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Synthesis and Unexpected Rearrangement of a Hydroxyphostone (1)

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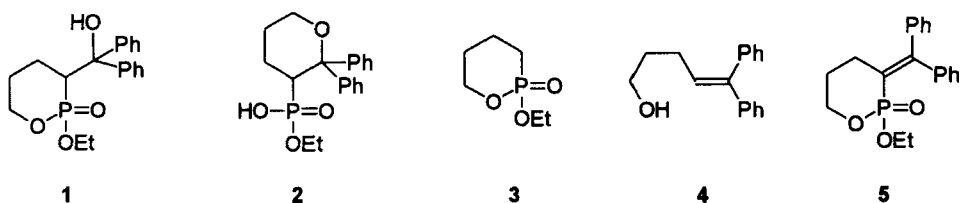
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SYNTHESIS AND UNEXPECTED REARRANGEMENT OF A HYDROXYPHOSTONE (1)

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During our investigations on the wide range of stereoselective alkylations of 6-membered ring phostones,¹ we uncovered a novel rearrangement of 3-(diphenylhydroxymethyl)-2-ethoxy-2-oxo-1,2-oxaphosphorinane (1). The *cis/trans* diastereomers of 1 were prepared by the reaction of benzophenone with the appropriate ylide of the parent phostone (3).² When *trans*-1 was left unattended at rt in CH₂Cl₂ a new compound, 2, was isolated which showed a significant downfield ³¹P shift and a higher melting point. Upon heating to the melting point 2 decomposed to give 4, which suggests that 2 may be an intermediate in the conversion of 1 to the Wittig-like product 4. The IR, ¹H, ¹³C, ³¹P, and 2-D NMR spectral data along with independent synthesis confirmed the identity of 2. Subsequently, 2 was also produced in 70% yield when *cis*-1 was treated with CH₂Cl₂/ether-HCl_{aq} at 50-60°C for 2 weeks, but this product was contaminated with 30% of the exocyclic alkene 5. No rearrangement was observed when 1 was treated with TsOH/EtOH or HPF₆; only 5 was produced. The stereochemistry and mechanisms of these transformations are presented.



1. O.P. Rodriguez, T.M. Lane, S.E. Cremer and D.W. Bennett, In preparation.
2. T.M. Lane, O.P. Rodriguez, S.E. Cremer and D.W. Bennett, *Phosphorus, Sulfur, and Silicon*, **103**, 63-75 (1995).