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Approaches to water-soluble phosphines

II. Free radical addition reactions of phenylphosphines

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Abstract

Free radical additions of diphenylphosphine, phenylphosphine and ethylenebis(phenylphosphine) to the following species are described: alkynols, alkyne ethers, unsaturated carboxylic acids and esters and β-lactones. In a number of cases, these lead to water-soluble phosphines. NMR spectroscopic characterization of all new products has been carried out.

Key words: Phosphine; Water soluble phosphines; Radical addition; Chirality

1. Introduction

We recently [1] described the preparation of water-soluble phosphines derived from allyl ethers of glycerine and several monosaccharides, which were subjected to a regioselective free radical addition of phenyl- and diphenylphosphine. In earlier work [2], we had described the free radical addition of diphenylphosphine to alkynes and allenes, the former also reacting in a regioselective manner. It thus appeared to us that the addition of phosphines under free radical conditions should provide a useful alternative to the well-known basic addition procedure [3–5] and, when applied to suitable substrates, should lead to further water-soluble phosphines, which could in addition be chiral. The present paper describes investigations carried out towards this end.

2. Results and discussion

2.1. Reactions of diphenylphosphine with alkynols and alkynyl ethers

The free radical addition of diphenylphosphine to 1-alkynes [2] is regiospecific, the $Ph_2P^{\cdot}$ radical attacking the terminal carbon atom, and is thus analogous to the hydrostannylation of such alkynes [6]. In contrast, alkynols and alkynyl ethers react non-regiospecifically with triorganotin hydrides, and so it appeared of interest to extend the addition of diphenylphosphine to include such species. This reaction can, in principle, give two regioisomers, as depicted in Scheme 1.

The detailed results are summarized in Table 1. The reactions were generally carried out in the presence of catalytic amounts of AIBN at 80°C; under UV irradiation conditions, the results are similar. Although NMR analysis showed that the products were formed in high yields, losses during work-up were high because of the small scale used, so that yields of isolated products were relatively poor.

The regiochemistry of the reaction apparently depends on two factors: (a) the distance of the oxygen atom from the triple bond; and (b) the number of substituents on the α-carbon atom. When the oxygen atom is bonded directly to the β-carbon atom, the reaction is regiospecific, as observed for 1-alkynes, whereas propargylic alcohols and esters give both regioisomers. Increasing substitution at the α-carbon atom results in terminal addition of the diphenylphosphino moiety. Isomer identification was carried out by multinuclear NMR spectroscopy; differentiation between *E* and *Z* isomers is based on the principles

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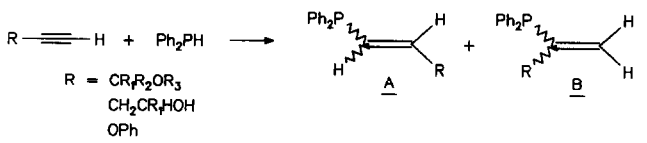


Scheme 1.

described previously [2]. Structure-relevant NMR data are listed in Tables 2 and 3. The water-solubility of all products obtained was unfortunately negligible.

2.2. *Reactions involving addition of phosphines to unsaturated carboxylic acids and esters*

Although the free radical addition of primary phosphines to carboxylic esters was reported previously [7], no spectroscopic proof of the structure of the adducts was provided. Addition reactions of secondary phosphines are known, but only base-catalysed reactions with unsaturated carboxylic esters have so far been carried out [8]. The resulting diphenylphosphinopropionic esters can be converted into the corresponding carboxylic acids by saponification.

TABLE 1. Consumption of starting material, reaction conditions, boiling points and yields of isolated product in additions of diphenylphosphine to alkynes to give products of the type $RHC=CHPPh_2$ (*E*/*Z*-**A**) and $H_2C=CRPPh_2$ (**B**) (Product ratios from ^{31}P NMR)

R	Reaction conditions	Cons. (%)	b.p. (°C/mmHg)	Isolated yield (%)	Amount *Z*-**A** (%)	Amount *E*-**A** (%)	Amount **B** (%)
CH_2OMe	4.5d [b]	35	$85–96/10^{-3}$	32	40	40	20
CHMeOH	4.5d [b]	45	$105–120/5\times10^{-2}$	16	50	20	30
CHPrOH	3.5d [c]	90	$150–160/5\times10^{-2}$	44	40	35	25
CHPrOH	4d [b]	90	–	–	50	25	25
CMe_2OH	4.5d [b]	80	$125–135/10^{-2}$	15	70	30	Trace
CEtMeOH	4.5d [b]	80	$130–136/5\times10^{-3}$	19	68	30	2
c-HexOH [a]	8.5d [b]	90	$180–185/10^{-3}$	5	60	35	5
CH_2CH_2OH	8.5d [b]	60	$90–115/10^{-3}$	36	85	10	5
$CH_2CHMeOH$	2.5d [b]	65	$125–132/5\times10^{-3}$	20	70	20	10
OPh	2.5d [b]	100	–	–	n.o. [d]	n.o.	n.o.

[a] 1-hydroxycyclohexyl. [b] In the presence of a catalytic amount of AIBN at 80°C. [c] Under UV irradiation at room temperature. [d] n.o., not observed.

TABLE 2. ^{31}P and ^{13}C chemical shifts (in ppm) and carbon–phosphorus coupling constants (in Hz) for the compounds of the type $R(H)^2C=^1C(H)PPh_2$ (*E*/*Z*-**A**) and $PPh_2(R)^1C=^2CH_2$ (**B**) (with $^3C = C\alpha$ to the double bond)

R	Isomer	$\delta(^{31}P)$	$\delta(^1C)$	$\delta(^2C)$	$\delta(^3C)$	$^1J(P^1C)$	$^2J(P^2C)$	$^3J(P^3C)$
CH_2OMe	*Z*-**A**	−31.3	h. [a]	142.8	70.2	h.	20.9	24.2
	E-**A**	−15.4	h.	141.9	73.2	h.	27.5	14.5
	B	−9.8	124.6	144.3	74.1	10.2	17.4	23.0
CHMeOH	*Z*-**A**	−32.3	127.1	150.3	65.7	13.3	20.3	24.2
	E-**A**	−15.8	h.	153.0	68.3	h.	18.3	13.3
	B	−12.4	125.0	153.0	69.9	12.7	18.3	30.3
CHPrOH	*Z*-**A**	−32.5	h.	149.6	69.2	h.	21.5	22.9
	E-**A**	−16.0	125.6	149.5	72.0	10.7	27.9	12.7
	B	−12.8	132.9	152.1	73.6	10.3	18.1	18.1
CMe_2OH	*Z*-**A**	−32.0	124.4	153.7	71.2	12.6	16.8	12.8
	E-**A**	−16.3	122.8	154.0	69.6	10.6	29.1	0
	B	−17.2 [b]						
CEtMeOH	*Z*-**A**	−31.9	125.0	152.8	73.7	11.6	16.1	12.1
	E-**A**	−15.9	123.9	153.0	70.8	10.3	28.6	0
	B	−15.4						
c-HexOH	*Z*-**A**	−31.2	125.1	154.1	72.3	11.8	15.4	12.6
	E-**A**	−15.8	123.6	154.1	73.9	10.7	34.2	0
	B	−17.0						
CH_2CH_2OH	*Z*-**A**	−32.7	h.	143.6	34.3	h.	22.1	20.3
	E-**A**	−15.1	h.	h.	38.1	h.	h.	12.7
	B	−4.9						
$CH_2CHMeOH$	*Z*-**A**	−33.1	129.8	143.5	40.1	9.9	24.3	19.5
	E-**A**	−15.2	130.3	143.2	44.4	11.5	28.8	12.2
	B	−5.0	124.7	145.2	45.8	8.0	17.4	20.9

[a] h., hidden. [b] Uncertain.

TABLE 3. ^1H chemical shifts (in ppm) and proton–phosphorus coupling constants (in Hz) for the compounds of the type $RC(^1H) = C(^2H)PPh_2$ (*E/Z*-**A**) and $RC(PPh_2)C = C^2H^1H$ (**B**) (with ^1H *trans* to the phosphorus atom)

R	Isomer	$\delta(^1H)$	$\delta(^2H)$	$^nJ(^1H^2H)$	$^3J(P^1H)$	$^nJ(P^2H)$
CH_2OMe	*Z*-A	6.47	6.22	12.6	29.7	< 2
	E-A	6.20	6.48	16.7	13.5	8.8
	B	5.28	6.00	1.5	8.7	12.3
CHMeOH	*Z*-A	6.46	6.32	11.5	23.4	3.0
	E-A	h. [a]	h.	h.	h.	h.
	B	5.03	6.01	1.2	8.2	15.5
CHPrOH	*Z*-A	6.46	6.33	11.5	22.5	0
	E-A	6.17	h.	16.7	13.8	h.
	B	5.00	5.91	< 2	7.2	15.6
CMe_2OH	*Z*-A	6.60	6.22	12.3	27.1	3.3
	E-A	6.83	6.49	16.8	14.5	7.0
CEtMeOH	*Z*-A	6.50	6.28	12.5	27.3	3.8
	E-A	6.23	6.47	16.3	16.3	5.3
	B	5.02	5.93	< 2	6.3	11.3
c-HexOH	*Z*-A	6.62	6.23	12.2	27.6	3.3
	E-A	6.33	6.53	16.8	14.8	6.9
	B	4.97	5.99	< 2	7.2	11.6
CH_2CH_2OH	*Z*-A	6.33	6.48	11.5	22.9	< 2
	E-A	h.	h.	h.	h.	h.
	B	5.04	5.71	< 2	8.7	18.8
$CH_2CHMeOH$	*Z*-A	6.51	6.37	11.7	22.6	1.6
	E-A	6.30	h.	16.8	14.6	h.
	B	4.97	5.69	1.5	7.9	17.8

[a] h., hidden.

The free radical addition pathway has two general advantages: (a) an aqueous workup is not necessary; (b) the phosphine can be added directly to the unsaturated carboxylic acid, thus eliminating the saponification step.

2.2.1. Free radical additions of diphenylphosphine

We find that the products obtained by free-radical addition are identical to those arising from the base-catalysed reaction [8]. The results are summarized in Table 4. The conversion of the esters into the sodium salts of the free acids can be brought about by treating a solution of the ester in deoxygenated ethanol/water with deoxygenated sodium hydroxide solution and heating the mixture under reflux. The sodium salts are highly water-soluble, and can readily be converted into the free acids. Attempts to eliminate the saponification step by adding the phosphine directly to substituted acrylic acids were moderately successful; the reaction occurred in a regioselective manner and in fairly high yields, and no by-products were detected. The ^{31}P chemical shifts for the free acids are in agreement with those reported previously [8].

TABLE 4. Consumption of starting material, NMR yield and reaction conditions for reactions of unsaturated compounds of the type $CR_3R_1 = CR_2 - COOR$ with diphenylphosphine (R_3 = H, if not otherwise stated)

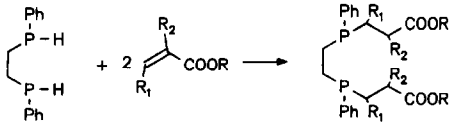
R_1/R_3	R_2	R	Reaction conditions	Phosphine consumption	Yield (%)
H	H	Me	3d, 80°C	100	98
H	Me	Me	2.5d, 80°C	100	100
COOEt [a]	H	Et	2.5d, 80°C	90	90
COOMe [b]	H	Me	6d, 80°C	90	90
Me/NH_2	H	Me	6d, 80°C	0	0
C(O)–	H	–	2.5d, 80°C	60	10
Ph	H	H	1.5d, 80°C, MeOH	40	40 [c]
Me	Me	H	6d, 80°C	60	60
Me	Me	H	6d, 80°C, MeOH	40	40

[a] *trans*. [b] *cis*. [c] Isolated yield: 18% with m.p. 158–160°C (from methanol).

2.2.2. Addition reactions of ethylenebis(phenylphosphine)

Free radical additions of ethylenebis(phenylphosphine) to unsaturated compounds have not previously been described, although some base-catalysed reactions with vinyl phosphines are known [9–12]; the latter lead to compounds in which both phosphorus atoms of the diphosphine are bonded to terminal carbon atoms of the vinylic moiety.

We find that the free radical addition of ethylenebis(phenylphosphine) to acrylic esters and acids occurs regioselectively, leading to products of the type shown in Scheme 2.



Scheme 2.

Details are given in Table 5. In three cases, small to moderate amounts of 1:1 adducts were formed as by-products, such an adduct indeed being the sole product when the reactions were carried out in the dark. As the bisphosphine used was a mixture of both diastereomers, the resulting addition products were also mixtures. In the case of methyl acrylate only two diastereomers are formed, but with substituted acrylic esters additional chiral centres were formed, leading to complex mixtures which could be characterized by ^{31}P NMR spectroscopy (see Section 3). The esters were saponified, and the water-soluble sodium salts converted into the free acids. Details are given in Section 3.

2.3. Reactions between phosphines and β-lactones

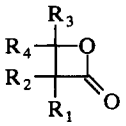
Cleavage reactions of β-lactones induced by various compounds containing polarized single bonds have been described previously [13–21]. Depending on the

TABLE 5. Consumption of starting material, NMR yield, ratio of 2:1 to 1:1 adduct and reaction conditions for reactions of ethylenebis(phenylphosphine) with acrylates of the type $R_1HC = CR_2-C(O)OR$

R_1	R_2	R	Reaction conditions	Phosphine consumption (%)	Yield (%) 2:1	Yield (%) 1:1
H	H	Me	9d, AIBN, 80°C	100	90	0
Me	H	Et	9d, AIBN, 80°C	97	80	10
H	Me	Me	4d, AIBN, 80°C	100	100	0
COOEt	H	Et	4d, AIBN, 80°C	100	95	0
Ph	H	Me	6d, AIBN, 80°C	100	70	30
Ph	H	Me	14d, MeOH [a]	40	0	40
Ph	H	H	5d, AIBN, 80°C	100	25 [b]	0

[a] Galvinoxyl, reaction carried out in the dark. [b] Remainder oxidation product.

TABLE 6. Phosphine consumption, yield as indicated by NMR spectroscopy, and reaction conditions for reactions of phosphines **A–C** with β-lactones of the type



Phosphines: **A**, Ph_2PH; **B**, $PhPH_2$, **C**, $PhHPCH_2CH_2PHPh$

Phosphine	R_1	R_2	R_3	R_4	Reaction conditions	Phosphine consumption (%)	NMR yield (%)
A	H	H	H	H	8d, AIBN, 80°C	20	20
A	H	H	Me	H	13d, AIBN, 80°C	65	50
A	H	H	Me	H	13d, 80°C [b]	60	50
A	Ph	Ph	H	H	9d, AIBN, 90°C	80	75 [f]
A	Ph	H	– [a]	– [a]	8d, AIBN, 80°C	0	0
A	Me	H	– [a]	– [a]	8d, AIBN, 80°C	0	0
B	H	H	H	H	10d, AIBN, 80°C	10	10
B	H	H	Me	H	9d, AIBN, 80°C	5	5
B	Ph	Ph	H	H	9d, AIBN, 90°C	100	100 [c]
B	Ph	H	– [a]	– [a]	10d, AIBN, 80°C	0	0
B	Me	H	– [a]	– [a]	8d, AIBN, 80°C	0	0
C	H	H	Me	H	15d, AIBN, 80°C	30	30 [d]
C	Ph	Ph	H	H	9d, AIBN, 90°C	100	100 [e]
C	Ph	H	– [a]	– [a]	8d, AIBN, 80°C	0	0
C	Me	H	– [a]	– [a]	8d, AIBN, 80°C	0	0

[a] $R_3 + R_4$: cyclohexylidene. [b] In the dark, galvinoxyl added. [c] 25% 1:1 and 75% 2:1 adduct (50% with decarboxylation, 25% without decarboxylation). [d] 20% 1:1 and 10% 2:1 adduct. [e] 50% 1:1 and 50% 2:1 adduct (with decarboxylation). [f] Decarboxylation.

nature of the compound involved two modes of reaction are observed: cleavage of the acyl carbon–oxygen bond or that of the alkyl carbon–oxygen bond.

2.3.1. Reactions of alkyl- and phenylsubstituted β-lactones

The reactions between phenylphosphine, diphenylphosphine and ethylenebis(phenylphosphine) and β-lactones can be carried out at 80°C in the presence of catalytic amounts of AIBN. The reactions occur regioselectively, to give phosphinocarboxylic acids, as shown in Scheme 3.

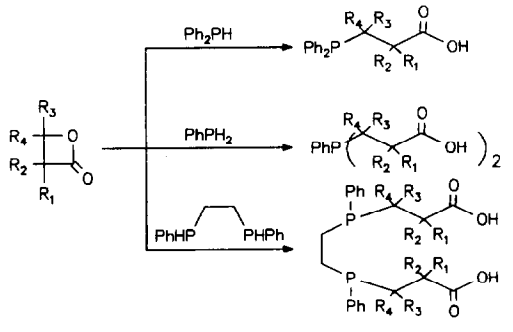
As can be seen from Table 6, the reactivity of the lactones depends on the nature of the substituents present on the carbon atom α to the oxygen ring atom, since these cause steric hindrance to the reaction. In all cases 3-cyclohexylidene-β-lactones fail to react, in spite of the relative instability of such spiro compounds. Yields otherwise vary from moderate to quantitative, but the situation is complicated in that phenylphosphine and ethylenebis(phenylphosphine) can give 1:1 as well as the required 2:1 adducts. In addition, the reactions of 2,2-diphenyl-β-lactone occur with decarboxylation. β-Lactones are thus apparently not suitable general precursors for phosphinocarboxylic acids of the type obtained.

In contrast to the β-lactones, γ-lactones do not react under these conditions.

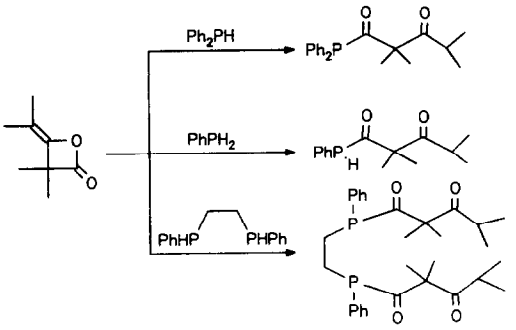
2.3.2. Reactions of the dimer of dimethyl ketene

Such dimers provide a "special case" of β-lactones, and some examples of their reactions with compounds containing polarized single bonds are known [22–30]; these proceed with cleavage of the acyl carbon–oxygen bond. In the case of the three phosphines, the same pattern is observed, as shown in Scheme 4.

The resulting acylphosphines were identified clearly by NMR spectroscopic analysis; the two carbonyl resonances appear at around 224 and 213 ppm, the former showing a moderate to large one-bond phosphorus–carbon coupling. The bisphosphine yields two diastereomeric products. Results and NMR data are given in Section 3. The acylphosphines were not isolated.



Scheme 3.



Scheme 4.

3. Experimental details

All manipulations involving phosphorus-containing materials were carried out under argon to preclude oxidation. NMR spectra were recorded on a Bruker AM 300 spectrometer (solutions in $CDCl_3$ and D_2O, standards TMS and external 85% H_3PO_4).

3.1. Hydrophosphinylation of alkynols and alkyne ethers

A mixture of diphenylphosphine (7.5 mmol) with an equimolar amount of the alkynol or alkyne ether was either heated at 80°C in the presence of AIBN (method A) or irradiated (with stirring) in a quartz Schlenk tube with light from a TQ 150 UV lamp (Heraeus, Hanau) (method B). Reaction times, isomer yields and isomer ratios are given in Table 1. Products could be purified by distillation in most cases. The elemental analysis data for the products that could be purified by distillation are as follows. $HOCHMeCH{=}CHPPh_2$: Found, C, 74.8; H, 6.1. $C_{16}H_{17}OP$ calcd, C, 75.0; H, 6.7%. $HOCHPrCH{=}CHPPh_2$: Found, C, 75.6; H, 7.6. $C_{18}H_{21}OP$ calcd, C, 76.0; H, 7.4%. $HOCMe_2CH{=}CHPPh_2$: Found, C, 75.4; H, 6.9. $C_{17}H_{19}OP$ calcd, C, 75.5; H, 7.1%. $HOCMe(Et)CH{=}CHPPh_2$: Found, C, 76.3; H, 7.0. $C_{18}H_{21}OP$ calcd, C, 76.0; H, 7.4%. $HOCH_2CH_2CH{=}CHPPh_2$: Found, C, 75.5; H, 6.7. $C_{16}H_{17}OP$ calcd, C, 75.0; H, 6.7%. $HOCHMeCH_2CH{=}CHPPh_2$: Found, C, 76.1; H, 7.1. $C_{17}H_{19}OP$ calcd, C, 75.5; H, 7.1%. $MeOCH_2CH{=}CHPPh_2$ underwent oxidation during analysis: Found, C, 70.2; H, 5.8. $C_{16}H_{17}O_2P$ calcd, C, 70.6; H, 6.3%.

3.2. Free radical additions of diphenylphosphine to carboxylic acids and esters

The hydrophosphinylation was carried out as for alkynols by method A. Reaction conditions and yields are given in Table 4.

The NMR data for the previously unknown diphenylphosphinosuccinic acid, its methyl ester, and its sodium salt, as well as the ^{31}P NMR data for the other (previously known) carboxylates and sodium salts are as follows.

^{31}P NMR data: $Ph_2P(ROOC)CH\text{-}CH_2\text{-}COOR$: R = Me; $\delta = -2.7$ ppm; R = Na; $\delta = -2.8$ ppm; R = H; $\delta = -3.4$ ppm. $Ph_2PCH_2CH_2COOR$: R = Me; $\delta = -17.5$ ppm; R = Na; $\delta = -15.0$ ppm. $Ph_2PCH_2CHMeCOOR$: R = Me; $\delta = -21.6$ ppm; R = Na; $\delta = -18.5$ ppm.

^{13}C NMR data for $Ph_2P(ROO^4C)^1CH\text{–}^2CH_2\text{–}^3COOR$: δ (ppm) (J(Hz)): R = Me: ^1C, 39.4 (23.6); ^2C, 33.8 (21.2), ^3C: 171.2 (15.4), ^4C: 171.3; R = Na: ^1C, 47.5 (14.2); ^2C, 40.5 (16.1); ^3C, 182.6 (14.5); ^4C, 182.1 (7.5); R = H: ^1C, 40.7 (25.1); ^2C, 34.6 (15.8); ^3C, 176.3 (13.7); ^4C, 176.9.

^1H NMR data for $Ph_2P(ROOC)C^3H\text{–}C^1H^2H\text{–}COOR$: R = Me: ^1H, 2.55 (^3J(HP) = 6.6); ^2H, 2.99 (^3J(HP) = 6.2); ^3H, 3.83 (^2J(HP) = 1.2); $^2J(^1H^2H) = -17.3$; $^3J(^1H^3H) = 3.7$; $^3J(^2H^3H) = 11.4$; R = Na: ^1H, 2.15 (^3J(HP) = 8.5); ^2H, 2.48 (^3J(HP) = 8.5); ^3H, 3.49 (^2J(HP) = 5.0); $^2J(^1H^2H) = -14.0$; $^3J(^1H^3H) = 4.5$; $^3J(^2H^3H) = 9.5$.

3.3. Saponification reactions of the diphenylphosphinocarboxylates

A solution of the ester (7.5 mmol) in deoxygenated ethanol/water (20 ml) was treated with deoxygenated sodium hydroxide solution (1 equiv., in the case of the succinate 2 equiv.) and the mixture was heated under reflux for 4 h. The solvent was removed under reduced pressure, leaving the sodium salt in quantitative yield. The water solubility of the sodium salts lies between 0.3 and 0.8 mol/l.

The conversion into the free acids was carried out as follows. The sodium salts were dissolved in deoxygenated water, and the resulting solution treated with concentrated HCl until the pH reached 3. The solution was extracted with chloroform, the organic layer separated and dried, and the solvent removed under reduced pressure. The carboxylic acids were obtained as extremely viscous oils in nearly quantitative yield.

3.4. Addition reactions of ethylenebis(phenylphosphine)

These were carried out with 3.5 mmol of the bisphosphine and 7 mmol acrylate as described for the diphenylphosphine additions, using method A. The results are given in Table 5.

3.5. Saponification of the ethylenebis(phenylphosphine) adducts

Saponification and conversion into the free acids was carried out as described above for the diphenylphosphine adducts. Yields were nearly quantitative, and the water solubility of the sodium salts was high (0.1–1.0 mol/l). The NMR data for the esters, sodium salts and free acids are given in Table 7.

3.6. Reaction of phosphines with lactones

The phosphines (5 mmol) and the lactones (5 mmol for Ph_2PH, 10 mmol for $PhPH_2$ and $(CH_2PHPh)_2$) were heated together at 80°C in the presence of a catalytic amount of AIBN. Reaction times, yields, and

TABLE 7. ^{31}P and ^{13}C chemical shifts (in ppm) for the ethylenebis(phenylphosphine) adducts $(^1CH_2(Ph)P\text{–}^2CR_1H\text{–}^3CHR_2\text{–}^4COOR)_2$

R_1	R_2	R	$\delta(^{31}P)$ 1:1	$\delta(^{31}P)$ 2:1	$\delta(^1C/^{1a}C)$	$\delta(^2C)$	$\delta(^3C)$	$\delta(^4C)$
H	H	Me		−22.2/−22.5	22.4 [a]	23.0 [c]	29.7 [d]	172.9 [f]
H	H	Me			22.5 [b]		30.0 [e]	173.0 [g]
Me	H	Et	−48/−8	−6.7/−7.5	20	29	39	172.0
H	Me	Me		−25/−27	23	32	37	176.1
COOEt	H	Et		−9.5/−12	20	40	27	172
Ph	H	Me	−48/−9	−5/−9	20/22	41/43	37/38	172
H	H	Na		−18.7/−20.3	24.3 [h]	25.2 [i]	35.7 [j]	185
Me	H	Na		−3.5/−6.5	32	44	40	183
H	Me	Na		−21.5/−25	26	35	43	188
COONa	H	Na		−7/−12	22	45	40	180
Ph	H	Na		−7/−11	20	48/52	35	172
H	H	H		−21.1/22.2	23	23	31	178
Me	H	H		−7/8.5	17	29	38	173
H	Me	H		−23/−32	24	32	37	182
COOH	H	H		−0.5/−11.5	20	41	34	170–175

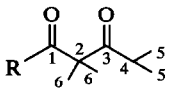
[a] $^1J = 23.3$. Hz/$^2J = 7.1$ Hz. [b] $^1J = 23.5$ Hz/$^2J = 5.5$ Hz [c] $^1J = 7.4$ Hz. [d] $^1J = 7.4$ Hz. [e] $^2J = 8.7$ Hz. [f] $^3J = 6.5$ Hz. [g] $^3J = 6.4$ Hz. [h] $^1J = 34.9$ Hz/$^2J = 0$ Hz. [i] $^1J = 54.6$ Hz [j] $^2J = 7.0$ Hz.

TABLE 8. ^{13}C chemical shifts (in ppm) and carbon–phosphorus coupling constants (in Hz) for compounds of the type $(HOO^3C-^2CR_1R_2-^1CR_3H)_nPPh_{3-n-o}H_o$ (I), $(CH_2PhP^1CHR_3-^2CR_1R_2-COOH)_2$ (II), $PhH^2PCH_2CH_2Ph^1P^1CHR_3-^2CR_1R_2-^3COOH$ (III), $(Ph_2{}^2CH-^1CH_2)_nPPh_{3-n-o}H_o$ (IV), $(CH_2PhP^1CH_2-^2CHPh_2)_2$ (V) and $PhH^2PCH_2CH_2Ph^1P^1CH_2-^2CHPh_2$ (VI); IV, V and VI: ^3C = quarternary carbon atom of the phenyl residue at C-2

Type/n/o	R_1	R_2	R_3	$\delta(^{31}P)$	$\delta(C_1)$ $^1J(C_1P)$	$\delta(C_2)$ $^2J(C_2P)$	$\delta(C_3)$ $^3J(C_3P)$	$\delta/{}^nJ$ (R_1/R_2)	$\delta/{}^nJ$ (R_3)
I/1/0	H	H	H	−16.8 [b]	19.0 (6.4)	29.4 (15.3)	175.8 (15.3)	–	–
I/1/0	H	H	Me	−3.7 [b]	26.1 (11.6)	37.5 (17.7)	170.7 (16.1)	–	15.8 (16.1)
I/2/0	H	H	H	−21.2	22.2 (3.8)	32.8 (12.7)	181.3 (11.4)	–	–
I/1/1	Ph	Ph	H	−57.3	40.7 (1.8)	59.8 (17.0)	178.9 (0)	144.3 (3.8)	–
II	H	H	Me	−8	29 [a] (n.o.)	38 (n.o.)	172/173 (n.o.)	–	16 (n.o.)
III	H	H	Me	−8(^{1}P)/−48(^{2}P)	29 [a] (n.o.)	38 (n.o.)	172/173 (n.o.)	–	–
IV/1/0	–	–	–	−22.4	35.6 (13.8)	47.9 (15.6)	144.1 (5.2)	–	–
IV/2/0	–	–	–	−31.1/−37.2	36.4 (14.1)	48.6 (16.5)	145.2 (7.6)	–	–
IV/1/1	–	–	–	−60.2	30.2 (14.7)	47.8 (13.4)	145.5 (6.4)	–	–
V	–	–	–	−27	35.5 [c] (15.0)	48.3 (12.9)	144 (n.o.)	–	–
VI	–	–	–	−27(^{1}P)/−43(^{2}P)	35 (n.o.)	48 (n.o.)	144 (n.o.)	–	–

[a] P–CH_2–CH_2–P: 19/22 ppm; n.o., not observed. [b] In agreement with [8]. [c] P–CH_2–CH_2–P: 23.8 ppm (12.7 Hz).

TABLE 9. ^{31}P, ^{13}C and ^1H chemical shifts (in ppm) and carbon–phosphorus coupling constants (in Hz) for compounds of the type



with R = Ph_2P (A), R = PhHP (B), R = Me_2-CHC(O)C(Me)$_2$C(O)PPhCH$_2$CH$_2$PPh (C)

R	A	B	C(1)	C(2)
$\delta(^{31}P)$	10.2	−36.2	2.3	2.3
$\delta(^1C)$	223.0	222.5	224.9	224.7
$^1J(^1CP)$	52.1	52.1	30.0	27.1
$\delta(^2C)$	66.6	66.3	66.1	62.2
$^2J(^2CP)$	30.5	20.4	13.7	14.9
$\delta(^3C)$	213.1	212.8	212.7	215.8
$^3J(^3CP)$	0	0	6.6	12.6
$\delta(^4C)$	38.5	38.4	36.7	38.4
$\delta(^5C)$	18.3	18.1	19.9	19.8
$\delta(^6C)$	15.9	15.7	15.8	15.8
$^3J(^6CP)$	14.1	n.o.	14.4	14.4
$\delta(^4H)$ [a]	2.88	2.74	2.64	3.05
$\delta(^5H)$ [b]	1.08	1.03	0.90	0.85
$^3J(^4H^5H)$	7.2	6.8	6.6	6.6
$\delta(^6H)$	1.47	1.39	Uncertain	Uncertain
$\delta(H_R)$	7.2–7.5	5.38	7.1–8.0; 1.55	7.1–8.0, 1.55
		$^1J(PH)$ = 231.3 Hz	$^2J(PH)$ = 13.7 Hz	$^2J(PH)$ = 13.7 Hz

[a] Doublet. [b] Septet.

product ratios are given in Table 6, and the NMR data for the products (including those of decarboxylation) in Table 8.

In the case of the dimethyl ketene dimer reaction times and results were as follows: Ph_2PH: 6 days, phosphine consumption 80%, NMR yield 30% (remainder Ph_4P_2). Ph_2PH (reaction in the dark): 7.5 days, consumption 70%, NMR yield 30% (remainder Ph_4P_2). $PhPH_2$: 9 days consumption 35%, NMR yield 35%. $(CH_2PHPh)_2$: 15 days, consumption 100%, NMR yield 80%. NMR data for the acyl phosphines are given in Table 9.

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