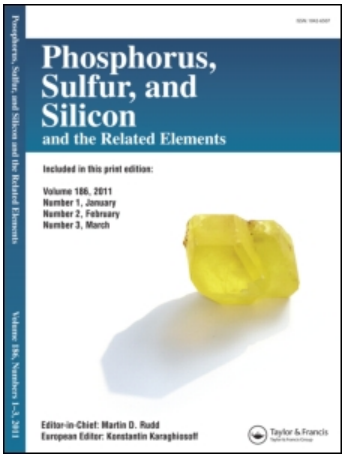

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NITROBENZYL (α-AMINO)PHOSPHONATES. PART 2[1]. CLEAVAGE OF 4-NITROBENZYL(α-AMINO)PHOSPHONIC ACIDS IN AQUEOUS SODIUM HYDROXIDE SOLUTION

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4-Nitrobenzyl(α-amino)phosphonic acids treated with an excess of aqueous sodium hydroxide undergo a C-P bond cleavage and subsequent transformation into a mixture of azoxybenzene and azobenzene derivatives. The observed cleavage is an example of the intramolecular redox reaction. The phosphonate moiety is oxidized to phosphate, and the remaining part of the molecule is reduced to azoxybenzene derivative **2**. After acidification of the reaction mixture two main products were isolated; 4,4′-diformylazoxybenzene (**3**) and 4-formyl-4′-hydroxyazobenzene (**4**). The product **4** was probably formed as a result of the Wallach type rearrangement of **3**.

Keywords: 4-Nitrobenzyl(α-amino)phosphonic acids; a C-P bond cleavage; azoxybenzene derivatives; phosphoric acid

INTRODUCTION

In the previous paper[1] we reported that 1-amino-2′-nitrobenzylphosphonic acids undergo a C-P bond cleavage in an aqueous NaOH solution. As a result of that cleavage mainly 3-amino-anthranil derivatives and phosphoric acid were found. We also found, that the corresponding 1-amino-4′-nitrobenzylphosphonic acids undergo a similar cleavage in basic medium, but the formed products were more complex. This reaction became a subject of our detailed studies and it is presented as a second part

of the previous work[1], describing now a cleavage of 4-nitrobenzylaminophosphonates in a basic medium.

The cleavage of 1-amino-4′-nitrobenzylphosphonic acids described here, is also an intramolecular redox reaction, similarly as it was observed previously[1], but the obtained products are different in this case, and do not resemble the cyclic products (anthranil derivatives)[1].

The reaction of splitting of 1-amino-4′-nitrobenzylphosphonic acids in aqueous NaOH solution proceeds analogously as a typical reduction of nitroaromatic compounds in the presence of a base. As it is widely known[13], the products of such a reduction are predominantly azoxybenzene derivatives. In 1969 Clark, Hobbs and Hutchinson reported[16], that 4-nitrophenylacetic acid in methanolic sodium hydroxide yielded a mixture of sodium salts of azo and azoxybenzene derivatives of glyoxylic acid. In our case, we have isolated a similar kind of species, as well.

As it was stated previously[1], contrary to 2- and 4-nitro derivatives the corresponding 1-amino-3′-nitrobenzylphosphonic acids are stable in an excess of aqueous NaOH solution and do not undergo a C-P bond cleavage.

RESULTS AND DISCUSSION

Synthesis of starting materials 1 and 5

The 1-amino-4′-nitrobenzylphosphonic acids **1** were obtained by hydrolysis of the corresponding esters **5** by means of 20% aqueous HCl. The esters **5** were prepared by an addition reaction of dialkyl phosphite to the corresponding aldimines, which is a classical method, frequently published in a literature[2,3].

In our case, for the synthesis of esters **5b,c** we used a previously described improved method, namely by heating of aldimine with dialkyl phosphite in toluene solution[1]. The formed esters were isolated and purified as oxalate salts. The esters were liberated from the oxalates in a pure state and then were hydrolysed with 20% aqueous HCl to 1-amino-4′-nitrobenzylphosphonic acids **1b,c**.

The cleavage of 1-amino-4′-nitrobenzylphosphonic acids 1a-c in aqueous NaOH

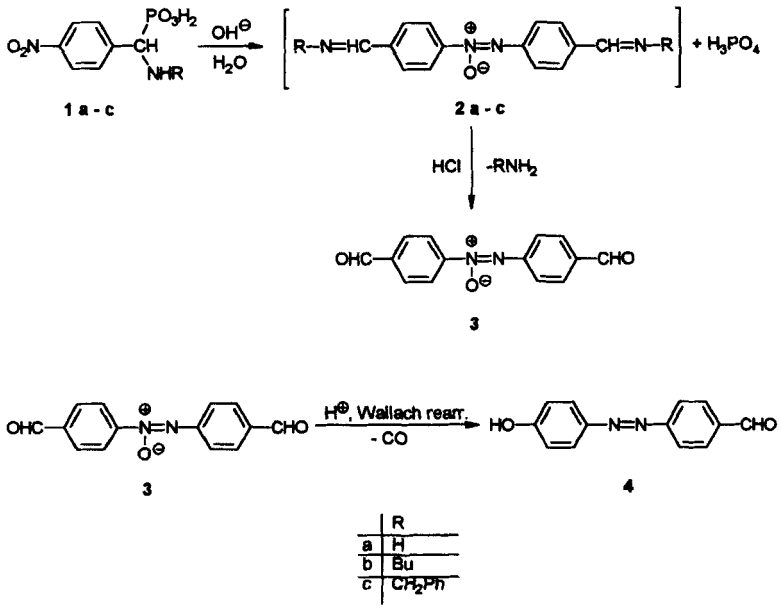
The 4-nitrobenzylphosphonic acid **1a-c** was dissolved in a ten-fold excess of aqueous sodium hydroxide and the solution was refluxed for 1 hour. The pale-yellow solution (at the beginning) quickly became red-brown, and then a brown precipitate appeared in the mixture. When the reflux was in progress, evolution of free amine from the reaction mixture was observed.

Further investigation of this reaction revealed that the products of this cleavage contain no phosphorus. In order to determine the products of a cleavage, the reaction mixture obtained in the case of acid **1b**, was investigated in some detail. Thus, after refluxing for 1 hr, it was cooled and extracted with diethyl ether. It allowed to isolate an intermediate, which turned out to be a bisbutylimine azoxybenzene derivative **2b**, as found on the basis of NMR and ESI±Q1MS spectra. (Scheme 1). The yield of imine **2b** was small, because a greater part of the cleavage product remained in the solution and it was not extractable by diethyl ether. Hydrolysis of the imine **2b** with dilute aq. HCl afforded the product **3**, which appeared to be 4,4′-diformylazoxybenzene, contaminated slighty with hydroxy compound **4**. The authenticity of **3** was confirmed by independent synthesis, according to the literature[5,6]. The physicochemical data of obtained **3** were in agreement with the literature ones[5,18].

Final neutralization of a reaction mixture with excess aqueous HCl caused precipitation of a brown solid, which was a mixture of several compounds and also some decomposition materials (tars).

The material obtained from the cleavage was examined by means of G.C.-M.S., ESI±Q1MS and NMR spectroscopy and individual compounds were separated by means of chromatography. It has been found, that the main product of the cleavage was the dialdehyde **3**. The second product, which appeared in lower amounts, was 4-hydroxy-4′-formylazobenzene[7] (**4**). Traces of other products were also detected by G.C.-M.S. technics as well as for example; 4-hydroxyazobenzene-4-carboxylic acid[9] and 4,4′-diformylazobenzene[6].

The amount of hydroxy compound **4** present in the precipitated material depended on the work-up of the reaction mixture. When the reaction mixture was treated with a large excess of aq. HCl and heated, the amount of **4**



SCHEME 1

was increased. It suggests, that the product **4** was formed from the dialdehyde **3**, as a result of its transformation.

It is known, that azoxybenzene deivatives treated with acids, especially with concentrated sulfuric acid rearreange to *p*-hydroxy azobenzene derivatives (the Wallach rearrangement)[4]. In our case there is a probability that the major product of phosphonate decomposition, dialdehyde **3** undergoes partially the Wallach type transformation to hydroxy compound **4**, during treatment of the precipitated material with hydrochloric acid. However, the way of formation of **4** seems to be unclear, because it requires substitution of one formyl group by hydroxy group. Maybe that the rearrangement of **3** undergoes with simultaneous substitution of a formyl by a hydroxyl group. Anyway, until now the mechanism of the Wallach rearrangement is not settled yet[8], and now it is difficult to explain also how it occurs in our case. But there is no doubt, that the dialdehyde **3** undergoes partial transformation to the hydroxy azobenzene derivative **4** during work-up of the reaction mixture. It was additionally proved by prolonged

heating of **3** in aqueous HCl solution. In this case, the hydroxyazobenzene derivative **4** was formed in considerable yield.

Similar transformation of **3** has been noticed many years ago by Alway and Bonner[6], and more recently by Japanese workers[9], who found that some 4,4′-disubstituted azoxybenzenes rearranged in sulfuric acid to 4-hydroxyazo compounds, with a loss of one substituent at the *p*- position. For example, when azoxybenzene-4,4′-dicarboxylic acid was heated with sulfuric acid, it yielded 49% of 4-hydroxyazobenzene-4-carboxylic acid and carbon dioxide[9]. In our opinion, a similar rearrangement might occur during work-up of the product of the cleavage of acids **1**; with a formyl group from **3** being removed as carbon monooxide and replaced by the hydroxide moiety.

The water layer, obtained after separation of a precipitate, contained some organic material and a phosphoric acid salt with amine, which was formed by decomposition of the imine **2** during neutralization of the reaction mixture. The phosphoric acid salt was analysed by means of ^{1}H and ^{31}P NMR spectra, performed on a residue, after evaporation of water. No traces of other phosphorus products (except of H_3PO_4) were found. The small amount of organic material in the water layer contained some 4-hydroxyazobenzene-4′-carboxylic acid[9] (detected by ESI±Q1MS method), and other indefinite tar-like products.

Transformations, which are similar to the presented ones here, were reported earlier[14,18] with 1-(4-nitrobenzyl)-pyridinium salts under treatment with NaOH. The products of those reactions were 4-carbonylo-azoxybenzene derivatives, formed by intramolecular oxidation of benzylic carbons by the nitro groups. The dialdehyde **3** was also formed by this way[18].

The cleavage of dialkyl esters of 1-amino-4′-nitrobenzylphosphonic acids 5a-c in aqueous NaOH

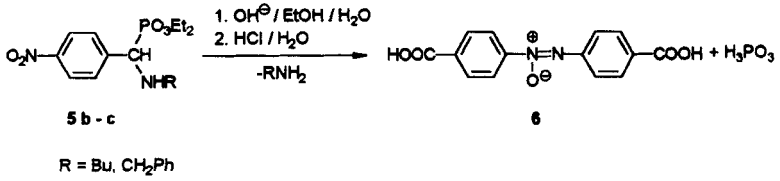
The dialkyl phosphonic esters **5** also underwent a cleavage in aqueous NaOH, with a pathway of a cleavage surprisingly different from phosphonic acids **1**. In general, the way of cleavage of the esters **5** was similar to the cleavage of 4-nitrophenylacetic acid in methanolic alkali, described by Clark and others[16].

The cleavage was particularly investigated in the case of esters **5b** and **5c**, being diethyl esters of the corresponding phosphonic acids **1b** and **1c**.

When the esters **5b,c** were heated with an excess of NaOH in aqueous ethanol, the solution become quickly red-brown, similarly as it was observed in the case of the acids. When the reaction was finished, a yellow-orange precipitate occurred in the solution, after cooling. The product appeared to be the sodium salt of azoxybenzene-4,4′-dicarboxylic acid (**6**). The remaining solution was concentrated and neutralized with aqueous HC to provide an additional amount of the free acid **6**. The authenticity of **6** was proved by ^{1}H NMR and other spectroscopical methods, and also by comparison with literature data[15–17].

The water layer (after removal of the product **6**) was evaporated and analysed by means of ^{1}H and ^{31}P NMR technics. Its examination by NMR spectra revealed that it was a mixture, containing mainly the phosphorous acid and some other phosphorus products in a considerably less amount. They included monoethyl phosphite and also traces of H_3PO_4.

Results of the cleavage of esters **5b,c** demonstrate that the phosphorus moiety does not take part in the redox reaction (which occurred during the cleavage of the acids), but it is simply removed from the molecule by the base and then hydrolysed to H_3PO_3. However, the remaining part of the molecule underwent some transformations, in which the nitro groups were reduced to azoxy ones with simultaneous oxidation of the benzylic CH moieties to the carboxyl groups (Scheme 2), yielding azoxybenzene-4,4′-dicarboxylic acid (**6**)



SCHEME 2

CONCLUSIONS

The investigation of a C-P bond cleavage in aminophosphonic acids, carried out up to now in our group[1,10], allows to recapitulate the obtained results, and make some basic conclusions. First, the cleavage of a C-P bond in aminophosphonates can occur in molecules possessing substitu-

ents, which have the ionization ability. It relates, first of all, to hydroxy and nitro groups, which are able to be ionized by a strong base (for example; sodium hydroxide) in aqueous solution. But, the ability for ionization is not a sufficient term for the occurrence of a C-P bond cleavage. Secondly, the substituents in aminophosphonates should provide a significant resonance effect in the molecule. In this case, the formed charge at the ionized group in the molecule can be transferred to a phosphonate group, *via* resonance effect, which is combined with delocalisation of conjugate double bonds in the molecule. It allows for a departure of the phosphonate group with a charge. This condition can be fulfilled, when the ionized group is situated at the definite position in the molecule. In the case of benzyl derivatives, it occurs obviously in the *ortho* and *para* position. This would explain the fact, that the *meta* substituted nitrobenzyl(amino)phosphonic acids do not undergo a C-P cleavage, in basic as well as in acidic media[1].

The similar phenomenon occurred in the case of *o*- and *p*-pyridylmethyl(amino)phosphonates, which were split in acidic conditions[10]. The protonation of 2- and 4-pyridylmethyl(amino)phosphonates by strong acid caused a C-P bond cleavage, and a departure of the phosphorus moiety as an intermediate with a positive charge.

Our findings also showed[11], that displacement of the group able to ionization by another one, not ionizable in reaction medium, caused a resistance for a C-P cleavage, even when the group is placed at *ortho* or *para* position. For example; diethyl *o*- or *p*-hydroxybenzyl(amino)phosphonates undergo a C-P bond cleavage in aq. NaOH solution, to form the corresponding hydroxybenzaldehydes and monoethyl phosphite[11]. However, when the hydroxy group in the *p*-hydroxybenzyl(amino)phosphonate is substituted by the methoxy group (which is not ionizable by a base), the obtained aminophosphonate, i.e *p*-methoxybenzyl (amino)phosphonate is stable in aqueous NaOH solution[11].

EXPERIMENTAL

NMR spectra were recorded on a Bruker Avance TM DRX 300 MHz in $CDCl_3$, DMSO-d_6 or D_2O solutions respectively, using 300.13 MHz for ^1H NMR, 75.477 MHz for ^{13}C NMR and 121.51 MHz for ^{31}P NMR spectra. G.C.-M. S. analyses were carried out with a Hewlett Packard HP 5971A apparatus, at an ionization potential of 70 eV, equipped with HP-1

capillary column, and also the M.S. analyses were performed on a Finnigan TSQ 700 instrument (electrospray ionization, on mode: ESI±Q1MS). IR spectra were recorded on a Perkin Elmer 2000 FT-IR spectrometer. Elemental analyses were done in the laboratory of Instrumental Analysis, in the Institute. Melting points were measured on a Digital Melting Point Apparatus Electrothermal 9200, and were uncorrected.

All commercially available reagents were used as received from the supplier (Aldrich Company).

Preparation of Diethyl 1-Amino-4′-nitrobenzylphosphonates (5b,c)

A procedure described for the preparation of diethyl 1-amino-2′- nitrobenzylphosphonates[1] was exactly followed. The obtained esters **5b,c** were purified as oxalate salts, according to the procedure[1]. Free esters were liberated from the oxalates by neutralization with aq. sodium bicarbonate, and then extracted with chloroform.

Diethyl 1-(N-butylamino)-4′-nitrobenzylphosphonate (5b): Oil. ^{1}H NMR($CDCl_3$) 8.12(d, 2H, J= 8.6 Hz), 7,51(m, 2H), 4.07(d, 1H, CH-P, J= 20.8 Hz), 3.97(m, 4H, OCH_2), 2.37(t, 2H, J= 6.6 Hz, CH_2N), 1.86(bs, 1H, NH), 1.38–1.10(m, 10H, CH_2, CH_3), 0.78(t, 3H, J= 7.2 Hz). ^{31}P NMR: 22.954(s). Oxalate: Yield: 71%. mp. 131 °C (dec.). ^{1}H NMR(D_2O + D_2SO_4): 8.41(d, 2H, J= 8.7 Hz), 7.85(d, 2H, J= 7.5 Hz), 5.09(d, 1H, CH-P, J= 18.3 Hz), 4.20(m, 4H, OCH_2), 3.13(m, 2H, CH_2N), 1.71(m, 2H, CH_2), 1.39–1.24(m, 8H, CH_2, CH_3), 0.88(t, 3H, J= 7.2 Hz). Anal. calc. for $C_{15}H_{25}N_2O_5P.(COOH)_2$: Calc. N, 6.45; P, 7.13; found: N, 6.47; P, 7.37.

Diethyl 1-(N-benzylamino)-4′-nitrobenzylphosphonate (5c): Oxalate: Yield: 53%. m.p. 125–129 °C (dec.). ^{1}H NMR(D_2O + D_2SO_4): 8.38(d, 2H, J= 8.6 Hz), 7.75(d, 2H, J= 8.6 Hz), 7.50–7.35(m, 5H), 4.96(d, 1H, CH-P, J= 18.7 Hz), 4.45–4.05(m, 6H, CH_2N, OCH_2), 1.35(t, 3H, J= 7.05 Hz, CH_3), 1.22(t, 3H, J= 7.1 Hz, CH_3). ^{31}P NMR: 15.912(s). Anal. calc. for $C_{18}H_{23}N_2O_5P.(COOH)_2$: N, 5.98; P, 6.61; found: N, 5.97; P, 6.44.

Preparation of 1-Amino-4′-nitrobenzylphosphonic Acids (1a-c)

The 1-amino-4′-nitrobenzylphosphonic acid[2,3] **(1a)** was obtained in *one-pot synthesis,* according to the described method[2]. The

1-(N-butylamino)-4′-nitrobenzylphosphonic acid **(1b)** and 1-(N-benzylamino)-4′-nitrobenzylphosphonic acid **(1c)** were obtained by hydrolysis of the corresponding esters **5b,c** by means of 20% aq. HCl, according to a standard procedure[1].

1-(N-butylamino)-4′–nitrobenzylphosphonic acid (1b): Yield: 56% m.p. 238–240°C. lit[12]. m.p. 238–240°C. ^{1}H NMR(D_2O + D_2SO_4): 8.37(d, 2H, J= 8.7 Hz), 7.78(d, 2H, J= 8.7 Hz), 4.83(d, 1H, CH-P, J= 17.4 Hz), 3.05(m, 2H, CH_2N), 1.71(m, 2H, CH_2), 1.33(m, 2H, CH_2), 0.86(t, 3H, CH_3, J= 7.3 Hz). ^{31}P NMR: 9.878 (s). Anal. calc. for $C_{11}H_{17}N_2O_5P$ N, 9.72; P, 10.75; found: N, 9.42; P, 10.37.

1-(N-benzylamino)-4′-nitrobenzylphosphonic acid (1c): Yield: 86%. m.p. 230–235°C. ^{1}H NMR(D_2O + D_2SO_4): 8.34(d, 2H, J= 8.5 Hz), 7.68(d, 2H, J= 8.4 Hz), 7.60–7.33(m, 5H), 4.72(d, 1H, CH-P, J= 17.8 Hz), 4.40–4.24(d,d, 2H, CH_2N). ^{31}P NMR: 9.616 (s). Anal. calc. for $C_{14}H_{15}N_2O_5P$: N, 8.69; P, 9.61; found: N, 8.77; P, 9.45.

The Basic Cleavage of 1-Amino-4′-Nitrobenzylphosphonic Acids (1a-c)

The phosphonic acid **1a-c** (5 mmol) was dissolved in aqueous sodium hydroxide solution (100 mL), containing 2.0g (50 mmol) NaOH. The solution was refluxed for 1 hr, cooled and neutralized with 6 M HCl to pH ≅ 2. The mixture was additionally refluxed for 10 min., and left several hours at room temp. The precipitated brown solid was filtered, washed with water and dried. Yield of the product: 0.60–0.70g (47%-55% yield, calculated for dialdehyde **3**), depending on the sample of the acid **1a-c** used.

The obtained material was separated by preparative chromatography (silica gel, eluant: $CHCl_3$-EtOAc, 20:1) to give the 4,4′diformylazoxybenzene **(3)** (~75% yield), 4-hydroxy-4′-formylazobenzene **(4)** (~15% yield) and tars remained. The dialdehyde **3** was additionally recrystalized from toluene.

4,4′-diformylazoxybenzene **(3)**: A yellow-orange solid. M.p. 178–180°C(dec.). Lit[5]. m.p. 194°C. Lit[18]. m.p. 190°C. ^{1}H NMR($CDCl_3$): 10.15(s, 1H, CHO), 10.07(s, 1H, CHO), 8.51(d, 2H, J=8.7 Hz, Ph), 8.28(d, 2H, J=8.7 Hz, Ph), 8.04(dd, 4H, J=8.7 Hz, Ph). ^{13}C NMR: 191.07(s, C=O), 190.71(s, C=O), 151.58(s, C_1), 147.96(s, $C_{1'}$), 138.61(s, C_4),

136.51(s, $C_{4'}$), 130.26(s, $C_{3,5}$+$C_{3',5'}$), 125.95(s, $C_{2,6}$), 123.05(s, $C_{2',6'}$). G.C.-M. S. (70 eV): 254(M, 35.5%), 238.1(3.4%), 226.1(M-CO, 81.7%), 197(2.5%), 141.1(5.3%), 133(27%), 121(43.9%), 105(100%), 93(90.6%), 77.1(38.1%), 65.1(37.5%).

4-hydroxy-4'-formylazobenzene **(4)**: A brown solid. M.p. 194–196°C. Lit. m.p[7]. 199°C. ^{1}H NMR ($CDCl_3$): 10.09(s, 1H, CHO), 8.04–7.86(m, 6H, Ph), 6.99–6.93(m, 2H, Ph). ^{13}C NMR: 192.60(s, C=O), 161.90(s), 155.40(s), 145.41(s), 136.78(s), 130.77(s, 2C), 125.51(d, J=10.57 Hz, 2C), 122.66(s, 2C), 116.14(s, 2C). G.C.-M.S. (70 eV): 226(M, 90.15%), 169(1.7%), 141(3.0%), 133(7.0%), 121(45.75%), 105(34.0%), 93(100%), 77(16.9%), 65.1(27.60%). ESI-QIMS: 225.3 (100%, M-1).

The water layer was evaporated to dryness and treated with 50 mL absolute ethanol in order to separate organic material from inorganic salts. The ethanolic extract was filtered and evaporated to give a semi-solid brown residue. A sample of evaporated material from the water layer was dissolved in D_2O and analysed by NMR. The ^{1}H NMR spectra showed the existence of traces of organic compound (probably 4-hydroxyazobenzene-4-carboxylic acid) and mainly the salt of butylamine with phosphoric acid [2.73(t, 2H, CH_2N), 1.36(q, 2H, CH_2), 1.10(sextet, 2H, CH_2), 0.64(t, 3H, CH_3) in the case of **1b**] and a salt of benzylamine [7.40(m, 5H, Ph), 3.99(s, 2H, CH_2N) in the case of **1c**]. The ^{31}P NMR spectra showed a single peak referring to phosphoric acid salt of amine (2.92 ppm in the case of **1a**, 2.186 ppm in the case of **1b** and 1.174 ppm in the case of **1c**).

The existence of the imine intermediate **2b** was proved in the case of the cleavage of **1b**. For this the reaction mixture prior to neutralization with aq. HCl, was extracted twice with diethyl ether (2x 50 mL). The ethereal extract was dried (anh. K_2CO_3), filtered and evaporated to give an orange-brown semisolid. The structure of the obtained product was established as the imine **2b**, on the basis of NMR, and ESI+1MS spectra.

Yield: 0.45g. ^{1}H NMR($CDCl_3$):8.32(m, 6H, Ph, CH=N), 7.85(m, 4H, Ph), 3.62(m, 4H, NCH_2), 1.70(m, 4H), 1.41(m, 4H), 0.95(m, 6H, CH_3). ESI+Q1MS: 365.3 (M+1, 100%).

The obtained product **2b** was heated with 50 mL 1M HCl for 5 min. and cooled. The undissolved material was filtered, washed with water and dried. The product obtained (m=0.22g, 69% yield) was mainly dialdehyde **3** (on the basis of ^{1}H NMR and G.C.-M.S spectra). The product was slightly contaminated with the hydroxy compound **4**.

The Basic Cleavage of Diethyl 1-Amino-4′-Nitrobenzylphosphonates (5b,c)

The phosphonic ester **5b,c** (5 mmol) was dissolved in a mixture of ethanol (40 mL) and water (40 mL), containing 2.0g (50 mmol) NaOH. The solution was refluxed for 1 hr and cooled. The formed yellow-orange precipitate (sodium salt of **6**) was collected by filtration, and the filtrate evaporated to a small volume (~ 30 mL) and neutralized with 6M HC1 to pH ≅ 2. It caused a separation of an additional amount of free acid **6**, as a brown precipitate. The total yield of **6** was 88% in the case of ester **5b** (0.46g of sodium salt and 0.24g of free acid **6**). The total yield in the case of ester **5c** was 66% (0.11g of sodium salt and 0.38g of free acid **6**). Treatment of the sodium salt with an excess of aq. HCl gave the acid **6**, as a yellow-brown powder, insoluble in water. The obtained acid **6** was additionally purified by recrystallization from DMF, to give a yellow powder.

Azoxybenzene-4,4′-dicarboxylic acid (6): m.p.: The acid **6** did not melt up to 350°C, but it darkened > 250°C. Lit.[16] m.p. 360°C. Lit.[17] m.p.: It darkened > 285°C, and did not melt. ^{1}H NMR(DMSO): 13.304(bs, 2H, COOH), 8.35(d, 2H, J= 8.55 Hz), 8.16(d, 2H, J= 8.60 Hz), 8.097(bs, 4H). ^{13}C NMR: 167.34(s, COOH), 167.01(s, COOH), 150.98(s, C_1), 147.32(s, $C_{1'}$), 135.09(, C_4), 132.16(s, $C_{4'}$), 131.30(s, C_3+C_5), 130.93(s, $C_{3'}$+$C_{5'}$), 125.76(s,C_2+C_6), 123.46(s, $C_{2'}$+$C_{6'}$). ESI +1QMS: 287.5 (M+1), 242.3, 169.3, 160.2, 149.3, 87.2. IR(KBr)(cm^{-1}): 2978, 2821, 2664, 2545, 2361, 1691 (C=O), 1602, 1462, 1424, 1291 (N-O), 1106, 916, 775.

Anal. calc for $C_{14}H_{10}N_2O_5$: C, 58.74, H, 3.52, N, 9.78; found: C, 58.89, H, 3.50, N, 9.87.

The water layer (after removal of the acid **6**) was evaporated to dryness and extracted with 50 mL of abs. ethanol, in order to remove inorganic salts. The ethanolic extract was filtered and evaporated to give a semisolid. A sample of the residue was dissolved in D_2O and NMR spectra were done. On the basis of ^{1}H and ^{31}P NMR spectra, the residue was composed mainly with phosphorous acid, some its monoethyl ester, and also phosphoric acid. The ^{1}H NMR spectrum demonstrated the characteristic dublet for the P-H bond of H_3PO_3 with a large coupling constant: $J_{P\text{-}H}$=717 Hz. The proportions of products based on the ^{31}P NMR spectrum for the cleavage of ester **5b** were as following: H_3PO_3 (86%, s, 5.417 ppm), monoethyl

phosphite (7.6%, s, 7.949 ppm), and H_3PO_4 (~ 6%, 1.515 ppm). For a cleavage of **5c**, the following values were found: H_3PO_3 (~ 60%, s, 5.513 ppm), monoethyl phosphite (~ 8%, 7.97 ppm), H_3PO_4 (~ 25%, 1.524 ppm) and also traces of other indefinite products.

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