A Simple Synthesis and Some Synthetic Applications of Substituted Phosphide and Phosphinite Anions

E. N. TSVETKOV, N. A. BONDARENKO, I. G. MALAKHOVA, M. I. KABACHNIK*

A. N. Nesmeyanov Institute of Organoelement Compounds, USSR Academy of Sciences, Vavilov Str. 28, Moscow V-334, U.S.S.R.

Based on data for the acidity relationship of phosphines and phosphinous acids and water in dimethyl sulfoxide and water, a simple method is reported for the generation of phosphide and phosphinite anions by the action of concentrated aqueous alkali on primary and secondary phosphines as well as phosphinous acids in dimethyl sulfoxide or other dipolar aprotic solvents. Alkylation of the anion yields secondary and tertiary phosphines, polyphosphines, functionally substituted phosphines as well as similarly substituted phosphine oxides. Phosphinous acids have been alkylated in various solvents in two-phase systems containing concentrated aqueous alkali and tetrabutylammonium iodide as phase transfer catalyst.

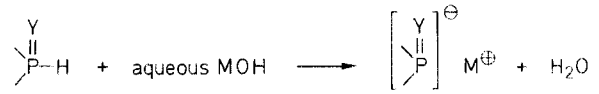
Primary and secondary phosphines[1] and secondary phosphine oxides[2], generally known as *PH*-acids, are important starting materials for the synthesis of tertiary phosphines and phosphine oxides. Phosphines and phosphine oxides are widely used and thus the development of simple syntheses is of considerable interest.

Usually, the syntheses do not start from the *PH*-acids themselves but from their anions. Due to the fact that *PH*-acids in aqueous solutions are weaker than water, the anions are obtained by use of anhydrous solvents such as ether, hydrocarbons, liquid ammonia, and strong bases such as

alkali metals, their hydrides and amides, as well as organometallic compounds. This fact is very inconvenient and restricts the application of these syntheses to laboratory.

We now report an improved method for the generation of anions of *PH*-acids. This improvement is based on the earlier studies on the determination of the *PH*-acidities of RPH_2, R_2PH, and R_2PHO in dimethyl sulfoxide[3,4,5]. The acidities of primary and secondary aromatic phosphines (pK 22–24)[3], alkylphenylphosphines (pK 27–28)[4] as well as dialkylphosphine oxides (pK 27–28) and diarylphosphine oxides (pK 18–23)[4,5] in dimethyl sulfoxide turned out to be higher than that of water in the same solvent (pK 31.4)[6]. Such a reversion of the acidity relationship between the *PH*-acids and water in dimethyl sulfoxide and water is probably due to the abnormally high water acidity in water as a result of the high energy of solvation of the hydroxide ion with water. The basicity of the hydroxide ion in dimethyl sulfoxide is much stronger than those of phosphide and phosphinite anions, therefore it can be used for their production. A solid alkali (even in a powdered form) is not convenient for this purpose because it is insoluble in dimethyl sulfoxide. Such a method is described in the literature[7,8] although it is not practised on a large scale.

Taking into account the fact that the acidity of the *PH*-acids in dimethyl sulfoxide is much higher than that of water (by 3–13 pK), we attempted to use a concentrated aqueous alkali solution for the generation of anions of *PH*-acids (Scheme **A**).



Y = unshared electron pair or oxygen; M = Na or K

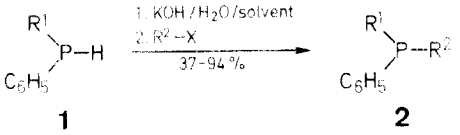
Scheme **A**

In fact, addition of a 40% aqueous solution of sodium hydroxide or a 50–56% aqueous solution of potassium hydroxide to a solution of diphenylphosphine in dimethyl sulfoxide gives rise to a gradual appearance of the brightly orange-red coloured diphenylphosphide anion. Under similar conditions, phenylphosphine forms the yellow coloured phenylphosphide anion. Due to the presence of water in the system, the phosphines seem to be converted to the corresponding phosphide anions only partially. For example, in the case of phenylalkylphosphines (pK 27–28) no colour develops at all. Diphenylphosphinous acid readily forms a phosphinite anion (pale yellow colour), which is explained by a large difference between its acidity and that of water, whereas in the case of dialkylphosphinous acid such a process does not occur so readily.

The phosphide anions can also be produced with the aid of other bipolar aprotic solvents such as dimethylformamide, dimethylacetamide, or hexamethylphosphoric triamide. However, use of these solvents required potassium carbonate to be added to the system as a water-removing substance in order to enhance concentration of the corresponding anion. Thus, phosphide and phosphinite anions can be conveniently produced in a variety of bipolar aprotic solvents, although dimethyl sulfoxide gives the best results. These methods have been used accordingly to develop syntheses of various phosphines and their oxides by alkylation of the corresponding anions.

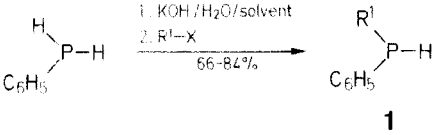
1. Phosphide Anions

This process is readily carried out by addition of an alkylating agent to a solution of the corresponding anion, the anion colour (if any) gradually disappearing. Thus, tertiary phosphines **2** are obtained from the alkylphenyl- or diphenylphosphide anion (Scheme **B** and Table 1)[9] and secondary phosphines **1** from the phenylphosphide anion (Scheme **C** and Table 2)[12].



1 **2**

Scheme **B**



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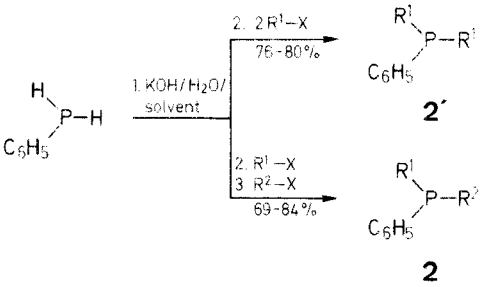
Scheme **C**

Dialkylphenylphosphines **2** can be synthesized both with isolation of secondary phosphines **1** and without their isolation via alkylation of a phenylphosphide anion with two mol of alkylating agent or successively with two different agents (Scheme **D** and Table 3)[13]. It is to be noted that a single-stage synthesis of dialkylphenylphosphines from phenylphosphine should proferably be effected in dimethyl sulfoxide since in other solvents the second alkalation sometimes does not go to completion, probably as a result of the low acidity of alkylphenylphosphines.



Scheme **D**

Along with monohalide alkylating agents, use is made of polyhaloalkanes as well as functionally substituted alkyl halides. Thereby certain di- and triphosphines are obtained (Scheme **E** and Table 4)[15]. Note that in the latter case, i.e. in the interaction of the diphenylphosphide anion with tetrakis[chloromethyl]methane (**4**), it has not been possible to substitute the fourth chlorine atom by the diphenylphosphine group to give **6** even on prolonged heating of the reaction mixture (75 °C, 8 h).

Among the functionally substituted alkyl halides, ω-chloro-substituted carboxylic acids and their esters **7** are used successfully. The corresponding ω-phosphinocarboxylic acids **8** are synthesized in fairly high yields (Scheme **F** and Table 5)[16]. It is natural that, in the course of the reaction, the esters are converted to the corresponding acids.

Table 1. Dialkylphenyl- and Alkyldiphenylphosphines **2** prepared according to Scheme **B**

R^1	R^2	X	Solvent[a]	Reaction Conditions: temperature[b]/heating temperature/time	Yield [%]	b.p. [°C]/torr	n_D^{20}	d_4^{20}	Literature Data
n-C_4H_9	n-C_3H_7	Br	DMSO	25–60°C/60°C/0.5 h	82	137–139°/14	1.5285	0.9216	b.p. 127–130°C/10 torr[10]
			HMPT/K_2CO_3	30–40°C/45–50°C/2 h	83				
n-C_4H_9	n-C_4H_9	Br	HMPT/K_2CO_3	30–40°C/40–50°C/2 h	80	106–108°/2	1.5238	0.9140	b.p. 83°C/0.2 torr[10]
n-C_8H_{17}	C_2H_5	Br	DMSO	20–40°C/50–60°C/1.5 h	87	132–134°/1	1.5162	0.9074	b.p. 132–134°C/1 torr[10]
C_6H_5	CH_3	O—SO_2—OCH_3	DMSO[c]	10–15°C[d]/20°C/0.5 h	82	121–122°/1	1.6257	1.0651	b.p. 146–147°C/7 torr[10]
		J	DMSO[c]	10°C[d]/10–20°C/0.5 h	70				
		O—SO_2—OCH_3	DMF/K_2CO_3[c]	10°C[d]/20°C/1 h	71				
C_6H_5	C_2H_5	Br	DMSO	15–18°C[d]/15–18°C/3 h	75	108–109°/1	1.6134	1.0457	b.p. 108–109°C/0.3 torr[10]
C_6H_5	n-C_3H_7	Br	DMSO	25–50°C/50°C/1 h	94	128–129°/2	1.5980	1.0300	b.p. 138°C/1 torr[10]
C_6H_5	n-C_4H_9	Br	DMSO	25–30°C/30–35°C/1 h	85	140–142°/2	1.5928	1.0167	b.p. 117–120°C/0.3 torr[10]
			DMSO/K_2CO_3	25–35°C/30–35°C/1 h	81				
			DMF/K_2CO_3	20–25°C/25°C/1 h	82				
			HMPT/K_2CO_3	20–25°C/20–25°C/2 h	88				
C_6H_5	$HOCH_2CH_2$	Cl	DMSO[e]	70–80°C/80–20°C/10 min	37	160–162°/1	–	–	b.p. 163.5–164.5°C/1 torr[11]
C_6H_5	$HOCH_2CH_2CH_2$	Cl	DMSO[e]	40–50°C/50°C/1.5 h	74	172–173°/1	–	–	b.p. 172–173°C/1 torr[11]
						m.p. 60–62°C (PE)			m.p. 60–61°C[11]

[a] DMSO = dimethyl sulfoxide, HMPT = hexamethylphosphoric triamide, DMF = dimethylformamide, DMA = dimethylacetamide.
[b] Temperature of reaction mixture during addition of alkylating agent.
[c] A 5% excess of alkylating agent is used.
[d] Reaction at higher temperature gives a lower yield, probably as a result of conversion of the tertiary phosphine to the corresponding phosphonium salt.
[e] 50% Aqueous potassium hydroxide solution is added to the diphenylphosphine/chlorohydrin mixture; molar ratio of diphenylphosphine to potassium hydroxide = 1 : 2.3.

Table 2. Alkylphenylphosphines **1** prepared according to Scheme **C**

R^1	X	Solvent[a]	Reaction Conditions: temperature[b]/heating temperature/time	Yield [%]	b.p. [°C]/torr	n_D^{20}	d_4^{20}	Molecular Formula[c] or Literature Data
CH_3	J	DMSO	10°C/20–25°C/0.5 h	80	51–52°/7	1.5733	0.9859	b.p. 59–60°C/10 torr[10]; n_D^{20}: 1.5695[10]
	$O—SO_2—OCH_3$	DMSO/K_2CO_3	10°C/15–20°C/0.5 h	79				
C_2H_5	Br	DMSO	15–18°C/20°C/0.5 h	75	92–92.5°/23	1.5582	0.9610	$C_8H_{11}P$ (138.2)
	Br	DMSO/K_2CO_3	25°C/25°C/0.5 h	83				
i-C_3H_7	Br	DMSO	40°C/50–60°C/1 h	72	87–88°/15	1.5452	0.9422	$C_9H_{13}P$ (152.2)
n-C_4H_9	Br	DMSO	30°C/25–30°C/0.5 h	79	96–97°/7	1.5412	0.9404	b.p. 102°C/9 torr[10]; n_D^{20}: 1.5400[10]
	Cl	DMSO	25–50°C/50–60°C/1 h	71				
	Br	DMF/K_2CO_3	20–30°C/30°C/1 h	77				
	Br	HMPT/K_2CO_3	30–40°C/40–50°C/2.5 h	75				
s-C_4H_9	Br	DMSO	25–60°C/60°C/1 h	84	105–106°/17	1.5395	0.9409	$C_{10}H_{15}P$ (166.2)
c-C_5H_9	Br	DMSO	25–60°C/60°C/1 h	81	135–136°/15	1.5685	1.0054	$C_{11}H_{15}P$ (178.2)
n-C_8H_{17}	Br	DMSO	40–50°C/50°C/2.5 h	80	102–103°/1	1.5192	0.9116	$C_{14}H_{23}P$ (222.3)
$HOCH_2CH_2CH_2$	Cl	DMSO[d]	20–50°C/50°C/1 h	66	115–116°/1	1.5775	1.0668	b.p. 107–110°C/2 torr[10]; n_D^{20}: 1.5745[10], d_4^{20}: 1.0696[10]

[a,b] See Table 1.
[c] Satisfactory microanalyses obtained: C ±0.24, H ±0.11, P ±0.25 (exception isopropylphenylphosphine: C −0.61).
[d] 50% Aqueous potassium hydroxide solution is added to the phenylphosphine/chlorohydrin mixture; molar ratio of phenylphosphine to potassium hydroxide = 1 : 2.3.

Table 3. Dialkylphenylphosphines **2,2'** prepared according to Scheme **D** in DMSO[a]

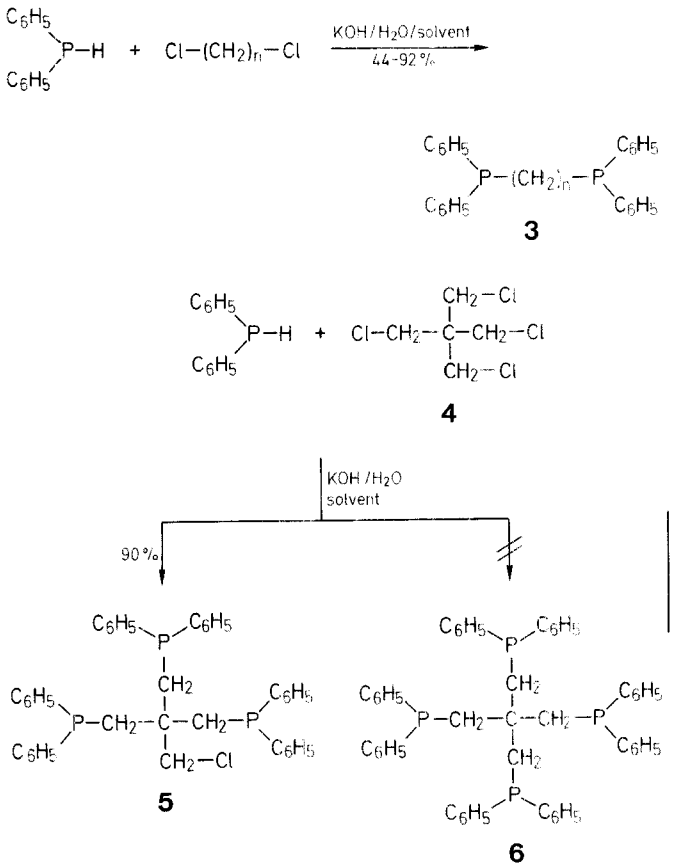
First Alkylation		Second Alkylation		Yield [%]	b.p. [°C]/torr	n_D^{20}	d_4^{20}	Molecular Formula[c] or Lit. Data
R^1-X	temp.[b]/heating temp./time	R^2-X	temp.[b]/heating temp./time					
$2C_2H_5—Br$	20–40°C/40–50°C/0.5 h	–	–	80	105–106°/18	1.5460	0.9458	b.p. 108–109°C/20 torr[10]
2*n*-$C_4H_9—Br$	20–50°C/60°C/2 h			76	120–121°/3	1.5230	0.9138	b.p. 83°C/0.2 torr[10]
2*n*-$C_4H_9—Br$	40–45°C/60°C/2 h[d]	–	–	78				
$H_3C—J$	10–15°C/30°C/20 min	$C_2H_5—Br$	20–25°C/50°C/1 h	80[e]	95–97°/18	1.5556	0.9581	b.p. 96–97°C/15 torr[10]
n-$C_4H_9—Br$	20–50°C/50°C/15 min	*n*-$C_3H_7—Br$	40–50°C/50–60°C/1 h	84	137–139°/16	1.5285	0.9216	b.p. 127–130°C/10 torr[10]
$C_2H_5—Br$	40°C/50°C/10 min	*n*-$C_8H_{17}—Br$	50°C/50–60°C/2 h	82[f]	122–125°/1	1.5162	0.9074	b.p. 132–134°/1 torr[10]
i-$C_3H_7—Br$	20–40°C/40–45°C/0.5 h	*n*-$C_8H_{17}—Br$	50°C/80°C/2 h	69[f]	148–149°/2	1.5127	0.9032	$C_{17}H_{29}P$ (264.4)

[a,b] See Table 1.
[c] Satisfactory microanalysis obtained: C −0.05, H +0.08, P ±0.00.
[d] Solvent used is HMPT/K_2CO_3.
[e] Product identified as dimethyl-ethyl-phenylphosphonium iodide; m.p. 149–150°C (Lit.[14], m.p. 148.5–150°C).
[f] When the order of addition of the alkylating agents is changed a mixture of secondary and tertiary phosphines is obtained.

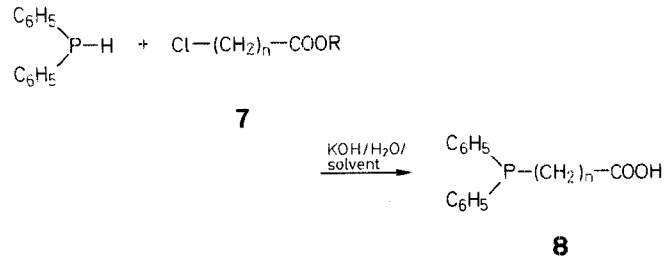
Table 4. Poly[diphenylphosphino]alkanes **3** and **5** prepared according to Scheme **E**

Product	Solvent[a]	Reaction Conditions temperature[b]/heating temperature/time	Yield [%]	m.p. [°C] (solvent)	Molecular Formula[c] or Lit. m.p. [°C]
3 (n = 1)	DMSO[d]	40–50 °C/50 °C/1 h	86	121–122° (C_2H_5OH)	122°[10]
	DMF/K_2CO_3	25–40 °C/45 °C/2 h	80		
	DMF	30–40 °C/45 °C/2 h	44		
	HMPT	20–40 °C/40–45 °C/1 h	83		
	$HMPT/K_2CO_3$	25–45 °C/40–45 °C/1 h	87		
	DMA/K_2CO_3	25–45 °C/40–45 °C/2 h	87		
3 (n = 2)	DMSO	25–28 °C/50 °C/1 h	92	143–144° (C_2H_5OH/C_6H_6)	143.5–144°[10]
3 (n = 4)	DMSO	50 °C/50 °C/1 h	80	133–134° (2-butanone)	137–138°[10]
5	$DMSO/K_2CO_3$	25–30 °C/40–50 °C/2 h	90	110.5–111° (C_2H_5OH)	$C_{41}H_{38}ClP_3$ (659.2)

[a,b] See Table 1.
[c] Satisfactory microanalysis obtained: C + 0.02, H − 0.12, Cl − 0.15, P + 0.08.
[d] 40% Aqueous sodium hydroxide solution is used.



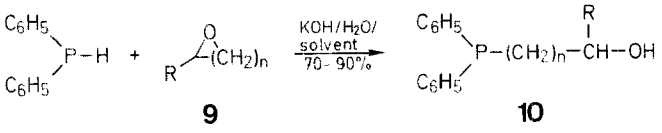
Scheme **E**



Scheme **F**

Less favourable results are obtained with chlorohydrins. Thus, the interaction of a two-fold excess of ethylene chlorohydrin with the diphenylphosphide anion in dimethyl sulfoxide gives the corresponding phosphinoalcohol in ~ 40% yield (Table 1). ω-Diphenylphosphinopropyl alcohol from trimethylene chlorohydrin is obtained in 65% yield (Table 1). Similarly, the phenylphosphide anion and trimethylene chlorohydrin gave monophenylated phosphinoalcohol (Table 2). Reaction of the diphenylphosphide anion with tetramethylene chlorohydrin does not give the corresponding phosphinoalcohol (with isolation of the starting diphenylphosphine).

The cleavage of oxiranes with the diphenylphosphide anion gives rise to β-diphenylphosphinoethyl alcohol and derivatives in high yields (Scheme **G** and Table 6)[17]. A similar reaction takes place between the diphenylphosphide anion and oxetane to give γ-diphenylphosphinopropyl alcohol[17].



Scheme **G**

However, in the system proposed, 2,3-dihydrobenzofuran is not cleaved by the diphenylphosphide anion even under vigorous conditions (120 °C, 3 h), although this reaction had been carried out by us earlier at 100 °C for 1 h[18]. This negative result can be explained by a lower reactivity of the anion in the system dimethyl sulfoxide/concentrated aqueous alkali, which is probably due to hydration.

The lower reactivity of the diphenylphosphide anion in the system dimethyl sulfoxide aqueous alkali is further indicated by the data on anisole dealkylation in these conditions. On heating anisole together with diphenylphosphine and aqueous potassium hydroxide in dimethyl sulfoxide (80 °C, 6 h) dealkylation is not completed. As shown by ^{1}H-N.M.R. data, the mixture isolated contains ~ 60% of diphenylmethylphosphine. During the reaction, part of the diphenylphosphine (~ 6%) is oxidized by the alkali to diphenylphosphinic acid[30]. In anhydrous tetrahydrofuran, anisole is dealkylated under reflux for 5 h[19], diphenylmethylphospine being isolated in 52% yield.

Table 5. ω-Diphenylphosphinocarboxylic Acids **8** prepared according to Scheme F

Substrate 7 R	n	Solvent[a]	Reaction Conditions temperature[b]/heating temperature/time	Yield [%] of 8	m.p. [°C] (solvent)	Lit. m.p. [°C]
H	1	DMSO	25–50 °C/50 °C/1 h[c]	72	120.5–121.5°	120–121°[10]
		$HMPT/K_2CO_3$	20–30 °C/30–40 °C/2 h[c]	64	(1/1 C_2H_5OH/H_2O)	
		HMPT	25 °C/30 °C/2 h[c]	51		
CH_3	1	DMSO	20–25 °C/20–25 °C/1 h	78		
		DMF/K_2CO_3	25 °C/25 °C/2 h	72		
		HMPT	25 °C/30 °C/2 h	50		
H	2	DMSO	20 °C/20 °C/1 h	91	130.5–131.5°	127–128°[10]
C_2H_5	2	DMSO	30–55 °C/50–55 °C/2 h[c]	94	(3/2 C_2H_5OH/H_2O or C_2H_5OAc)	
		DMF/K_2CO_3	25–28 °C/25 °C/2 h[c]	84		
		$HMPT/K_2CO_3$	25–30 °C/25–30 °C/4 h[c]	86		
C_2H_5	3	DMSO	20–25 °C/20–25 °C/12 h[d]	81	100–101° (3/2 C_2H_5OH/H_2O)	97–98°[10]

[a,b] See Table 1.
[c] 50% Aqueous potassium hydroxide solution is added to the diphenylphosphine/alkylating agent mixture.
[d] Molar ratio of diphenylphosphine to ester to potassium hydroxide = 1 : 2 : 5.

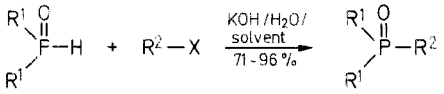
Table 6. ω-Diphenylphosphinoalkyl Alcohols **10** prepared according to Scheme G

Substrate 9 R	n	Solvent[a]	Reaction Conditions temperature[b]/heating temperature/time	Yield [%]	b.p. [°C]/torr	Lit. b.p. [°C]/torr
H	1	DMSO	0–5 °C/20 °C/0.5 h[c]	80	168–170°/1.5	163.5–164.5°/1[11]
		DMF/K_2CO_3	5–8 °C/20 °C/0.5 h[c]	77		
		$HMPT/K_2CO_3$	5–8 °C/20 °C/0.5 h[c]	73		
H	2	DMSO	30 °C/85–95 °C/1 h	83	195–196°/3	171–173°/1[11]
		$HMPT/K_2CO_3$	30–40 °C/85–95 °C/3 h	80	m.p. 60–61° (PE)	m.p. 60–61°[11]
CH_3	1	DMSO	20–25 °C/40 °C/2 h	90	157–157.5°/1	192–193°/3[10]
C_6H_5	1	DMSO	45–50 °C/45–50 °C/3 h	70	172–174°/0.06	218–222°/3[10]

[a,b] See Table 1.
[c] A two-fold excess of oxirane is used.

2. Phosphinite Anions

As demonstrated by the data on the acidities of diaryl- and dialkylphosphinous acids[11] in dimethyl sulfoxide, concentrated aqueous alkali can be used to advantage for the production of the corresponding substituted phosphinite anions which can then be used in to the Michaelis-Becker reaction. Thus, alkylation of phosphinite anions gives the corresponding tertiary phosphine oxides **12** (Scheme H and Table 7)[20] as well as tertiary 1, ω-bis[phosphinyl]alkanes **13** (Scheme I and Table 8)[22].



11 **12**

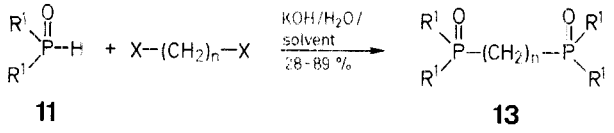
Scheme H

The situation is complicated by the fact that the phosphinous acid is oxidized by the alkali to the phosphinic acid. In the case of diphenylphosphinous acid, the reaction proceeds fairly slowly. In

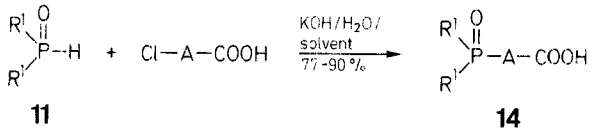
Table 7. Tertiary Phosphine Oxides **12** prepared in DMSO[a] according to Scheme H

R^1	R^2	X	Reaction Conditions temperature[b]/heating time	Yield [%]	m.p. [°C] (solvent)	Lit. m.p. [°C]
n-C_4H_9	n-C_4H_9	Br	20–30 °C/60 min	91	b.p. 130 °C/2 torr	b.p. 300 °C[21]
n-C_4H_9	$C_6H_5CH_2$	Cl	20–30 °C/60 min	86	64–65° (PE)	64–65°[21]
$C_6H_5CH_2$	$C_6H_5CH_2$	Cl[c]	20–60 °C/60 min	77	213–214° (C_6H_6)	214°[21]
C_6H_5	CH_3	J	20 °C/10 min	80	111–112° (1/5 C_2H_5OAc/PE)	111.5–112°[21]
C_6H_5	C_2H_5	Br	20–50 °C/30 min	92	120–121° (1/1 C_2H_5OAc/PE)	121°[21]
C_6H_5	n-C_4H_9	Br	20–50 °C/10 min	96	94–95° (1/5 C_2H_5OAc/PE)	95°[21]
C_6H_5	$C_6H_5CH_2$	Cl[c]	20 °C/10 min	81	195–196° (C_2H_5OH)	195–196°[21]
4-Cl—C_6H_4	C_2H_5	Br	20 °C/30 min	71	98.5–99° (1/5 C_2H_5OAc/PE)	98.5–99°[21]

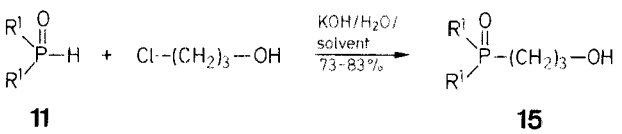
[a,b] See Table 1.
[c] The alkali solution is added to the phosphinous acid/alkyl halide mixture.



Scheme I



Scheme J



Scheme K

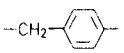
this case the phosphinous acid reacts with a concentrated aqueous alkali solution is dimethyl sulfoxide for 20 h at 20 °C or 5 h at 60 °C to give diphenylphosphinic acid in 80 % yield. The diphenylphosphinous acid is quantitatively oxidized by aqueous alkali in ethanol under reflux for 4 h (see Experimental Section). If alkylation proceeds rapidly, the side reaction does not affect the final results of the process.

Table 8. Tertiary 1,ω-Bis[phosphinyl]alkanes **13** prepared in DMSO[a] according to Scheme **I**

R^1	n	X	Reaction Conditions: temperature[b]/heating temperature/time	Yield [%]	m.p. [°C] (solvent)	Molecular Formula[c] or Lit. m.p. [°C]
n-C_4H_9	2	Cl	20–30 °C/50 °C/1 h	55	174–175° (1/5 C_6H_6/PE)	174–175°[21]
n-C_4H_9	4	Br	20–60 °C/50 °C/1 h	89	118–119° (hexane)	116–118°[21]
$C_6H_5CH_2$	4	Br	20–60 °C/50 °C/1 h[d]	83	232–233° (C_2H_5OH)	$C_{32}H_{36}O_2P_2$ (514.6)
C_6H_5	1	Cl	20–60 °C/50 °C/1 h	30	181–182° (5/1 C_2H_5OH/H_2O)	181–182°[21]
		Br	20–65 °C/65–20 °C/1 h[e]	28		
		J	25–55 °C/25 °C/1 h	35[f]		
C_6H_5	2	Cl	20–50 °C/50 °C/20 min	82	271–272° (C_2H_5CH)	269–270°[21]
C_6H_5	3	Br	20–50 °C/50 °C/10 min	80	142–143° (C_6H_6)	142–143°[21]
C_6H_5	4	Br	20–50 °C/50 °C/100 min	89	259–260° (DMF)	258–260°[21]

[a,b] See Table 1.
[c] Satisfactory microanalysis obtained: C +0.17, H +0.09, P +0.22.
[d] 40% Aqueous sodium hydroxide solution is used.
[e] 50% Aqueous potassium hydroxide solution is added to the diphenylphosphinous acid/dichloromethane mixture.
[f] Diphenylphosphinic acid (33%) is also obtained.

Table 9. ω-Phosphinylcarboxylic Acids **14** prepared in DMSO[a] according to Scheme **J**

R^1	A	Reaction Conditions: temperature[b]/heating temperature	Yield [%]	m.p. [°C] (solvent)	Molecular Formula[c] or Lit. m.p. [°C]
n-C_4H_9	$-CH_2-$	20–50 °C/55 °C	89	46–47° (ether)	46–47°[24]
$C_6H_5CH_2$	$-CH_2-$	20–60 °C/50 °C	85	170–171° (2-butanone/CH_3CN)	$C_{16}H_{17}O_3P$ (288.3)
C_6H_5	$-CH_2-$	20–40 °C/40 °C	90	146.5–147.5° (2-butanone/CH_3CN)	145–146°[21]
C_6H_5	$-CH_2CH_2-$	25–40 °C/50 °C	90	136–137° (C_2H_5OAc)	133–134°[21]
C_6H_5		20–45 °C/60 °C	77[d]	248–249° (C_2H_5OH)	248–249°[25]

[a,b] See Table 1.
[c] Satisfactory microanalysis obtained: C +0.12, H +0.14, P +0.04.
[d] 4-Bromomethylbenzoic acid and 40% aqueous sodium hydroxide solution are used.

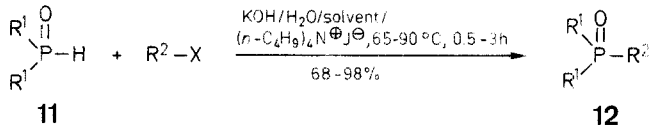
Table 10. γ-Phosphinylpropyl Alcohols **15** prepared in DMSO[a] according to Scheme **K**

R^1	Reaction Conditions: temperature[b]/heating temperature/time	Yield [%]	m.p. [°C] (solvent)	Molecular Formula[c] or Lit. m.p. [°C]
$C_6H_5CH_2$	40–65 °C/50 °C/2 h	73	102.5–103.5° (C_2H_5OAc)	$C_{17}H_{21}O_2P$ (288.3)
C_6H_5	40–45 °C/45 °C/0.5 h	83	102–103° (C_2H_5OAc)	102–103°[11]
4-$H_3C-C_6H_4$	30–50 °C/60 °C/2 h	82	125–125.5° (C_2H_5OAc/hexane)	$C_{17}H_{21}O_2P$ (288.3)

[a,b] See Table 1.
[c] Satisfactory microanalyses obtained: C ±0.12, H ±0.08, P ±0.15.

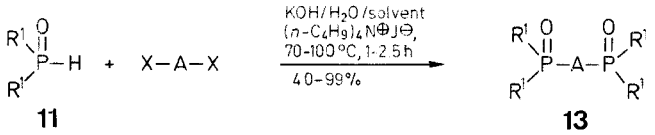
The phosphinite anions react with ω-halocarboxylic acids and trimethylene chlorohydrin to give ω-phosphinyl substituted carboxylic acids **14** (Scheme **J** and Table 9)[24] and γ-phosphinylpropyl alcohols **15** (Scheme **K** and Table 10)[26], respectively.

Tertiary phosphine oxides **12** (Scheme **L** and Table 11)[27] and tertiary 1,ω-bis[phosphinyl]alkanes **13** (Scheme **M** and Table 12)[28] can be obtained via alkylation of phosphinous acids with the corresponding agents also in a two-phase system in the presence of phase transfer catalyst (tetrabutylammonium iodide). In this case the best results can be obtained with such solvents as hydrocarbons (hexane, benzene), although some other solvents can be used such as butyl alcohol, dibutyl ether, dimethylformamide.



11 **12**

Scheme **L**



11 **13**

Scheme **M**

However, this method is not suitable for the production of phosphine oxides and 1,ω-bis[phosphinyl]alkanes containing alkyl groups at the phosphorus atom, which can be synthesized using dimethyl sulfoxide as solvent. This is probably due to an insufficient acidity of dialkylphosphinous acids to give their anions in a two-phase system.

3. Conclusions

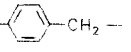
1. Based on the data for the acidity relationship of phosphines and phosphinous acids and water in dimethyl sulfoxide and in water, a simple method has been developed for the production of phosphide and phosphinite anions under the action of concentrated aqueous alkali on the primary and secondary phosphines, as well as phosphinous acids in dimethyl sulfoxide or other bipolar, aprotic solvents dimethylformamide, dimethylacetamide, hexamethylphosphoric triamide, in the presence of potassium carbonate as a water-removing agent).

2. Alkylation of the phosphide and phosphinite anions has yielded secondary and tertiary phosphines, polyphosphines, functionally substituted phosphines as well as similarly structured phosphine oxides.

Table 11. Tertiary Phosphine Oxides **12** prepared in a Two-Phase system according to Scheme **L**

R^1	R^2	X	Solvent	Temperature/Time	Yield [%]	m.p. [°C] (solvent)	Molecular Formula or Lit. m.p. [°C]
C_6H_5	CH_3	J	C_6H_6	80 °C/2 h	97	111–112° (1/5 C_2H_5OAc/PE)	111.5–112°[21]
C_6H_5	C_2H_5	Br	C_6H_6	80 °C/2 h	98	120–121° (1/1 C_2H_5OAc/PE)	121°[21]
C_6H_5	n-C_4H_9	Br	C_6H_6	80 °C/2 h	97	94–95° (1/5 C_2H_5OAc/PE)	95°[21]
C_6H_5	$C_6H_5CH_2$	Cl	C_6H_6	80 °C/1 h	86	195–196° (C_2H_5OH)	195–196°[21]
			hexane	70 °C/1 h	96		
			n-C_4H_9OH	65 °C/0.5 h	86		
			DMF	80 °C/1 h	86		
			$(n$-$C_4H_9)_2O$	80 °C/0.5 h	68		
$C_6H_5CH_2$	CH_3	J	C_6H_6	80 °C/1.5 h	98	133–133.5° (1/5 C_6H_6/PE)	133.5–134°[21]
$C_6H_5CH_2$	$C_6H_5CH_2$	Cl	C_6H_6	80 °C/3 h	97	213–214° (C_6H_6)	214°[21]
			o-xylene	90 °C/1.5 h	91		

Table 12. Tertiary 1,ω-Bis[phosphinyl]alkanes **13** prepared in a Two-Phase System according to Scheme **M**

R^1	A	X	solvent	Temperature/ Time	Yield [%]	m.p. [°C] (solvent)	Molecular Formula[a] or Lit. m.p. [°C]
C_6H_5	$-(CH_2)_2-$	Cl	C_6H_6	80 °C/2 h	95	271–272° (C_2H_5OH)	269–270°[21]
C_6H_5	$-(CH_2)_4-$	Br	C_6H_6	80 °C/1 h	98	259–260° (DMF)	258–260°[21]
$C_6H_5CH_2$	$-(CH_2)_2-$	Cl	C_6H_6	80 °C/2.5 h	46	231–232° (C_2H_5OH)	$C_{30}H_{32}O_2P_2$ (486.4)
$C_6H_5CH_2$	$-(CH_2)_3-$	Br	C_6H_6	80 °C/2 h	40	210–211° (C_2H_5OH)	$C_{31}H_{34}O_2P_2$ (500.6)
			o-xylene	100 °C/2 h	84		
			DMF	100 °C/2 h	40		
			n-C_4H_9OH	100 °C/2 h	80		
			hexane	70 °C/2 h	98		
$C_6H_5CH_2$	$-(CH_2)_4-$	Br	C_6H_6	80 °C/2 h	99	232.5–233.5° (C_2H_5OH)	$C_{32}H_{36}O_2P_2$ (514.6)
C_6H_5		Br	C_6H_6	80 °C/2 h	90	320–321° (C_2H_5OH)	322°[21]

[a] Satisfactory microanalyses obtained: C ±0.55, H ±0.16, P ±0.22.

3. Phosphinous acids have been alkylated in various solvents in a two-phase system containing concentrated aqueous alkali and tetrabutylammonium iodide as phase transfer catalyst.

All operations with phosphorus(III) compounds were conducted under argon. The solvents and water used in phosphine syntheses are recommended to be distilled under argon. Typical experiments are described below. In each case the reaction conditions are shown in the Tables. In phosphine syntheses the ratio of the solvent to the water contained in the alkali solution should be ~ 10:1. Potassium carbonate was taken in an equimolecular amount with respect to the total amount of water contained in the alkali solution and formed during the formation of the phosphide anion. Alkylation reactions occurred exothermically. The Tables show temperature ranges of the spontaneous heating of the reaction mixture on addition of the alkylating agent. Melting points were measured with Anschütz thermometers.

Tertiary Dialkylphenyl- and Alkyldiphenylphosphines[9] 2 (Scheme B and Table 1)[1]:

In dimethyl sulfoxide: To a solution of the secondary phosphine **1** (24 mmol) in dimethyl sulfoxide is added at 20 °C with stirring a 50–56% aqueous solution of potassium hydroxide (32 mmol) and then dropwise at 10–60 °C an alkylating agent (29 mmol). The mixture is stored for 0.5–3 h at 10–60 °C, diluted with water, and extracted with benzene or pentane[31]. The extract is dried with sodium sulfate. The solvent is distilled off at an atmospheric pressure and the residue is distilled in vacuum.

In dimethylformamide or hexamethylphosphoric triamide: To a solution of the secondary phosphine **1** (22 mmol) in the solvent (20 ml) is added at 20 °C powdered potassium carbonate (111 mmol) and then gradually with vigorous stirring a 50–56% aqueous solution of potassium hydroxide (29 mmol). To the mixture is added dropwise at 10–40 °C the alkylating agent (24 mmol). After heating for 1–2 h at 20–50 °C the mixture is diluted with water and extracted with benzene or pentane[31]. The extract is dried with sodium sulfate. The solvent is distilled off at atmospheric pressure and the residue is distilled in vacuum.

Secondary Alkylphenylphosphines[12] 1 (Scheme C and Table 2):

In dimethyl sulfoxide: To a solution of phenylphosphine (50 mmol) in dimethyl sulfoxide (30 ml) is added with stirring a 50–56% aqueous solution of potassium hydroxide (65 mmol) and then at 10–60 °C dropwise an alkylating agent (50 mmol). After heating for 0.5–2.5 h at 20–60 °C the mixture is diluted with water and extracted with pentane[31]. The extract is washed with water and dried with sodium sulfate. The solvent is distilled off at an atmospheric pressure and the residue is distilled in vacuo.

In dimethylformamide or hexamethylphosphoric triamide: To a solution of phenylphosphine (54 mmol) in the solvent (30 ml) is added at 20 °C powdered potassium carbonate (216 mmol) and then gradually with vigorous stirring a 56% aqueous solution of potassium hydroxide (70 mmol). To the mixture is added dropwise at 20–40 °C alkyl halide (54 mmol). After heating for 1–2.5 at 30–50 °C the mixture is diluted with water and extracted with pentane[31]. The extract is washed with water and dried with sodium sulfate. The solvent is distilled off at atmospheric pressure and the residue is distilled in vacuum.

Tertiary Dialkylphenylphosphines 2,2′ from Phenylphosphine[13] (Scheme D and Table 3):

In dimethyl sulfoxide using 2 mol of alkylating agent: To a solution of phenylphosphine (60 mmol) in dimethyl sulfoxide (70 ml) is added at 20 °C with stirring a 56% aqueous solution of potassium hydroxide (132 mmol) and then dropwise at 20–50 °C alkyl halide (132 mmol). After heating for 0.5–2 h at 40–50 °C the mixture is diluted with water and extracted with benzene or pentane[31]. The extract is washed with water and dried with sodium sulfate. The solvent is distilled off at atmospheric pressure and the residue is distilled in vacuum.

Di-n-butyl-phenylphosphine in hexamethylphosphoric triamide: To a solution of phenylphospine (4.6 g, 42 mmol) in hexamethylphosphoric triamide (50 ml) is added at 20 °C powdered potassium carbonate (42.8 g, 310 mmol) and then gradually with vigorous stirring a solution of potassium hydroxide (5.6 g, 101 mmol) in water (4.2 ml). To the mixture is added dropwise at 40–45 °C *n*-butyl bromide (12.6 g, 92 mmol). After heating for 2 h at 50 °C the mixture is diluted with water (150 ml) and extracted with pentane. The extract is dried with sodium sulfate. The solvent is distilled off at atmospheric pressure and the residue is distilled in vacuo to give di-*n*-butylphenylphosphine; yield: 7.3 g (78%); b.p. 120–121 °C/3 torr.

In dimethyl sulfoxide using two different alkylating agents: To a solution of phenylphosphine (45 mmol) in dimethyl sulfoxide (45 ml) is added at 20 °C with stirring a 56% aqueous solution of potassium hydroxide (108 mmol) and then dropwise at 10–50 °C the first alkyl halide R^1-X (45 mmol). After heating for 10–30 min at 30–50 °C, the second alkyl halide R^2-X (45 mmol) is added dropwise to the mixture. After heating for 1–2 h at 50–80 °C the mixture is diluted with water and extracted with benzene or pentane[31]. The extract is washed with water and dried with sodium sulfate. The solvent is distilled off at atmospheric pressure and the residue is distilled in vacuum.

Poly[diphenylphosphino]akanes[15] 3 and 5 (Scheme E and Table 4):

In dimethyl sulfoxide: To a solution of diphenylphosphine (24 mmol) in dimethyl sulfoxide (15 ml) is added at 20 °C with stirring a 56% aqueous solution of potassium hydroxide (33 mmol) and then dropwise at 25–50 °C the dihaloalkane (13 mmol) in dimethyl sulfoxide (5 ml). After heating for 1–2 h at 40–50 °C, the mixture is diluted with water and the precipitate is filtered off.

In dimethylformamide, dimethylacetamide, or hexamethylphosphoric triamide: To a solution of diphenylphosphine (12 mmol) in the solvent (20 ml) is added at 20 °C powdered potassium carbonate (61 mmol) and then gradually with vigorous stirring a 50% aqueous solution of potassium hydroxide (16 mmol). To the mixture is added dropwise at 20–45 °C the dihaloalkane (6 mmol) in the solvent (5 ml). After heating for 1–2 h at 40–45 °C, the mixture is diluted with water and the precipitate is filtered off.

Tris[diphenylphosphinomethyl]chloromethylmethane **(5)**: To a solution of diphenylphosphine (4.4 g, 24 mmol) in dimethyl sulfoxide (15 ml) is added at 20 °C powdered potassium carbonate (13.8 g, 100 mmol) and then gradually with vigorous stirring a solution of potassium hydroxide (1.7 g, 30 mmol) in water (1.3 ml). To the mixture is added dropwise at 25–30 °C tetrakis[chloromethyl]methane (4; 1.6 g, 8 mmol) in dimethyl sulfoxide (5 ml). After heating for 2 h at 40–50 °C, the mixture is diluted with water (120 ml) and the precipitate is filtered off to give **5**; yield: 4.8 g (90%); m.p. 110.5–111 °C.

$C_{41}H_{38}ClP_3$	calc.	C 74.71	H 5.81	Cl 5.38	P 14.10
(659.2)	found	74.73	5.69	5.23	14.18

ω-Diphenylphosphinocarboxylic Acids[16] 8 (Scheme F and Table 5):

In dimethyl sulfoxide: To a solution of diphenylphosphine (18 mmol) in dimethyl sulfoxide (20 ml) is added at 20 °C with stirring a 50% aqueous solution of potassium hydroxide (47 mmol) and then dropwise at 20–50 °C ω-chlorocarboxylic acid or its ester **7** (20 mmol) in dimethyl sulfoxide (5 ml). After heating for 1–2 h at 20–55 °C the mixture is diluted with water. The aqueous solution is washed with benzene and acidified with diluted hydrochloric acid (1:5). The precipitated oil is extracted with benzene. The extract is dried with sodium sulfate and evaporated in vacuum.

ω-Diphenylphosphinoalkyl Alcohols[17] 10 (Scheme G and Table 6):

In dimethyl sulfoxide: To a solution of diphenylphosphine (25 mmol) in dimethyl sulfoxide (10 ml) is added at 20 °C with stirring a 56% aqueous solution of potassium hydroxide (30 mmol) and then dropwise at 0–50 °C the oxacycloalkane **9** (25 mmol) in dimethyl sulfoxide (5 ml). After heating for 0.5–3 h at 20–95 °C, the mixture is diluted with water and extracted with benzene. The extract is dried with sodium sulfate, evaporated in vacuum, and the residue is distilled.

In dimethylformamide or hexamethylphosphoric triamide: To a solution of diphenylphosphine (26 mmol) in the solvent (20 ml) as

added at 20 °C powdered potassium carbonate (100 mmol) and then gradually with vigorous stirring a 56% aqueous solution of potassium hydroxide (31 mmol). To the mixture is added dropwise at 0–50 °C the oxacycloalkane **9** (26 mmol). After heating for 0.5–3 h at 20–95 °C, the mixture is diluted with water and extracted with benzene. The extract is dried with sodium sulfate, evaporated in vacuum, and the residue is distilled.

Tertiary Phosphine Oxides[20] 12 (Scheme H and Table 7):
To a solution of the phosphinous acid **11** (9 mmol) in dimethyl sulfoxide (15 ml) is added at 20 °C with stirring a 40–56% aqueous solution of potassium hydroxide (12 mmol) and then dropwise at 20–60 °C the alkyl halide (12 mmol). After heating for 10–60 min at 50 °C, the mixture is diluted with water and extracted with chloroform. The extract is dried with sodium sulfate and evaporated in vacuum.

Tertiary 1,ω-Bis[phosphinyl]alkanes[22] 13 (Scheme I and Table 8):
To a solution of the phosphinous acid **11** (25 mmol) in dimethyl sulfoxide (20 ml) is added at 20 °C with stirring a 40–56% aqueous solution of potassium hydroxide (32 mmol) and then dropwise at 20–50 °C the 1,ω-dihaloalkane (14 mmol). After heating for 10–100 min at 50 °C, the mixture is diluted with water. The precipitated crystalline product is filtered off. If the product precipitates in the form of oil, it is extracted with chloroform, the extract is dried with sodium sulfate, and evaporated in vacuum.

Oxidation of Diphenylphosphinous Acid with Aqueous Alkali in Dimethyl Sulfoxide:
To a solution of diphenylphosphinous acid (2.0 g, 10 mmol) in dimethyl sulfoxide (15 ml) is added dropwise with stirring at 20 °C a solution of potassium hydroxide (0.7 g, 13 mmol) in water (0.7 ml). After heating for 5 h at 60 °C, the mixture is diluted with water (50 ml). The aqueous solution is washed with benzene and acidified with hydrochloric acid. The precipitate is filtered off to give diphenylphosphinic acid; yield: 1.8 g (80%); m.p. 193–195 °C. (Ref.[29], m.p. 194–196 °C).

A similar procedure is used to oxidize diphenylphosphinous acid with aqueous alkali in dimethyl sulfoxide at 17–20 °C for 20 h; yield: 80%; m.p. 194–195 °C.

Oxidation of Diphenylphosphinous Acid with Aqueous Alkali in Ethanol:
A mixture of diphenylphosphinous acid (2.0 g, 10 mmol), potassium hydroxide (0.7 g, 13 mmol), and water (0.7 ml) in ethanol (15 ml) is refluxed for 4 h and then diluted with water (50 ml). The aqueous solution is washed with benzene and acidified with hydrochloric acid. The precipitate is filtered off to give diphenylphosphinic acid; yield: 2.1 g (~ 100%); m.p. 194–194.5 °C.

ω-Phosphinylcarboxylic Acids[23] 14 (Scheme J and Table 9):
To a solution of the phosphinous acid **11** (22 mmol) and ω-halocarboxylic acid (24 mmol) in dimethyl sulfoxide (10 ml) is added dropwise at 20–60 °C with stirring a 30–56% aqueous solution of potassium hydroxide (57 mmol). After heating for 1 h at 40–60 °C, the mixture is diluted with water. The aqueous solution is acidified with dilute hydrochloric acid (1:5). The precipitated crystalline product is filtered off. If the product precipitates in the form of oil, it is extracted with chloroform. The extract is dried with sodium sulfate and evaporated in vacuum.

γ-Phosphinylpropyl Alcohols[26] 15 (Scheme K and Table 10):
To a solution of the phosphinous acid **11** (22 mmol) and trimethylene chlorohydrin (22 mmol) in dimethyl sulfoxide (10 ml) is added dropwise at 30–65 °C with stirring a 50% aqueous solution of potassium hydroxide (57 mmol). After heating for 0.5–2 h at 45–60 °C, the mixture is diluted with water and extracted with chloroform. The extract is dried with sodium sulfate and evaporated in vacuum.

Tertiary Phosphine Oxides 12 in a Two-Phase System[27] (Scheme L and Table 11):
To a solution of the phosphinous acid **11** (10 mmol) in the solvent (20 ml) at 20 °C is added at 40–56% aqueous solution of potassium hydroxide (15 mmol), tetra-*n*-butylammonium iodide (1 mmol), and the alkyl halide (13 mmol). After heating for 0.5–3 h at 65–90 °C, the mixture is diluted with water and extracted with chloroform. The extract is dried with sodium sulfate and evaporated in vacuum. If the product precipitates in the form of crystals, it is filtered off.

Tertiary 1,ω-Bis[phosphinyl]alkanes 13 in a Two-Phase System[28] (Scheme M and Table 12):
To a solution of the phosphinous acid **11** (10 mmol) in the solvent (20 ml) at 20 °C is added a 50% aqueous solution of potassium hydroxide (15 mmol), tetra-*n*-butylammonium iodide (1 mmol), and 1,ω-dihaloalkane (0.006 mol). After heating for 1–2.5 h at 70–100 °C, the mixture is diluted with water and extracted with chloroform. The extract is dried with sodium sulfate and evaporated in vacuum. If the product precipitates in crystalline form, it is filtered off.

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[30] Heating the diphenylphosphine together with 56% aqueous potassium hydroxide in dimethyl sulfoxide (80°C, 6 h) affords 10–15% of diphenylphosphinic acid. In the same conditions but without alkali no diphenylphosphinic acid is formed. Under reflux for 4 h together with 56% aqueous potassium hydroxide in alcohol the diphenylphosphine is not converted to diphenylphosphinic acid.

[31] Phosphines whose boiling points are close to that of the solvent used in the reaction (dimethyl sulfoxide, dimethylformamide, hexamethylphosphoric triamide) should be extracted with pentane or petroleum ether (b.p. 40–70°C), which do not extract these solvents from water.