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Experimental

ESR spectra were recorded on a Varian-E12A radiospectrometer. The solutions under investigation were placed in quartz tubes which were carefully degassed and filled with argon. The irradiation was performed with the focused light of a DRSh-1000 lamp. A Unipan-660 regulator was used for maintaining constant sample temperature in the spectrometer resonator. Organomercuryphosphorus compounds were synthesized in a way similar to the methods described earlier.[10]

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References

1. A. G. Davies, D. Griller, and B. P. Roberts, *J. Am. Chem. Soc.*, 1972, **94**, 1782.
2. K. S. Chen, P. J. Krusic, and J. K. Kochi, *J. Am. Chem. Soc.*, 1972, **94**, 2030.
3. B. L. Tumanskii, V. V. Kadyrov, O. A. Popova, L. T. Lantseva, N. N. Bubnov, S. P. Solodovnikov, and K. N. Makarov, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1991, 1018 [*Bull. Acad. Sci. USSR, Div. Chem. Sci.*, 1991, **40**, 903 (Engl. Transl.)].
4. Ya. A. Levin and E. I. Vorkunova, in *Gomoliticheskaya khimiya fosfora* [*The Homolytic Chemistry of Phosphorus*], Nauka, Moscow, 1978, 61 (in Russian).
5. B. L. Tumanskii, V. V. Bashilov, N. N. Bubnov, S. P. Solodovnikov, and V. I. Sokolov, *Izv. Akad. Nauk, Ser. Khim.*, 1992, 1457 [*Bull. Russ. Acad. Sci., Div. Chem. Sci.*, 1992, **41**, 1140 (Engl. Transl.)].
6. B. L. Tumanskii, V. V. Bashilov, S. P. Solodovnikov, and V. I. Sokolov, *Izv. Akad. Nauk, Ser. Khim.*, 1992, 1936 [*Bull. Russ. Acad. Sci., Div. Chem. Sci.*, 1992, **41**, 1519 (Engl. Transl.)].
7. I. G. Neil and B. P. Roberts, *J. Organomet. Chem.*, 1975, **102**, C17.
8. J. E. Wertz and J. R. Bolton, *Electron Spin Resonance: Elementary Theory and Practical Applications*, McGraw-Hill, New York, 1972.
9. M. A. Cremonini, L. Lunazzi, G. Placucci, and P. J. Krusic, *J. Org. Chem.*, 1993, **58**, 4735.
10. D. L. Venezky and R. B. Fox, *J. Am. Chem. Soc.*, 1956, **78**, 1664.

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Synthesis of alkyl (3-pyridyl)hydroxymethylphosphonates and their IR spectra

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The reaction of dialkyl H-phosphonates with pyridine-3-carbaldehyde gives alkyl (3-pyridyl)hydroxymethylphosphonates. In liquid systems, the hydrogen atom is localized at the oxygen atom of the hydroxyl group; in crystals, the existence of a zwitter-ionic form could not be excluded. In $CHCl_3$ solutions, isolated molecules and cyclic dimeric H-complexes exist in an equilibrium.

Key words: alkyl (3-pyridyl)hydroxymethylphosphonates, H-bond; IR spectra.

The interaction of pyridine-3-carbaldehyde with dialkyl H-phosphonates has been studied. In the presence of MeONa, the reaction proceeds exothermically with the formation of alkyl (3-pyridyl)hydroxymethylphosphonates **1**—**4** (Scheme 1). The IR spectra of ethyl (3-pyridyl)hydroxymethylphosphonate (**2**) and ethyl α-hydroxybenzylphosphonate (**5**)[1] (Fig. 1) contain characteristic absorption bands (ν/cm^{-1}): 2600—3300 (AH), 1230—1260 (P=O), 1010—1070 (PO—C), as well as ~3000 and 1600 (CH and $\mathrm{C}\overset{\cdots}{-}\mathrm{C}$, respectively).[2]

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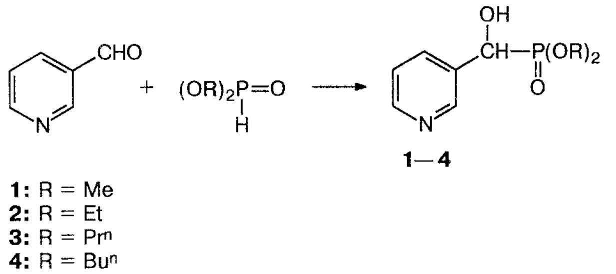
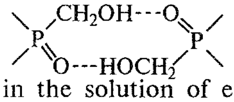
Scheme 1



Crystalline compound **2** has νAH absorbance in the 3000 cm^{-1} region, which is strongly shifted to lower frequencies and overlaps the bands of the stretching vibration of C—H bonds and their possible overtones. This produces a complex contour similar to Fermi-resonance. These spectra are usually observed for ν$^+$NH,[2] which suggests the probable existence of a zwitter-ionic structure:

To clarify this point, the IR spectra of solutions of esters **2** and **5** were recorded in chloroform.

It is known that νOH and ν$^+$NH frequencies can coincide in the case of formation of H-bonds, whereas they differ considerably for isolated molecules (in inert solvents): ~3600 cm^{-1} (OH) and ~3500 cm^{-1} ($^+$NH).[2] The results shown in Fig. 1 unambiguously attest to the existence of hydroxyl groups in esters **2** and **5**, as bands with maxima at 3588 and 3257 cm^{-1} for ester **2** and at 3589 and 3289 cm^{-1} for ester **5** appear in the spectra of the solutions of both compounds in the νAH region. As the solutions are diluted, the wide low-frequency bands disappear in both spectra and only the peaks at ~3600 cm^{-1} remain, which are almost identical in frequency and belong to hydroxyl groups free from intermolecular H-bonds. The bands in the ~3600 cm^{-1} region are asymmetrical, which is explained by the possible existence of a conformational equilibrium between the molecular forms with intramolecular hydrogen bonds O···H directed to different proton-acceptor centers (P=O, P—O, Ph, Py).[3] The concentration sensitive bands at 3257 cm^{-1} for ester **2** and at 3289 cm^{-1} for ester **5** belong to OH groups participating in intermolecular hydrogen bonds. The fact that the frequencies of the latter are almost identical for ester **5** in the crystalline state and in solution indicates that they belong to cyclic intermolecular dimers of the type



(see Ref. 3). The same is observed in the solution of ester **2**, however, in the crystalline state a considerable shift of νAH to low frequencies is observed. This is explained by the fact that the partner in the AH...B chain changes from P=O to the pyridine ring N atom, which has higher proton-acceptor ability, and by the formation of a longer chain of H-bonds. For ester **2** in the crystalline state, the formation of a zwitter-ionic structure also is possible. One can observe a similar spectral pattern for compound **1**.

The IR spectra of liquid esters **3** and **4** have νOH absorption bands at ~3280 cm^{-1}, which are characteris-

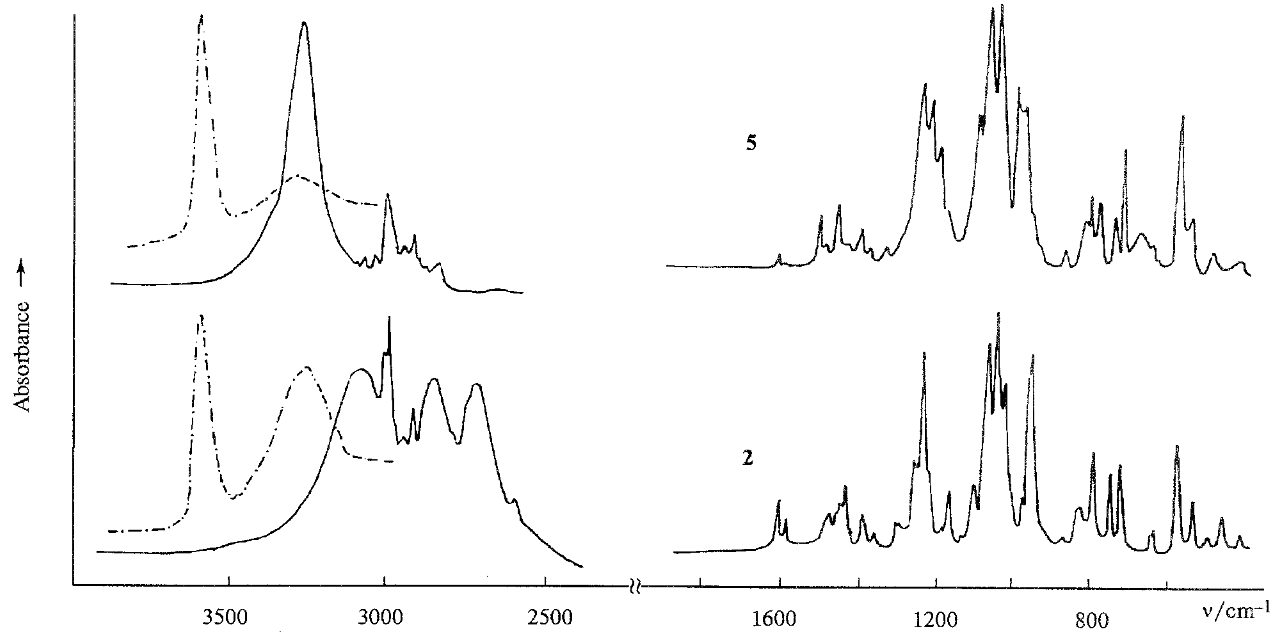


Fig. 1. IR spectra of free esters **2** and **5** (solid line) and their chloroform solutions (dotted line).

Table 1. Characteristics of alkyl (3-pyridyl)hydroxymethylphosphonates

Compound	Yield (%)	M.p. /°C	d_4^{20}	n_D^{20}	Found / Calculated (%)				Molecular formula	^{31}P NMR, δ
					C	H	N	P		
1	50	120—121	—	—	44.03 44.25	5.55 5.57	6.37 6.45	14.50 14.26	$C_8H_{12}NO_4P$	26.0
2	86	84	—	—	48.65 48.98	6.71 6.58	5.57 5.71	12.80 12.63	$C_{10}H_{16}NO_4P$	23.0
3	82	—	1.0992	1.4910	53.00 52.74	7.46 7.38	4.88 5.13	11.54 11.33	$C_{12}H_{20}NO_4P$	23.0
4	90	—	1.0780	1.4890	56.00 55.81	7.95 8.02	4.72 4.64	10.30 10.28	$C_{14}H_{24}NO_4P$	23.0

tic of solutions of **2** and **5** in chloroform. Apparently, cyclic H-dimers are formed in esters **3** and **4** by analogy with those described above for ester **5** and for solutions of **1** and **2**.

Experimental

^{31}P NMR spectra were recorded on an NMR KGU-4 instrument at 10.2 MHz (with 85 % H_3PO_4 as the external standard). Water was used as a solvent for crystalline compounds **1** and **2**, and acetone was used for compound **5**.

IR spectra were obtained with a Bruker IFS-113V Fourier IR-spectrometer. Samples of crystalline compounds were prepared in the form of pellets with KBr. Liquid substances were placed between KBr plates.

Alkyl (3-pyridyl)hydroxymethylphosphonates (1—4). One drop of a freshly prepared saturated solution of MeONa in MeOH was added to an equimolar mixture of dialkyl H-phosphonate and pyridine-3-carbaldehyde, and the temperature of the reaction mixture increased from ~20 °C to 50—70 °C. Esters **1** and **2** were recrystallized from anhydrous acetone. Liquid substances were purified by dissolving them in anhydrous acetone followed by precipitation with hexane. The upper solvent layer was decanted, and the rest was removed by vacuum evaporation. Characteristics of esters **1—4** are given in Table 1. Ethyl α-hydroxybenzylphosphonate **5** (m.p. 82 °C, from acetone, δP 22) was prepared by the known procedure.[1]

References

1. K. Fields, US Pat. 2579810; *Chem. Abstrs.*, 1952, **46**, 6140.
2. N. B. Colthup, L. H. Daly, and S. E. Wiberly, in *Introduction to Infrared and Raman Spectroscopy*, Academic Press, New York—London, 1964, 511.
3. R. R. Shagidullin, A. V. Chernova, and E. P. Trutneva, *Vnutrimolekulyarnaya vodorodnaya svyaz' v oksifosforil'nykh i oksitiofosforil'nykh soedineniyakh* [*Intramolecular Hydrogen Bonds in Oxyphosphoryl and Oxythiophosphoryl Compounds*], Moscow, 1981, Dep. VINITI 12.05.1981, 2192-81 (in Russian).

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