

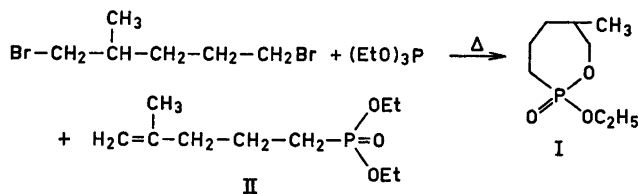
Geometric Isomerism in a Seven-membered Ring Phosphonate

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Five- and six-membered cyclic compounds with phosphorus as heteroatom in the ring have been resolved by several workers in their geometric isomers.¹⁻⁸ However, isolation of geometric isomers in seven-membered cyclic compounds containing phosphorus in the ring, has not yet been reported in the literature.

This paper reports the preparation and gas liquid chromatographic (GLC) isolation of *cis* and *trans* isomers of the seven-membered cyclic phosphonate, 2-ethoxy-6-methyl-2-oxo-1,2-oxaphospha-cycloheptane (I). The compound was prepared on heating a mixture of triethylphosphite and 2-methyl-1,5-dibrompentane. In addition to the cyclic phosphonate, about 20% of 4-methyl-4-pentene-diethoxy-phosphonate (II), was also isolated.



The structures of I and II were established by infrared and proton magnetic resonance spectra, as well as by elementary analysis.

The cyclic compound I was separated in its *cis-trans* isomers on a preparative

gas chromatographic column. The isomers were present in the ratio approx. 1:4. Refractive indexes, P=O frequencies, and retention times for the isomers, are given in Table 1.

The NMR spectra of the isomer (I) mixture showed two doublets for the 6-methyl group at $\delta = 0.90$ ($J = 7$ cps) and $\delta = 1.07$ ($J = 7$ cps) ppm, their relative areas were 1:4 in accordance with the ratio between the isomers found gas chromatographically. That the separation between these signals is a chemical shift difference, and not due to spin-spin coupling, is confirmed by the NMR spectra of the pure isomers, (A) and (B), which each showed only one doublet for the ring C-CH₃ absorption at $\delta = 1.07$ and $\delta = 0.90$ ppm, respectively. The doublets arise from the different positions of the 6-methyl group in the seven-membered ring: *cis* resp. *trans* to the ethoxy group attached to the phosphorus atom. In accordance with the NMR spectra of some substituted dioxaphospholanes and dioxaphosphorinanes,^{1,4} these observations also indicate configurational stability about the phosphorus atom.

It is tentatively proposed that the isomer (A) with the more downfield 6-methyl doublet has *trans* configuration, since the methyl group in *trans* position is nearest to the deshielding phosphoryl group.

Table 1. Physical data of the I isomers.

Compound	Isomer	n_D^{20}	P=O cm ⁻¹	Retention time (min) 170°	Tentative conformation
	A	1.4580	1250	43	<i>trans</i>
	B	1.4600	1260	40	<i>cis</i>

This assignment agrees with the relative retention time of the isomer (A), as the *trans* isomers usually have longer retention time than *cis* isomers. The structural relationship of the *cis-trans* pair and related isomers of seven-membered ring phosphonates, are investigated further.

Experimental. 2-Ethoxy-6-methyl-2-oxo-1,2-oxaphospha-cycloheptane (I), and 4-methyl-4-pentene-diethoxy phosphonate (II). Triethylphosphite (50 g) and 2-methyl-1,5-dibromopentane (20 g) were kept with stirring for 7 h at 200°C. The ethyl bromide was continuously distilled off, and the remaining reaction mixture fractionated *in vacuo* in a heated jacket column to give 6.0 g (39 %) of I and 2.8 g (20 %) of II. The esters have the following specifications:

I: b.p.₁₀ 134°, n_D^{20} : 1.4590 (Found: C 49.89; H 8.85; Calc. for C₈H₁₇O₃P: C 50.02; H 8.86.)
II: b.p.₁₀ 130°, n_D^{20} : 1.4425 (Found: C 54.28; H 9.47. Calc. for C₁₀H₂₁O₃P: C 54.55; H 9.54.)

The isomers (A) and (B) were separated by means of an Aerograph Autoprep A-700 gas chromatograph. GLC purity of the isomers was above 99 %.

1. Goldwhite, H. *Chem. Ind. (London)* **1964** 494.
2. Fontal, B. and Goldwhite, H. *Tetrahedron Letters* **22** (1966) 3275.
3. Gagnaire, D., Robert, J. B. and Venier, J. *Bull. Soc. Chim. France* **1966** 3719.
4. Denney, D. Z. and Denney, D. B. *J. Am. Chem. Soc.* **88** (1966) 1830.
5. Quin, L. D. and Shook, H. E. *Tetrahedron Letters* **1965** 2193.
6. Quin, L. D., Gratz, J. P. and Montgomery, R. E. *Tetrahedron Letters* **1965** 2187.
7. Bergesen, K. *Acta Chem. Scand.* **21** (1967) 578.
8. Wadsworth, W. S., Jr. *J. Org. Chem.* **32** (1967) 1603.

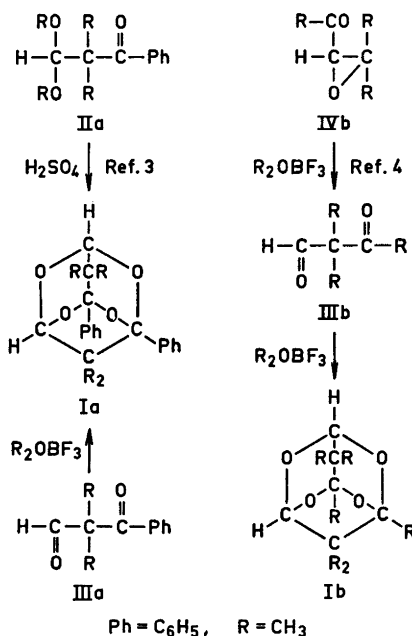
Received March 30, 1968.

Some 2,4,6,8-Tetraoxadamantanes

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Unlike their phospho¹ and thia analogues (IS),² 2,4,6,8-tetraoxadamantanes (I) seem to be unknown, except for the compound Ia, obtained from the acetal IIa by treatment with 80 % sulphuric acid.³



The (co)dimerization of several β -dicarbonyl compounds to I in the presence of boron fluoride-dimethyl ether (BD) or zinc chloride-acetic acid was discovered during the synthesis of IS. The structures of I were proved like those of IS. The observed GLC * retentions, PMR chemical shifts and fragmentation on electron impact accorded perfectly with those extrapolated from the corresponding data for IS, although the high oxygen contents

* Unless stated otherwise, the abbreviations and symbols in Ref. 2 are used.