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Abstract

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ON DERIVATIVES OF CARBALKOXYMETHYLPHOSPHINIC ACIDS

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In a number of works it was established that α-metallated carbonyl compounds containing a system of conjugated metal–carbon and carbon–oxygen bonds exhibit a pronounced dual reactivity. It was further shown that esters of α-metallated carboxylic acids are also capable of reacting in two ways ([1,2]). Thus, on acylation of these compounds, either esters of β-keto acids or α-alkoxyvinyl acylates were obtained:

$$R_3SnCH_2C(=O)OR + R'COX \longrightarrow \begin{cases} R'COCH_2C(=O)OR, \\ CH_2=C(OR)-OCOR' \end{cases}$$

Of particular interest is the reaction of esters of α-metallated carboxylic acids with halosilanes ([3]). Conditions were found under which the interaction proceeded both with transfer of the reaction center (formation of α-silyloxyvinylalkyl esters) and without transfer of the reaction center (formation of esters of α-silylated carboxylic acids). It should be noted that the reaction of α-metallated aldehydes and ketones with halo derivatives of silicon and phosphorus in all cases proceeded with transfer of the reaction center and led to the formation only of vinyloxy derivatives ([4]).

In continuation of these works, we have investigated the reaction of esters of α-stannated carboxylic acids with halides of trivalent phosphorus.

As might have been expected, in the case of esters of α-metallated carboxylic acids the phenomenon of transfer of the reaction center is expressed much more weakly than was observed for α-metallated aldehydes and ketones.

In all the experiments we carried out, the reaction proceeded practically without transfer of the reaction center and made it possible to obtain a series of derivatives of the previously undescribed class of carbalkoxymethylphosphinic acids.

For the synthesis of these compounds, esters of α-stannated carboxylic acids proved preparatively convenient. In the reaction of the latter with trivalent

phosphorus, by simply changing the ratio of the reagents one may replace one, two, or three chlorine atoms.

$$R_3SnCH_2COOR' + PCl_3 \begin{cases} \xrightarrow{1:1} Cl_2PCH_2COOR' \\ \xrightarrow{2:1} ClP(CH_2COOR')_2 \\ \xrightarrow{3:1} P(CH_2COOR')_3 \end{cases}$$

The yields of the compounds obtained in this way range from 80 to 90%. The trialkyltin chlorides formed simultaneously are readily separated by distillation of the reaction mixture.

Table 1

Formula	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, %
$RPCl_2$	80	79/15	1.4980	1.3860	37.00	37.34	20.83	2.94	17.89	20.58	2.88	17.71
$R'PCl_2$	81	73/8	1.4908	1.3103	41.76	41.99	25.68	3.82	16.06	25.42	3.73	16.40
R_2PCl	80	113/3	1.4825	1.2045	57.04	57.44	40.08	5.97	13.08	39.95	5.87	12.87
R_3P	90	141/2	1.4865	1.2025	58.79	58.89	43.27	6.27	12.40	43.24	6.03	12.39
R'_3P	89	160–161/1	1.4753	1.1346	73.21	72.84	49.50	7.36	10.40	49.65	7.29	10.67
$RP(OC_2H_5)_2$	79	84–85/8	1.4420	1.0662	48.18	48.25	43.25	7.79	16.01	43.30	7.79	15.96
$R'P(OC_2H_5)_2$	74	95–96/9	1.4380	1.0349	52.79	52.90	46.82	8.43	14.70	46.17	8.23	14.88
$R'_2POC_2H_5$	78	109.5–110.5/1	1.4580	1.0836	63.01	62.87	48.18	7.84	12.48	48.00	7.65	12.38
R_3PO	96	38–40*	–	–	–	–	40.61	5.68	11.64	40.49	6.07	11.96
R'_3PO	98	74–75*	–	–	–	–	46.60	7.31	10.28	46.76	6.87	10.05

* melting point.

Analogously, alkyldichlorophosphites and dialkylchlorophosphites react to give esters of functionally substituted phosphinic acids:

$$R_3SnCH_2COOR' + (R''O)_2PCl \rightarrow (R''O)_2PCH_2COOR'.$$

These compounds can also be obtained by esterification of chlorophosphines formed in the reaction of phosphorus trichloride with esters of α-stannylated carboxylic acids.

In the IR spectra of the compounds obtained, absorption was found in the region 1728–1735 cm^{-1}, corresponding to vibrations of the $C = O$ bond in the ester group.

All synthesized derivatives of trivalent phosphorus oxidize in air with self-heating. When air is passed through an ethereal solution of tris-(carbalkoxy)methylphosphines, the corresponding oxides are formed.

The yields, constants, and analyses of the compounds obtained are given in Table 1.

Experimental Part

All operations were carried out in a stream of nitrogen.

Reaction of phosphorus trichloride with α-stannylated esters of acetic acid.

1. Carbomethoxymethyldichlorophosphine. To a solution of 30.2 g (0.22 mole) of phosphorus trichloride in 100 ml of absolute ether, with stirring, a solution of 79.2 g (0.22 mole) of the methyl ester of tributylstannylacetic acid in 50 ml of absolute ether was slowly added dropwise. After heating for 30 min, the ether was distilled off and the residue was distilled in vacuo. This gave 31.1 g (80% of theory) of carbomethoxymethyldichlorophosphine and 69.1 g (96% of theory) of tributylchlorostannane.

2. Di-(carbethoxymethyl)-chlorophosphine. To a solution of 8.2 g (0.06 mole)

phosphorus trichloride in 20 ml of abs. benzene was added dropwise, with stirring, a solution of 35.5 g (0.12 mole) of ethyl triethylstannylacetate. The reaction proceeded with self-heating. The benzene was distilled off and the residue was distilled in vacuo. 10.5 g (80% of theory) of di-(carbethoxymethyl)-chlorophosphine and 28.2 g (97.6% of theory) of triethylchlorostannane were obtained.

3. **Tris-(carbomethoxymethyl)-phosphine.** To a solution of 43.7 g (0.156 mole) of methyl triethylstannylacetate in 40 ml of abs. benzene, 7.1 g (0.053 mole) of phosphorus trichloride in 70 ml of abs. benzene was slowly added with stirring. The benzene was distilled off, and the residue was distilled in vacuo. 35.4 g (92% of theory) of triethylchlorostannane and 12.3 g (90% of theory) of tri-(carbomethoxymethyl)-phosphine were obtained.

4. **Diethyl ester of carbethoxymethylphosphinous acid.** To a solution of 24.6 g (0.065 mole) of ethyl tributylstannylacetate in 100 ml of abs. benzene, a solution of 10.2 g (0.065 mole) of diethyl chlorophosphite in 10 ml of abs. benzene was added dropwise with stirring. The mixture was boiled for 30 min. After distillation of the benzene, the residue was distilled in

vacuo. 10 g (74% of theory) of the diethyl ester of carbethoxymethylphosphinous acid and 20.4 g (96% of theory) of tributylchlorostannane were obtained.

5. **Ethyl ester of di(carbethoxymethyl)-phosphinous acid.** To a solution of 59.8 g (0.203 mole) of ethyl triethylstannylacetate, a solution of 14.7 g (0.1 mole) of ethyldichlorophosphite was added. The mixture was boiled for 30 min, the benzene was distilled off, and the residue was distilled. 16 g (78% of theory) of the ethyl ester of di-(carbethoxymethyl)-phosphinous acid and 48 g (99% of theory) of triethylchlorostannane were obtained.

6. **Oxidation of tris-(carbethoxymethyl)-phosphine.** Through a solution of 2.9 g (0.1 mole) of tris-(carbethoxymethyl)-phosphine in 30 ml of abs. ether, a stream of dry air was passed. 3.01 g (98% of theory) of the oxide of tris-(carbethoxymethyl)-phosphine was obtained.

Ethyl tributylstannylacetate was obtained by the interaction of ethoxytributylstannane with ketene by the method of I. F. Lutsenko and S. V. Ponomarev ([5]).

Ethoxytributylstannane. Yield: 80%, b.p. 96/1 mm, n_D^{20} 1.4686, d_4^{20} 1.1097. MR_D found 84.04; calculated 84.44.

Found %:		C 50.19; H 9.84; Sn 35.44
$C_{14}H_{32}OSn$.	Calculated %:	C 50.18; H 9.63; Sn 35.12

Ethyl tributylstannylacetate. Yield: 82%, b.p. 129/1 mm, n_D^{20} 1.4750, d_4^{20} 1.1271. MR_D found 93.56; calculated 94.26.

Found %:		C 50.88; H 9.02; Sn 31.63
$C_{16}H_{34}O_2Sn$.	Calculated %:	C 50.95; H 9.09; Sn 31.48

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named after M. V. Lomonosov

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REFERENCES CITED

[1] A. N. Nesmeyanov, I. F. Lutsenko, E. M. Tumanova, *Izv. AN SSSR, OKhN*, **1949**, 601.
[2] S. V. Ponomarev, I. F. Lutsenko, *ZhOKh* **34**, No. 10 (1964).
[3] Yu. I. Baukov, G. S. Burlachenko, I. F. Lutsenko, *DAN* **157**, No. 1 (1964).
[4] A. N. Nesmeyanov, I. F. Lutsenko, V. A. Brattsev, *DAN* **128**, No. 3 (1959).
[5] I. F. Lutsenko, S. V. Ponomarev, *ZhOKh* **31**, 2025 (1961).

Note: Figure translations are in progress. See original paper for figures.