

Preliminary communication

THE TETRAAMIDODIPHOSPHINE MONOXIDE \rightleftharpoons PHOSPHORODIAMIDOUS ANHYDRIDE TAUTOMERISM

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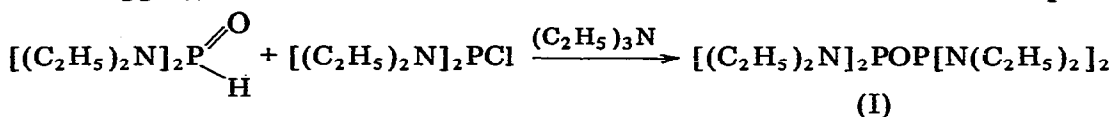
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Summary

Tautomerism in the system $\text{>P-O-P<} \rightleftharpoons \text{>P-P(=O)<}$ has been observed for the first time.

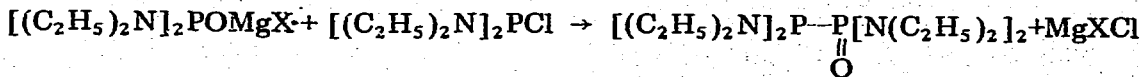
We have found that the compound $\text{R}_2\text{P(O)-P(NR}'_2)_2$ when treated under conditions identical to those used in the rearrangement found recently [1] gives, initially, the mixed anhydride $\text{R}_2\text{P-O-P(NR}'_2)_2$ which further isomerises to yield $\text{R}_2\text{P-P(O)(NR}'_2)$. This allows one to suppose that the (earlier unknown) phosphorodiamidous anhydrides $(\text{R}_2\text{N})_2\text{P-O-P(NR}_2)_2$ (I) may also rearrange to the isomeric monoxides $(\text{R}_2\text{N})_2\text{P-P(NR}_2)_2$ (II).

Phosphorotetraethyldiamidous acid condensed with phosphorotetraethyldiamidous chloride in the presence of triethylamine to give the anhydride I ($\delta(^{31}\text{P}) - 123.5$ ppm), which is stable for about two weeks at -2 to -4°C . If it is kept



for a longer time I starts rearranging to the monoxide II ($\delta(^{31}\text{P}^{\text{III}}) - 67.2$ ppm, $\delta(^{31}\text{P}^{\text{V}}) - 32.9$ ppm, $^1J(\text{PP}) 124.5$ Hz), with the process accelerating on heating or on addition of magnesium halides. For example, addition of a small portion of a magnesium halide lowers the content of I, raises the content of II and leads to a 15:85 (percentage throughout) I/II mixture in four to five days. On maintaining the mixture under the same conditions for a longer time, this ratio is only slightly affected.

Compound II was also obtained by us from magnesium phosphorotetraethyldiamidite [2] and phosphorotetraethyldiamidous chloride:



However, the II obtained could not be purified (by the action of pyridine and light petroleum) from salt admixtures completely. The I to II rearrangement is reversible. High-vacuum distillation of the 15 : 85 I/II mixture containing several per cent (mol/mol) of MgX_2 results in a distillate which comprises 40–70% of I, depending on the operating conditions. On storage the distillate is transformed again to a mixture containing ca. 15% I and 85% II. Redistilling this mixture raises the content of I markedly. The possibility of repeatedly controlling the I/II ratio in the same sample suggests that we are dealing with $P(O)-E \rightleftharpoons P-O-E$ tautomerism (well known for $E = H$). The study of tautomeric transformations in systems containing E's other than H is under way.

References

- 1 V.L. Foss, V.V. Kudinova, Yu.A. Veits and I.F. Lutsenko, *Zh. Obshch. Khim.*, 44 (1974) 1209.
- 2 E.E. Nifant'ev and I.V. Shilov, *Zh. Obshch. Khim.*, 43 (1973) 2564.