Reaction of dialkyl H-phosphonates with azines and 1,2-bis(*tert*-butylimino)ethane

A. N. Pudovik,* R. R. Shagidullin, V. K. Khairullin, I. I. Vandyukova, A. V. Chernova, A. M. Kibardin, and M. A. Pudovik

A. E. Arbuzov Institute of Organic and Phyzical Chemistry, Kazan' Scientific Center of the Russian Academy of Sciences,
8 ul. Akad. Arbuzova, 420083 Kazan', Russian Federation.
Fax: +7 (843 2) 75 2253

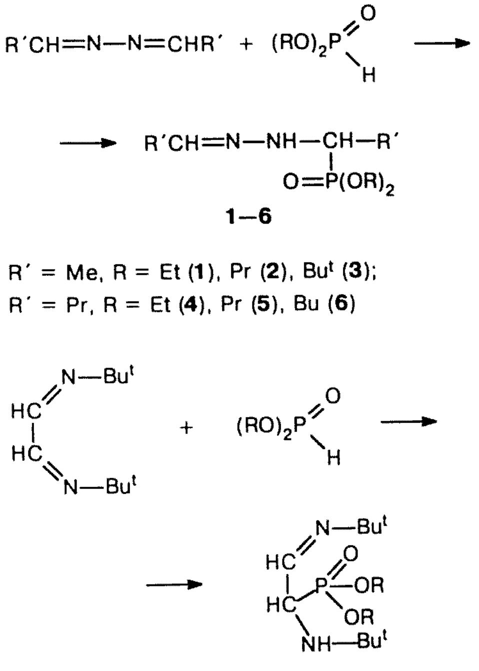
Acetaldehyde and butyraldehyde azines and 1,2-bis(*tert*-butylimino)ethane add only one molecule of dialkyl H-phosphonate at room temperature to form alkyl (α-aminoalkyl)phosphonates. IR spectra of compounds obtained are discussed.

Key words: dialkyl H-phosphonates, IR spectra, 1,2-bis(*tert*-butylimino)ethane, aldehyde azines.

Dialkyl H-phosphonates react smoothly with benzaldehyde azine to give alkyl α-aminobenzylphosphonates.[1] The reaction of aliphatic-aromatic azomethines with dialkyl H-phosphonates yields alkyl aminophosphonates.[2]

In this work, we describe the reaction of dialkyl H-phosphonates with acetaldehyde and butyraldehyde azines (AA and BA) and with 1,2-bis(*tert*-butylimino)ethane (BBE). Only one molecule of dialkyl H-phosphonate adds to these compounds at room temperature (Scheme 1).

Scheme 1



1—6

R' = Me, R = Et (**1**), Pr (**2**), Bu^t (**3**);
R' = Pr, R = Et (**4**), Pr (**5**), Bu (**6**)

7—9

R = Et (**7**), Pr (**8**), Bu (**9**)

The adducts formed (Table 1) are transparent viscous substances. During distillation even under high vacuum, they partly decompose to the initial compounds and other organophosphorus products with δ_P 16 and 10. The products were purified by high-vacuum distillation of excess dialkyl H-phosphonate and unreacted initial azine upon gentle heating.

In addition to the well known absorption peaks at 3000 (νCH_n), 1460 ($\delta_{as}CH_n$), and 1370 (δ_s Me) cm^{-1}, the IR spectra of compounds **1—9** contain bands corresponding to the functional groups present in the molecules of the compounds studied (Table 2).[3,4]

The NH group in compounds **1—9** can be involved in both intermolecular and intramolecular hydrogen bonds with marked proton acceptors such as phosphoryl groups, nitrogen atoms, or multiple bonds. It is this diversity of possibilities in the liquid phase that apparently accounts for the broadening of the νNH bands noted in Table 2. It can also be mentioned that the νP=O absorption frequency is too low for this particular environment of the phosphorus atom, which should also be attributed to the existence of an H-bond.

Experimental

^{31}P NMR spectra were obtained on a YaMR KGU-4 instrument operating at 10.2 MHz. 85 % H_3PO_4 was used as the external standard. IR spectra were recorded on a Bruker IFS-113V FTIR spectrometer (KBr).

Diethyl α-(ethylidenehydrazino)ethyl phosphonate (1). AA (0.02 mol) and diethyl H-phosphonate (0.025 mol) were placed in an NMR tube filled with argon. The tube was sealed and kept at room temperature for 30 days until the intensity of the ^{31}P NMR signal corresponding to the phosphonate no longer increased and that of the signal for diethyl H-phosphonate no longer decreased. Excess diethyl H-phosphonate and unreacted AA were distilled off from the reaction mixture at a bath temperature of 50—55 °C and a residual pressure of 0.01 Torr.

Translated from *Izvestiya Akademii Nauk. Seriya Khimicheskaya,* No. 8, pp. 2063—2065, August, 1996.

Table 1. Properties of dialkyl α-(alkylidenehydrazino)alkylphosphonates **1—6** and dialkyl α-(*tert*-butylamino)-β-(*tert*-butylimino)ethylphosphonates **7—9**

Compound	Yield (%)	d_4^{20}	n_D^{20}	^{31}P NMR, δ_P	Found / Calculated (%)		Molecular formula
					N	P	
1	61.0	1.1089	1.4750	28	12.37 12.60	13.96 13.94	$C_8H_{19}N_2O_3P$
2	44.5	1.0600	1.4735	28	11.28 11.19	12.60 12.38	$C_{10}H_{23}N_2O_3P$
3	49.8	1.0320	1.4696	28	9.88 10.06	11.40 11.13	$C_{12}H_{27}N_2O_3P$
4	64.0	1.0097*	1.4640*	26	9.92 10.06	10.86 11.13	$C_{12}H_{27}N_2O_3P$
5	51.4	0.9985*	1.4600*	28	9.02 9.14	10.17 10.11	$C_{14}H_{31}N_2O_3P$
6	56.5	0.9875*	1.4575*	28	8.21 8.38	9.44 9.26	$C_{16}H_{35}N_2O_3P$
7	59.0	1.0212	1.4680	24	9.01 9.14	9.78 10.11	$C_{14}H_{31}N_2O_3P$
8	91.0	1.0022	1.4665	24	8.15 8.38	8.64 9.26	$C_{16}H_{35}N_2O_3P$
9	66.0	0.9802	1.4670	23	7.50 7.73	8.30 8.54	$C_{18}H_{39}N_2O_3P$

* At 16 °C.

Table 2. Characteristic frequencies of the IR absorption maxima (ν/cm^{-1}) of the functional groups in molecules **1—9**

Compound	νNH	νC=N	νP=O	νP—OR
1	3241 w, br	1631 w	1232 s	1056 vs, 1031 vs, 968 s
2	3230 w, br	1631 w	1226 s	1014 vs, 998 vs
3	3245 w, br	1633 w	1254 s	1067 s, 1026 s, 977 vs
4	3240 m, br	1630 w	1237 s	1060 vs, 1040 vs, 970 s
5	3240 w, br	1635 w	1235 s	1070 s, 1007 vs
6	3245 m, br	1630 w	1242 s	1073 s, 1033 vs, 989 vs
7	3316 w, br	1629 s	1225 vs	1055 vs, 1035 vs, 953 vs
8	3317 w, br	1629 s	1229 vs	1067 vs, 1029 vs, 973 vs
9	3299 w, br	1627 s	1224 vs	1067 vs, 993 vs

This gave compound **1** as the residue. Compounds **2**, **3**. and dialkyl α-(butylidenehydrazino)butyl phosphonates **4—6** were prepared in a similar way. Characteristics of these compounds and the ^{31}P NMR spectral data are presented in Table 1, and the IR spectral data are listed in Table 2.

Diethyl α-(*tert*-butylamino)-β-(*tert*-butylimino)ethylphosphonate (7). BBE (0.01 mol) and diethyl H-phosphonate (0.02 mol) were placed in an NMR tube filled with argon, and the tube was sealed. After storing the tube for 18 days at room temperature, excess diethyl H-phosphonate and unreacted BBE were distilled off at a bath temperature of 50—60 °C and a residual pressure of 0.008 Torr. Compounds **8** and **9** were prepared in a similar way. Characteristics of these compounds and the ^{31}P NMR spectral data are presented in Table 1, and the IR spectral data are listed in Table 2.

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Received January 12, 1996