(40), 95 (38), 85 (70), 59 (25). Anal. Calcd for $C_{11}H_{16}O_4$: C, 62.25; H, 7.60. Found: C, 62.60; H, 7.73.

Cyclization of Compound 5. Compound **5** (185 mg, 0.6 mmol) was cyclized according to the standard procedure. Flash chromatography (hexane/ethyl acetate (4:1)) gave compound **13** (45 mg, 33%) and compound **14** (59 mg, 44%). After recrystallization from hexane we obtained pure the major (7*S*)-**13** isomer: mp 106–108 °C; $[\alpha]^{25}_D$ +7.5° (*c* 0.48, $CHCl_3$); IR (KBr) 3595 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) (see Table I, supplementary material); MS *m/z* 213 (M^+ – 15, 100). Anal. Calcd for $C_{12}H_{20}O_4$: C, 63.13; H, 8.83. Found: C, 63.39; H, 8.57. **14**: mp 42–44 °C; $[\alpha]^{25}_D$ –3.2° (*c* 3.4, $CHCl_3$); IR (KBr) 3500 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) (see Table II, supplementary material); MS *m/z* 213 (M^+ – 15, 100). Anal. Calcd for $C_{12}H_{20}O_4$: C, 63.13; H, 8.83. Found: C, 62.98; H, 8.79.

Cyclization of Compound 6. Compound **6** (232 mg, 0.56 mmol), was cyclized according to the standard procedure. Flash chromatography (hexane/ethyl acetate (19:1)) gave compound **15** (63 mg, 34%) and compound **16** (83 mg, 46%). After recrystallization from hexane we obtained pure the major (7*S*)-**15** isomer: 109–111 °C; $[\alpha]^{25}_D$ –4° (*c* 1.0 $CHCl_3$); IR (KBr) 1730 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) (See Table I, supplementary material); MS *m/z* 317 (M^+ – 15, 20), 105 (100). Anal. Calcd for $C_{19}H_{24}O_5$: C, 72.12; H, 7.65. Found: C, 71.25; H, 7.49. **16**: mp 76–78 °C; $[\alpha]^{25}_D$ –37° (*c* 0.4 $CHCl_3$); IR (KBr) 1725 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) (see Table II, supplementary material); MS *m/z* 332 (2), 105 (100). Anal. Calcd for $C_{19}H_{24}O_5$: C, 72.12; H, 7.65. Found: C: 72.37; H, 7.67.

Cyclization of Compound 7. Compound **7** (214 mg, 0.66 mmol) was cyclized according to the standard procedure to give after flash chromatography (hexane/ethyl acetate (9:1)) compound **17** (30 mg, 18% (25% taking into account the recovered starting material **7**)). After crystallization we could obtain major (8*R*)-**17** isomer: mp 99–101 °C; $[\alpha]^{25}_D$ +4° (*c* 0.3, $CHCl_3$); IR (KBr) 3500 cm^{-1}; ^1H NMR (300 MHz, C_6D_6) (see Table II; supplementary material); MS *m/z* 227 (M^+ – 15, 100). Anal. Calcd for $C_{13}H_{22}O_4$: C, 64.44; H, 9.15. Found: C, 64.03; H, 9.47.

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Supplementary Material Available: Schemes IV–VI, synthetic procedures and spectral data of the intermediates in the synthesis of compounds **2–7**, ^1H NMR data for compounds (7*S*)-**13**, (7*S*)-**15**, **14**, **16**, and **17**, ORTEP representation of compound (7*S*)-**15**, and the rest of the crystallographic data (32 pages). Ordering information is given on any current masthead page.

Addition of Triphenylphosphonium Salts to Aldehydes. Remarkable Counter Ion Effects on Phosphorus Proton Couplings

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As part of a program aimed at developing synthetic methods based on divalent germanium and divalent tin,[1] we had the opportunity to examine the chemistry of triphenylphosphonium salts **1**. Phosphonium salt **1a**, a precursor to dichloro- or bisamidogermylenes, can be obtained in nearly quantitative yield by the addition of tributyltin hydride[2] to an ethereal solution of germanium tetrachloride and triphenylphosphine (eq 1).[3] Tin and zinc analogues **1b**, **1c** can also be prepared in high yield.[3]

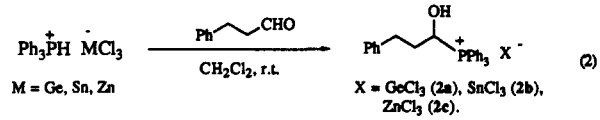
$$Ph_3P + GeCl_4 \xrightarrow[Et_2O,\ rt]{nBu_3SnH} Ph_3\overset{+}{P}H\ \overset{-}{M}Cl_3 \qquad (1)$$

1a, M = Ge
b, M = Sn
c, M = Zn

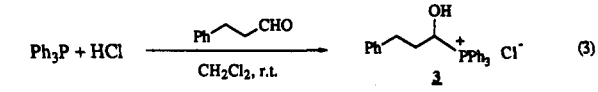
We were interested in preparing 1-hydroxytrichlorogermanes via the addition of **1a** to aldehydes. This approach was based on work by Mironov that had shown that 1-hydroxytrichlorogermanes could be prepared by the addition of $HGeCl_3$ to aldehydes.[4] In our system it was not clear whether the triphenylphosphine would compete with the germanate anion for addition to the carbonyl carbon.

Recent work by Lee and Trogler showed that a variety of 1-hydroxy phosphonium salts could be prepared in high yield by the addition of an anhydrous acid to acetone, acetaldehyde, or benzaldehyde in the presence of PMe_3 or PEt_3.[5] However, no reaction was observed with triphenylphosphine.[5] Interestingly, Anders et al. prepared 1-hydroxy triphenylphosphonium tetrafluoroborate salts from triphenylphosphine, benzaldehyde or acetaldehyde, and tetrafluoroboric acid.[6] In addition, triphenylphosphonium tetrafluoroborate reacts with thiodienes to give thioallylphosphonium tetrafluoroborates[7] and triphenylphosphonium bromide[8] adds to enol ethers to give 1-alkoxy phosphonium bromides.[9] Thus, whether triphenylphosphine would add to an aldehyde or whether it could compete against trichlorogermanate or trichlorostannate was unclear.

When **1a–c** were added to hydrocinnamaldehyde, 1-hydroxy triphenylphosphonium salts **2a–c** were obtained irrespective of the counterion (eq 2). We similarly pre-



(2)



(3)

pared phosphonium salt **3** from triphenylphosphine, hydrogen chloride, and hydrocinnamaldehyde without incident (eq 3).[10] Thus, triphenylphosphine readily adds to aldehydes under anhydrous acidic conditions and it is more nucleophilic than trichlorogermanate, trichlorostannate, or chloride anions.

Due to significant differences in the ^1H NMR and IR spectra of compounds **2** and **3** (see below) their structures were determined based on the following information: (i) the spectra for **2a–c** were very similar, (ii) $^-ZnCl_3$ is not a nucleophile, unlike $^-GeCl_3$ or $^-SnCl_3$, and thus it cannot add to an aldehyde, (iii) there were no observable tin satellite peaks in the ^1H NMR spectra for the C_1-H proton

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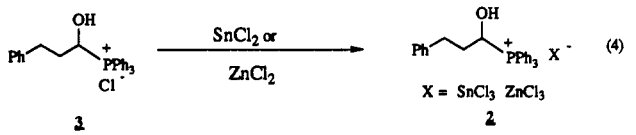
Table I. Selected ^1H NMR Values for Compounds 2 and 3

compd no.	ppm O*H*	*J* (Hz)	ppm P-C-*H*	J_{PCH} (Hz)
3	8.5 (s)	~0	5.9 (d)	10.2
2a	5.0 (t)	8.5	6.2 (m)	3.0
2b	5.1 (dd)	8.0, 9.1	6.3 (dt)	<3.0
2c	5.4 (t)	8.6	6.1 (m)	

in **2b**, suggesting tin was not bonded to this carbon, and (iv) when tin dichloride or zinc dichloride was added to **3**, they yielded compounds **2b** and **2c**, respectively (eq 4). It thus became clear that germanate and stannate anions had not added to hydrocinnamaldehyde but that triphenylphosphine had added instead to form a 1-hydroxy phosphonium salt.



(4)

3 **2**

A comparison of the ^1H NMRs of **2** and **3** revealed some interesting differences. For compound **3** the P-C_1-H coupling was 10.2 Hz, the hydroxyl proton was consistently a singlet at 8.5 ppm, and the C(2) protons were clearly diastereotopic (Table I). For compound **2a** the P-C_1-H coupling was ca. 3 Hz,[11] the hydroxyl proton appeared as a sharp triplet (J = 8.5 Hz) at 5.0 ppm, and the C(2) protons were overlapping. There were also significant differences in the IR spectra of compounds **3** and **2**. Whereas **2** has a hydroxyl stretch at 3380 cm^{-1}, the hydroxyl stretch of **3** resembled that of a carboxylic acid. Thus, there appears to be an interaction between the hydroxy proton and Cl^- in **3**, but no such interaction between the counter ions of the type **2**. Apparently, this interaction also effects the proximal phosphorus-proton couplings. On the other hand, the ^{13}C and ^{31}P spectra were very similar for compounds **2** and **3**.

In summary, triphenylphosphonium salts add to aldehydes, irrespective of the counter ion, yielding 1-hydroxy phosphonium compounds. The ^1H NMR and IR spectra clearly indicate the presence of hydrogen-bonding interactions between the chloride counter ion and the hydroxyl proton, whereas no such interaction is observed between the $^-GeCl_3$, $^-SnCl_3$, or $^-ZnCl_3$ counter ions.

Experimental Section

^1H NMR spectra were recorded at 400 MHz on a Varian XLA-400 spectrometer. ^{13}C NMR spectra were recorded at 100 or 75 MHz. ^{31}P NMR spectra were recorded at 160 MHz. Infrared spectra: all infrared spectra were obtained on a Perkin-Elmer Model 283 IR. C, H, N analyses: analyses were obtained for all new compounds from G. D. Searle, Skokie, IL.

Preparation of (3-Phenyl-1-hydroxypropyl)triphenylphosphonium Trichlorogermanate (2a). Hydrocinnamaldehyde (0.14 g, 1.04 mmol) was added to triphenylphosphonium trichlorogermanate (0.46 g, 1.04 mmol) in methylene chloride (5 mL) and stirred for 2 h. The volume of the reaction was reduced under vacuo, ethyl ether was added (ca. 1:1), and the reaction mixture was placed in a freezer (-30 °C). The crystals were isolated by filtration, washed with ether, and dried under vacuo (0.55 g, 92%): ^1H NMR ($CDCl_3$) δ 7.81-7.65 (m, 15 H), 7.27-7.16 (m, 6 H), 6.20-6.15 (m, 1 H), 5.05-5.00 (t, 1 H, J = 8.5 Hz, OH), 3.15-3.07 (m, 1 H), 3.00-2.93 (m, 1 H), 2.13-2.06 (m, 2 H); ^{13}C NMR ($CDCl_3$) δ 140.22, 135.11 (d, $^4J_{PC}$ = 2.9 Hz), 134.21 (d, J_{PC} = 9.1 Hz), 130.43 (d, J_{PC} = 12.1 Hz), 128.66, 128.57, 126.30, 116.75 (d, $^1J_{PC}$ = 81.3 Hz), 67.62 (d, $^1J_{PC}$ = 61.1 Hz), 34.65 (d, $^3J_{PC}$ = 4.9 Hz), 31.86 (d, $^2J_{PC}$ = 13.8 Hz); ^{31}P ($CDCl_3$) δ 23.6 (s); IR (neat, cm^{-1}) 3380 (m), 3060 (w), 3000 (m), 2960 (m), 2920 (m), 2900 (w), 1590 (m), 1480 (w), 1430 (m), 1110 (s), 1060 (m), 990 (m), 520 (m), 480 (m). Anal. Calcd: C, 56.26; H, 4.55. Found: C, 55.87; H, 4.66.

2b: ^1H NMR ($CDCl_3$) δ 7.80-7.76 (m, 9 H), 7.70-7.66 (m, 6 H), 7.26-7.16 (m, 5 H), 6.35-6.30 (dt, 1 H, $^3J_{HH}$ = 5.7, 7.3, 7.9 Hz, $CH_2CHOH(PPh_3)$), 5.13-5.09 (dd, 1 H, $^3J_{HH}$ = 8.0 Hz, $^3J_{PH}$ = 9.1 Hz, OH), 3.15-3.08 (m, 1 H), 3.04-2.94 (m, 1 H), 2.79-2.04 (m, 2 H); ^{13}C NMR ($CDCl_3$) δ 140.37, 135.00 (d, $^4J_{PC}$ = 2.9 Hz), 134.21 (d, J_{PC} = 9.0 Hz), 130.35 (d, J_{PC} = 12.2 Hz), 128.61, 128.47, 126.18, 116.66 (d, $^1J_{PC}$ = 81.4 Hz), 67.16 (d, $^1J_{PC}$ = 60.8 Hz), 34.47 (d, $^3J_{PC}$ = 5.3 Hz), 31.83 (d, $^2J_{PC}$ = 13.9 Hz); ^{31}P ($CDCl_3$) δ 23.72 (s); IR ($CHCl_3$, cm^{-1}) 3320 (m), 2990 (s), 2300 (w), 1440 (w), 1370 (w), 1250 (s), 1100 (m), 890 (m). Anal. Calcd: C, 52.09; H, 4.21. Found: C, 52.02; H, 4.17.

2c: ^1H NMR (CD_2Cl_2) δ 7.8-7.7 (m, 9 H), 7.67-7.63 (m, 6 H), 7.2-7.1 (m, 5 H), 6.11 (br t, 1 H), 5.41 (t, 1 H, J = 8.6 Hz), 3.12-3.02 (m, 1 H), 3.0-2.9 (m, 1 H), 1.8 (m, 2 H); ^{13}C NMR (CD_2Cl_2) δ 140.79, 135.54 (d, $^4J_{PC}$ = 3.0 Hz), 134.69 (d, J_{PC} = 9.0 Hz), 130.93 (d, J_{PC} = 14.0 Hz), 129.09, 128.92, 126.64, 116.99 (d, $^1J_{PC}$ = 81.5 Hz), 68.61 (d, $^1J_{PC}$ = 61.3 Hz), 34.92 (d, $^3J_{PC}$ = 4.9 Hz), 32.26 (d, $^2J_{PC}$ = 14.0 Hz); ^{31}P (CD_2Cl_2) δ 25.68; IR (CH_2Cl_2, cm^{-1}) 3520 (m), 3320 (m), 1600 (w), 1470 (w), 1120 (m). Anal. Calcd: C, 56.97; H, 4.60. Found: C, 56.65; H, 4.63.

Preparation of (3-Phenyl-1-hydroxypropyl)triphenylphosphonium Chloride (3). Hydrogen chloride (1 mL, 1 mmol, 1 M in ethyl ether) was added to a solution of triphenylphosphine (0.26 g, 1 mmol) in methylene chloride (5 mL) at room temperature and stirred for 5 min. Hydrocinnimaldehyde (0.13 g, 1 mmol) was added, and the reaction was stirred for 15 min. The volatiles were removed under vacuo to yield a white solid that was recrystallized form methylene chloride and ethyl ether (ca. 1:1): ^1H NMR ($CDCl_3$) δ 8.51 (s, 1 H, OH), 7.77-7.72 (m, 9 H), 7.65-7.60 (m, 6 H), 7.29-7.25 (m, 5 H), 5.92 (d, 1 H, J_{PH} = 10.17 Hz, $CH_2CHOH(PPh_3)$), 3.19-3.13 (m, 1 H), 2.98-2.90 (m, 1 H), 2.16-2.11 (m, 1 H), 2.00-1.96 (m, 1 H); ^{13}C NMR ($CDCl_3$) δ 140.77, 134.74 (d, $^4J_{PC}$ = 2.9 Hz), 134.2 (d, J_{PC} = 8.9 Hz), 130.15 (d, J_{PC} = 12.1 Hz), 128.90, 128.50, 126.10, 117.79 (d, $^1J_{PC}$ = 80.5 Hz), 67.03 (d, $^1J_{PC}$ = 58.8 Hz), 35.09 (d, $^3J_{PC}$ = 6.7 Hz), 31.80 (d, $^2J_{PC}$ = 14.5 Hz); ^{31}P ($CDCl_3$) δ 22.63 (s); IR ($CHCl_3$, cm^{-1}) 3040 (m), 2940 (s), 2800 (m), 1430 (w), 1250 (m), 1190 (m), 1100 (s). Anal. Calcd: C, 74.91; H, 6.05. Found: C, 74.81; H, 6.12.

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Registry No. 1a, 137516-56-4; **1b**, 137516-57-5; **1c**, 137516-58-6; **2a**, 137516-60-0; **2b**, 137516-61-1; **2c**, 137516-62-2; **3**, 137516-55-3; $PhCH_2CH_2CHO$, 104-53-0; PPh_3, 603-35-0.

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Metal-Halogen Exchange between Polybromoanisoles and Aliphatic Grignard Reagents: A Synthesis of Cyclopenta[*b*]benzofurans

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Metal-halogen exchange between aromatic halides and aliphatic organometallic reagents is a versatile method for preparing aromatic organometallic species.[1] Although organolithium reagents are usually used for this purpose,

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