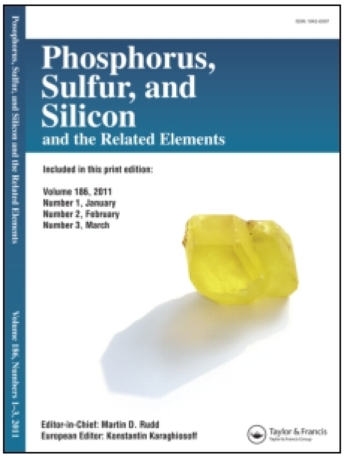

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METHYL PHOSPHINEACETATES—SYNTHESIS AND CHARACTERIZATION AS POTENTIAL LIGANDS

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METHYL PHOSPHINEACETATES—SYNTHESIS AND CHARACTERIZATION AS POTENTIAL LIGANDS

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Two series of methyl phosphineacetates with the general formulae $Ph_{3-n}P(CH_2CO_2Me)_n$, $n = 1$-3, and $RP(CH_2CO_2Me)_2$, R═Me, Et, *i*-Pr, were synthesized by a BF_3-catalyzed reaction of the acids or their hydrohalides with methanol. The products were characterized by IR, ^1H, ^{13}C and 31P NMR and mass spectra and their properties that are important for the coordination behaviour (basicity, electronic parameters and cone angles) were determined. A new method for cone angle estimation based on a systematic search for crystal structure data was proposed.

INTRODUCTION

Functionalized phosphines now constitute a separate, rapidly growing class of compounds.[1] This is mainly the consequence of their use as ligands in metal complexes which are interesting both for theoretical coordination chemistry and in homogeneous catalysis.[2] While the soft phosphorus atom in these complexes is firmly bonded to a (usually) soft metal atom, a hard atom inherent frequently to the functional group may behave as a second, labile donor occupying a site where substitution reactions may take place with substrate molecules. Some phosphines bearing alkoxy-carbonyl groups have already been studied from this standpoint. A typical representative of such ligands is ethyl diphenylphosphineacetate[3] which, besides the types of bonding mentioned above, is capable of C-metallation through the methylene carbon adjacent to phosphorus. It is well known that the

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coordination properties of tertiary phosphines are sensitive to seemingly unimportant changes in the ligand structure. It therefore appeared interesting to synthesize a series of methyl phosphineacetates, **1**–**6**, and to investigate the properties potentially determining their coordination behaviour.

$(C_6H_5)_2PCH_2CO_2CH_3$	(**1**)	$CH_3P(CH_2CO_2CH_3)_2$	(**4**)
$C_6H_5P(CH_2CO_2CH_3)_2$	(**2**)	$CH_3CH_2P(CH_2CO_2CH_3)_2$	(**5**)
$P(CH_2CO_2CH_3)_3$	(**3**)	$(CH_3)_2CHP(CH_2CO_2CH_3)_2$	(**6**)

The esters **1**–**3** were already known[4] but they have not been studied in any systematic way.

RESULTS AND DISCUSSION

The esters were prepared in good yields by a BF_3-catalyzed esterification[5] of acids or their hydrohalides.[6] The reaction rate is strongly affected by the thermodynamic and/or kinetic stability of the appropriate ester. BF_3 adduct, the further transformation of which, according to a TLC tracing of the reaction course, clearly represents the rate-determining step. After purification by distillation, the esters are colourless liquids, unstable in the air because of oxidation to phosphine oxides. As expected, the phenyl-containing derivatives are more resistant to oxidation than the remaining compounds, which even tend to ignite spontaneously in the air when finely dispersed.

The spectral parameters of the products confirm unambiguously their structures. In the IR spectra, the existence of rotamers around the P—CH_2COO and C═O bonds is reflected in broadening of the ν(C═O) and splitting of the ν(C—H) bands respectively. The NMR spectra are presented in Table I. Their parameters are in accord with general trends for related phosphines;[7] the zero value of the $^2J_{P,H}$(acetate) coupling constant in **1** is surprising and probably reflects a value close to 45° for the lone pair-P—C—H torsion angle.[8] The rotation around the P—C bonds must be fast on the NMR time scale in all cases since no signs for the presence of rotamers have been observed at room temperature.

The mass spectra display many common and some specific features of the fragmentation induced by electron impact ionization. with the exception of the diphenyl derivative, **1** (see below), the products of fission of the methoxycarbonyl group are dominating in all spectra. The common decomposition pattern, as revealed by metastable transitions and by the elemental composition of the ions, involve simple bond dissociations, hydrogen transfers and rearrangements, leading to the formation of the P—O bond (Scheme 1). Specific differences in the behaviour of **2** to **6** are related to different propensities of phenyl and alkyl groups toward fragmentation. In the case of the phenyl and the methyl derivative, **2** and **4**, no well-defined dissociation of these groups can be observed, whereas with the ethyl derivative, **5**, the loss of ethylene[9] is observable, e.g. from the molecular ions and $(M—CH_3OH)^+$ ions. In the fragmentation of the isopropyl derivative, **6**, propylene is split off in an analogous way but to a higher extent,

TABLE I

^{31}P, ^{1}H and ^{13}C NMR parameters of compounds **1–6**

	^{31}P NMR	^{1}H NMR[a]			^{12}C NMR[a]						
Compound	δ_P	δ_{CH_2} ($^2J_{H,P}$)	δ_{OCH_3}	$\delta_{C_6H_5}$	δ_{CH_2} ($^1J_{C,P}$)	δ_{CO} ($^2J_{C,P}$)	δ_{CH_3}	$\delta_{C\text{-}1}$ ($^1J_{C,P}$)	$\delta_{C\text{-}2,6}$ ($^2J_{C,P}$)	$\delta_{C\text{-}3,5}$ ($^3J_{C,P}$)	$\delta_{C\text{-}4}$
1	−15.9	3.34s (0)	3.68s	7.49–7.72m	35.0 (21.0)	171.1 (8.9)	51.9	138.6 (14.5)	133.3 (19.9)	129.3 (6.9)	129.8
2	−27.2	3.05dd; 3.18dd[b] (1.7) (3.6)	3.67s	7.51–7.78m	33.6 (22.6)	170.9 (6.4)	51.8	131.4 (10.0)	132.8 (21.0)	129.3 (7.3)	130.3
3	−34.0	2.88d (3.2)	3.80s	—	32.1 (23.9)	170.9 (6.7)	52.0	—	—	—	—
				Alkyl δ_{PCH} ($^2J_{H,P}$)	Alkyl δ_{CH_3} ($^3J_{H,P}$)					Alkyl δ_{PC} ($^1J_{C,P}$)	Alkyl δ_{CH_3} ($^2J_{C,P}$)
4	−38.3	2.96dd; 2.79dd[c] (3.0) (1.7)	3.79s	(.79d (4.6)	—	34.0 (23.5)	171.1 (4.9)	51.7		11.2 (17.4)	—
5	−24.8	2.71dd; 2.79dd[c] (2.2) (2.8)	3.79s	1.70m[d] (1.3)	1.22m[d] (16.3)	32.0 (25.1)	171.2 (5.1)	51.8		20.0 (14.2)	9.6 (16.5)
6	−12.7	2.73dd; 2.82dd[c] (2.0) (1.9)	3.78s	1.93dd[d] (3.8)	1.23dd[e] (26.7)	30.7 (26.7)	171.5 (5.1)	51.8		25.8 (12.3)	19.1 (16.7)

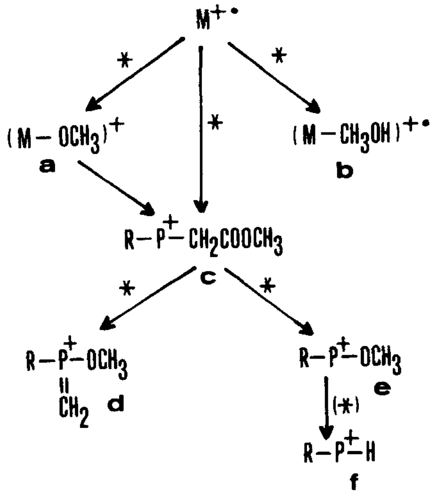
[a] The absolute values of coupling constants are given;

[b] $^2J_{H(A),H(B)} = 13.9$;

[c] $^2J_{H(A),H(B)} = 13.6$;

[d] $^3J_{CH_2CH_3} = 7.7$;

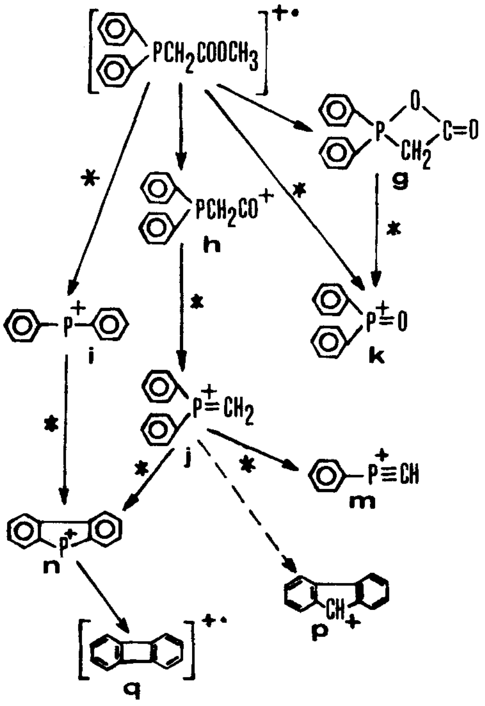
[e] $^3J_{CH,CH_3} = 7.0$



SCHEME 1 Fragmentation of compounds **2**–**6**.

especially from the $(M—CH_3OH)^+$ ion. In addition, loss of isopropyl may be observed as a result of the low dissociation energy of the P—C bond(s). The $P(COOCH_3)_2^+$ ion which is abundant especially in the spectrum of phosphinetriacetate, **3**, is subjected to a twofold rearrangement and subsequent elimination of two ketene molecules, yielding the $P(OCH_3)_2^+$ ion. This ion decomposes further losing formaldehyde through hydrogen transfer. The fragmentation of the diphenyl derivative, **1**, is quite different in that it is dictated by the properties of the diphenyl-phosphine fragment. The origin of the most abundant fragment ions, as revealed from metastable transitions and elemental compositions, is depicted in Scheme 2. The ions with two aromatic residues have probably the same structures as the corresponding ions originating from triphenylphosphine.[10] The loss of the phosphorus atom from the $C_{12}H_8P^+$ ion may also be observed in a metastable transition.[10] The loss of methyl from the molecular ion is undoubtedly connected with a rearrangement[11] leading to formation of the P—O bond. The decomposition of the $(C_6H_5)_2P{=}CH_2^+$ ion yielding benzene and the $C_6H_5P{=}CH^+$ phosphonium ion is related to the high stability of both originating species.

Of the many parameters designating the coordination behavior of phosphines, the basicity, electronegativity and steric requirements are known to be of the greatest importance. Table II summarizes the pK_a values,[12] Tolman's v electronic parameters[13] and cone angles. For the determination of the cone angles, the substitution reaction with nickel tetracarbonyl in toluene[14] provided values of poor precision ranging between 120 and 150° and displaying trends which are evidently inconsistent with the phosphine structure. It cannot be excluded that the origin method,[13] besides suffering in principle from the assumption that the absorptivities of CO in the individual species are the same, is further affected in this special case by competitive coordination of carbonyl oxygen(s).[3] Clearly, an alternative method for cone angle estimation is needed. Of a number of available methods,[15] the search for crystal structure data[16] with respect to the



SCHEME 2 Fragmentation of compound **1**.

P—C—C(O)—O—C fragment yielded reliable results. All six directly related structures average to the half-cone-angle[17] of 69(3)° for the alkyl phosphineacetate substituent. This value is independent of the alkyl type since it is invariantly determined by "bending out" of the carbonyl oxygen unless, of course, it is coordinated to a metal. The combination with the cone angles of symmetrical phosphines[14] then yielded the values summarized in Table II.

Attempted correlation of spectral data and/or coordination behaviour of tertiary phosphines have convincingly demonstrated[7,14] that both parameters are closely interrelated and cannot be safely separated even for large series of specifically designed phosphines. Among the compounds studied in this work, electronic effects clearly dominate for **1** to **3** and steric effects for **4** to **6**. Despite

TABLE II

Basicities, electronic and steric parameters of compounds **1–6**

Compound	pK_a	νA_1 (cm^{-1})	Θ (°)
1	3.46	2071.2	143
2	3.94	2073.9	140
3	4.34	2076.0	138
4	5.54	2072.6	131
5	5.58	2071.7	136
6	5.57	2070.9	145

the limitations, the following well-known relations in combination with the constants determined here for the $CH_2CO_2CH_3$ group may be of practical value in predicting the properties of tertiary phosphines bearing this substituent:

$$\delta_P = 62 - \sum \delta_i \qquad (\text{see}^{18};\ \delta_{CH_2CO_2Me} = -10(1))$$

$$\nu_{A_1}[\text{cm}^{-1}] = 2056.1 + \sum \nu_i \qquad (\text{see}^{18};\ \nu_{CH_2CO_2Me} = 7.1(1))$$

$$\Theta[^\circ] = \sum \tfrac{2}{3}_{i/2} \qquad (\text{see}^{14};\ \vartheta_{CH_2CO_2Me} = 69(3))$$

$$\text{pK}_a = 7.85 - 2.67 \sum \sigma_i^* \qquad (\text{see}^{12};\ \sigma^*_{CH_2CO_2Me} = 0.44(3))$$

EXPERIMENTAL

General. Manipulations with phosphines were carried out in the absence of air using standard bench-top and syringe techniques. Solvents were purified and degassed by conventional procedures. The synthesis of starting phosphineacetic acids has been described elsewhere.[6]

Methods. IR: Perkin-Elmer 664 with Data Station 3600, neat liquids or solutions in dichloromethane and toluene, NaCl windows. NMR: Varian XL-200, solutions in d_6-acetone at *ca.* 22°C; ^{1}H- and ^{13}C NMR spectra were referenced to the solvent signal and the shift values were recalculated to the δ-scale (TMS) using the relations $\delta_H(d_6\text{-acetone}) = 2.20$, $\delta_C(d_6\text{-acetone}) = 29.8$; ^{31}P NMR were referenced to external 85% H_3PO_4 ^{13}C and ^{31}P NMR spectra were measured with a broad-band proton decoupling; chemical shifts (δ_H) and coupling constants were obtained by a first-order analysis except for **5** where the CH_3CH_2P fragment needed simulation as an A_3B_2X system. MS: Jeol MS D 100 (75 eV, 300 μA), direct-probe inlet; exact *m/z* values for elemental analysis were measured by peak-matching; metastable transitions in the first field-free region were registered by a defocusing technique. pK_a-Values: the method of Allman and Goel[12] modified for a semi-micro scale; Radiometer PHM 64 instrument with a GK 2302 combination electrode thoroughly pre-conditioned in nitromethane. Substitution reactions with $Ni(CO)_4$: the method of Tolman;[14] no reduction to nickel metal occurred even at 110°C/60 hrs. The calibration of the last two methods with pure triphenylphosphine showed an excellent agreement with the literature values.

Synthetic procedure. A sample of either phosphineacetic acid, its hydrohalide, or its sodium salt (in this last case pre-evaporated with excess HCl) containing 10 milimoles of the carboxyl group was refluxed with 50 ml of a 1% BF_3 solution in methanol until TLC spots (after quenching by water) of the acid and/or acid esters disappeared. This book minutes for the free acids and hours for the hydrohalides. The cooled mixture was then partitioned between saturated aqueous NaCl and methyl acetate, the organic layer was washed with water and dried with sodium sulphate. Fractional distillation afforded the products in given yields.

1: 75%, b.p. 142°C/0.8 torr. Anal. calcd. for $C_{15}H_{15}O_2P$: C, 69.79; H, 5.85; P, 11.99. Found: C, 70.01; H, 5.90; P, 11.83. IR: 1731 vs, 1737 sh ν(C=O); 1261, 1116 s (C—O—C). MS: *m/z*(%): 258($M^{+\cdot}$; 85), 243(5), 227(h; 3), 201(k; 22), 199(j; 38), 186(18), 185(i; 98), 183(100), 165(p; 10), 152(q; 15), 121(m; 52), 105(18), 91(16), 77(31), 51(27).

2: 82%, b.p. 125°C/0.4 torr. Anal. calcd. for $C_{12}H_{15}O_4P$: C, 56. 70; H, 5.95; P, 12.18. Found: C, 56.55; H, 6.00; P, 12.22. IR: 1731 vs ν(C=O); 1265, 1119 vs (C—O—C). MS: 254($M^{+\cdot}$; 17), 223(a; 7), 222(b; 19), 181(c; 13), 153(d; 11), 149(12), 139(e; 100), 121(24), 109(f; 44), 91(15), 78(18), 77(21).

3: 66%, b.p. 126°C/0.8 torr. Anal. calcd. for $C_6H_{15}O_6P$: C, 43.21; H, 6.04; P, 12.38. Found: C, 43.50; H, 6.01; P, 12.14. IR: 1727 vs, b ν(C=O); 1265, 1119 vs (C—O—C). MS: 250($M^{+\cdot}$; 5), 219(a; 12), 218(b; 20), 177(c; 8), 149(d; 4), 145(11), 135(e; 48), 107(24), 103(43), 93(100), 57(17), 42(17).

4: 62%, b.p. 105°C/0.6 torr. Anal. calcd. for $C_7H_{13}O_4P$: C, 43.76; H, 6.82; P, 16.12. Found: C, 43.85; H, 6.73; P, 16.14. IR: 1729 vs, b ν(C=O); 1264, 1119 vs (C—O—C). MS: 192($M^{+\cdot}$; 24), 161(a; 23), 160(b; 36), 119(c; 85), 93(21), 91(d; 53), 87(20), 77(e; 100), 63(40), 45(22), 42(21).

5: 77% b.p. 107–108°C/0.8 torr. Anal. calcd. for $C_8H_{15}O_4P$: C, 46.61; H, 7.33; P, 15.02. Found: C, 46.48; H, 7.51; P, 14.96. IR: 1727 vs, b ν(C=O); 1266, 1116 vs (C—O—C). MS: 206($M^{+\cdot}$; 46), 175(a; 36), 174(b; 47), 133(c; 88), 105(d; 95), 93(48), 91(e; 100), 73(40), 61(f; 19), 59(42), 45(32), 43(40).

6: 80%, b.p. 119–121°C/0.8 torr. Anal. calcd. for $C_9H_{17}O_4P$:C, 49.09; H, 7.78; P, 14.06. Found: C, 48.96; H, 7.78; P, 14.03. IR: 1727 vs, b ν(C=O); 1265, 1116 vs (C—O—C). MS: 220($M^{+\cdot}$; 37), 189(a; 29), 188(b; 17), 147(c; 48), 166(44), 135(27), 119(d; 9), 105(e; 75), 104(100), 103(21), 93(72), 77(44), 73(24).

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