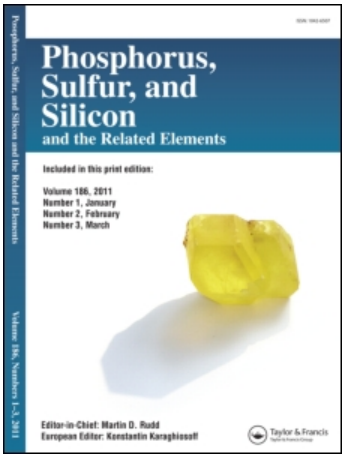

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AN N-THIOPHOSPHINYL CARBOXAMIDE: [O,S] TRANSPOSITION WITH DISPROPORTIONATION AND HYDROLYSIS

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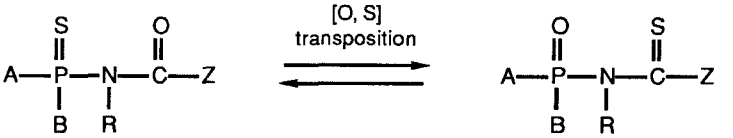
Abstract N-Diphenylthiophosphinyl-N-methyl carboxamide (**1aab**) undergoes an uncatalyzed "[O,S]-transposition" in CCl_4 to form a 75:25 equilibrium mixture of **1aab** and N-diphenylphosphinyl-N-methyl thiocarboxamide (**2aab**). This equilibrium mixture then slowly undergoes a disproportionation to initially form the unsymmetrical diphenylthiophosphinic diphenylphosphinic anhydride (**9**) and the corresponding N-benz(methylimino)-N-methyl thiobenzamide (**8**). Parallel or subsequent processes result in the formation of N-methyl thiobenzamide (**6**), N-methyl benzamide (**7**), bis-diphenylphosphinic anhydride (**10**), and bis-diphenylthiophosphinic anhydride (**11**). Pathways for these transformation are suggested.

INTRODUCTION

We recently reported[1] the discovery of an interesting process whereby N-thiophosphyl carboxamides (**1xyz**) undergo an uncatalyzed "[O,S] transposition" in inert solvents to form N-phosphyl thiocarboxamides (**2xyz**). A general reactivity order of N-thiophosphoryl (**1cab**) > N-thiophosphonyl (**1bab**) > N-thiophosphinyl (**1aab**) was observed. Stereochemical studies on **1bab** (apparent inversion) and crossover studies on a mixture of **1cba** and **1bab** revealed[2] a mechanism for the [O,S] transposition that involves a combination of phosphatropic migrations and a dissociation-recombination process (see top of Scheme I). Hydrolysis of the transposition products (**2caa, 2cab,** or **2ccb**) proceeds[3] with predominant cleavage of the N-phosphyl group to form the corresponding thiocarboxamides (**6**). Some carboxamides (**7**) were also formed during the neutral hydrolysis but acidic hydrolysis of *e.g.* **2ccb** gives only thiocarboxamide.



1xyz **2xyz**

x	A	B	y	R	z	Z
a	Ph	Ph	**a**	Me	**a**	Me
b	Ph	MeO	**b**	Ph	**b**	Ph
c	MeO	MeO	**c**	Bn		

It was noticed at the time that the transposition products (**2xyz**) undergo slow subsequent transformations upon standing. We have probed the time dependence of the [O,S] transposition and subsequent transformations of N-diphenylthiophosphinyl-N-methyl benzamide (**1aab**) to provide some insite into the pathways involved.

RESULTS AND DISCUSSION

The [O,S] transposition of **1aab** to **2aab** and subsequent transformations were followed as a function of time by ^{31}P NMR and ^{1}H NMR (N-methyl region) on aliquots taken from a CCl_4 solution at 60° C. Within the first 500 min, the transposition has occurred to form an equilibrium mixture (*ca.* 75:25) of **1aab** and **2aab** (Figure 1 - ^{31}P chemical shifts of the isomers are indicated in brackets in the legend).

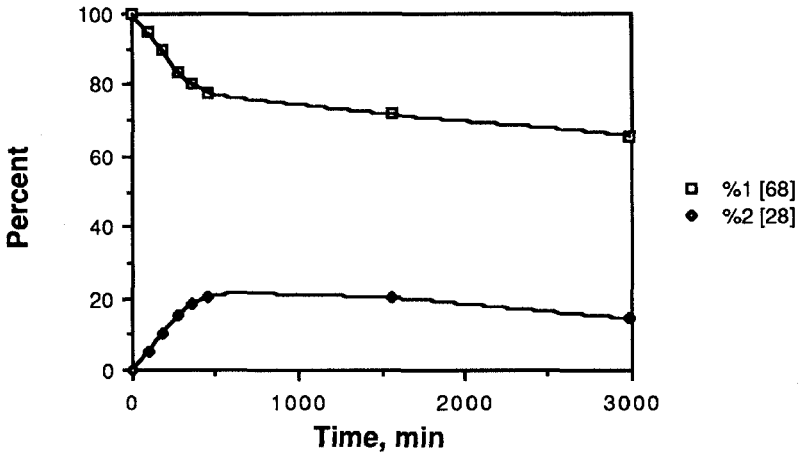
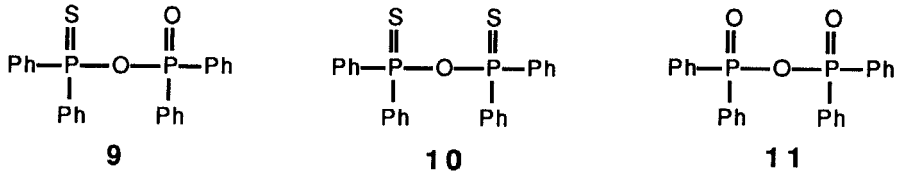
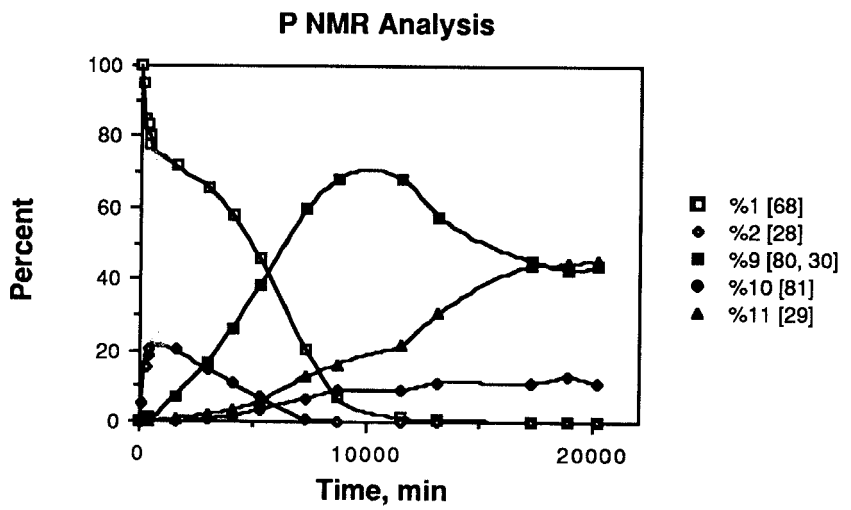
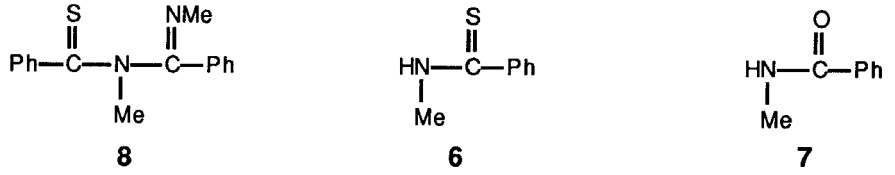


FIGURE 1 Time dependence of [O,S] transposition of **1aab** to **2aab**.

Following the reaction mixture for an additional 20,000 min (2 weeks) revealed the slow further transformations of **1aab** and **2aab** into compounds **9** - **11** derived only from the phosphinyl portion (top of Figure 2 - followed by ^{31}P NMR) and compounds **6** - **8** derived from the carboxamide portion (bottom of Figure 3 - followed by ^{1}H NMR of the N-methyl region) of the reactants. Appropiate chemical shifts are given in the legends. There is an apparent initial buildup of **9** and **8** which subsequently convert into **10** & **11** and **6** & **7**, respectively. The general similarities in the two plots indicate some correlation between the subsequent reactions of **9** and those of **8**. The early production of small amounts of **8** is probably due to some competitive hydrolysis reacton.







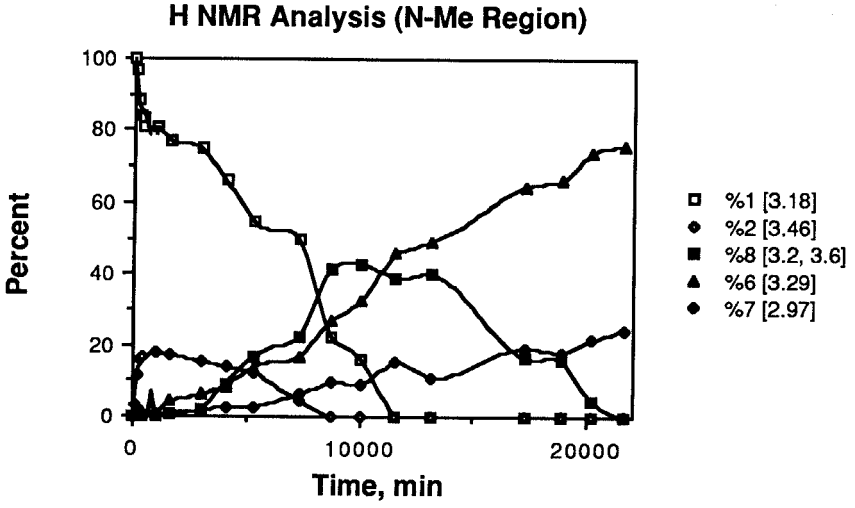
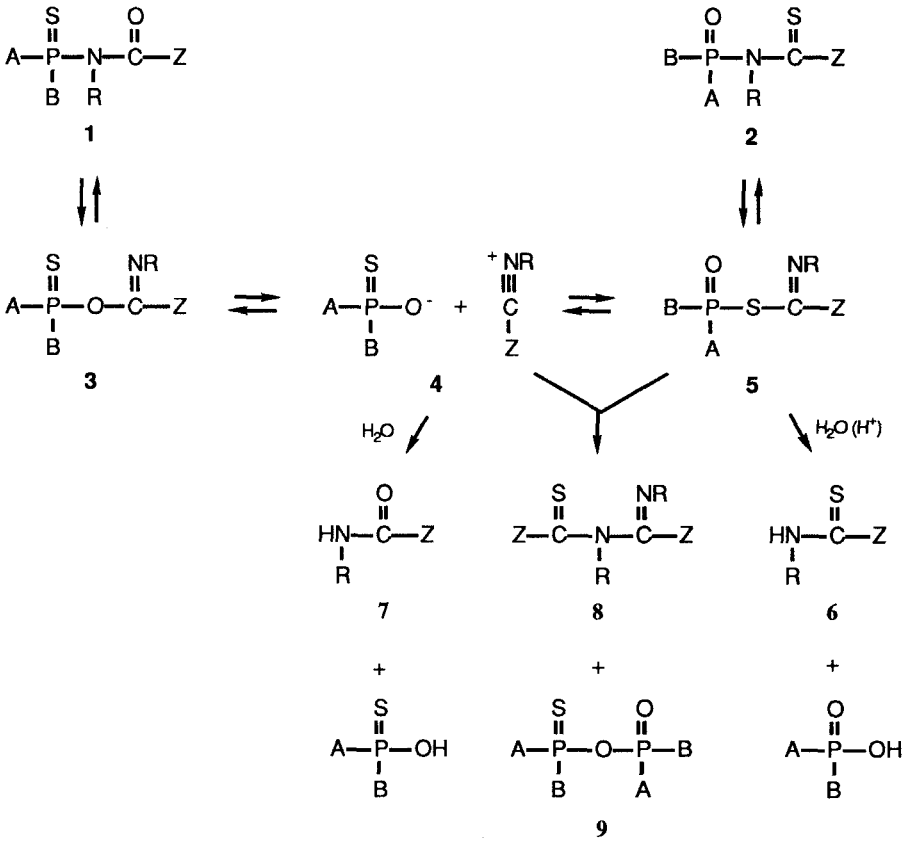


FIGURE 2 ^{31}P AND ^{1}H Analysis of time dependent transformations.

A possible mechanistic pathway to the initial formation of **8** and **9** is shown in Scheme I. Subsequent hydrolysis of **8** by trace amounts of water would result in the formation of equal amounts of **6** and **7**. However, since **6** is clearly formed in excess, some other process (in addition to hydrolysis of **5**) must be operating. Compounds **10** and **11** could arise by a disproportionation of **9**; but again, equal amounts would result. It appears that **9** may be acting as a thionation reagent and is converted to **11** while transforming **7** into **6**.

Scheme I



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