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SYNTHESIS OF DIETHYL 2-{[3-(TRIETHOXYSILYL)PROPYL]AMINO}ETHYLPHOSPHONATE

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Diethyl 2-{[3-(triethoxysilyl)propyl]amino}ethylphosphonate is promising reagent for the modification of silica surface and thus for the creation of chelate adsorbents for extraction of *d*-metals ions from water media.

Diethyl 2-{[3-(triethoxysilyl)propyl]amino}ethylphosphonate was synthesized by alkylation of 3-aminopropyltriethoxysilane (APTES) with diethyl vinylphosphonate under quick neat heating. The possible alternative approaches to the synthesis of this compound were investigated (alkylation of APTES and N-acetylAPTES) as well as behavior of APTES towards heating in absolute ethanol and THF. APTES was shown to be not stable in absolute ethanol, that is caused by polycondensation processes. Because of this fact, previously reported protocol of diethyl 2-{[3-(triethoxysilyl)propyl]amino}ethylphosphonate synthesis in ethanol turned to be impossible.

Keywords: 3-aminopropyltriethoxysilane (APTES), alkylation, polycondensation, surface modification.

Introduction

3-Aminopropyltriethoxysilane (APTES) is a widely used agent for development of robust hydrophobic coatings on glass surface [1, 2] and, in general, for obtaining of 3-(aminopropylsilyl)modified surfaces [3–6].

Two general pathways are used for the synthesis of 3-(aminopropylsilyl)modified silica: grafting and sol-gel synthesis. Grafting process consists of reaction of silanol groups on the surface of silica and APTES [7–9], while the sol-gel procedure is the simultaneous hydrolytic condensation of APTES with tetraethoxysilane (TEOS) [10–12]. Moreover, 3-aminopropyl groups on the surface may be further functionalized [13, 14]. However, such “double grafting” on the surface inevitably leads to uneven filling of the surface layer with both modified and unchanged amino and silanol groups, and the control of this process is quite difficult.

We have lately proposed a general strategy for *N*-modified 3-(aminopropyl)silica synthesis, which consisted of *N*-prefunctionalization of APTES with hydrolytically, air and time stable functional groups and further synthesis of surface-modified silica on the base of the latter precursor. In our previous work we worked up the synthesis of diethyl {[3-(triethoxysilyl)propyl]amino}-methylphosphonates, which after grafting of SiO_2 surface and further hydrolysis should produce sorption material with five-membered chelate binding structure [15].

The purpose of the present work is to obtain, starting from APTES, diethyl 2-{[3-(triethoxysilyl)propyl]amino}ethylphosphonate **1** which after a grafting of SiO_2 or sol-gel synthesis in reaction with TEOS should create a layer of the uniform substituted 2-(phosphonatoethyl)amino groups on the silica surface, producing after the stage of acidic hydrolysis a promising six-membered chelate binding structures (Figure 1).

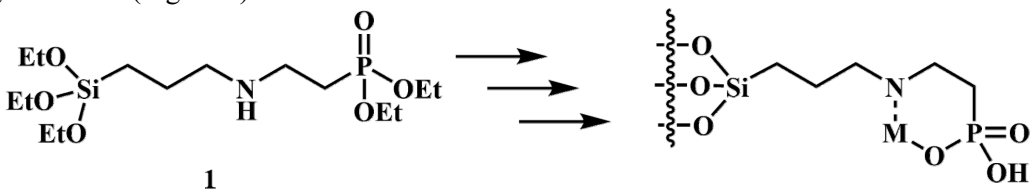

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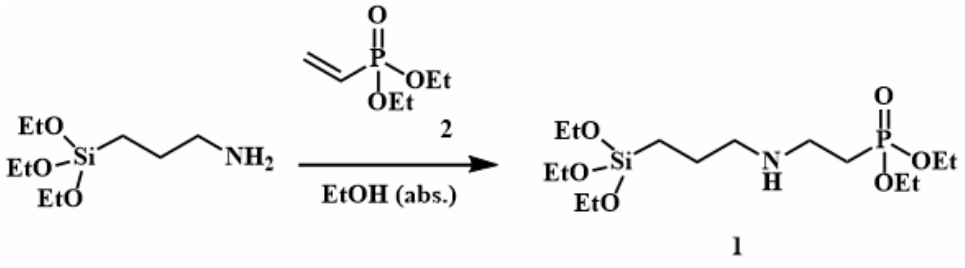
Figure 1. Structure of the target diethyl 2-{[3-(triethoxysilyl)propyl]amino}ethylphosphonate **1** and estimated structure of chelate complexes.

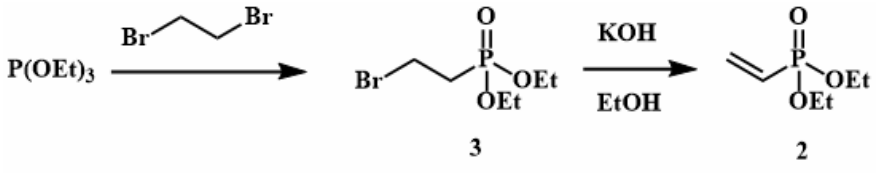
Results and discussion

The synthesis of the compound **1** is described in literature, but full characterization is given in the only article [16] while the other publications contain incomplete spectral data [17–19] or information about mixtures obtaining [20]. The synthesis reported by the authors [16] consisted of simple heating of APTES with diethyl vinylphosphonate **2** in absolute EtOH for 24 h. (Scheme 1).



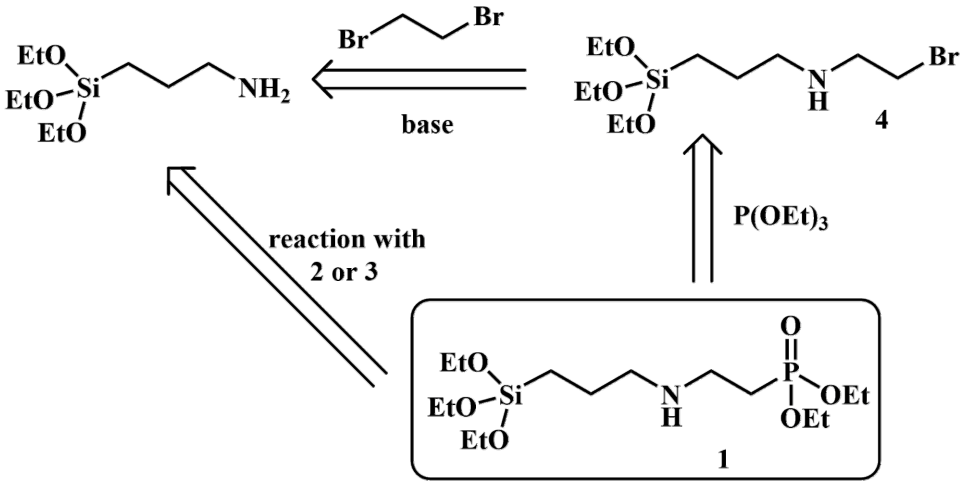
Scheme 1. Reported pathway of compound **1** synthesis [16].

First we reproduced the protocol, cited in ref. [16]. Starting APTES was commercially available, and diethyl vinylphosphonate **2** was obtained in two stages, starting from commercially available triethyl phosphite and 1,2-dibromoethane through the synthesis of intermediate diethyl 2-bromoethylphosphonate **3** (analogously to data [21–25]), Scheme 2.



Scheme 2. Synthesis of diethyl vinylphosphonate **2**.

However, it turned out that the samples of the reaction mixture, taken sequentially during heating (according to Scheme 1), indicate not only the formation of the target product **1**, but the gradual disappearance of EtO-groups near the silicon atom, indicating the polycondensation of APTES and/or reaction product **1** (Figure 2).



Scheme 3. Retrosynthetic analysis of the compound **1** as secondary amine (starting from APTES).

We assumed that such a process should occur spontaneously in absolute EtOH as in a proton donor solvent. We tested our hypothesis by heating APTES at a bath temperature of 70°C a) in absolute THF (dried over molten potassium); b) in absolute EtOH (dried under activated zeolites). It turned out that in absolute EtOH after 13 h. of heating the processes that indicate polycondensation of APTES took place (decreasing of EtO-groups signals intensity in ^{1}H NMR spectrum). In contrast, according to

^{1}H NMR spectrum, no changes happened with the original APTES after heating it in absolute THF for 24 h. and removal of the solvent.

This, unfortunately, testified about the unreliability of the publication data [16] and the need to develop a protocol for the synthesis of compound **1** from the beginning.

The obvious common pathways for the synthesis of the compound **1** as secondary amine starting from APTES (primary amine) are shown on the Scheme 3 (retrosynthetic scheme is given), Scheme 3.

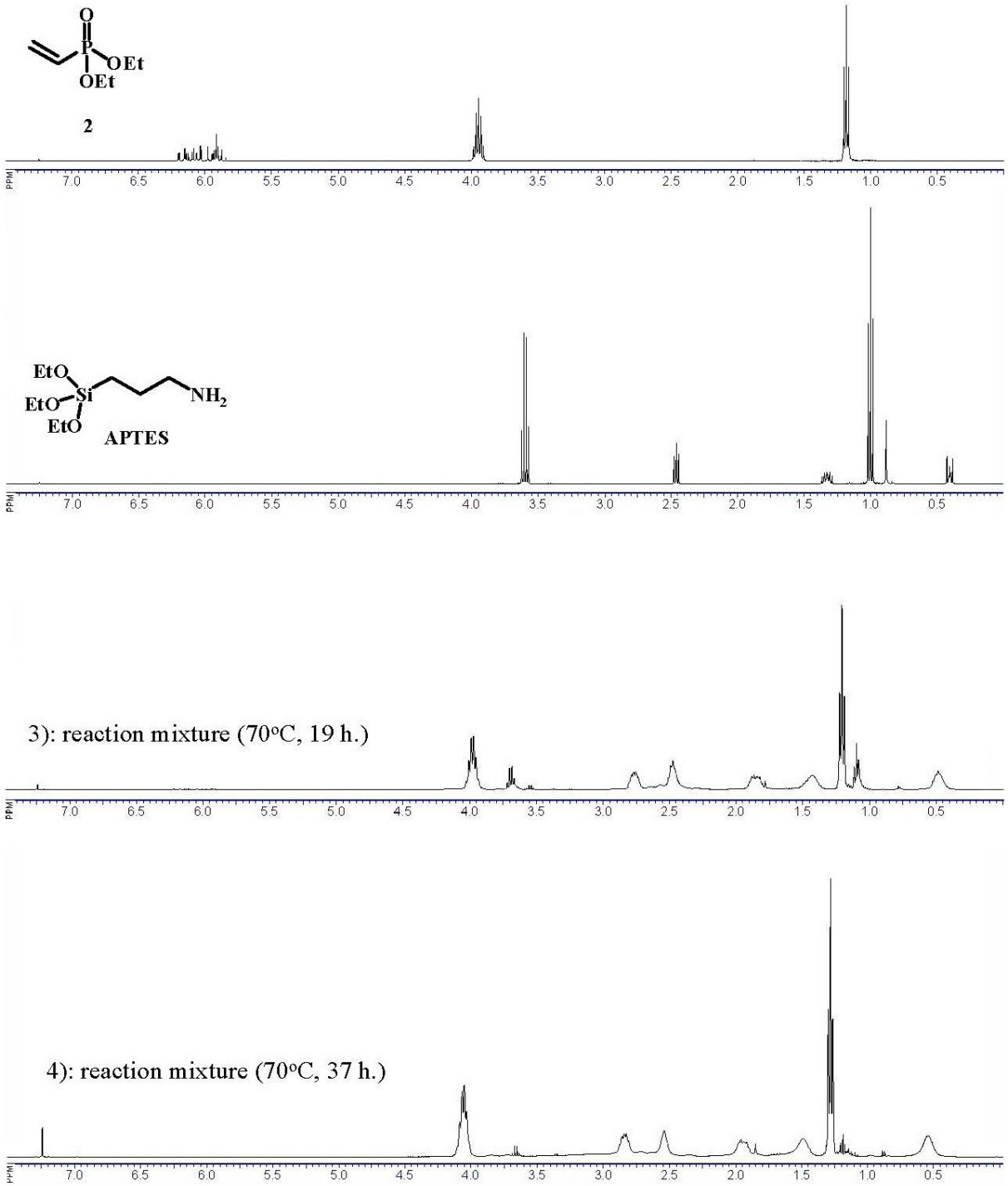
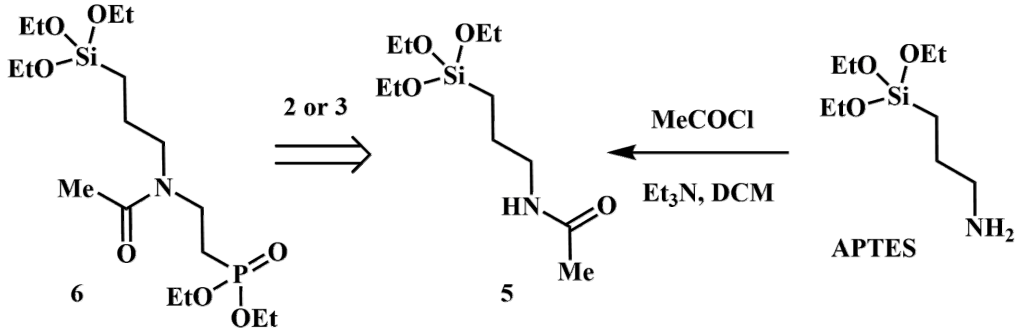


Figure 2. ^{1}H NMR spectra ($CDCl_3$): 1) diethyl vinylphosphonate **2**; 2) APTES; 3) the reaction mixture (ethanol was removed by vacuum distillation) after 19 h. of heating at 70°C under argon; 4) the reaction mixture (ethanol was removed by vacuum distillation) after 37 h. of heating at 70°C under argon.

Noteworthy, that the most obvious drawback of these pathways is possible poly-*N*-alkylation of APTES with 1,2-dibromoethane, ethyl vinylphosphonate **2** or diethyl 2-bromoethylphosphonate **3**.

That is why we also considered the alkylation of compound **5** (obtained by APTES acetylation) by compound **2** or **3** as a synthetic route of the nearest precursor of compound **1** – substance **6** (Scheme 4).



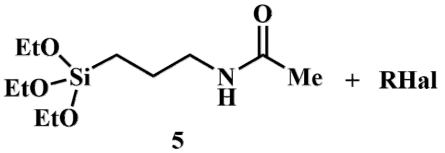
Scheme 4. Retrosynthetic analysis of the compound **6**.

N-Acetyl group of compound **6** should be completely removed after grafting on the surface of SiO_2 and subsequent acid hydrolysis, so compounds **1** and **6** are synthetically equivalent in the case of surface-modified silica obtaining. Generally, the pathway of the synthesis of secondary amine derivatives starting from secondary amides seemed more selective and convenient, comparing with the synthesis of compounds **1** and **4** by direct alkylation of APTES.

We studied the interaction of compound **5** with diethyl 2-bromoethylphosphonate **3** in systems traditionally used for *N*-alkylation of amides: a) $CHCl_3$, NEt_3 (r. t.); b) K_2CO_3, methyl ethyl ketone (reflux); c) NaH, THF (r. t.). After treatment of the reaction mixtures it was found that alkylation of compound **6** did not occur in any case (established by ^{1}H NMR ($CDCl_3$)), and the only new component of the mixtures was ethyl vinylphosphonate **2**, which was apparently formed by the elimination of HBr from compound **3**.

Since the side formation of ethyl vinylphosphonate **2** was obvious because of using diethyl 2-bromoethylphosphonate **3** in basic media, we performed model alkylations of compound **5** with available bromides, which are unable to eliminate HBr under mild basic conditions, in different media (Table 1). Absolute solvents were used, syntheses were performed in an inert atmosphere.

Table 1. Model alkylation of compound **5**.



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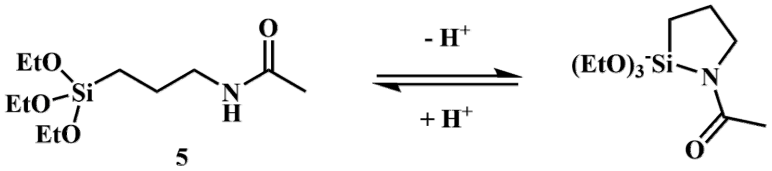
RHal	Reaction conditions
n-BuBr	K_2CO_3, methyl ethyl ketone, 90ºC
n-BuBr	NaH, THF, 25ºC
n-BuBr	NaH, DMF, 25ºC
1-Bromo-3-chloropropane	NaH, THF, 25ºC
1-Bromo-3-chloropropane	NaH, DMF, 25ºC
Diethyl 3-chloropropylphosphonate (**7**)	K_2CO_3, DMF (50ºC, 2 h.; then 80ºC, 2 h.; then 100ºC, 2 h.; then 120ºC, 2 h.)

Unfortunately, in any case the result was negative, and the starting compound **5** was returned back in the amount of 50–70 %.

We attribute such a passivity of amide **5** in the basic media to the formation of an anion, which is stabilized by intramolecular complexation by the silicon atom (due to the reversibility of the process after work-up of the reaction mixtures the starting material is regenerated, Scheme 5).



Scheme 5. Possible explanation of the stability of *N*-anion of amide **5**.

As we previously expected, attempts to obtain the *N*-butyl derivatives of APTES by its direct alkylation in K_2CO_3/THF and K_2CO_3/DMF systems at reflux also failed due to the formation of complex mixtures of reaction products.

Thus, the only reaction we still counted on was alkylation (Michael addition) of APTES with diethyl vinylphosphonate **2**, but the reaction conditions had to be investigated, keeping in mind the negative result of the process in absolute ethanol.

We expected, that the positive result should consist primarily of the quantitative (90 % or more) yield of the target compound **1**, because the formation of a significant number of possible impurities (e.g., products of *N*,*N*-dialkylation of APTES) should lead to extreme difficult purification of compound **1** by vacuum distillation (its estimated boiling point is about 170ºC at 0.1 mm Hg). Purification of the target compound **1** by recrystallization was definitely not possible (viscous oil at room temperature), and the use of chromatographic methods was impossible due to the interaction of compound **1** with the surface of the sorbent. More, compound **1** was assumed to be hydrolytically unstable, and this fact caused additional inconvenience to work with it. Additionally, the obvious disadvantage of using DMAP as organic base (instead of DIPEA) was the difficulty of its removal by vacuum/distillation from the reaction mixture because of involatility, which should cause the presence of inevitable and undesirable impurities. Noteworthy, that ^{1}H NMR spectra of all the synthesized compounds and reaction mixtures were measured in $CDCl_3$, because APTES and its derivatives are hydrolyzed even by water, containing in $(CD_3)_2SO$.

The results of the experiments are summarized in Table 2. The conditions and the result of the most successful experiment are highlighted in bold.

Interestingly, that the most convenient approach to the successful synthesis of the target compound **1** turned out to be instant immersion of the flask with the stirred mixture of the reagents without any catalyst in hot oil bath.

^{1}H NMR spectrum of the target compound **1** is given in the Figure 3.

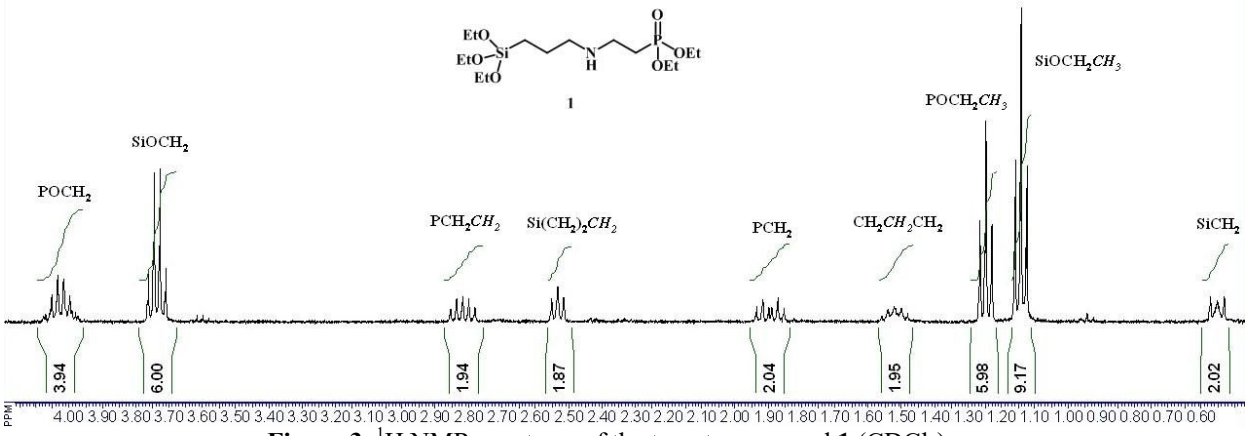
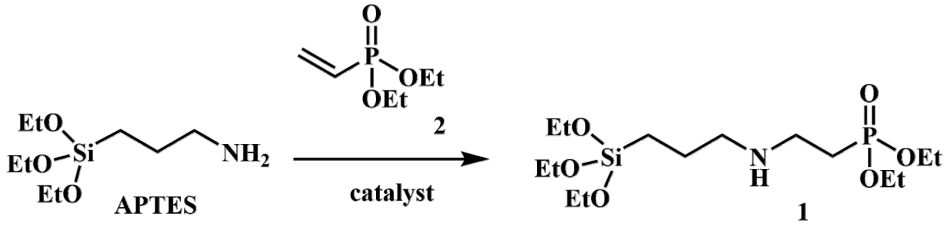


Figure 3. ^{1}H NMR spectrum of the target compound **1** ($CDCl_3$).

The ^{1}H NMR spectrum of the compound **1** contains signals of EtO-groups of both ester fragments and separate signals of each of the five CH_2-groups (see Figure 3 and Experimental part). Noteworthy, that the signals of protons of PCH_2- and $POCH_2$-groups are multiplets due to the spin-spin coupling of the corresponding protons and ^{31}P nuclei.

Compound **1** is a viscous liquid, sensitive to water. However, compound **1** is stable over time (at least for several months) in the absence of moisture and in an inert atmosphere, as evidenced by identical ^{1}H NMR spectra of samples taken immediately after its synthesis and after prolonged storage.

Table 2. Interaction of APTES with diethyl vinylphosphonate **2**.



№	Molar ratio APTES : **2**	Catalyst, 10 mol. % (if any)	Time, min.	Temperature of the bath, ºC	Time of reaching the temperature, min.	Purity of compound **1** after vacuum distillation, %	Amount of compound **1** in the reaction mixture (according to ^{1}H NMR data, $CDCl_3$, mol. %
1	1:1	–	60	100	10	–	traces
2	1:1	–	120	100	10	–	64
3	1:1	–	240	100	10	–	64
4	1:1	–	180	100	10	85[3]	65
5	3:1	–	660	100	10	–	58
6	1:1	DMAP[1]	120	100	10	–	55
7	1:1	DMAP[1]	480	100	10	–	30
8	1:1	DIPEA[2]	120	100	10	85[3,4]	45
9	1:1	DIPEA[2]	480	70	7	85[3,4]	60
10	1.5:1	DIPEA[2]	120	100	10	85[3,4]	47
11	1:1.5	DIPEA[2]	120	100	10	85[3,4]	55
12	1:1	DIPEA[2]	120	20	0	–	0[5]
13	1:1	DIPEA[2]	240	20	0	–	5[5]
14	1:1	DIPEA[2]	360	20	0	–	10[5]
15	1:1	DIPEA[2]	120	40	4	–	0[5]
16	1:1	DIPEA[2]	120	60	6	–	8[5]
17	1:1	DIPEA[2]	120	80	8	–	12[5]
18	1:1	DIPEA[2]	120	100	10	–	16[5]
19	**1:1**	**–**	**120**	**100**	**instantly[6]**	**97**	**85**

[1] DMAP – 4-dimethylaminopyridine. [2] DIPEA – di(*i*-propyl)ethylamine. [3] 170ºC, 0.1 mm Hg (see Experimental). [4] Yield after distillation of combined samples (entries 8–11). [5] As mixture with starting compounds. [6] Immersion of a flask with the stirred reaction mixture in an oil bath of a given temperature.

Conclusion

As a result, we proposed a suitable protocol of the synthesis of diethyl 2-{[3-(triethoxysilyl)propyl]amino}ethylphosphonate by alkylation of APTES with diethyl vinylphosphonate under quick heating and further mixing at 100ºC in neat. Additionally, the impossibility of carrying out the processes with APTES derivatives in absolute EtOH due to their polycondensation was shown.

Experimental

^{1}H NMR spectra were registered in $CDCl_3$ (δ_H = 7.26 ppm) and in $(CD_3)_2SO$ (δ_H = 2.50 ppm) at 400 MHz using Varian MR-400 spectrometer with $Si(CH_3)_4$ as an internal standard, chemical shifts are given in ppm, coupling constants are given in Hz. Resonance multiplicity was described as s (singlet), t (triplet), q (quartet), m (multiplet) and br (broad signal). Syntheses with APTES derivatives were performed in argon (99.993 %) atmosphere. Starting APTES, acetyl chloride, 1,2-dibromoethane, triethyl phosphite, DMAP, DIPEA, triethylamine, 1-bromo-3-chloropropane, inorganic reagents and solvents were commercially available. Silica of 400–230 mesh (40–60 μm) by Swambe Chemicals was used. APTES was distilled under reduced pressure before use and stored under argon. Acetyl chloride was distilled under atmospheric pressure before use and stored under argon. All the solvents for the synthesis with APTES (except hexane) were dried over active zeolites. Activation of zeolites (CaA and NaA from «Reakhim») was performed by 400ºC during 3 h., then cooling in

desiccator over KOH. THF was dried over KOH and distilled over molten potassium before use. Dichloromethane (DCM) was dried over K_2CO_3. Triethylamine was dried over KOH. K_2CO_3 was activated by heating at 400ºC for 3 h., then cooled in desiccator over KOH. Ethanol was dried over K_2CO_3, then over active zeolites and stored over active zeolites. Diethyl 2-bromoethylphosphonate **3** was obtained as shown elsewhere [22–24], diethyl vinylphosphonate **2** was obtained analogously to been reported [21, 25].

3-(*N*-Acetylamino)propyltriethoxysilane 5. A solution of CH_3COCl (7.8 g, 99 mmol) in 40 ml of dry CH_2Cl_2 was added under cooling (ice/water) during 5 min. to the solution of APTES (20 g, 90 mmol) and NEt_3 (12.0 g, 119 mmol) in 200 ml of dry CH_2Cl_2. The resulting mixture was stirred for 12 h., then washed 5 times with 120 ml of water, 250 ml of 1% water solution of HCl, 250 ml of saturated water solution of $NaHCO_3$ and twice with 100 ml of saturated water solution of NaCl. Organic phase was dried over Na_2SO_4. After filtration and evaporation of the solvent 19.5 g (82 %) of colorless oil **5** was obtained. ^{1}H NMR ($CDCl_3$), δ, ppm (*J*, Hz): 6.02 (1H, br. s, NH), 3.76 (6H, q, *J* = 7.2, OCH_2), 3.13–3.21 (2H, m, CH_2N), 1.91 (3H, s, $COCH_3$), 1.51–1.62 (2H, m, CH_2CH_2N), 1.16 (3H, t, *J* = 7.2, CH_3CH_2), 0.55–0.61 (2H, m, CH_2Si).

Diethyl 3-chloropropylphosphonate 7. A mixture of triethyl phosphite (20.0 g, 0.12 mol) and 1-bromo-3-chloropropane (38.0 g, 0.24 mol) was heated to reflux with Dean-Stark trap during 5 h. The mixture was cooled and distilled under 15 mm Hg. The fraction with boiling point of 140–150ºC was collected and 11.1 g (43 %) of colorless liquid **7** were obtained. ^{1}H NMR ($(CD_3)_2SO$), δ, ppm (*J*, Hz): 3.90–4.08 (4H, m, $POCH_2$), 3.52–3.70 (2H, m, CH_2Cl), 1.60–2.20 (4H, m, $(CH_2)_2P$), 1.19 (6H, t, *J* = 7.2, CH_3).

Diethyl 2-{[3-(triethoxysilyl)propyl]amino}ethylphosphonate 1. A well-stirred homogeneous mixture of APTES (7.0 g, 31.6 mmol) and diethyl vinylphosphonate **2** (5.19 g, 31.6 mmol) was quickly immersed in preheated (100ºC) oil bath. Stirring and heating continued during 2 h. Reaction mixture was cooled and distilled at 0.1 mm Hg. The fraction with boiling point of 163–171 ºC was collected and 7.80 g (64 %) of viscous colorless oil **1** was obtained. ^{1}H NMR ($CDCl_3$), δ, ppm (*J*, Hz): 3.95–4.09 (4H, m, $POCH_2$), 3.74 (6H, q, *J* = 7.2, $SiOCH_2$), 2.77–2.87 (2H, m, CH_2CH_2P), 2.53 (2H, t, *J* = 7.2, $Si(CH_2)_2CH_2$), 1.83–1.96 (2H, m, CH_2P), 1.47–1.57 (2H, m, $CH_2CH_2CH_2$), 1.25 (6H, t, *J* = 7.2, CH_3CH_2OP), 1.14 (9H, t, *J* = 7.2, CH_3CH_2OSi), 0.51–0.59 (2H, m, CH_2Si).

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Ю.И. Чуйко, Ю.В. Холин, М.А. Колосов. Синтез диэтил-2-{[3-(триэтоксисилил)пропил] амино}этилфосфоната.

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Диэтил 2-{[3-(триэтоксисилил)пропил]амино}этилфосфонат – перспективный реагент для модификации поверхности кремнеземов и, таким образом, создания адсорбентов для извлечения ионов *d*-металлов из водных сред.

Диэтил-2-{[3-(триэтоксисилил)пропил]амино}этилфосфонат был синтезирован путем алкилирования 3-аминопропилтриэтоксисилана (APTES) диэтилвинилфосфонатом при быстром нагревании без растворителя. Были исследованы возможные альтернативные подходы к синтезу этого соединения (алкилирование APTES и N-ацетилAPTES), а также поведение APTES при нагревании в абсолютном этаноле и тетрагидрофуране. Показано, что APTES нестабилен в абсолютном этаноле, что вызвано процессами поликонденсации. Из-за этого факта ранее описанный подход к синтезу диэтил-2-{[3-(триэтоксисилил)пропил]-амино}этилфосфоната в этаноле оказался невозможным.

Ключевые слова: 3-аминопропилтриэтоксисилан (APTES), алкилирование, поликонденсация, модификация поверхности.

Ю.І. Чуйко, Ю.В. Холін, М.О. Колосов. Синтез діетил-2-{[3-(тріетоксисиліл)пропіл]аміно}етилфосфонату.

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Діетил-2-{[3-(тріетоксисиліл)пропіл]аміно}етилфосфонат – перспективний реагент для модифікації поверхні кремнеземів і, таким чином, створення хелатних адсорбентів для вилучення іонів *d*-металів з водних середовищ.

Задум отримання діетил-2-{[3-(тріетоксисиліл)пропіл]аміно}етилфосфонату, як і інших функціональних N-похідних 3-амінопропілтріетоксисилану (APTES), полягає в отриманні шляхом органічного синтезу конкретної речовини (прекурсора) з надійно доведеною структурою, стабільної впродовж тривалого часу при зберіганні за кімнатної температури; ця сполука після одноразового прищеплення на поверхню кремнезему формує шар однотипних функціональних груп (вторинних аміногруп та залишків фосфонової кислоти, поєднаних вуглеводневим ланцюгом), стабільних у водному середовищі, на повітрі та у часі. Такий підхід вигідно відрізняється від поетапного прищеплення APTES та взаємодії поверхні APTES-модифікованих кремнеземів з певними реагентами, оскільки в останньому випадку після кожної стадії залишається незміненою частина поверхневих груп вихідного сорбенту, а будова функціональних груп є неоднозначною.

Діетил-2-{[3-(тріетоксисиліл)пропіл]аміно}етилфосфонат був синтезований шляхом алкілування APTES діетилвінілфосфонатом при швидкому нагріванні без розчинника. Окрім того, було досліджено можливі підходи до синтезу цієї сполуки (алкілування APTES і N-ацетилAPTES у різних умовах, які використовуються для N-алкілювання, відповідно, амінів та амідів), але, нажаль, усі вони не призвели до бажаного результату. Зокрема, негативний результат алкілування N-ацетилAPTES у присутності основи ми пояснюємо формуванням пасивного циклічного Si-вмісного аніону. Вивчено також поведінку APTES при нагріванні в абсолютному етанолі та тетрагідрофурані. Показано, що APTES нестабільний в абсолютному етанолі (зменшення кількості EtOSi-груп у спектрах ^{1}H ЯМР), що, вірогідно, викликано процесами поліконденсації, тому описаний раніше підхід до синтезу діетил-2-{[3-(тріетоксисиліл)пропіл]аміно}етилфосфонату в етанолі виходячи з APTES та діетилвінілфосфонату виявився неможливим.

Ключові слова: 3-амінопропілтріетоксисилан (APTES), алкілування, поліконденсація, модифікація поверхні.