (**1**-**4**) occur suprafacially, suggests that the rearrangements follow a sigmatropic, nondissociative mechanism (Scheme II).[4-6]

The reactivity, however, of various cyclic systems studied is sensitive to structure, and the detailed mechanism is not clear. For example, the 5α-hydroperoxides derived from the O-methyl, O-trimethylsilyl and O-acetyl derivatives of cholesterol rearrange much more readily than **2**, the hydroperoxide derived from cholesterol itself.[6] Further, the mechanism of the related rearrangement of β-(acyloxy)-alkyl radicals appears to be different in cyclic and acyclic systems.[7]

In an attempt to understand further some of the structural factors that affect the reactivity, we have now examined the rearrangement of a number of allyl hydro-

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