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Phosphorus, Sulfur, and Silicon and the Related Elements

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Phosphonates Containing Sulfur and Silicon: New Stereochemical and Mechanistic Aspects

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PHOSPHONATES CONTAINING SULFUR AND SILICON: NEW STERFOCHEMICAL AND MECHANISTIC ASPECTS

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Abstract - Synthesis, reactivity and conformation of cyclic S,S-thioacetals of formylphosphonates are described. The chemistry of α -trimethylsilyl- α -methylthiometanephosphonate is briefly discussed.

For the past few years, work in this Laboratory has centered on the preparations and reactions of the phosphonates containing α -organosulfur substituents of general formula $(\underline{1})$. Among them S,S-thioacetals of formyl-phosphonates $(\underline{2})$ are of special interest because they

$$(RO)_{2}^{PCH-X}$$
 $X,Y = SR$ $(RO)_{2}^{PCH-X}$ SR $S(O)_{2}^{R}$ O SR

are reagents of choice for the synthesis of ketene S,S-thioacetals via the Wittig-Horner reaction with carbonyl compounds 1 .

$$\begin{array}{c} \text{1.Base} \\ \text{(RO)}_{2} \text{P(O)CH(SR)}_{2} & \xrightarrow{2.R^{1}R^{2}CO} \\ \hline \text{3.H}_{3}O^{+} & \text{(RS)}_{2}C = CR^{1}R^{2} + \text{(RO)}_{2}\text{PO}_{2}\text{H} \end{array}$$

The present communication describes the results of our further studies on this class of compounds.

SYNTHESIS OF 2

As far as the synthesis of $\underline{2}$ is concerned 2 , it was found now that they may conveniently be prepared by the reaction of diazomethanephosphonates with organic disulfides in the presence of the proper catalysts.

$$(RO)_2 P(O) CHN_2 + (RS)_2 \xrightarrow{Et_2 O \cdot BF_3} \underline{2}$$

The best results in terms of the yield and purity of products were obtained with ${\rm Et_20\cdot BF_3}$. The use of ${\rm Rh_2(OAc)_4}$ as a catalyst was found to give α -phosphoryl sulfides.

CONFORMATION OF 2-PHOSPHORYL 1,3-DITHIANES

2-Substituted 1,3-dithianes in solution have eiter dynamic or rigid chair structure with substituents occupying axial or equatorial position. Therefore, it was of interest to investigate conformation of 1,3-dithiane with the phosphorus containing groups at the anomeric carbon atom.

To this end the model compounds $\underline{3}$ and $\underline{4}$ were synthesized and their structures were elucidated by means ^1H , ^{31}P and $^{13}\text{C-NMR}$ spectroscopy and X-ray analysis.

$$X = CH_2, tBuCH, Me_2C, S$$
 $X = CH_2, tBuCH, Me_2C, S$
 $X = CH_2, Me_2$

All the data obtained so far point to a rigid chair conformation of the six-membered ring with the axial

phosphoryl group 3 , 4 . Conformation of $\underline{4}$ will be briefly discussed.

REACTION OF 2 WITH α , β -UNSATURATED CARBONYL COMPOUNDS

In an extension of our earlier work 1 , the reaction of 2 with α , β -unsaturated aldehydes and ketones was investigated. It was found that aldehydes give the corresponding Wittig-Horner reaction products in high yields (65-80%) via the hydroxy-adduct (1,2-addition) as detected by 31 P-NMR spectroscopy.

However, the reaction with α , β -unsaturated ketones proceeds in a different way. All the experimental results lead to formulation of the following general reaction course.

$$\frac{\text{Li}}{(\text{RO})_2 \text{P(O)C(SR)}_2} \frac{\text{R}^1 \text{CH=CHC(O)R}^2}{-78^{\circ} \text{C}} \qquad \text{[1,4-adduct]Li}$$

$$\frac{\text{the Wittig-Horner}}{\text{reaction products}}$$

In this context, it is of interest that the reaction of the lithium salts of α -phosphoryl sulfides with α , β -unsaturated ketones gives 1,4-adducts as the final reaction products and was found to proceed as follows:

$$\frac{(RO)_2 P(O) CHSMe}{-78^{\circ}C} \xrightarrow{R^1 CH = CHC(O)R^2} [1,2-adduct]Li$$

$$\frac{}{25^{\circ}C} [1,4-adduct]Li \xrightarrow{H^+} 1,4-adduct$$

SYNTHESIS AND REACTIVITY OF α -TRIMETHYLSILYL- α -METHYL-THIOMETHANEPHOSPHONATE (5)

The title compound was prepared in three different ways: (a) by silylation of α -phosphoryl sulfide, (b) by sulfenylation of α -trimethylsilyl methanephosphonate and (c) by the Arbusov reaction of triethyl phosphite with the appropriate bromide.

$$(Et0)_{2}P(0)CH_{2}Me$$

$$(Et0)_{2}P(0)CH_{2}SiMe_{3}$$

$$(Et0)_{3}P$$

$$(Et0)_{3}P$$

$$(Et0)_{3}P$$

$$(Et0)_{2}PrCH SiMe_{3}$$

$$Me_{3}Si(MeS)CHBr$$

$$0$$

$$5$$

The lithium salt of $\underline{5}$ on treatment with aliphatic, aromatic and α , β -unsaturated aldehydes gives the Peterson reaction products in high yields (60-85%).

$$(Et0)_2P(0)C(Me_3Si)SMe \xrightarrow{RCH0} (Et0)_2P(0)C(SMe)=CHR$$

The reaction with ketones is more complicated, the Peterson reaction product is formed in 5% yield only. In summary, the phosphonates 2 and 5 are useful synthetic intermediates and their chemistry is connected with interesting stereochemical and mechanistic aspects.

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