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Reactions of dialkyl phosphonates and phosphinates with bis(benzylideneimino)toluene

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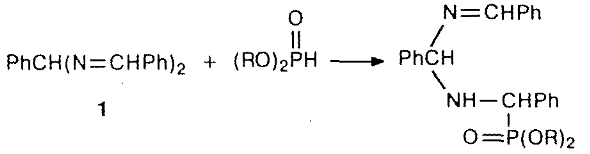
Dialkyl phosphonates bind to the C=N bond of bis(benzylideneimino)toluene, with formation of dialkyl (benzylideneimino)benzylaminobenzyl phosphonates. The complicated character of IR spectra of these compounds is connected with the possibility of formation of dimeric cyclic associates and intramolecular hydrogen bonding. Phosphinic acid reacts with bis(benzylidenimino)toluene in a 2 : 1 ratio to afford *N,N'*-benzylidenebis(α-aminobenzylphosphonic) acid.

Key words: dialkyl phosphonates; phosphinic acid; dialkyl (benzylideneimino)benzylaminobenzyl phosphonates, hydrogen bond.

Previously,[1] it was shown that dialkyl phosphonates attach to *N,N'*-dibenzylideneazine at one of the two C=N bonds at ~20 °C. For this reason, it was appropriate to introduce into this reaction the compounds containing two isolated C=N bonds.

Reactions of dialkyl phosphonates and phosphinates with bis(benzylidenimino)toluene (**1**) are described in this work.

Dialkyl phosphonates add only to one of the two C=N bonds of compound **1** at 20 °C to form dialkyl (benzylideneimino)benzylaminobenzyl phosphonates **2—4**.



1 **2—4**

R = Et (**2**), Pr (**3**), Bu (**4**)

The resulting amino phosphonates are transparent viscous liquids. They decompose into the initial compounds upon heating. Their main physicochemical parameters are presented in Table 1, and their spectral characteristics are shown in Table 2.

Table 2 does not contain the frequencies of NH bond stretching vibrations, whose identification is important to confirm the structures of the compounds obtained, but in fact it is a rather complicated task. IR spectra of the pure substances (films and pellets with KBr) contain only several very weak diffuse bands in the frequency range of ν(NH) higher than 3000 cm^{-1} (Fig. 1). At the same time, a well pronounced absorption maximum at 3393 cm^{-1} is registered in the IR spectra of the solutions of amino phosphonates in CCl_4. This absorption characterizes the stretching vibrations of the NH group. We assigned less intense low-frequency components manifesting themselves additionally at 3327 and 3267 cm^{-1} to ν(NH) of conformers with intramolecular hydrogen bond and an overtone of stretching vibrations of the C=N group, respectively.[2] The absence of pronounced absorption bands ν(NH) in the IR spectra of amines and their derivatives

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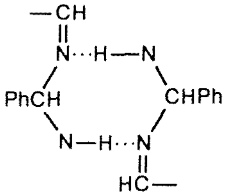
Table 1. The main physicochemical parameters of aminophosphonates **2**—**4**

Compound	Yield (%)	n_D^{20}	d_4^{20}	Found/Calculated (%) N	Found/Calculated (%) P	Molecular formula
2	90.0	1.1416	1.5458	6.42 6.44	7.10 6.86	$C_{25}H_{29}N_2O_3P$
3	97.0	1.1035	1.5415	6.13 6.03	6.67 6.51	$C_{27}H_{33}N_2O_3P$
4	100.0	1.0730	1.5270	5.72 5.68	6.28 5.99	$C_{29}H_{37}N_2O_3P$

was also observed earlier.[3] In our opinion, this is explained by the existence of strong hydrogen bonds, resulting in a shift of ν(NH) band to the range of the CH bond stretching vibrations and masking by them. The analysis of the available data allowed us to conclude that a cyclodimerization of molecules occurs in pure solvents as a result of intermolecular hydrogen bonding, as takes place, for example, with amidines.[4]



The ^1H NMR spectrum of compound **3** has a doublet at 5.08 ppm (CHP, ^2J = 18.31 Hz), quadruplet at 3.93 ppm ($POCH_2$, ^3J = 20.14 Hz), and two multiplets within the 1.49—1.65 and 0.81—0.95 ppm ranges (CH_2 and CH_3, respectively). A doublet at 8.55 ppm (^4J = 4.88 Hz) corresponds to the methine proton at a multiple bond. One would expect that cyclic phosphonate **5** will be a product of the interaction between diimine **1** and phosphinic acid. Instead, *N,N'*-benzylidenebis(α-aminobenzylphosphinic) acid (**6**) was isolated as a result of the exothermic reaction (ratio of reagents 1 : 1) (Scheme 1).

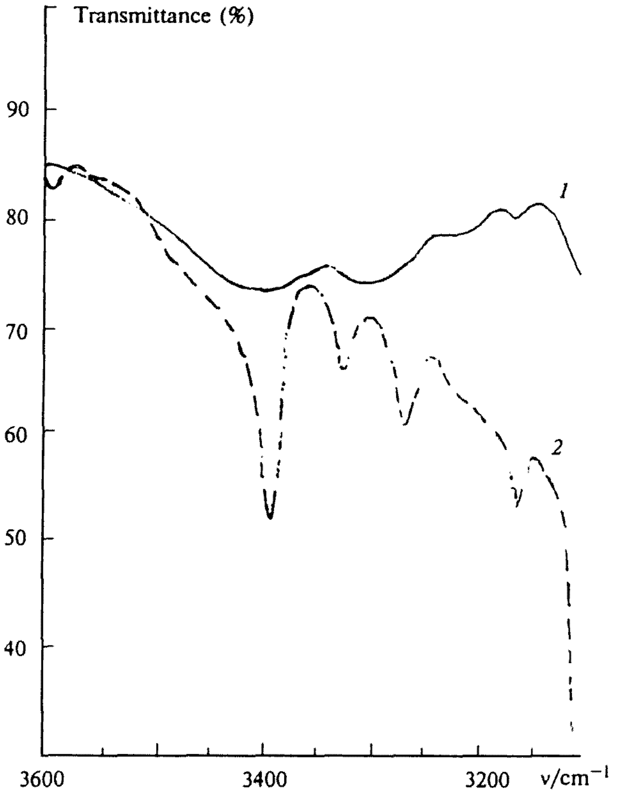


Fig. 1. IR spectrum of dipropyl (benzylideneamino)benzylaminobenzyl phosphonate **3** in liquid phase (*1*) and in solution in CCl_4 (*2*).

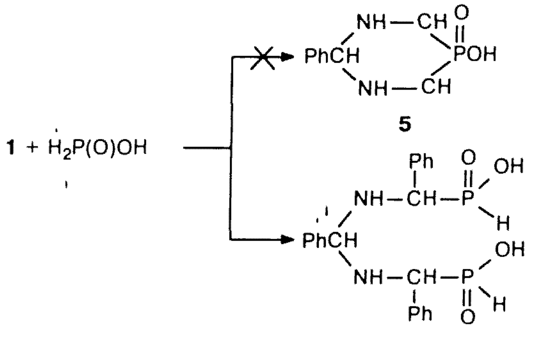
The structure of compound **6** is confirmed by the presence of ν(NH) and ν(OH) absorption bands in its IR spectrum in the 3600—2000 cm^{-1} range with the main maximum at ~3000 cm^{-1} (see Ref. 2), and those for ν(PH) at 2344 cm^{-1}, as well as bands corresponding to the vibrations of aromatic fragments (1599, 1495, 760, and 698 cm^{-1}).[5,6]

Table 2. Spectral characteristics of compounds **2**—**4**

Compound	IR, ν/cm⁻¹ ν(C=N)	ν(CH)*	ν(C=C)*	γ(CH)*, δ(CC)*	ν(P=O)	ν(P—O)	^{31}P NMR, δ
2	1637m	3086 w 3063 w 3031 w	1602 w 1581 w 1494 w	758 m 698 m	1252 s	1054 vs 1028 vs 965 s	20
3	1638 m	3086 сл 3065 w 3032 w	1602 w 1581 w 1494 w	756 m 647 m	1251 s	1066 vs 998 vs	20
4	1638 m	3086 w 3062 w 3031 w	1602 w 1581 w 1494 w	756 m 607 m	1253 s	1066 vs 1032 vs 981 vs	20

*The vibrations of the phenyl groups.

Scheme 1



Experimental

IR spectra of compounds **2**—**4** were recorded in the films placed between KBr plates, and IR spectra of crystal compound **6** were recorded in pellets with KBr on a Bruker IFS-113v IR-FT-spectrometer in the 4000—400 cm^{-1} range (resolution is 1 cm^{-1}).

^{31}P NMR spectra were recorded on an NMR KGU-4 instrument (10.2 MHz) with 85 % H_2SO_4 as standard. ^{31}P NMR spectrum of compound **6** was obtained on a Bruker CXP-100 instrument (34.48 MHz) in CH_2Cl_2. The ^1H NMR spectrum was recorded on a Bruker WM-250 spectrometer (250.13 MHz) in $(CD_3)_2CO$.

Bis(benzylideneimino)toluene (1). A mixture of freshly distilled benzaldehyde (21.5 g) and 15 % aqueous ammonia (30 mL) was allowed to stand at ~20 °C for 2 days. The product was filtered off, washed with water, and then recrystallized from ethanol. Compound **1** (17 g, 85 %) was obtained; m.p. 110 °C.[7]

Reaction of bis(benzylideneimino)toluene with dialkyl phosphonates. A mixture of compound **1** (0.01 mol) and dialkyl phosphites (0.025 mol) was heated in a vial at 90 °C for 1 h and allowed to stand at ~20 °C for 10 days. The excess of the initial ester as well as the rest of compound **1** which did not enter into the reaction was removed *in vacuo* at 70—90 °C (0.006 Torr). Dialkyl (benzylideneimino)benzylaminobenzyl phosphonates **2**—**4** were obtained; their constants and spectral characteristics are presented in Tables 1 and 2, respectively.

***N,N'*-benzylidenebis(α-aminobenzylphosphinic) acid (6).** Phosphinic acid (0.66 g) was added to a solution of bis(benzylideneimino)toluene (3 g) in 15 mL of anhydrous benzene under argon. Anhydrous CH_2Cl_2 (6 mL) and anhydrous ethanol (10 mL) were added to the resulting emulsion. Crystals precipitated were filtered off and washed with ether and anhydrous acetone. *N,N'*-benzylidenebis(α-aminobenzylphosphinic) acid (1.5 g, 70 %) was obtained, m.p. 129—131 °C. ^{31}P NMR, δ: 19.83 (s).

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