

CCA-1056

YU ISSN 0011-1643

547.233:547.241

Original Scientific Paper

Synthesis and Spectral Properties of Hydroxy- and Methoxy-Substituted Benzeneazophosphonates

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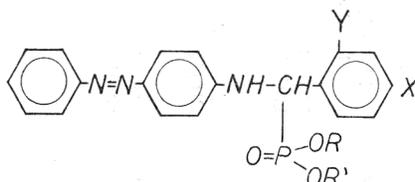
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Received April 7, 1977

Diethyl and dibutyl hydroxy- and methoxy-substituted [α -(4-benzeneazoanilino)-*N*-benzyl]phosphonates have been prepared. The corresponding monoesters were obtained by the partial hydrolysis of the diesters. Molecular weight determination in chloroform solution showed that the monoesters are dimeric. Infrared spectra, recorded in chloroform solution as well as in the solid state, confirmed this association as being due to the hydrogen bonding between the P=O and P—OH group. In the hydroxy-substituted compounds, the phenolic OH group also participates in such a bonding.

INTRODUCTION

Continuing our investigation of benzeneazophosphonic acid derivatives, some new hydroxy- and methoxy-substituted [α -(4-benzeneazoanilino)-*N*-benzyl]phosphonates have been prepared. In our previous works^{1,2} it has been shown that the site of the benzeneazo group attachment has a major influence on the properties of the corresponding monoesters. With this regard monoesters exhibit either a zwitterion or a dimerized structure. Although the alkaline hydrolysis of diesters of various α -anilinobenzylphosphonic acid derivatives afforded in most cases the corresponding sodium salts of the monoesters^{1,3}, the hydroxy-substituted diethyl [4-(2-naphtolazo)- α -anilinobenzyl]phosphonates failed to do so and gave instead products of decomposition⁴. This observation initiated our interest to synthesize a number of the cited diesters in order to investigate the influence of the substituents on their alkaline hydrolysis. The following compounds have been prepared:



R=R'	X	Y	R	R'	X	Y	R	R'	X	Y
1 Et	H	OH	7 Et	Na	H	ONa	13 Et	H	H	OH
2 Et	OH	H	8 Et	Na	OH	H	14 Et	H	OH	H
3 Et	OMe	H	9 Et	Na	OMe	H	15 Et	H	OMe	H
4 Bu	H	OH	10 Bu	Na	H	ONa	16 Bu	H	H	OH
5 Bu	OH	H	11 Bu	Na	OH	H	17 Bu	H	OH	H
6 Bu	OMe	H	12 Bu	Na	OMe	H	18 Bu	H	OMe	H

TABLE I
Physical, Spectral, and Analytical Data of Substituted Benzeneazo Phosphonic Acid Derivatives

Compd.	Formula	M. p./°C Recr. solv.	Yield/%	Anal. Calc'd/% Found			Characteristic group frequencies/cm ⁻¹ in the infrared spectrum						
				C	H	N	P	ν P=O	δ(O)—C	ν P—O—(C)	ν NH, ν OH		
1	C ₂₃ H ₂₆ N ₃ O ₄ P	173—174 EtOH	90	62.86 63.09	5.96 5.67	9.56 9.84	7.05 7.23	1235 vs	1156 w 1144 s	1052 s 1028 s	3260 m 3160 m		
2	C ₂₃ H ₂₆ N ₃ O ₄ P	156.5—157.5 EtOH—H ₂ O, 9:1	98	62.86 62.68	5.96 6.19	9.56 9.83	7.05 7.05	1235 vs	1143 s	1040 s 1020 vs	3250 s 3160 m		
3	C ₂₄ H ₂₈ N ₃ O ₄ P	151—152 EtOH	86	63.56 63.62	6.12 6.53	9.27 9.49	6.80 6.87	1240 vs	1154 m 1140 s 1125 m	1045 s ^c 1025 vs	3270 m 3175 w 3118 w		
4	C ₂₇ H ₃₄ N ₃ O ₄ P	129—130 EtOH	64	65.44 65.36	6.92 7.21	8.48 8.78	6.25 6.31	1235 vs br	1146 vs 1130 sh	1068 s 1030 vs	3260 s 3170 m 3060 m br		
5	C ₂₇ H ₃₄ N ₃ O ₄ P	146—147 EtOH	75	65.44 65.30	6.92 7.18	8.48 8.32	6.25 6.39	1220 s	1158 m 1145 w	1060 m 1025 s	3390 w 3200 m br		
7	C ₂₁ H ₂₀ N ₃ O ₄ PNa ₂	265 ^a EtOH	60	10.10 10.37		9.23 9.45	6.80 7.06	ν P=O ν _{as} PO ₂ ⁻	ν _{sym} PO ₂ ⁻	δ(O)—C	ν P—O—(C)	ν NH, ν OH, H ₂ O	
8	C ₂₁ H ₂₁ N ₃ O ₄ PNa 1.5 H ₂ O	240—242 ^a EtOH	78	5.00 4.81	5.86 6.65	9.13 9.36	6.73 6.65	1245 s br 1190 m 1180 s	1075 vs 1140 m	1060 s br 1045	3700—3200 m		
9	C ₂₂ H ₂₃ N ₃ O ₄ PNa H ₂ O	220 ^a EtOH	92	4.94 4.65	3.87 3.18	9.03 9.29	6.66 6.68	1250 m 1200 m 1180 s	1078 vs 1155 sh 1145 s	1050 vs ^c 1032 vs	3520 m br 3380 m br 3300 m br		

RESULTS AND DISCUSSION

Physical properties, analytical and infrared data of diesters **1**—**5**, sodium salts of the monoesters **7**—**12** and monoesters **13**—**18** are given in Table I. Diesters were obtained as yellow or orange crystals. Methoxy-substituted dibutyl ester **6** was obtained as an oil difficult to purify and it was hydrolyzed without previous purification. When refluxed with an excess of alcoholic sodium hydroxide none of the diesters exhibited any significant rupture of the P—C bond and they gave the anticipated sodium salts of the monoesters in 60—90% yield. This behavior is in contrast with the observed instability of a hydroxy-naphthyl derivative in alkaline medium¹, but is in accord with the properties of other hydroxyphenyl substituted diesters³. During the hydrolysis of the *ortho*-hydroxybenzyl diesters **1** and **4**, also the hydrogen of the phenolic OH group was exchanged with sodium, while in *para*-hydroxybenzyl diesters **2** and **5** the OH group remained free, though the same excess of the alkali was used in both instances.

Sodium salts were obtained as yellow or orange solids. Although they all crystallize with water of crystallization and some are hygroscopic, after drying in vacuo **7**, **10** and **12** were obtained anhydrous. The amount of water in other salts was determined by thermogravimetric analysis.

Molecular weight determinations of the monoesters (Table II) was possible to carry out only for the methoxy **15** and **18** and *para*-hydroxy **14** and **17** substituted compounds. *Ortho*-hydroxy **13** and **16** derivatives were insufficiently soluble. In chloroform solution the monoesters are dimeric, presumably owing to the hydrogen bonding between the P=O and P—OH groups. Properties of *para*-methoxy-substituted monoesters are similar to those of the monoesters of unsubstituted [α -(4-benzeneazoanilino)-*N*-benzyl]-phosphonic acid¹, though the solubility of the former monoesters in common organic solvents is somewhat decreased. Hydroxy-substituted monoesters are dark red, brown or violet compounds, very slightly soluble in organic solvents owing to the existing hydrogen bonding between the phosphonic and phenolic OH groups.

TABLE II
Molecular Weights of Monoesters

Compd.	Mol. wt. found	Mol. wt. calc'd for dimer
14	833 ^a	823
15	846 ^a	851
17	920 ^b	879
18	890 ^b	907

Determined in chloroform: ^aby ebullioscopic method; ^bby Signer's method.

Spectral Studies

Neutral esters give sharp and strong bands between 1220—1240 cm^{-1} presumably of the P=O stretching. In monoesters and their sodium salts the ionized PO_2^- group exists along with the P=O group as these compounds show multiple bands in the region 1175—1260 cm^{-1} . The absorption in this region has been ascribed to the P=O group and to the asymmetric stretching vibrations of the P_2^- group. Because of the dimeric structure arising from the hydrogen bonding between the P=O and P—OH groups, the methoxy-substituted monoesters give broad and complex band in vicinity of 1245 cm^{-1} , with a shoulder at 1230 cm^{-1} . The hydroxy-substituted monoesters show a very broad band, medium to strong intensity, at about 1170 cm^{-1} . The low frequency of this band indicates the presence of the PO_2^- group, presumably as the result of participation of the phenolic OH group in the above mentioned hydrogen bonding.

The complexity of the bands in sodium salts is due to the water of crystallization. Bonded presumably to the PO_2^- group, the water may change the polarity of the oxygen atoms and bring about the appearance of such a spectrum². Symmetric vibration of the PO_2^- ion is found in sodium salts between 1070—1110 cm^{-1} .

Hydrogen bonded P(O)OH group should exhibit three typical bands in the region 1600—2800 cm^{-1} (^{2,4,5}). Such bands are found only in the methoxy-substituted monoesters. From the foregoing discussion, the hydroxy derivatives are not expected to show these bands. Indeed, the band that should appear at 1600—1740 cm^{-1} is missing, while the other two bands if present, are masked by the hydrogen bonded phenolic OH group.

All the compounds absorb in the region 1125—1160 cm^{-1} and between 1000—1070 cm^{-1} . The former bands have been assigned to the C—O—(P) bond⁶ and the latter to the P—O—(C) vibration⁷. The bands are more complex in monoesters and their sodium salts than in neutral esters. In sodium salts the bands are partly superimposed on the symmetric PO_2^- vibration and in monoesters on the symmetric PO_2^- and P—O—(H) stretching frequencies.

The N—H stretching frequencies in neutral esters are lower than in the corresponding monoesters probably due to hydrogen bonding between the NH and P=O groups. In the monoesters, because of their association, such type of hydrogen bonding is sterically unlikely.

Only diesters were sufficiently soluble in chloroform for recording and studying the ¹H NMR spectra. As shown in Table III, the resonances of the methyl groups in diethyl esters are doubled. Such doubling is caused by the relative position of the ester groups with respect to the benzene ring. The same phenomenon has been observed with some dialkyl esters of phenyl-substituted organophosphorus compounds^{8,9}, as well as with diesters of α -anilinobenzylphosphonic acid³. Due to the coupling with the phosphorus and to the nonequivalency of the protons, the methylene groups appear as multiplets. Dibutyl esters give too complex spectrum to allow the analysis.

The broad doublets observed in **1**, **2**, **4**, and **5** at δ 4.7—5.3 were assigned to the benzylic OH proton coupled to the phosphorus and the NH proton. Only diester **3** showed clearly a doublet of a doublet ($J = 24$ and 8.5 Hz) as result of these couplings. The NH proton was found as a broad singlet between δ 5—6 while the phenolic OH group was usually hidden by the aromatic protons.

TABLE III
¹H NMR Spectra of Phosphonic Acid Diesters

Compound	Chemical shift δ in ppm (J in Hz) ^a
1	1.14, 1.24 (two t, each 3 H, $J = 6.5$, two CH ₂ CH ₃), 3.64—4.44 (m, 4 H, two OCH ₂), 5.27 (broad d, 1 H, $J = 23.5$, PCH), 5.4 (broad s, 1 H, NH ^b), 6.60—7.96 (m, 13 H, ArH), 8.92 (s, 1 H, OH ^b)
2	1.07, 1.20 (two t, each 3 H, $J = 7$, two CH ₂ CH ₃), 3.47—4.37 (m, 4 H, two OCH ₂), 4.75 (broad d, 1 H, $J = 23$, PCH), 5.2 (broad s, 1 H, NH ^b), 6.50—7.95 (m, 14 H, ArH + OH ^b)
3	1.13, 1.28 (two t, each 3 H, $J = 6.5$, two CH ₂ CH ₃), 3.48 (s, 3 H, OCH ₃), 3.56—4.43 (m, 4 H, two OCH ₂), 4.73 (dd, 1 H, $J = 24$ and 8.5, PCH), 6.43 (s, 1 H, NH ^b), 6.52—7.88 (m, 13 H, ArH)
4	0.60—1.88 (m, 14 H, two CH ₂ CH ₂ CH ₃), 3.60—4.34 (m, 4 H, two OCH ₂), 5.21 (broad d, 1 H, $J = 23$, PCH), 5.4 (broad s, 1 H, NH ^b), 6.58—7.96 (m, 13 H, ArH), 8.90 (s, 1 H, OH ^b)
5	0.54—1.83 (m, 14 H, two CH ₂ CH ₂ CH ₃), 3.56—4.23 (m, 4 H, two OCH ₂), 4.71 (broad d, 1 H, $J = 23$, PCH), 5.0 (broad s, 1 H, NH ^b), 6.38—7.92 (m, 14 H, ArH + OH ^b)

^a In CDCl₃ at 60 MHz; ^b D₂O exchangeable proton.

EXPERIMENTAL

Melting points were uncorrected. The infrared spectra were recorded for Nujol mulls and for solutions in chloroform with Perkin-Elmer 257 spectrophotometer. ¹H NMR spectra were obtained with a Varian A-60A spectrometer in deuteriochloroform solutions with tetramethylsilane as the internal standard. Thermogravimetric analyses were performed with a Cahn RG electromicro balance applying a heating rate of 2°/min and an atmosphere of static air. Molecular weights were determined by Clark's modification of Signer method¹⁰ and with a Beckmann's ebullioscope. As a standard solute, penta-acetylglucose (B.D.H. micro-analytical reagent) was used.

The analyses were performed in the Analytical Laboratory of the »Ruder Bošković« Institute.

Materials

Diethyl and dibutyl phosphonate were purchased from Eastman Organic Co. and were freshly distilled. The required Schiff's bases 4-benzeneazo-*N*-(2-hydroxybenzaldehyde), 4-benzeneazo-*N*-(4-hydroxybenzaldehyde) and 4-benzeneazo-*N*-(4-methoxybenzaldehyde) were prepared as described¹¹.

General Method for the Preparation of Esters of Benzeneazophosphonic Acid

Diethyl esters 1—3 and dibutyl esters 4—6 were prepared by heating of diethyl and dibutyl phosphonate, respectively, with an equimolar amount of the appropriate Schiff base in an oil bath at 100 °C for 6—8 h. Contrary to the original method of preparation¹², this condensation was carried out without any catalyst. Only for the preparation of diesters 4—6, some abs ethanol was added to the above mixture. Addition of a few drops of water to the reaction product and subsequent cooling afforded 1—5 as crystalline solids.

Sodium salts of the monoesters 7—12 were obtained by the hydrolysis of 1—6 as previously described⁴. The only modification was the amount of sodium hydroxide which was increased to 2.5—3 mol/mol of diester.

For the preparation of monoesters 13—18, the solution of the corresponding sodium salt in water was acidified by a small excess of 5% hydrochloric acid added

dropwise. After allowing the mixture to stand at room temperature for a few hr, the precipitates formed were collected by filtration, washed with cold water, dried and recrystallized.

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SAŽETAK

Sinteza i spektralna svojstva hidroksi i metoksi supstituiranih benzenazofosfonata

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Sintetizirani su dietil i dibutilesteri hidroksi i metoksi supstituirane [α -(4-benzenazoanilino)-*N*-benzil]fosfonske kiseline. Odgovarajući monoesteri dobiveni su djelomičnom hidrolizom diestera. Određivanja molekularne težine monoestera u otopini kloroforma pokazuju da se radi o dimernim spojevima. Infracrveni spektri potvrđuju ovu asocijaciju koja je uzrokovana vodikovim vezama između P=O i P—OH grupa. U hidroksi supstituiranim monoesterima i fenolna OH skupina također učestvuje u ovoj vezi.

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Prispjelo 7. travnja 1977.