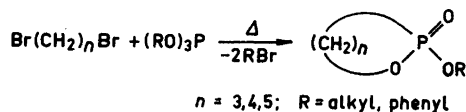


Isolation of *cis* and *trans* Isomers of Some Oxaphosphorinans

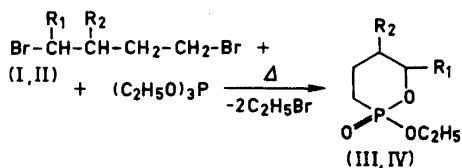
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Trialkyl phosphites and triphenyl phosphites upon heating react with aliphatic dibromides forming five-, six-, and seven-membered rings with phosphorus as heteroatom.^{1,2}



In a study of the hydrolysis of the geometric isomers of six-membered cyclic phosphonates the two compounds, 5-methyl-2-oxo-2-ethoxy-1,2-oxaphosphorinan (III), and 6-methyl-2-oxo-2-ethoxy-1,2-oxaphosphorinan (IV), were needed. They were prepared according to the above principle from triethylphosphite and the dibromides 2-methyl-1,4-dibromobutane (I) and 1,4-dibromopentane (II).



I, III: $\text{R}_1 = \text{H}, \text{R}_2 = \text{CH}_3$

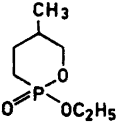
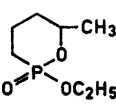
II, IV: $\text{R}_1 = \text{CH}_3, \text{R}_2 = \text{H}$

The identity of the cyclic compounds was established by infrared and proton magnetic resonance spectra, elementary analysis and equivalent weights.

The preparations (III) and (IV) were both found by gas liquid chromatography (GLC) to contain geometric isomers in the ratio approx. 1:2. The isomers were separated by preparative gas chromatography. Refractive index, density, retention time, and $\text{P}=\text{O}$ frequency of each isomer are given in Table I.

The isomers, (A) – (D), most probably exist in the chair conformation, as characteristic for cyclohexane derivatives, and might therefore be expected to obey the modified Auwers-Skita rule.³⁻⁵ This rule states that *cis* isomers of 1,4- and *trans*

Table I. Physical data of the (III) and (IV) isomers.

Compounds	Isomer	n_D^{20}	d_4^{20}	$\text{P}=\text{O}$ cm^{-1}	Retention time (min) 185°C	Tentative conformation
	A	1.4597	1.148	1240	31.5	<i>cis</i>
	B	1.4541	1.134	1250 1275	42.5	<i>trans</i>
	C	1.4492	1.095	1240 1255	27.5	<i>cis</i>
	D	1.4525	1.106	1250	46.0	<i>trans</i>

isomers of 1,3-disubstituted cyclohexanes have the higher refractive indexes and the higher densities. According to this, the data of Table I indicate the *cis* structure for isomers (A) and (C), and the *trans* structure for (B) and (D). These assignments agree with the relative retention times of isomers (A) and (C), as the *cis* isomers usually has shorter retention time than the *trans* isomer. The structural relationship of the two *cis-trans* pairs are at present being further investigated.

Experimental. *5-Methyl-2-oxo-2-ethoxy-1,2-oxaphosphorinan (III)*. Triethyl phosphite (50 g) and 2-methyl-1,4-dibromobutane (20 g) were stirred for 2 h at 180°C. The ethyl bromide was continuously distilled off, and the remaining reaction mixture fractionated *in vacuo* in a heated jacket column to give 6.2 g (40%), b.p., 130°, n_D^{20} 1.4588. (Found: C 47.06; H 8.50; E 177.5. Calc. for $C_7H_{10}O_3P$: C 47.20; H 8.43; E 178.2).

6-Methyl-2-oxo-2-ethoxy-1,2-oxaphosphorinan (IV) was synthesized from triethyl phosphite (50 g) and 1,4-dibromopentane (20 g) using the same procedure as above. 4.7 g (30%), b.p., 95°, n_D^{20} 1.4496. (Found: C 46.94; H 8.36; E 176.1. Calc. for $C_7H_{10}O_3P$: C 47.20; H 8.43; E 178.2).

GLC purity of III and IV > 99%. The isomers were separated by means of an Aerograph Autoprep A-700 gas chromatograph using a $20' \times 1/4''$ column containing 10% PDEAS on Fluoropak 80, at 185°, and with a helium flow of 40 ml/min. GLC purity of the isomers was above 99%.

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Some Comments on a Reported Quinuclidine Synthesis

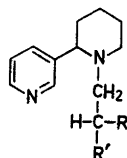
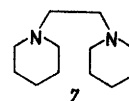
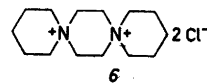
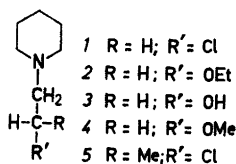
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In the beginning of this century Knorr¹ and even others carefully investigated the chemical behaviour of tertiary β -chloroethylamines like *N*-(β -chloroethyl)-piperidine, *1*. Knorr found that compound *1* in ethanol partly dimerizes to the bis-quaternary salt *6* and partly yields the ether *2*. He found further that Hofmann cleavage of *6* effected with aqueous potassium hydroxide yields dipiperidinoethane, *7*, piperidinoethanol, *3*, and acetylene.

In 1963 Sadykov and coworkers reported the formation of quinuclidine,² *11*, from compound *1* by treatment with methanolic potassium hydroxide and in a second paper³ an analogous formation of the quinuclidine derivative *13* from compound *8* by the same base treatment. In 1964 these authors, in an extension of the previous work, reported³ an analogous formation of compounds *12* and *14*, when the corresponding β -chloropropylamines *5* and *10*, respectively, were used as starting materials.

In 1965 Rubtsov and coworkers⁴ published a paper titled "Hofmann cleavage of 6,9-diazoniadispiro-(5.2.5.2)-hexadecane dichloride (compound *6*) with methanolic



- 11 R = R' = H
 12 R = Me; R' = H
 13 R = H; R' = 3-pyridyl
 14 R = Me; R' = 3-pyridyl