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REACTION OF 2-DIALKOXYPHOSPHORYL-1,3,2-DITHIAPHOSPHOLANES (PHOSPHORINANES) WITH NUCLEOPHILIC REAGENTS

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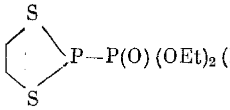
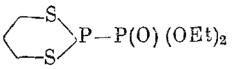
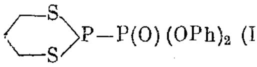
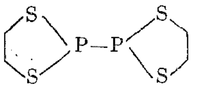
It has already been shown [1] that in the reaction of 2-chloro-1,3,2-dithiaphospholane (phosphorinane) with trialkylphosphites, and also with dialkyl phosphite salts, 2-dialkoxyphosphoryl-1,3,2-dithiaphospholanes (phosphorinanes) are formed. These are compounds with a P—P bond, and P atoms with different valences participate in their formation, with a tricoordinated P atom being included in the composition of the heterocycle. It is known [2] that the reactivity of the P—P bond is appreciably dependent on the character of the substituents at the P atoms. Mainly compounds with alkyl, aryl, and alkoxyl substituents have previously been studied. It was interesting to clarify the influence of alkylthiol substituents, both cyclic and acyclic, on the reactivity of the compounds with the P—P bond. In the case of cyclic compounds we could expect that, because of the lability of the P—S bonds in the ring, the attack of the nucleophile would lead either to a cleavage of the P—P bond, or to cleavage of the P—S bond and opening of the ring. To clarify the influence of the substituents at the two P atoms on the direction and rate of the reaction of the compounds with a P(III)—P(V) bond, we studied the reaction of the following compounds with water and alcohols: 2-Diethoxyphosphoryl-1,3,2-dithiaphospholane (I), 2-diethoxyphosphoryl-1,3,2-dithiaphosphorinane (II), 2-diphenoxyphosphoryl-1,3,2-dithiaphosphorinane (III) and diethoxyphosphoryl dibutyl dithiophosphite (IV).

 (I)  (II)

 (III) $(BuS)_2P—P(O)(OEt)_2$ (IV)

The reaction was controlled by the ^{31}P NMR and TLC methods.

Reaction with Water. For a qualitative evaluation of the reactivity of compounds (I)-(III), we determined the time of completion of their hydrolysis by an excess of water at ~20°C (1.5 mmoles of (I)-(III), 20 mmoles of H_2O in 2 ml of THF). The end of the reaction was determined from the disappearance of the starting compound by the TLC method (Silufol, absolute ether, development with iodine vapors). Under these conditions, (I) is hydrolyzed completely in the course of a week, (II) after three weeks, and (III) after 2 h. However, the character of the products obtained in the hydrolysis depends on the ratio between the reagents, temperature and duration of the reaction.

During the hydrolysis of phospholane (I) by an equimolar amount or a small excess of water in THF, 1,2-bis(1,3,2-dithiaphosphorinan-2-ylthio)ethane (VII) was isolated, which is probably a product of disproportionation of the intermediately formed 2-hydroxy-1,3,2-dithiaphospholane (V). In [3], it was also shown that (V) is unstable and disproportionates to form bistrithiophosphite (VII) and phosphorous acid. According to ^{31}P NMR data, as a result of the hydrolysis of (I), not only bistrithiophosphite (VII) is formed, but also diethyl phosphite and phosphorous acid, and also small amounts of a compound with a chemical shift (CS) of 37.6 ppm, which is probably a hypophosphite  ; its formation was observed in [4]. From the literature data, the following scheme of hydrolysis can be suggested

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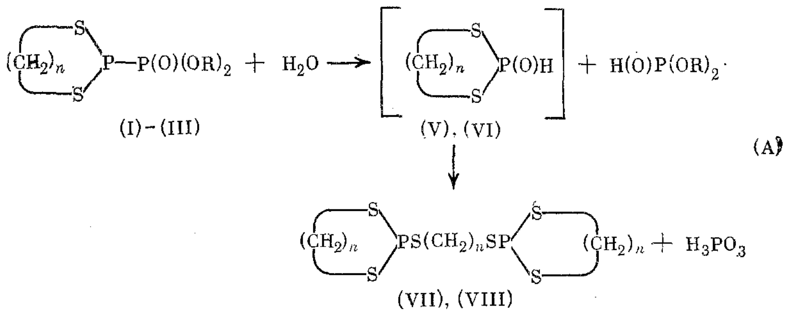


$n = 2$, $R = Et$ (I), $n = 3$, $R = Et$(II); $n = 3$, $R = Ph$ (III), $n = 2$ (V), (VII); $n = 3$ (VI), (VIII).

In the hydolysis of phosphorinane (II) with an equimolar amount of water, according to ^{31}P NMR data, diethyl phosphite and phosphorous acid are formed, as well as a compound with CS of 80.6 ppm, which is bistrithiophosphite (VIII), as confirmed by its alternative synthesis from 2-chloro-1,3,2-dithiaphosphorinane and propanedithiol. The hydrolysis of (II) also proceeds, probably by scheme A. However, in reaction with an equimolar amount of water, (II) is consumed incompletely, since under the reaction conditions bistrithiophosphite (VIII) also undergoes hydrolysis to propanedithiol and phosphorous acid. In the hydrolysis of (II) by an excess of water (ratio of reagents 1:6 and more), only phosphorous acid, diethyl phosphite, and propanedithiol are formed. The latter was detected in all reaction mixtures by the TLC method (Silufol, absolute benzene, iodine vapors), and also by a qualitative reaction for the SH group with sodium aqua-ferricyanide in a saturated solution of $NaHCO_3$ [5].

The hydrolysis of (III) by an excess of water proceeds rapidly and under mild conditions (2 h at ~20°C), and therefore the bistrithiophosphite (VIII) formed has no time to hydrolyze, and it can be recorded by means of ^{31}P NMR.

Thus, in the hydrolysis of (I)-(III), probably, first the hydrophosphoryl compounds (V), (VI) are formed, which disproportionate under the reaction conditions (see scheme A). In the hydrolysis of (II) without heating, at the beginning of the reaction a low-intensity doublet is observed at 4.5 ppm, $J_{PH} = 674$ Hz in the ^{31}P NMR spectrum, which can be assigned to (VI) (comp. [6]). However, the concentration of the initial (II) at that time is several times higher than that of the products formed, and the doublets of (II), phosphorous acid, and diethyl phosphite partially overlap. There is indirect evidence that in the hydrolysis of (I)-(III), first the P—P bond is cleaved, while the cleavage of the P—S bond is the result of secondary processes: in the hydrolysis products, a cyclic fragment at P(III) is retained, while the products in which the P—S bonds (one or both of them) would be destroyed with the retention of the P—P bond, were not recorded.

The hydrolysis of (I) and (II) is accelerated by the action of dilute HCl or KOH solutions.

The reactivity in the hydrolysis reaction increases in the series (II) < (I) < (III). Most stable to the action of water is the compound with a phosphorinane ring at P(III) and ethoxy groups at P(V). Replacement of the ethoxy groups by phenoxy at P(V) increases the rate of hydrolysis more than replacement of the phosphorinane ring by phospholane ring at P(III).

Reaction with Alcohols. As in the case of hydrolysis, the alcoholysis of compounds (I)-(IV) proceeds with cleavage of the P—P bond, and the corresponding O-alkyl dithiophosphites (IX)-(XI) are thus formed

$$\underset{\text{(I)—(IV)}}{R_2P{-}P(O)(OR')_2} + R''OH \rightarrow \underset{\text{(IX)—(XI)}}{R_2P{-}OR''} + H(O)P(OR')_2 \qquad \text{(B)}$$

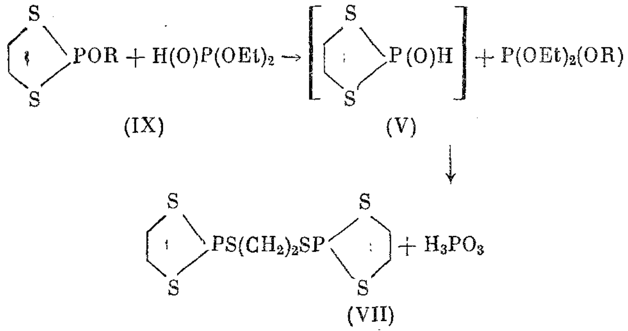
$R_2 = SCH_2CH_2S$ (I), (IX); $SCH_2CH_2CH_2S$ (II), (III), (X);

$(BuS)_2\!<$ (IV), (XI); $R' = Et$ (I), (II), (IV); Ph (III), $R'' = Me$, Et.

In the case of cyclic compounds, the process becomes complicated by side reaction that affect the P—S bonds in the ring and depend on the structure of the ring, the ratios of reagents, (B) the temperature, and the duration of reaction.

Compounds (I) and (II) react with an equimolar amount of alcohol in a sealed ampule at 90°C in concentrated solutions. Phospholane (I) reacts after 1 h quantitatively, whereas only half the amount of phosphorinane (II) reacts after 4 h. The rate of the reaction is practically independent of the alcohol used (MeOH, EtOH).

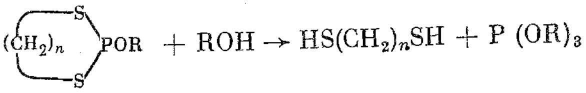
According to ^{31}P NMR data, in the alcoholysis of (I) not only 2-alkoxy-1,3,2-dithiaphospholane (IX) and diethyl phosphite are formed, but also a small amount of bistrithiophosphite (VII) is observed in the reaction mixture, which is probably formed as the result of an exchange reaction between (IX) and diethyl phosphite



(C)

If the reaction mixture is held for a few days (at ~20°C), compound (VII) precipitates (mp 127°C).

Under the same conditions, in the reaction of (I) and (II) with excess of alcohol, the reaction does not stop at stage B, but the P—S bonds become cleaved to form the corresponding dithiol and trialkyl phosphite



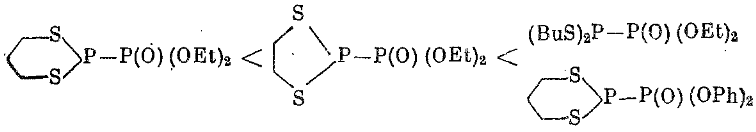
$$(CH_2)_n\langle S_2 \rangle POR + ROH \rightarrow HS(CH_2)_nSH + P(OR)_3 \quad (D)$$

$n = 2$ (IX); $n = 3$ (X).

In the ethanolysis of (II), the appearance of signals of diethyl phosphite (6.0 ppm) and (X) (155.5 ppm) is observed in the ^{31}P NMR spectrum, and then a signal of triethyl phosphite (138 ppm [7]) appears, while after 6 h of heating, only the signals of diethyl phosphite and triethyl phosphite are recorded, and propanedithiol is detected in the reaction mixture. When phospholane (I) is heated in excess of ethanol, the side process proceeds so rapidly that it is impossible to record the formation of 2-ethoxy-1,3,2-dithiaphospholane (IX), and only signals of triethyl phosphite (138.7 ppm) and diethyl phosphite (6.4 ppm) are recorded in the ^{31}P NMR spectrum. In addition, ethanedithiol is detected in the reaction mixture.

To compare the reactivity of compounds (I)-(IV) in reactions with alcohols, the time of their quantitative alcoholysis was determined in excess of ethanol (1.5 mmole of (I)-(IV) in 15 mmole of EtOH) at ~20°C. The end of the reaction was determined by the TLC method from the disappearance of the initial compound. Under these conditions, compounds (III) and (IV) react quantitatively after 24 h, (I) after a month, and (II) very slowly (after one month most of it remains unreacted). In the case of (IV), only diethyl phosphite and $(BuS)_2P(OEt)$ are formed, and there is no cleavage of the P—S bonds, possibly because the alcoholysis of (IV) proceeds fairly rapidly. In the case of (I), the alcoholysis is accompanied by an exchange reaction (scheme C), and bistrithiophosphite (VIII) precipitates.

The reactivity of compounds (I)-(IV) in reactions with nucleophilic reagents is thus dependent on the type of substituents at both the tricoordinated and tetracoordinated P atoms, and increases in the series:



EXPERIMENTAL

The ^{31}P NMR spectra were run on a S-60 spectrometer (24.3 MHz), with H_3PO_4 as external standard (the shifts to the weak field are positive). All the reactions were carried out in dry nitrogen.

Hydrolysis of 2-Diethoxyphosphoryl-1,3,2-dithiophospholane (I). a) A mixture of 1.3 g (5 mmoles) of (I) and 0.09 g (5 mmoles) of water in 1.7 ml of THF was heated in a sealed ampule for 2 h at 90°C, then evaporated to 1/4 of its volume, and the precipitate was filtered, washed with ether, and dried in vacuo. The yield 1,2-bis(1,3,2-dithiaphospholan-2-ylthio)ethane (VII) was 0.41 g, mp 128°C (cf. [3, 8]), $\delta^{31}P$ 110 ppm (cf. [3, 8]). Found, %: C 21.70; H 3.73. $C_6H_{12}S_6O_2$. Calculated, %: C 21.29; H 3.57.

b) A mixture of 1.2 mmoles of (I) and 1.2 mmoles of water in 0.4 ml of THF was heated in a sealed ampule for 2 h. The following signals are observed in the ^{31}P NMR spectrum: 110.6 ppm, corresponding to bistrithiophosphite (VII); two doublets at 6.2 ppm, J_{PH} = 702 Hz and 7.1 ppm, J_{PH} = 702 Hz, corresponding to phosphorous acid [7] and diethyl phosphite (for the latter in THF, δP 6.0 ppm, H_{PH} = 700 Hz); 37.6 ppm, a low intensity signal probably corresponding to hypophosphite [4].

1,3-Bis(1,3,2-dithiaphosphorinan-2-ylthio)propane (VIII). A solution of 1.64 g (16.2 mmoles) of triethylamine in benzene was added slowly, with stirring, to a mixture of 2.8 g (16.2 mmole) of 2-chloro-1,3,2-dithiaphosphorinane and 0.87 g (8.1 mmoles) of propanedithiol in 20 ml of benzene. The mixture was then stirred for 2 h at 80°C. The precipitate of triethylamine hydrochloride was filtered, and the solvent was removed in vacuo. Since (VIII) decomposes during distillation, it was purified by the successive addition and decantation of small amounts of hexane, benzene, and ether; the residual solvents were removed in vacuo. The yield of (VIII) was 1.45 g (47%), $\delta^{31}P$ 79.3 ppm. Found, %: C 28.87; H 4.73; P 16.74. $C_9H_{18}S_6P_2$. Calculated, %: C 28.40; H 4.77; P 16.28.

Hydrolysis of 2-Diethoxyphosphoryl-1,3,2-dithiaphosphorinane (II). a) A mixture of 1.2 mmole of (II) and 1.2 mmole of water in 0.4 ml of THF was heated in a sealed ampule for 2 h at 90°C. In the ^{31}P NMR spectrum signals appear at 6.7 and 7.5 ppm, corresponding to diethyl phosphite and phosphorous acid, and a signal at 80.6 ppm corresponding to bistrithiophosphite (VIII). A 1.2 mmole portion of water was added to the reaction mixture, which was then heated for 2 h, and the intensity of the 80.6 ppm signal then considerably decreased.

b) A mixture of 1.2 mmoles of (II) and 7.3 mmoles of water was heated under the conditions of reaction (a). After 2 h, doublets of diethyl phosphite and phosphorous acid (5.6 ppm, J_{PH} = 690 Hz and 6.7 ppm, J_{PH} = 692 Hz) were recorded in ^{31}P NMR spectrum.

Hydrolysis of 2-Diphenoxyphosphoryl-1,3,2-dithiaphosphorinane (III). A mixture of 1.5 mmole of (III) and 20 mmoles of water in 2 ml of THF was stirred at ~20°C. After 2 h, signals of (VIII) (76.5 ppm) and diphenylphosphite (doublet at 0.0 ppm, J_{PH} = 730 Hz (cf. [7]) were recorded in the ^{31}P NMR spectrum.

Alcoholysis of 2-Diethoxyphosphoryl-1,3,2-dithiaphosphorinane (II). a) A mixture of 1.2 mmole of (II) and 1.2 mmole of alcohol in 0.4 ml of THF was heated in a sealed ampule at 90°C. After 4 h, the signals of following compounds were recorded in the ^{31}P NMR spectrum: 2-methoxy-1,3,2-dithiaphosphorinane (155 ppm) and 2-ethoxy-1,3,2-dithiaphosphorinane (157.5 ppm), respectively (cf. [9]); diethyl phosphite (6.7 ppm), unreacted initial (II) (doublet of doublets of P(III) −18.3 ppm, P(V) 27.0 ppm; J_{PP} = 264 Hz [1]).

b) A 1.5 mmole portion of (II) in 15 mmoles of ethanol was held at ~20°C for two weeks. Signals of diethyl phosphite (6.0 ppm), triethyl phosphite (138.7 ppm), (X) (148 ppm), and unreacted initial (II) (−18.0 and 25.5 ppm) were recorded in the ^{31}P NMR spectrum.

Alcoholysis of 2-Diethoxyphosphoryl-1,3,2-dithiophospholane (I). A mixture of 1.2 mmole of (I) and 1.2 mmole of ethanol was heated in a sealed ampule at 90°C. After 1 h, the signals of 2-ethoxy-1,3,2-dithiaphospholane (IX) (149.3 ppm) (cf. [8]), diethyl phosphite (7.1 ppm, J_{PH} = 701 Hz), and bistrithiophosphite (VII) (113.6 ppm, a low intensity signal) were recorded in the ^{31}P NMR spectrum.

Alcoholysis of Diethoxyphosphoryl Dibutyl Dithiophosphite (IV). A mixture of 1.5 mmole of (IV) in 15 mmole of ethanol was heated for 24 h at ~20°C. Signals of diethyl phosphite (6.4 ppm) and $(BuS)_2P(OEt)$ (XI) (159 ppm) were recorded in ^{31}P NMR spectrum (for $(RS)_2P(OR)$ 153.5-162.1 ppm [7]).

CONCLUSIONS

The reaction of 2-dialkoxyphosphoryl-1,3,2-dithiaphospholanes (phosphorinanes) with nucleophilic reagents proceeds with the initial cleavage of the P—P bond. The rate of reaction depends on the structure of the ring, and also on the type of substituents at the tetracoordinated P atom.

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INTERACTION OF 2-DIETHOXYPHOSPHORYL-1,3,2-DITHIAPHOSPHORINANE WITH CHLORAL IN THE PRESENCE OF WATER

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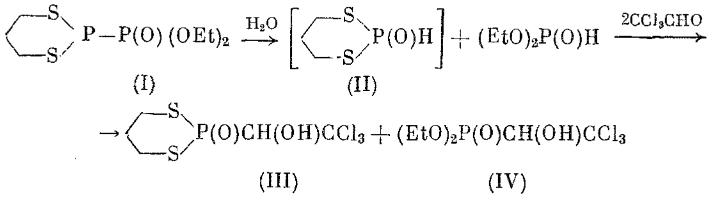
The cyclic phosphite (II) is formed initially on hydrolysis of 2-diethoxyphosphoryl-1,3,2-dithiaphosphorinane (I) and rapidly disproportionates under the reaction conditions according to [1]. However, if the hydrolysis is carried out in the presence of chloral, which vigorously adds hydrophosphoryl compounds, then (II) reacts with chloral and is not subject to secondary conversions. Evidently the reaction goes according to the following scheme.



On adding water to the mixture of (I) and chloral (at a reactant ratio of chloral:(I) = 2:1) a rapid exothermal reaction occurred. Compound (III) was isolated in 86% yield from the reaction mixture. Only two signals were recorded in the ^{31}P NMR spectrum of a solution of the reaction mixture in DMSO, viz., 63.0 ppm corresponding to (III) and 15.2 ppm corresponding to (IV) (cf. 14.4 ppm in [2]). In the absence of water (I) did not interact with chloral even on boiling for 2 h.

When hydrolysis of (I) was carried out with a deficiency of chloral (ratio of chloral:(I) = 1:1) only the latter interacts with (II) and diethyl phosphite did not react. In this case only signals of (III) (63.7 ppm) and diethyl phosphite (doublet 8.2 ppm, J_{PH} = 694 Hz [1]) were observed in the ^{31}P NMR spectrum of a solution of the reaction mixture in DMSO.

Compound (I) interacted with chloral hydrate only on heating. At a reactant ratio of 1:1 in contrast to the reaction with chloral, both α-hydroxyphosphoryl compounds (III) and (IV) and also diethyl phosphite and $\overline{S(CH_2)_3S}P\overline{S(CH_2)_3S}P\overline{S(CH_2)_3S}$ (V) were observed according to data of ^{31}P NMR spectra. It is probable that under these conditions the initially formed

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