with chloroform (30 mL). The aqueous phase was separated, neutralized, and evaporated in vacuo. The resulting crude residue was recrystallized from water (10 mL) to give **2**: 430 mg (91%); colorless needles; mp 262–265 °C dec; TLC (silica gel, B) R_f 0.23; $[\alpha]^{20}_D$ −77.0° (*c* 1.06, H_2O); UV (methanol) λ_{max} 217, 257, 281 (sh) nm (ϵ 19 500, 12 900, 7300); ^1H NMR (Me_2SO-d_6) δ 2.05 (1 H, m, H-2′b), 2.40 (1 H, m, H-2′a), 3.48 (2 H, m, H-5′), 3.75 (1 H, m, H-4′), 4.28 (1 H, m, H-3′), 4.89 (1 H, t, OH-5′, *J* = 5.5 Hz), 5.20 (1 H, d, OH-3′, *J* = 3.8 Hz), 6.23 (2 H, br s, NH_2), 6.26 (1 H, d, H-5, *J* = 3.6 Hz), 6.30 (1 H, d of d, H-1′, $J_{1',2'a}$ = 8.4 Hz, $J_{1',2'b}$ = 6.0 Hz), 6.92 (1 H, d, H-6, *J* = 3.6 Hz), 10.35 (1 H, br s, NH), ^{13}C NMR (Me_2SO-d_6) δ 39.50 (C-2′), 61.92 (C-5′), 70.84 (C-3′), 82.23 (C-1′), 86.85 (C-4′), 100.08 (C-4a), 102.09 (C-5), 116.67 (C-6), 150.50 (C-7a), 152.50 (C-2), 158.51 (C-4). Anal. Calcd for $C_{11}H_{14}N_4O_4$: C, 49.61; H, 5.30; N, 21.04. Found: C, 49.66; H, 5.31; N, 21.18.

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Registry No. **2**, 86392-75-8; **4**, 84955-32-8; **5**, 4330-21-6; **6**, 86392-74-7.

Chemistry of Organosilicon Compounds. 171. Isoprenylation of Carbonyl Compounds with 2-[(Trimethylsilyl)methyl]-1,3-butadiene Initiated by a Catalytic Amount of Tetra-*n*-butylammonium Fluoride. The Most Convenient Route to Ipsenol and Ipsdienol

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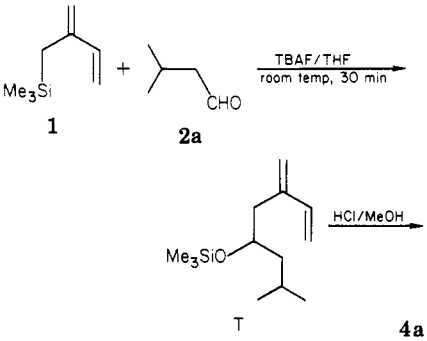
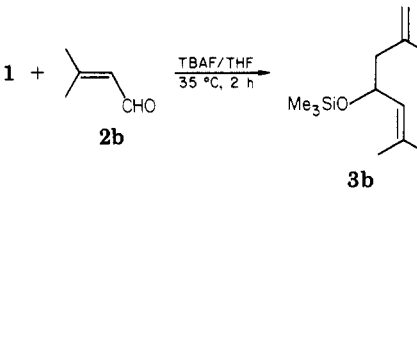
Many efforts have been directed to the synthesis of isoprenylated naturally occurring materials,[1] especially to the synthesis of ipsenol and ipsdienol, principal components of the aggregation pheromones of *Ips paraconfusus*, a bark beetle of California Ponderosa Pine.[2] During the course of studies on the application of allylsilanes to organic synthesis,[3] we have found that 2-[(trimethylsilyl)methyl]-1,3-butadiene (**1**)[1p] provides one of the most convenient and simple route to these compounds.

Isoprenylsilane (**1**) reacted with isovaleraldehyde (**2a**) or 3-methyl-2-butenal (**2b**) very smoothly in the presence of a catalytic amount of tetra-*n*-butylammonium fluoride (TBAF)[4] in tetrahydrofuran to give ipsenol (**4a**) and ipsdienol (**4b**) in 74% and 70% yields, respectively, after careful acid-catalyzed hydrolysis by use of a "one pot" operation (eq 1 and 2). The formation of the silyl ethers



(1)

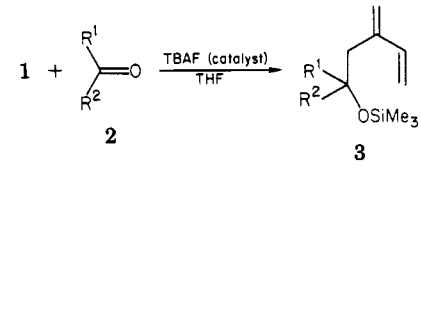


(2)

(**3**) was confirmed by GC/MS spectroscopic analysis of the reaction mixture before hydrolysis.

This is the most efficient and concise procedure of the synthesis of ipsenol (**4a**) and ipsdienol (**4b**) in the highest yield from the readily available starting materials among various methods known hitherto.

The wide utility and general superiority of the present isoprenylating system to **4a** and **4b** have been further demonstrated by the isoprenylation of a variety of carbonyl compounds (**2**) such as aldehydes and ketones. Thus, when a mixture of **1**, **2**, and a catalytic amount of TBAF was stirred in THF at room temperature or at slightly higher temperature (around 30–50 °C) for 1.5–4 h, the corresponding isoprenylated derivatives were obtained in high yield (eq 3). The results are summarized in Table I.



(3)

The alcohols **4** and their silyl ethers **3** involving an isoprenyl moiety should be treated carefully during the hydrolysis under acid conditions in order to avoid lowering the yields, presumably due to polymerization and other side reactions. In the case of enolizable aldehydes and

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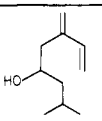
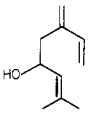
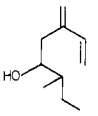
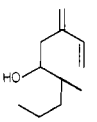
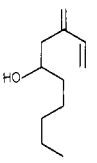
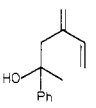
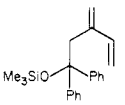
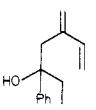
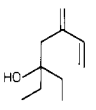
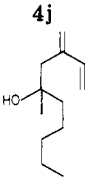
(4) Hosomi, A.; Shirahata, A.; Sakurai, H. *Tetrahedron Lett.* **1978**, 3043.

0022-3263/83/1948-3122$01.50/0

Table I. Isoprenylations of Carbonyl Compounds 2 with Isoprenylsilane (1) Initiated by Tetra-*n*-butylammonium Fluoride

entry	carbonyl compound	conditions[d]	product	% yield[a]
1	$(CH_3)_2CHCH_2CHO$ **2a**	rt, 30 min	 **4a**	74
2	$(CH_3)_2C{=}CHCHO$ **2b**	35 °C, 2 h	 **4b**	70
3	$CH_3CH_2CH(CH_3)CHO$ **2c**	45 °C, 1.5 h	 **4c**	75
4	$CH_3(CH_2)_2CH(CH_3)CHO$ **2d**	45 °C, 35 min	 **4d**	81
5	PhCHO **2e**	40 °C, 1 h	 **4e**	90
6	$CH_3(CH_2)_4CHO$ **2f**	45 °C, 4 h	 **4f**	38[c]
7	$PhCOCH_3$ **2g**	rt, 2.5 h	 **4g**	87
8	Ph_2CO **2h**	50 °C, 2.5 h	 **3h**	100[b]
9	$PhCOCH_2CH_3$ **2i**	rt, 3 h	 **4i**	89
10	$CH_3CH_2COCH_2CH_3$ **2j**	rt, 4 h	 **4j**	61
11	$CH_3CO(CH_2)_4CH_3$ **2k**	45 °C, 3.5 h	 **4k**	33[c]

[a] Yield after isolation by TLC. [b] Isolation by column chromatography. [c] Besides **4**, a considerable amount of the aldol was obtained. [d] rt = room temperature.

ketones, the aldol condensation competes with the addition of **1** to **2** to bring less satisfactory results.

In conclusion, we have found the most simple, versatile, economical, and mild conditions for isoprenylations of carbonyl compounds with the in situ generated isoprene allylic anion **5**.

Experimental Section

Infrared spectra were determined on a Hitachi EPI-G2 spectrophotometer. The abbreviation TF donates thin film. NMR spectra were determined on Varian T-60 and EM-390 and JEOL FX-90Q spectrometers. Mass spectra were taken on a JEOL JMS-300D GC/MS spectrometer. Gas chromatographic analyses were carried out on Hitachi Model 063 and 163 chromatographs equipped with a thermal-conductivity detector.

3-Methyl-2-butenal [2b, bp 50 °C (35 mm) (lit.[1e] bp 133–135 °C)] was prepared from 3-methyl-2-butenol by the pyridinium dichromate (PDC) oxidation[5] in dichloromethane in 85% yield. Other carbonyl compounds are commercially available and used without purification. TBAF was prepared from tetra-*n*-butylammonium bromide by passing it through a column of ion-exchange resin, Amberlite IRA-400 (OH), followed by hydrogen fluoride titration of the resulting hydroxide according to the reported procedure.[6]

General Procedure for the Reaction of Isoprenylsilane (1) with Aldehydes and Ketones. To a solution (5 mL) of 0.2 mL of TBAF in THF (1.0 M, 0.2 mmol) under an argon atmosphere at room temperature was added a mixture of isoprenyltrimethylsilane (1, 1.5–2 molar equiv/mol of carbonyl group) and a carbonyl compound (2 mmol) in THF (1 mL). After being stirred under the conditions given in Table I, the reaction mixture was passed through a short silica gel column (2 cm), and the solvent was evaporated under reduced pressure. The residue was hydrolyzed with methanol (10 mL) containing 0.05 mL of hydrochloric acid (1 M) for 3–5 min at room temperature. Evaporation of the solvent afforded an oil which was chromatographed on three 20 × 20 cm silica gel preparative thin-layer plates in an appropriate solvent. All products were identified by spectroscopic and elemental analyses.

Spectral Data for 4. 2-Methyl-6-methylene-7-octen-4-ol (4a):[1] TLC (Hex/Et_2O, 5/1) R_f 0.32; NMR (CCl_4) δ 0.91 (d, J = 6 Hz, 3 H), 0.94 (d, J = 6 Hz, 3 H), 1.04–1.43 (m, 2 H), 1.48 (s, 1 H), 1.53–2.00 (m, 1 H), 2.00–2.53 (m, 2 H), 3.70 (septet, J = 4.2 Hz, 1 H), 4.93–5.37 (m, 4 H), 6.32 (dd, J = 10.9, 17.4 Hz, 1 H); ^{13}C NMR ($CDCl_3$) δ 21.93 (q), 23.30 (q), 24.54 (d), 40.47 (t), 46.35 (t), 67.50 (d), 113.91 (t), 118.08 (t), 138.45 (d), 143.09 (s); IR (TF) 3370 (s), 3090 (m), 2960 (s), 2940 (s), 2880 (s), 1810 (w), 1600 (m), 1460 (m), 1390 (m), 1370 (m), 1145 (w), 1080 (m), 1030 (w), 1000 (s), 905 (s) cm^{-1}; mass spectrum (70 eV), m/e (relative intensity) 154 (M^+, 0.1), 136 (3), 121 (1), 110 (1), 103 (1), 85 (17), 68 (100), 43 (41), 41 (40); high-resolution mass spectrum, $C_{10}H_{18}O$ (M^+) obsd m/e 154.1369 (calcd 154.1380).

2-Methyl-6-methylene-2,7-octadien-4-ol (4b):[1] TLC (Hex/Et_2O, 5/1) R_f 0.23; NMR (CCl_4) δ 1.63 (d, J = 1.3 Hz, 3 H) 1.70 (d, J = 1.3 Hz, 3 H), 1.91 (br s, 1 H), 2.14–2.42 (m, 2 H), 4.35 (dt, J = 8.4, 6.7 Hz, 1 H), 4.77–5.33 (m, 5 H), 6.27 (dd, J = 10.6, 17.4 Hz, 1 H); ^{13}C NMR ($CDCl_3$) δ 18.02 (q), 25.39 (q), 39.82 (t), 66.45 (d), 113.45 (t), 118.15 (t), 127.42 (d), 134.4 (s), 138.39 (d), 142.44 (s); IR (TF) 3360 (s), 3080 (m), 2980 (s), 2920 (s), 1800 (w), 1660 (m), 1590 (s), 1440 (s), 1380 (s), 1160 (w), 1120 (w), 1020 (s), 990 (s), 900 (s) cm^{-1}; mass spectrum (70 eV), m/e (relative intensity) 152 (M^+, 1), 134 (7), 119 (12), 85 (100), 67 (11), 55 (9), 41 (30); high-resolution mass spectrum, $C_{10}H_{16}O$ (M^+) obsd m/e 152.1211 (calcd 152.1221).

3-Methyl-6-methylene-7-octen-4-ol (4c): TLC (Hex/Et_2O, 5/1) R_f 0.33; NMR (CCl_4) δ 0.77–1.06 (m, 6 H), 1.10–1.77 (m, 4 H), 3.37–3.68 (m, 2 H), 4.90–5.33 (m, 4 H), 6.32 (dd, J = 10.5, 17.4 Hz, 1 H); IR (TF) 3400 (s), 3080 (m), 2960 (s), 2930 (s), 2880 (s), 1595 (s), 1460 (s), 1380 (m), 1060 (m), 1000 (s), 900 (s) cm^{-1}; mass spectrum (70 eV), m/e (relative intensity) 136 ($M^+ - H_2O$, 7), 121 (6), 107 (15), 69 (46), 68 (100), 57 (41), 45 (68), 41 (71); high-resolution mass spectrum, $C_{10}H_8$ ($M^+ - H_2O$) obsd, m/e 136.1253 (calcd 136.1252). Anal. Calcd for $C_{10}H_{18}O$: C, 77.87; H, 11.76. Found: C, 77.96; H, 11.84.

6-Methyl-3-methylene-1-octen-5-ol (4d): TLC (Hex/Et_2O, 5/1) R_f 0.39; NMR (CCl_4) δ 0.79–1.05 (m, 6 H), 1.05–1.75 (m, 5 H), 1.92–2.65 (m, 2 H), 4.97–5.35 (m, 4 H), 6.33 (dd, J = 10.5, 17.1 Hz, 1 H); IR (TF) 3420 (m), 3095 (w), 2970 (s), 2880 (s), 1600 (m), 1460 (m), 1385 (m), 1060 (m), 1040 (m), 1000 (m), 910 (s) cm^{-1}; mass spectrum (70 eV), m/e (relative intensity) 150 ($M^+ - H_2O$, 3), 121 (6), 83 (41), 68 (100), 55 (46), 41 (69); high-resolution mass spectrum, $C_{11}H_{18}$ ($M^+ - H_2O$) obsd m/e 150.1410 (calcd 150.1409). Anal. Calcd for $C_{11}H_{20}O$: C, 78.51; H, 11.98. Found: C, 78.21; H, 12.02.

3-Methylene-1-phenyl-4-pentenol (4e): TLC (PhH) R_f 0.33; NMR (CCl_4) δ 2.17 (s, 1 H), 2.42 (dd, J = 7.5, 13.5 Hz, 1 H), 2.58 (dd, J = 5.9, 13.5 Hz, 1 H), 4.67 (dd, J = 7.5, 5.9 Hz, 1 H), 4.90–5.35 (m, 4 H), 6.29 (dd, J = 10.8, 17.4 Hz, 1 H), 7.03–7.30 (m, 5 H); IR (TF) 3380 (s), 3080 (m), 3020 (m), 2980 (w), 2920 (m), 1598 (s), 1490 (w), 1450 (m), 1390 (m), 1200 (w), 1060 (s), 1030 (s), 1000 (s), 905 (s), 760 (s), 705 (s) cm^{-1}; mass spectrum (70 eV), m/e (relative intensity) 174 (M^+, 2), 156 (12), 107 (100), 105 (55), 79 (47), 77 (51), 68 (43), 53 (16), 51 (18); high-resolution mass spectrum, $C_{12}H_{14}O$ (M^+) obsd m/e 174.1053 (calcd 174.1045).

3-Methylene-1-decen-5-ol (4f): TLC (Hex/Et_2O, 5/1) R_f 0.39; NMR (CCl_4) δ 0.91 (t, J = 5.9 Hz, 3 H), 1.07–1.80 (m, 9 H), 2.13 (dd, J = 8.1, 14.1 Hz, 1 H), 2.42 (dd, J = 4.5, 14.1 Hz, 1 H), 3.37–3.83 (m, 1 H), 4.90–5.37 (m, 4 H), 6.29 (dd, J = 10.9, 17.9 Hz, 1 H), IR (TF) 3400 (s), 3080 (w), 2955 (s), 2920 (s), 2860 (s), 1600 (w), 1460 (w), 1380 (w), 1030 (w), 1000 (w), 905 (w) cm^{-1}; mass spectrum (70 eV), m/e (relative intensity) 168 (M^+, 1), 150 (1), 107 (1), 99 (17), 83 (27), 68 (100), 55 (43), 41 (33); high-resolution mass spectrum, $C_{11}H_{20}O$ (M^+) obsd m/e 168.1509 (calcd 168.1512).

4-Methylene-2-phenyl-5-hexen-2-ol (4g): TLC (PhH) R_f 0.45; NMR (CCl_4) δ 1.48 (s, 3 H), 1.93 (br s, 1 H), 2.65 (s, 2 H), 4.77–5.33 (m, 4 H), 6.23 (dd, J = 10.8, 17.1 Hz, 1 H), 7.02–7.40 (m, 5 H); IR (TF) 3450 (s), 3080 (w), 3060 (w), 2980 (s), 2940 (m), 1680 (m), 1600 (s), 1495 (w), 1450 (s), 1380 (m), 1365 (m), 1270 (m), 1080 (s), 1040 (m), 1000 (m), 910 (s), 775 (s), 710 (s) cm^{-1}; mass spectrum (70 eV), m/e (relative intensity) 170 ($M^+ - H_2O$, 37), 155 (31), 121 (100), 105 (15), 43 (62); high-resolution mass spectrum, $C_{13}H_{16}O$ (M^+) obsd m/e 188.1219 (calcd 188.1201).

3-Methylene-5,5-diphenyl-5-(trimethylsiloxy)pentene (3h): NMR (CCl_4) δ −0.12 (s, 9 H), 3.20 (br s, 2 H), 4.62–5.15 (m, 4 H), 6.00 (dd, J = 10.3, 17.2 Hz, 1 H), 6.95–7.38 (m, 10 H); IR (TF) 3090 (m), 3060 (m), 3020 (m), 2960 (s), 2900 (m), 1810 (w), 1600 (m), 1495 (m), 1450 (m), 1260 (s), 1110 (s), 1080 (s), 1030 (m), 1000 (m), 970 (m), 960 (m), 940 (m), 905 (s), 870 (s), 850 (s), 770 (s), 710 (s) cm^{-1}; mass spectrum (70 eV), m/e (relative intensity) 322 (M^+, 0.2), 307 (3) 255 (100), 75 (11), 73 (70); high-resolution mass spectrum, $C_{21}H_{16}OSi$ (M^+) obsd m/e 322.1746 (calcd 322.1751).

5-Methylene-3-phenyl-6-hepten-3-ol (4i): TLC (PhH) R_f 0.52; NMR (CCl_4) δ 0.70 (t, J = 7.3 Hz, 3 H), 1.63–2.07 (m, 3 H), 2.69 (s, 2 H), 4.73–5.33 (m, 4 H), 6.20 (dd, J = 10.7, 17.0 Hz, 1 H), 6.93–7.43 (m, 5 H); IR (TF) 3520 (m), 3080 (m), 3060 (m), 3020 (m), 2980 (s), 2940 (s), 2880 (m), 1680 (m), 1595 (m), 1490 (m), 1450 (s), 1180 (m), 955 (s), 900 (s), 760 (s) cm^{-1}; mass spectrum (70 eV), m/e (relative intensity) 202 (M^+, 0.1), 184 (8), 169 (8), 155 (24), 135 (100), 105 (32), 77 (24), 57 (67); high-resolution mass spectrum, $C_{14}H_{18}O$ (M^+) obsd m/e 202.1350 (calcd 202.1356).

3-Ethyl-5-methylene-6-hepten-3-ol (4j): TLC (Hex/Et_2O, 5/1) R_f 0.42; NMR (CCl_4) δ 0.83 (t, J = 7 Hz, 3 H), 0.87 (t, J = 7.1 Hz, 3 H), 1.17 (br s, 1 H), 1.30–1.60 (m, 4 H), 2.30–2.36 (m, 2 H), 4.93–5.40 (m, 4 H), 6.35 (dd, J = 10.7, 17.0 Hz, 1 H); IR (TF) 3460 (m), 3080 (w), 2960 (s), 2940 (s), 2880 (m), 1590 (m), 1450 (m), 1370 (w), 1120 (m), 970 (m), 900 (s) cm^{-1}; mass spectrum (70 eV), m/e (relative intensity) 154 (M^+, 0.5), 136 (1), 125 (10), 107 (6), 87 (78), 57 (100), 45 (38); high-resolution mass spectrum, $C_{10}H_{18}O$ (M^+) obsd m/e 154.1369 (calcd 154.1358).

5-Methyl-3-methylene-1-decen-5-ol (4k): TLC (Hex/Et_2O, 5/1) R_f 0.28; NMR (CCl_4) δ 0.91 (t, J = 6 Hz, 3 H), 1.08 (s, 3 H), 1.13–1.70 (m, 9 H), 2.34 (s, 2 H), 4.90–5.43 (m, 4 H), 6.31 (dd, J = 11, 17.1 Hz, 1 H); IR (TF) 3440 (m), 3080 (w), 2950 (s), 2920 (s), 2860 (s), 1590 (m), 1450 (m), 1370 (m), 1140 (m), 990 (m), 900 (s) cm^{-1}; mass spectrum (70 eV), m/e (relative intensity) 182 (M^+, 0.3), 162 (2), 115 (72), 97 (12), 68 (43), 55 (67), 43 (100); high-resolution mass spectrum, $C_{12}H_{22}O$ (M^+) obsd m/e 182.1652 (calcd 182.1669).

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Nuclear Magnetic Resonance Phosphorus-31 Relaxation Times for Diastereomeric Phosphines and Phosphine Oxides

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In conjuction with our studies[2] of homogeneous asymmetric hydrogenations using chiral phosphine/rhodium I catalysts, we prepared and characterized four diastereomeric organophosphines, $(R)_P$- and $(S)_P$-menthylmethylphenylphosphines **1** and **2** and $(R)_P$- and $(S)_P$-neomenthylmethylphenylphosphines **3** and **4**, and the four corresponding oxides **5–8** (Figure 1). These same compounds have been made and studied by Valentine et al.[3] Proper interpretation of our asymmetric hydrogenation experiments ideally required the use of phosphine ligands which were diastereomerically pure. Since the synthetic route used to prepare the phosphines could lead to racemization,[2] an analytical method capable of distinguishing and quantifying the phosphorus diastereomers was required; Fourier transform (FT) ^{31}P NMR proved to be an appropriate convenient method.[4]

Although it is known that organophosphorus relaxation times can vary widely depending upon structure,[5] the magnitude of the difference does not seem to be widely appreciated; we were made aware of this phenomenon when we were attempting to quantify spectral data of samples containing known amounts of a phosphine and the corresponding oxide. A series of NMR spectra, in which the pulse width was varied, were taken of the same sample. The spectra did not accurately reflect the known relative amounts of phosphine and phosphine oxide present. We then determined that the two compounds had widely different ^{31}P relaxation times and that improper data collection conditions were responsible for saturating the signals so that the signal intensities did not accurately measure the relative amount of each nucleus present.

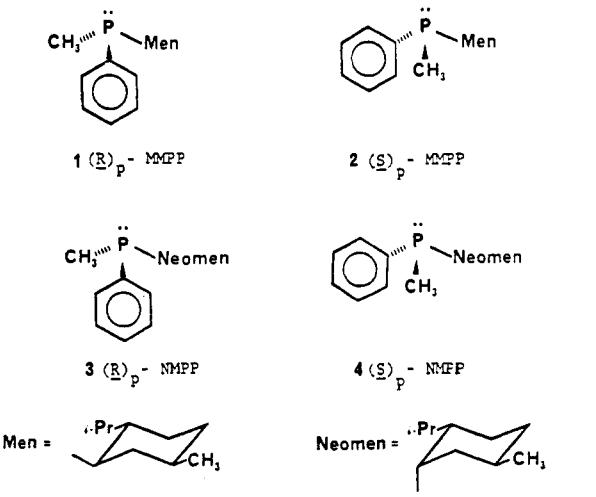
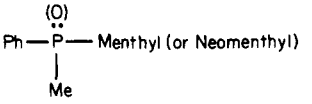


Figure 1. Structures for diastereomeric phosphines 1–4. The phosphine oxides (oxygen atom bonded to the electron pair) corresponding to 1–4 are respectively $(R)_P$-MMPP oxide (**5**), $(S)_P$-MMPP oxide (**6**), $(R)_P$-NMPP oxide (**7**), and $(S)_P$-NMPP oxide (**8**).

Table I. Structures,[a] Relaxation Times,[b] and Chemical Shifts[c] of Diastereomeric Menthyl- and Neomenthylphosphines and -Phosphine Oxides in C_6D_6



compd	substituent	config at phosphorus[a]	T_1 times,[b] s	chem shifts, δ [c]
1	menthyl	(*R*)-phosphine	15.4	34.7
2	menthyl	(*S*)-phosphine	14.6	31.9
3	neomenthyl	(*R*)-phosphine	16.0	38.9
4	neomenthyl	(*S*)-phosphine	17.0	36.4
5	menthyl	(*S*)-phosphine oxide	2.5	−37.6
6	menthyl	(*R*)-phosphine oxide	5.2[d] 7.1[e]	−35.9 −35.9
7	neomenthyl	(*S*)-phosphine oxide	9.9	−36.2
8	neomenthyl	(*R*)-phosphine oxide	11.0	−38.8

[a] Structures determined by X-ray crystallography.[2,3] Because of the *R,S* sequence rules, (*R*)-phosphine is configurationally related to (*S*)-phosphine oxide when oxygen takes the place of the electron pair. [b] See ref 2a for standard inversion-recovery data curves. [c] Chemical shifts are in parts per million from H_3PO_4: positive, upfield; negative, downfield. [d] Concentration in C_6D_6 15 mg/0.4 mL. [e] Concentration in C_6D_6 45 mg/0.4 mL.

Relatively few papers have appeared in the literature which report ^{31}P relaxation times (T_1) for organophosphorus compounds. Stanislawski and Van Wazer[6] and Pregosin and Kunz[4c] have addressed the problems involved with obtaining quantitatively accurate ^{31}P NMR spectra of organophosphorus compounds, and Ojima[7] is also aware of this potential problem. Yet, papers reporting the use of ^{31}P NMR as a chemical probe are appearing with increasing frequency in the organic literature without substantiating evidence for the quantitative accuracy of the measurements. *We hope that our results involving ^{31}P relaxation times will make others more cognizant of the conditions necessary for obtaining quantitative ^{31}P NMR data.*

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