Vanadium salts are commonly used to catalyze the oxidation of alkanols to carboxylic acids with nitric acid. The use of vanadium catalyst can greatly influence the oxidation of cyclohexanol and cyclohexanone with nitric acid.[11] Vanadium appears to have little effect on the oxidation[14] of **1** by N_2O_4 and HNO_3 to **12**. In our work, it was found that traces of vanadium cause the destruction of citric acid (**7**) by nitric acid.[15]

The yields of **6** and **7** were surprisingly high when the oxidation was carried out with aqueous nitric acid in the absence of vanadium. Several model diols and triols were oxidized with aqueous nitric acid. It was found that the yield of polycarboxylic acids decreased with increasing number of hydroxyl groups. The oxidation of 3-(hydroxymethyl)-1,3,5-pentanetriol[16] with nitric acid gave yields of only 3–12% citric acid. Oxidation of 3-methyl-1,5-pentanediol at 50 and 60 °C with 70 wt % of nitric acid containing 1.4 wt % of N_2O_4 gave 33 and 23% yields of 3-methylpentanedioic acid and 45 and 62% yields of 2-methylbutanedioic acid, respectively. The yields of **6** and **7** from **2** and **3** were much higher than would be predicted from the results of the oxidation of these model polyols. Very little degradation occurs during the oxidation of the monohydric alcohol **2**. The yield of citric acid (**7**) from the diol **3** was about 65 mol %, compared to a maximum yield of 33% in the apparently analogous oxidation of 3-methyl-1,5-pentanediol to 3-methylpentanedioic acid. It is possible that the terminal carbon of the double bonds in **2** and **3** is rapidly oxidized to a carboxyl group, and this forms a lactone such as **5**, which may oxidize to the polycarboxylic acid in a higher yield than the free alcohol. This is speculative at present, as no evidence is available on the factors influencing yields for oxidation of this type in nitric acid.

Registry No. 2, 763-32-6; **3**, 40760-35-8; (*E*)-**4**, 16933-29-2; (*Z*)-**4**, 39149-97-8; **6**, 597-44-4; **7**, 77-92-9; N_2O_4, 10544-72-6; 3-methyl-2,5-furandione, 616-02-4.

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Synthesis and Nuclear Magnetic Resonance Spectra of Some Substituted Vinyldiphenylphosphines

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Some substituted vinyl tertiary phosphines have been synthesized by the reaction of the substituted vinyl Grignard reagents with $(C_6H_5)_2PCl$ and $C_6H_5PCl_2$. The compounds include $(C_6H_5)_2PC(CH_3)=CH_2$, (*Z*)- and (*E*)-$(C_6H_5)_2PCH=CHCH_3$, $(C_6H_5)_2PCH=C(CH_3)_2$, (*Z*)- and (*E*)-$(C_6H_5)_2PC(CH_3)=CHCH_3$, and the compound mixture (*Z,E*)-, (*Z,Z*)-, and (*E,E*)-$(C_6H_5)P(CH=CHCH_3)_2$. ^{31}P and ^{1}H NMR data are reported. Those phosphines which have a methyl group cis to phosphorus in the ethylene group have unusually large upfield (highly shielded) ^{31}P chemical shifts.

The utility of vinyl tertiary phosphines for the synthesis of unsymmetrical bis(tertiary phosphines),[1-3] poly(tertiary phosphines),[4-6] and some other novel tertiary phosphines[7] via addition of an alkali metal diorganophosphide or a phosphorus–hydrogen bond to the vinyl group has been clearly demonstrated. In the pursuit of some unsymmetrical bis(tertiary phosphines) with two carbons bridging the phosphorus atoms, we have prepared several substituted vinyldiphenylphosphines and substituted divinylphenylphosphines, which have some unusual ^{31}P NMR chemical shifts. The synthesis, ^{31}P NMR, and ^{1}H NMR results are presented here.

Table I. Phosphorus-31 Chemical Shifts of Substituted Vinyl Tertiary Phosphines

compd	$\delta_P{}^a$
$(C_6H_5)_2PCH=CH_2$	$-11.7,^b -13.8^c$
$(C_6H_5)_2PC(CH_3)=CH_2$	-0.9
$(C_6H_5)_2PCH=C(CH_3)_2$	-28.3
(*E*)-$(C_6H_5)_2PCH=CHCH_3$	-14.2
(*Z*)-$(C_6H_5)_2PCH=CHCH_3$	-32.7
(*E*)-$(C_6H_5)_2PC(CH_3)=CHCH_3$	$+5.9$
(*Z*)-$(C_6H_5)_2PC(CH_3)=CHCH_3$	-18.5
(*E,E*)-$(C_6H_5)P(CH=CHCH_3)_2$	-21.4
(*E,Z*)-$(C_6H_5)P(CH=CHCH_3)_2$	-39.8
(*Z,Z*)-$(C_6H_5)P(CH=CHCH_3)_2$	-57.9

[a] Positive values are downfield from 85% H_3PO_4. [b] Reference 8. [c] Reference 22.

Results and Discussion

The reaction of chlorodiphenylphosphine with the Grignard reagent of a mixture of (*Z*)- and (*E*)-2-bromo-2-butene produces a crude reaction mixture of (*Z*)- and (*E*)-$(C_6H_5)_2PC(CH_3)=CHCH_3$, which have ^{31}P chemical shifts of −18.5 and 5.9 ppm, respectively (Table I lists the ^{31}P NMR data). Since the corresponding saturated alkyldiphenylphosphine has a chemical shift of −3.2 ppm,[8] the highly shielded resonance at −18.5 ppm was quite

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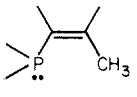
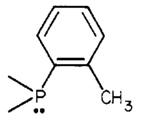
unexpected. In a similar fashion, the ^{31}P chemical shifts of (*Z*)-$(C_6H_5)_2PCH{=}CHCH_3$ and (*E*)-$(C_6H_5)_2PCH{=}CHCH_3$ are −32.7 and −14.2 ppm, respectively, whereas the corresponding saturated compound, $(C_6H_5)_2PCH_2CH_2CH_3$, has a ^{31}P chemical shift of −17.6 ppm. Again, the shift in the *Z* isomer apparently is unpredictably highly shielded. That these chemical shifts are indeed due to the isomers indicated, and not to some other rearranged product or other side product, was shown by carrying out the following procedures. First, hydrogenation of the mixture of (*Z*)- and (*E*)-$(C_6H_5)_2PCH{=}CHCH_3$ isomers produced diphenylpropylphosphine as the only product, and hydrogenation of the mixture of (*Z*)- and (*E*)-$(C_6H_5)_2PC(CH_3){=}CHCH_3$ produced 2-butyldiphenylphosphine as the only product. Second, after gas chromatographic separation of the isomers from the mixture of (*Z*)- and (*E*)-1-bromopropene, the Grignard reagent of each of the isomers reacted with chlorodiphenylphosphine to produce principally the respective (*Z*)- and (*E*)-$(C_6H_5)_2PCH{=}CHCH_3$ compounds. The (*Z*)-1-bromopropene produced about 95% of the (*Z*)-propenylphosphine. The (*E*)-1-bromopropene produced about 70% of the (*E*)-propenylphosphine (30% was the *Z* isomer). It should be noted that 1-bromopropenes as well as their vinyl Grignard reagents undergo isomerization at moderate temperatures.[9-11] The 1-bromopropenes were identified by their characteristic infrared (*Z*, 935, 1300 cm^{-1}; *E*, 1217, 1438 cm^{-1}) and ^1H NMR (*Z*, $^3J_{HCCH(cis)} = 70$ Hz; *E*, $^3J_{HCCH(trans)} = 13.5$ Hz) spectra.[12,13] Third, the *Z*:*E* ratio (86:14) for the (*Z*)- and (*E*)-$(C_6H_5)_2PC(CH_3){=}CHCH_3$ products, as measured from the ^{31}P NMR spectrum of the isomer mixture, is the same as the *Z*:*E* ratio (85:15) in the starting 2-bromo-2-butenes, as measured from the gas chromatogram. Fourth, gas chromatographic separation of (*Z*)- and (*E*)-$(C_6H_5)_2PC(CH_3){=}CHCH_3$ produced the individual compounds which can easily be identified by characteristic ^1H NMR spectra, e.g., $^3J_{PH(cis)} \approx 10$ Hz whereas $^3J_{PH(trans)} \approx 25$ Hz, for similar compounds.[14] Taken together, these results conclusively demonstrate that the assignments of the ^{31}P chemical shifts to the correct isomers can be made unequivocally and that those substituted vinyl compounds with a methyl group cis to phosphorus have a more greatly shielded phosphorus than those isomeric compounds with a proton cis to phosphorus. This is another classic example of an exaggerated γ effect on the ^{31}P chemical shift.[15,16] One of the explanations of this effect in trivalent phosphorus chemistry is a steric "compression" of the phosphorus lone-pair electrons. In this respect, the steric effect of the *Z*-isomer vinyl groups is quite similar to the steric effect of the *o*-tolyl group in tertiary phosphines, which were previously reported to have unusually large (upfield) group contributions.[16]





The group contributions of the substituted vinyl groups can be used to assign the ^{31}P chemical shifts in the reaction mixture of the Grignard of (*Z*)- and (*E*)-1-bromopropene with dichlorophenylphosphine. The distilled product, which is expected to contain the three isomers of di-1-propenylphenylphosphine, viz., the *Z*,*Z*, *Z*,*E*, and *E*,*E* compounds, exhibits ^{31}P NMR peaks at −57.9, −39.8, and −21.4 ppm. The group contribution of the (*Z*)-1-propenyl group, calculated from the chemical shift of (*Z*)-diphenyl-1-propenylphosphine by using the accepted phenyl group contribution[8] of −3 ppm, is −27 ppm. That of the (*E*)-1-propenyl group, obtained in the same manner, is −8 ppm. Therefore, the calculated chemical shift of (*Z*,*Z*)-di-1-propenylphenylphosphine is $2(-27) + (-3) = -57$ ppm, that of the *Z*,*E* isomer is $-27 - 8 - 3 = -38$ ppm, and that of the *E*,*E* isomer is $2(-8) - 3 = -19$ ppm. These are in quite good agreement with the experimental values of −57.9, −39.8, and −21.4 ppm, respectively.

Except for the vinyl groups with cis substitution relative to phosphorus, the ^{31}P group contributions of the substituted vinyl groups bear a relationship to each other similar to that of the group contributions of the alkyl groups. For example, the group contribution of the isopropenyl group (ca. 5 ppm) is 13 ppm downfield from that of (*E*)-1-propenyl (−8 ppm), whereas the group contribution of isopropyl (6 ppm) is 17 ppm downfield from *n*-propyl (−11 ppm). The (*E*)-1-propenyl group (GC = −8 ppm) is 2 ppm upfield from the vinyl group (GC = −6 ppm),[8] whereas propyl (GC = −11 ppm) is 4 ppm upfield from ethyl (GC = −7 ppm). Other relationships hold similarly.

The ^1H NMR spectra of these compounds have varying degrees of complexity and were analyzed by LAOCOON III computer simulation with final refinement performed with a Varian SIMEQ spin simulation program available with the Varian FT80A instrument.[17] The NMR analyses were complicated in some cases due to isomer impurities. The results are given in Table II and are in reasonable agreement with previous studies[14] and expected coupling constants.[18]

Experimental Section

^{31}P NMR spectra were obtained on the neat liquids with a Varian Associates DP-60 spectrometer at 24.3 MHz with 85% H_3PO_4 as an external standard. Chemical shifts are reported as positive when downfield from the reference. ^1H NMR spectra were obtained on a Varian A60A spectrometer. Microanalyses were performed by Dr. Franz Kasler of the University of Maryland. Synthetic operations were carried out in a nitrogen atmosphere.

Diphenylisopropenylphosphine. This compound was prepared by the reaction of the Grignard reagent (0.4 mol) of 2-bromopropene (Aldrich Chemical Co.) in 200 mL of tetrahydrofuran (THF) with $(C_6H_5)_2PCl$ (0.32 mol, Aldrich) in 150 mL of THF. The yield of product, bp 111–117 °C (0.3 mmHg) [lit.[14] bp 117–119 °C (1 mmHg), lit.[19] bp 105–120 °C (1 mmHg)] was 0.20 mol (63%). Anal. Calcd for $C_{15}H_{15}P$: C, 79.63; H, 6.68. Found: C, 79.67; H, 6.56.

Diphenyl(2-methyl-1-propenyl)phosphine. This compound was prepared from the Grignard of $BrCH{=}C(CH_3)_2$ (0.25 mol prepared by the method of Krestinsky[20]) and $(C_6H_5)_2PCl$ (0.20 mol) in THF. The yield of product, bp 171–177 °C (4 mmHg) [lit.[14] bp 119–121 °C (1 mmHg)], was 54%. Anal. Calcd for

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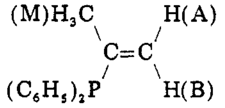
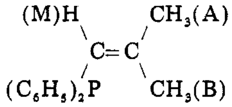
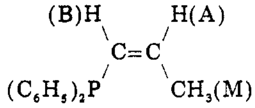
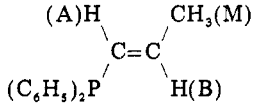
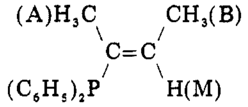
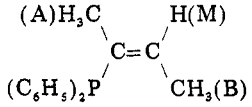
Table II. Proton NMR Data for Some Substituted Vinyldiphenylphosphines[a]

	δ_A	δ_B	δ_M	J_{PA}	J_{PB}	J_{PM}	J_{AB}	J_{AM}	J_{BM}
	5.58 5.56[b]	5.12 5.17[b]	1.82	25.3 26.5[b]	10.7 10.5[b]	9.2	1.7 2.3[b]	−1.7	−1.1
	1.82	1.98	5.92 5.6[b]	0.3	0.5	4.0 6.0[b]	0	−2.0	−1.5
	6.37	6.24	1.91	20.0	2.7	0	8.5	6.0	−0.8
	6.2	6.1	1.85	7.0	10.0	0.3	13	1.5	4.9
	1.67	1.68	5.88	8.5	0.3	10.0	0	−1.1	6.0
	1.58	1.95	6.26	3.0	0.5	23.7	1.6	1.4	7.0

[a] Chemical shifts are in parts per million and coupling constants in hertz. [b] Reference 14.

$C_{16}H_{17}P$: C, 79.97; H, 7.13. Found: C, 79.79; H, 7.08.

(*Z*)- and (*E*)-1-Bromopropene. The mixture of isomers of 1-bromopropene (Aldrich) was separated by gas chromatography (GC); a 600 cm × 0.6 cm column, packed with 20% Carbowax on Chromosorb F at a column temperature of 100 °C was used. The collected isomers were kept at −78 °C to prevent isomerization. The isomer with the shortest retention time was identified as the *Z* isomer by ^{1}H NMR and infrared spectra.[12,13]

Diphenyl-(*Z*)-1-propenylphosphine. This compound was made from the Grignard reagent of 0.018 mol of (*Z*)-1-bromopropene in 4 mL of THF with 0.012 mol of $(C_6H_5)_2PCl$ in 4 mL of THF. The final product, bp 142–146 °C (1.1 mmHg), weighed 1.2 g (0.0053 mol, 44%). The ^{31}P spectrum had a major peak at −32.7 ppm with only a minor peak (ca. 5%) due to the *E* isomer at −14.2 ppm. Anal. Calcd for $C_{15}H_{15}P$: C, 79.63; H, 6.68. Found: C, 79.25; H, 6.71.

Diphenyl-(*E*)-1-propenylphosphine. This compound was prepared from the Grignard reagent of 9.2 mmol of (*E*)-1-bromopropene in 4 mL of THF with 7.1 mmol of $(C_6H_5)_2PCl$ in 4 mL of THF. The yield of product, bp 125–127 °C (0.5 mmHg), was 0.89 g (4.0 mmol, 56%). The ^{31}P NMR spectrum had a principal peak at −14.2 ppm (ca. 70%) with a lesser peak (30%) at −32.7 ppm due to the *Z* isomer. Anal. Calcd for $C_{15}H_{15}P$: C, 79.63; H, 6.68. Found: C, 79.44; H, 6.77.

(*Z*)- and (*E*)-(1-Methyl-1-propenyl)diphenylphosphine. The compounds were prepared from the Grignard reagent of a mixture of (*Z*)- and (*E*)-2-bromo-2-butene (0.45 mol, J. T. Baker Chemical Co.) and 0.35 mol of $(C_6H_5)_2PCl$ in THF. The yield of the isomer mixture, bp 129–133 °C (0.8 mmHg), was 74%. The ^{31}P NMR spectrum had peaks at −18.5 (86%) and +5.9 ppm (14%), due to the (*Z*)-$(C_6H_5)_2PC(CH_3){=}CHCH_3$ and (*E*)-$(C_6H_5)_2PC(CH_3){=}CHCH_3$ isomers, respectively. This mixture was GC separated by using a 180 cm × 0.6 cm column packed with 10% Carbowax 20 M on 60/80 Chromosorb W at a column temperature of 225 °C. The isomer of shorter retention time (peak area, 85%) was identified by ^{31}P and ^{1}H NMR as the *Z* isomer, while the second peak (15%) was identified as the *E* isomer. Anal. Calcd for (*Z*)-$C_{16}H_{17}P$: C, 79.98; H, 7.13. Found: C, 79.70; H, 6.98. Calcd for (*E*)-$C_{16}H_{17}P$: C, 79.98; H, 7.13. Found: C, 79.68; H, 6.90.

In addition, the isomers of 2-bromo-2-butene were separated by GC in the same manner as the 1-bromopropenes. The Grignard of the *Z* isomer (6.6 g, 0.049 mol) was used to prepare the (*Z*)-$(C_6H_5)_2PC(CH_3){=}CHCH_3$ compound from $(C_6H_5)_2PCl$ (0.035 mol) in 16 mL of THF. The yield of product, bp 122–126 °C (0.5 mmHg), was 4.1 g (0.017 mol, 49%). The ^{31}P NMR spectrum had the major peak at −18.6 ppm with a minor peak (ca. 5%) at 6.0 ppm due to a slight impurity of the *E* isomer.

Reduction of a Mixture of Diphenyl-(*Z*)- and (*E*)-1-propenylphosphine to Diphenylpropylphosphine. A mixture of 4.13 g (0.018 mol) of (*Z*)- and (*E*)-$(C_6H_5)_2PCH{=}CHCH_3$ in 50 mL of dry THF was charged in a glass Parr bomb with about 1.5 g of W-6 Raney nickel.[21] After evacuation, the bomb was filled with H_2 at a pressure of about 2 atm and allowed to shake overnight. After filtration, the filtrate was distilled to yield $(C_6H_5)_2PC_3H_7$, bp 195–202 °C (9 mmHg) [lit.[22] bp 138 °C (1 mmHg)], which was identified by the single peak in the ^{31}P NMR spectrum at −17.0 ppm (lit.[8] −17.6 ppm).

Reduction of a Mixture of (*Z*)- and (*E*)-(1-Methyl-1-propenyl)diphenylphosphine to 2-Butyldiphenylphosphine. The mixture of isomers (10.0 g, 0.042 mol) was hydrogenated as described above. The product was distilled to give 4.6 g (0.019 mol, 46%) of $(C_6H_5)_2PCH(CH_3)CH_2CH_3$, bp 183–190 °C (6 mmHg) [lit.[22] bp 141–145 °C (1.5 mmHg)]. The ^{31}P NMR spectrum of the product had a single resonance at −3.0 ppm (lit.[8] −3.2 ppm). The ^{1}H NMR spectrum was identical with that of an authentic sample of the compound prepared in a different way.

Acknowledgment. Support from the National Science Foundation (Grant No. CHE78-09536) is gratefully acknowledged.

Registry No. $(C_6H_5)_2PC(CH_3){=}CH_2$, 16433-97-9; $BrC(CH_3){=}CH_2$, 557-93-7; $(C_6H_5)_2PCl$, 1079-66-9; $(C_6H_5)_2PCH{=}C(CH_3)_2$, 34193-25-4; $BrCH{=}C(CH_3)_2$, 3017-69-4; (*Z*)-$BrCH{=}CHCH_3$, 590-14-7; (*E*)-$BrCH{=}CHCH_3$, 590-15-8; (*Z*)-$(C_6H_5)_2PCH{=}CHCH_3$, 28691-78-3; (*E*)-$(C_6H_5)_2PCH{=}CHCH_3$, 72138-55-7; (*Z*)-$(C_6H_5)_2PC(CH_3){=}CHCH_3$, 72138-56-8; (*E*)-$(C_6H_5)_2PC(CH_3){=}CHCH_3$, 72138-57-9; (*Z*)-$BrC(CH_3){=}CHCH_3$, 3017-68-3; (*E*)-$BrC(CH_3){=}CHCH_3$, 3017-71-8; $(C_6H_5)_2PC_3H_7$, 7650-84-2; $(C_6H_5)_2PCH(CH_3)CH_2CH_3$, 7650-79-5; $(C_6H_5)_2PCH{=}CH_2$, 2155-96-6; (*E*,*E*)-$(C_6H_5)P(CH{=}CHCH_3)_2$, 72138-58-0; (*E*,*Z*)-$(C_6H_5)P(CH{=}CHCH_3)_2$, 72138-59-1; (*Z*,*Z*)-$(C_6H_5)P(CH{=}CHCH_3)_2$, 72138-60-4.

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