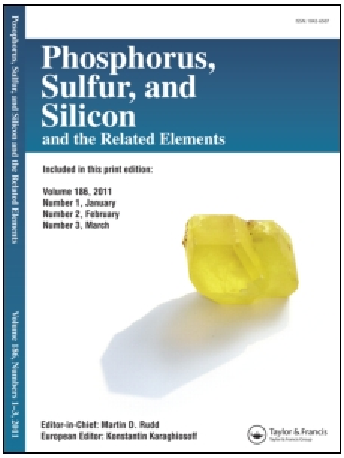

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SHORT COMMUNICATION

Synthesis of S-Sulfonyl-Phosphinothioates and Phosphinodithioates, a Novel Organophosphorus-sulphur Structure

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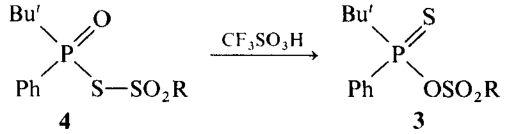
Racemic and optically active S-sulphonylphosphinothioates $R\text{-}SO_2\text{-}S\text{-}P(O)Bu^tPh$ and dithioates $R\text{-}SO_2\text{-}S\text{-}P(S)Bu^tPh$ (R = Me, *p*-tolyl) have been prepared for the first time by the reaction of the corresponding acids $Bu^tPhP(S)SH$ (X = O,S) of their salts with sulphonylating reagents $RSO_2\text{-}Y$ (Y = Cl, $O\text{-}SO_2R$, triazolide).

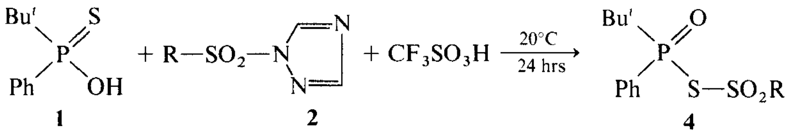
It has been observed that the main products of the reaction of methane- and *p*-methylbenzenesulphonyl chloride with trialkylammonium tert-butylphenylphosphinothioate $Bu^tPhP(S)O^- \; R_3NH^+$ are the corresponding sulphonic anhydrides $R\text{-}SO_2\text{-}O\text{-}P(S)Bu^tPh$ **3**.[1] We have subsequently studied the reaction under various conditions and with different sulphonylating reagents with a view to find an optimum yield. A closer study of the reaction revealed the formation of unexpected products: S-sulphonyl-*t*-butylphenylphosphinothioates $R\text{-}SO_2\text{-}S\text{-}P(O)Bu^tPh$ **4** isomeric with the anhydride **3**. The proper choice of a sulphonylating reagent and solvent allowed us to control the reaction towards selective formation of **3** or **4**.

When *t*-butylphenylphosphinothioic acid $Bu^tPhP(S)OH$ **1** was reacted with triazolide **2a** in the presence of an equimolar amount of trifluoromethanesulphonic acid in nitromethane the formation of **4a** was observed as major product. The reaction mixture also contained a small amount of anhydride **3a**.

It seems likely that the mixed anhydride $RSO_2OSO_2CF_3$ is formed as an intermediate.[2] The yield of **4a** estimated by ^{31}P NMR was 75% and a ratio **4a**:**3a** = 9:1. Pure crystalline **4a** was isolated in 40% yield. The reaction with triazolide **2b** in acetonitrile solution took a similar course.[3] In the case of optically active acid (R^+) **1**, $|\alpha|_D^{20} = {}^{+}25.2°$ the compound (R^+) **4a** $|\alpha|_D^{20} = +212.5°$ was formed. It was possible to demonstrate in independent experiments that **4** isomerises slowly at room temperature into **3** in the presence of catalytic amounts of CF_3SO_3H to form an equilibrium mixture shifted towards the structure **3**.



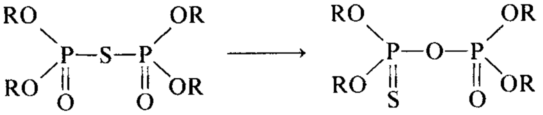
This is a new type of thiolo-thiono rearrangement in phosphorus-sulphur chemistry similar to that of monothiopyrophosphates.[4]



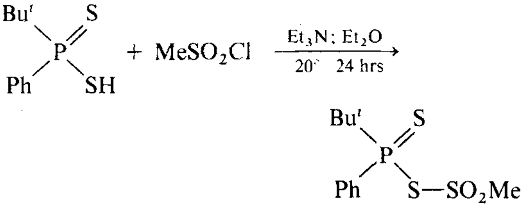
(1)

a: R = Me
b: R = *p*-tolyl

4a m.p. 108–110°; $\delta(^{31}P)$ + 64.0
$\nu_{P=O}$ 1170 cm^{-1}
4b m.p. 134–136°; $\delta(^{31}P)$ + 63.8
$\nu_{P=O}$ 1150 cm^{-1}

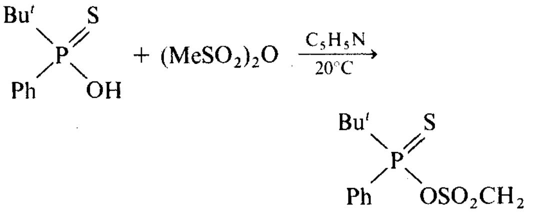


The analogous S-sulphonyl-*t*-butylphenylphosphinodithioate **6a** was prepared in high yield by condensation of *t*-butylphenyl-phosphinodithioic acid with mesyl chloride in the presence of triethylamine.


(2)

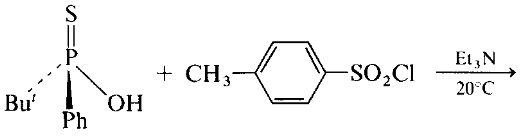
6a

In contrast to reaction (**1**) we further found that the sulphonylation reactions (**3**) and (**4**) in acetonitryl solution, afforded exclusively anhydrides **3** in 80% yield.

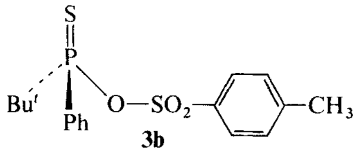

(3)

3a

m.p. = 113–114°C
$\delta(^{31}P) = +112.7$



$(-)S[\alpha]_D^{20} = -10.2$

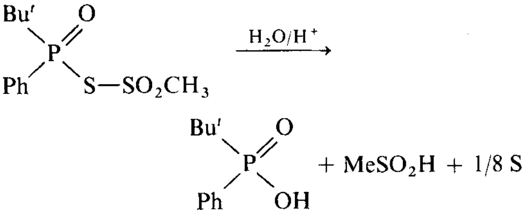

(4)

3b

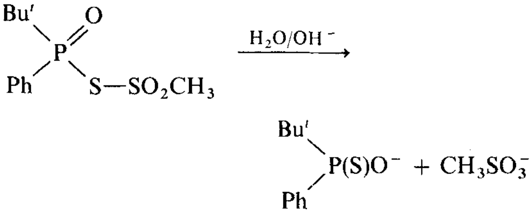
$(+)S[\alpha]_D^{20} = +16.9°$
m.p. = 64–66°
$\delta(^{31}P) = +111.6$

However, when reactions (**3**) and (**4**) were carried out in nonpolar solvent, a mixture of isomeric products **3** and **4** was formed.

S-sulphonylphosphinothioate **4a** was hydrolised in acid-aqueous medium to the corresponding-*t*-butylphenylphosphinic acid with parallel formation of the elemental sulphur.


(5)

In alkaline medium **4a** hydrolises into the monothioacid **1**.


(6)

These observations suggest that reaction (**5**) proceeds via nucleophilic attack of water on the phosphorus centre and reaction (**6**) involves sulphene ($SO_2{=}CH_2$) as a reactive intermediate.[5,6] It is of interest to note that the behaviour of phosphorus monothioacids towards sulphonylating agents described in this communication cannot be predicted on the basis of "hard soft acid and base" (HSAB) approach. In contrast to alkylating, silylating and phosphorylating reagents, which follow the HSAB rules[7] the sulphonylating agents, in spite of their "hard" character tend to form relatively stable sulphur-sulphur bonds. Further studies on this discrepancy are underway.

ACKNOWLEDGEMENT

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