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Abstract

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ON THE STRUCTURE OF THE PRODUCT OF THE INTERACTION BETWEEN PHOSPHITE AND ETHANOLAMINE

(Presented by Academician B. A. Arbuzov on 31 VII 1964)

In February 1960, at the annual session of the Kazan Branch of the Academy of Sciences of the USSR, we reported on the results of a study of the reaction of phosphites with ethanolamine. Since our conclusions concerning the structure of the products of this reaction differ from the opinion of the author of a recently published work ([1]), we considered it necessary to publish them.

In the interaction of ethanolamine with triethyl phosphite, only two molecules of ethanolamine are required to displace from the latter three molecules of alcohol. This conclusion agrees with the result of Burgada ([1]). The experimental procedure was also analogous. Such a course of the reaction undoubtedly indicates the formation of a cyclic product with a five-membered ring. From three phosphites we obtained identical products:

$$\begin{array}{l} \mathrm{CH_2-O} \\ \quad | \quad \backslash \\ \mathrm{CH_2-NH\ \ P(OCH_2-CH_2NH_2).} \end{array}$$

An open chain of molecules may be represented in two variants with trivalent phosphorus:

$$\begin{array}{l} \mathrm{CH_2-O} \\ \quad | \quad \backslash \\ \mathrm{CH_2-NH\ \ POCH_2CH_2NH_2,} \end{array} \qquad \text{(A)}$$

$$\begin{array}{l} \mathrm{CH_2-O} \\ \quad | \quad \backslash \\ \mathrm{CH_2-NH\ \ PNHCH_2CH_2OH} \end{array} \qquad (\ )$$

or as an isomerized structure with pentavalent phosphorus:

$$\begin{array}{c} CH_2-O \quad O \\ | \quad \backslash \| \\ CH_2-NH \quad PCH_2CH_2NH_2. \end{array} \qquad (\ )$$

Determination of the molecular weight (calculated 150, found 144 and 149) and analysis give results corresponding to the empirical formula: $C_4H_{11}N_2O_2P$.

The qualitative reaction for a free amino group proved negative, which contradicts structures (A) and ( ). It was also not possible chemically to establish the presence of a free hydroxyl (formula).

Thus, the data given above did not make it possible to answer definitely the question of the structure of the product. Spectral methods were applied to elucidate it.

Figure 1 gives the infrared absorption spectra of the compound under discussion*: *a*—a suspension in Vaseline oil, *b*—a solution in benzene. As can readily be seen, the spectra contain no appreciable absorption bands in the region 1500-1700 cm^{-1}, where the deformation vibrations of NH_2 appear as intense maxima (2). The absence of this group in the molecule is also confirmed by the spectrum of solution *b*, in which, otherwise, two absorption peaks, ν_{as} and ν_s of NH_2, would have to be observed. Also in agreement with the chemical data cited above, spectrum *b* shows no signs of a hydroxyl group

Fig. 1

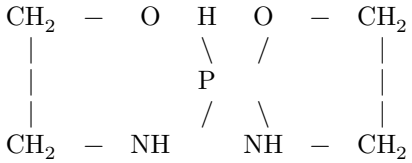
Fig. 1

(of an unassociated group, equal to 3600-3700 cm^{-1}). The intense broad absorption band at 3400 cm^{-1} in the spectrum of the solid sample *a*, in solution, on dilution, disappears, and in its place a narrow peak at 3474 cm^{-1} appears, which, according to its frequency, should be assigned to ν_{N-H} of an unassociated secondary amine group.

The band of considerable absorption in spectrum *a*, with a maximum at $\sim$ 2350 cm^{-1}, is noteworthy. In solution the maximum apparently shifts somewhat toward higher frequencies ($\sim$ 2370 cm^{-1}) and decreases in intensity. No group in (A), (B), or (C) has vibrational frequencies in this region. At the same time it is characteristic of the $P-H$ bond (2). Peaks corresponding to $P-H$ also appear in the NMR and PMR spectra.**

Thus, none of the structures presented (A, B, C) describes the structure of the product of the reaction of phosphites with ethanolamine. R. Burgada (1) assigned to it structure (A), although he also had at his disposal the IR spectrum of the compound, which he mentions but does not present or interpret.

On the basis of the results described, we believe that, in the final analysis, the reaction under discussion leads to double cyclization and that its product has a spiro structure:



with H − P and two P − O/P − N bonds as shown.

* The spectra were obtained on a UR-10 spectrophotometer with slit program 4. In spectrum (a), arrows indicate Vaseline bands; the dotted line in the spectrum corresponds to the absorption band of benzene itself. In the latter case the cuvette thickness was $d = 0.15$ mm; the concentration was not determined.

** The NMR spectrum was studied in the problem laboratory of Kazan University under the direction of Yu. Yu. Samitov, for which the authors express their deep gratitude.

A possible interpretation of the spectra in accordance with this structure (in the sense of the predominant participation of individual bonds and angles in vibrations of different frequency) is given in the spectrogram (a). Four bands, whose relative intensity and frequency decrease in the spectrum of the solution, are assigned to deformation vibrations of N–H and P–H because of their ability to form hydrogen bonds ($1425, 1316, 1139, 966$ cm^{-1} in the solid phase and $1397, 1304, 1127, 968$ cm^{-1}, respectively, in solution).

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CITED LITERATURE

[1] R. Burgada, *Ann. Chim.*, **8**, 347 (1963). [2] L. Bellamy, *Infrared Spectra of Complex Molecules*, IL, 1963, pp. 357, 454.

Note: Figure translations are in progress. See original paper for figures.