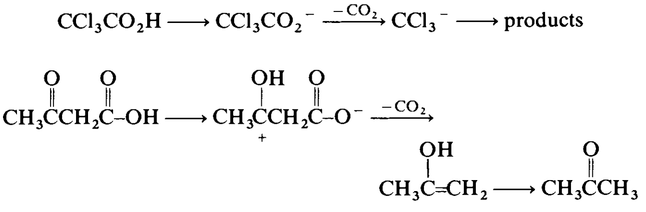
Thermal Stability of Phosphinoacetic Acids

Johannes A. van Doorn* and Nico Meijboom
Koninklijke/Shell-Laboratorium, Amsterdam (Shell Research B.V.), P.O. Box 3003, 1003 AA Amsterdam, The Netherlands

Phosphinoacetic acids decarboxylate smoothly in toluene solution at 99 °C and the corresponding alkylphosphine is formed in quantitative yields. Electron-withdrawing substituents at the α position of the carboxylic acid lead to a large increase in the reaction rate. In contrast, electron-withdrawing substituents at the phosphorus atom lead to a small decrease in the rate. We have concluded from the substituent effects, solvent effects, and the influence of bases and acids that both the lone pair of the phosphorus atom and the carboxylate hydrogen atom play a crucial role in the reaction. A mechanism is proposed that proceeds *via* an ylide. Sodium phosphinocarboxylates do not decarboxylate in an aqueous solution at 95 °C. Instead a carbon–phosphorus bond cleavage occurs probably by an intramolecular nucleophilic substitution.

The thermal stability of carboxylic acids varies greatly. Alkanoic acids generally do not decarboxylate below 300 °C, however, functional groups and heteroatoms have a profound effect on the rate of this reaction and they may cause the decarboxylation to take place at temperatures well below 100 °C. In addition, the functional groups determine by which of the two possible mechanisms the carboxylic acid will decarboxylate. For instance, the decarboxylation of trichloroacetic acid[1] and mercaptoacetic acids[2] proceeds *via* the carboxylate anion and the substituents stabilize the negative charge at the incipient carbanion. By contrast, acetylacetic acids and related compounds first form a zwitterion by an intramolecular protonation before the reaction occurs. The negative charge that develops is accommodated by the cationic centre with formation of a double bond[1] (Scheme 1). The thermal decarboxylation of phosphinoacetic acids has previously been reported on two occasions. Mann *et al.*[3] have observed this reaction during an acid-catalysed hydrolysis of a phosphinoacetic ester. Podlahova and Ludvik[4] have concluded from the weight loss in a thermal gravimetric analysis (TGA) of 1,2-bis-[phenyl(carboxymethyl)phosphino]ethane that a decarboxylation occurs. No details were given and the mechanism by which the reaction proceeds is not known. We have studied the reaction in more detail in order to elucidate this mechanism.

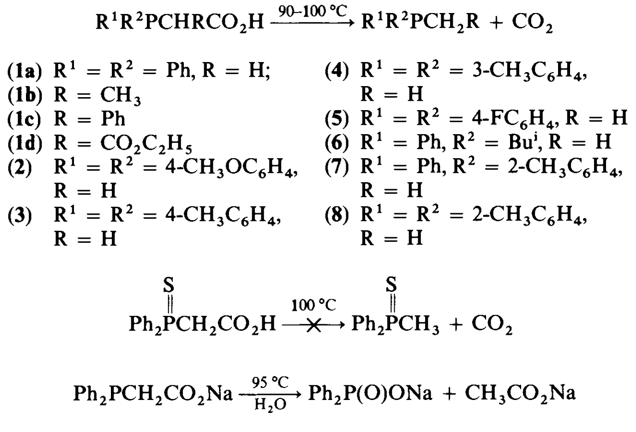


$CCl_3CO_2H \longrightarrow CCl_3CO_2^- \xrightarrow{-CO_2} CCl_3^- \longrightarrow$ products

$CH_3\overset{O}{\overset{\|}{C}}CH_2\overset{O}{\overset{\|}{C}}\text{-}OH \longrightarrow CH_3\underset{+}{\overset{OH}{\overset{|}{C}}}CH_2\overset{O}{\overset{\|}{C}}\text{-}O^- \xrightarrow{-CO_2} CH_3\overset{OH}{\overset{|}{C}}{=}CH_2 \longrightarrow CH_3\overset{O}{\overset{\|}{C}}CH_3$

Scheme 1.

Two reports exist on the thermal stability of phosphinocarboxylates. Issleib and Zimmermann[5] have shown that a complex of Ni^{II} and diphenylphosphinobenzoic acid decomposes exothermally at 135 °C. However, the exact structure of the products was not determined. Podlahova and Podlaha[6] have found that a carbon–phosphorus bond cleavage occurs when the sodium salt of 1,2-bis(dicarboxymethylphosphino)ethane, a phosphorus analogue of ethylenediaminetetra-acetic acid, is heated in an aqueous alkaline solution at 80 °C. We have studied the cleavage reaction of phosphinoacetic acids as a function of substituents.



$R^1R^2PCHRCO_2H \xrightarrow{90\text{–}100\,°C} R^1R^2PCH_2R + CO_2$

(**1a**) $R^1 = R^2 = Ph, R = H$;
(**1b**) $R = CH_3$
(**1c**) $R = Ph$
(**1d**) $R = CO_2C_2H_5$
(**2**) $R^1 = R^2 = 4\text{-}CH_3OC_6H_4, R = H$
(**3**) $R^1 = R^2 = 4\text{-}CH_3C_6H_4, R = H$
(**4**) $R^1 = R^2 = 3\text{-}CH_3C_6H_4, R = H$
(**5**) $R^1 = R^2 = 4\text{-}FC_6H_4, R = H$
(**6**) $R^1 = Ph, R^2 = Bu^t, R = H$
(**7**) $R^1 = Ph, R^2 = 2\text{-}CH_3C_6H_4, R = H$
(**8**) $R^1 = R^2 = 2\text{-}CH_3C_6H_4, R = H$

$Ph_2\overset{S}{\overset{\|}{P}}CH_2CO_2H \xrightarrow[\times]{100\,°C} Ph_2\overset{S}{\overset{\|}{P}}CH_3 + CO_2$

$Ph_2PCH_2CO_2Na \xrightarrow[H_2O]{95\,°C} Ph_2P(O)ONa + CH_3CO_2Na$

Scheme 2.

Results

We have found that decarboxylation occurs exclusively with phosphinoacetic acids. Diphenylphosphinoacetic acid (**1a**) readily forms diphenylmethylphosphine and carbon dioxide, in a [$^2H_8$]toluene solution at 90–100 °C. By contrast, the corresponding ω-phosphinopropionic and butyric acids are stable for 15 h at 200 °C in the melt. Unexpectedly, the sulphide of diphenylphosphinoacetic acid is perfectly stable for 21 h at 100 °C in tetrachloroethane. Solutions of the sodium carboxylate in water are not stable at 95 °C because of phosphorus–carbon bond cleavage ($k = 3.3 \pm 0.1\ 10^{-5}\ s^{-1}$ at 95.1 °C, see Scheme 2) but no decarboxylation can be observed.

In order to obtain information on the mechanism of the decarboxylation reaction we wanted to study the rate of the reaction as a function of substituent and added acid and base. Unfortunately, a plot of log *C versus* time for the decomposition of diphenylphosphinoacetic acid in a [$^2H_8$]toluene solution at 99.2 °C does not give a straight line, as would be expected for a first-order process. Instead a curved line is obtained and the apparent rate constant of the reaction gradually increases with an increase in the conversion of the carboxylic acid (See Figure 1). Furthermore, we have found that the apparent rate constant increases upon dilution: the rate for a 0.1 mol dm^{-3} solution being larger than that for a 0.2 mol dm^{-3} solution. However, on a log *C* plot the line obtained for the 0.1 mol dm^{-3} solution has exactly the same shape as that of the 0.2 mol dm^{-3} solution after 50% conversion. Separate experiments have shown that this increase in rate is not the result of an autocatalytic process

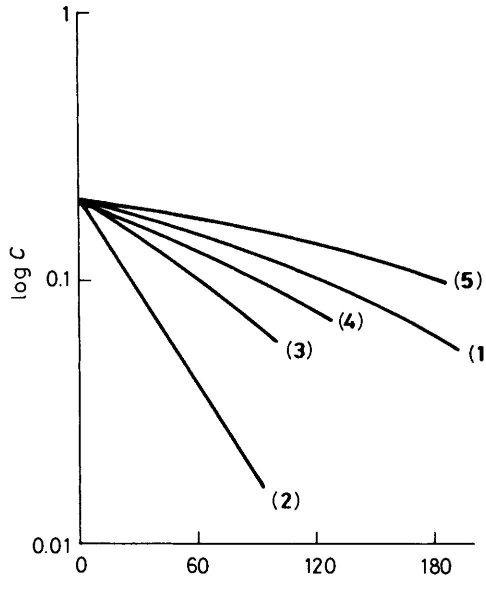


Figure 1. Plot of log *C versus t* for various phosphinoacetic acids. Reaction in [$^2H_8$]toluene at 99.2 °C.

Table 1. Conversion of (**1a**) in [$^2H_8$]toluene as a function of concentration and temperature.

Temp./°C	C_0/mol dm^{-3}	$t_{\frac{1}{2}}$/h
80.8	0.2	12
90.2	0.2	3.7
99.1	0.2	2
99.1	0.1	1.5
107.9	0.2	0.4
107.9	0.05	0.3

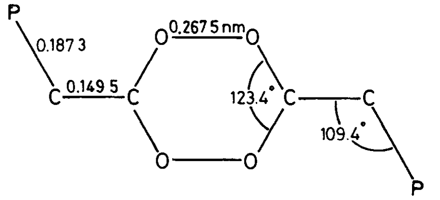
Table 2. Conversion of various phosphinoacetic acids.[a]

Compound	$t_{\frac{1}{2}}$	δ ^{31}P of $R^1R^2PCH_2R$
(**1a**)	120 m[b]	−27.6
(**1b**)	14 h	−12.3
(**1c**)	5 m[c]	−10.5
(**1d**)	⩽0.1 h at 20 °C[d]	
(**2**)	27 m	
(**3**)	60 m	−24.7
(**4**)	96 m	−28.0
(**5**)	190 m	
(**6**)	29 m[e]	−36.4
(**7**)	110 m	−32.1
(**8**)	150 m[f]	−42.1

[a] 0.2 mol dm^{-3} in [$^2H_8$]toluene at 99.2 °C; see Figure 1. [b] k = 3.10^{-4} s^{-1}; K = 0.03 mol dm^{-3}. [c] The acid dissolves completely at the reaction temperature. [d] The acid decarboxylates as it is formed by acidification of the lithium salt. [e] k = 6.10^{-4} s^{-1}; K = 0.36 mol dm^{-3}. [f] k = 1.10^{-4} s^{-1}; K = 0.36 mol dm^{-3}.

caused by the product, the feebly basic diphenylmethylphosphine. Deliberate addition of 1 equiv. of this compound at the beginning of the reaction gives exactly the same curve as that obtained without added product.

It is a well-known fact that carboxylic acids are hydrogen-bridged dimers in the solid state and that the dimer and the monomer may coexist in apolar solutions.[7] Similar structures have been observed with phosphinocarboxylic acids[8,9] and protonated phosphinocarboxylic acids.[10] It has further been confirmed by *X*-ray analysis[11] that diphenylphosphinoacetic acid is a classical hydrogen-bridged cyclic dimer in the solid state. The i.r. spectrum of a solution of diphenylphosphinoacetic acid in toluene (0.1–0.005 mol dm^{-3}) shows a strong absorption at 1 702.2 cm^{-1}. A small peak is present at 1 740 cm^{-1}, but this peak does not become stronger upon dilution. Thus, in solution and at room temperature the compound is predominantly present as a dimer. However, it is to be expected that appreciable amounts of monomer will be present at elevated temperatures. The kinetics of the reaction suggest that the monomer undergoes the decarboxylation reaction and that the dimer is relatively stable. On dilution or consumption by reaction the dimer–monomer equilibrium shifts to the monomer side and thus the rate increases. We have attempted to find the rate constant *k* and the equilibrium constant *K* by a computer simulation. Indeed we were able to find a value for both constants that leads to a perfect simulation of the observed line. Unfortunately, it appears that this solution is not unique and in fact an infinite amount of mathematically correct solutions exist. Therefore we had to derive these constants by comparing the apparent rate constants at various stages in the conversion. According to Ostwald's law:



$$[R^1R^2PCHRCO_2H]_2 \overset{\text{fast}}{\rightleftharpoons} R^1R^2PCHRCO_2H \xrightarrow{\text{slow}} R^1R^2PCH_2R$$

Scheme 3.

$$K_{t=0} = \frac{\alpha^2 C_0}{1-\alpha} = K_{t=n} = \frac{\alpha_n^2 C_0}{1-\alpha_n}$$ assuming first-order kinetics $C_{t=n} = nC_0$, $n = 1$-conversion

This equation leads to:

$$\alpha_n = \frac{f^2 - 1/n}{f - 1/n}, \quad \text{where } f = \frac{\alpha_n}{\alpha_0} = \frac{k_n}{k_0}; \quad k = \frac{k_{\text{obs}}}{\alpha}$$

Thus from the ratio of the apparent rate constants at t_0 and t_n, the degree of dissociation α, the equilibrium constant *K* and the rate constant *k* can be calculated. In this way we have derived the values α = 0.24, *K* = 0.03 mol dm^{-3}, and *k* = 3.10^{-4} s^{-1} for the reaction of (**1a**) at 99.2 °C in [$^2H_8$]toluene. The values for α and *K* are well within the range obtained for hexanoic acid in benzene.[7a] Furthermore, the value for *k* obtained in this way is close to the apparent rate constant at very high conversion (>85%).

We have not analysed the curves for all the compounds in this way because we have found that the data are not very accurate in all cases. In particular, if the curve is relatively flat, poor results are obtained. We found it convenient in most cases to use the $t_{\frac{1}{2}}$ value, *i.e.* the time in which half of the starting material is converted (see Tables 1 and 2), for 0.2 mol dm^{-3} solutions.

The electronic nature of substituents at the α position of the phosphinocarboxylic acid has a profound effect on the rate of the decarboxylation reaction (see Table 2). It appears that electron-withdrawing substituents lead to a very fast conversion of the acid. We have calculated from the shape of the line of log *C versus t* that *ca.* 25% of (**1a**) is present as the monomer at the reaction temperature. It is likely that the amount of monomer

Table 3. Decarboxylation of (**1a**) in various solvents.[a]

Solvent	$t_{\frac{1}{2}}$/h	ε
[$^2H_8$]toluene	2	2.4
[$^2H_5$]bromobenzene	1.6	5
1,2-dichlorobenzene	1.4	9.9
[$^2H_6$]DMSO	13	46.7
[$^2H_7$]DMF	30	36.7
[$^2H_5$]pyridine	9	12.3
$CF_3CF_2CF_2CO_2H$ + 20% [$^2H_8$]toluene[b]	no reaction in 2 h	—

[a] 0.2 mol dm^{-3} at 99.2 °C. [b] In this medium the phosphorus atom is protonated according to n.m.r. spectroscopy.

Table 4. Rate of carbon–phosphorus bond cleavage of $Ar_2PCHRCO_2$-Na.[a]

Ar	R	$t_{\frac{1}{2}}$/h	$k/10^{-5}$ s^{-1}
Ph	H	5.8	3.3 ± 0.1
Ph	CH_3	11.5	1.64 ± 0.03
4-$CH_3C_6H_4$	H	27[b]	0.5 ± 0.2[b]
4-FC_6H_4	H	10.5	1.82 ± 0.03
3-FC_6H_4	H	16.5	1.03 ± 0.03

[a] 0.2 mol dm^{-3}, 0.8 mol dm^{-3} NaOH, 95.1 °C. [b] Estimate $t_{\frac{1}{2}}$, precipitation of material prevents accurate measurement of k.

for (**1b**–**d**) will be different. However, a possible increase in the amount of monomer could at the most account for an increase of the rate constant by a factor of four. Thus it is clear that the increase in the rate observed when electron-withdrawing groups are attached to the α-carbon atom must be ascribed mainly to an increase in the rate constant of the decarboxylation reaction.

The electronic nature of substituents R^1 and R^2 attached to the phosphorus atom has a less profound effect on the rate of the reaction: by varying the electronic properties of R^1 and R^2 whilst keeping their steric influence constant as in compounds (**1a**), and (**2**)–(**6**) we have found that electron-withdrawing substituents lead to a small decrease in the reaction rate (see Figure 1). Analysis of the curve obtained for compound (**6**) as depicted above reveals that this decrease is due both to a shift in the dimer–monomer equilibrium to the dimer side and to a small decrease in the rate constant of the decarboxylation reaction (see Table 1).

In addition, we have found that the rate constant of the decarboxylation is moderately decreased in sterically congested phosphinoacetic acids. The value obtained for bis(2-tolyl)-phosphinoacetic acid is 1×10^{-4} s^{-1}.

Solvents may have a major effect on the rate of the decarboxylation reaction of (**1a**), see Table 3. It appears that the solvents [$^2H_6$]DMSO, [$^2H_7$]DMF, and [$^2H_5$]pyridine, which can all form a hydrogen bond with the carboxylic acid, lead to a large increase of the $t_{\frac{1}{2}}$ value, *i.e.* a large decrease in the reaction rate. Compound (**1a**) showed no detectable decarboxylation within 2 h at 99.2 °C in a mixture of perfluorobutyric acid and [$^2H_8$]toluene (4:1, v/v). N.m.r. spectroscopy indicates that the phosphorus atom is protonated in this mixed solvent.

We have found in another series of solvents (which are neither acids, nor bases, and which do not bind to the carboxylic acid) that an increase in the relative permittivity of the solvent leads to an increase in the rate.

We have observed that sodium diphenylphosphinoacetate decomposes readily in an aqueous solution of sodium hydroxide at 95 °C. According to ^{13}C n.m.r. spectroscopy, sodium acetate and sodium diphenylphosphinate are formed as the only products. The phosphinate is probably a secondary product derived from diphenylphosphine oxide. In an independent experiment we have found that this oxide is converted into the phosphinate under the reaction conditions. It appears that there is no simple relation between the rate of the cleavage reaction and the electronic nature of the aryl group (see Table 4). Both electron-donating and electron-withdrawing substituents lead to a decrease in the reaction rate. The cleavage reaction is not observed with 3-diphenylphosphinopropionic acid and 2-diphenylphosphinobenzoic acid. Both compounds are perfectly stable in an alkaline solution at 95 °C for 20 and 65 h, respectively.

Discussion

The very large effect exerted on the rate of the decarboxylation reaction by the electronic nature of the substituent at the α-carbon atom clearly shows that, as expected, a negative charge is developed at that atom.[1] Obviously, one would expect that electron-withdrawing substituents at the phosphorus atom would also lead to an increase in rate. However, the rate constant is slightly decreased and this suggests that a more basic phosphorus atom leads to an increase in the rate of decarboxylation.*

In Figure 2(*a*) we have plotted the $t_{\frac{1}{2}}$ value of the decarboxylation reaction of $R^1R^2PCH_2CO_2H$ *versus* the value of $\chi_{R^1R^2}$. Figure 2(*b*) shows a plot of the $t_{\frac{1}{2}}$ value of $R_2PCH_2CO_2H$ *versus* the pK value of the corresponding tertiary phosphine R_3P. Both plots suggest that indeed a relation does exist between the basicity of the phosphorus atom and the rate of the decarboxylation. However, the point for the sterically congested compound (**8**) deviates from both curves. The rate is lower, as is to be expected from the pK value. The crucial role that the lone pair of the phosphorus atom plays in the mechanism was further demonstrated in other experiments. If the lone pair is used in bonding of a sulphur atom or a proton then the phosphinoacetic acid does not decarboxylate at 100 °C.

An equally important role is played by the carboxylic hydrogen. If this hydrogen is bonded by a hydrogen bridge to another carboxylic acid (dimerization) or to solvents such as DMF, DMSO, and pyridine then the decarboxylation reaction is retarded or does not occur at all. If the proton is totally absent, as in the carboxylate anion, no ready decarboxylation is observed ($k < 3 \times 10^{-5}$ s^{-1}).

We propose a mechanism in which the carboxylate hydrogen protonates the phosphorus atom. The resulting zwitterion, a phosphonium carboxylate, which obviously cannot be formed in the presence of strong acids or bases, will readily lose carbon dioxide, analogous to triphenylphosphonium carboxylate ion.[13] The negative charge at the incipient carbanion is stabilized by the positively charged phosphorus atom and an ylide is formed as an intermediate. Ylides in which the phosphorus atom bears a hydrogen atom are known compounds, and their stability is governed by the electronic nature of the substituents attached to both the phosphorus atom and the ylidic carbon atom.[14] With the array of substituents as obtained by decarboxylation of the phosphinocarboxylic acids the alkylphosphine will be more stable than the corresponding ylide and consequently the alkylphosphine will be formed by a hydrogen shift. Molecular models show that considerable steric hindrance is present in the ylide

---

* These findings are completely in line with observations made by Issleib *et al.*[12] These authors were able to purify primary phosphinoacetic acids ($R^1 = R^2 = H$, $\chi_{R^1R^2} = 16.6$) by a vacuum distillation (R = H, b.p. 70–72 °C/6 mm Hg; R = CH_3, b.p. 73–74 °C/5 mmHg) whereas a distillation was not advantageous for phosphinoacetic acids with more electron-donating substituents (R^1 = H, R^2 = Ph, cyclohexyl, C_2H_5, R = H; R^1 = H, R^2 = Ph, R = CH_3).

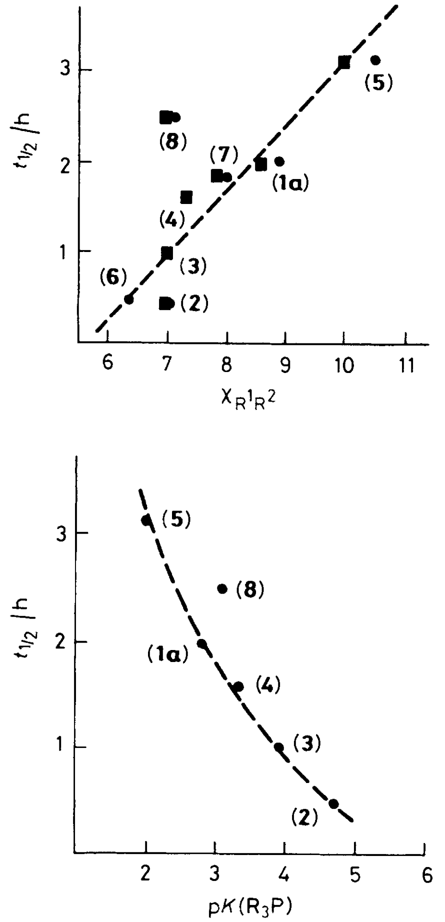
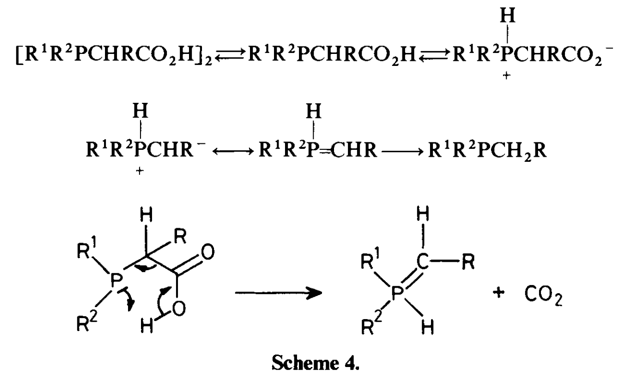


Figure 2. (*a*) Plot of $t_{\frac{1}{2}}$ value of the compounds $R^1R^2PCH_2CO_2H$ *versus* the electronic parameter $\chi_{R^1R^2}$ ■ data from ref. 18, ● data from ref. 19; 2(*b*) plot of $t_{\frac{1}{2}}$ value of the compounds $R_2PCH_2CO_2H$ *versus* the p*K* value of R_3P.[20]

derived from (**8**). Consequently this ylide will be destabilized and this may account for the fact that compound (**8**) decarboxylates at a relatively low rate.



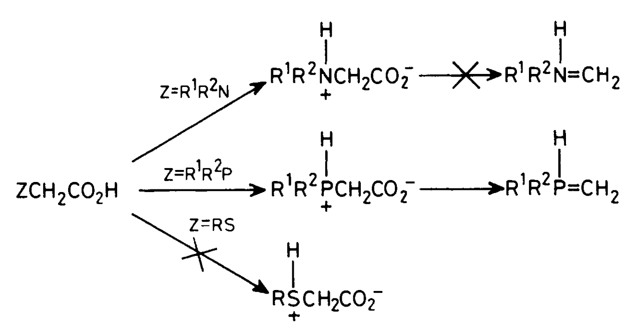
$$[R^1R^2PCHRCO_2H]_2 \rightleftarrows R^1R^2PCHRCO_2H \rightleftarrows R^1R^2\overset{H}{\underset{+}{P}}CHRCO_2^-$$

$$R^1R^2\overset{H}{\underset{+}{P}}CHR^- \longleftrightarrow R^1R^2\overset{H}{P}{=}CHR \longrightarrow R^1R^2PCH_2R$$

Scheme 4.

We wonder whether the phosphonium carboxylate is a distinct intermediate in an apolar solvent. It may be that the decarboxylation occurs simultaneously with the protonation of the phosphorus atom.

The unique combination that exists when Z = R^1R^2P, *viz*. that the phosphorus atom is both a basic centre and is able to form ylides, explains the relatively high decarboxylation rate for phosphinoacetic acids. Both amino and mercaptoacetic acids are thermally much more stable.



Conclusions

Diphenylphosphinoacetic acids decarboxylate readily at a relatively low temperature in apolar solvents. In the so-called complexing solvents, and in basic solvents or at high concentrations the compounds are stabilized due to hydrogen bonding. The presence of the lone pair at the phosphorus atom is essential for the reaction to occur and furthermore, the basicity of the phosphorus atom plays a crucial role in the mechanism. The reaction proceeds *via* a zwitterion that decarboxylates to form an ylide and a subsequent hydrogen shift leads to an alkylphosphine. This mechanism is strongly reminiscent of the mechanism of the decarboxylation of keto-acids and malonic acid and differs from that of mercaptoacetic and trichloroacetic acids.

Experimental

Manipulations with phosphines were either performed in an argon atmosphere using Schlenk techniques or under nitrogen in a glove box. Solvents were dried with sodium wire or with molecular sieves. The synthesis of the phosphinocarboxylic acids was reported before.[16] Diphenylphosphinobenzoic acid was prepared according to ref. 17. The conversion of the acids was monitored by measurement and integration of the ^{31}P and ^1H n.m.r. spectra at regular intervals. The spectra were measured with Varian 200 and 300 MHz spectrometers.

Attempted Synthesis of 2-*Ethoxycarbonyl*-2-*diphenylphosphinoacetic Acid*.—To a solution of lithium di-isopropylamide, prepared from 23 cm^3 of butyl-lithium (1.6 mol dm^{-3} in hexane) and 5.2 cm^3 of di-isopropylamine, in 100 cm^3 of diethyl ether was added 10.0 g of ethyldiphenylphosphinoacetate at 0 °C in 15 min with stirring. The mixture was stirred for 1 h at 0 °C and subsequently a rapid stream of CO_2 was passed through the solution. Water was added, the aqueous layer was separated and hydrochloric acid was added until pH 3. A thick oil separated off, from which bubbles readily developed. The eventual product was pure starting material. This ester itself is not soluble in a 10% NaOH solution and this clearly shows that initially a carboxylic acid had been obtained.

Acknowledgements

We are indebted to J. B. van Mechelen for allowing us to use some data of the crystal structure determination of diphenylphosphinoacetic acid prior to publication and to E. Dorland for practical assistance.

References

1 'Methoden der Organischen Chemie (Houben-Weyl),' Thieme Verlag, Stuttgart, 1952, vol. 8, p. 484.

2 (*a*) K. Uneyama, W. Tagaki, I. Minamida, and S. Oae, *Tetrahedron*, 1968, **24**, 5271; (*b*) S. Oae, W. Tagaki, K. Uneyama, and I. Minamida, *ibid*., p. 5283.

3 F. G. Mann, B. P. Tong, and V. P. Wystrack, *J. Chem. Soc.*, 1963, 1155.
4 J. Ludvik and J. Podlahova, *J. Inorg. Nucl. Chem.*, 1978, **40**, 967.
5 K. Issleib and H. Zimmermann, *Z. Anorg. Allgm. Chem.*, 1967, **353**, 197.
6 J. Podlahova and J. Podlaha, *Collect. Czech Chem. Commun.*, 1983, **48**, 1552.
7 (*a*) O. Levy, G. Y. Markovits, and I. Perry, *J. Phys. Chem.*, 1975, **79**, 239; (*b*) S. Kopacz, J. Kalembkiewicz, and J. Szantulja, *J. Gen. Chem. USSR*, 1984, **54**, 639; (*c*) 'The Chemistry of Functional Groups,' ed. S. Patai, suppl. B: 'The Chemistry of Acid Derivatives. Part 1,' John Wiley and Sons, New York, 1979, ch. 6.
8 K. Issleib and R. Kümmel, *Chem. Ber.*, 1967, **100**, 3331.
9 J. Podlahova, *Collect. Czech. Chem. Commun.*, 1978, **43**, 57.
10 J. Podlahova, B. Kratochvil, V. Langer, J. Silha, and J. Podlaha, *Collect. Czech. Chem. Commun.*, 1981, **46**, 3063.
11 J. B. van Mechelen, to be published.
12 K. Issleib, R. Kümmel, and H. Zimmermann, *Angew. Chem., Int. Ed. Engl.*, 1965, **77**, 172.
13 W. J. Considine, *J. Org. Chem.*, 1962, **27**, 647.
14 O. I. Kolodiazhnyi, *Tetrahedron Lett.*, 1980, **21**, 2269.
15 'Methoden der Organischen Chemie (Houben–Weyl),' Thieme Verlag, Stuttgart, vol. 11/1, p. 991.
16 J. A. van Doorn and N. Meijboom, *Phosphorus Sulfur*, in press.
17 *Inorg. Synth.*, 1982, **21**, 175.
18 C. A. Tolman, *Chem. Rev.*, 1977, **77**, 313.
19 T. Bartik, T. Himmler, H. G. Schulte, and K. Seevogel, *J. Organomet. Chem.*, 1984, **272**, 29.
20 T. Allman and R. G. Goel, *Can. J. Chem.*, 1982, **60**, 716.

Received 7th December 1988; *Paper* 8/04832K