

Stereochemistries of the Reactions of *cis*- and *trans*-2-Methoxy-4-methyl-1,3,2-dioxaphosphorinan with Methyl Iodide

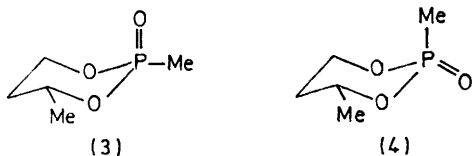
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Summary Under appropriate conditions the title compounds react stereospecifically with methyl iodide; these results are in total agreement with a two-step ionic

mechanism, and they eliminate the requirement for the production of a five-co-ordinate phosphorus compound as intermediate.

THE Michaelis-Arbusov reaction involves reaction of a trivalent phosphorus compound with an alkyl halide to give an intermediate phosphonium salt which decomposes to alkyl halide and a phosphoryl compound. The generally accepted mechanism for the overall transformation involves two ionic reactions, S_N1 and/or S_N2 .¹ Recently Bodkin and Simpson² reported that *cis* and *trans*-2-alkoxy-



4-methyl-1,3,2-dioxaphosphorinans reacted with alkyl iodides to give phosphonates with varying degrees of loss of stereochemistry about phosphorus, the loss of stereochemistry most probably occurring prior to the formation of the phosphonium salt. They suggested that the initial reaction involved formation of a five-co-ordinate phosphorus compound which could undergo intramolecular transposition of the ligands, 'pseudorotation,' prior to ionization of the iodide ion. Such a process would result in loss of stereochemistry. They also noted that at lower temperatures the *cis*-isomers were isomerizing into the *trans*-isomers, and suggested that the isomerization arose by return of the five-co-ordinate compound to starting materials. Thermal isomerization of the *cis*-phosphites into the *trans*-phosphites was ruled out as being too slow under the conditions of the reaction.

The thermodynamic equilibrium mixtures of these phosphites strongly favours the *trans*-structure, and it is

¹ R. G. Harvey and E. R. DeSombre, 'Topics in Phosphorus Chemistry,' eds., M. Grayson and E. J. Griffith, Interscience, New York, vol. 1, 1964.

² (a) C. L. Bodkin and P. Simpson, *Chem. Comm.*, 1970, 1579; (b) C. L. Bodkin and P. Simpson, *J.C.S. Perkin II*, 1972, 2049.

³ G. Aksnes, R. Erickson, and K. Mellinger, *Acta. Chem. Scand.*, 1967, 21, 1028.

⁴ J. A. Mosbo and J. G. Verkade, *J. Amer. Chem. Soc.*, 1973, 204.

known that adventitious catalysis by traces of acid can cause rapid isomerization of the *cis*-isomers.³ With this in mind we have studied *trans*-2-methoxy-4-methyl-1,3,2-dioxaphosphorinane (1), the *cis*-isomer (2), and their co-reactant MeI. Reactions of a 95:5 mixture of (1) and (2) under a variety of conditions (neat reactants at 70°; reactants in CH_2Cl_2 at 25 and 70°) gave products of a stereospecific reaction.

The results with the reaction of (2) and MeI were considerably different and varying ratios of the isomeric cyclic phosphonate products were found as the conditions and additives were varied. Additives such as trimethyl-*NN*-diethylaminosilane, an acid scavenger, and charcoal, an iodine scavenger, changed the ratio of products towards a more stereospecific product mixture. Finally it was found that a freshly prepared mixture of 21:79 (1) and (2) reacted in CH_2Cl_2 at 70° to give a 21:79 mixture of products. These results show that in this series the reactions can be made completely stereospecific, and they strongly support an S_N2 displacement by phosphorus on MeI to give an intermediate which decomposes by an S_N2 attack by iodide ion on the methyl group of the methoxy.

The products and starting materials were studied by ¹H and ³¹P n.m.r. spectroscopy. The product (3) from (1) had δ (³¹P) - 28 p.p.m. relative to 85% H_3PO_4 and that, (4), from (2) had δ - 23 p.p.m.; $\nu(P=O)$ for (3) 1229 cm^{-1} and for (4) 1250 cm^{-1} . These data support assignment of axial P=O for (3) and equatorial P=O for (4).⁴ The mechanism of the reaction also predicts such structures.

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