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N-ALKYLPENTAMETHYLPHOSPHORAMIDES: NOVEL CATALYSTS IN TWO-PHASE REACTIONS

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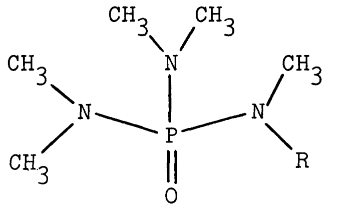
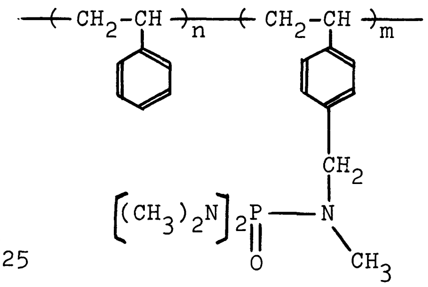
Phosphoramides having hydrophobic groups in the molecule, e.g. N-dodecylpentamethylphosphoramide or N-benzylpentamethylphosphoramide, can be used as phase-transfer catalysts in two-phase reactions. Polymeric phosphoramides, which were prepared by the copolymerization of N-(p-vinylbenzyl)pentamethylphosphoramide with styrene, were found to catalyze phase-transfer reactions more efficiently than their monomeric analogs.

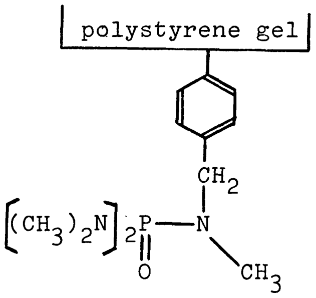
Aqueous organic two-phase reactions are catalyzed by quaternary ammonium or phosphonium salts,$^{1)}$ crown ethers,$^{2)}$ cryptates,$^{3)}$ and α-phosphoryl sulfoxides.$^{4)}$ We found that phosphoramides, with a suitable structure, can be effectively used as phase-transfer catalysts in two-phase reactions. Compounds (I)—(III) were prepared and the catalytic activity of these phosphoramides was tested for some substitution reactions. The results are described in this communication.



(Ia) R = CH_3 (If) R = n-$C_{12}H_{25}$
(Ib) R = $C_6H_5CH_2$ (Ig) R = n-$C_{16}H_{33}$
(Ic) R = p-$CH_2{=}CHC_6H_4CH_2$
(Id) R = n-C_8H_{17}
(Ie) R = α-$C_{10}H_7CH_2$



(IIa) m/(n+m) = 0.095
(IIb) m/(n+m) = 0.25
(IIc) m/(n+m) = 0.44



(III)

Table 1. Phase-transfer reactions catalyzed by phosphoramides (Ia)—(Ig)

Substrate[a)]	Reagent[b)]	Phosphoramide[c)]	Temp, °C	Time, hr	Yield,[d)] %	Product
n-$C_8H_{17}Br$	KI	(Ia)	80	4	6.5	n-$C_8H_{17}I$
n-$C_8H_{17}Br$	KI	(Ib)	80	4	70	n-$C_8H_{17}I$
n-$C_8H_{17}Br$	KI	(Ic)	80	4	83	n-$C_8H_{17}I$
n-$C_8H_{17}Br$	KI	(Id)	80	4	77	n-$C_8H_{17}I$
n-$C_8H_{17}Br$	KI	(Ie)	80	4	47	n-$C_8H_{17}I$
n-$C_8H_{17}Br$	KI	(If)	80	4	83	n-$C_8H_{17}I$
n-$C_8H_{17}Br$	KI	(Ig)	80	4	86	n-$C_8H_{17}I$
n-$C_8H_{17}Br$	CH_3COOK	(Ic)	80	24	88	n-$C_8H_{17}OCOCH_3$
n-$C_8H_{17}Br$	NaCN[e)]	(Ib)[f)]	80	8	62	n-$C_8H_{17}CN$
n-$C_8H_{17}Br$	NaCN[e)]	(Ie)[g)]	80	8	>96	n-$C_8H_{17}CN$
trans-Stilbene	$KMnO_4$[h)]	(If)	25	6	82[i)]	C_6H_5COOH

a) Benzene was used as solvent in the permanganate oxidation, otherwise no solvent was used for the substrate. b) Saturated aqueous solution, 5.0 mol. equiv. c) 0.15 Mol. equiv. d) By g.l.c. analysis. e) 20.7 Mol. equiv. f) 0.11 Mol. equiv. g) 0.10 MOl. equiv. h) 2.7 Mol. equiv. i) Isolated product.

Phosphoramides (Ib)—(Ig) were synthesized by the reaction of sodium salt of pentamethylphosphoramide with the corresponding alkyl halides. Compound (II), polymers containing phosphoramide groups, was prepared by the copolymerization of N-(p-vinylbenzyl)-pentamethylphosphoramide (Ic) with styrene. Compound (III), an insoluble polymer containing phosphoramide groups, was prepared by the reaction of chloromethylated polystyrene—divinylbenzene beads with sodium salt of pentamethylphosphoramide.

As shown in Table 1, the halogen exchange reaction of n-octyl bromide with potassium iodide is catalyzed by phosphoramides (Ib)—(Ig), while is not catalyzed by hexamethylphosphoramide (Ia). This result indicates that the replacement of one of the methyl groups of (Ia) by a higher aliphatic or an aralkyl groups induced catalytic activity for the halogen exchange reaction. These phosphoramides also were effective as catalysts for the reactions of n-$C_8H_{17}Br$ with NaCN or CH_3COOK, and for the oxidation of trans-stilbene.

Table 2. Phase-transfer reactions catalyzed by polymeric phosphoramides (II)—(III)[a]

Reagent[b]	Phosphoramide[c]	Time, hr	Yield,[d] %	Reagent[b]	Phosphoramide[c]	Time, hr	Yield,[e] %
KI	(Ib)	48	10	CH_3COOK	(Ib)	48	23
KI	(Ic)	24	2	CH_3COOK	(IIa)	48	35
KI	(IIa)	24	38	CH_3COOK	(IIb)	48	37
KI	(IIb)	24	43	CH_3COOK	(IIc)	48	47
KI	(IIc)	25	87				
KI[f]	(III)[g]	9	67[h]				

a) n-Octyl bromide and toluene were used as substrate and solvent, respectively; temp, 80°C. b) Saturated aqueous solution, 5.0 mol. equiv.

c) 0.05 Mol. equiv. based on phosphoramide group. d) Product, n-octyl iodide.

e) Product, n-octyl acetate. f) Temp, 100°C; 13.4 mol. equiv. g) 0.12 Mol. equiv.

h) >96 % After 24 hr.

Compound (II), polymers having phosphoramide groups, was effective as catalysts for two-phase reactions (Table 2). The catalytic activity of the polymers was superior to that of their monomeric analogs, e.g., (Ib) or (Ic). In addition, the catalytic activity of the polymers increased with an increase in phosphoramide content of the polymers, that is, in the order of (IIc) > (IIb) > (IIa). This result can be explained in terms of "cooperative effect" of phosphoramide groups on cation binding properties (Fig. 1).[5] Such a cooperative coordination of phosphoramide groups upon cations must result in efficient extraction of ion pairs from an aqueous phase to an organic phase, and thereby results in efficient catalysis for two-phase reactions. In practice, the cation binding ability of polymers (IIa)—(IIc) was found to be superior to that of their monomeric analogs, and to decrease in the order (IIc) > (IIb) > (IIa) (see Table 3).[6] This result supports the presence of cooperative effect of phosphoramide groups on catalysis for two-phase reactions.

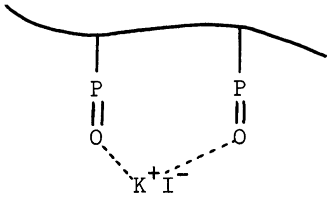


Fig. 1.

Recently, it has been demonstrated by Regen[7] that two-phase reactions are catalyzed by a solid phase catalyst containing quaternary ammonium groups. Compound (III), a solid phase catalyst containing phosphoramide groups, was found to catalyze the halogen exchange reaction of n-octyl bromide with potassium iodide (Table 2).

Table 3. Extraction of picrate salts by phosphoramides[a)]

Phosphoramide	% Picrate salt extracted[b)]				
	Cation	Li^+	Na^+	K^+	Ba^{2+}
(Ia)[c)]		3	1	1	1
(Ib)		3	2	4	—
(IIa)		29	25	25	31
(IIb)		35	31	32	37
(IIc)		62	49	49	55

a) Solvent system, $H_2O—CH_2Cl_2$(50:50, v/v); [Picric acid] = 7.2×10^{-5}M; [P=O units] = 7.0×10^{-3}M; [Metal hydroxide] = 0.01 M.

b) Based on total amount of picrate salt. c) 7.0×10^{-2}M.

These experimental results suggest that compounds having both polar groups such as S=O, or N-C=O, and hydrophobic groups may be effective as phase-transfer catalysts. Further research on the application of this concept is in progress.

References

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5) Cf. for example S. Kopolow, T. E. Hogen Esch, and J. Smid, Macromolecules, 6, 133 (1973).

6) The binding efficiencies of polymeric phosphoramides and their monomeric analogs were evaluated by a procedure described by Smid et al.[5)]

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