SYNTHESIS OF METHYL- AND DIMETHYL-SUBSTITUTED ETHYLENE

DIPHOSPHINE DIOXIDES AND THEIR COMPLEX-FORMING PROPERTIES

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Alkylation of diphenylphosphonous acid by allyl bromide leads (depending on the reaction conditions) to the formation of both diphenylallylphosphine oxide and diphenylpropenylphosphine oxide. Addition of phosphonous acids to diphenylpropenylphosphine and diphenyl(2-methyl)propenylphosphine oxides resulted in the formation of a series of methyl- and dimethyl-substituted ethylenediphosphine dioxides. The complex forming ability of diphosphine dioxides with respect to alkali metal cations was studied. It was shown that 1-diphenylphosphinyl-2-methyl-2-dioctylphosphinylpropane (X) has the highest Li/Na selectivity (β (Li)/ β (Na) = 50).

The synthesis, the complex-forming and extraction properties of tetraphenylethylenediphosphine dioxides substituted in the ethylene bridge have been previously described in [1-3]. These compounds have increased solubility in nonpolar and slightly polar solvents and are fairly effective complex forming agents with respect to alkali metal cations [2] and promising extractants for the trans-plutonium elements [3], comparable in their effectiveness with diphenylcarbamoylmethylphosphines. The present work is devoted to the synthesis and study of the complex-forming properties with respect to alkali metal cations of related compounds, ethylenediphosphine dioxides, substituted by methyl- and dimethyl-groups in the ethylene bridge, and containing various substituents at the phosphorus atoms.

A convenient method for the synthesis of ethylenediphosphine dioxides with an asymmetric structure is the addition of phosphonous acids to vinylphosphine oxides [4, 5]. Diphenylpropenylphosphine oxide (I) [1] and diphenyl(2-methylpropenyl)phosphine oxide (II) were chosen as the starting materials. Compounds (I) and (II) are formed by the reaction of diphenylphosphonous acid with allyl bromide or methallyl chloride at a 1:1 ratio of the reagents in a two-phase system (benzene-45% NaOH or KOH, 5 h, 80°C, in the absence of an interphase transfer catalyst).

$$Ph_{2}P(O)H = XCH_{2} = C = CH_{2} \xrightarrow{KOH} Ph_{2}P = CH = C$$

$$R$$

$$X = Br, R = H (I), X = CI, R = CH_{3} (II).$$

We should note that previously, during alkylation of diphenylphosphonous acid with allyl bromide in a two-phase system in the presence of powdered KOH and an interphase transfer catalyst, a product with mp 96-97°C was obtained to which the structure of diphenylallylphosphine oxide was ascribed [6].* This difference in the result prompted us to make a detailed study of the alkylation of diphenylphosphonous acid by allyl halides.

In fact, in the reaction of diphenylphosphonous acid with allyl bromide or methallyl chloride in a two-phase system (benzene-45% KOH) in the presence of an interphase transfer catalyst Bu₄NI or Bu₄NBr for 1 h at 65° C and at a 1:1 ratio of the reagents, diphenylallyl-phosphine (III) and diphenylmethallylphosphine (IV) oxides are formed

*According to our data and those published in [7], diphenylallylphosphine oxide has mp 108-109°C, while the mp 96-97°C probably corresponds to a mixture of isomeric oxides of diphenylallyl- and diphenylpropenylphosphines.

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However, on further heating of the reaction mixture, phosphine oxides (III) and (IV) are converted into phosphine oxides (I) and (II), respectively.

The dynamics of alkylation of diphenylphosphonous acid by allyl bromide in a two-phase system was studied in detail using ³¹P NMR spectroscopy. When the reaction was carried out in the absence of an interphase transfer catalyst, a decrease in the diphenylphosphonous acid signal (δP 18.7 ppm) and intensification of the signal of diphenylallylphosphine (δP 27.9 ppm) were observed in the ³¹P NMR spectrum of the reaction mixture. After 1.5 h from the beginning of the reaction, the signal of the diphenylphosphonous acid disappeared, and the only product of the phosphine oxide type was allylphosphine oxide (III). Subsequently, it signal disappeared and the accumulation of the signal of the isomerized phosphine oxide (I) (SP 21.0 ppm) took place. After 5 h from the beginning of the reaction, the rearrangement of the allyl oxide (III) into the propenyl oxide (II) was complete. Carrying out the reaction in the presence of the interphase transfer catalyst accelerated the formation of phosphine oxide (III), and 1 h after the beginning of the reaction, its content in the reaction mixture reached a maximum. Phosphine oxide (III) subsequently rearranged into phosphine oxide (I). Thus, in order to obtain diphenylallylphosphine oxide, the reaction must be carried out in the presence of an interphase catalyst and must be ended after 1 h. To obtain diphenylpropenylphosphine oxide, the duration of the reaction should be not less than 5 h. Phosphine oxides (II) and (IV) can be obtained in a similar way.

The addition of phosphonous acids to phosphine oxides (I) and (II) in a DMSO medium during catalysis with 45% KOH leads to methyl- and dimethylethylenediphosphine dioxides (V)-(XII), in most cases in high yields



The values of R and R', the yields and certain properties of dioxides (V)-(XII) are given in Table 1.

<u>Complex-Forming Properties</u>. Table 2 shows the logarithms of the stability constants $(\log \beta)$ of complexes [M⁺L] of ethylenediphosphine dioxides (V)-(VIII), (X), (XI) with Li⁺, Na⁺, and K⁺ cations and the values of Li/Na⁻ and Na/K-selectivity of these ligands, which were evaluated from the ratio of stability constants of two different cations. The same table also shows similar characteristics for methyl- and dimethyl-substituted tetraphenyl-ethylenediphosphine dioxides (XIII) and (XIV) previously studied by us in [2]. It is not difficult to see that, compared with the "tetraphenyl" dioxides (XIII) and (XIV), the complex forming ability of the "mixed" dioxides with respect to Li⁺, Na⁺, and K⁺ cations noticeably increases as a result of increase in the nucleophilicity of one of the phosphoryl oxygen atoms when corresponding substituents are introduced to the phosphorus atom. This fact is particularly clearly manifested in the case of dioxides (VII) and (VIII) with ethyl radicals at one of the phosphorus atoms.

The selective properties of the "mixed" dioxides studied are determined by successive decrease in the stability of the complexes on increase in the radius of the cation $Li^+ > Na^+ > K^+$, i.e., these compounds are selective first of all with respect to the Li^+ cation. The maximal value of the Li/Na selectivity (50) is reached in the case of dimethyl-substituted dioxide (X) with n-octyl radicals attached to one of the phosphorus atoms. The Li/Na selectivity of the dioxide (8) exceeds not only that of the simplest crown ethers, for which this property is always uncharacteristic, but also that of all phosphorus-containing complex forming agents known in the literature, including the most effective dioxide (XIV) [2].

phosp	hine	Dioxide	s Ph ₂ P ¹ (0)C	CR	[P ² (0)R ₂ ¹]	CH3					
Com-				Found Calct	1 ulated	*	. %	Mp, °C	δ₽'.	61%,	J pr Pr.	Dup constraint ô
punod	۳. ۲	Ж	Empirical formula	0	=	- -	,blsil	(solvent)	ррп		Hz	FIN Spectrum () Frm
(A)	н	p-Tol	C ₂₉ H ₃₀ O ₂ P ₂	73,6	6,3	13,1	82	121-123 (benzene-hexane,1:1)	31.7	7.8:	48,6	.2d.d(3H) (Jup=15 Hz, Jun=0Hz), 2,3s(6H), 2.5m(2H), 2,9 m (1H), 5 9 − 7 8 m(1H)
(IA)	Me	p-Tol	C ₃₀ H ₃₂ O ₂ P ₂	73.9	6.3 6.6	12.8 12.8	88	189-191 (benzene-hexane, 1:2)	29,9	38.	48.6	1, 2 - 1, 0 m (1017) $1, 45 d(611) (J_{107} - 1, 1, 1, 2, 2, 45 (611)), 2, 75 m(211), 7, 2, 75 m(211), 7, 2, 7, 8 m(1, 811)$
(III)	Ξ	E E	C ₁₉ H ₂₆ O ₂ P ₂	65.6 65.5	7,5	17.8	16	129-130,5 (benzene-hexane, 1:2)	32.4	56.1	44.0	1.0 - 1.4 m (9H), $1.7 m (4H)$, $2.3 m (2H)$, $2.3 m (2H)$, $2.9 m (1H)$, $7.4 - 7.9 m (10H)$
(IIII)	Me	E	C20H28O2P2	<u>66,0</u> 66.3	7.7	17,4	87	143-144 (benzene-hexane, 1:4)	29,5	58.6	44.0	1.25 $m(1211)$, 1.7 $m(411)$, 2.7 $d.d(211)$, ($J_{HP}(=10Hz)$, 2.7 $d.d(211)$, ($J_{HP}(=10Hz)$, $J_{LUZ}=24z$), 7 $d-7gm(10H1)$
(XI)	Η	Oct	C ₃₁ 11 ₅₀ O2P2	72,1	9,6	11.9	50	Bp 220-233 (10-4 mm)	32.2	53.2	44.0	0.94(311), $1.2-1.7(3111)$, $0.94(311)$, $1.2-1.7(3111)$, $0.323(211)$, $3.000(111)$, $7.3-8.000(10111)$
(X)	Me	Oct	Ca21152O2P2	72.3	9.8 9.8	11.8	78	1	27,3	54,4	14.5	0.95t(6H), 1.2 - 1.7 (35H), 2.6m(2H), 7.3 - 7.9m(10H)
(IX)	2	PhCH ₂	C291130()2P2	73,5	6.3 6.4	13,2	87	1/40 - 1/12 (benzene-hexane,1 : 1)	33,3	47,9	45.0	1.3 d.d (311) (J_{HP} = (5 Hz, J_{H11} = 5,5Hz), 2.5m (211), 2 = 3 (m (5H), 7.2 - 7 8m (20H))
(IIX)	Me	PhCH ₂	C30H32O2P2	73.9	6.4 6,6	12,7	80	158-160 (benzene-hexane, 1:1)	33.2	44,7	44.8	1,4d(6H) (7,1p = 14H2), 2,8(6H), 7,2-7,8 m (20H)

Physical Constants, Analytical and NMR Data of Methyl- and Dimethyl-Substituted Ethylenedi-TABLE 1.

TABLE 2. Logarithms of Stability Constants $(\log \beta)$ of Complexes M⁺L of Methyl- and Dimethyl-Substituted Ethylenediphosphine Dioxides Ph₂P(0)CH₂CR(CH₃)P(0)R₂' with Alkali Metal Cations (THF-CHCl₃, 4:1, per volume, at 25°C)

Com-	R	R	lg β			Selectivity	
pound			Li+	Na+	K≁	6 (Li+)/f (Na+)	β (Na+) 'β (K+)
(V) (VI) (VII) (VIII) (X) (XI) (XII) * (XIV) *	H Me H Me H H Me	p-Tol p-Tol Et Et Oct PhCH ₂ Ph Ph	4.1 4.3 4.7 4.7 4.6 4.4 4.0 4.2	2.8 2,9 3.3 3.2 2.9 3.1 2.6 2.6	1,5 1,6 2,1 1,7 1,5 2,0 1,5 1,5	$ \begin{array}{ c c c c c c c c c c c c c c c c c c c$	20 20 16 32 25 13 13 13

*See [2].

EXPERIMENTAL

All the reactions in which phosphonous acids participated were carried out in a dry argon atmosphere. The purity of the compounds was monitored by TLC on Silufol UV-254 plates in systems chloroform-acetone (1:1) and chloroform-alcohol (20:1). The melting points were determined on a "Boetius RNMK-05" apparatus. The ¹H and ³¹P NMR spectra were recorded on a "Bruker CXP-200" spectrometer using TMS (internal) and 85% H_3PO_4 (external) as standards, and CDCl₃ as solvent. The weak-field signals in the ³¹P NMR spectra were considered to be positive. The averaged results of the elemental analyses are given in Table 1. The quantitative evaluation of the complex-forming ability of the ligands (L) was carried out in relation to the values of the stability constants of the complexes $[M^+]L$ which were determined conductometrically. The method of conductometric measurements at 25°C in a mixed THF-CHCl₃ (4:1) solvent was described previously in [8]. The random error in the determination of the stability constants of the only error in the determination of the stability constants of the only error in the determination of the stability constants of the only error in the determination of the stability constants of the only error in the determination of the stability constants of the complexes than 0.1 log. units. Alkali metal 2,4-dinitro-phenolates served as salts in the investigation.

<u>Diphenyl(2-methylpropenyl)phosphine Oxide (II)</u>. A 20-ml portion of 45% KOH was added to a mixture of 30.5 g of $Ph_2P(0)H$ and 13.7 g of methallyl chloride in 200 ml of benzene. The mixture was stirred for 5 h at the boiling point. Benzene was removed under vacuum, and the residue was dissolved in CHCl₃ (100 ml), the solution was washed with water (3 × 40 ml), and dried over MgSO₄. Chloroform was evaporated under vacuum, and the residue was chromatographed on a column of silica gel L100 × 250 μ , using a chloroform-acetone (1:1) mixture as eluent. Yield, 22.4 g (58%) of phosphine oxide (II), mp 154-156°C (benzene:hexane, 2:3). PMR spectrum (δ , ppm, J, Hz): 2.0 s (3H), 2.1 d.d (3H, J_{HH} = 1, J_{HP} = 2), 5.95 d (1H, J_{HP} = 12.5), 7.5-7.8 m (10H). ³¹P NMR spectrum: δ 21.3 ppm. Found, %: C 74.8; H 6.5; P 12.1. C₁₆H₁₇OP. Calculated, %: C 75.0; H 6.6; P 12.1.

<u>Diphenylallylphosphine Oxide (III)</u>. A 47.0-ml portion of 45% KOH ws added to a mixture of 44.0 g of $Ph_2P(O)H$, 26.0 g of allyl bromide and 2.0 g of Bu_4NI in 400 ml of benzene. The reaction mixture was stirred for 1 h at 65°C, and cooled to 20°C. The organic layer was washed with water (3 × 100 ml), dried over MgSO₄, and the solvent was evaporated under vacuum. After recrystallization of the residue from a benzene—hexane (1:1) mixture, 43.0 g (75%) of phosphine oxide (III), mp 108-109°C [7] was obtained. PMR spectrum (δ , ppm, J, Hz): 3.2 m (2H, J_{HP} = 14.5, J_{HH} = 7.5), 5.2 m (2H), 5.8 m (1H), 7.3-7.8 m (10H). ³¹P NMR spectrum: δ 30.2 ppm. Found, %: C 74.2; H 6.4; P 13.0. C₁₅H₁₅OP. Calculated, %: C 74.3; H 6.3; P 12.8.

<u>Diphenyl(2-methallyl)phosphine Oxide (IV)</u>. A 40.0-ml portion of 45% KOH was added to a mixture of 40.5 g of $Ph_2P(0)H$, 18.2 g of methallyl bromide and 3.0 g of Bu_4NBr in 400 ml of benzene. The reaction mixture was stirred for 1 h at 65°C. Benzene was evaporated under vacuum, the residue was dissolved in chloroform (150 ml), the solution was washed with water (3 × 60 ml), dried over MgSO₄, and chloroform was evaporated under vacuum. After recrystallization of the residue from a benzene-hexane (1:1) mixture, 28.8 g (56%) of phosphine oxide (IV) was obtained, mp 136-138°C [7]. PMR spectrum (δ , ppm, J Hz): 1.9 m (3H), 3.05 d (2H, J_{HP} = 14), 4.8 m (2H), 7.3-7.8 m (10H). ³¹P NMR spectrum: δ 29.5 ppm. Found, %: C 74.7; H 6.6; P 11.8. C₁₆H₁₇OP. Calculated, %: C 75.0; H 6.6; P 12.1. <u>1-Diphenylphosphinyl-2-di(p-tolyl)phosphinylpropane (V)</u>. A 1.2-ml portion of 45% KOH was added to a mixture of 2.1 g diphenylpropenylphosphine oxide [1] and 2.0 g of $(p-Tol)_2$ -P(0)H [9] in 15 ml of DMSO. The reaction mixture was stirred for 5 h at 60°C, then cooled to 20°C, diluted with water (15 ml) and extracted with chloroform (4 × 15 ml). The combined extract was washed with water (3 × 10 ml), dried over MgSO₄, and the solvent was evaporated under vacuum. Yield, 4.0 g (91%) of compound (V). After recrystallization from a benzene-hexane (1:1) mixture, the yield was 3.6 g (82%).

Compounds (VI)-(VIII), (XI), (XII) (Table 1) were obtained in a similar way.

<u>1-Diphenylphosphinyl-2-dioctylphosphinylpropane (IX)</u>. A 1.1-ml portion of 45% KOH was added to a mixture of 2.4 g of diphenylpropenylphosphine oxide [1] and 2.8 g of Oct₂-P(O)H [10] in 20 ml of DMSO. The reaction mixture was stirred for 5 h at 60°C, then cooled to 20°C, diluted with water (20 ml) and extracted with chloroform (4 × 15 ml). The combined extract was washed with water (3 × 20 ml), and dried over MgSO₄. The solvent was evaporated under vacuum, and the residue was chromatographed on a column of silica gel L100 × 250 μ , using a mixture of chloroform and alcohol (50:1) as eluent. Yield 2.6 g (50%) of compound (IX) in the form of colorless oil. After distillation under vacuum (bp 220-223°C, 10⁻⁴ mm), the yield of compound (IX) was 0.63 g (11.7%) (see Table 1).

<u>1-Diphenylphosphinyl-2-methyl-2-dioctylphosphinylpropane (X)</u>. A 1.5-ml portion of 45% KOH was added to a mixture of 2.6 g of oxide (II) and 2.8 g of $Oct_2P(0)H$ [10] in 30 ml of DMSO. The reaction mixture was stirred for 3 h at 60°C, cooled to 20°C, diluted with water (30 ml) and extracted with chloroform (4 × 20 ml). The combined extract was washed with water (3 × 20 ml), dried over MgSO₄, and the solvent was evaporated under vacuum. The residue was chromatographed on a column of silica gel L100 × 250 μ using chloroform as eluent. Yield, 4.2 g (78%) of compound (X) in the form of a colorless oil (see Table 1).

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