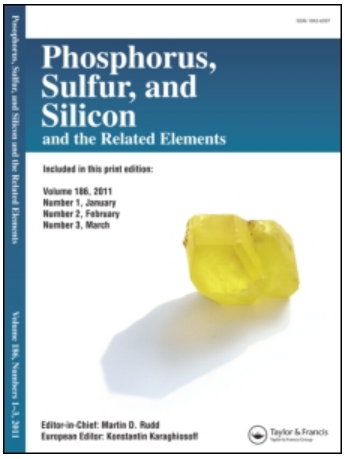

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ADDITION PRODUCTS OF DIALKYL PHOSPHITES TO A DIFURYL-CONTAINING SCHIFF BASE

I. Kraicheva[a]
[a] Institute of Polymers, Bulgarian Academy of Sciences, Sofia, Bulgaria

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ADDITION PRODUCTS OF DIALKYL PHOSPHITES TO A DIFURYL-CONTAINING SCHIFF BASE

I. KRAICHEVA

Institute of Polymers, Bulgarian Academy of Sciences, 1113 Sofia, Bulgaria

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New difuryl-containing diesters of aminophosphonic acids were synthesized through addition of dialkyl phosphites (dimethyl- and diisopropyl phosphite) to bis[4-(furfurylidene amino)-phenyl]methane. The reaction was carried out in the presence of an alkaline catalyst at ambient temperature. The structure of the compounds prepared was confirmed by means of IR, ^{1}H- and ^{31}P-NMR spectroscopy. TLC data are also presented.

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

INTRODUCTION

In the last years, much attention has been paid to the synthesis of various aminophosphonic esters[1–6]. Some of these compounds were found to exhibit antifungal activity[1,2,7]. The relationship between the chromatographic parameters of some substituted aminomethylphosphonates and their fungicidal effect has been investigated[8].

On the other hand, our earlier studies revealed that some esters of aminophosphonic acids can be used as monomers for the synthesis of polymers with increased burning resistance or to modify polymeric materials[9,10]. With the present work we continue the attempts to prepare polyfunctional compounds of this type.

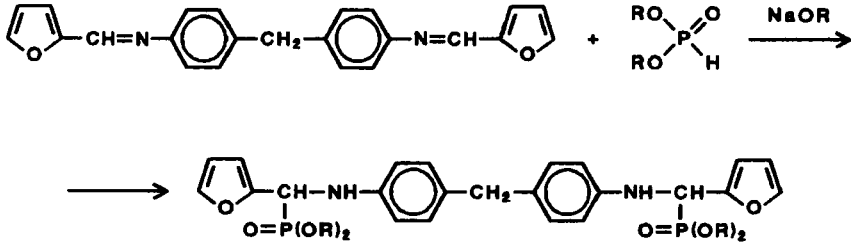
The addition of dialkyl- and diaryl phosphites to azomethines is known to be the simplest method for the synthesis of aminophosphonic esters[1].

RESULTS AND DISCUSSION

Novel difuryl-containing diesters of aminophosphonic acids, 4,4′-bis[N-methyl-(dimethoxyphosphonyl)-1-(2-furyl)]diaminodiphenylmethane (**1**) and 4,4′-bis[N-methyl(diisopropoxyphosphonyl)-1-(2-furyl)]diaminodiphenylmethane (**2**), were synthesized through addition of dialkyl phosphites (dimethyl- and diisopropyl phosphite) to a Schiff base, prepared from furfural and 4,4′-diaminodiphenylmethane. The reaction of dialkyl phosphites with bis[4-(furfurylidene amino)phenyl]methane proceeds according to Scheme 1. The reagents interact at ambient temperature in the presence of catalytic amounts of a saturated solution of sodium alkoxide in the corresponding alcohol. Earlier, under the same conditions, the addition of diethyl phosphite to the same Schiff base was achieved[9]. The use of solvent to homogenize the reaction mixture is not obligatory. Crystalline compounds were obtained with good yields.

Some of the compounds of this type, described in the literature, are unstable and they hydrolyze even by the moisture of air[11] or under recrystallization from 96% ethanol[3]. The products of the interaction of dialkyl phosphites with bis[4-(furfurylidene amino)phenyl]methane are stable and therefore, after completion of the reaction the catalyst can be removed by washing with water or after recrystallization from the corresponding alcohol.

The homogenity of the novel compounds was proved by means of thin layer chromatography, R_f-values being 0.50 (**1**) and 0.75 (**2**). The product of the addition of diethyl phosphite to the same Schiff base had an R_f-value of 0.57[9], *i.e.* an increase of the R_f-values of the compounds with the increase of the size of the alkoxygroups takes place.



R = CH_3 (1), *i*-C_3H_7 (2)

SCHEME 1

The composition and structure of compounds **1** and **2** were established on the basis of elemental analysis data and IR-, ^{1}H- and ^{31}P-NMR spectroscopic studies. The P- and N-analyses revealed that the addition of dialkyl phosphites concerns both C=N bonds of the Schiff base.

The assignment of the IR spectra of **1** and **2** is in accordance with literature data for similar compounds[12–14].

The ambiguity in the literature data about the formation mechanism of the target products of the addition of dialkyl phosphites to Schiff bases[5,11,15–17] required a more detailed study of the structure of the novel compounds analysing their ^{1}H- and ^{31}P-NMR spectra.

In the ^{31}P-NMR spectra of the compounds single signals are present in the region characteristic for a phosphonate phosphorus atom. In the ^{1}H-NMR spectra of the reaction products, no signal at 8.29 ppm (s), assignable to the methine (CH=N) proton of the starting Schiff base was observed. In the proton spectra of the compounds, taken in $CDCl_3$, resonance signals of CH(P)-fragment were registered: doublet of doublets for **1** and doublet of **2** (Figure 1 a, b). Furthermore, the doublet of **2** appeared in the range of the multiplet signal of the POCH-proton (Figure Ib). The broad singlet signals shown in Figure 1 a, b were ascribed to the protons of the secondary NH-groups of **1** and **2**. In the spectra of **1** and **2**, registered after D_2O-exchange, the signals of NH-protons disappeared and the CH(P)-protons gave doublet signals (Figure 1 c, d).

In the ^{1}H-NMR spectra of the compounds, measured in DMSO-d_6, the resonance signals of the CH(P)- and NH-fragments were down-field shifted and appeared as doublets of doublets, *i.e.* the splitting of the NH-signal was also

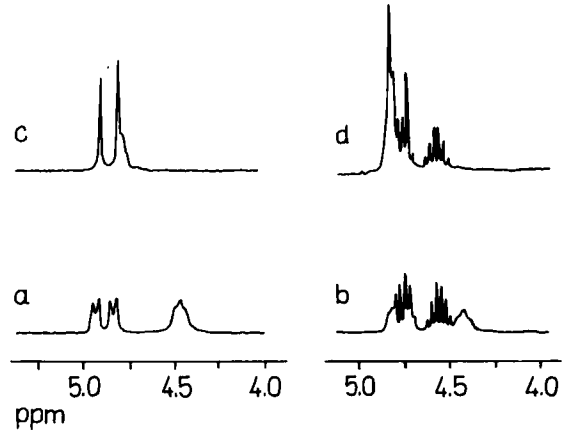


FIGURE 1 ^{1}H-NMR spectra of the compounds: a), b) **1** and **2** respectively in $CDCl_3$; c), d) **1** and **2** respectively—in $CDCl_3$, D_2O.

registered (Figure 2a, 3a). It is evident that the couple of doublets of doublets in the spectra of **1** and **2** are due to coupling of the proton in: i) the CH(P)-fragment to both the phosphorus and the imino proton, and ii) the NH-group to both the phosphorus and the CH(P)-proton. Coupling between the amino proton and the proton at the α-C-atom has been registered for some aminophosphines[18], aminophosphonates[19], ammonium salts[20] and N-substituted aliphatic and aliphato-aromatic amines[21–23].

After partial D_2O-exchange the NH-signal appeared as doublet of doublets with decreased intensity as compared to that before the exchange. The CH(P)-proton gave two types of signals: together with the doublet of doublets, one more doublet signal was observed (Figures 2b, 3b). This occurs because the deuteroexchange is not complete.

Earlier[9] we described an addition product of the same Schiff base and diethyl phosphite. The ^{1}H-NMR spectrum of this compound was now re-examined, indicating analogous features. In $CDCl_3$ solution: CH(P), δ = 4.84 ppm (dd), $^2J_{CHP}$ = 23.86 Hz, $^3J_{CHNH}$ = 9.25 Hz; NH, δ = 4.43 ppm (br. s). In DMSO-d_6: CH(P), δ = 5.07 ppm (dd), $^2J_{CHP}$ = 24.18 Hz, $^3J_{CHNH}$ = 10.37 Hz; NH, δ = 5.77 ppm (dd), $^3J_{NHCH}$ = 10.24 Hz, $^3J_{NHP}$ = 4.66 Hz.

A common NMR-feature of the three addition products of dialkyl phosphites and bis[4-(furfurylidene amino)phenyl]methane is the coupling registered between the protons at N- and α-C-atom. The coupling constants $^3J_{CHNH}$ measured in DMSO-d_6 were approximately equal for the three compounds ($^3J_{CHNH} \approx 10$

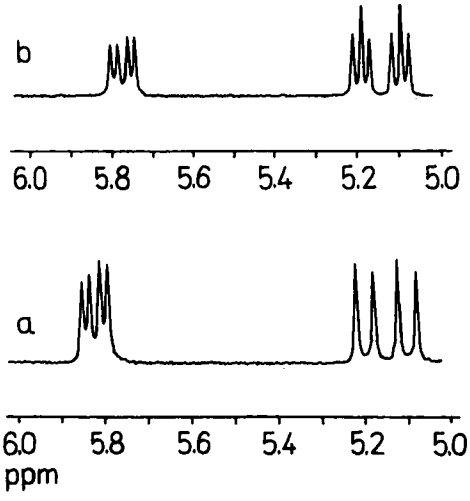


FIGURE 2 ^{1}H-NMR spectra of compound **1**: a) in DMSO-d_6; b) in DMSO-d_6, D_2O.

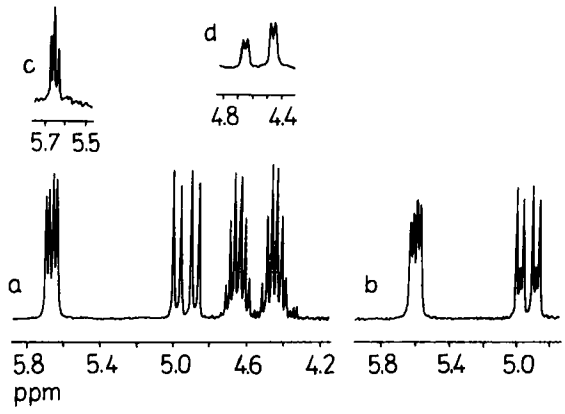


FIGURE 3 ^{1}H-NMR spectra of compound **2**: a) in DMSO-d_6; b) in DMSO-d_6, D_2O; c), d) spin-decoupling of CH(P) and CH_3 respectively.

Hz), because of the equal surrounding of the nitrogen atom[21]. The multiplicity of the signals indicates the presence of a secondary amino group. This is one more evidence in favor of the structure proposed for the compounds.

Figure 3c, d represent the results of spin-decoupling for compound **2**. Irradiation on the CH(P)-proton does not lead to a total decoupling with NH-protons because of the insufficient difference in chemical shifts (0.74 ppm). Thus the shape of the NH-signal is changed (Figure 3c). After irradiation of CH_3-protons (four doublets in the range of 1.3 to 0.9 ppm) the two multiplets of POCH-fragment centered at 4.65 and 4.45 ppm disappeared. A couple of doublets arose, allowing to calculate the coupling constant of the proton of the fragment mentioned and the ^{31}P-nucleus (Figure 3d).

The observed chemical shift non-equivalence of the CH_3O-groups in **1** is obviously due to the presence of a chiral center. By the same reason the CH-protons of the isopropoxy fragments of **2** give also two signals (Figure 3a, d). The CH_3-groups of these fragments give, however, four signals. This is an example of "double non-equivalence" in the presence of a chiral atom and three prochiral centers (the P-atom and the two secondary isopropyl carbons)[24,25]. The four CH_3-groups in **2** have different environments, they are diastereotopic and anisochronous. Moreover, the fast rotation around the O-$CH(CH_3)_2$-bond would not remove their non-equivalence[26].

The chemical shifts and coupling constants of the protons of the molecular fragments confirm the structure suggested for compounds **1** and **2**. The ratio between the integrals of the signals is as expected. When keeping **1** and **2** for a

long time at normal conditions, no change in the spectra *i.e.* in the structure of the substances was observed. This does also not occur after purification procedures (water washing or recrystallization from ethanol).

EXPERIMENTAL

Starting compounds: Dialkyl phosphites (Fluka, purum) purified by distillation, *i.e.* dimethyl phosphite, b.p. 56°C/3 mmHg, n_D^{20} = 1.4039; diisopropyl phosphite, b.p. 91°C/20 mmHg, n_D^{20} = 1.4090; Schiff base—bis[4-(furfurylidene amino)phenyl]methane, m.p. 94°C, prepared according to Ref. 27. The melting of the compounds was examined 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 WM-250 spectrometer operating at 250.13 MHz in FT mode at room temperature. DMSO-d_6 and $CDCl_3$ as solvents and TMS as internal standard were used. ^{31}P-NMR-spectra were registered on a Bruker WM-250 spectrometer in $CDCl_3$ applying 85% H_3PO_4 as external standard. TLC were performed on Kieselgel-60 F_{254} plastic sheets (Merck). The samples were applied as CH_3OH solutions. The chromatograms were developed ascendingly using the ethylacetate—tetrahydofyran—methanol (12:3:1) solvent system. The spots were detected under UV light and in iodine vapours.

4,4'-Bis[N-methyl(dimethoxyphosphonyl)-1-(2-furyl)]diaminodiphenylmethane (1): Bis[4-(furfurylidene amino)phenyl]methane (4.72 g, 0.0133 mol) and dimethyl phosphite (3.82 g, 0.0347 mol) were mixed in a flask equipped with a mechanical stirrer, reflux condenser, thermometer, an argon inlet and a dropping funnel. A saturated methanolic CH_3ONa solution was added dropwise with stirring until exothermicity ceased. Stirring was continued for an hour at ambient temperature. The reaction mixture was distilled under vacuum to remove the methanol and unreacted dimethyl phosphite. After water washing and filtering a white precipitate was obtained and purified by recrystallization from ethanol. The product was dried *in vacuo* to constant weight. Yield: 65.3% (5.00 g); m.p. 216°C.

Analysis: Calcd. for $C_{27}H_{32}O_8N_2P_2$: N, 4.88%; P, 10.80%. Found: N, 4.62%; P, 10.41%.

IR (KBr-disk), $\tilde{\nu}$(cm^{-1}): 775, 890, 965, 1535—furan ring; 1040—C-O-C moiety; 1256—ν(P=O); 1187—ν(P-OCH$_3$); 3230—ν(NH).

^{31}P-NMR (in $CDCl_3$), δ(ppm): 22.16.

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

TABLE I ^{1}H-NMR parameters of compounds **1** and **2**

Chemical shifts, δ(ppm)										*Coupling constants, J(Hz)*					
Cmpd.	*Solvent*	*CH_3*	*CH*	*CH(P)*	*NH*	*CH_2*	*$H_{\beta,\gamma}$ (Furan)*	*H_δ (Furan)*	*C_6H_4*	*^3J ($CHCH_3$)*	*^3J (POCH)*	*^2J (CHP)*	*^3J (CHNH)*	*^3J (NHCH)*	
	DMSO-d_6	3.67(d)		5.15(dd)	5.82(dd)	3.57(s)	6.41(m)	7.59(m)	6.78(m)		10.60	24.26	10.33	10.39	
		3.57(d)									10.62				
	$CDCl_3$	3.81(d)		4.88(dd)	4.47(s,br)	3.71(s)	6.35(m)	7.39(m)	6.76(m)		10.59	24.03	8.54		
		3.62(d)									10.64				
	DMSO-d_6	1.23(d)	4.65(m)	4.93(dd)	5.67(dd)	3.56(s)	6.39(m)	7.56(m)	6.77(m)	6.28	7.30	24.51	10.26	10.35	
		1.20(d)	4.45(m)							6.24	7.48				
		1.14(d)								6.18					
		1.01(d)								6.18					
	$CDCl_3$	1.32(d)	4.77(m)	4.77(d)	4.42(s, br)	3.71(s)	6.32(m)	7.35(m)	6.74(m)	6.17		24.37			
		1.29(d)	4.56(m)							6.21					
		1.24(d)								6.20					
		1.05(d)								6.20					

4,4'-Bis[N-methyl(diisopropoxyphosphonyl)-1-(2-furyl)]diaminodiphenylmethane (2): This was prepared similarly by reaction of diisopropyl phosphite (1.89 g, 0.0114 mol) and bis[4-(furfurylidene amino)phenyl]methane (1.55 g, 0.0044 mol) in 2-propanol (60 ml). i-C_3H_7ONa was used as a catalyst. The reaction mixture was stirred for 4 hours at ambient temperature and a yellow precipitate was obtained in a good yield. The crude product (2.67 g, 88.6%) was purified by recrystallization from 2-propanol and dried to constant weight *in vacuo*. Yield: 73.0% (2.20 g); m.p. 191°C. Analysis: Calcd. for $C_{35}H_{48}O_8N_2P_2$: N, 4.08%; P, 9.04. Found: N, 4.13%; P, 9.20%.

IR (KBr-disk), $\tilde{\nu}(cm^{-1})$: 775, 965, 990, 1535—furan ring; 1030—C-O-C moiety; 1248—ν(P=O); 1185—ν(P-OC_3H_7-i); 3230—ν(NH).

^{31}P-NMR (in $CDCl_3$), δ(ppm): 18.47.

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

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