

Synthetic and NMR Spectrometric Studies on the Aminolysis of Methylphosphonothioic Dichloride

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ABSTRACT. The methods of preparation and possible reaction mechanisms for the formation of cyclodiphosph (V) azanes, $[\text{MeP}(\text{S})\text{NR}]_2$, are discussed. These compounds and their monomeric precursors, $\text{MeP}(\text{S})(\text{NHR})_2$, have been investigated using ¹H, ¹³C, ³¹P nmr spectrometry.

The thermal condensation of phenylphosphonothioic di(monoalkylamide), $\text{PhP}(\text{S})(\text{NHR})_2$, leads to a variety of different products (Trippett 1962, Mel'nikov *et al.* 1967, Flint *et al.* 1971 and Argent *et al.* 1981). When R=Me, Et, Prⁿ, Buⁿ, Buⁱ, Pr^c and CH₂Ph the corresponding, 1,3-dialkyl-2, 4-diphenyl-2, 4-dithiocyclo-diphosph (V) azane, $[\text{PhP}(\text{S})\text{NR}]_2$, is obtained. The *trans*-form was found to be the predominating reaction product (Trippett 1962, Ibrahim *et al.* 1971, Bullen *et al.* 1973 and Cameron *et al.* 1975). The *cis*-isomer has also been isolated in certain cases (Healy *et al.* 1971, and Bullen and Tucker 1973).

However, when R=H, Prⁱ, Bu^s, Bu^l, the dealkylated cyclotriphosph(V)azane, $[\text{PhP}(\text{S})\text{NH}]_3$, is the product (Ibrahim *et al.* 1971, Bullen *et al.* 1973, Bullen and Tucker 1973 and Cameron *et al.* 1975), whilst with R=Hex^c, a most unusual fused bicyclic compound is formed (Healy *et al.* 1971 and Argent *et al.* 1981).

The thermolysis of phenylphosphonothioic di(monoarylamides), $\text{PhP}(\text{S})(\text{NHC}_6\text{H}_4\text{X})_2$ (X=H; o-; m-; p-Me, o-; m-; p-OMe) leads to the corresponding cyclodiphosph(V)azanes, $[\text{PhP}(\text{S})\text{NC}_6\text{H}_4\text{X}]_2$. The reaction products have been assigned the *trans*-structures on the basis of the ¹H nmr evidence, but the *cis*-isomer was detected only in some cases (Argent *et al.* 1981).

Experimental

A method for the synthesis of cyclodiphosph(V)azanes in the solution have been developed (Hursthouse *et al.* 1985). In the present work a series of methylphosphonothioic di(monoalkylamides) were prepared by the interaction of methylphosphonothioic dichloride with primary aliphatic amines in polar non-aqueous solvents. ^1H , ^{31}P and ^{13}C nmr spectral data of the various methylphosphonothioic diamides were measured and structural inferences were drawn from these data (Table 1).

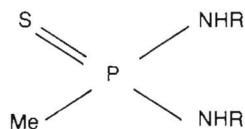
Table 1. ^1H , ^{13}C of the Me-P and ^{31}P nmr spectrometric data of methylphosphonothioic di(monoalkylamides)

Compound	δ Me $^1\text{H}^*$	J P-H **	δ $^{31}\text{P}^*$	$\delta^{13}\text{C}$ (Me) *	J C-P **
MeP(S)Cl $_2$	2.82	14.58	78.65	39.00	80.59
MeP(S)(NHMe) $_2$	1.77	13.83	68.86	20.00	90.12
MeP(S)(NHPr i) $_2$	1.77	13.83	60.53	23.30	90.12
MeP(S)(NHBu i) $_2$	1.78	14.08	66.23	21.50	90.11
MeP(S)(NHBu s) $_2$	1.78	14.05	66.76	21.85	90.12
MeP(S)(NHBu t) $_2$	1.78	14.15	53.25	22.50	90.15

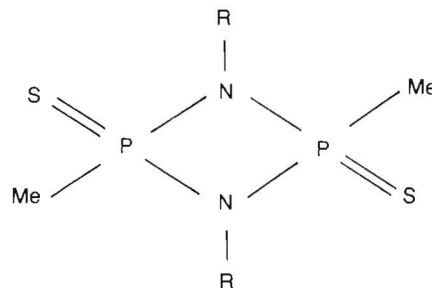
* in ppm

** in Hz

The reaction of methylphosphonothioic dichloride MeP(S)Cl $_2$, with alkylamines, NH $_2$ R(R=Me, Et, Pr i , Bu i , Bu s , Bu t), in acetonitrile for 2 hrs at room temperature yields methylphosphonothioic di(monoalkylamides), MeP(S)(NHR) $_2$, (I) and 1,3-dialkyl-2,4-dimethyl-2,4-dithiocyclodiphosph(V)azanes, [MeP(S)NR] $_2$ (II).



(I)



(II)

Monitoring the reaction of methylphosphonothioic dichloride and isopropylamine by ^{31}P nmr at room temperature, only signals due to the starting material, MeP(S)Cl_2 , the di(monoalkylamide), $\text{MeP(S)(NHPr}^i)_2$ and the cyclodiphosph(V)azane, $[\text{MeP(S)NPr}^i]_2$, were observed.

The reaction proceeds very quickly under a variety of concentration conditions. At lower amine concentration, dimeric cyclodiphosph(V)azanes (II) predominate, whilst at higher amine concentration the di(monoalkylamide) (I) is the predominant reaction product. It was found that the optimum ratio of methylphosphonothioic dichloride to isopropylamine is 1:3 to obtain the highest yield (36% yield) of the four-membered cyclic dimer $[\text{MeP(S)NPr}^i]_2$.

^{31}P nmr spectra were recorded using a F.T. spectrometer operating at 24.15MHz and using 0.05M solutions in chloroform with a deuterated solvent as an external standard (8 mm tube in 10 mm). The shifts are measured relative to 85% H_3PO_4 (0.0 ppm) and reported on the same scale in ppm.

As a pilot experiment, an attempt to trap the possible intermediate $[\text{MeP(S)=NR}]$ in the reaction solution was carried out in the presence of benzil or acrolein. No reaction between the trapping agents and any of the reaction constituents was detected.

The t.l.c. for the reaction products of methylphosphonothioic di(monoisobutylamide) showed that the mixture contains at least three components and that the diamide is the predominate constituent. By working out this mixture and separating the different components by column chromatography over silica gel, it was possible to isolate $[\text{MeP(S)NBu}^i]_2$ as a colourless unstable liquid. By means of ^{31}P nmr it was shown that the ^{31}P chemical shift of this dimer is at $\delta=84.2712$ ppm.

Results and Discussion

^1H , ^{13}C , and ^{31}P nmr spectra of all methylphosphonothioic di(monoalkylamides) were in accordance with the expected structure of such diamides (see Table 1). However, in the ^1H nmr spectrum of $\text{MeP(S)(NHPr}^i)_2$ the two methyl groups of each isopropyl show chemical shift non-equivalence because they are diastereotopic (Flint *et al.* 1971, Ibrahim *et al.* 1971 and Argent *et al.* 1981). Similar non-equivalence is also observed in the ^{13}C nmr spectrum of this compound.

By contrast such non-equivalence is not observed in the two methyl groups of the isobutyl chain in the corresponding $\text{MeP(S)(NHBu}^i)_2$ in both ^1H and ^{13}C nmr spectra.

From the ^1H nmr spectrum of the di(isopropylamide), the methyl proton signals (a) appear at $\delta=1.15-1.20$ ppm as two doublets and the methine proton signal (b) appears as a complex pattern of multiplets presumably due to the overlap of two septets at $\delta=3.35-3.55$ ppm. The signal at $\delta=2.33$ ppm is that of the N-H protons (c). Also, from ^{13}C nmr spectra of the di(isopropylamide), the two methyl carbons (a) are magnetically non-equivalent leading to two overlapping doublets at $\delta=25.45-25.80$ ppm, whilst the methine carbon (b) give rise to a doublet at $\delta=43.20-43.35$ ppm.

A plot of ^{31}P nmr chemical shifts for the cyclic dimers against those of the corresponding monomeric precursors, showed that the shifts of the monoalkylamides of the two series $\text{PhP}(\text{S})(\text{NHR})_2$ and $\text{MeP}(\text{S})(\text{NHR})_2$ which have common alkyl groups are approximately similar (Fig. 1), irrespective of the nature of the

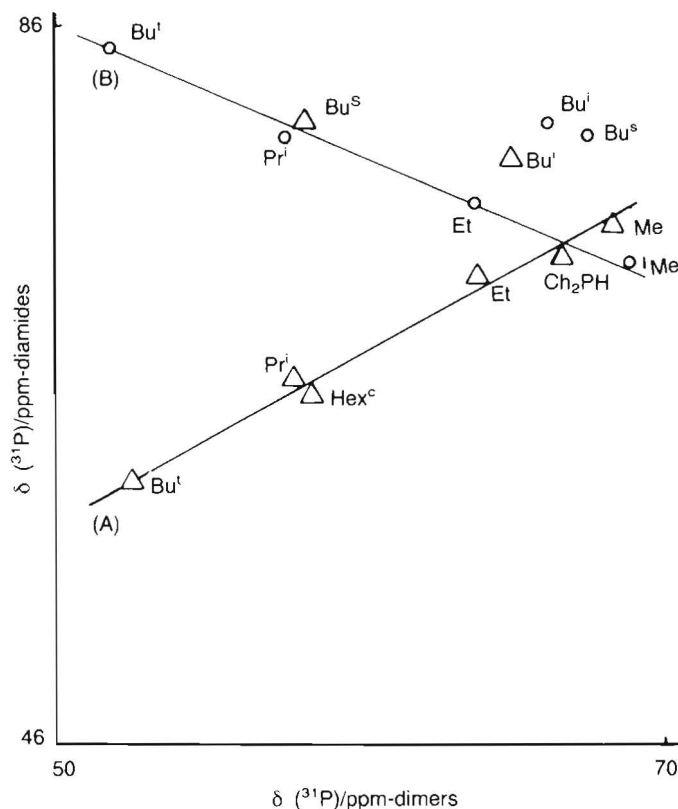


Fig. 1. ^{31}P nmr chemical shifts for diamides versus dimers:

A: $\text{PhP}(\text{S})(\text{NHR})_2$ VS. $[\text{PhP}(\text{S})\text{NR}]_2$

B: $\text{MeP}(\text{S})(\text{NHR})_2$ VS. $[\text{MeP}(\text{S})\text{NR}]_2$

parent phosphorus chloride. These findings suggest that the phosphorus nuclei in these compounds are influenced by a consistent shielding mechanism.

Major differences of ^{31}P nmr chemical shifts are observed for the dimers in each of the series even when they have common alkyl groups. It is not out of place to mention that the electron delocalisation within the four-membered ring system (Islam *et al.* 1974 and Ibrahim 1968), may have a direct influence on the deshielding of the phosphorus nuclei.

It should be noted that the ^{31}P nmr chemical shifts for the iso-butyl dimer derivatives is anomalous in these series. The reason for this anomaly is not yet well understood.

For the derivatives of MeP(S)Cl_2 (curve B) (Fig. 1), the change in the chemical shifts of the cyclic dimers is less pronounced and opposite in sense to the changes for PhP(S)Cl_2 (curve A) derivatives. As a possible explanation to this discrepancy is the difference in hybridisation encountered in the two series, where the ipso-carbon atom attached to phosphorus in the Ph-P series is sp^2 hybridised, whilst the methyl-carbon in the Me-P series is sp^3 hybridised and its bonds are directed tetrahedrally.

It has been reported that the plot between $\delta^{31}\text{P}$ and $\delta^{13}\text{C-1}$ (C-1 is the ipso-carbon) nmr chemical shifts for both PhP(S)(NHR)_2 and $[\text{PhP(S)NR}]_2$ show a straight line relationship (Hursthouse *et al.* 1985).

In the present work a similar relationship has also been observed for the series MeP(S)(NHR)_2 in which the correlation between $\delta^{31}\text{P}$ and $\delta^{13}\text{C}$ showed a straight line relationship. These findings indicate that the inductive effect of the alkyl groups attached to nitrogen is one of the controlling factors in the electron flow towards the phosphorus atom. These curves (Fig. 2) again reflect the regularity of the behaviour of the diamide derivatives and confirm that deviations from regularity only occur in some cyclic dimers, notably those of Bu^i and Bu^{sec} derivatives.

The proposed reaction mechanisms leading to the formation of the diamides and their corresponding dimers is represented in Scheme 1. However, there is no ^{31}P nmr evidence, at the present time, to support the existence of the "linear dimer" or "trigonal phosphorus" intermediates. In attempting to trap the possible intermediate $[\text{MeP(S)=NR}]$ by carrying out the solution reaction in the presence of benzil or acrolein, no reaction between these reagents and phosphorus moiety was detected.

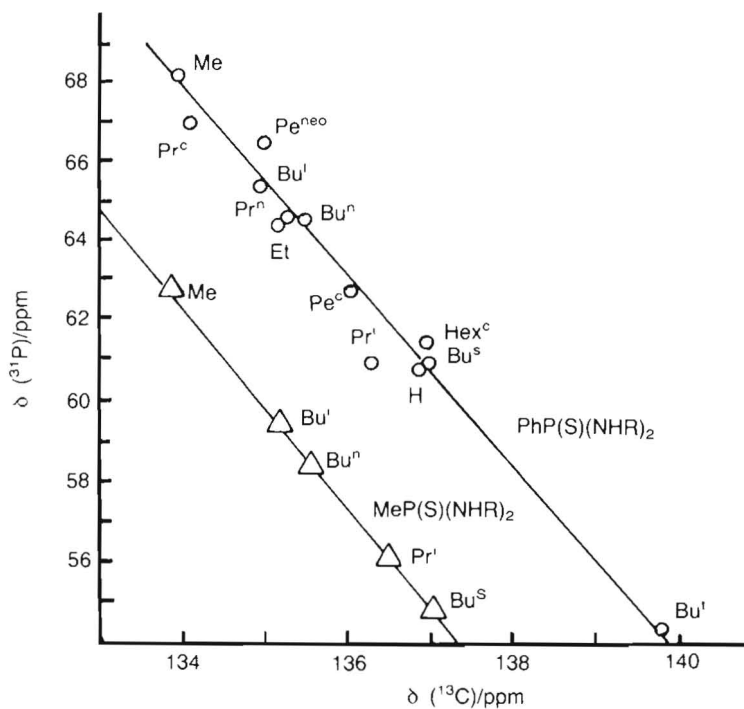
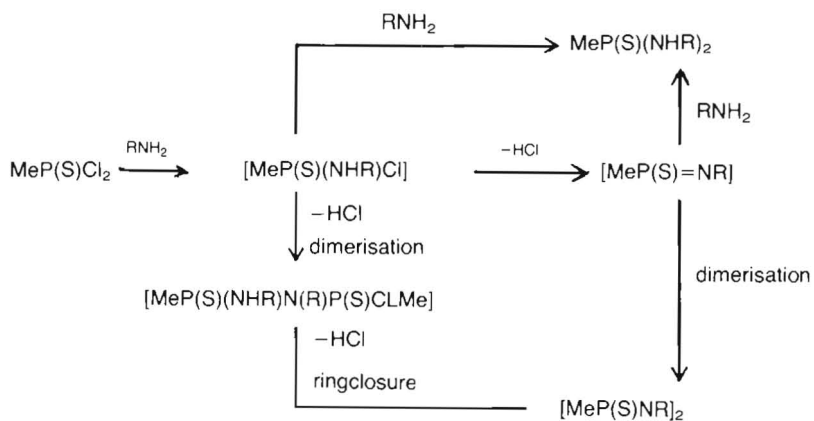


Fig. 2. ^{13}C Versus ^{31}P nmr chemical shifts for the diamides: $\text{MeP}(\text{S})(\text{NHR})_2$ and $\text{PhP}(\text{S})(\text{NHR})_2$



Scheme 1

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دراسات تخليقية وطيفية عن طيف الرنين النووي المغناطيسي لنواتج تفاعل ثنائي كلوريد ميثيل فوسفونوثيويك مع الأمينات

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يستعرض البحث طرق تخليق بعض دايمرات ثنائي الفوسفازانات الحلقية من تفاعل ثنائي كلوريد ميثيل فوسفونوثيويك مع بعض الأمينات. حيث نوقشت الآلية المحتملة لتكوين هذه الدايمرات لثنائي الفوسفازانات الحلقية $[MeP(S)NR]_2$. وتمت دراسة هذه الدايمرات والمونوميرات التي إشتقت منها بتحليل أطياف الرنين النووي المغناطيسي لها. كما إشمئل البحث على إيجاد العلاقات بين الإزاحات الكيميائية للكربون ١٣ (^{13}C) والفوسفور ٣١ (^{31}P) لأطياف الرنين النووي المغناطيسي لهذه النوى في المركبات المذكورة، حيث أظهرت هذه النتائج علاقة خطية بين الإزاحة الكيميائية للكربون ١٣ (^{13}C) والإزاحة الكيميائية للفوسفور ٣١ (^{31}P) يدل هذا على أن الإزاحة الكيميائية لهاتين النواتين تعتمد اعتماداً كلياً على طبيعة المجموعات التي ترتبط بذرة الفوسفور.