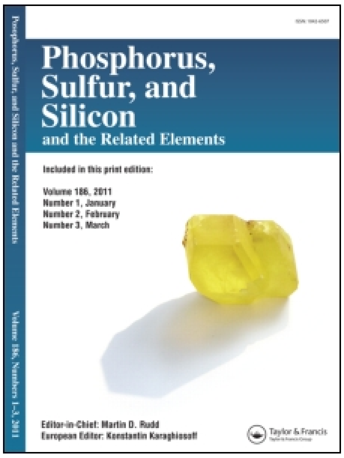

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THE REACTION OF DIMETHYL HYDROGEN PHOSPHONATE AND AMINOALCOHOLS

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THE REACTION OF DIMETHYL HYDROGEN PHOSPHONATE AND AMINOALCOHOLS

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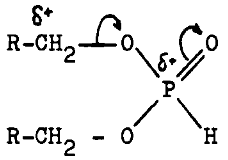
The interaction between dimethyl hydrogen phosphonate (DMHP) and aminoalcohols was examined. It was found that at the temperature of 80°C the basic reaction is that of alkylation of the aminoalcohols. The structure of the end products was proved by the aid of ^{1}H- and ^{31}P-NMR spectroscopy.

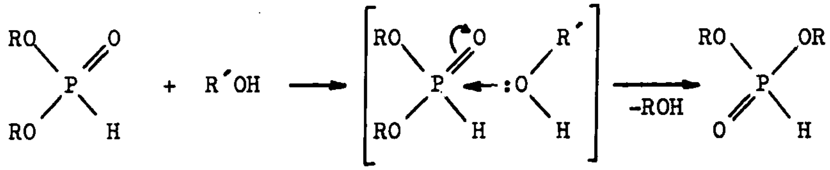
Key words: Dimethyl hydrogen phosphonate (DMHP); aminoalcohols; alkylated products; ^{1}H- and ^{31}P-NMR spectroscopy.

INTRODUCTION

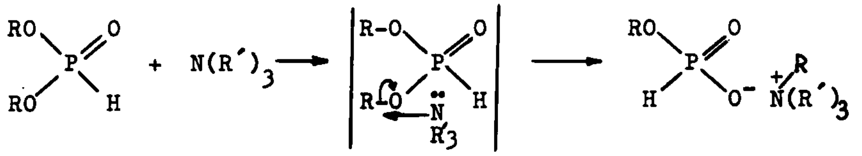
The dialkyl hydrogen phosphonate esters possess two electrophilic centres—the phosphorus atom and the alpha carbon atom of the alkoxyl group.



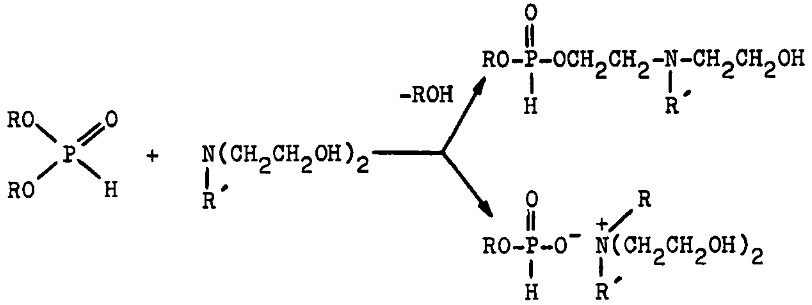
The electrophilic phosphorus atom is the site of the reaction of transesterification of the dialkyl hydrogen phosphonates with compounds which contain a hydroxyl group.[1]



The alpha carbon atom of the alkoxyl group is the site of the alkylation reaction which occurs between dialkyl hydrogen phosphonate and tertiary amines.[2,3]



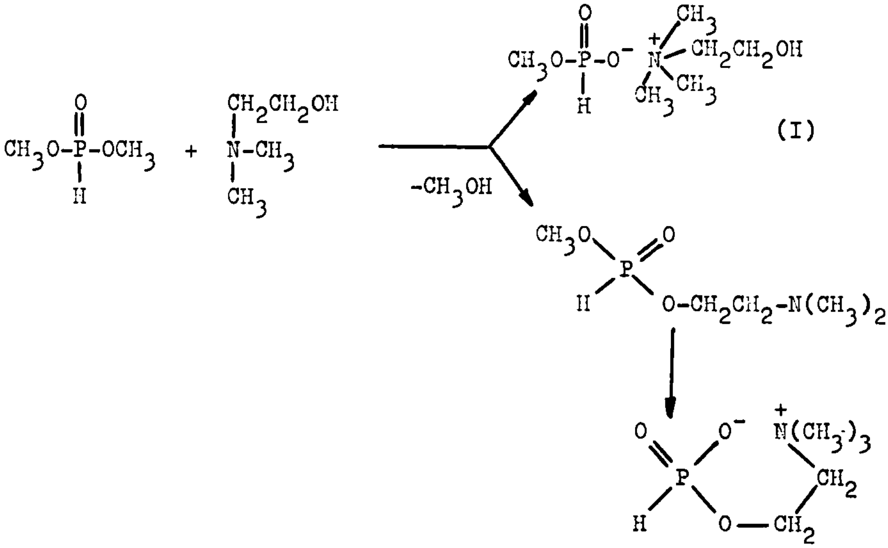
It was established as well, that in the interaction between dialkyl hydrogen phosphonates and aminoalcohols[4] at temperatures higher than 90°C one may observe both reactions—transesterification and alkylation, i.e. both electrophilic centres take part in the reaction.



The aim of the present study was to investigate the interaction between dimethyl hydrogen phosphonate with aminoalcohols at 80°C, a temperature lower than the initial temperature of trans-esterification. We anticipated that a predominance of alkylation would occur.

RESULTS AND DISCUSSION

Unlike tertiary amines, aminoalcohols (dimethylethanolamine, N-methyldiethanolamine, diethanolamine and triethanolamine) are able to cause both transesterification and alkylation of dialkyl hydrogen phosphonates. The simultaneous participation of the two electrophilic centres is established at temperatures higher than 90°C.[4] In this connection a reaction between dimethyl hydrogen phosphonate and dimethylethanolamine was carried out at a temperature lower than 90°C. The examination of the reaction product by ^{1}H-NMR spectroscopy showed that P—H



Scheme 1

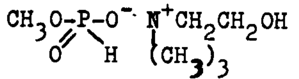
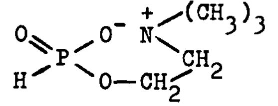
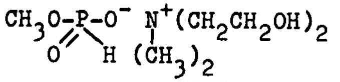
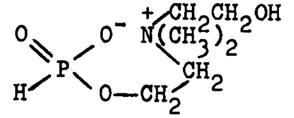
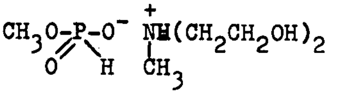
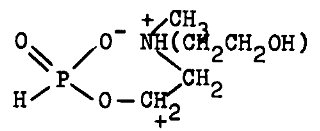
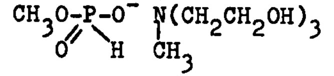
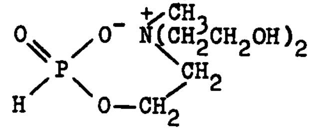
protons were present-δ = 6.68 ppm (d), J_{PH} = 608.6 Hz; for P—OCH_3 protons – δ = 3.54 ppm (d), J_{POCH3} = 12.2 Hz; for $\overset{+}{N}$—CH_3 protons – δ = 3.22 ppm (s). Besides, there were signals for $\overset{+}{N}$—CH_2 protons – δ = 3.33 ppm (t); for O—CH_2 – δ = 4.0 ppm (m). The distribution of the protons shows that the integral intensity to δ = 3.22 ppm corresponds to 9 protons, i.e. the product contains a $\overset{+}{N}(CH_3)_3$ group, due to alkylation of the dimethylethanolamine with dimethyl hydrogen phosphonate.

In addition to these signals, there were signals for a second compound: P—H protons δ = 6.79 ppm (d), J_{PH} = 624.1 Hz and also a signal for $\overset{+}{N}$—CH_3 δ = 3.25 ppm (s). From the ratio of the integral intensity of the two kinds of P—H protons, the percent of the two compounds was determined, 93% I and 7% II (Scheme 1).

From the ^{31}P-NMR spectrum (Table I) it can be seen that the signal at δ = 7.69 ppm and $^3J_{POCH_3}$ = 11.8 Hz is a doublet of quartets, characteristic of the

TABLE I

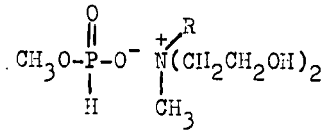
^{31}P-NMR data of the products, obtained by reaction of DMHP and aminoalcohols in a molar ratio 1:1

Initial compounds	End Products	Yield, (%)	Chem-shift, (ppm)	Coupling constants, (Hz)		
				$^1J_{PH}$	$^3J_{POCH_3}$	$^3J_{POCH_2}$
DMHP and dimethyl-ethanolamine		93.0	7.69	625.8	11.8	—
DMHP and dimethyl-ethanolamine		7.0	5.05	627.3	—	8.8
DMHP and N-methyl-diethanolamine		83.3	7.72	613.3	12.0	—
DMHP and N-methyl-diethanolamine		16.7	5.07	627.4	—	7.3
DMHP and diethanol-amine		80.7	7.81	618.1	12.0	—
DMHP and diethanol-amine		19.3	6.14	630.0	—	8.9
DMHP and triethanol-amine		81.2	7.76	615.9	12.1	—
DMHP and triethanol-amine		18.8	5.54	629.2	—	9.1

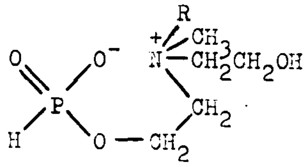
$CH_3O—P(O)H$ fragment; the signal at $\delta = 5.05$ ppm, $^2J_{POCH_2} = 8.8$ Hz is a doublet of triplets, which is characteristic of the $—CH_2—O—P(O)H$ fragment.

These data are consistent with product I formed from the alkylation of dimethylethanolamine with dimethyl hydrogen phosphonate and product II from transesterification of dimethyl hydrogen phosphonate with dimethylethanolamine and subsequent alkylation.

Under the same conditions alkylation of N-methyldiethanolamine, diethanolamine and triethanolamine with dimethyl hydrogen phosphonate were carried out. The ^1H- and ^{31}P-NMR spectra were consistent with the structural assignments (Table I).



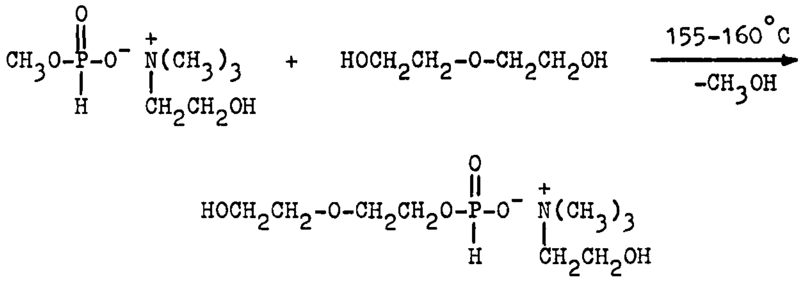
$$CH_3O-\overset{\overset{O}{\|}}{\underset{H}{P}}-O^- \ \overset{+}{\underset{CH_3}{N}}(R)(CH_2CH_2OH)_2$$



where R = H, CH_3, CH_2CH_2OH

The alkylated product contains an ionic bond between the oxygen and nitrogen atom (O^-N^+). The presence of this kind of bond in the product will probably influence the character of the other bonds in the molecule. In fact, the J_{PH} coupling constant of 710 Hz for dimethyl hydrogen phosphonate is decreased to 608–625 Hz for the alkylated products. Most probably this change is due to the presence of the ionic bond. The negative charge of the oxygen atom will determine the electron density at P—H, P—O and C—O bonds. The increase of the electron density of the phosphorus atom will determine the shift of the electron pair towards the hydrogen atom. The polarity of the bond P—H will decrease; the strength of the bond will increase. The change in the character of the P—H bond can be proved also by the IR data. The band of absorption for P—H shifts from 2438 cm^{-1} for dimethyl hydrogen phosphonate to 2342 cm^{-1} for the alkylated product. The increased electron density of the phosphorus atom will also enhance the ionic character of the P=O bond. That can be seen by the shift of the absorption band from 1258 cm^{-1} for the dimethyl hydrogen phosphonate to 1207 cm^{-1} for the alkylated product.

The suggestion that the negative charge on oxygen increases the electron density of the phosphorus atom can also be proved by transesterification of the alkylated product with diethyleneglycol.



$$CH_3O-\overset{\overset{O}{\|}}{\underset{H}{P}}-O^- \ \overset{+}{\underset{CH_2CH_2OH}{N}}(CH_3)_3 + HOCH_2CH_2-O-CH_2CH_2OH \xrightarrow[-CH_3OH]{155-160^\circ C}$$

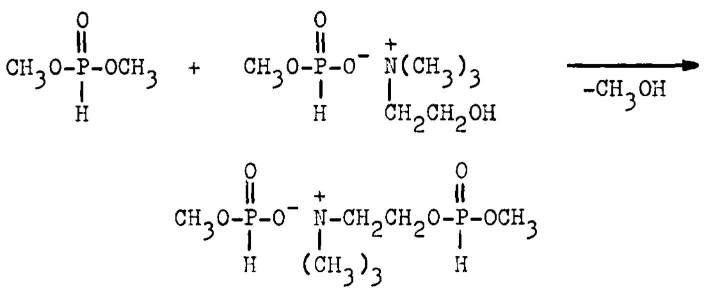
$$HOCH_2CH_2-O-CH_2CH_2O-\overset{\overset{O}{\|}}{\underset{H}{P}}-O^- \ \overset{+}{\underset{CH_2CH_2OH}{N}}(CH_3)_3$$

A transesterification reaction can be observed at 155–160°C, which reaches 70% conversion after 2½ hours. Unlike the alkylated product the dimethyl hydrogen phosphonate is transesterified by diethyleneglycol at 122–125°C.[5]

The transesterification reaction begins with a nucleophilic attack of the oxygen atom of the hydroxyl group towards the phosphorus atom. In the transesterification of the alkylated product such an attack will be hampered by the increased electron density of the phosphorus atom, which will slow the reaction rate.

The observed low conversion of the transesterification reaction of triethanolamine, diethanolamine and N-methyldiethanolamine[4] is due probably to an alkylation reaction. It has made possible a decrease in the transesterification rate by the means of increase of the electron density of the phosphorus atom of the alkylated product. The ^{31}P-NMR spectroscopic data shows that an internal alkylation of the monotransesterified product can be observed.

The experimental results showed that the hydroxyl group in the alkylated product is less reactive towards transesterification, compared with the hydroxyl group of the aminoalcohols.



The trasesterification of dimethyl hydrogen phosphonate with the hydroxyl containing alkylated product takes place at the temperature of 130°C, whereas the reaction of dimethyl hydrogen phosphonate with aminoalcohols takes place at 88–90°C. The decreased reactivity of the hydroxyl group of the alkylated product can be attributed to the influence of the positive charge of the nitrogen atom, which causes a shift of the electron density towards the nitrogen, which will cause a lowering in the electron density of the oxygen.

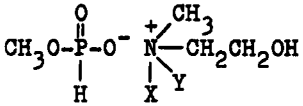
A similar influence of the negative charge on the reaction ability of the hydroxyl group may exist under conditions that the alkylated product exists in the form of free ions.

The data from ^{1}H-NMR spectroscopy show (Table II) that there is a correlation between the P—H coupling constants and the kind of the substituents on the nitrogen atom.

The decrease in the number of the substituents with donor character and the increase in the number of the substituents with acceptor character lead to the increase of the coupling constant. The change of the $^{1}J_{PH}$ is determined by the presence of negative charge of the oxygen atom and the degree of that change will probably depend on the magnitude of the negative charge of the nitrogen atom. It will depend on the type of the substituents present.

TABLE II

Relationship between the P—H coupling constants and the kind of the substituents of the quaternary nitrogen atom.



$$CH_3O-\underset{H}{\overset{O}{P}}-O^{-}\ \ \overset{+}{N}(CH_3)(X)(Y)-CH_2CH_2OH$$

Kind of substituents on the nitrogen atom		Coupling constant
X	Y	${}^1J_{PH}$ (Hz)
CH_3	CH_3	608.6
CH_3	CH_2CH_2OH	615.5
H	CH_2CH_2OH	619.0
CH_2CH_2OH	CH_2CH_2OH	620.7

Substituents with donor character such as methyl group for example, will increase the electron density of the phosphorus atom and strengthen the *s*-character of the P—H bond. Vice versa, the decrease in the number of the substituents with donor character and increase of the substituents with acceptor character will decrease the electron density of the phosphorus atom, i.e. it will reduce the *s*-character of the P—H bond.

The alkylated aminoalcohols are of interest as monomers for synthesis of polymers, containing an ionic bond in their structure, or as modifiers for polymers to improve their fire resistance.

EXPERIMENTAL

Methods of analysis: ^{1}H-NMR spectra were recorded at a Bruker WM (250 MHz), inner standard—TMS, in a solution of CD_3OD. ^{31}P-NMR were recorded at the same apparatus with an external standard of 85% H_3PO_4. The IR spectra were taken on a film using a UR-20 instrument (Carl Zeiss-Jena).

Initial compounds: dimethyl hydrogen phosphonate, Fluka, purified by vacuum distillation, n_D^{20} = 1.4025; dimethylethanolamine, N-methyldiethanolamine, diethanolamine and triethanolamine, Fluka, purified by vacuum distillation.

Procedure for the reaction of dimethyl hydrogen phosphonate with aminoalcohols at a molar ratio 1:1. An amount of 22 g, 0.2 mol of freshly distilled DMHP was placed into a four-neck flask, provided with a stirrer, a thermometer, an addition funnel and an argon inlet. The liquid was heated up to a temperature of 70–72°C. At that temperature 0.2 mol aminoalcohol was added dropwise with such rapidity that the temperature of the reaction mixture must not exceed 80°C despite the exothermic effect. After the addition of all the aminoalcohol the reaction mixture was warmed for two hours at 80°C. After that the volatile compounds in the reaction mixture were removed under vacuum.

The obtained products—colorless viscous liquids were soluble in water, methyl alcohol, ethyl alcohol, and dimethylsulphoxide.

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