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## STEREOCHEMISTRIES OF SOME REACTIONS OF CYCLIC STEREOISOMETRIC PHOSPHITES

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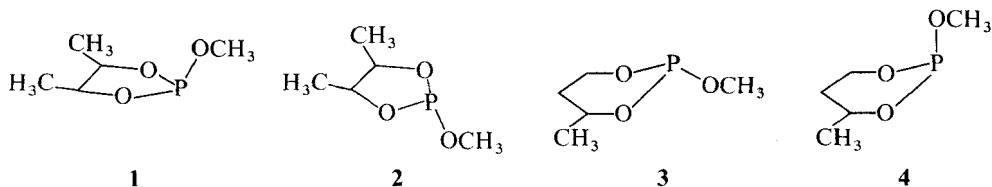
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The reaction of the isomeric phosphites, **1** and **2**, with ozone have been shown to be stereospecific and to proceed with retention of configuration about phosphorus. Similarly ozonization of mixtures of **3** and **4** were found to be stereospecific or very nearly so with retention of configuration about phosphorus. The mechanistic implications of these findings are discussed. Reactions of **1** and **2** with neopentyl and *t*-butyl hypochlorites proceed in a stereochemically random manner. The formation of a pentacoordinated intermediate is implicated. Reactions of a mixture of **1** and **2** with ethyl thiyl radicals provided phosphorothionates with complete retention of configuration.

The stereochemistries of the conversions of tricoordinate phosphorus compounds into tetra-coordinate phosphorus compounds have been studied for many reactions. The information obtained from these studies is often valuable in understanding the mechanisms of these conversions. In a general way ionic reaction mechanisms usually lead to well-defined stereochemistries in the products. For example, there are numerous reactions in which tricoordinate phosphorus compounds behave as nucleophiles, and in many cases the initial displacement can be shown to occur with retention of configuration. Other reactions take place with the formation of pentacoordinated intermediates. Such intermediates can be formed in a stereochemically random manner, or if formed in a stereochemically homogeneous manner their stereochemical identity can be lost by intramolecular permutational isomerization, "pseudorotation". In this report various reactions of the pairs of phosphites, **1**, **2**, and **3**, **4** will be presented. Compounds, **1**, **2**, are found at equilibrium as a mixture of 12% **1**, and 88% **2**.<sup>2</sup> It has not been possible to obtain nonequilibrium mixtures of **1**

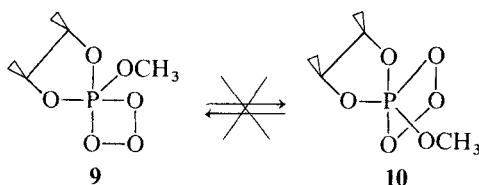
and **2**. The equilibrium mixture of **3** and **4** consists of 5% **3**, and 95% **4**. It has been possible to prepare nonequilibrium mixtures of **3** and **4**<sup>3</sup> and thus the products of different ratios of reactants can be compared. The use of *cis-trans*-isomers in determining stereochemistries of reactions is subject to certain limitations. In the case of cyclic phosphites, it has been shown for example that **3** is more reactive than **4** in some reactions.<sup>4</sup> If **3** is consumed and then by some process **4** is converted to **3** to reestablish the equilibrium, the stereochemical results will be meaningless. Similarly product isomerization can lead to spurious results. With these restrictions in mind, appropriate experiments can provide useful information.

**Ozonization of cyclic phosphites** Ozonizations of **1** and **2** under a variety of conditions led to product mixtures which had the same ratio of phosphates *cis-5* and *trans-6* as were present in the starting material. The reactions then proceeded with complete retention of stereochemistry. Similarly a 5% **3**, 95% **4** mixture was ozonized to give a product mixture whose ratio of phosphates, *cis-7* and

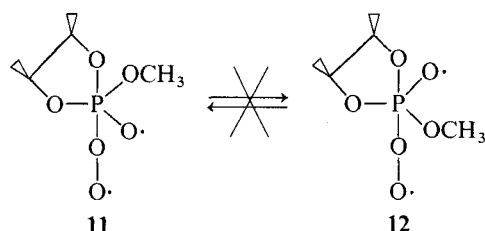


*trans*-**8** was 5:95. Ozonization of a mixture of 78.5% **3**, and 21.5% **4** gave a mixture of **7** and **8** whose ratio was 69:31. The small loss in stereochemistry cannot be easily explained. The results do show though that no common intermediate was obtained from the two mixtures of differing ratios of **3** and **4**.

Earlier work has shown that the phosphite reaction involves the formation of an adduct with a 4-membered ring.<sup>5</sup> The adduct then decomposes with the production of singlet oxygen and



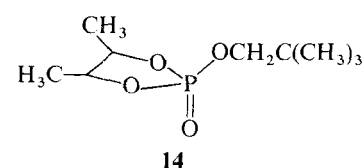
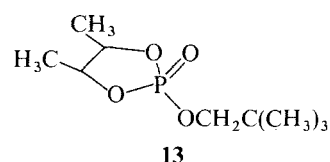
phosphate. In the case of **1** and **2** as well as **3** and **4** the results clearly show that the intermediate ozonides, for example, **9** and **10** do not interconvert, nor do they open to intermediates such as **11** and **12** which interconvert. Perhaps the most easy way to accommodate the data is to postulate that the ozonides decompose in a concerted manner to give phosphates. Stephenson and McClure<sup>5b</sup> have investigated the effect of changing the structure of the phosphites on the rates of decomposition of the ozonides. They suggest



that there are two mechanisms for the decompositions. The results obtained in the present study do not eliminate the dual mechanism hypothesis. The results do impose rather stringent restrictions on its application.

**Reactions of 1 and 2 with hypochlorites** In earlier work it was shown that **3** and **4** react with neopentyl hypochlorite to give product phosphates which arise with loss of some stereochemistry.<sup>6</sup> It was postulated that pentacoordinated intermediates were formed and that they underwent varying amounts of interconversion in competition with their decompositions.

The reactions of an equilibrium mixture of **1** and **2** with neopentyl hypochlorite have now been studied under a variety of conditions. The products, **13** and **14**, were synthesized by an independent method for comparison purposes.

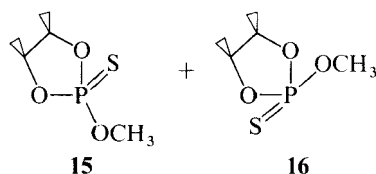


In all cases the product ratios of **13**:**14** were essentially 1:1.<sup>7</sup> These results are in general agreement with those reported earlier and are strongly supportive of the formation of pentacoordinated intermediates from **1** and **2** and neopentyl hypochlorite. The finding that the ratio of products does not vary with reaction conditions is suggestive of formation of an equilibrium mixture of pentacoordinated materials. Such was certainly not the case in the reactions of neopentyl hypochlorite with **3** and **4**. It is not surprising to find this difference. The five-membered ring containing pentacoordinated intermediates from **1** and **2** should be more stable towards chloride loss and subsequent Arbusov reaction than those from **3** and **4**.<sup>8</sup>

Reaction of *t*-butyl hypochlorite with **1** and **2**, 12:88, gave a mixture of **5** and **6**, 42:58. These results are also in agreement with the formation of pentacoordinated intermediates from the reactants.

**Reaction of 1 and 2 with ethyl disulfide** Bentrude and co-workers<sup>9</sup> investigated the stereochemistries of the reactions of various mixture of *cis*- and *trans*-2-methoxy-5-*t*-butyl-1,3,2-dioxaphosphorinanes, isomeric six-membered ring phosphites, with *n*-butyl thiyl radicals generated by the photolysis of *n*-butyl disulfide. The reactions were found to be essentially stereospecific and to yield phosphorothionates with retention of configuration. There is no doubt that these reactions involve phosphoranyl radicals  $(\text{RO})_3\text{P}-\text{SR}^{10}$  and in the case cited above they are formed and decompose in a stereospecific manner.

Reaction of **1** and **2**, 12:88, with ethyl disulfide under photolytic conditions afforded a mixture of **15** and **16** in a totally stereospecific manner, i.e. a



ratio of 10:90 of mixed products was found. The assignment of the stereochemistries of these products is based upon observations of Bentrude and Tan.<sup>11</sup> They allowed series of 5-membered ring containing phosphorus heterocycles similar to **1** and **2** to react with sulfur. In all cases they found the reactions to be stereospecific and that the predominant isomer was *trans*. When **1** and **2** were allowed to react with sulfur, mixtures of **15** and **16** ca. 30:70 were formed under a variety of conditions. On the basis of these results and those from the ethyl thiyl reactions it is concluded that the reaction of **1** and **2** with ethyl thiyl radicals involves complete retention of configuration. This result is of course in complete accord with the earlier work of Bentrude *et al.*<sup>9</sup>

## EXPERIMENTAL SECTION

<sup>1</sup>H NMR spectra were recorded with Varian A-60 and HA-100 spectrometers; <sup>31</sup>P NMR spectra were recorded with a Varian HA-100 spectrometer. Chemical shifts are related to external 85% phosphoric acid with upfield shifts being reported as negative and downfield as positive. GC analyses were conducted under a variety of conditions; full details can be found in the thesis of S. Schutzbank, Rutgers University, 1971.

**Reaction of 1 and 2 with ozone.** In a typical experiment, 0.93 g (0.0062 mol) of **1**, **2**,<sup>2</sup> relative ratio 12:88 in 30 ml of methylene chloride was treated with ozone at -68°C until the blue color of excess ozone persisted. Argon was then bubbled through the mixture to displace the ozone. After removal of the solvent *in vacuo* there was obtained 1.02 g of product, theory 1.03 g, which was analyzed by <sup>31</sup>P NMR spectroscopy<sup>2</sup> and GC. The relative percentages were 12:88.

In another experiment a solution of **1** and **2** was added to a saturated solution of ozone at -72°C. Isolation and analysis gave an average ratio of percentages of 10:90.

**Reaction of 3 and 4 with ozone.** The relative percentages of the two starting phosphites were determined by integrating the absorptions of the hydrogens of the ring methyl groups. The *trans* is found at  $\delta$  1.15 ( $J_{\text{HCH}} = 6\text{Hz}$ ) and the *cis* at  $\delta$  1.36 ( $J_{\text{HCH}} = 6\text{Hz}$ ). The ozonolyses were conducted at -40°C, and the GC analyses were carried out with a 16'  $\times$  1/8" stainless steel column packed with 5% GE XE60 at 180°C. The two phosphates had retention times of 28 and 42 min.

**Reaction of 1 and 2 with neopentyl hypochlorite.** In a typical experiment, there was added to 0.53 g (0.0035 mol) of **1** and **2** in 20 ml of methylene chloride a solution of neopentyl hypochlorite,<sup>6</sup> in methylene chloride, 0.35 M 10 ml, at -75°C over a period of one hour. The solvent was removed and the <sup>31</sup>P NMR spectrum revealed two resonances at  $\delta$  + 14.9 and + 13.7. Addition of authentic phosphates augmented these resonances. GC analysis gave a relative ratio of isomers of 48:52. Under other conditions the ratio of products varied slightly. After storage in a refrigerator for 13 months the ratio changed from 48:52 to 33:67. This result indicates that the material that absorbs at + 13.7 is the *trans*-isomer.

**Preparation of 5 and 6.** To a stirred solution of 5.09 (0.055 mol) of meso-2,3-butanediol and 11.21 g (0.111 mol) of triethylamine in 130 ml of methylene chloride at 0°C was added dropwise 11.36 g (0.055 mol) of neopentyl phosphorodichloridate in 20 ml of methylene chloride. The reaction mixture was cooled to -75°C and forced through a filter stick to remove triethylamine hydrochloride. The solvent was removed and the residue was distilled at 95-110°C (0.5 mm) to give 7.3 g (59%) of mixed phosphates. The <sup>31</sup>P NMR spectrum of this mixture had two resonances at  $\delta$  + 15 and + 13.5 in the ratio 46:54. The <sup>1</sup>H NMR spectrum although complicated is in agreement with the structural assignment.

**Reaction of 1 and 2 with *t*-butyl hypochlorite.** To a solution of 0.61 g (0.004 mol) of **1** and **2** in 20 ml of methylene chloride at -72°C was added 10 ml of a 0.41 M solution of *t*-butyl hypochlorite in methylene chloride. The <sup>31</sup>P NMR spectrum after concentration had two resonances at  $\delta$  + 17 and + 15 which are in agreement with those reported for the known phosphates. GC analysis gave relative ratios of 48:52 and further the two peaks were augmented by authentic phosphates.

**Reaction of 1 and 2 with ethyl thiyl radicals.** To a 5 mm quartz NMR tube was added 0.17 g (0.0013 mol) of **1** and **2**, 0.73 ml of a 1.55 M solution of ethyl disulfide in methylene chloride and a catalytic amount of  $\alpha,\alpha$ -azodi-*iso*-butyronitrile. The reaction mixture was irradiated at room temperature for 3.5 hr. The <sup>31</sup>P NMR spectrum had resonances at  $\delta$  + 84.6 and + 82, which correspond to those found for authentic thiophosphates prepared by allowing **1** and **2** to react with sulfur. GC analysis gave relative ratios of 10:90, and the peaks were augmented by authentic thiophosphates.

**Reaction of 1 and 2 with sulfur.** To a stirred solution of 0.028 g (0.000875 mol) of sulfur in 0.91 g of carbon disulfide was added 0.128 g (0.000853 mol) of **1** and **2**. The <sup>31</sup>P NMR spectrum had two resonances at  $\delta$  + 83 and + 81. GC analysis gave relative ratio of 27:73.

## ACKNOWLEDGEMENT

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