10.83; Si 21.56%; MR 40.58. PMR spectrum (δ, ppm): 0.09 s (9H, CH_3Si); 3.59 s (1H, OH); 4.06 dd (2H, CH_2, $^3J = 3.5$, $^4J = 0.9$ Hz); 5.85 dt (1H, SiCH, $^3J = 18.8$ Hz); 6.08 dt (1H, =CH).

Compound (VIb), $(CH_3)_3SiCH=CHCOCH_3$, had n_D^{20} 1.4480 [7]. The same ketone was prepared by oxidation of (IVb) with CrO_3 in H_2SO_4. The PMR spectrum was identical to that described in [7].

CONCLUSIONS

Reaction of α- and β-(trialkylsilyl)acroleins with methylmagnesium iodide forms the corresponding secondary unsaturated organosilicon alcohols. The reactions of α-(trialkylsilyl)acroleins are accompanied by cleavage of the Si—C bond. The byproducts from β-(trialkylsilyl)acroleins are primary unsaturated alcohols and α, β-unsaturated organosilicon ketones.

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SYNTHESIS AND ACID—BASE AND COMPLEXING PROPERTIES OF AMINO-SUBSTITUTED α-HYDROXYALKYLIDENEDIPHOSPHONIC ACIDS

M. I. Kabachnik, T. Ya. Medved',
N. M. Dyaglova, Yu. M. Polikarpov,
B. K. Shcherbakov, and F. I. Bel'skii

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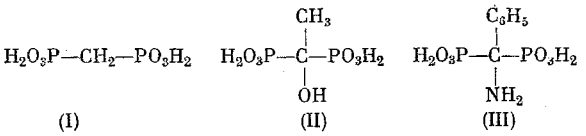
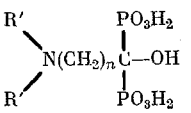
Methylenediphosphonic acid (I) and its derivatives, notably hydroxyethylenediphosphonic acid (II), because of their accessibility [1] and ability to form stable complexes with a series of metal cations, find various uses [2, 3]. We have made detailed studies of the complexing properties of (II) [4] and of aminobenzylidenediphosphonic acid (III) [5] and have measured the stability constants of metal complexes with these ligands by potentiometric titration



(I) (II) (III)

These acids in some cases display greater complexing ability than polyaminopolyphosphonic acids [2]. We decided to synthesize and study the properties of acids containing together with the hydroxymethylenediphosphonic acid grouping an additional coordination site, an amino group. Hence we prepared amino-substituted α-hydroxyalkylidenediphosphonic acids (IV)-(VII)



R=R'=H, $n=2$ (IV); R=R'=H, $n=3$ (V); R=H, R'=C_2H_5, $n=2$ (VI); R=R'=C_2H_5, $n=2$ (VII) R=R'=CH_3, $n=2$ (VIII)

Institute of Heteroorganic Compounds, Academy of Sciences of the USSR, Moscow.

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TABLE 1. Acid Dissociation Constants* [25°C, ionic strength μ = 0.1 (0.1 M KCl)]

Compound	pK_1	pK_2	pK_3	pK_4
(I) [4]	1,7	2,75	7,33	10,42
(II) [4]	1,7	2,47	7,28	10,29
(III) [5]	1,6	5,29	8,17	10,29
(IV)	2,55	5,83	9,9	10,8
(V)	2,72	8,73	10,5	11,6
(VI)	2,49	6,70	10,4	11,5
(VII)	2,50	5,92	10,0	11,2
(VIII)	2,35	5,89	9,7	10,8

*The error in pK_1 and pK_2 is ± 0.05 pK units and in pK_3 and pK_4 is ± 0.1 pK units (reliability 0.95).

The literature describes only one representative of this class of compound, namely α-hydroxy-γ-aminopropylidenediphosphonic acid (IV) [6], which was synthesized by the method normally used for the preparation of hydroxyalkylidenediphosphonic acids [7]. Acid (IV) was prepared in 59% yield by the reaction of β-alanine with phosphorous acid and PCl_3 in chlorobenzene at 100°C followed by aqueous hydrolysis

$$H_2N(CH_2)_2COOH + H_3PO_3 + PCl_3 \rightarrow H_2N(CH_2)_2C(PO_3H_2)_2OH \quad (IV)$$

The literature lacks information on the complexing ability of (IV).

Starting from γ-aminobutyric acid we synthesized α-hydroxy-δ-aminobutylidenediphosphonic acid (V), in which the phosphorus atoms and amino group are separated by four carbons. Both γ-amino acid (IV) and δ-amino acid (V) possess limited solubility in water [(V) is far less soluble].

We synthesized N-alkyl-substituted acids (VI)-(VIII) from N-alkyl-substituted β-aminopropionic acids, prepared by the procedure of [8] by addition of amines to methyl acrylate followed by hydrolysis of the intermediate amino acid ester with water at room temperature. Thus we synthesized N-ethyl-, N,N-diethyl-, and N,N-dimethyl-β-aminopropionic acids, which were converted by H_3PO_3 and PCl_3 into the aminohydroxydiphosphonic acids (VI)-(VIII). These compounds are amorphous powders, which on prolonged standing in air are converted into colorless oils and are highly soluble in water, unlike compounds with an unsubstituted amino group. We verified the structures of the synthetic compounds by elemental analysis and, in the case of α-hydroxy-γ-N,N-diethylaminopropylidenediphosphonic acid, by the ^{31}P NMR spectrum, which shows one signal with δ-17.36 ppm, characteristic of α-hydroxyalkylidenediphosphonic acids, implying the equivalence of both phosphorus atoms.

We evaluated the acid — base and complexing properties of the synthetic compounds by pH-metric titration. The neutralization curves of acids (IV), (VI)-(VIII) are similar in character. The buffer region $0 < a < 1$ corresponds to dissociation of the first proton; the buffer region $1 < a < 2$ to dissociation of the second; and finally the last two protons are lost in the buffer region $2 < a < 4$ (a denotes the equivalents of alkali consumed per mole of acid). Acid (V) has two buffer regions: the first corresponds to dissociation of the first proton ($0 < a < 1$), the second to loss on the second, third, and fourth protons ($1 < a < 4$). We were unable to reach any conclusions regarding the dissociation of the protons of the aliphatic hydroxyl groups (no potential discontinuities).

The acid dissociation constants calculated following [9] are summarized in Table 1. For comparison we include the dissociation constants of acids (I)-(III). Acids (IV)-(VIII) are distinguished from acids (I), (II), and (III) by the higher pK_1 and also the unusually high pK_3, comparable with pK for dissociation of the betaine protons of aminophosphonic acids [2].

We characterized the complexing properties of the synthetic compounds by titrating these acids in the presence of Ca^{2+}, Co^{2+}, and Cu^{2+} cations. The neutralization curves were shifted toward more acidic pH, implying complexation. We calculated the stability constants of the protonated and normal complexes (Table 2) by Schwarzenbach's algebraic method [9, 10].

TABLE 2. Stability Constants of Compounds (I)-(VIII) (25°C, ionic strength $\mu = 0.1$)

Compound	Ca^{2+}			Co^{2+}			Cu^{2+}		
	MH_2L	MHL	ML	MH_2L	MHL	ML	MH_2L	MHL	ML
(I) [4]	—	3,88	6,03	—	6,11	12,03	—	6,78	13,29
(II) [4]	—	—	6,04	—	5,29	9,36	—	6,26	12,48
(III) [5]	—	4,82	6,56	—	7,36	10,63	—	10,01	15,63
(IV)	2,85	5,7*	5,8*	4,4*	8,5*	9,9*	5,8*	10,9*	13,6*
(V)	5,37	6,01	6,10	6,4*	7,9*	8,8*	7,73	11,31	12,92
(VI)	4,21	6,09	6,17	5,23	8,88	10,15	6,65	11,67	13,73
(VII)	3,37	5,62	5,73	4,20	6,94	7,71	5,99	11,08	12,68
(VIII)	3,38	5,57	5,71	4,74	7,89	9,01	6,00	10,76	12,95

*These constants are less reliable, since the calculation did not allow for the formation of the precipitate.

Introduction of an amino group into these complexons does not increase the stability of the normal complexes by comparison with acids (I) and (II). We note the extremely high stability of the MHL protonated complexes, which are invariably more stable than those of acids (I), (II), and (III). Remarkably, the MHL complexes differ only slightly in stability from the normal ML complexes (particularly with Ca^{2+}; the stability constants of the MHL and ML complexes lie within an order of magnitude of each other). Apparently as a result of steric hindrance, closure of an additional ring to form an M — N bond after loss of the betaine proton very slightly stabilizes the complex. Thus the synthetic acids are distinguished from (I), (II), and (III) by their ability to form strong complexes at acidic and neutral pH.

An important feature of the complexes of these acids is their greater solubility in comparison with those of acids (I)-(III). Thus the complexes of acid (II) with Ca^{2+} and Cu^{2+} are insoluble in all pH ranges, with the exception of strongly acidic solutions; acid (I) forms insoluble complexes with Co^{2+} while acid (III) forms insoluble MH_2L complexes with Ca^{2+} and Cu^{2+}. In contrast acids (VI)-(VIII) form soluble complexes at all pH's. Acid (V) gives a precipitate only with Co^{2+} and only at pH > 9. The least soluble are complexes of acid (IV): with Ca^{2+} a precipitate forms at pH 6.5 and persists to the end of the titration; with Cu^{2+} an intense precipitate appears at pH 4 and then completely dissolves at pH 7; while with Co^{2+} the precipitate appears at pH 4.7 and dissolves at pH 9.7.

EXPERIMENTAL

α-Hydroxy-γ-aminopropylidenediphosphonic Acid (IV). A mixture of β-alanine (4.5 g, 0.05 mole) H_3PO_3 (6.2 g, 0.076 mole) and C_6H_5Cl (25 ml) was heated on a steam bath under an inert gas. After dropwise addition of PCl_3 (10.3 g, 0.075 mole) to the stirred mixture, heating was continued for a further 3 h. The lower, initially more mobile layer of the reaction mixture gradually thickened and toward the end almost completely solidified. After cooling the solvent was decanted and the residue was kept under vacuum. Water (30 ml) was added. The mixture was heated on a steam bath for 25-30 min and then filtered; traces of HCl were removed under vacuum. Compound (IV) crystallized from the aqueous solution on cooling, mp 226-228°C (water). Addition of alcohol to the mother liquor gave more acid: yield 6.1 g (51%). Found: C 15.0; H 4.7; N 5.9; P 25.9%; $C_3H_{11}NO_7P_2$. Calculated: C 15.3; H 4.7; N 5.8; P 26.4%.

α-Hydroxy-δ-aminobutylidenediphosphonic Acid (V). Similarly γ-aminobutyric acid (5.1 g, 0.049 mole), H_3PO_3 (6.2 g, 0.076 mole), and PCl_3 (10.3 g, 0.075 mole) gave (V) (5.7 g, 46%), mp 233-235°C (decomposition). Found: C 19.5; H 5.1; N 5.4; P 25.4%. $C_4H_{13}NO_7P_2$. Calculated: C 19.3; H 5.2; N 5.2; P 24.9%.

α-Hydroxy-γ-N-ethylaminopropylidenediphosphonic Acid (VI). The reaction was carried out as above, except that after removal of HCl (IV) was precipitated with alcohol. The solution was decanted; and precipitation was twice repeated. The resulting thick colorless oil was kept for 30 min under an oil-pump vacuum at 100°C. β-N-Ethylaminopropionic acid (3 g, 0.026 mole), H_3PO_3 (3.1 g, 0.038 mole), and PCl_3 (5.1 g, 0.037 mole) gave (VI) (3.3 g, 49%) as an amorphous powder. Found: N 5.1; P 23.2%. $C_5H_{11}HO_7P_2$. Calculated: N 5.3; P 23.6%.

α-Hydroxy-γ-N, N-diethylaminopropylidenediphosphonic Acid (VII). By the procedure used for (VI), β-N, N-diethylaminopropionic acid (8 g, 0.055 mole), H_3PO_3 (6.2 g, 0.076 mole), and PCl_3 (10.3 g, 0.075 mole) gave (VII) (8.5 g, 53%) as an amorphous powder. Found: C 29.2; H 6.5; N 4.8; P 21.7%. $C_7H_{19}NO_7P_2$. Calculated: C 28.9; H 6.5; N 4.8; P 21.2%.

α-Hydroxy-γ-N,N-dimethylaminopropylidenediphosphonic Acid (VIII). By the procedure used for (VI), β-N,N-dimethylaminopropionic acid (5.8 g, 0.049 mole), H_3PO_3 (6.1 g, 0.074 mole), and PCl_3 (10.3 g, 0.075 mole) gave (VIII) (7.5 g, 57%) as an amorphous powder. Found: C 22.9; H 5.8; N 5.3; P 23.5%. $C_7H_{15}NO_7P_2$. Calculated: C 22.8; H 5.7; N 5.3; P 23.6%.

Potentiometric titrations were carried out in water with a pH-262 potentiometer (glass and silver chloride electrodes). Initial acid concentrations were 1×10^{-3} mole/liter. The metal:ligand ratio in all runs was maintained at 1:1. Titrations were carried out in a thermostated cell in a stream of N_2 at 25±0.1°C with ionic strength $\mu = 0.1$ (0.1 M KCl). The electrodes were calibrated with standard buffer solutions with pH 1.68, 4.01, and 9.18. Metal solutions were prepared from the chlorides (chemically pure grade); the metal content in the stock solutions was determined complexometrically [11].

CONCLUSIONS

1. We have synthesized new amino-substituted α-hydroxyalkylidenediphosphonic acids.

2. We have measured the acid dissociation constants of these compounds and the stability constants of their complexes with Ca^{2+}, Co^{2+}, and Cu^{2+} ions.

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