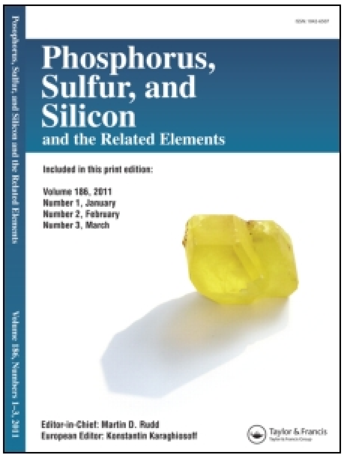

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PSEUDOROTATION IN MONOCYCLIC OXYPHOSPHORANES WHICH CONTAIN CHIRAL CENTERS

Donald B. Denney[a]; Dorothy Z. Denney[a]; Micah N. Raab[a]
[a] Department of Chemistry, Rutgers, The State University of New Jersey, New Brunswick, N.J.

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PSEUDOROTATION IN MONOCYCLIC OXYPHOSPHORANES WHICH CONTAIN CHIRAL CENTERS

DONALD B. DENNEY, DOROTHY Z. DENNEY
and MICAH N. RAAB

Department of Chemistry, Rutgers, The State University of New Jersey, New Brunswick, N.J. 08853

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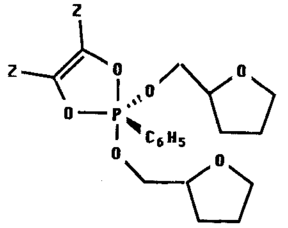
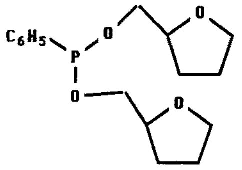
Phenylbis[2-methyl-1-butoxy]phosphine has been allowed to react with butanedione to produce 2,2-bis[2-methyl-1-butoxy]-2-phenyl-4,5-dimethyl-1,3,2-dioxaphophol-4-ene. This material is a mixture of three diastereomers. It has been reported that 2,2-bis[tetrahydrofurfuyloxy]-2-phenyl-4,5-dimethyl-1,3,2-dioxaphosphol-4-ene is a mixture of only two diastereomers. The present work suggest that two of the diastereomers of the tetrahydrofurfuryloxy compound interconvert via hexacoordinated zwitterionic intermediates which involve addition of the oxygen of the tetrahydrofuran ring to phosphorus.

Key words: Pseudorotation, monocyclic phosphoranes, strain rule, hexacoordinate phosphorus.

Recently, Koole *et al.*[1] reported the preparation of the phosphoranes, **1** and **2**. The precursor to these materials, **3**, is found as a mixture of diastereomers, two meso forms and a dl-pair. Interestingly, **1** and **2**, appeared from their ^{31}P NMR spectra, which contained only two resonances in both cases, to consist of only two diastereomers. The authors concluded that there is a rapid interconversion of the two meso isomers. They further showed that these interconversions must be remarkably facile. There was no change in the ^{31}P NMR spectra of 1 and 2 on cooling to −70°C. They suggested that the interconversions occur by an intramolecular rearrangement. This process requires that the five membered rings adopt diequatorial dispositions. This requirement represents a violation of the strain rule.[2] Although there are known violations of the strain rule, they have only been found under exceptional circumstances. There has also always been a ready explanation for the violation. No such explanation has been offered for the



1 Z = CH_3
2 Z = CF_3



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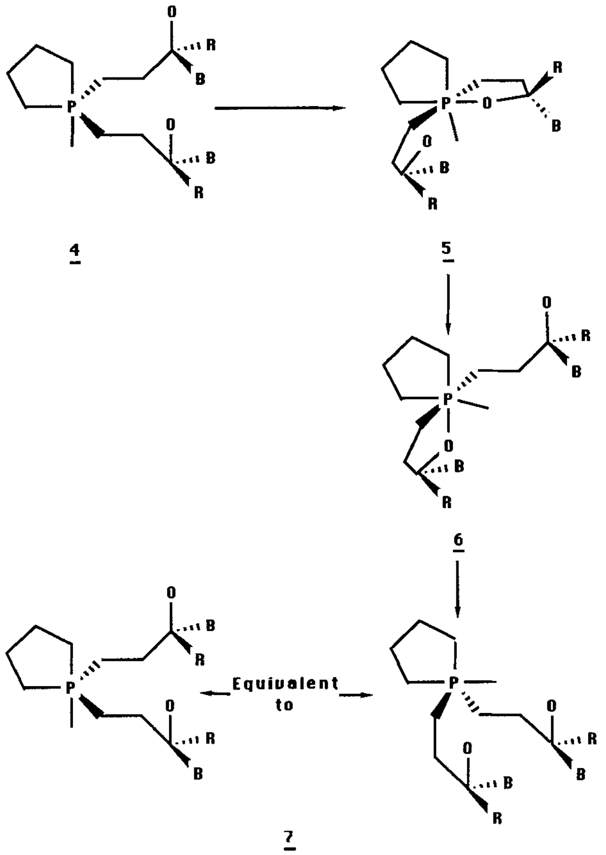
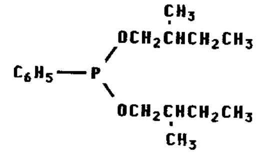
apparent behavior of 1 and 2. The difference between 1 and 2 and monocyclic oxyphosphoranes which do not violate the strain rule is the presence of the oxygens of the tetrahydrofuran rings. If these oxygens can add to phosphorus to form zwitterionic hexacoordinated compounds an explanation for their NMR spectra is found. The process is schematically represented by considering one meso form 4 which cyclizes to 5. Attack by the remaining ligand with ring opening yields 6 which on reversion to the phosphorane gives rise to 7, the other meso isomer. Alternate routes to an hexacoordinate intermediate are available and they lead to the same result.



If this explanation is correct then it can be tested by preparing a phosphonite from an alcohol which contains a chiral center but which does not contain oxygens that can interact with the phosphorus in its derived phosphoranes. Compound **8** is such a material. This substance has been prepared and it is found as a mixture of three diasteromers as is expected. Conversion to **9** by condensation with biacetyl yielded a mixture of diasteromers as evidenced by the presence of three resonances in the ^{31}P NMR spectrum. This is exactly what is predicted if there is not violation of the strain rule and if formation of a zwitterionic intermediate is precluded. Clearly these results favor the alternate explanation for the NMR data obtained from **1** and **2**.



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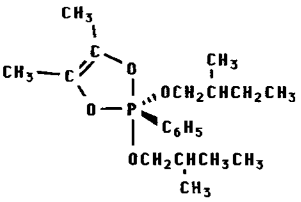

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EXPERIMENTAL SECTION

SPECTROSCOPY. All spectra were obtained using a Varian VXR-200 WB. All NMR data are reported in Tables I and II.

Phenylbis(2-methyl-1-butoxy)phosphine (**8**). To a mixture of racemic 2-methyl-1-butanol (10.3 g, 0.117 mol) and triethylamine (12.0 g, 0.119 mol) in 140 mL of heptane at 0°C and under a nitrogen atmosphere, was added, dropwise and with stirring, phenyldichlorophosphine (9.29 g, 0.052 mol) dissolved in 93 mL of heptane. After the addition was complete, the reaction mixture was allowed to warm to room temperature. The triethylamine hydrochloride was separated by filtration and the heptane was removed by distillation at atmospheric pressure. The residual oil was distilled to yield 5.94 g of 8 (0.024 mol, 46%) as a colorless oil, bp 98-100°C (0.076 mm). The approximate ratio of isomers as determined by ^{31}P NMR spectroscopy was 1:2:1.

2,2-Bis(2-methyl-1-butoxy)-2-phenyl-4,5-dimethyl-1,3,2-dioxaphosphol-4-ene (**9**). Butanedione (0.6 g, 7.2 mmol) was added slowly, under a nitrogen atmosphere, to a cooled (0°C) stirred solution of phenylbis(2-methyl-1-butoxy)phosphine (1.00 g, 3.98 mmol) in 2.5 mL of anhydrous acetonitrile-d_3. An aliquot was removed after the reaction mixture had warmed to room temperature and this was immediately analyzed by NMR spectroscopy. The approximate ratio of isomers as determined by 31P NMR spectroscopy was 1:2:1.

TABLE I

^{31}P and ^{1}H NMR Spectral Data

Compound	^{31}P[c]	^{1}H[d]
8[a]	154.94	0.81 (t, 7.2, 6H)
	154.85	0.88 (d of d, 6.4, 2.0, 6H)
	154.76	1.1–1.6 (mult, 6H)
		3.7 (mult, 4H)
		7.2–7.6 (mult, 5H)
9[b]	−34.49	0.83 (t, 7.8, 6H)
	−34.52	0.90 (d, 6.6, 6H)
	−34.56	1.1–1.5 (mult, 6H)
		1.72 (s, 12H)
		3.79 (mult, 4H)
		7.1–7.7 (mult, 5H)

[a] The solvent is benzene-d_6.

[b] The solvent is acetonitrile-d_3.

[c] Chemical shift values relative to 85% phosphoric acid.

[d] ^{1}H NMR data include chemical shift, multiplicity, coupling constants and relative intensities.

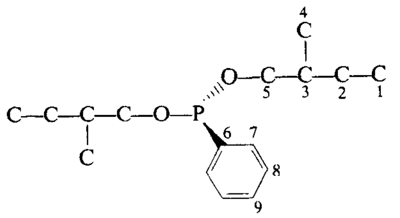
TABLE II

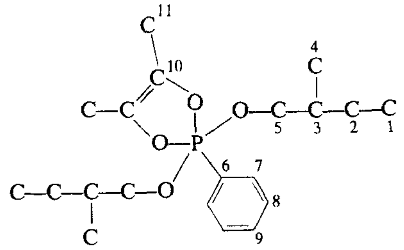
^{13}C NMR Spectral Data[a]

Cpd/C#[b]	1	2	3	4	5	6	7	8	9	10	11
8[c]	11.5	26.2	36.7 (5.1)	16.7 (2.2)	71.12 71.14 (7.9)	142.1 (22.3)	130.2 (2.7)	128.4 (5.2)	129.2		
9[d]	11.8	26.8	36.9 (7.7)	17.1	71.4 (10.7)	142.0 (247.3)	130.3 (9.7)	128.2 (17.9)	129.9 (3.6)	130.7 (?)	10.9 (10.0)

[a] The chemical shifts are reported in ppm relative to TMS, the coupling constants in Hz are in brackets. All spectra are proton decoupled so all coupling constants reflect coupling to phosphorus.

[b] The numbering systems are as follows:





[c] The solvent is benzene-d_6.

[d] The solvent is acetonitrile-d_3.

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