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LETTERS TO THE EDITOR

Acid-catalyzed Condensation of 2-Oxoazepan with Dimethyl Hydrogen Phosphite and Formaldehyde

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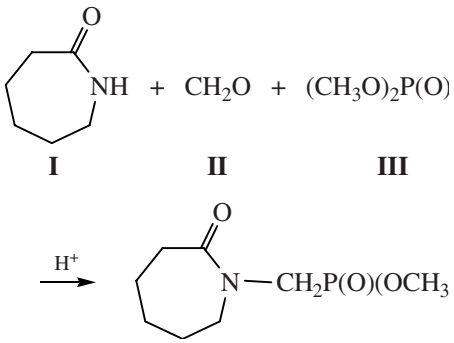
Amines, aldehydes and dialkyl hydrogen phosphites are known to enter to the Kabachnik–Fields reaction to form aminoalkylphosphonates [1].

We found that azepan-2-one (**I**) reacts with formaldehyde (**II**) and dimethyl hydrogen phosphite (**III**) under the conditions of acid catalysis to form *N*-(dimethoxyphosphinoylmethyl)azepan-2-one (**IV**).

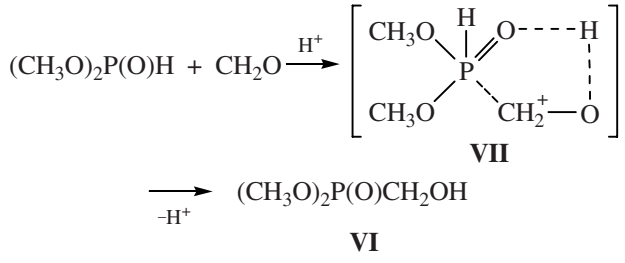


The reaction is performed at an equimolar reagent ratio in aqueous medium in the presence of catalytic amonus of sulfuric acid at 60°C for 2 h. The yield of the reaction product is 75–80%. The structure of compound **IV** is evidenced by its IR and ^{1}H NMR spectra. The IR spectrum contains the following characteristic absorption bands, cm^{-1}: ν(C=O) 1618 [amide **I**; 1660 in **I**], amide **II** 1486, ν(P=O) 1320, and ν(P–O–CH$_3$) 1186 cm^{-1}.

The ^{1}H NMR spectrum (in D$_2$O) contains signals of the following proton groups, δ, ppm: 3.34 d (OCH$_3$), 3.69 t (CH$_2$–P), 2.36 t [CH$_2$C(O)–], 3.20 s (–CH$_2$N–), 1.57 m (β-CH$_2$), 1.29 m (γ-CH$_2$) (the latter four signals rrelate to ε-lactam ring). These data were compared with a theoretical ^{1}H NMR spectrum simulated by means Chemoffice Ultra 2004 v8.0.

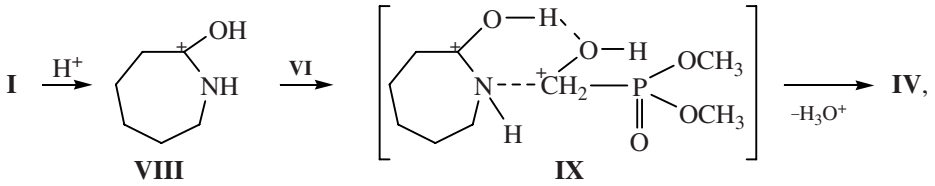
The contents of nitrogen and phosphorus in compound **IV** corresponds to its empirical formula.

The electronic structure of the starting, intermediate, and final compounds was studied by MNDO calcualtions with the Dewar and Thiel parameters [2]. As follows from the calculations, the most probable reaction pathway involves initial formation of (dimethoxyphosphinoyl)methanol (**VI**). Energetically, the most advantageous participant of the acid-catalyzed reaction is a five-coordinate phosphorus phosphite structure that forms with **II** an energetically favorable transition state **VII**.



The formation of transition state **VII** decreases the total energy by 210.34 kJ mol^{-1}. The total energy of phosphorus-containing alcohol **VI** is 0.34% lower than that of complex **VII**.

Phosphorylated alcohol **VI** then reacts with the protonated form of cyclic amide **VIII**, affording a six-membered transition state **IX**.



IX → **IV** + H_3O^+.

According to [3], the protonation of **I** at the carbonyl oxygen to form cation **VIII** is energetically equally probable with the protonation at the NH group. The energy gain in the reaction of alcohol **VI** with cation **VIII**, forming transition state **IX**, is –21.46 kJ mol^{-1}. This promotes reorganization of **IX** to final reaction product **IV**, which decreases the total energy by 4.4%.

***N*-(Dimethoxyphosphinoylmethyl)azepan-2-one (IV).** To 30 ml of distilled water, 10.0 g of azepan-2-one (**I**) and then 2.5 ml of 40% formaldehyde were added. Dimethyl hydrogen phosphine, 8.1 ml, containing a catalytic amount of sulfuric acid (1–2 drops) was then added in portions to the mixture at room temperature. When the temperature began to fall, the mixture was heated to 60°C and kept for 2 h. The water and unreacted starting compounds were removed in a vacuum (0.5 mm Hg) at 150°C. Yield 15.9–16.96 g (75–80%), n_D^{20} 1.4795, d_4^{20} 1.0208. Found, %: N 5.31; P 12.73. $C_9H_{18}NPO_4$. Calculated, %: N 5.96; P 13.2.

The ^1H NMR spectrum of compound **IV** in D_2O was registered on a Varian Mercury instrument at 300 MHz. The IR spectrum was recorded on a Specord M-82 instrument.

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