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# Alkylation Reactions of Tris(dialkylamino)phosphines. A Kinetic Study

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The reactions of methyl iodide with various tris(dialkylamino)phosphines, $(R_2N)_3P$, in acetonitrile at 25.0° C have been studied kinetically. The reactivity order was found to be: Tris(piperidino)phosphine ∼ tris(dipropylamino) phosphine ∼ tris(diethylamino)phosphine ≥ tris(dimethylamino)phosphine > tris(morpholino)phosphine.

With the exception of tris(morpholino)phosphine which is approximately as reactive as is triphenylphosphine, these aminophosphines are all at least as reactive toward methyl iodide as is tributylphosphine.

The various factors determining the nucleophilicity of tris(dialkylamino)phosphines are discussed.

Within the last decade, a large volume of synthetic work dealing with tris(dialkylamino)phosphines, $(R_2N)_3P$, has been published. The nucleophilic atom in this class of tervalent phosphorus compounds is generally the phosphorus atom, although, toward methyl trifluoroacetate [1] and when the phosphorus atom is a member of a five-membered ring system,[2] there is some evidence that the nitrogen atoms may be able to compete with the phosphorus atom for the electrophilic center.

Competition experiments [3,4] and numerous semi-quantitative studies [5–11] have shown that these compounds range among the most reactive ones of all the usual tervalent phosphorus compounds. However, this exceptional reactivity is by no means general and toward certain substrates, molecular oxygen and some metal carbonyls,[12] tris(dialkylamino)phosphines are less reactive than are the usual trialkyl phosphites and trialkyl- and triarylphosphines.

Due to the limited ability of tris(dialkylamino)phosphines to act as electrophilic species[7,13], their low reactivity in many reactions can readily be accounted for. However, the complete lack of systematic kinetic studies of reactions of this class of tervalent phosphorus compounds with any substrate leaves much to be known with regard to the factors determining their reactivity.

In this paper the results from a kinetic study of the reactions between some tris(dialkylamino)phosphines and alkyl halides in acetonitrile are presented, eqn. 1.

$$(R_2N)_3P + RX \xrightarrow{\text{MeCN}} (R_2N)_3\overset{+}{P}R + X^- \qquad (1)$$

The reactions depicted by eqn. 1 should in principle be well suited for kinetic studies since the products, the phosphonium salts, are obtained in almost quantitative yield and are in most reactions studied easily purified and characterized. However, serious experimental difficulties were encountered in the present study due to the high reaction rates and to the unstable nature of some of the tris(dialkylamino)phosphines (see Experimental Part).

The principle alkyl halide employed in this study was methyl iodide, since several kinetic studies of reactions between this substrate and other tervalent phosphorus compounds have been reported, (for leading references, see Ref. 14), allowing a direct comparison to be made. Furthermore, some reactions between tris(morpholino)phosphine, $Mor_3P$, and various 4-substituted benzyl halides were studied in an attempt to obtain information with regard to the structure of the transition state in alkylation reactions of this class of phosphorus nucleophiles.[14]

## EXPERIMENTAL

Acetonitrile was purified as described[14] and flushed with dry nitrogen or argon prior to use. Light petroleum (40 – 60 °C), diethyl ether, benzene, and toluene were dried with metallic sodium. The various amines were fractionated from potassium hydroxide pellets. Methyl iodide and the benzyl halides were purified as previously reported.[14]

*Tervalent phosphorus reagents.* $(Me_2N)_3P$, Fluka prakt., was first distilled under vacuum and then dissolved in a large volume of light petroleum (40 – 60 °C), 500 ml to 25 g compound, and set aside for 24 h at – 20 °C to completely precipitate dimethylamine hydrochloride. After filtration, performed in a dry box, the light petroleum was removed in vacuum and the aminophosphine repeatedly distilled in vacuum prior to use.

$(Et_2N)_3P$ and $(Pr_2N)_3P$ were prepared according to standard procedures and purified as $(Me_2N)_3P$.

Tris(piperidino)phosphine, $Pip_3P$, was prepared and purified in a similar way, but finally crystallized from diethyl ether at dry-ice temperature; m.p. 37 °C.

Tris(morpholino)phosphine, $Mor_3P$, was prepared and purified as described,[11] m.p. 157 °C (lit.[11] 156 °C).

$Mor_2PPh$ was made according to Hudson and co-workers,[15] m.p. 115 – 116 °C (113 – 115 °C).[15]

$MorPPh_2$, apparently a new compound, was prepared from freshly distilled chlorodiphenylphosphine, $ClPPh_2$, and 2 mol of morpholine in toluene. The product was crystallized from toluene, then from diethyl ether and finally from acetonitrile. Since this compound is very sensitive to moisture, no attempt was made to determine the ultimate yield of the reaction. M.p. 192 °C. (Found: C 71.54; H 6.44; N 4.94; P 11.41. Calc. for $C_{16}H_{18}NOP$: C 70.85; H 6.64; N 5.17; P 11.44).

All operations with the aminophosphines, including the synthesis of the phosphonium salts and the preparations of solutions for the kinetic studies were performed in a dry-box under nitrogen or argon.

*Phosphonium salts.* The phosphonium salts were prepared in nearly quantitative yield by adding the alkyl halides in slight excess to the aminophosphines dissolved in acetonitrile. The following salts were crystallized from acetonitrile or from acetonitrile/diethyl ether mixture:

Methyl tris(dimethylamino)phosphonium iodide, m.p. > 350 °C (> 350 °C [5]). Methyl tris(piperidino)phosphonium iodide, m.p. 254 °C (242 °C [16]). Methyl tris(morpholino)phosphonium iodide, m.p. 310 °C (dec). Bis(morpholino)methylphenylphosphonium iodide, m.p. 205 – 206 °C. Diphenylmethylmorpholinophosphonium iodide, m.p. 204 – 205 °C. Methyl triphenylphosphonium iodide, m.p. 183 °C (182 – 183 °C [17]). Benzyl tris(morpholino)phosphonium bromide, m.p. 297 °C (dec). 4-Nitrobenzyl tris(morpholino)phosphonium bromide, m.p. 268 – 269 °C (dec). 4-Methylbenzyl tris(morpholino)phosphonium bromide, m.p. 247 – 248 °C.

The phosphonium salts from $(Et_2N)_3P$ and $(Pr_2N)_3P$ and methyl iodide, MeI, could not be obtained as crystalline solids from reactions performed in acetonitrile upon addition of diethyl ether. Only when the reactions were performed in diethyl ether could crystalline phosphonium salts be obtained. All attempts to crystallize methyl tris(diethylamino)phosphonium iodide, m.p. 72 – 92 °C, from the usual dipolar aprotic solvents upon addition of large quantities of diethyl ether or light petroleum failed. Methyl tris(dipropylamino)phosphonium iodide could be crystallized from acetone/diethyl ether mixture after several days at – 20 °C. M.p. 135 – 138 °C. These two phosphonium salts, contrary to the phosphonium salts mentioned above, are very hygroscopic.

*Kinetic studies.* The second order rate constants for most of the reactions were calculated from kinetic runs performed under both pseudo first order and second order conditions. The conductivity method,[14] and, for reactions with methyl iodide, the UV method measuring the rate of formation of iodide ions at 247.5 nm, were applied.

For the reactions of methyl iodide with $(Me_2N)_3P$, $(Et_2N)_3P$, and $(Pr_2N)_3P$, the aminophosphines purified by distillation, none of these methods were entirely satisfactory and the reproducibility of the rate constant was generally poor. The rate constants given in Table 1 for $(Et_2N)_3P$ and $(Pr_2N)_3P$ are therefore assumed to be no better than ± 10 %. $(Me_2N)_3P$ was especially difficult to handle, and the various methods could only give a rough estimate of the rate constant for its reaction with methyl iodide at 25 °C. Competition experiments between $(Et_2N)_3P$ and $(Me_2N)_3P$ toward methyl iodide were therefore performed: To a 1:1 mixture of $(Me_2N)_3P$ and $(Et_2N)_3P$ in acetonitrile, each $3 \times 10^{-3}$ M, was added an equivalent amount of methyl iodide, dissolved in acetonitrile. After 1 h at room temperature the reaction mixture was evaporated to dryness in vacuum. The residue was washed several times with diethyl ether to remove unreacted aminophosphine, then dissolved in trideuterioacetonitrile, $CD_3CN$, and the relative amounts of the phosphonium salts from $(Me_2N)_3P$ and $(Et_2N)_3P$ determined by integration of the *N*-alkyl Me-signals in the NMR. Repeating the experiments with varying relative concentrations of the competing nucleophiles showed $(Et_2N)_3P$ to be 1.8 – 2.0 times as reactive as $(Me_2N)_3P$ toward methyl iodide at room temperature, in agreement with the suggested rate constants from the rate studies.

The reactions of $Pip_3P$, $Mor_3P$ and the various morpholino-substituted phosphines with methyl iodide showed second order kinetics of good precision and these rate constants are probably well within ± 5 %.

The second order rate constants for the reactions between $Mor_3P$ and the benzyl halides were determined only by the conductivity method under pseudo first order conditions.[14]

All measurements were performed at 25.0 °C maintained within ± 0.05 °C in an thermostated oil-bath.

*Comments on the kinetic methods.* The conductivity method appeared to be the most reliable one, even though solutions of solely tris(dialkylamino)phosphines in acetonitrile were not entirely stable as viewed from the increasing conductivity of the solutions with time, especially for solutions of the liquid aminophosphines. This instability in acetonitrile appeared to be a function of ageing of the aminophosphines and was kept to a minimum by working with freshly purified samples.

Presumably, part of these difficulties arose from the presence of impurities in the aminophosphines. Regardless of how carefully the liquid aminophosphines, $(Me_2N)_3P$, $(Et_2N)_3P$, $(Pr_2N)_3P$, were distilled, traces of the corresponding amines, $R_2NH$, were always found to be present as indicated by the red colour of the solutions due to the presence of the corresponding phosphoranes when these aminophosphines were allowed to react with 4-nitrobenzyl bromide.[18]

The solid aminophosphines, on the other hand, which were purified by crystallization, gave colourless solutions of the corresponding phosphonium salts when added to 4-nitrobenzyl bromide. The presence of dialkylamines in the solutions of the liquid aminophosphines in acetonitrile could thus not be due to hydrolysis of these compounds [16,19] by residual water in the applied solvent.

The UV method measuring the rate of formation of iodide ions at 247.5 nm was less reliable due to the extreme dilution necessary and to the high extinction coefficient of the aminophosphines at this wavelength.[20]

## RESULTS

In Table 1 are listed the results from the present study for the reactions between the various aminophosphines and methyl iodide in acetonitrile at 25 °C. For comparison, the rates of reaction of triphenylphosphine, $Ph_3P$, tributylphosphine, $Bu^t_3P$, and trimethyl phosphite, $(MeO)_3P$, for reactions with the same substrate in acetonitrile at the same temperature are included in the table. In column 2 in Table 1, the basicity constants in water for the parent dialkylamines, $R_2NH$, are listed.

*Table 1.* Second order rate constants for the reactions between various tervalent phosphorus compounds and methyl iodide in acetonitrile at 25 °C.

| | $k_2 \times 10^3$ ($l\ mol^{-1}\ s^{-1}$) | $pK_a$ of $HNR_2$ in water [f] |
|---|---|---|
| $(Me_2N)_3P$ | ~200 [a] | 10.73 |
| $(Et_2N)_3P$ | 480 [b] | 10.98 |
| $(Pr_2N)_3P$ | 530 [b] | 11.00 |
| $Pip_3P$ | 480 | 11.11 |
| $Mor_3P$ | 22 | 8.33 |
| $Mor_2PPh$ | 11 | |
| $MorPPh_2$ | 6.1 | |
| $Ph_3P$ | 5.9 [c] | |
| $Bu^t_3P$ | 240 [d] | |
| $(MeO)_3P$ | 0.035 [e] | |

[a] Approximate value only. [b] Rate constants only accurate to ± 10 %. [c] Ref. 14. [d] Calculated value ($Bu^t_3P$ is ~ 40 times as reactive as is $Ph_3P$ toward MeI in both acetone and methanol).[21,22] [e] Ref. 23. [f] Ref. 24.

Although the accuracy of the calculated second order rate constants for some of the reactions studied is somewhat limited, the data in Table 1 indicate the following reactivity sequence: $Pip_3P \sim (Pr_2N)_3P \sim (Et_2N)_3P \geq (Me_2N)_3P > Mor_3P \geq Ph_3P$. Thus, $(Me_2N)_3P$, the commonly applied tris(dialkylamino)phosphine and, as shown in the Experimental Part, the most difficult one to handle, is the least reactive one with the exception of tris(morpholino)phosphine, $Mor_3P$. The data in Table 1 readily suggest that in reactions where a tris(dialkylamino)phosphine is desired, tris(piperidino)phosphine, $Pip_3P$, is the compound of choice since, being a solid compound at room temperature, its purification and handling is quite simple.

Tris(morpholino)phosphine, $Mor_3P$, is considerably less reactive than are the other aminophosphines studied and is only slightly more reactive than triphenylphosphine. A slight, but smooth increase in reactivity is observed from $Ph_3P$ to $Mor_3P$ with increasing number of morpholino groups attached to the reacting phosphorus atom.

With the possible exception of $(Me_2N)_3P$, the remaining tris(dialkylamino)phosphines are all at least as reactive as is tributylphosphine toward methyl iodide. Since the reactivity of trialkylphosphines toward alkyl halides is only slightly dependent upon the substituents linked to the phosphorus atom,[21] it can thus be concluded that tris(dialkylamino)phosphines range

*Table 2*. Second order rate constants for reactions between tris(morpholino)phosphine and triphenylphosphine and some benzyl halides in acetonitrile at 25 °C. (Relative rates in parenthesis).

| | $k_2 \times 10^3$ l mol$^{-1}$ s$^{-1}$ | | |
|---|---|---|---|
| | 4-Methylbenzyl bromide | Benzyl bromide | 4-Nitrobenzyl bromide |
| $Mor_3P$ | 12 (1.45) | 8.30 (1.00) | 8.50[a] (1.02) |
| $Ph_3P$ | 3.50 (1.63) | 2.15 (1.00) | 2.34[b] (1.09) |

[a] $k_2$ for RI $= 5.0 \times 10^{-2}$ l mol$^{-1}$ s$^{-1}$, $k_2(RI)/k_2(RBr) = 5.9$. [b] Ref. 14. $k_2$ for RI $= 1.63 \times 10^{-2}$ l mol$^{-1}$ s$^{-1}$, $k_2(RI)/k_2(RBr) = 7.0$.

among the most reactive ones of all tervalent phosphorus compounds toward methyl iodide.

In Table 2 are listed the rate constants for the reactions between tris(morpholino)phosphine and some 4-substituted benzyl halides. For comparison, the results from a recent study on similar reactions of triphenylphosphine [14] are included. Tris(morpholino)phosphine is seen to retain its slightly higher reactivity toward these substrates compared to triphenylphosphine. The effect of the substituents in the benzyl halides on reaction rates are of the same order of magnitude, and as for triphenylphosphine, a slight increase from benzyl bromide to 4-nitrobenzyl bromide is observed. The effect of the leaving group, as exemplified by the $k_2(RI)/k_2(RBr)$ ratios, is slightly lower for tris(morpholino)phosphine, 5.9, than for triphenylphosphine, 7.0.

## DISCUSSION

Little is known with regard to the factors determining the nucleophilicity of tris(dialkylamino)phosphines. From several thermodynamic studies, however, two important factors seem to have been established which govern their basicity toward Lewis acids. Since the nucleophilicity is generally closely related to the basicity in a series in which the nucleophilic atom remains constant,[22] it is natural to assume that the nucleophilicity of tris(dialkylamino)phosphines depends on these two factors as well.

*A. The lone pair-lone pair repulsion.* The *p*-orbital lone pairs on the nitrogen atoms are interacting with the phosphorus lone pair in a repulsive manner, raising the energy of the latter and rendering it both more basic and nucleophilic.[20] Thus, when the nitrogen lone pairs are not constrained to be orthogonal to the phosphorus lone pair, which is not the case in any of the aminophosphines studied in the present investigation, the basicity and the nucleophilicity of this class of tervalent phosphorus compounds should parallel the basicity of the dialkylamines from which they are derived. The reactivity sequence for aminophosphines found in the present study, Table 1, is in agreement with this theory.

*B. The* $p_N\pi$*-*$d_P\pi$ *electronic transfer.*[20,25,26] This type of electronic transfer should be facilitated by $sp^2$ hybridization of the nitrogen lone pairs since lone pairs in $sp^3$ hybrids are expected to be less effective in donating $\pi$-density to the phosphorus atom than when contained in a *p*-orbital. Although structural data on tris(dialkylamino)phosphines are scarce, an electron diffraction study of tris(dimethylamino)phosphine [27] and a recent X-ray structure determination of tris(morpholino)phosphine [28] indicate that the nitrogen atoms have considerable $sp^2$ character. The limited structural data, however, do not allow any conclusions to be made with regard to a possible correlation between the hybridization of the nitrogen atoms and the substituents linked to these atoms.

The $\pi$ electron transfer should especially be favoured in reactions where considerable positive charge is accumulated on the phosphorus atom in the transition state since the consequent contraction of its *d*-orbitals will render these more available for interaction with the nitrogen orbitals. The very short P−N bond distance of 1.63 Å [29] in dimethylaminodifluorophosphine, $Me_2NPF_2$, due to the electronegative fluorine atoms is in accord with this suggestion.

However, the data in Table 2 suggest that the transition state for alkylation reactions of tris(dialkylamino)phosphines is quite comparable with that of alkylation reactions of triphenylphosphine. Recently,[14] it has been proposed that this transition state is somewhat "tight" but rather reactant-like with rather small amount of bond breaking, causing the phosphorus atom to have only a negligible fractional charge in the transition state. It thus appears conceivable that tris(dialkylamino)phosphines do not owe their high reactivity toward alkyl halides to $\pi$-electron transfer in the transition state.

Actually, the lower rate increase from benzyl bromide to 4-methylbenzyl bromide for reactions of $Mor_3P$ than for $Ph_3P$ suggests even less dependence upon fractional charge on the carbon atom and thus less bond breaking in the transition state in alkylation reactions of aminophosphines than for triphenylphosphine. The smaller effect of the leaving group as exemplified by the $k_2(RI)/k_2(RBr)$ ratios accords with this suggestion. The transition state for alkylation reactions of tris(dialkylamino)phosphines should thus be even less ionic and "tighter" than for the corresponding reactions of triphenylphosphine. Presumably, the ability of tervalent phosphorus compounds to enter into a "tight" transition state is related to the stability of the corresponding phosphoranes.[14,23] The very stable nature of phosphoranes derived from tris(dialkylamino)phosphines is well documented.[30] Tris(dialkylamino)phosphines seem to be the only tervalent phosphorus compounds which can make stable adducts with triphenylmethyl isocyanide, $Ph_3CNC$.[31]

The $\pi$ electron transfer may well be the cause for the exceptional reactivity of tris(dialkylamino)phosphines in reactions with highly electron deficient electrophiles or when the reactions go through highly ionic transition states. The NPN bond angles in these compounds, $97-98°$,[27,28] invalidates the possible argument that tris(dialkylamino)phosphines owe their high reactivity in certain reactions to a large bond angle in their ground state. With Lewis acids like borane, $BH_3$,[26,32] the triphenylmethyl carbenium ion, $Ph_3C^+$,[33] and organic azides, $RN_3$,[20] with which tris(dialkylamino)phosphines make more stable adducts than do other tervalent phosphorus species, a considerable charge transfer from the phosphorus atom to the accepting atoms is known to take place. The very stable nature of chloro- and bromotris(dialkylamino)phosphonium cations, $XP^+(NR_2)_3$,[34,35] supports this argument.

The results in the present study indicate that the nucleophilicity of tris(dialkylamino)phosphines toward aliphatic carbon is mainly governed by the availability of the free electron pair on the reacting phosphorus atom. Their reactivity toward this class of substrates does not seem to require $\pi$ electron transfer from the nitrogen atoms to the phosphorus atom. In reactions with alkyl halides these compounds therefore do not appear to act as $\alpha$-nucleophiles. The $\alpha$-effect is generally known to be negligible in alkylation reactions.[36,37] By applying the Brønsted equation [38] one can thus speculate that the proton basicity of the phosphorus atom in tris(dialkylamino)phosphines is comparable to that of trialkylphosphines while tris(morpholino)phosphine should be slightly more basic than triphenylphosphine.

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