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LETTERS TO THE EDITOR

Reaction of 4-Oxo-5,6-benzo-1,3,2-dioxaphosphinin-2-yl Isocyanate with Dialkyl Arylcarbonylphosphonates

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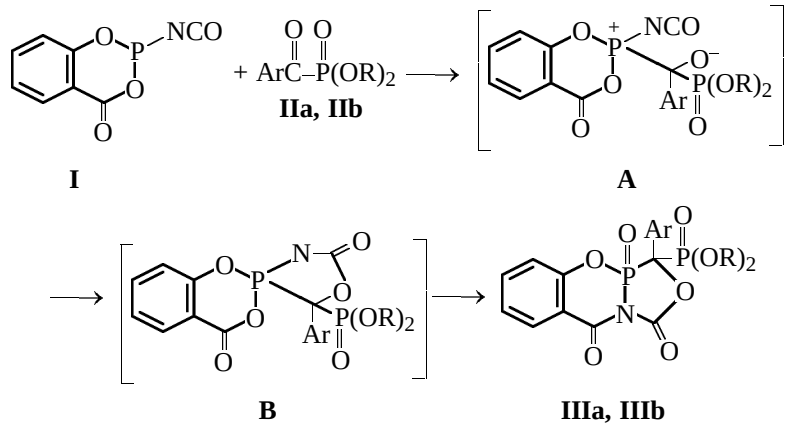
4-Oxo-5,6-benzo-1,3,2-dioxaphosphinin-2-yl isocyanate (**I**) ("salicyl isocyanatophosphite"), which contains both exo- and endocyclic carbonyl groups, can enter reactions with carbonyl compounds, involving the isocyanate group and yielding spirophosphoranes and diazadiphosphetidines, (2) involving the endocyclic carbonyl group and yielding ring-expansion products (6,7-benzo-1,3,2-dioxaphosphepines) [1], or (3) involving both functionalities and yielding phosphabicyclononanes with phosphorus–oxygen and phosphorus–nitrogen bonds [2].

Here we report for the first time that phosphite **I** can react with dialkyl arylcarbonylphosphonates **II** (80°C, 8 h, C_6H_6) to give cyclic compounds, viz. substituted phosphabicyclononanes **III** with a phosphorus–carbon bond. The cyclization process involving the isocyanate group probably occurs at the stage of formation of dipolar ion **A** by attack of the phosphorus atom of phosphite **I** on the electropilic center of phosphonate **II** (carbonyl carbon atom). Intermediate phosphimine **B** further undergoes the iminophosphonate–amidophosphonate rearrangement to give final product **III**.



Ar = *n*-ClC_6H_4 (**a**), 1-naphthyl (**b**); R = Et (**a**), Me (**b**).

The structures of the substituted phosphabicyclononanes were proved by physicochemical methods. The $^{31}P–\{^1H\}$ NMR spectra contain two doublets at δ_P 8–10 and 11–13 ppm, characteristic of phosphonate phosphorus atoms. The stereoselectivity of the process is quite high (diastereomeric ratio 9 : 1). The ^{13}C NMR spectra contain double sets of signals of carbon atoms of the same kind, implying formation of two diastereomers, while the presence of a doubled doublet at 82.15–82.18 ppm with expected coupling constants

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($^1J_{PC}$ 153.0–153.7 and 110.3–110.9 Hz) provide unequivocal evidence for the formation of a P–S–P fragment.

7-(*p*-Chlorophenyl)-2-(diethoxyphosphinoyl)-1-aza-3,4-benzo-5,8-dioxa-6-phosphabicyclo[4.2.0]-nonane-2,6,9-trione (IIIa). A mixture of 4.26 g of phosphite **I**, 5.64 g of diethyl (*p*-chlorophenylcarbonyl)phosphonate (**IIa**), and 10 ml of benzene was heated at 80°C for 8 h under dry argon. The reaction mixture was reprecipitated into pentane to isolate 6.93 g (70%) of compound **IIIa**, mp 164–166°C. IR spectrum, ν, cm^{-1}: 2965, 1835, 1720, 1660, 1605, 1490, 1455, 1370, 1310, 1285, 1255, 1205, 1170, 1115, 1090, 1040, 1010, 980, 940, 865, 820, 755, 720. $^{31}P–\{^1H\}$ NMR spectrum (CH_2Cl_2), δ_P, ppm (*J*, Hz): 12.87 and 8.88 d.d ($^2J_{PCP}$ 12.7), d_2, 22%; 11.40 and 9.72 d.d ($^2J_{PCP}$ 20.4), d_1, 78%. Found, %: C 46.80; H 3.60; P 12.50. $C_{19}H_{18}ClNO_8P_2$. Calculated, %: C 46.96; H 3.70; P 12.77.

7-(Dimethoxyphosphinoyl)-7-naphthyl-1-aza-3,4-benzo-5,8-dioxa-6-phosphabicyclo[4.2.0]-nonane-2,6,9-trione (IIIb) was obtained similarly to compound **IIIa** from 4.93 g of phosphite **I** and 6.23 g of dimethyl (naphthylcarbonyl)phosphonate (**IIb**). Yield 6.74 g (60%), mp 174–176°C. IR spectrum, ν, cm^{-1}: 2960, 2930, 1835, 1720, 1675, 1612, 1515, 1460, 1400, 1380, 1345, 1315, 1300, 1225, 1185, 1160, 1120, 1090, 1065, 1030, 970, 950, 898, 880, 775, 760. $^{31}P–\{^1H\}$ NMR spectrum (DMSO-d_6), δ_P, ppm (*J*, Hz): 9.42 and 17.0 d.d ($^2J_{PCP}$ 22.8). Found, %: C 53.33; H 3.71; P 12.92. $C_{21}H_{17}NO_8P_2$. Calculated, %: C 53.28; H 3.59; P 13.10.

The IR spectra were obtained on a Specord M-80 spectrometer in Vaseline oil. The NMR spectra were measured on Varian Unity-300 ($^{31}P–\{^1H\}$, 121.42 MHz) and Bruker MSL-400 (^{13}C, $^{13}C–\{^1H\}$, 100.6 MHz) spectrometer against internal HMDS and external H_3PO_4.

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