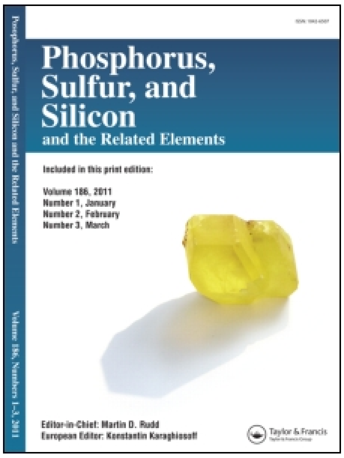

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A NEW ROUTE TO PHOSPHORYL THIOCARBONYL MIXED IMIDES - STRUCTURE LIMITATIONS

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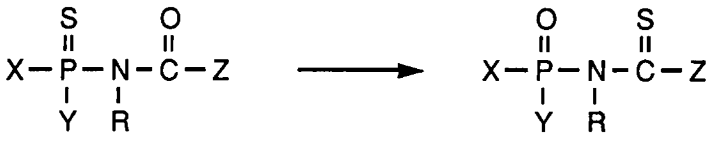
Abstract The rearrangement of N-methyl thiophosphoryl carbonyl mixed imides (**I**, XYP(S)N(Me)C(O)Z) to N-methyl phosphoryl thiocarbonyl mixed imides (**II**, XYP(O)N(Me)C(S)Z) was studied as a function of substitution on phosphorus (**Ia**: X = Y = MeO; **Ib**: X = Ph, Y = MeO; and **Ic**: X = Y = Ph) with Z = Ph and as a function of substitution on carbon (**Ia**: Z = Ph; **Id**: Z = Me; and **Ie**: Z = OiBu) with X = Y = MeO. For **Ia**, **Ib**, and **Id**, rearrangement is complete and quantitative. In contrast, **Ic** rearranges to a 10/90 equilibrium mixture of **IIc**/**Ic** and **Ie** gives no evidence for rearrangement to the phosphoryl thiocarbonyl mixed imide **IIe**. A relative reactivity order for **Ia**, **Ib**, **Ic**, and **Id** of 1.00, 0.15, 0.036, and 0.11 respectively, was observed in the rearrangements.

INTRODUCTION

Phosphoryl carbonyl mixed imides of general structure XYP(O)N(R)C(O)Z are being widely investigated as potential crop protection chemicals. These studies have also prompted mechanistic investigations into their chemical and biochemical modes for reaction. We were interested in studying thiophosphoryl analogues of these compounds and, in the course of synthesis, discovered[1] that N-substituted (R = Me, Ph; $R \neq H$) thiophosphoryl carbonyl mixed imides (**I**, X = Y = MeO; Z = Ph) undergo a rearrangement. This rearrangement occurs without a catalyst, in an inert solvent, to give the corresponding phosphoryl thiocarbonyl mixed imides (**II**) as shown in equation (1). Apparently, the



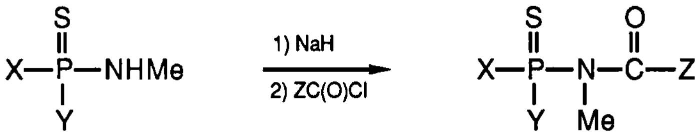
$$X-\underset{\underset{Y}{|}}{\overset{\overset{S}{\|}}{P}}-\underset{\underset{R}{|}}{N}-\overset{\overset{O}{\|}}{C}-Z \longrightarrow X-\underset{\underset{Y}{|}}{\overset{\overset{O}{\|}}{P}}-\underset{\underset{R}{|}}{N}-\overset{\overset{S}{\|}}{C}-Z \qquad (1)$$

I **II**

thiophosphoryl sulfur atom and the carbonyl oxygen atom simply switch positions. As such, this rearrangement could provide a practical route to mixed imides which have a thiocarbonyl functionality. We would like to report our studies on the generality of this rearrangement.

RESULTS AND DISCUSSION

The synthetic route we used[2] for preparing thiophosphoryl carbonyl mixed imides (**I**) is shown in equation (2). The compounds were obtained in 62-90% yields, after purification, and gave satisfactory elemental analyses. Selected spectral data on each of the mixed imides prepared is given in Table I.



$$X{-}\overset{\overset{S}{\|}}{\underset{\underset{Y}{|}}{P}}{-}NHMe \xrightarrow[2)\ ZC(O)Cl]{1)\ NaH} X{-}\overset{\overset{S}{\|}}{\underset{\underset{Y}{|}}{P}}{-}\underset{\underset{Me}{|}}{N}{-}\overset{\overset{O}{\|}}{C}{-}Z \qquad (2)$$

TABLE I Selected spectral data on N-methyl thiophosphoryl carbonyl mixed imides (**Ia** - **Ie**).

XYP(S)N(Me)C(O)Z				^{1}H NMR, ppm (J_{HP}, Hz)		IR, cm^{-1}
No.	X	Y	Z	$POCH_3$	$PNCH_3$	ν_{CO}
Ia	MeO	MeO	Ph	3.63 (14)	3.13 (9)	1665
Ib	Ph	MeO	Ph	3.65 (14)	3.15 (10)	1675
Ic	Ph	Ph	Ph	------------	3.17 (10)	1662
Id	MeO	MeO	Me[a]	3.83 (15)	3.20 (10)	1680
Ie	MeO	MeO	OiBu	3.83 (15)	3.20 (10)	1726

[a] These protons appear as a singlet at 2.40 ppm.

The rearrangements were studied by dissolving the thiophosphoryl carbonyl mixed imide (**I**) in carbon tetrachloride and heating to 40 °C in a constant temperature bath. Formation of **II** is readily noticed by the appearance of a yellow color due to the thiocarbonyl chromophore. The degree of rearrangement can be easily followed by ^{1}H NMR since the N-methyl doublet of the product is shifted significantly downfield, and both O-methyl and N-methyl protons are coupled less strongly with phosphorus (Table II).

TABLE II Selected ^{1}H NMR data on N-methyl phosphoryl thiocarbonyl mixed imides (**IIa** - **IId**).

	XYP(O)N(Me)C(S)Z			^{1}H NMR, ppm (J_{HP}, Hz)	
No.	X	Y	Z	$POCH_3$	$PNCH_3$
IIa	MeO	MeO	Ph	3.59 (12)	3.54 (7)
IIb	Ph	MeO	Ph	3.65 (12)	3.58 (7)
IIc	Ph	Ph	Ph	----------	3.46 (7)
IId	MeO	MeO	Me[a]	3.87 (12)	3.53 (7)

[a] These protons appear as a singlet at 2.97 ppm.

For the mixed imides **Ia**, **Ib**, and **Id**, rearrangement is complete and quantitative. In contrast, the mixed imide **Ic** only partially rearranged to a 10/90 equilibrium mixture of **IIc**/**Ic** and **Ie** gave no evidence of a rearranged product after several days. From a bond energy viewpoint, the rearrangement should be exothermic if the P=O vs P=S bond strength difference is greater than the C=O vs C=S bond strength difference. Apparently, relative to phenyl substitution, an alkoxy group on phosphorus increases the P=O vs P=S bond strength difference[4] and encourages product formation while an alkoxy group on carbon increases the C=O vs C=S bond strength difference[5] sufficiently to prevent product formation.

The rearrangements of **Ia**[1], **Ib**, and **Id** were followed kinetically in carbon tetrachloride at 40.0 °C by observing the appearance of the thiocarbonyl absorbance (400-440 nm) in the visible spectrum. For **Ic**, the approach to equilibrium was followed under similar conditions by ^{1}H NMR. First-order kinetics were observed over greater than four half-lives, and the rate constants for product formation are given in Table III. The data rules out a bimolecular process and any buildup of an intermediate during the reaction.

The rearrangement could involve either initial attack on phosphorus by the carbonyl oxygen atom or initial attack on the carbonyl carbon by the thiophosphoryl sulfur atom. However, the effect on reactivity by substituents (X,Y) on phosphorus (**Ia** > **Ib** > **Ic**) is not the typical effect seen[6] in reactions involving a rate-limiting nucleophilic attack at phosphorus. In addition, the effect on reactivity by substituents (Z) on carbon (**Ia** > **Id**) is not typical for a rate-limiting nucleophilic attack at a carbonyl center. Studies are underway to further elucidate the mechanism and rate-limiting step of the rearrangement.

TABLE III First-order rate constants for the formation of phosphoryl thiocarbonyl mixed imides (**IIa-IId**) from the corresponding thiophosphoryl carbonyl mixed imides (**Ia-Id**).[a]

No.	X	Y	Z	$10^6 k_f$, sec^{-1}	$t_{1/2}$, hr
Ia	MeO	MeO	Ph	49.7 (± 1.9)	3.87
Ib	Ph	MeO	Ph	7.4 (± 0.1)	26.0
Ic	Ph	Ph	Ph	1.8 (± 0.2)[b]	------
Id	MeO	MeO	Me	5.5 (± 0.3)	35.0

[a] Solvent = CCl_4. Temp = 40° C. [b] The observed rate constant ($k_f + k_r$) for approach to a 10/90 equilibrium was 1.8 (± 0.2) x 10^{-5} s^{-1}.

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