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Synthesis of β-Carbonylphosphine Oxides and Phenyl-Substituted Ethylenediphosphine Oxides. Study of Their Complexing with Alkali Metals Cations

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Abstract—The synthesis of some β-carbonylphosphine oxides and phenyl-substituted ethylenediphosphine oxides was carried out. Their complexing with alkali metals cations was studied. Compounds obtained were shown to possess clearly expressed Li/Na selectivity.

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We reported earlier on developing chemical methods to utilize toxic organoelemental compounds, including sulfur and cyano-containing [1] and organochlorine pesticides [2]. To continue these works we studied the development of chloro-acetophenone (CAP) utilization methods. Great amount of this substance were stored on the chemical arsenals, during which the warranty period of its storage expired.

For this purpose we studied reaction of CAP with hydrophosphoryl compounds [phosphinous acids $R_2P(O)H$]. The reaction was not examined earlier. We presumed that some substituted β-carbonylphosphine oxides might be obtained. These compounds containing two donor centers are of interest as potential bidentate ligands and extracting agents.

We found that reaction of chloroacetophenone with phosphinous acids proceeds by the following scheme:

$$\mathrm{PhC(O)CH_2Cl + R_2P(O)}$$

$$\xrightarrow{\mathrm{KOH}} \mathrm{PhC(O)CH_2P(O)R_2 + KCl + H_2O.}$$

I–V

Reaction was carried out under mild conditions using DMSO or DMFA as solvents at 60–65°C for 1.5–2 h. Yields and some constants are given in Table 1.

The considerably low yield of compound **II** in comparison with analogs has engaged our attention. Evidently, this fact was due to high losses on the isolation stage.

All of the compounds obtained are well soluble in aromatic hydrocarbons (benzene, toluene) and non-polar organic solvents. It should be pointed out especially that compound **II** is soluble at room temperature in hydrocarbons of normal structure up to *n*-pentane.

We synthesized series of phenyl-substituted ethylenediphosphine oxides unreported earlier to obtain comparative characteristics of ligand possibility of the new prepared β-carbonylphosphine oxides against the others bidentate ligands and extracting agents. The choice of the phenyl group as a substituent in the ethylene bridge was done to increase the diphosphine oxides solubility in non-polar and aromatic solvents.

$$\mathrm{2\,R_2P(O)H + C_6H_5CHClCH_2Cl + 2\,NaOH}$$

$$\xrightarrow[\mathrm{(DMF)}]{\mathrm{DMSO}} \mathrm{R_2P^1(O)CH_2CH[P^2(O)R_2]C_6H_5 + 2\,NaCl + 2\,H_2O.}$$

VI–IX

Yields, some constants, and NMR spectra parameters for phenyl-substituted ethylenephosphine oxides are given in Tables 2, 3.

Table 1. Yields, melting points, elemental analysis data and NMR spectra parameters for β-carbonylphosphine oxides

Comp. no.	R	Yield, %	mp, °C	Found, %			Formula	Calculated, %			δ_P, ppm
				C	H	P		C	H	P	
I	C_2H_5	68	118–120	64.31	8.01	14.01	$C_{12}H_{17}O_2P$	64.27	7.64	13.81	31.3
II	*n*-C_8H_{17}	41	– (bp 220–228/10^{-4} mm)	73.80	10.29	7.67	$C_{24}H_{41}O_2P$	73.43	10.53	7.88	29.4
III	C_6H_5	78	212–214	75.30	5.19	9.41	$C_{20}H_{17}O_2P$	74.99	5.34	9.67	30.6
IV	$C_6H_5CH_2$	81	159–161	76.13	6.11	9.13	$C_{22}H_{21}O_2P$	75.91	6.08	8.90	33.2
V	*n*-$CH_3C_6H_4$[a]	73	–	77.01	5.58	9.38	$C_{22}H_{21}O_2P$	75.91	6.08	8.90	37.1

[a] In this work technical ditolylphosphinous acid was used (by NMR spectrum data, 90–94%).

Table 2. Yields, melting points and elemental analysis data for phenyl-substituted ethylenediphosphine oxides

Comp. no.	R	Yield, %	mp, °C	Found, %			Formula	Calculated, %		
				C	H	P		C	H	P
VI	C_2H_5	54	106–109	61.09	8.67	19.56	$C_{16}H_{28}O_2P_2$	61.13	8.98	19.71
VII	*n*-C_8H_{17}	32	–	73.19	12.41	10.20	$C_{38}H_{76}O_2P_2$	72.80	12.22	9.88
VIII	C_6H_5	88	192–194	75.78	5.81	12.27	$C_{32}H_{28}O_2P_2$	75.88	5.57	12.23
IX	$C_6H_5CH_2$	82	–	77.12	6.62	11.35	$C_{36}H_{36}O_2P_2$	76.85	6.45	11.01

As follows from Table 2, the target products yields are sufficiently high except for compound **VII.** This fact may also originate from high losses on the isolation stage.

As early as the nineteen seventies phosphine oxides and alkylenediphosphine oxides were established to form complex compounds of various stability with metal cations [3]. Various methods for quantitative estimation of the ligand properties of alkylenediphosphonates with respect to metal cations were used, but electroconductivity measurement method was the most common [4].

Table 3. NMR spectra parameters for phenyl-substituted ethylenediphosphine oxides

Comp. no.	$\delta(P^1)$, ppm	$\delta(P^2)$, ppm.	$J(P^1P^2)$, Hz
VI	29.1	56.9	44.0
VII	32.0	52.8	44.2
VIII	27.1	54.5	44.6
IX	29.9	38.1	48.6

Properties of compounds obtained were evaluated by stability constant values of their complexes with alkali metals cations of the corresponding 2,4-dinitrophenolates. The ratio of stability constants values of lithium and sodium complexes was used for selectivity estimating. Data about complexing ability and selectivity are given in Table 4.

As follows from these data, all of the compounds obtained are effective ligands for alkali metals cations. Compound **III** is of greater practical interest since it combined the sufficiently high absolute value log β with high Li/Na-selectivity close to the most effective from the known [5] organophosphorus compounds.

EXPERIMENTAL

All the reactions involving phosphonous acids were carried out under a dry argon atmosphere. Purification and individuality of compounds obtained were monitored by TLC on Silufol UV-254 plates eluting with systems chloroform-acetone (1:1) and chloroform–ethanol (20:1). Melting points were determined on a Boetius PHMK-05 device. The ^{31}P NMR spectra were registered on a spectrometer Bruker

Table 4. Logarithms of stability constants (log β) for complexes M^+L with alkali metals cations in the mixture THF–$CHCl_3$ 4:1 at 25°C

Comp. no.	log β		Selectivity B(Li)/β(Na)
	Li	Na	
I	3.4	2.6	6.3
II	3.7	2.9	6.3
III	4.6	3.0	35
IV	3.3	2.8	3.2
V	3.1	2.2	7.9
VI	3.0	2.0	10
VII	3.6	2.9	5.0
VIII	4.2	3.1	12.5

CXP-200 relative to external 85% H_3PO_4 using $CDCl_3$ as a solvent. The downfield chemical shifts were considered to be positive. Quantitative estimation of ligand ability (L) was made using stability constants values $[M^+]L$ measured by conductometric method. Procedure of these measurements performed at 25°C in THF–$CHCl_3$ (4:1) system is described in [4]. Precision error < 0.1 log units. Alkali metals 2,4-dinitrophenolates were used as salts.

Phosphine oxide (III). To a solution of 10.5 g of diphenylphosphonous acid and 7.7 g of chloroacetophenone in 70 ml of DMSO at 60°C was added 4.3 ml of 45% of potassium hydroxide solution. The reaction mixture was stirred for 2 h, then cooled, diluted with water (70 ml), and extracted with chloroform (370 ml). Organic layer was separated, washed with water (4× 50 ml), and dried with $MgSO_4$. Solvent was removed in a vacuum. Yield 12.5 g (78%), after recrystallization from dioxane, 11.5 g (72%).

Diphosphine oxide (VIII) was prepared similarly from 10.5 g of diphenylphosphinous acid, 8.7 g (6.9 ml) of 1-phenyl-1^b,-dichloroethane and 9.0 ml of 45% potassium hydroxide solution (10% excess). Yield 25.3 g (88%), after recrystallization from dioxane, 17.7 g (69%).

REFERENCES

1. Antoshin, A.E., Lermontov, S.A., Reikhov, Yu.N., Tugushov, V.I., and Tugushov, K.V., *Khim. i Biol. Bezop.*, 2006, no. 6 (30), p. 10.
2. Antoshin, A.E., Lermontov, S.A., Reikhov, Yu.N., and Tugushov, K.V., *Khim. i Biol. Bezop.*, 2008, nos. 1–2 (37–38), p. 12.
3. Medved’, T.Ya., Polikarpov, Yu.M., Bertina, L.E., and Kabachnik, M.I., *Usp. Khim.*, 1975, no. 6, p. 1003.
4. Yatsimirskii, K.B., Kabachnik, M.I., Medved’, T.Ya., and Sinyavskaya, E.I., *Izv. Akad. Nauk SSSR Ser. Khim.,* 1988, no. 1, p. 58.
5. Yevreinov, V.I., Vostroknutova, Z.N., Baulin, V.E., Syundyukova, V.Kh., and Tsvetkov, E.N., *Zh. Obshch. Khim.*, 1989, vol. 59, no. 1, p. 79.