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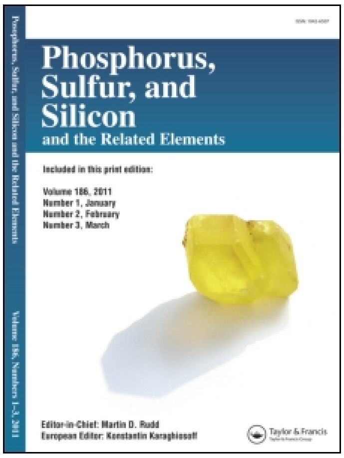

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ADDITION PRODUCTS OF DIBUTYL PHOSPHITE TO SCHIFF BASES

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1,4-Bis[N-methyl(dibutoxyphosphonyl)-1-(2-furyl)]diaminobenzene and 4,4′-bis[N-methyl (dibutoxyphosponyl)-1-phenyl]benzidine have been synthesized through addition of dibutyl phosphite to Schiff bases (N,N′-difurfurylidene-p-phenylenediamine and N,N′-dibenzylidene-benzidine, respectively) in the presence of sodium butoxide or triethylamine. The compounds have been characterized by elemental analysis, TLC and IR spectra. A detailed analysis of their ^{1}H-NMR spectra (1D and COSY) has been carried out.

Keywords: Schiff bases; aminophosphonic dibutyl esters; furan derivatives; phosphonic acid esters; NMR; IR; TLC

INTRODUCTION

Aminophosphonate derivatives[1–3] as well as aminophosphonic acids dibutyl esters[3–6] continue to be of considerable interest. Dibutyl esters of aminophosphonic acids have been prepared by reacting dibutyl phosphite with cyclohexyl-, pyridyl- or tetrazolyl-containing Schiff bases[7–9]. Stereoselective addition of dibutyl phosphite to chiral imines has also been performed[10–12]. Some of these compounds were found to exhibit antibacterial, antifungal or antitumor activity[4,5,9].

Our present attempts to synthesize novel aminophosphonate derivatives were stimulated by our earlier studies revealing that some of these substances can be used as additives to polymers with specific properties or for the synthesis of new monomers[13,14]. It is expected that the elongation of

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the alkyl chain in the phosphonate moiety of the compounds will increase their compatibility with the polymer[15].

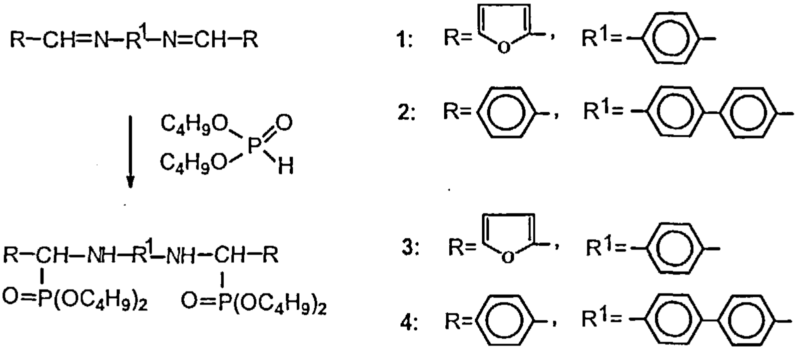
The aim of the present work is the synthesis of dibutyl esters of aminophosphonic acids and the study of their structure by means of spectral methods. The objective is to apply them further as antipyrenes for polymers.

RESULTS AND DISCUSSION

Addition of dibutyl phosphite to Schiff bases, prepared from furfural and p-phenylenediamine (**1**) or benzaldehyde and benzidine (**2**) was carried out. Two novel diesters of aminophosphonic acids were synthesized: 1,4-bis[N-methyl(dibutoxyphosphonyl)-1-(2-furyl)]diaminobenzene (**3**) and 4,4′-bis[N-methyl(dibutoxyphosphonyl)-1-phenyl]benzidine (**4**). The reaction was carried out in the presence of catalytic amounts ofa saturated solution of C_4H_9ONa in butanol or triethylamine, as shown in Scheme 1. According to literature data[7], the elongation of the alkyl chain in the alkoxy groups of dialkyl phosphites reduces their reactivity. Thus, upon addition of dibutyl phosphite to some cyclohexyl - or tetrazolyl-containing Schiff bases the yields of reaction products have been rather low[7,9]. However, the condensation of dibutyl phosphite and Schiff bases 1 and 2 in the presence of C_4H_9ONa was easily performed, the yield of compounds **3** and **4** being good. Depending on the catalyst used, dibutyl phosphite and the azomethine **1** react at room temperature (C_4H_9ONa) or upon heating (triethylamine). The increase of temperature favours the formation of resinous compounds from the furyl-containing Schiff base. For this reason the yield of the product **3** was low when triethylamine was applied as a catalyst. Compound **4** was synthesized at higher temperature in order to increase the solubility of azomethine 2 in dibutyl phosphite.

The spectroscopic data for compounds 3 and **4** confirm the structure proposed. In accordance with the literature data[6,16,17] in the IR spectra of **3** and **4** the absorption bands of the corresponding groups were observed (see Experimental).

The ^{1}H-NMR spectroscopic parameters of **3** and **4** are summarized in Table I. No signal of NH proton was observed in the spectrum of **3** taken in $CDCl_3$. The signal of the CH(P) – proton appeared in this spectrum as a doublet of doublets because of the coupling with ^{31}P and the NH proton.



SCHEME 1

D_2O exchange eliminated the smaller splitting converting the signal into a doublet. Comparison of the relative intensities of the signals before and after D_2O exchange revealed that the signal of the NH proton falls in the region of the multiplet signals for OCH_2 protons. In the spectrum of **4** measured in $CDCl_3$, the signals of the protons of CH(P) and NH groups overlapped (Figure 1a). After D_2O exchange a signal of the CH(P) proton appeared as a doublet at 4.75 ppm (Figure 1b). The signals of CH(P) and NH protons of **3** and **4** (Figure 1c) were shifted downfield and both of them appeared as a doublet of doublets in DMSO-d_6 solution, similarly to the pattern reported earlier[18]. After adding D_2O to the DMSO-d_6 solutions, partial exchange was observed in the spectrum of **3**, whereas in the spectrum of **4** the signal of NH was completely eliminated and a doublet of CH(P) appeared (Figure 1d).

The butoxy groups in the compounds **3** and **4** are attached to a prochiral phosphorus atom bound to an asymmetric carbon atom. Therefore non-equivalence of the alkoxy groups as well as of the protons of particular CH_2 groups takes place and this has been experimentally observed[6,17–21]. The signals of the methylene protons in the $OCH_2C^{\beta}H_2C^{\gamma}H_2CH_3$ fragments of **3** and **4** are rather complex. As seen from Table I three multiplets corresponding to OCH_2 protons were distinguished in the $CDCl_3$ spectra (both **3** and **4**) and in DMSO-d_6 spectrum (**4**). The relative intensity of these multiplets is 2:1:1, i.e. the chemical shift difference of two of these diastereotopic protons is insignificant and their signals are overlapped. The C^{β} H_2 and $C^{\gamma}H_2$ protons often give a common multiplet which is

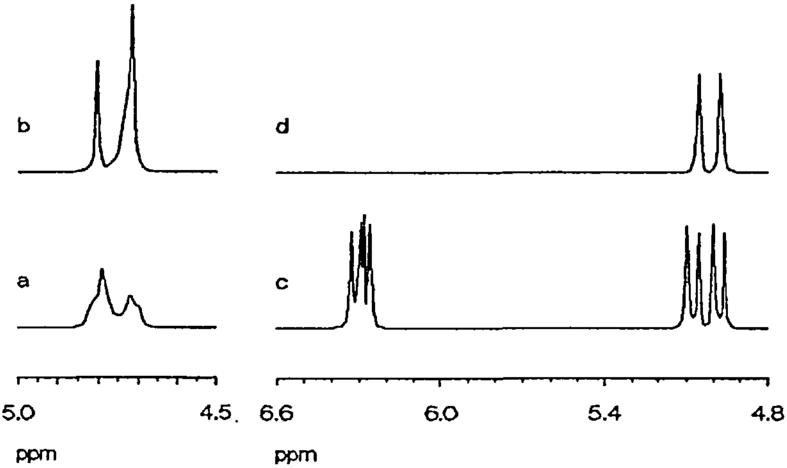


FIGURE 1 ^{1}H-NMR spectra of compound 4: a), b) in $CDCl_3$ and in $CDCl_3$, D_2O, respectively; c), d) in DMSO-d_6 and in DMSO-d_6, D_2O, respectively

sometimes overlapped with the signals of CH_3 or other protons[7,17]. In the spectrum of **3** (in both DMSO-d_6 and $CDCl_3$) the signal of each of these groups appears as an individual multiplet. The H,H-COSY spectrum indicates that the lower-field multiplet corresponds to $C^{\beta}H_2$ and the higher-field one – to the $C^{\gamma}H_2$ protons. The H,H-COSY spectrum of **4** is presented in Figure 2. The correlation patterns indicate that the signal at 1.52 ppm belongs to the $C^{\beta}H_2$ protons and in the range of 1.43–1.09 ppm the signals of both $C^{\beta}H_2$ and $C^{\gamma}H_2$ protons appear.

EXPERIMENTAL

Starting compounds: Dibutyl phosphite (Fluka), b.p. 122°C/9 mmHg, n_D^{20} = 1.4254; Schiff bases: N,N′-difurfurylidene-p-phenylenediamine (**1**), m.p. 171°C, IR (KBr-disk) $\bar{\nu}$ (cm^{-1}) – 1620 (ν C=N), ^{1}H-NMR ($CDCl_3$) δ (ppm) – 8.33 (s, CH=N), prepared according to Ref. 22; N,N'dibenzylidene-benzidine (**2**), m.p. 236°C, IR (KBr-disk) $\bar{\nu}$ (cm^{-1}) – 1670 (ν C=N), ^{1}H-NMR ($CDCl_3$) δ (ppm) – 8.54 (s, CH=N), prepared according to Ref. 23; triethylamine, b.p. 89°C. The melting of the compounds was examined

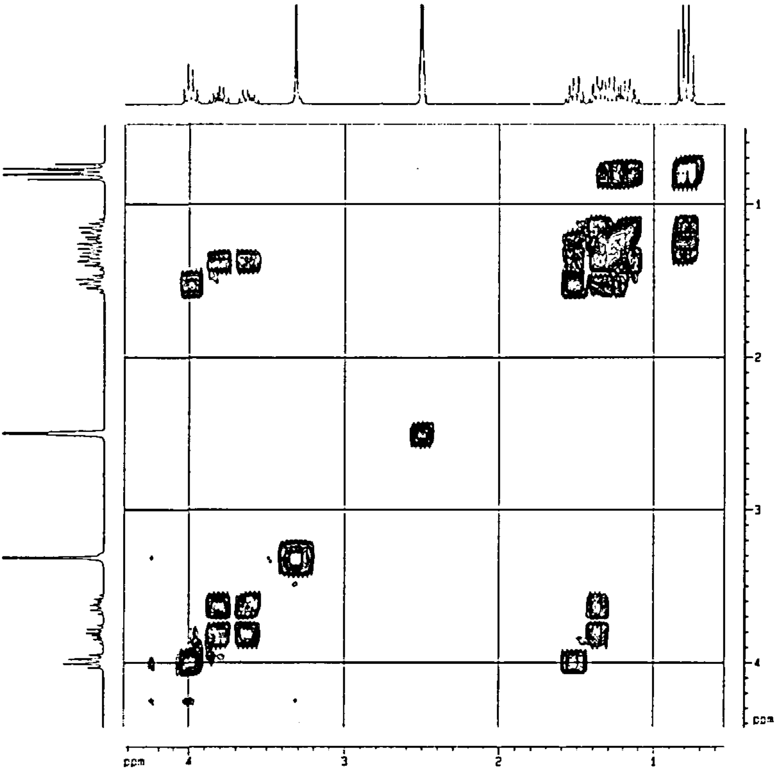


FIGURE 2 H,H-COSY spectrum of compound 4 in DMSO-d_6 showing the butyl protons ($OCH_2C^{\beta}H_2C^{\gamma}H_2CH_3$) region

on a Kofler microscope. The IR spectra were taken on a UR-20 spectrophotometer (KBr-disks). ^{1}H-NMR spectra were recorded on a Bruker DRX-250 spectrometer at room temperature; DMSO-d_6 and $CDCl_3$ as solvents and TMS as internal standard were used. Typical measurement conditions: 1D – spectra – 250.13MHz, 30° pulse, 64 scans, 16 K data points; H,H-COSY - 64 increments with 8 scans, 512 × 256 word matrix, sinebell window in both dimensions. TLC were performed on Kieselgel-60F_{254} plastic sheets (Merk). The samples were applied as CH_3OH solutions. The chromatograms were developed ascendingly using the ethylacetate-tetrahydrofuran-methanol (12:3:1) solvent system. The spots were detected under UV light and in iodine vapours.

TABLE I ^{1}H-NMR parameters of compounds **3** and **4**[*]

Comp. N°	Solvent	Chemical shifts, δ(ppm)							Coupling constants, J (Hz)				
		CH_3	$CH(P)$	NH	OCH_2	$C^{\beta}H_2$**	$C^{\gamma}H_2$**	C_6H_4	^3J (CH_2CH_3)	^2J (CHP)	^3J $(CHNH)$	^3J $(NHCH)$	^3J (NHP)
3	DMSO-d_6	0.82(t) 0.81(t)	4.93(dd)	5.15(dd)	3.94(m) 3.76(m)	1.48(m)	1.26(m)	6.60(s)	7.33 7.24	23.75	10.66	10.70	4.42
	$CDCl_3$	0.88(t) 0.86(t)	4.74(dd)	-	4.08(m) 3.96(m) 3.78(m)	1.56(m)	1.31(m)	6.52(s)	7.32 7.29	23.78	8.65	-	-
4	DMSO-d_6	0.81(t) 0.77(t)	5.03(dd)	6.29(dd)	3.99(m) 3.80(m) 3.63(m)	1.52(m) 1.43–1.09 (m)	1.43–1.09 (m)	6.97(m)	7.32 7.26	24.65	10.07	10.07	6.51
	$CDCl_3$	0.88(t) 0.82(t)	4.79–4.71	4.79–4.71	4.04(m) 3.88(m) 3.59 (m)	1.60(m) 1.49–1.14 (m)	1.49–1.14 (m)	6.90(m)	7.27 7.24	-	-	-	-

[*] ^{1}H-NMR in DMSO-d_6 and in $CDCl_3$, δ (ppm) : 3 – 6 . 3 8 and 6.31, respectively (m, $H_{\beta,\gamma}$ Furan) , 7.55 and 7.36, respectively (m, H_{δ} Furan) ; 4 – 7.38 and 7.37, respectively (m, C_6H_5).

[**] Methylene protons of $OCH_2C^{\beta}H_2C^{\gamma}H_2CH_3$.

Preparation of 1,4-Bis(N-methyl (dibutoxyphosphonyl)-1-(2-furyl)]diaminobenzene *(3)*

a) N,N′-difurfurylidene-p-phenylenediamine (3.51g, 0.0133 mol) and dibutyl phosphite (6.70 g, 0.0345 mol) were mixed and stirred in a flask. A saturated solution of C_4H_9ONa in butyl alcohol was added dropwise until exothermicity ceased. After stirring for three hours at ambient temperature, the reaction mixture was washed with water and filtered to obtain a crude product in a good yield (7.87 g, 90.80%). The product was purified by recrystallization from cyclohexane. The white crystalline powder obtained was dried in vacuo to constant weight.

Yield: 68.9% (5.97g); m.p. 114°C; R_f 0.82

Analysis

Calcd. for $C_{32}H_{50}N_2O_8P_2$: N, 4.29%; P, 9.51%.
Found: N, 4.11%; P, 9.59%.

IR (KBr-disk) $\bar{\nu}$ (cm^{-1}) :1020 and 1538 (furan ring) - ν (C-O-C) and ν (C=C), respectively; 1245 - ν (P=O); 1040, 1080 – ν ($P\text{-}OC_4H_9$) ; 1135, 1155 - δ ($O\text{-}C_4H_9$) ; 3240 – ν (NH).

^1H-NMR (in DMSO-d_6 and in $CDCl_3$) see Table I.

b) To a mixture of N,N′-difurfurylidene-p-phenylenediamine (2.84 g, 0.0108 mol) and dibutyl phosphite (5.43 g, 0.0280 mol) was added $(C_2H_5)_3N$ as a catalyst. After stirring and heating at 80°C for 3.5 hours, a dark-coloured reaction product was obtained. A hot cyclohexane solution of the crude product was filtered through Al_2O_3 in inert atmosphere. After three recrystallizations a white crystalline powder of **3** was obtained.

Yield: 15.70% (1.10g); m.p. 114°C; R_f 0.82.

Preparation of 4,4′-Bis[N-methyl(dibutoxyphosphonyl)-1-phenyl]benzidine *(4)*

This was prepared by reaction of N,N′-dibenzylidene-benzidine (4.66 g, 0.0129 mol) and dibutyl phosphite (6.53g, 0,0337 mol) in the presence of C_4H_9ONa as a catalyst. The mixture was refluxed at 110–115°C for three hours by stirring.

After washing with water and filtering a yellow precipitate (8.16g, 84.21%) was obtained. The crude product was recrystallized from methanol. Yield: 69.0% (6.68 g) ; m.p. 173°c; R_f 0.84.

Analysis

Calcd. for $C_{42}H_{58}N_2O_6P_2$: N, 3.74%; P, 8.29%.

Found: N, 3.89% ; P, 8.17%.

IR (KBr-disk) $\bar{\nu}$ (cm^{-1}) :1460, 1510, 1620 (aromatics) – ν (C=C); 1240 – ν (P=O) ; 1035, 1078 – ν ($P\text{-}OC_4H_9$) ; 1110, 1160 – δ ($O\text{-}C_4H_9$) ; 3310 ν (NH).

^1H-NMR (in DMSO-d_6 and in $CDCl_3$) see Table I.

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