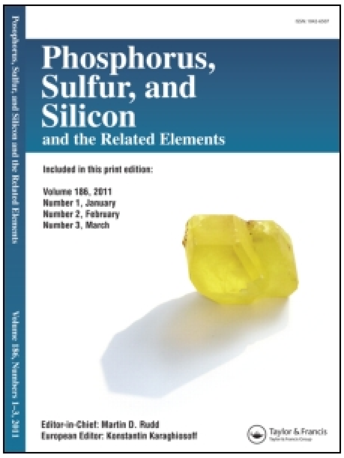

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THE REACTION OF CARBOXYLIC ACID CHLORIDES WITH 2,4-BIS(4-METHOXYPHENYL)-1,3,2,4-DITHIADIPHOSPHETANE 2,4-DISULFIDE

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Carboxylic acid chlorides react with 2,4-bis(4-methoxyphenyl)-1,3,2,4-dithiadiphosphetane 2,4-disulfide to give the intermediates **2**a,b; **2**'a,b) which are useful as thioacylating agents. Compounds **2** react with amines under mild conditions to give the corresponding thioamides.

INTRODUCTION

Known thioacylating agents[1–4] are few and rather expensive. Recently,[5] we have reported the reaction of carboxylic acid chlorides with dialkyldithiophosphoric acids and/or with 2,4-bismethylthio)-1,3,2,4-dithiodiphosphetane 2,4-disulfide which led to the corresponding dithioester.

In a continuation of this work, we studied the reaction of carboxylic acid chlorides with compound (**1**), since the resulting intermediates are thioacylating reagents.

RESULTS AND DISCUSSION

Acetyl and benzoyl chlorides react with compound (**1**) to give compounds (**2**). Attempts to purify or identify these compounds by GLC gave benzoyl chloride and compound (**1**). For this reason we used these compounds (**2**) *in situ*. We succeeded in trapping the intermediate (**2**) using sodium ethoxide to give stable compound (**3**). The structure of compound (**3**) was proved by I, R, ^{1}H and ^{13}C NMR, M.S., and microanalysis.

It is known that compound (**1**) reacts with amides[9] when held at 110°C for a long time to give the corresponding thioamides. The intermediates (**2a**,**b**: **2**^{1}**a**,**b**) react with aniline, dibenzyl-aniline and/or morpholine under mild conditions (70°C; 2–4 mins.) to give the corresponding thioamide derivatives (**4a**–**d**); Table I.

EXPERIMENTAL

Compounds **3** and **4** were separated on a silica gel column (CH_2Cl_2- pet. ether, 50%). ^{1}H NMR spectra were recorded at 60 MHZ on a Varian EM 360

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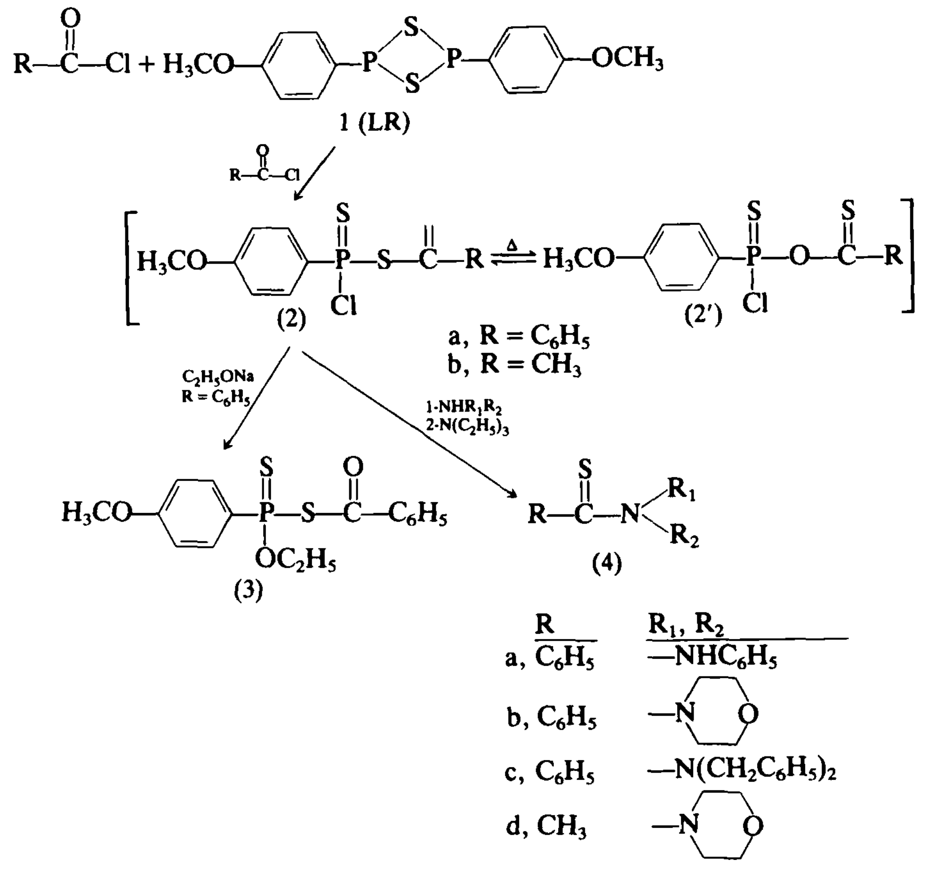
† Presented at 11th international conference on the organic Chemistry of Sulfur, Lindau, W Germany, 1984.



SCHEME 1

Spectrometer. ^{13}C and ^{31}P NMR spectra were recorded at 20 and 32 MHZ, respectively, on a Varian CFT-20 spectrometer. TMS was used as internal standard and chemical shifts are expressed in δ-values. ^{31}P chemical shifts were related to 85% H_3PO_4. IR spectra were recorded on a Beckman IR-18 spectrometer. MS spectra were recorded on a micromass 7070 f spectrometer

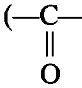
TABLE I

Experimental and physical data for the reaction of intermediates **2** with sodium ethoxide and amides

Product	Reaction temp. °C	Reaction time min.	Yield %
3	20	15	50
4a	70	3	47[6]
4b	70	2	95[7]
4c	70	4	74[8]
4d	70	3	71[6]

operating at 70 ev using a direct inlet. Silica Gel 60 (Merck) was used for chromatography.

Benzoyl chloride (0.01 mole) reacts with compound **1** (2.2 g; 0.006 mole) in 10 ml toluene at 110°C after 1 hour to give a red viscous oil (**2a**,**b**; $\mathbf{2^1a}$,**b**). 0.01 mole of compound (**2a**; $\mathbf{2^1a}$) in 10 ml toluene reacts with sodium ethoxide (0.25 g Na in 15 ml abs. ethanol) at 40°C for 1 hour to give S- benzoyl-O-ethyl-4-methoxyphenylphosphonothiolothionate, **3**. The following data for compound **3** was found:-

^{1}H NMR 1.2(*t*, CH_3), 3.8 (*s*, OCH_3), 4.4 (*q*, CH_2), 6.8–8 (or, 9H aromatics); IR ($CHCl_3$) 1700 cm^{-1} ($C=O$); M.S. M^+ at 352 low intensity; ^{13}C NMR 190.8 ppm  $(\text{—}\underset{\underset{\displaystyle O}{\|}}{C}\text{—}S\text{—})$; ^{31}P NMR 25.3 ppm; and analysis: Found; C, 54.33, H, 4.54, S, 18.1; $C_{16}H_{17}O_3PS_2$ requires C, 54.52 H, 4.86 S, 18.2%.

The intermediates (**2a**,**b**; $\mathbf{2^1a}$,**b**) 0.01 mole in 10 ml toluene react with 0.01 mole of aniline, dibenzylaniline and/or morpholine in the presence of a few drops of triethylamine at 70°C to give the corresponding thiobenzo-, and thioacetamide derivatives **4a**–**d** in high yields (Table I). The compounds **4a**–**d** are known[6] and were identified by m.p. and mixed m.p., IR, M.S. All are identical with compounds synthesized earlier.

CONCLUSION

Carboxylic acid chlorides react with compound **1**(LR) to give the intermediates **2** which are useful as thioacylating agents. This method is simple, starts from readily available and cheap reagents, and furthermore avoids the use of obnoxious thiols.

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