## LITERATURE CITED

1. V. S. Blagoveshchenskii, O. P. Yakovleva, A. A. Borisenko, N. V. Zyk, and S. I. Vol'fkovich, Dokl. Akad. Nauk SSSR, 230, 845 (1976); L. V. Ermanson, V. S. Blagoveshchenskii, and N. N. Godovikov, Izv. Akad. Nauk SSSR, Ser. Khim., 2788 (1980).
2. I. F. Lutsenko and M. V. Proskurnina, Usp. Khim., 48, 1648 (1978).
3. E. E. Nifant'ev, A. I. Zavalishina, S. F. Sorokina, and A. A. Borisenko, Zh. Obshch. Khim., 46, 471 (1976).
4. R. Burgada, M. Willson, H. Goncalves, and H. Boudjebel, Bull. Soc. Chim. France, 2207 (1975).
5. K. Bauer, Analysis of Organic Compounds [Russian translation], Inostr. Lit., Moscow (1953), p. 311.
6. O. P. Yakovleva, V. S. Blagoveshchenskii, A. A. Borisenko, E. E. Nifant'ev, and S. I. Vol'fkovich, Izv. Akad. Nauk SSSR, Ser. Khim., 2060 (1975).
7. V. Mark, H. Dungan, M. M. M. Crutchfield, and J. R. Van Waxer, Top. in Phosph. Chem., 4, 261 (1967).
8. H. Goncalves, R. Burgada, M. Willson, H. Boudjebel, and F. Mathis, Bull Soc. Chim. France, 621 (1975).
9. E. E. Nifant'ev, A. I. Zavalishina, S. F. Sorokina, V. S. Blagoveshchenskii, O. P. Yakovleva, and E. V. Esenina, Zh. Obshch. Khim., 44, 1694 (1974).

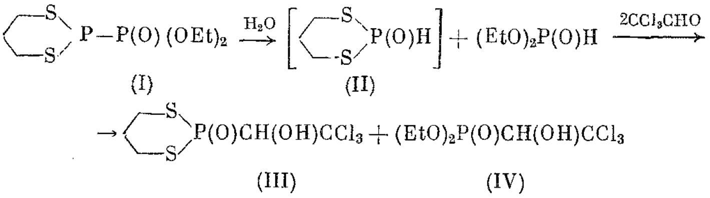
---

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

L. V. Ermanson, N. N. Godovikov,
and V. S. Blagoveshchenskii

UDC 542.91:547.1'118

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.



(I) (II) (III) (IV)

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 $S(CH_2)_3SPS(CH_2)_3SPS(CH_2)_3S$ (V) were observed according to data of $^{31}P$ NMR spectra. It is probable that under these conditions the initially formed

---

A. N. Nesmeyanov Institute of Heteroorganic Compounds, Academy of Sciences of the USSR, Moscow. Translated from Izvestiya Akademii Nauk SSSR, Seriya Khimicheskaya, No. 2, pp. 427-429, February, 1986. Original article submitted September 10, 1984.

0568-5230/86/3502-0395$12.50

cyclic phosphite (II) succeeds in partially disproportionating with the formation of the bistrithiophosphite (V) [1] and the remaining chloral reacts with diethyl phosphite. However, hydrolysis of (I) in the presence of chloral occurs vigorously and is not accompanied by side processes.

Evidently the reaction of 2-diethoxyphosphoryl-4-methyl-1,3,2-dithiaphosphorinane with chloral in the presence of water occurs similarly. Two signals were observed in the $^{31}P$ NMR spectrum at 64.1 and 61.5 ppm probably corresponding to the two geometric isomers of $\overline{SCH_2CH_2CH(CH_3)SP}(O)CH(OH)CCl_3$. Attempts to isolate the individual substances failed.

## EXPERIMENTAL

The $^{31}P$ NMR spectra were taken on a S-60 (24.3 MHz) instrument, internal standard was $H_3PO_4$, downfield shifts were considered positive. IR spectra were drawn on a UR-20 instrument in KBr disks.

2-Hydroxy-(2,2,2-trichloro-1-hydroxyethyl)-1,3,2-dithiaphosphorinane (III). Water (0.15 g: 0.008 mole) was added to a mixture of (I) (1.92 g: 0.007 mole) and freshly distilled chloral (2.06 g: 0.014 mole). On agitating, the water rapidly dissolved with strong evolution of heat and the mixture crystallized. The powdered crystalline mass was stirred in benzene at 80°C for 30 min, the hot mixture was filtered, and the crystals were decanted sequentially with ether and $CH_2Cl_2$. After drying in vacuum (III) (1.81 g: 86%) was obtained having mp 140°C (cf. [3]). Found, %: P 9.81; S 21.10. $C_5H_8S_2PO_2Cl_3$. Calculated, %: P 10.06; S 21.26. $\delta^{31}P$ 63.7 ppm in DMSO {for $(EtS)_2P(O)CH(OH)CCl_3$ $\delta P$ 65.5 ppm [4]}. IR spectrum ($\nu$, $cm^{-1}$): 1260 (P=O), 3110 (OH).

Interaction of 2-Diethoxyphosphoryl-1,3,2-dithiaphosphorinane (I) with Chloral Hydrate. Chloral hydrate (0.41 g: 0.0025 mole) and (I) (0.68 g: 0.0025 mole) were heated at 85°C with stirring for 30 min, cooled, and dissolved in DMSO. Signals (ppm) were recorded in the $^{31}P$ NMR spectrum of the obtained solution at 63.6 (III), 15.0 (IV), 79.4 for bistrithiophosphite (V) [1], and at 7.1 for diethyl phosphate.

## CONCLUSION

2-Oxo-2-(2,2,2-trichloro-1-hydroxyethyl)-1,3,2-dithiaphosphorinane was formed on interaction of 2-diethoxyphosphoryl-1,3,2-dithiaphosphorinane with chloral in the presence of water.

## LITERATURE CITED

1. L. V. Ermanson, N. N. Godovikov, and V. S. Blagoveschenskii, Izv. Akad. Nauk SSSR, Ser. Khim., 423 (1986).
2. N. A. Vorontsova, O. N. Vlasov, L. Ya. Bogel'fer, and N. N. Mel'nikov, Zh. Obshch. Khim., 47, 2698 (1977).
3. É. E. Nifant'ev, A. I. Zavalishina, S. F. Sorokina, and S. M. Chernyak, Dokl. Akad. Nauk SSSR, 203, 593 (1972).
4. N. A. Kardanov, N. P. Provotorova, P. V. Petrovskii, N. N. Godovikov, and M. I. Kabachnik, Izv. Akad. Nauk SSSR, Ser. Khim., 2114 (1983).