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HYDROGEN BOND IN SOME PHOSPHORUS-SUBSTITUTED ALIPHATIC ALCOHOLS

N. A. Bondarenko, E. I. Matrosov,

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E. N. Tsvetkov, and M. I. Kabachnik

Of the large number of hydroxyalkylphosphoryl compounds, in which the formation of an intramolecular hydrogen bond is possible, the various  $\alpha$ -hydroxy derivatives have been investigated in greatest detail [1-3]. In the condensed phase and in solutions in carbon tetrachloride to a concentration of  $10^{-3}$  M these compounds exist in the form of dimeric associates on account of interaction between the P=0 and OH groups. The intramolecular hydrogen bonds are only formed in very dilute solutions and are fairly weak (structure  $\alpha$ ):



TABLE 1. The  $\omega-Diphenylphosphino-$  and  $\omega-Diphenylphosphoryl-Substituted Alcohols$ 

Compound	Yield %	m <del>p</del> , °C (solvent), bp, °C (p, mm Hg)	Published data		
Ph <sub>2</sub> PCH <sub>2</sub> CH <sub>2</sub> OH (I)	70	163,5-164,5(1)	178–184(1,8) [10] 229–222(3)		
Ph <sub>2</sub> PCH <sub>2</sub> CH <sub>2</sub> CH <sub>2</sub> OH (II)	80	60-61 pet.ether 172-173(1)	60-61 [10]		
Ph <sub>2</sub> PCH <sub>2</sub> CH <sub>2</sub> CH <sub>2</sub> CH <sub>2</sub> OH (III)	81	$196-197 (2), \\ n_{D}^{20} 1,6104$	$ \begin{vmatrix} 170(0,16), & & \\ n_D^{20} & 1,6103 & [12] \\ 160-163(0,02), & & \\ n_D^{20} & 1,6101 & [11] \\ 160-164(0,2) & [13] \end{vmatrix} $		
$Ph_2P(O)CH_2CH_2OH * (IV)$	68 (A) 95 (B)	100,5-101,5 ethy1 acetate 100,5-101,5 ethy1 acetate, MEK †	94-95 [4] 94,5-95,5 [7] 88-89 [8] 111~114 [10]		
Ph <sub>2</sub> P(O)CH <sub>2</sub> CH <sub>2</sub> CH <sub>2</sub> OH (V)	60 (A) 97 (B)	102-103 ethy1 acetate-hexane 102-103	102-103 [4,9]		
Ph <sub>2</sub> P(O)CH <sub>2</sub> CH <sub>2</sub> CH <sub>2</sub> CH <sub>2</sub> OH <b>‡(VI)</b>	91 (B)	62-63 ether-MEK	$ \begin{bmatrix} 267-269 & [4] \\ 164(0,01), \\ n_{D}^{20} & 1,5959 & [12] \end{bmatrix} $		

\* Found: C 68,4; H 6.3; P 12,5%. C14H15O2P. Calculated: C 68.3; H 6.1; P 12.6%.

†MEK = methyl ethyl ketone.

<sup>‡</sup> Found: C 69.9; H 7.2; P 11,1%. C<sub>18</sub>H<sub>19</sub>O<sub>2</sub>P. Calculated: C 70.1; H 7.0; P 11.3%.

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TABLE 2. The Frequencies  $(v, \text{ cm}^{-1})$  of the Maxima in the Absorption Bands of the OH Group of Ph<sub>2</sub>P(0)-(CH<sub>2</sub>)<sub>n</sub>OH in Solutions in Carbon Tetrachloride (c =  $6 \cdot 10^{-4}$  M)

n	No. of members in ring	free 'OH	intra ⁰OHO=₽	intra free intra $\Delta v_{OH} = v_{OH} - v_{OH}$	K <sup>25°</sup>	
1	5	3600	3580 [5]	20 [5]		
2	6	3640	3450	190		
3	7	3645	3350	295		
4	8	3645	3375	270		

The  $\beta$ -hydroxy derivatives, in which the intramolecular hydrogen bonds (structure b) exist in more concentrated solutions than in the  $\alpha$ -hydroxyalkylphosphoryl compounds, have been investigated less; six-membered rings with an intramolecular hydrogen bond are more stable than the analogous five-membered rings [1].

The  $\gamma$ - and  $\delta$ -hydroxyalkylphosphoryl compounds formed by closure of the intramolecular hydrogen bond in seven- and eight-membered rings respectively (structures c and d), for which only data in [4] are known, have hardly been investigated at all. However, as shown more recently, the relationships obtained in [4] characterize the relative stability of the intermolecular associates of the investigated compounds [1-3, 5].

In the present work we studied the character of the H bond in  $\beta$ -,  $\gamma$ -, and  $\delta$ -diphenyl-phosphoryl-substituted aliphatic alcohols Ph<sub>2</sub>P(0)(CH<sub>2</sub>)<sub>n</sub>OH (n = 2, 3, 4), the formation of intramolecular hydrogen bonds in which leads to closure of six-, seven-, and eight-membered rings.

The investigated compounds have been described in the literature and were obtained by two methods: A) by alkaline cleavage of  $\omega$ -hydroxyalkyltriphenylphosphonium chlorides [4, 6-9]; B) by oxidation of  $\omega$ -diphenylphosphino alcohols (I-III), synthesized by the cleavage of ethylene and trimethylene oxides [10] and also THF [11-13] with metal diphenylphosphides. However, the constants of the  $\omega$ -diphenylphosphoryl-substituted alcohols (IV-VI) obtained by these methods do not always coincide.



It is first of all necessary to note the sharp difference in the constants given by various authors for  $\delta$ -diphenylphosphorylbutyl alcohol (VI). The discrepancy is so large that it suggests that the compounds described as (VI) have different structures. Thus, the compound obtained by method A was described [4] as crystalline with mp 269°C, while the compound synthesized by method B was described as a liquid [12].

There are differences too in the melting points of  $\beta$ -diphenylphosphorylethyl alcohol (IV). The compound obtained by method A from  $\beta$ -hydroxyethyltriphenylphosphonium chloride [4, 6] melted at 94-95°C. In this case triphenylphosphine oxide may be formed as such a product, as demonstrated during the alkaline decomposition of  $\beta$ -hydroxyethyltriphenylphosphonium iodide [7]. A sample of the same alcohol obtained from ethylene oxide and potassium diphenylphosphide, followed by oxidation of the phosphine (I) [10] (method B), melted at 111-114°C. Owing to the above-mentioned contradictions we used both methods with small experimental modifications for the synthesis of the investigated compounds.

By the reaction of triphenylphosphine with the corresponding chlorides followed by alkaline decomposition of the phosphonium chloride (method A) we obtained the alcohols (IV)

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	p-	n=2		n=3			n=4			
Solvent	PrOH	free VOH	inter	intra	free ™OH	inter intra	- <b>f</b> ree	inter	intra	
	чон		<sup>v</sup> OH inter <sup>∆v</sup> OH	intra ∆vOH		inter <sup>Δ</sup> VOH	intra <sup>∆v</sup> OH	OH	inter <sup>Δv</sup> OH	ΔvOH
	1			0/50			2250			2275
CC14	3645	3640	-	<u>3450</u> 190	3645	-	295	3645	·	270
C <sub>6</sub> H <sub>8</sub>	3620	3600		3425 ‡ 215	3610	· ·	3350 295	3610		<u>3375</u> 270
CHCl <sub>3</sub>	3630	3630	_	$\frac{3420}{220}$	3630	. –	3330 315	3630	·	<u>3350</u> 295
CH <sub>3</sub> CN	3555	_	3520 120	<u>3450</u> 190		3540	<u>3325</u> 320	-	3545 100	3400 245
THF	3490	-	<u>3440</u> 200	-	-	3470 175	3330 315	"	3475 170	3380 265
DMFA	3460	-	3430 210	- -	: 	3440	. <b></b>		3450 195	
DMSO	3390	-	<u>3340</u> 310	-	-	3355 290		· _ ·	3370	-
Hexamethyl-	3350	-	3310 320	-	-	3330 315	-	-	<u>3350</u> 295	-
1 A 6.			a sector		44194					

TABLE 3. The Frequencies  $(v, cm^{-1})$  of the Absorption Maxima of the OH Group in Ph<sub>2</sub>P(0)(CH<sub>2</sub>)<sub>n</sub>OH in Various Solvents\* (c = 0.15-0.10 M)

inter free inter intra free intra  $\Delta v_{OH} \approx v_{OH} \operatorname{CCh}_{4} - v_{OH} \approx \Delta v_{OH} \approx v_{OH} \operatorname{CCh}_{4} - v_{OH}$ .  $C \approx 3 \cdot 10^{-3} M$ .  $C \approx 1 \cdot 10^{-2} M$ , the band has a low-frequency shoulder.

and (V). The alkaline decomposition of  $\delta$ -hydroxybutyltriphenylphosphonium chloride, according to TLC data, gave a mixture of at least two products with similar Rf values, and we were therefore unable to isolate the individual compounds. In this case method A showed common disadvantages, which rested in the difficulty of purification of the initial phosphonium salts (with chlorohydrins and HCl as impurities) and also the uncertainty in the realization of their alkaline decomposition and, by virtue of this, the difficulty in separating the phosphoryl-substituted alcohols from the side products.

Method B gave the best results in the production of the alcohols (IV-VI). For the synthesis of the phosphino alcohols (I-III) we used the cleavage of ethylene and trimethylene oxides and also of THF with sodium diphenylphosphide. In the first two cases the reaction occurs readily and gives good yields of the products. For the cleavage of THF we used rigorous conditions (200°C, 30 h), and this made it possible to increase the yield of the phosphine (III) to 81%. The phosphino alcohols (I-III) were converted into the oxides (IV-VI) by oxidation with hydrogen peroxide.

The alcohol (IV) obtained both by method A and by method B had the same melting point  $(100.5-101.5^{\circ}C)$ , which was higher than that given for method A [4, 6-8] but lower than that given for method B [10] (Table 1). The constants of the  $\gamma$ -diphenylphosphorylpropyl alcohol (V) synthesized by both methods coincide with the published data [4, 9]. Unlike the compound synthesized by method B [12] and described as a liquid, the alcohol (VI) was a crystalline substance melting at 63°C. At the same time, this temperature differs from that given in [4] (269°C). It should be noted that the IR spectrum of this high-melting substance does not contain an absorption band for the OH group, and there is moreover a large discrepancy between the found and calculated carbon contents for (VI). In the IR spectrum of the alcohol (VI) which we synthesized there are absorption bands corresponding to the hydroxyl and phosphoryl groups. The constants of the obtained compounds are given in Table 1.

The character of the hydrogen bond in the synthesized compounds was investigated by IR spectroscopy in solutions in carbon tetrachloride, benzene, chloroform, acetonitrile, THF, DMFA, DMSO, and hexamethylphosphorotriamide. In the IR spectrum of the saturated solution of (IV) in carbon tetrachloride ( $c \sim 3.10-3$  M) in the region of the vibrations of the OH group there are two bands: at 3640 cm<sup>-1</sup> corresponding to the absorption of the free OH group ( $v_{OH}^{free}$ ) and an asymmetric band at 3450 cm<sup>-1</sup> with a shoulder on the low-frequency side. symmetrical, and the observed intensity ratio of this band  $v_{OH}^{free}$  does not change. This makes it possible to assign vOH 3450 cm<sup>-1</sup> to the absorption of the OH group taking part in the formation of an intramolecular hydrogen bond of type b.\* In order to investigate the reasons for the unsymmetrical nature of vOH 3450  $cm^{-1}$  in a saturated solution of the alcohol (IV) in carbon tetrachloride we investigated the IR spectra of the compound in concentrated solutions in benzene (c =  $3 \cdot 10^{-1}$  to  $1 \cdot 10^{-2}$  M), since the compound has limited solubility in carbon tetrachloride. In the spectrum of a benzene solution of the alcohol (IV) ( $c = 3 \cdot 10^{-1}$ M) there is one symmetrical band at  $3350 \text{ cm}^{-1}$ , and this indicates the presence of one type of association with participation of the OH group. When the solution is diluted a shoulder appears on the high-frequency side of this band. With further reduction in the concentration the shoulder develops into a v(OH) band at 3425 cm<sup>-1</sup>. The intensity of the v(OH) band at 3350 cm<sup>-1</sup> decreases on dilution, being converted into a shoulder on the v(OH) band at 3425 cm<sup>-1</sup> when c =  $1 \cdot 10^{-2}$  M. This makes it possible to assign the v(OH) band at 3350 cm<sup>-1</sup> to the absorption of the OH group participating in the formation of an intermolecular hydrogen bond. Thus, on the basis of these data it is possible to explain the unsymmetrical nature of the v(OH) band at 3450 cm<sup>-1</sup> in a saturated solution of the alcohol (IV) in carbon tetrachloride by the fact that at this concentration intermolecular associates, which only decompose at high degrees of dilution, are present in addition to the monomeric molecules with intramolecular hydrogen bonds.

In the IR spectra of saturated solutions of the alcohols (V) and (VI) in carbon tetrachloride (c =  $3 \cdot 10^{-3}$  M) (Table 2), as in the case of the alcohol (IV), there are two v(OH) bands: vfree at 3645 cm<sup>-1</sup> and symmetrical bands at 3350 cm<sup>-1</sup> (V) and 3375 cm<sup>-1</sup> (VI), corresponding to OH groups participating in the formation of an intramolecular hydrogen bond with the P=0 groups, as confirmed by the invariability of the form and position of the vbond band and also by the constant intensity ratio of the observed bands with dilution.

Thus, in solutions of the phosphorus-containing alcohols (IV-VI) in carbon tetrachloride at  $c = 6 \cdot 10^{-4}$  M there are only monomeric molecules, for which an equilibrium exists between the "open" and "closed" forms A and B:



The value of v(OH) bonded by an intramolecular hydrogen bond ( $\Delta v_{OH}^{intra}$ , Table 2) increases

with increse in the length of the polymethylene chain, and this shows that the strength  $(\Delta H)$  of the intramolecular hydrogen bond increases in the transition from five- to sixand seven-membered rings and that the intramolecular hydrogen bond in the eight-membered ring is a little weaker. However, in addition to the increase in the strength of the intramolecular hydrogen bond which forms the constant of the intramolecular hydrogen bond (K, see Table 2) decreases with increase in the length of the polymethylene chain, i.e., the equilibrium (1) is shifted toward the molecules with the "open" form A. Thus, in the transition from the  $\beta$ -substituted alcohol (IV) to the  $\delta$ -substituted alcohol (VI) the fraction of molecules with an intramolecular hydrogen bond in carbon tetrachloride decreases from 83 to 55%. The number of conformers in which the formation of an intramolecular hydrogen bond is structurally impossible probably increases with increase in the number of methylene groups in the molecule, and form B with an intramolecular hydrogen bond becomes less favorable with respect to entropy.

Thus, with increase in the number of methylene units in the ring the strength of the intramolecular hydrogen bond changes in the order five-membered < six-membered < seven-membered < eight-membered. The seven-membered ring is the most stable. Earlier [14], during examination of the v(OH) bands of five-, six-, seven-, and eight-membered rings with intramolecular hydrogen bonds in phosphorylated alcohols, a somewhat different relationship was observed: the strength of the intramolecular hydrogen bond increased in the order five-

(1)

<sup>\*</sup>In the IR spectrum of a solution of an equimolar mixture of  $Ph_2P(0)(CH_2)_2OEt$  and p-PrOH in carbon tetrachloride on dilution (from  $3 \cdot 10^{-2}$  to  $6 \cdot 10^{-4}$  M) the intensity of v(OH), due to an intermolecular hydrogen bond with the P=O group (3405 cm<sup>-1</sup>), decreases sharply with a simultaneous increase in the intensity of the free v(OH) (3645 cm<sup>-1</sup>).

membered < six-membered < seven-membered < eight-membered, i.e., the last ring is the most stable. However, during compilation of this series, the authors examined substances with nonuniform structures. Thus, in the compound

 $(EtO)_{3}P=0...H=-0$   $-C-(CH_{3})_{2}-C -C-(CH_{3})_{2}-C -H...O=P(OEt)_{3}$ 

which forms an eight-membered ring, the OH group is simultaneously at the  $\alpha$  position to one P=0 group and at the  $\delta$  position to the other; this does not make it possible to compare it with the other phosphoryl-containing alcohols. In addition, the compared compounds have different substituents at the phosphorus atom, and this can also affect the strength of the intramolecular hydrogen bond in addition to the size of the ring which forms.

The relationship which we obtained is similar to the order of variation in the strength of the intramolecular hydrogen bond and also the position of equilibrium between the "open" and "closed" forms A and B as a function of the size of the ring in the diols  $HO(CH_2)_nOH$ and their monomethyl ethers  $MeO(CH_2)_nOH$  [15], amino alcohols  $Et_2N(CH_2)_nOH$  [16], and esters of hydroxycarboxylic acids  $ROOC(CH_2)_nOH$  [17]. The observed relationship between the strength of the intramolecular hydrogen bond and the size of the ring is confirmed by the data from the IR spectra of the alcohols (IV-VI) in solvents with different basicities. Table 3 gives the v (OH) values for compounds (IV-VI) and also p-PrOH in solutions in benzene, chloroform, acetonitrile, THF, DMFA, DMSO, and hexamethylphosphorotriamide.

In a solution of the alcohol (IV) in benzene with  $c = 1 \cdot 10^{-2}$  M, intermolecular associates through interaction between the P=O and OH groups also exist together with the monomeric molecules A and B; the absorption of the OH group bonded by an intermolecular hydrogen bond appears as a low-frequency shoulder on the v(OH) band at 3425 cm<sup>-1</sup>, due to the absorption of the OH group in the monomers with intramolecular hydrogen bonds. In benzene solutions of the alcohols (V) and (VI) the intermolecular associates decompose at a higher concentration. [Solutions with  $c \leq 3 \cdot 10^{-1}$  M only contain the monomeric molecules; on dilution the position and form of the v(OH) bands involved in the formation of intramolecular hydrogen bonds do not change.]

In the IR spectra of the phosphoryl-substituted alcohols (IV-VI) in chloroform in the region of the absorption of the OH group there are two bands, i.e., a high-frequency v(OH) band belonging to the free OH group and a low-frequency v(OH) band for the OH bonded by an intramolecular hydrogen bond. In this case, as in carbon tetrachloride and benzene, an equilibrium (1) exists between forms A and B. A similar pattern is observed in solutions of the alcohols (IV-VI) in acetonitrile. The monomeric molecules with intramolecular hydrogen bonds are in equilibrium with the molecules which form hydrogen bonds with the solvent. (In this case the absorption band of the free OH group is shifted toward the low-frequency region compared with  $v_{\text{free}}^{\text{free}}$  in carbon tetrachloride, benzene, and chloroform.) The presence of molecules with intramolecular hydrogen bonds in solutions of the alcohols (IV-VI) in acetonitrile confirms the high strength of the intramolecular hydrogen bond in the six-, seven-, and eight-membered rings compared with the five-membered rings, in which there are no intramolecular hydrogen bonds in acetonitrile [2].

In the IR spectra of the substituted ethyl alcohol (IV) in THF there is one v(OH) band at 3440 cm<sup>-1</sup>, corresponding to the OH group of the "open" form A of the monomeric molecule bonded with the solvent by an intermolecular hydrogen bond, in contrast to the substituted propyl (V) and butyl (VI) alcohols, in solutions of which in THF there are also monomeric molecules with intramolecular hydrogen bonds in addition to the intermolecular alcohol—THF associates (the "open" form A). In DMFA, DMSO, and hexamethylphosphorotriamide in the alcohols (IV-VI) there are no intramolecular hydrogen bonds, and all the molecules are combined with the solvent by intermolecular hydrogen bonds, i.e., the equilibrium (1) is shifted fully toward the "open" form.

Comparison of the strength of the intramolecular hydrogen bond with the strength of the intermolecular hydrogen bond obtained from the shift of the absorption band for the combined OH group ( $\Delta v_{OH}^{intra}$  and  $\Delta v_{OH}^{inter}$  in Table 3) shows that the intramolecular hydrogen bond in the six-membered ring [alcohol (IV)] is similar to the intermolecular hydrogen bond of this compound with DMFA, while in the seven- and eight-membered rings [alcohols (V) and (VI)] it is stronger than the intermolecular hydrogen bond with this solvent. The intermolecular

hydrogen bonds between the substituted propyl (V) and butyl (V) alcohols and DMSO are also comparable with the intramolecular hydrogen bonds in these molecules, and the intramolecular hydrogen bond is only stronger with hexamethylphosphorotriamide. In solutions of the alcohol (IV) in THF and DMFA and also of the alcohols (V) and (VI) in DMFA and DMSO, however, only the substance-solvent intermolecular hydrogen bond exists, in spite of the fact that the  $\Delta v_{OH}^{intra}$  value is greater than or comparable with  $\Delta v_{OH}^{inter}$ . This fact can evidently be explained by the more favorable entropy conditions for the formation of the intermolecular hydrogen bond than the intramolecular hydrogen bond.

## EXPERIMENTAL

All the operations with trivalent phosphorus were carried out in an atmosphere of argon. The melting points were measured by specially short Anschutz thermometers. During determination of the boiling points corrections were not made for the projecting mercury column. The individuality of the compounds was confirmed by TLC (one spot in the alcohol and 1:3 alcohol-acetone systems on Silufol UV-254 plates). The IR spectra were recorded on a UR-20 instrument with a scanning rate of 64 cm<sup>-1</sup>/min and slit program 4. Calibration was realized against the absorption spectrum of polystyrene. Anhydrous solvents, purified by known methods, were used. The K<sub>ac</sub> values were determined on a Hitachi EPS-3T spectrophotometer in thermostated quartz cuvettes with a thickness of 10 cm (on the scale T = 90-100% at 25 ± 0.1°C) from the intensity of the first overtone of the free OH band at 1420 nm calculated according to [15]. All the compounds were thoroughly dried, and the solutions were prepared just before the spectra were recorded. The PMR spectra were recorded on a Hitachi-Perkin-Elmer R-20 spectrometer in chloroform (c =  $3 \cdot 10^{-1}$  M) with HMDS as internal standard. The spectral parameters of the phenyl protons are not given.

<u>B-Diphenylphosphinoethyl Alcohol (I)</u>. To a solution of 2.1 g of sodium in 400 ml of dry liquid ammonia (dried with sodium, evaporated, and recondensed) we added, while stirring, 14.2 g of diphenylphosphine. The ammonia was removed, and 70 ml of absolute THF was added to the residue. To the mixture at  $-5^{\circ}$ C we added dropwise with stirring 4.1 g of ethylene oxide in 10 ml of absolute THF. After 30 min we added 100 ml of benzene and, dropwise, 30 ml of water to the mixture at  $20^{\circ}$ C. The organic layer was separated, and the aqueous layer was extracted with benzene. The combined extract was dried with sodium sulfate and evaporated under vacuum, and the residue was distilled. The yield of (I) was 12.2 g.

<u> $\gamma$ -Diphenylphosphinopropyl Alcohol (II)</u>. To sodium diphenylphosphide, obtained from 3.5 g of sodium and 18.6 g of diphenylphosphine in 400 ml of dry liquid ammonia [see the synthesis of the alcohol (I)] in 200 ml of absolute benzene at 20°C we added dropwise 6.7 g of trimethylene oxide. After boiling for 1 h we added dropwise 30 ml of alcohol, while cooling with cold water, and then 75 ml of water. The organic layer was separated, and the aqueous layer was extracted with benzene. The combined extract was dried with sodium sulfate and evaporated under vacuum. The residue was distilled. The yield of (II) was 19.5 g.

 $\delta$ -Diphenylphosphinobutyl Alcohol (III). A mixture of 18.1 g of diphenylphosphine, 2.2 g of sodium, and 60 ml of absolute THF was heated in a glass tube in an autoclave at 200°C (bath temperature) for 30 h. The contents of the tube were poured into 100 ml of benzene. To the mixture we added dropwise with stirring dilute hydrochloric acid (1:1) to an acidic reaction and then dry sodium bicarbonate to a neutral reaction. The benzene layer was separated, and the aqueous layer was extracted with benzene. The extract was dried with sodium sulfate and evaporated under vacuum. The residue was distilled, and the yield of (III) was 19.2 g.

<u>β-Diphenylphosphorylethyl Alcohol (IV).</u> Method A. A mixture of 5.0 g of β-hydroxyethyltriphenylphosphonium chloride [6] (mp 237°C), 10.0 g of a 40% solution of sodium hydroxide, and 5 ml of water in 10 ml of alcohol was boiled for 8 h and then evaporated under vacuum. The yield of (IV) was 2.3 g.

<u>Method B.</u> To a solution of 12.4 g of (I) in 50 ml of acetone we added dropwise with stirring 12.3 g of 30% hydrogen peroxide and 15 ml of acetone. The solution was boiled for 1 h and evaporated under vacuum. The residue, dissolved in 30 ml of chloroform, was washed with a saturated solution of sodium bicarbonate, dried with sodium sulfate, and evaporated under vacuum. The yield of (IV) was 12.5 g. PMR spectrum ( $\delta$ , ppm): 2.5 dt (CH<sub>2</sub>-P), J<sub>CH<sub>2</sub>-CH<sub>2</sub> = 5.9 Hz, J<sub>CH<sub>2</sub>-P = 10.3 Hz, 3.9 dt (CH<sub>2</sub>-O), J<sub>CH<sub>2</sub>-CH<sub>2</sub> = 5.9 Hz, J<sub>CH<sub>2</sub>-P = 15.2 Hz, 4.7 s (OH).</sub></sub></sub></sub>

 $\gamma$ -Diphenylphosphorylpropyl Alcohol (V). Method A. Compound (V) was obtained similarly to (IV) (method A) from  $\gamma$ -hydroxypropyltriphenylphosphonium chloride [9]; mp 225°C, cf. [9].

<u>Method B.</u> The compound was obtained from (II) similarly to (IV) (method B). PMR spectrum  $(\delta, \text{ ppm})$ : 1.8, 2.3 m (CH<sub>2</sub>CH<sub>2</sub>P), 3.6 t (CH<sub>2</sub>O), J<sub>CH<sub>2</sub>-CH<sub>2</sub> = 5.9 Hz, 4.8 s (OH).</sub>

 $\frac{\delta-\text{Diphenylphosphorylbutyl Alcohol (VI).}}{\text{IV} \text{ (IV) (method B). PMR spectrum ($\delta$, ppm): 1.3-13.1 m (CH_2CH_2CH_2-P), 3.5 t (CH_2O), JCH_2-CH_2 = 5.9 Hz, 4.3 s (OH).}$ 

 $\beta$ -Diphenylphosphorylethyl Ethyl Ether. The ether was obtained by a method similar to that in [18]; mp 75-78°C (from ether).

## CONCLUSIONS

1.  $\omega$ -Diphenylphosphino-substituted alcohols  $Ph_2P(CH_2)_nOH$  (n = 2, 3, 4) were synthesized by the cleavage of ethylene and trimethylene oxides and also of THF with sodium diphenylphosphide.  $\omega$ -Diphenylphosphoryl-containing alcohols  $Ph_2P(0)(CH_2)_nOH$  (n = 2, 3, 4) were obtained by oxidation of the phosphino alcohols with hydrogen peroxide.

2. In dilute solutions in carbon tetrachloride the  $\omega$ -diphenylphosphoryl-substituted aliphatic alcohols  $Ph_2P(0)(CH_2)_nOH$  (n = 2, 3, 4) exist in the form of both monomeric molecules stabilized by intramolecular hydrogen bonds P=0...HO and molecules with a free OH group. The dependence of the strength of the intramolecular hydrogen bond on the ring size was investigated. Intramolecular hydrogen bonds in a six-membered ring are absent in solutions of the  $\omega$ -diphenylphosphoryl-substituted alcohols in THF; this bond is preserved in the seven- and eight-membered rings. In DMFA, DMSO, and hexamethylphosphorotriamide the molecules exist as associates with the solvent.

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