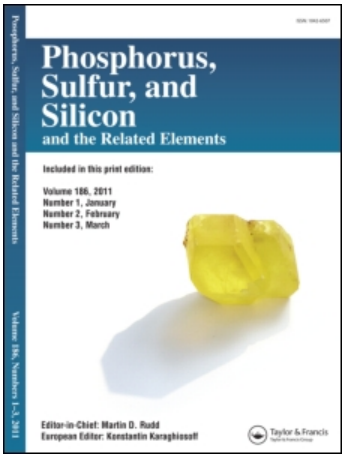

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ON THE REVERSIBILITY OF HYDROXYPHOSPHONATE FORMATION IN THE KABACHNIK-FIELDS REACTION

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ON THE REVERSIBILITY OF HYDROXYPHOSPHONATE FORMATION IN THE KABACHNIK-FIELDS REACTION

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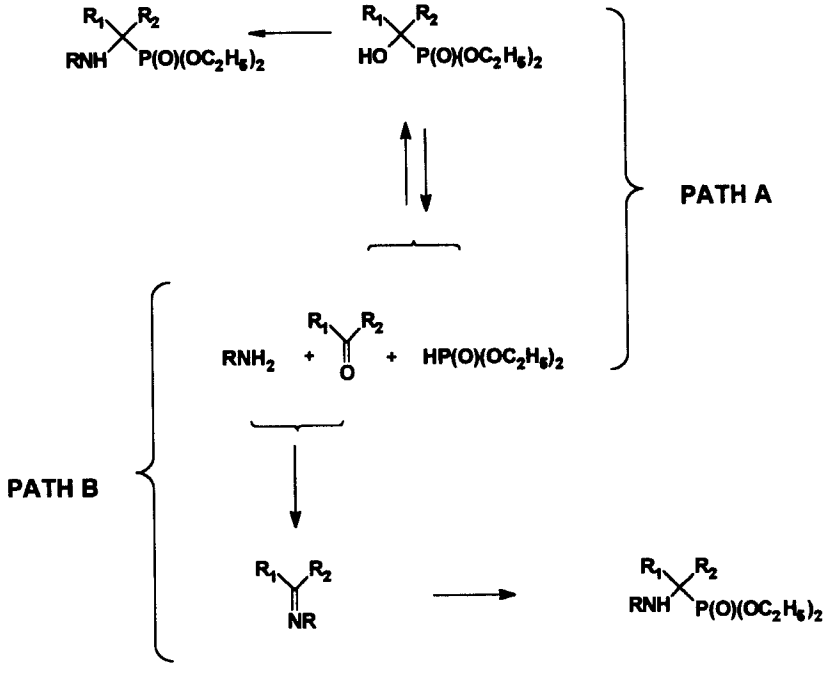
The reversibility of hydroxyphosphonate synthesis in the Kabachnik-Fields synthesis was studied. It was found that in all studies cases which included aliphatic and aromatic aldehydes or ketones the hydroxyphosphonates decompose to the starting ketone and dialkyl phosphite in the presence of aliphatic amines as determined by ^{1}H-, ^{13}C-, ^{31}P-NMR.

Key words: Kabachnik-Fields synthesis, hydroxyphosphonate, aminophosphonate.

INTRODUCTION

Aminophosphonates and aminophosphonic acids are known since the 1968. Today they are a subject of many papers mostly due to their biological activity.[1] One of the very first method of their synthesis was the procedure described by Kabachnik and Medved[2–3] in which carbonyl compound, ammonia and dialkyl phosphite reacted at temperatures 70–120°C.[2–4] Modification of this reaction was described by Fields.[4] He replaced the ammonia with primary or secondary amines, which allowed him to obtain N-mono-, and N,N-disubstituted-aminophosphonates. These methods are known as Kabachnik-Fields reaction. Although it is widely applied, its mechanism is still not clear. Kabachnik and Medved[2,3] suggested that first the hydroxyphosphonate is formed via ammonia catalysed addition of dialkyl phosphite to carbonyl compound and then aminophosphonate is formed via nucleophilic substitution of the hydroxyl group by an amino moiety. His conclusion was based on the fact that aminophosphonates are obtained only at elevated temperatures, while formation of hydroxyphosphonates are observed at room temperature after mixing of the reagents. On heating the hydroxyphosphonates dissappear and aminophosphonates are formed, (see Scheme I path A). An alternative mechanism was proposed by Petrov.[4] Based on the Fields idea,[5] he presented the arguments that hydroxyphosphonates are formed reversibly from carbonyl compound and dialkyl phosphite, and aminophosphonates are formed as addition products of dialkyl phosphites to imines, (see Scheme I path B). Both mechanisms are presented on scheme below.

The fact that the methoxy group of methoxymethylphosphonate $(RO)_2P(O)(CH_2)OCH_3$ did not exchange and that hydroxymethyl phosphonate when heated with amine yielded the aminophosphonate with higher yield if the



SCHEME I

alcoholate was added were additional evidences for the Petrov mechanism.[4] In the last case alcoholate acts as a base and accelerates the decomposition of hydroxyphosphonate into the carbonyl compound and diethyl phosphite. Very recently the question on the mechanism was raised again. Galkin and coworkers studied the mechanism for benzaldehyde and aniline.[6] They concluded that the mechanism operates via the imine path. This system however is not representative since aniline is a too weak base to promote the addition of phosphite to the carbonyl compound.[7] On the other hand, Krutikov and coworkers,[8] based on the NMR studies, suggested that aminophosphonates are formed via nucleophilic substitution of the hydroxy group of the hydroxyphosphonate by the amino group. One of the main arguments was the same—the disappearance of hydroxyphosphonate and formation of aminophosphonate during the course of the reaction.

RESULTS AND DISCUSSION

The formation of aminophosphonates from hydroxyphosphonates via nucleophilic displacement of the hydroxyl group by the amine seems to be unlikely. We agree with the Petrov arguments for the mechanism via the imine path. Since Petrov studied only formaldehyde as the carbonyl compound we decided to set up a series of experiments to check the reversibility of hydroxyphosphonate formation in other cases. Thus the hydroxyphosphonates obtained from aliphatic and aromatic alde-

hydes and ketones were heated in the presence of an aliphatic primary amine (butylamine), tertiary amine (triethylamine), and tertiary amine in the presence of a protonic solvent (triethylamine with ethyl alcohol). The amines and ethanol were used in a 3–5 fold excess. The results are presented in Table I. All the reaction products were identified by means of ^{1}H, ^{31}P and ^{13}C-NMR spectroscopy of the reaction mixture using the Brucker 300 MHz instrument and by comparison with the pure compounds prepared as described in the experimental part.

From the Table I one can see that for all the used hydroxyphosphonates there are some conditions in which the hydroxyphosphonate decomposes to the carbonyl compound and diethyl phosphite.

In the experiments where the hydroxyphosphonates were heated with butylamine, the decomposition of hydroxyphosphonates were substantial, although the degree of decomposition depends on the structure of substrates. After 4 hours of treatment with butylamine at 60°C the hydroxyphosphonates from aliphatic ketone and aromatic aldehyde or ketones were almost absent in the reaction mixture. When aromatic groups are attached to the carbon bearing the hydroxy and phosphonate moieties the process of reversing of the hydroxyphosphonate synthesis is accompanied by the rearrangement of hydroxyphosphonate to phosphate. In some cases formation of the carbonyl compound is followed by the imine or even the aminophosphonate synthesis. In these conditions in the case of aliphatic aldehyde 92% of starting material was unchanged.

With the exception of two cases refluxing the hydroxyphosphonate with butylamine moves the reaction further in the same direction. For the hydroxyphosphonates made from benzophenone and fluorenone the reaction mixture is more complex since in these conditions the phosphate formation becomes also reversible. The prolonged heating of these mixtures gives several products of radical reactions.[9]

Triethylamine is either inert or acts in the similar manner but with a much smaller effect. However the addition of ethanol accelerates the reaction in the presence of triethylamine.

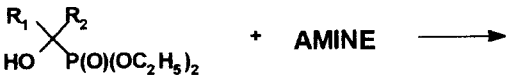
The above observations can be explained in the following manner. The formation of hydroxyphosphonates from carbonyl compound and dialkyl phosphite is easily reverted by the aliphatic amine; tertiary amines are very weak catalysts of this reaction. They become much more effective in the presence of a protic compound. This fact was additionally confirmed by the kinetic studies which showed that the reaction is about 100 times faster in ethanol than in methylene chloride.[10] It suggests that hydrogen bond formation can play an important role here. Summing up these observations we propose a two path mechanism of hydroxyphosphonate decomposition (Scheme II):

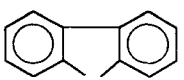
Both paths A and B, from Scheme II, are promoted by some hydrogen bond formation between an amine and phosphoryl oxygen. The presence of electron attracting groups, like aromatic ones, stabilizes the carbanion and thus the rearrangements to the phosphates were observed. Substitution of the aromatic hydrogens with halogens or nitro group promotes the formation of phosphates.[10]

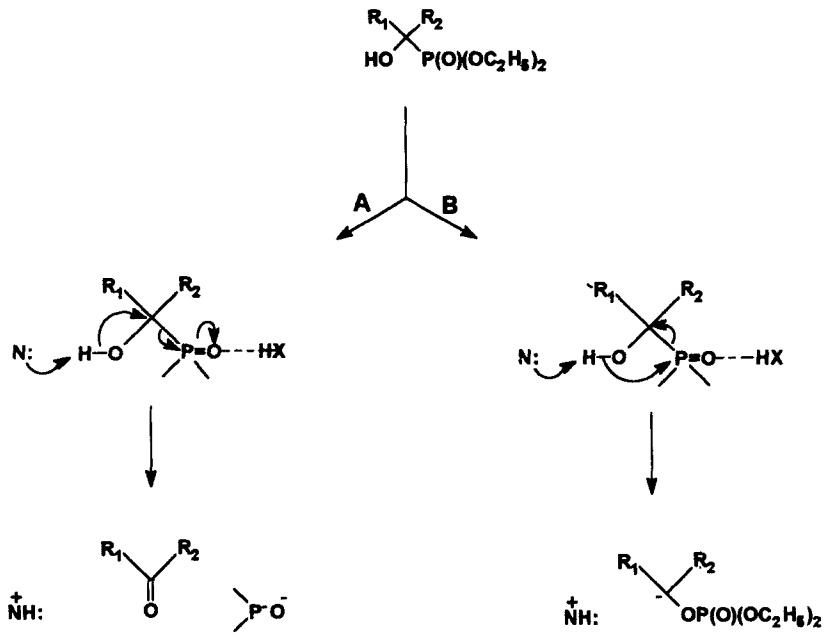
For the thermal decomposition of hydroxyphosphonates the intramolecular rearrangement reaction via a cyclic five membered transition state[11] was proposed. This mechanism could be an alternative to the one, presented above, however, it does not explain the formation of phosphates. We think that both paths A and B

TABLE I

Products of the reaction of hydroxyphosphonates with amines. Ex. No. 1. butylamine, 4 hrs, 60°C; 2. triethylamine, 4 hrs, 60°C; 3. Triethylamine and ethanol, 4 hrs, 60°C; 4. butylamine, reflux 2 hrs. For more details see experimental parts.



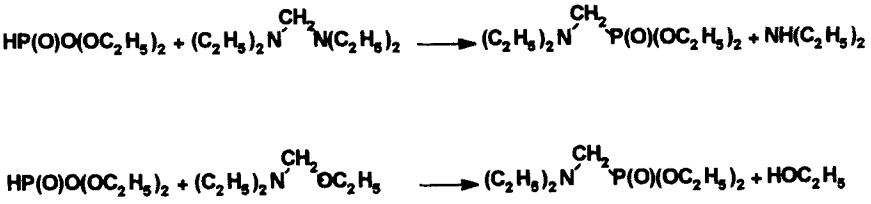
R_1	R_2	Ex. No	$R_1(R_2)C{=}O$	$R_1(R_2)C{=}NC_4H_9$	$HP(O)(OC_2H_5)_2$	$R_1(R_2)C(OH)P(O)(OC_2H_5)_2$	$R_1(R_2)CHOP(O)(OC_2H_5)_2$	$R_1(R_2)C(NHC_4H_9)P(O)(OC_2H_5)_2$
H—	$CH(CH_3)CH_2CH_3$	1	0	0.08	0.08	0.92	0	0
		2	0	0	0	1.00	0	0
		3	0	0	0	1.00	0	0
		4	0	0.29	0.56	0.17	0	0.27
H—		1	0	0.90	0.90	0.10	0	0
		2	0	0	0	1.00	0	0
		3	0	0	0.10	0.99	0	0
		4	0	0.96	0.96	0.01	0.03	0
$-CH_3$	$-CH_3$	1	0.32	0.40	0.72	0.08	0	0.20
		2	0.22	0	0.22	0.73	0	0
		3	0.30	0	0.30	0.70	0	0
		4	0.30	0.40	0.70	0	0	0.30
$-CH_3$		1	0.45	0.55	0.96	0.04	0	0
		2	0.01	0	0.01	0.99	0	0
		3	0.55	0	0.55	0.45	0	0
		4	0.46	0	0.46	0.41	0.03	0
		1	0.60	0.05	0.65	0	0.35	0
		2	0.16	0	0.16	0.76	0.08	0
		3	0.70	0	0.70	0	0.30	0
		4	0.15	0.48	0.63	0.11	0.26	0
		1	0	0	0	0	1.0	0
		2	0	0	0	1.0	0	0
		3	0.15	0	0.15	0.19	0.66	0
		4	0.09	0	0.09	0.34	0.57	0



SCHEME II

start from the same point and only when the more stable carbanion is involved the phosphates are formed.

The above study shows that the formation of aminophosphonates via the imine path is possible even if the formation of hydroxyphosphonates is much faster and all the carbonyl compound is used up for their formation before the imine is formed. Decomposition of hydroxyphosphonate to dialkyl phosphite and carbonyl compound was observed in all cases. This, however does not explain how the reaction proceeds in the case of secondary amines, where the N,N-dialkylaminophosphonates are formed, since in this case the imine formation is not possible. This was one of the Krutikov arguments against the imine path.[8] In this case the reaction can proceed via iminium salt or by nucleophilic substitution of a hydroxy or an amine group of the formed hemiaminal or aminal, respectively, by the phosphonic group. Those two possibilities were pointed out by Petrov,[4] who even obtained the aminophosphonates in the reaction of the N,N,N′,N′ tetraethylmethylenediamine or N,N,O triethylaminoacetal with dibutyl phosphite (Scheme III).



SCHEME III

EXPERIMENTAL

All NMR spectra were taken on a Bruker Avance DRX 300 MHz instrument (sponsored by Komitet Badań Naukowych-grant 653/1A/119/93).

Imine Synthesis

Method a. Carbonyl compound and butylamine were mixed in a molar ratio of 1:1.1 and dry potassium carbonate added. After 1 hr the product was filtered and the residue was evaporated on a warm water bath under reduced pressure. In all cases the product was pure enough for analysis and synthesis of aminophosphonates.

N-benzylidenebutylamine; oil, ^{1}H-NMR ($CDCl_3$) 8.24 (s, 1H, PhC<u>H</u>=N), 7.87–7.29 (m, 5H, Ar<u>H</u>), 3.58 (t, 2H, C<u>H</u>$_2$N, J_{HH} = 6.70 Hz), 1.72–1.63 (m, 2H, C<u>H</u>$_2$CH$_2$N), 1.42–1.30 (m, 2H, C<u>H</u>$_2$CH$_3$), 0.92 (t, 3H, C<u>H</u>$_3$, J_{HH} = 8.13 Hz).

N-(α-methylbenzylidene)-butylamine; oil, ^{1}H-NMR ($CDCl_3$) 8.00–7.30 (m, 5H, Ar<u>H</u>), 3.48 (t, 2H, C<u>H</u>$_2$N, J_{HH} = 7.14 Hz), 2.23 (s, 3H, C<u>H</u>$_3$) 1.80–1.65 (m, 2H, C<u>H</u>$_2$CH$_2$N), 1.50–1.35 (m, 2H, C<u>H</u>$_2$CH$_3$), 0.98 (t, 3H, C<u>H</u>$_3$, J_{HH} = 8.13 Hz).

N-isopropylidenebutylamine; oil, ^{1}H-NMR ($CDCl_3$) 3.11 (t, 2H, C<u>H</u>$_2$N, J_{HH} = 6.91 Hz), 1.93 (s, 6H, C<u>H</u>$_3$) 1.56–1.48 (m, 2H, C<u>H</u>$_2$CH$_2$N), 1.40–1.25 (m, 2H, C<u>H</u>$_2$CH$_3$), 0.92 (t, 3H, C<u>H</u>$_3$, J_{HH} = 8.13 Hz).

N-isoamylidenebutylamine; oil, ^{1}H-NMR ($CDCl_3$) 7.49 (t, 1H, C<u>H</u>=N, J_{HH} = 5.32), 3.20 (t, 2H, C<u>H</u>$_2$N, J_{HH} = 6.95 Hz), 1.99 (t, 2H, C<u>H</u>$_2$—CH, J_{HH} = 6.26), 1.85–1.65 (m, 1H, (CH$_3$)$_2$C<u>H</u>), 1.50–1.35 (m, 2H, C<u>H</u>$_2$CH$_2$N), 1.30–1.20 (m, 2H, C<u>H</u>$_2$CH$_3$), 0.80 (t, 3H, C<u>H</u>$_3$, J_{HH} = 6.66 Hz) 0.76 (d, 6H, CH(C<u>H</u>$_3$)$_2$).

Method b. For low reacting carbonyl compounds a mixture of carbonyl compound with a 2–3 fold excess of butylamine and a catalytic amount of aluminium chloride was refluxed for a period of 2–3 hrs. Reaction was monitored by taking the IR spectra. When the reaction was completed the mixture was dissolved in dry ethyl ether, dried over potassium carbonate, filtered and evaporated from a hot water bath under reduced pressure. The obtained imine was used without further purification.

N-benzhydrylidenebutylamine; oily solid, ^{1}H-NMR ($CDCl_3$) 7.75–7.20 (m, 8H, Ar<u>H</u>), 3.71 (t, 2H, C<u>H</u>$_2$N, J_{HH} = 7.05 Hz), 1.70–1.60 (m, 2H, C<u>H</u>$_2$CH$_2$N), 1.50–1.40 (m, 2H, C<u>H</u>$_2$CH$_3$), 0.91 (t, 3H, C<u>H</u>$_3$, J_{HH} = 8.00 Hz).

N-fluorenylidenebutylamine; oily solid, ^{1}H-NMR ($CDCl_3$) 7.70–7.20 (m, 10H, Ar<u>H</u>), 3.81 (t, 2H, C<u>H</u>$_2$N, J_{HH} = 6.98 Hz), 1.70–1.60 (m, 2H, C<u>H</u>$_2$CH$_2$N), 1.50–1.40 (m, 2H, C<u>H</u>$_2$CH$_3$), 0.92 (t, 3H, C<u>H</u>$_3$, J_{HH} = 8.10 Hz).

Hydroxyphosphonate Synthesis

Method a. Some of the hydroxyphosphonates were prepared according to the literature data.[12,13]

Diethyl (±)-1-hydroxy-3-methylbutylphosphonate, ^{1}H-NMR ($CDCl_3$), 4.25–4.05 (m, 4H, C<u>H$_a$H$_b$</u>—O, CH$_c$C<u>H^d</u>—O,), 3.90 (dxdxd, 1H, C<u>H</u>P, J_{HH}, J_{HP} = 11, 5.5, 3 Hz), 3.0 (bs, 1H, O<u>H</u>), 1.95–1.80 (m, 1H, C<u>H</u>(CH$_3$)$_2$), 1.75–1.55 (m, 1H, CH$_a$<u>H$_b$</u>), 1.45–1.30 (m, 1H, C<u>H$_a$</u>H$_b$), 1.31 (t, 3H, C<u>H</u>$_3$, J_{HH} = 7.16), 1.30 (t, 3H, C<u>H</u>$_3$, J_{HH} = 7.15), 0.96 (d, 3H, C<u>H</u>$_3$CH, J_{HH} = 6.65 Hz), 0.91 (d, 3H, C<u>H</u>$_3$CH, J_{HH} = 6.56); ^{31}P-NMR ($CDCl_3$), 26.32.

Diethyl 1-hydroxy-1-methylethylphosphonate, ^{1}H-NMR ($CDCl_3$), 4.10–4.00 (m, 4H, C<u>H$_a$H$_b$</u>—O), 2.72 (bs, 1H, O<u>H</u>), 1.46 (d, 6H, C<u>H</u>$_3$C, J_{HP} = 15.16), 1.30 (t, 6H, C<u>H</u>$_3$CH$_2$, J_{HH} = 7.14); ^{31}P-NMR ($CDCl_3$), 27.25.

Diethyl (±)-1-hydroxy-1-phenylmethylphosphonate, ^{1}H-NMR ($CDCl_3$), 7.57–7.28 (m, 5H, Ar<u>H</u>), 5.04 (d, 1H, C<u>H</u>, J_{HP} = 10.99 Hz), 4.64 (bs, 1H, O<u>H</u>), 4.15–3.95 (m, 4H, C<u>H$_a$H$_b$</u>—O, C<u>H$_c$H$_d$</u>—O), 1.27 (t, 3H, C<u>H</u>$_3$CH$_2$, J_{HH} = 6.98), 1.22 (t, 3H, C<u>H</u>$_3$CH$_2$, J_{HH} = 7.41); ^{31}P-NMR ($CDCl_3$), 21.96.

Diethyl (±)-1-hydroxy-1phenylethylphosphonate, ^{1}H-NMR ($CDCl_3$), 7.70–7.20 (m, 5H, Ar<u>H</u>), 4.20–3.75 (m, 4H, C<u>H$_a$H$_b$</u>—O, C<u>H$_c$H$_d$</u>—O), 1.84 (d, 3H, C<u>H</u>$_3$CPh, J_{HP} = 15.37), 1.28 (t, 3H, C<u>H</u>$_3$CH$_2$, J_{HH} = 7.06), 1.20 (t, 3H, C<u>H</u>$_3$CH$_2$, J_{HH} = 7.06); ^{31}P-NMR ($CDCl_3$), 24.51.

Method b. For more reactive ketones (benzophenone, fluorenone) the following procedure of hydroxyphosphonate synthesis was applied in order to avoid the formation of phosphates.

The ketone was dissolved in the diethyl phosphite in 1:1 molar ratio (slightly heating if necessary) and the mixture was saturated with dry ammonia. Then it was left to stand for a couple of hours. If necessary the mixture was put into a refrigerator to promote crystallization. The resulting hydroxyphosphonate was filtered and purified by crystallization.

Diethyl 1-hydroxy-1,1-diphenylmethylphosphonate, ^{1}H-NMR ($CDCl_3$), 7.70–7.20 (m, 10H, ArH) 4.20–3.90 (m, 4H, CH_aH_b—O), 3.70 (bs, 1H, OH), 1.21 (t, 6H, CH_3CH_2, J_{HH} = 7.01); ^{31}P-NMR ($CDCl_3$), 21.10.

Diethyl 9-hydroxy-9-fluorenylphosphonate, ^{1}H-NMR ($CDCl_3$), 7.90–7.30 (m, 8H, ArH), 4.10–3.80 (m, 4H, CH_aH_b—O), 2.72 (bs, 1H, OH), 1.10 (t, 3H, CH_3CH_2, J_{HH} = 7.37); ^{31}P-NMR ($CDCl_3$), 21.81.

Aminophosphonate Synthesis

A mixture of imine and diethyl phosphite was heated at 70°C until the imine disappeared (by TLC method). It takes about 2–5 hrs. Then the mixture was dissolved in dry acetone to which the acetone solution of anhydrous oxalic acid was added and the mixture was kept at low temperatures. The oxalate was filtered off, and aqueous ammonia was added followed by extraction of the free aminophosphonate with ether or chloroform. After drying over potassium carbonate the solvent was removed and the residue was crystallized. In the cases of noncrystalline aminophosphonates they were used without further purifications or their oxalates were crystallized before converting them to the free aminophosphonates.

Diethyl (±)-1-butylamino-3-methylbutylphosphonate, microanalytical data (calculated/found) N-2.97/2.80%, P-6.57/6.31%, m.p. for oxalate 70–73°C, ^{1}H-NMR ($CDCl_3$), 4.15–3.90 (m, 4H, CH_aH_b—O, CH_cH_d—O), 2.80–2.60 (m, 2H, CH_2N), 2.60–2.40 (m, 1H, CHP), 1.95–1.80 (m, 1H, $CH(CH_3)_2$), 1.45–1.30 (m, 2H, $CHCH_aH_b$), 1.25–1.10 (2xt, 6H, CH_3CH_2O, J_{HH} = 7.16, 7.10), 0.95–0.85 (m, 9H, $(CH_3)_2CH$, $CH_3CH_2CH_2CH_2$); ^{31}P-NMR ($CDCl_3$), 29.69.

Diethyl 1-butylamino-1-methylethylphosphonate, microanalytical data (calculated/found) N-3.16/3.30%, P-6.99/7.12%, m.p. for oxalate 132–135°C, ^{1}H-NMR ($CDCl_3$), 4.15–4.05 (m, 4H, CH_aH_b—O), 2.66 (t, 2H, CH_2N, J_{HH} = 7.14), 1.5–1.3 (m, 4H, CH_2CH_2), 1.28 (t, 6H, CH_3CH_2O, J_{HH} = 6.90); 1.25 (d, 6H, CH_3C, J_{HP} = 17.42 Hz), 0.86 (t, 3H, CH_3, J_{HH} = 7.07); ^{31}P-NMR ($CDCl_3$), 31.54.

Diethyl (±)-1-butylamino-1-phenylmethylphosphonate, microanalytical data (calculated/found) N-2.85/2.95%, P-6.30/6.12%, m.p. for hydrochloride 64–69°C, ^{1}H-NMR ($CDCl_3$), 7.5–7.2 (m, 5H, ArH), 4.20–3.70 (m, 4H, CH_aH_b—O, CH_cH_d—O), 2.60–2.35 (m, 2H, CH_aH_bN), 2.25–2.05 (b.s, 1H, NH), 1.50–1.40 (m, 2H, CH_2CH_2N), 1.40–1.30 (m, 2H, $CH_2CH_2CH_2N$), 1.27 (t, 3H, CH_3CH_2O, J_{HH} = 6.99); 1.14 (t, 3H, CH_3CH_2O, J_{HH} = 7.19), 0.85 (t, 3H, CH_3, J_{HH} = 7.06); ^{31}P-NMR ($CDCl_3$), 23.95.

Diethyl (±)-1-butylamino-1-phenylethylphosphonate, microanalytical data (calculated/found) N-2.77/2.90%, P-6.13/6.05%, m.p. for oxalate 85–89°C, ^{1}H-NMR ($CDCl_3$), 7.5–7.15 (m, 5H, ArH), 4.15–3.70 (m, 4H, CH_aH_b—O, CH_cH_d—O), 2.60–2.40 (m, 1H, CH_aH_bN), 2.35–2.20 (m, 1H, CH_aH_bN), 2.25–2.05 (b.s, 1H, NH), 1.77 (d, 3H, CH_3, J_{HP} = 16.41), 1.55–1.40 (m, 2H, CH_2CH_2N), 1.40–1.30 (m, 2H, $CH_2CH_2CH_2N$), 1.24 (t, 3H, CH_3CH_2O, J_{HH} = 7.04); 1.16 (t, 3H, CH_3CH_2O, J_{HH} = 7.08) 0.88 (t, 3H, $CH_3CH_2CH_2CH_2N$, J_{HH} = 7.08); ^{31}P-NMR ($CDCl_3$), 27.29.

Diethyl 9-butylamino-9-fluorenylphosphonate, m.p. 104°C, for hydrochloride 137–139°C[14] microanalytical data (calculated/found) N-2.48/2.61%, P-5.48/5.60%, ^{1}H-NMR ($CDCl_3$), 7.90–7.30 (m, 8H, ArH), 4.00–3.70 (m, 4H, CH_aH_b—O), 1.99 (t, 2H, CH_2N, J_{HH} = 6.85), 1.40–1.11 (m, 4H, $CH_2CH_2CH_2N$), 1.08 (t, 6H, CH_3CH_2O, J_{HH} = 7.02), 0.77 (t, 3H, $CH_3CH_2CH_2CH_2N$, J_{HH} = 7.24); ^{31}P-NMR ($CDCl_3$), 23.16.

Phosphates Synthesis

Phosphates were prepared as described in Reference 7.

ACKNOWLEDGEMENTS

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