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Abstract

Full Text

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Phosphorus and Phosphinic Esters of Enols

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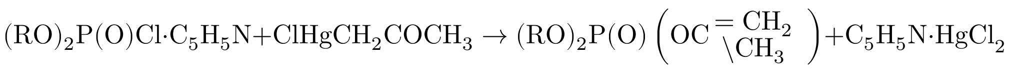
In previous papers (¹) we described methods for the synthesis of vinyl esters of phosphorous and phosphinic acids, based on the readily occurring interaction of mercuric acetaldehyde with the corresponding halogenophosphorus compounds. In all the cases studied, the interaction proceeded with transfer of the reaction center of the molecule. In order to broaden the scope of application of this reaction, we also studied the action of acid chlorides of phosphoric and phosphinic acids on α-mercurated aldehydes and ketones. However, the very first experiments showed that acid chlorides of pentavalent phosphorus acids, in contrast to acid chlorides of trivalent phosphorus acids, do not react with organomercury compounds in ether or benzene medium. The reaction also did not proceed on heating acid chlorides of phosphoric and phosphinic acids with mercurated oxo compounds in the absence of a solvent.

In studying the properties of α-mercurated aldehydes and ketones it was established that salts (NaJ, KCl, etc.) readily cleave the metal–carbon bond in these compounds (²). This observation was subsequently successfully used by us for the synthesis of vinyloxysilanes (³). Alkylchlorosilanes, which did not react directly with mercurial aldehydes and ketones, readily entered into reaction in the form of salts with pyridine.

We also studied this variant in the case of acid chlorides of pentavalent phosphorus acids. The salt formed upon dissolving the acid chloride of phosphoric or phosphinic acid in pyridine reacts readily, even in the cold, not only with the complete organomercury compound (for example, with mercuric acetaldehyde), but also with organomercury salts of ketones



$$(RO)_2P(O)Cl\cdot C_5H_5N + ClHgCH_2COCH_3 \rightarrow (RO)_2P(O)\left(OC\begin{matrix}=CH_2\\ \backslash CH_3\end{matrix}\right) + C_5H_5N\cdot HgCl_2$$

with formation of the ester of phosphoric or phosphinic acid with the enol form of the carbonyl compound.

The reaction we have found makes it possible to obtain phosphoric acid esters with one, two, and three unsaturated groups, and phosphinic acid esters with either one or two unsaturated groups. The yield in this case reaches

50–85%. The α-mercurated derivatives of acetaldehyde, acetone, diethyl ketone, cyclopentanone, cyclohexanone, and the following halogenophosphorus compounds were introduced into this reaction: methyl, ethyl, and butyl dichlorophosphates; diethyl and dibutyl chlorophosphates; ethylphosphinic acid chloride; ethoxyethylphosphinic acid chloride; and phosphorus oxychloride.

Isolation of the enol esters from the reaction mixture in the presence of mercury salts is extremely difficult, owing to polymerization reactions and resinification caused by these salts. To remove mercury salts, the following method was used: the main quantity of mercury salt, which precipitated after completion of the reaction as a complex with pyridine, was filtered off, and

Table 1

Compound	Yield, %	B.p., °C/mm	n_D^{20}	d_4^{20}	MR_D, found	MR_D, calc.	Found, % C	Found, % H	Found, % P	Calculated, % C	Calculated, % H	Calculated, % P
$(C_2H_5O)_2P(O)-OC(=CH_2)CH_3$	57	77.5–78°/3	1.4198	1.0715	45.84	46.05	43.45	7.88	15.77	43.30	7.78	15.96
$(C_4H_9O)_2P(O)-OC(=CH_2)CH_3$	53	115–116°/3	1.4300	1.0056	64.29	64.50	52.51	9.18	12.10	52.78	9.26	12.38
$(C_2H_5O)_2P(O)-(OC(=CHCH_3)C_2H_5)$	84	90–91°/2	1.4298	1.0428	55.02	55.26	48.64	8.43	13.71	48.65	8.62	13.94
$(C_2H_5O)_2P(O)-(O-C_6H_5)$	85	116–117°/2	1.4621	1.1029	57.30	57.68	51.26	8.05	12.83	51.30	8.18	13.22
$C_2H_5P(O)(OC_2H_5)(OC(=CH_2)CH_3)$	77	67–67.5°/3	1.4318	1.0349	44.64	44.92	47.02	8.43	17.23	47.19	8.48	17.39
$(CH_3O)P(O)(OC(=CH_2)CH_3)_2$	39	79–80°/3	1.4361	1.1011	45.37	45.58	44.00	6.73	16.08	43.75	6.82	16.12
$(C_4H_9O)P(O)(OC(=CH_2)CH_3)_2$	51	94.5–95°/2	1.4356	1.0355	59.08	59.42	51.28	8.29	12.93	51.28	8.18	13.23
$(CH_3O)P(O)(OC(=CH-CH_3)C_2H_5)_2$	50	106–107°/2	1.4468	1.0419	63.70	64.03	53.21	8.44	12.34	53.21	8.52	12.48
$(C_2H_5O)P(O)(O-C_6H_5)_2$	74	139–140°/2	1.4761	1.1406	63.90	64.25	55.40	7.52	12.02	55.80	7.42	11.99
$C_2H_5P(O)(OC(=CH_2)CH_3)_2$	64	71.5–72°/3	1.4451	1.0394	48.75	49.07	50.39	7.85	16.44	50.52	7.95	16.29
$C_2H_5P(O)(O-C_6H_5)_2$	70	131–132°/2	1.4892	1.1138	62.80	63.15	59.52	7.98	12.51	59.49	7.95	12.79
$OP(OC(=CH_2)CH_3)_3$	51	80–80.5°/2.5	1.4428	1.0720	53.95	54.33	49.57	6.84	14.05	49.53	6.93	14.20
$OP(OC(=CHCH_3)C_2H_5)_3$	76	125.5–126°/2	1.4588	1.0107	81.75	82.03	59.50	9.03	9.94	59.58	9.00	10.24
$OP(OCH=CH_2)_3$	86	58–58.5°/4	1.4289	1.1209	40.50	40.48	40.84	5.20	17.26	40.92	5.15	17.59

hydrogen sulfide was passed through the filtrate in the presence of an excess of pyridine,

$$HgCl_2 + H_2S + 2C_5H_5N \rightarrow HgS + 2C_5H_5N \cdot HCl.$$

The mercuric sulfide and pyridine hydrochloride were filtered off, and the filtrate was distilled. The yields and constants of the enol ethers obtained are given in Table 1.

Experimental Part

1. **Preparation of diethyl 3-penten-2-phosphate.** In 50 ml of dry pyridine, 35.2 g (0.11 mole) of α-chloromercuridiethyl ketone was dissolved, cooled to 0°, and, with stirring, 17.2 g (0.1 mole) of diethyl chlorophosphate dissolved in 20 ml of absolute ether was added; after 1.5 h of stirring, 150 ml of absolute ether was added. The crystalline precipitate was filtered off, and a stream of dry hydrogen sulfide was passed through the filtrate to decompose the mercury salts. The precipitate was filtered off, and ether and pyridine were distilled from the filtrate. Distillation of the residue in vacuum gave 18 g (84% of theory) of diethyl 3-penten-2-phosphate.

2. **Preparation of ethyl di-(cyclopenten-1)-phosphate.** In 100 ml of pyridine, 65 g (0.21 mole) of α-chloromercuricyclopentanone was dissolved and cooled to 0°. To the reaction mixture, with stirring, 16.3 g (0.1 mole) of ethyl dichlorophosphate was added, after which stirring was continued for 1.5 h. Then 200 ml of ether was added, the crystalline precipitate was filtered off, and a stream of dry hydrogen sulfide was passed through the filtrate. After separation of the precipitate, the solvent and pyridine were distilled off, and the residue was distilled in vacuum. 19.1 g (74% of theory) of ethyl di-(cyclopenten-1)-phosphate was obtained.

3. **Preparation of tri-(3-penten-2)-phosphate.** In 120 ml of pyridine, 105.6 g (0.33 mole) of α-chloromercuridiethyl ketone was dissolved, cooled to 0°, and, with stirring, 15.3 g (0.1 mole) of phosphorus oxychloride in 20 ml of absolute ether was added, after which the reaction mixture was stirred for 2 h. Then 200 ml of absolute ether was added. The crystalline precipitate that formed was filtered off, and a stream of dry hydrogen sulfide was passed through the filtrate. After separation of the precipitate, the ether and excess pyridine were distilled off, and the residue was distilled in vacuum. 23 g (76% of theory) of tri-(3-penten-2)-phosphate was obtained.

4. **Preparation of ethyl isopropenyl ethylphosphinate.** In 70 ml of dry pyridine, 32.2 g (0.11 mole) of chloromercuriacetone was dissolved. The mixture was cooled to 0°, and, with stirring, 15.6 g (0.1 mole) of ethoxyethylphosphinic acid chloride in 20 ml of absolute ether was added. The mixture was stirred for 1.5 h, after which 150 ml of absolute ether

was added. The crystalline precipitate was filtered off, and a stream of dry hydrogen sulfide was passed through the filtrate. The precipitate was separated, the ether and excess pyridine were distilled off, and the residue was distilled in vacuum. 13.7 g (77% of theory) of ethyl isopropenyl ethylphosphinate was obtained.

5. **Diisopropenyl ethylphosphinate.** In 100 ml of pyridine, 64.4 g (0.22 mole) of chloromercuriacetone was dissolved, cooled to 0°, and, with stirring, 14.7 g (0.1 mole) of ethylphosphinic acid chloride in 20 ml of absolute ether was added, after which the mixture was stirred for 2 h. Then 150 ml of absolute ether was added, the crystalline precipitate was filtered off, and a stream of dry hydrogen sulfide was passed through the filtrate. After separation of the precipitate, the ether and excess pyridine were distilled off, and the residue was distilled in vacuum. 12.2 g (64% of theory) of diisopropenyl ethylphosphinate was obtained.
6. **Preparation of trivinyl phosphate.** In 100 ml of pyridine, 45 g (0.15 mole) of mercuribisacetaldehyde was dissolved; the mixture was cooled to ...

0°, and, with stirring, 15.3 g (0.1 mole) of phosphorus oxychloride was added; after this the mixture was stirred for 1.5 hours. Then 150 ml of absolute ether was added, and the crystalline precipitate of the pyridine-sulfuric acid complex was filtered off. Dry hydrogen sulfide was passed through the filtrate; the precipitate was separated, and after distilling off the ether and pyridine the residue was distilled in vacuo. 15.2 g (86% of theory) of trivinyl phosphate was obtained.

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