REACTION OF DERIVATIVES OF TRIVALENT PHOSPHORUS WITH 2-OXO-1,3-DITHIO-1,3-DIPHENYLPROPANE

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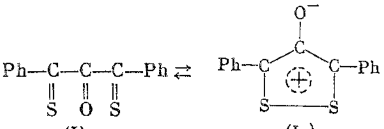
UDC 542.91:547.1'118

The reaction of α-diketones and vicinal triketones with trialkyl phosphites leads to the formation of 1,3,2-dioxaphospholenes with a pentacoordinated phosphorus atom [1-3]. On the example of reacting monothiobenzil with phosphites and phosphonites it was shown [4] that cyclic phosphoranes, the 1,3,2-oxathiaphospholenes, are also formed when the C = O group is replaced by the C = S group.

It was shown for the recently described [5, 6] 2-oxo-1,3-dithio-1,3-diphenylpropane (I) that it exists in equilibrium with the mesoionic form (Ia), which at 20°C is strongly shifted toward (Ia).



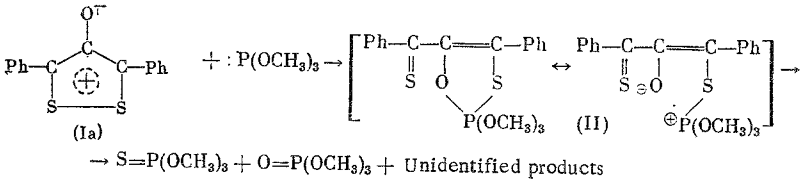
(I) (Ia)

The reaction of (I) with trimethyl phosphite, tri(dimethylamino)phosphine, triphenylphosphine, and dimethylphosphorous acid is described in the present paper.

The reaction of (I) with trimethyl phosphite was run in hot benzene. At a reactant ratio of 1 : 1 and 1 : 2 a part of the starting (I) was recovered from the reaction mixture independent of the heating time; (I) reacts completely with a larger excess of the phosphite to give trimethyl phosphate and trimethyl thiophosphate (1 : 2), which were identified on the basis of the IR and ^{31}P NMR spectral data ($\delta_{^{31}P}$ 0 and −73 ppm, respectively). Unidentified sulfur-containing compounds were also isolated when the reaction mixture was chromatographed on silica gel.

The reaction of tri(dimethylamino)phosphine and triphenylphosphine with (I) proceeds in a similar manner to give the corresponding oxides and thiooxides. Dimethylphosphorous acid also reacts with (I), with the cleavage of oxygen and sulfur from the latter. Based on the IR and ^{31}P NMR spectral data, the dimethylphosphoric and dimethylthiophosphoric acids were identified among the reaction products.

Deoxidation and desulfurization, which are the sole direction when 2-oxo-1,3-dithio-1,3-diphenylpropane is reacted with derivatives of trivalent phosphorus acids, indicate that the mesoionic form (Ia) takes part in the reaction in the investigated temperature range. The reactions apparently begin by nucleophilic attack of the P atom on the S atom to give the unstable intermediate (II). A temperature study of the ^{31}P NMR spectra disclosed that in the range 80-100° the signal of trimethyl thiophosphate (−73 ppm) appears somewhat before the signal of trimethyl phosphate (0 ppm).



Similar nucleophilic attack on the S atom occurs when trialkyl phosphites [7-9] and trialkylphosphines [9, 10] are reacted with disulfides. Here it was observed that the trialkyl phosphites are more reactive than triphenylphosphine.

A. M. Butlerov Chemical Institute of the V. I. Ul'yanov – Lenin Kazan State University. Translated from Izvestiya Akademii Nauk SSSR, Seriya Khimicheskaya, No. 9, pp. 2101-2103, September, 1976. Original article submitted December 25, 1975.

TABLE 1

T., °C	Derivatives of phosphorus acids				
	$P(OCH_3)_3$	$P[N(CH_3)_2]_3$	PPh_3	$H(O)P(OCH_3)_2$	$P(OCH_3)_3 +$ $+ CH_3COOH$
Start of effect	95	55	147	97	65
Maximum of effect	108	67	171	104	83

The prior protonation of (I) on the oxygen probably occurs when (I) is reacted with dimethylphosphorous acid, with subsequent nucleophilic attack by phosphite anion on the sulfur of the positively charged dithiol ring. The relatively high reactivity of the dialkyl phosphites toward (I), comparable to that of the trialkyl phosphites, can be explained by this, whereas disulfides react only with the salts of dialkylphosphorous acids or with dialkyl phosphites in the presence of amines; the dialkylphosphorous acids themselves react only with disulfides of the acyl type [11, 12].

The fact that trimethyl phosphate in the presence of CH_3COOH reacts at a lower temperature than without it is also explained by the prior protonation of (I) by acetic acid, although trimethyl phosphate and trimethyl thiophosphate are the reaction products in both cases.

EXPERIMENTAL

Reaction of 2-Oxo-1,3-dithio-1,3-diphenylpropane (I) with Trimethyl Phosphite. A mixture of 3.2 g of (I) and 2.9 g of $P(OCH_3)_3$ in 50 ml of abs. benzene was stirred at 100-110° for 14 h. Then the benzene was removed in vacuo and the residue was treated with CH_2Cl_2. The CH_2Cl_2-insoluble portion (0.8 g) is unreacted (I). From the CH_2Cl_2-soluble portion was isolated by vacuum distillation a mixture of $O=P(OCH_3)_3$ and $S=P(OCH_3)_3$ with bp 42-54° (0.1 mm), δ_{31P} 0 and −73 ppm. The residue was chromatographed on silica gel (II activity) (1 g of product per 10 g of silica gel). As eluants we used petroleum ether, its mixture with benzene (9:1, 4:1, 1:1), benzene, and its mixture with ether (9:1, 4:1, 1:1). The course of the chromatography was checked by TLC and the IR spectra. Here we isolated 3 greenish-brown solid products, which contained sulfur (15-17% S) and were free of phosphorus, and whose structure could not be established.

Reaction of (I) with $P(OCH_3)_3$ in the Presence of CH_3COOH. A mixture of 0.5 g of (I), 0.5 g of $P(OCH_3)_3$, and 0.25 g of glacial CH_3COOH in 45 ml of benzene was heated at ~80° for 6.5 h. Vacuum distillation gave a mixture of $O=P(OCH_3)_3$ and $S=P(OCH_3)_3$, δ_{31P} 0 and − 73 ppm.

Reaction of (I) with Tri(dimethylamino)phosphine, Triphenylphosphine, and Dimethylphosphorous Acid. The reactions were run by heating (I) with an excess of the phosphorus reagent in a sealed ampul at temperatures that were determined by the DTA method (Table 1). Based on the IR and NMR spectral data, the respective formation of the following compounds was recorded: $S=P(NMe_2)_3$ (−82 ppm) and $O=P(NMe_2)_3$ (−24 ppm); $S=PPh_3$ (−44 ppm) and $O=PPh_3$ (−24 ppm); $(MeO)_2PSOH$ (−66 ppm) and $(MeO)_2POOH$ (0 ppm).

The authors express their gratitude to É. I. Gol'dfarb for taking the ^{31}P NMR spectra.

CONCLUSIONS

When trimethyl phosphite, tri(dimethylamino)phosphine, triphenylphosphine, and dimethylphosphorous acid are reacted with 2-oxo-1,3-dithio-1,3-diphenylpropane the latter is desulfurized and deoxidized.

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X-RAY STUDY OF TETRABUTYLAMMONIUM HYDROXIDE TRIHYDRATE

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UDC 543.422.8:541.49:547.233.4-36:546.212

Data on the physical properties of tetrabutylammonium hydroxide and its hydrates are lacking in the literature. In the present communication, as an expansion of the research by the authors on the physicochemical characteristics of tetraalkylammonium hydroxides, are given the results of an x-ray study of tetrabutylammonium hydroxide trihydrate (I). $[(C_4H_9)_4N]OH \cdot 3H_2O$ (I) was synthesized by the method described in [1].

The x-ray patterns of the samples were taken by the Debye – Sherrer method on a URS-55 apparatus. Using an airtight chamber at –60 to –80°C the powdered (I) was placed in thin-walled capillaries, which were then sealed. The recording was done at the temperature of liquid N_2. The exposure time was 10 h. The reproduction of the x-ray patterns was good.

Indexing based on the Hall – Davey curves gave a good agreement (Table 1) of the measured interplanar distances and those calculated for a rhombic system with the parameters $a = 13.06$; $b = 11.20$; $c = 10.50$ Å. The number of formula units was calculated to be $Z = 4$; $\rho_{\text{peaks}} = 1.10$; $\rho_{\text{x-ray}} = 1.16$ g/cm³.

A comparison of the data for the lattice parameters of the tetramethyl-, tetraethyl-, and tetrabutylammonium hydroxides (Table 2) shows that these compounds are isomorphous and that the lattice parameters increase somewhat with increase in the mass of the cation.

TABLE 1. X-Ray Data for $[(C_4H_9)_4N]OH \cdot 3H_2O$

I	d_{meas}, Å	d^*_{meas}, Å	d_{calc}, Å	*hkl*	*I*	d_{meas}, Å	d^*_{meas}, Å	d_{calc}, Å	*hkl*
w	5,20	5,51	5,60	020	Ditto	2,17	2,19	2,19	224, 333
v.w	4,68	4,98	5,20	002	»	2,05	2,08	2,10	602, 440
m	3,91	4,02	4,02	202, 311	»	1,96	1,98	2,00	442
v.w	4,28	4,30	4,35	220	»	1,79	1,81	1,83	144, 060
m	3,41	3,48	3,48	131	»	1,73	1,75	1,75	162
m	3,18	3,24	3,22	222, 231	»	1,69	1,71	1,72	062
m	2,80	2,85	2,85	040, 031	»	1,48	1,49	1,50	126, 064, 264
v.w	2,61	2,64	2,63	240	»	1,44	1,45	1,45	146
Ditto	2,47	2,50	2,48	004	»	1,30	1,31	1,31	334
»	2,36	2,39	2,41	242	»	1,14	1,14	1,14	048
»	2,23	2,26	2,28	024	»	1,01	1,01	1,01	068

*d_{meas}, with a correction for the sample thickness.

TABLE 2. Lattice Parameters of Tetraalkylammonium Hydroxides (Å)

Hydroxide	*a*	*b*	*c*	Literature reference
$[(CH_3)_4N]OH \cdot 5H_2O$	12,57	10,96	7,91	[2]
$[(C_2H_5)_4N]OH \cdot 2H_2O$	13,23	11,02	9,34	[3]
$[(C_4H_9)_4N]OH \cdot 3H_2O$	13,96	11,20	10,50	

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Translated from Izvestiya Akademii Nauk SSSR, Seriya Khimicheskaya, No. 9, pp. 2103-2104, September, 1976. Original article submitted December 29, 1975.