the insoluble bis(carboxymethyl) trithiocarbonate (m.p. 171–173°C) was filtered off. The filtrates were treated with charcoal, concentrated and diluted with petroleum ether, whereupon the products crystallized.

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Conformational Isomers of 1,2-Oxaphospholanes

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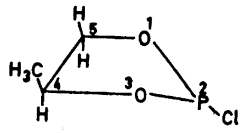
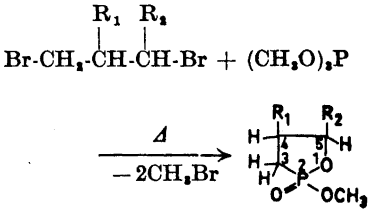
Conformational isomers of disubstituted five-membered rings, containing tervalent and quadruply linked phosphorus as heteroatom, are observed by several workers.[1–4] Goldwhite [1] has shown that the proton magnetic resonance spectrum of the cyclic compound, 2-chloro-4-methyl-1,3,2-dioxaphospholane (I), contains two



I

doublets centered at 0.95 and 1.20 ppm. The doublets were assigned to the methyl group placed in two different conformational environments, *cis* and *trans* to the 2-chlorosubstituent in compound (I). A similar interpretation accounts for the PMR spectra of other substituted 1,3,2-oxaphospholanes.[1,3] This paper reports the preparation of 2-methoxy-5-methyl-2-oxo-1,2-oxaphospholane (II) and 2-methoxy-4-methyl-2-oxo-1,2-oxaphospholane (III), prepared from trimethylphosphite and the dibromides 1,3-dibromobutane and 2-methyl-1,3-dibromopropane, respectively, on heating:



II: $R_1 = H, R_2 = CH_3$
III: $R_1 = CH_3, R_2 = H$

The structures of (II) and (III) were established by infrared and PMR spectra, as well by elementary analysis. Gaschromatographic analysis of (II) and (III) under several conditions has given one major peak only, but the PMR spectra indicate that these compounds are mixtures of conformational isomers in ratio approx. 2:1.

The PMR signal of the methyl group in position 5 in (II) is well separated from the rest of the spectrum and consists of two double doublets (Fig. 1). This is due

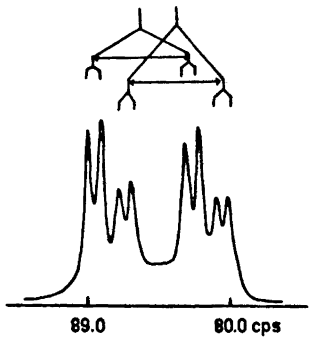
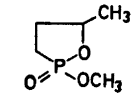
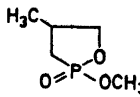


Fig. 1. Spectrum at 60 Mc of the methyl group in II in $CDCl_3$ with TMS as internal standard.

to the methyl groups in two different conformational environments coupled to the methine proton and to the phosphorus atom (Table 1). The PMR signal of the methyl groups in position 4 in (III) consists of two triplets (Fig. 2). It is assumed that the methyl group is coupled to phosphorus in only one of the two conformations of (III). A corresponding observation is also reported for 2-chloro-*trans*-4,5-dimethyl-1,2,3-dioxaphospholane(IV),[3] where one of the methyl groups occurs as a doublet and the other as a double doublet. Mixtures

Table 1. Chemical shifts and coupling constants for the methyl- and methoxy groups in (II) and (III).

Compound	Chemical shift Hz from TMS		Coupling constant Hz [a]			
	methyl	methoxy	J_{H-CH_3}	$J_{P-O-C-CH_3}$	$J_{P-C-C-CH}$	J_{P-O-CH_3}
	85.5	227.0	6.1	0.8		11.1
	83.5	226.6	6.1	0.8		11.2
	68.9	226.8	6.8		2.0	11.1
	68.8	226.2	7.0		~0	11.1

[a] From first order analysis. The accuracy is probably ±0.1 Hz.

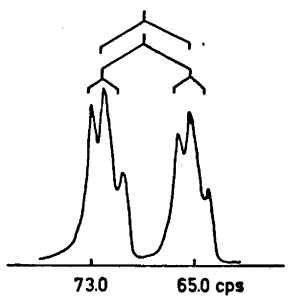
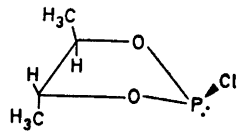


Fig. 2. Spectrum at 60 Mc of the methyl group in III in $CDCl_3$ with TMS as internal standard.

of conformational isomers in (II) and (III) are also confirmed by the two doublets for the $P-OCH_3$ absorption (Table 1). The structural relationship of the isomers is at present being further investigated.

Experimental. 2-Methoxy-5-methyl-2-oxo-1,2-oxaphospholane (II). Trimethylphosphite (50 g) and 1,3-dibrombutane (20 g) were stirred for 3 h at 100°C. The methyl bromide was continuously distilled off, and the remaining reaction mixture fractionated *in vacuo* in a heated jacket column to give 7 g (41 %) $b.p._{10}$ 132°, n_D^{21}: 1.4480. (Found: C 39.97; H 7.29; P 32.08. Calc. for $C_5H_{11}O_3P$: C 40.02; H 7.33; P 32.01).



IV

2-Methoxy-4-methyl-2-oxo-1,2-oxaphospholane (III) was synthesized from trimethylphosphite (50 g) and 2-methyl-1,3-dibromopropane (20 g) using the same procedure as above. 5.1 g (32 %), $b.p._1$ 129°, n_D^{21}: 1.4540. (Found: C 39.89; H 7.31; P 31.98. Calc. for $C_5H_{11}O_3P$: C 40.02; H 7.33; P 32.01).

GLC purity of (II) and (III) > 99 %. The PMR spectra were measured at 60 Mc (JEOL C-60 H) in 20 % solution of the compounds in $CDCl_3$ at 25°C.

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