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INTERACTION OF LITHIUM ALKYLAMIDES OR LITHIUM DIALKYLAMIDES WITH TETRAPHENYLPHOSPHONIUM CHLORIDE. REACTION COURSE AS A FUNCTION OF REACTION CONDITIONS AND DIALKYLAMIDE STRUCTURES

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Summary

Reaction of $Ph_4P^+Cl^-$ with LiNHR (where R = CH_3, C_2H_5, i-C_3H_7, n-C_4H_9, but not $C(CH_3)_3$) gives phosphineimines III, whereas the reaction with $LiNR_2$ proceeds via three routes depending on the size of R and the dialkylamide excess. With larger R groups, homolytic decomposition of pentacoordinate phosphorus compounds occurs. With smaller R groups, Ph_3P and $PhNR_2$ are formed. Higher excesses of lithium amide result, probably, in ligand exchange at the pentacoordinate phosphorus followed by decomposition of the exchange products. Charge transfer complex intermediates are assumed to be formed in all the reactions.

Introduction

In a short communication [1] we have described some reactions of lithium dialkyl amides with phosphonium chloride. In the present paper we wish to present ^{31}P NMR spectra of the reaction mixtures and discuss the effect of the reactant excess upon the product compositions.

Sodium amide with bis(*o,o'*-biphenylene)phosphonium iodide gave the aminophosphorane [2], lithium diethyl amide with tetraphenylphosphonium bromide gave 9-phenyl-9-phosphafluorene (I), [3]. The same phosphine resulted from the reaction of lithium piperidide and t-butyltriphenylphosphonium bromide [4]. The authors [3,4] believed that the first step of the reaction was metalation.

We have found that the reaction of lithium dialkyl amides with tetraphenylphosphonium chloride is complicated, involving a set of parallel reactions. The prevailing direction of the reaction depends on the substituents at the nitrogen and on the ratio of the reactants.

Results and discussion

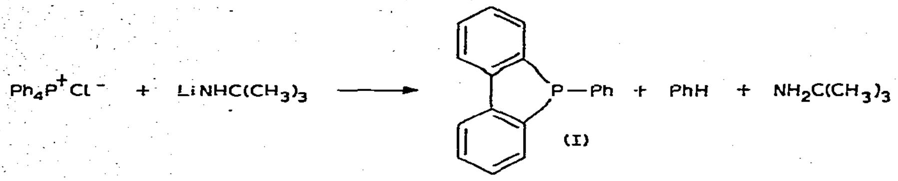
Principal reactions and their interpretation

The reaction of tetraphenylphosphonium chloride with primary lithium alkylamides to give *N*-alkyltriphenylphosphineimines (III) proceeds, probably, via the pentacoordinate phosphorus intermediate II * (eq. 1) (Table 1). Lithium

$$Ph_4PCl + LiNHR \longrightarrow \underset{(II)}{[Ph_4P{-}NHR]} \longrightarrow \underset{(III)}{Ph_3P{=}NR} + PhH \qquad (1)$$

$(R = CH_3, C_2H_5, CH(CH_3)_2, n\text{-}C_4H_9)$

t-butyl amide, however, reacts quite differently. The cyclic phosphine I is formed in a yield of 80—85% (eq. 2), together with benzene. This may be due to the presence of the bulky t-butyl group and the difficulties inherent in forming the P—N bond.



(2)

In reaction of tetraphenylphosphonium chloride with secondary lithium dialkyl amides the size of substituents at the nitrogen atom is also decisive. Lithium diethyl amide or lithium di-i-propyl amide react by eq. 3 exclusively, whereas in the case of lithium dimethyl amide, lithium piperidide and lithium morpholide reaction by eq. 4 interferes **. The yields of the products of these

$$Ph_4P^+Cl^- + LiNR_2 \longrightarrow I + PhH + NHR_2 \qquad (3)$$

TABLE 1

REACTION PRODUCTS FROM THE REACTIONS OF TETRAPHENYLPHOSPHONIUM CHLORIDE (1×10^{-1} mol/l) WITH PRIMARY LITHIUM AMIDES IN A THF/ETHER MIXTURE

Lithium amide	Reactants ratio ($Ph_4PCl/RNHLi$)	Temp. (°C)	Reaction time (h)	Product yield (%)		
				PhH	$Ph_3P{=}NR$	Others
CH_3NHLi	1/3	20	3	90	70 [a]	none
C_2H_5NHLi	1/3	20	1	90	70 [b]	none
i-C_3H_7NHLi	1/3	20	5	95	75 [c]	none
n-C_4H_9NHLi	1/3	20	2	50	93 [d]	none
t-C_4H_9NHLi	1/3 [e]	50	3	60	none	I (85)

[a] $Ph_3\overset{+}{P}N(CH_3)_2I^-$ isolated, m.p. 185°C [20]. [b] $Ph_3\overset{+}{P}N(C_2H_5)_2I^-$ isolated, m.p. 174°C [20]. [c] $(Ph_3\overset{+}{P}N(CH_3)\text{-}i\text{-}C_3H_7)I^-$ isolated, m.p. 211°C [20]. [d] $(Ph_3\overset{+}{P}N(CH_3)\text{-}n\text{-}C_4H_9)I^-$ isolated, m.p. 240°C. [e] 1.8×10^{-1} mol/l $Ph_4P^+Cl^-$.

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* Similar reactions are known; sodium amide and CH_3Li with Ph_4PCl give $Ph_3P{=}NH$ [5] and $Ph_3P{=}CH_2$ [6,7] respectively.

** The fact that the diethylamide group is effectively larger than the piperidide group has been stated previously [8,9].

TABLE 2

REACTION PRODUCTS FROM THE REACTIONS OF TETRAPHENYLPHOSPHONIUM CHLORIDE WITH LITHIUM DIALKYLAMIDES AND LITHIUM t-BUTYLAMIDE (1×10^{-1} mol/l Ph_4PCl in THF/ether)

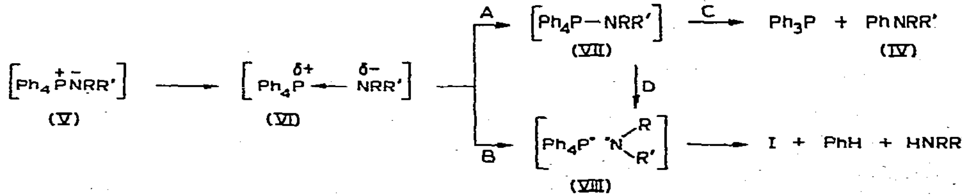
Lithium amide	Concentration ratio (Ph_4PCl/R_2NLi)	Temp. (°C)	Reaction time (h)	Product yield (%)			
				Ph_3P	I	PhH	$PhNR_2$
$(CH_3)_2NLi$	1/3	50	3	24	64	60	15
	1/15	50	3	98	traces (ca. 2)	82	traces (ca. 1)
$(CH_2)_5NLi$	1/3	50	3	34	66	41	34
	1/10	50	3	93	7	69	24
	1/15	50	3	97	traces	80	18
$O(CH_2CH_2)_2NLi$	1/3 [a]	50	2	47	25	44	27
	1/15	50	3	80	none	40	30
$CH_2(CH_2-CH(CH_3)-)_2NLi$	1/3	50	1		64	61	
$(C_2H_5)_2NLi$	1/3	20	5	traces (ca. 3)	98	90	
	1/7	20	3	10	90	91	
$(i\text{-}C_3H_7)_2NLi$	1/3	20	3	traces (ca. 2)	94	90	
$t\text{-}C_4H_9NHLi$	1/3 [b]	50	3	traces	85	60	
	1/7 [b]	20	3	4	82	80	

[a] 5×10^{-2} mol/l Ph_4PCl. [b] 1.8×10^{-1} mol/l Ph_4PCl.

$$Ph_4P^+Cl^- + LiNR_2 \longrightarrow \underset{(IV)}{PhNR_2} + Ph_3P \qquad (4)$$

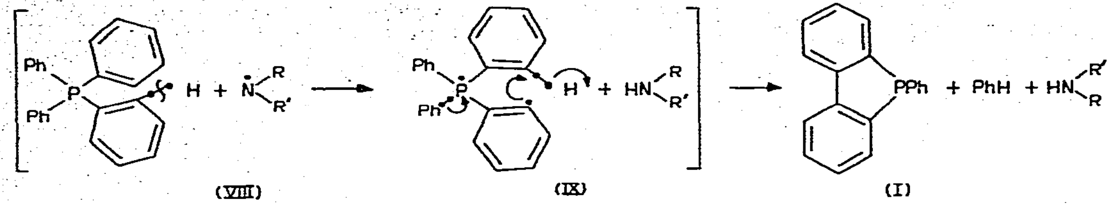
reactions are listed in Table 2. The size effect is also evident on comparing the reactions of lithium piperidide and lithium 2,6-dimethyl piperidide with tetraphenylphosphonium chloride: eq. 3 and 4 operate in the former case and only eq. 3 in the latter. The reaction sequence is shown in Scheme 1.

SCHEME 1



The ion pair V gives a fairly stable complex VI, which may involve partial charge transfer, as the deep colour of the solution (λ_{max} = 420 nm) disappears during the course of the reaction. The complex VI may either give the pentacoordinate phosphorus compound VII (Route A) or the radical pair VIII (Route B). Route A yields triphenylphosphine and the dialkylaniline IV while Route B gives the phosphine I, benzene and the amine. The radical pair may also form from the aminophosphorane VII via P—N bond homolysis. The transformations of VIII are presented in Scheme 2.

SCHEME 2



The amine radical abstracts a hydrogen atom from the *ortho* position of one of the phenyls, which leads to concerted homolytic decomposition of the diradical intermediate IX. The radicals do not escape out of the cage (no reaction with the solvent has been observed). Radical decomposition of pentaphenylphosphorus to the phosphine I and benzene was proposed by Razuvaev [10].

An increase in the lithium dialkyl amide excess lowers the yield of phosphine I (Table 2), therefore the assumption [2,3] that the formation of I involves phosphonium *o*-metalation is no longer applicable.

The amide radical size effect may be explained by assuming that larger radicals destabilise the phosphorane VII, hinder its formation and facilitate its homolysis. As a result, Route C (Scheme 1) becomes less, and Route D (or B) more easily accessible.

The formation of the pentacoordinate phosphorus intermediate agrees with the formation of *N*-alkyltriphenylphosphineimines (III) from primary lithium amides and $Ph_4P^+Cl^-$ (eq. 1) and also with the ^{31}P NMR spectra discussed below.

^{31}P NMR spectra and their interpretation

^{31}P NMR spectra of the reaction mixtures were recorded, at about 20% concentration of $Ph_4P^+Cl^-$, as a function of time.

The spectra in Fig. 1 were recorded for the reaction of tetraphenylphosphonium chloride with a six-fold excess (mol/mol) of lithium piperidide in a tetrahydrofuran—ether mixture. After 150 h at 20—30°C, only the signals due to tertiary phosphines are seen, for Ph_3P $\delta(^{31}P) = 6$ ppm [11], and 9-phenyl-9-phosphafluorene (I) $\delta(^{31}P) = 10.4$ ppm [11], whereas the spectrum recorded directly after the reactants have been mixed contains signals due to intermediates. The signal at —20.8 ppm may be due to the initial phosphonium salt or to the ion pair V ($\delta^{31}P = -24$ ppm [11] for $Ph_4P^+I^-$ in ethanol).

The signal at —11.7 ppm, very intense at the beginning of the reaction, may be assigned to the complex VI (CTC) because, being close to the ion pair signal, it is shifted to higher field. The highfield signal at 74.3 ppm increases and then decreases with time. It may be assigned to the *N*-piperydyltetraphenylphosphorane [VII, R + R' = $(CH_2)_5$] since $\delta(^{31}P)$ is known to be 86 ppm for pentaphenylphosphorus [12] and 95 ppm for amino-bis(*o*,*o*'-biphenylene)phosphorane [2].

Tetraphenylphosphonium chloride reacts with lithium diethylamide much faster In 30—50 min at 20—35°C the signal due to VI (—11 ppm) disappears from the spectrum and only the signal due to phosphine I (10 ppm) remains unaffected. The reactions with lithium t-butyl amide and lithium n-butyl amide are even

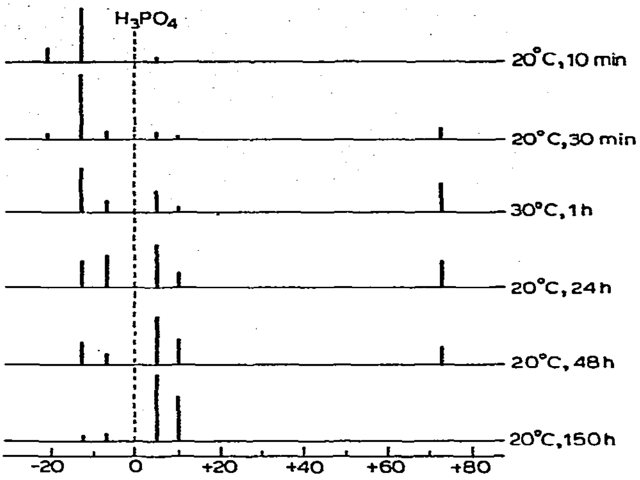


Fig. 1. $^{31}P\{^1H\}$ NMR spectra of the mixture of tetraphenylphosphonium chloride and lithium piperidide, $Ph_4P^+Cl^-/LiN(CH_2)_5$ 1/6 in ether/THF 1/4 *.

faster, and only signals due to phosphine I at 10 ppm and the *N*-n-butyltriphenylphosphineimine (III) signal at —2.9 ppm were observed 7—10 min (the spectrum cannot be recorded earlier) after the reagents have been mixed. Consequently, ^{31}P NMR spectroscopy verifies the assumptions made above. The spectral data are shown in Table 4.

Effect of lithium dialkylamide excess upon the reaction course

Equations 3 and 4 are valid only when the lithium dialkylamide excess is not too high. The normal ratio was three equivalents of the amide to one equivalent of the phosphonium salt. If the excess was lower, the reaction was not

TABLE 3

9-PHENYL-9-PHOSPHAFLUORENE (±) AND BENZENE YIELDS AS A FUNCTION OF THE SALT CONCENTRATION IN THE REACTION OF $Ph_4P^+Cl^-$ WITH $LiNEt_2$, IN ETHER AT 20° C

Run No.	Salt concentration (mol/l)	Concentration ratio (salt/amide)	Reaction time (h)	Yield (%)	
				I	PhH
1	1×10^{-1}	1/3	50	96	51
2 [a]	5×10^{-2}	1/3	60	46	50
3 [a]	5×10^{-2}	1/3	90	42	40
4 [b]	5×10^{-3}	1/3	90	4	3

[a] 50% Ph_4PCl isolated. [b] 90% Ph_4PCl isolated.

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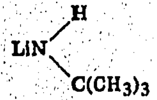
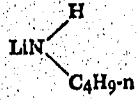
* The phosphonium salt will not dissolve in THF or ether before the amide is added, so its spectra in these solvents could not be recorded. $Ph_4P^+Cl^-$ in ethanol gives a signal at $\delta^{31}P$ of —24 ppm [11]. The signal at —6.3 ppm may belong to one of the ion pairs.

TABLE 4

$^{31}P\{^1H\}$ NMR DATA OF REACTION MIXTURES FOR REACTIONS OF $Ph_4P^+Cl^-$ WITH $LiNR_2$, (ca. 20% Ph_4PCl in THF/ether 4/1, from 85% phosphoric acid reference)

Lithium amide	Concentration ratio ($Ph_4PCl/LiNR_2$)	Reaction time (h)	Temp. (°C)	^{31}P Chemical shifts (ppm)					
				Ph_4PX	Intermediates			Products	
					CTC	Unidentified species	Ph_4P-NR_2 (VII)	Ph_3P	Phosphine I
$LiN(CH_2)_5$	I/6	0.2	20	−20.8	−11.7	none	none	none	none
		0.5	20	−20.8	−11.7	−6.3	+74.3	+5.9	+10
		1; 24; 48	20	none	−11.7	−6.3	+74.3	+5.9	+10
		150	20	none	none	−6.3	none	+5.9	+10
	I/15	0.5	20	−20.7	−11.6	−6.4	+74.1	+5.8	none
		1.5	29	none	−11.6	−6.4, +51.3	+74.1	+5.8	none
		3.5	50	none	none	−6.4	none	+5.8	none
		4.5	50	none	none	none	none	+5.8	none
$LiN(CH_3)_2$	I/15	0.3	23	none	−11.9	none	+75.4	none	none
		2.0	23	none	−11.9	−7.1	none	+5.9	none
		24	23	none	none	−7.1	none	+5.9	none
$LiN(C_2H_5)_2$	I/6	0.25	20	none	−11.2	none	none	none	+10.5
		0.5	20	none	−11.2	−6.5	+72.6	+5.9	+10.5
		1.5	20	none	none	none	none	+5.9	+10.5
		0.1	20	none	none	none	none	none	+10.2
 [a]		0.1	20	none	none	none	none	none	none

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[a] Only one signal is observed for *N*-butyltriphenylphosphineimine.

complete, and noticeable amounts of the tetraphenylphosphonium chloride were recovered. A higher dilution of the reaction mixture (Table 3) also inhibited the reaction. These data may suggest that complex VI formation is reversible (eq. 5).

$$\mathrm{Ph_4P^+Cl^-} + \mathrm{LiNR_2} \rightleftharpoons \underset{\text{(V)}}{[\mathrm{Ph_4P^+NR_2^-}]} + \mathrm{LiCl} \rightleftharpoons \underset{\text{(VI)}}{[\mathrm{Ph_4}\overset{\delta+}{\mathrm{P}} \longleftarrow \overset{\delta-}{\mathrm{N}}\mathrm{R_2}]} \qquad (5)$$

The data in Table 2 show that an increase in the amide excess lowers the phosphine I yield and, in parallel, raises the triphenylphosphine and benzene yields *. The amount of phenylated amide is also slightly affected.

These facts cannot be explained in terms of eq. 3 and 4 alone. Probably, aminophosphorane VII decomposition via Routes C and D (Scheme 1) competes with ligand exchange in VII (eq. 6), under the action of a higher lithium amide excess **.

$$\underset{\text{(VII)}}{\mathrm{Ph_4PNR_2}} + \mathrm{LiNR_2} \longrightarrow \underset{\text{(X)}}{\mathrm{Ph_3P(NR_2)_2}} + \mathrm{PhLi} \qquad (6)$$

Phenyllithium reacts with an excess of the free amine to give benzene. The increase in the triphenylphosphine yield may be due to fast decomposition of the diaminophosphorane via eq. 7 ***.

$$\underset{\text{(X)}}{\mathrm{Ph_3P[N(CH_2R')_2]_2}} \rightarrow \mathrm{Ph_3P} + \mathrm{R'CH{=}NCH_2R'} + \mathrm{HN(CH_2R')_2} \qquad (7)$$

Predominant formation of $\mathrm{Ph_3P}$, practically complete absence of the phosphine I and the decrease in the yields of dialkylaniline †, in the reactions with a 15-fold excess of the amide, indicates a faster ligand exchange in the phosphorane VII when compared with Routes C and D in Scheme 1.

$$\mathrm{Ph_4SbOCH_3} \rightarrow \mathrm{Ph_3Sb} + \mathrm{PhH} + \mathrm{OCH_2} + \mathrm{CH_3OPh} \qquad (8)$$

$$\mathrm{Ph_4SbC_2H_5} \rightarrow \mathrm{Ph_3Sb} + \mathrm{CH_2{=}CH_2} + \mathrm{PhH} \qquad (9)$$

The data in Table 2 show that the effect of the reactants ratio is especially noticeable in reactions with smaller lithium amides such as dimethyl amide, piperidide and morpholide, but is much weaker with the larger amides such as

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* Note that the results are very sensitive to reaction conditions such as dilution, temperature, solvent and, probably, irradiation. On the whole, however, the pattern is quite definite.

** Similar exchanges involving organolithium compounds are known for a quite extensive number of pentacovalent phosphorus compounds [11, 13] and also for $\mathrm{Ph_5P}$ (the potassium amide reagent) [14].

*** β-Elimination (cf. eq. 7), caused by thermolysis of pentacoordinate compounds of the Group V elements, was found for alkyl-bis(2,2′-biphenylene)arsenic [17], alkoxytetraphenylantimony [18] (eq. 8), and alkyltetraphenylantimony [19] (eq. 9).

† Dialkylaniline disappears completely only in the reaction with a 15-fold lithium dimethyl amide excess, whereas its yield is decreased by 10% in the reactions with lithium piperidide or lithium morpholide. Probably an $S_N2(o)$ substitution at the carbon atom occurs in parallel, similar to the case of triphenylsulphonium salts and alkoxides [16] or sodium piperidide [15].

diethylamide and t-butyl amide. This may reflect the effect of the substituent size on the lifetimes of *N,N*-dialkylaminotetraphenylphosphorane (VII).

Experimental

GLC analyses of reactions products were made on a Varian—Aerograph 1200 instrument with a flame ionisation detector and nitrogen as a carrier gas. The columns were made as follows:

1. 5% XE-60 on Chromaton N-AW-DMCS, grain diameter 0.16—0.25 mm, column length 1.5 m, temperature programmed at 100—230°C, carrier gas flow rate 12 ml min^{-1}.
2. 3% Polymethylsiloxane PMS-100 on Chromaton N-AW-DMCS, grain diameter 0.10—0.16 mm, column length 1 m, temperature programmed at 100—200°C, carrier gas flow rate 20 ml min^{-1}.
3. 15% Carbowax-20M on Chromaton N-AW-DMCS, grain diameter 0.16—0.25 mm, column length 1.5 m, temperature programmed at 65—90°C, carrier gas flow rate 10 ml min^{-1}.

Columns 1 and 2 were used for analysing tertiary phosphines and dialkylanilines, columns 1 and 3 for benzene. Quantitative data were obtained as calibration against an internal reference was made.

Reaction technique

All reactions were carried out over a dry argon atmosphere in anhydrous solvents. Tetraphenylphosphonium salt was added to a lithium amide solution, prepared from the amine and a butyllithium solution. The reaction mixture became quickly homogeneous and acquired a dark red colour. The reaction was terminated when a thin-layer chromatography test, on alumina, showed that none of the initial salt was present. The mixture was poured into water, extracted with toluene and the extract dried and analysed by GLC. The results are shown in Tables 1 and 2.

N-n-butyltriphenylphosphineimine

$Ph_4P^+Cl^-$ (3.4 g, 9 mmol) was added to a lithium n-butyl amine solution in an ether/THF (2/3) mixture, prepared from n-butylamine (4 ml, 40 mmol) and butyllithium (18.4 ml of a 1.63 *N* solution, 30 mmol). The mixture was stirred for 2 h, the solvent removed in an argon atmosphere and the residue triturated in anhydrous hexane. The resulting crystals were extracted with chloroform, the solution was filtered, the solvent removed and the residue heated with 15 ml of CH_3I for 3 h. The crystals were reprecipitated from chloroform with ethyl acetate and frozen from a methanol/ethyl acetate (1/5) mixture, to give $(C_6H_5)_3\overset{+}{P}—N(C_4H_9)CH_3I^-$, 4 g (93%), m.p. 240°C. (Found: C, 58.28; H, 5.68; I, 26.86; N, 2.76; P, 6.57. $C_{23}H_{27}INP$ calcd.: C, 58.11; H, 5.74; I, 26.70; N, 2.95; P, 6.51%.)

Methoiodides or ethoiodides of the other *N*-alkyltriphenylphosphineimines, $Ph_3P{=}NR$ (R = CH_3, C_2H_5, i-C_3H_7), were obtained in a similar way. Their yields and melting points are shown in Table 1.

NMR techniques

The spectra were recorded on a Brucker-HX-90 instrument at 36.43 MHz operating frequency. Fresh dark red reaction solutions were placed into the ampoule filled with argon. Table 4 shows the spectral parameters for some reactions, Fig. 1 shows the spectral pattern for the reaction $Ph_4P^+Cl^-$ with lithium piperidide.

The intensities are not listed, since the measurements were made on a pulse instrument where the intensity is broadly dependent on the relaxation time. Slow accumulation was impossible under the conditions adopted.

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