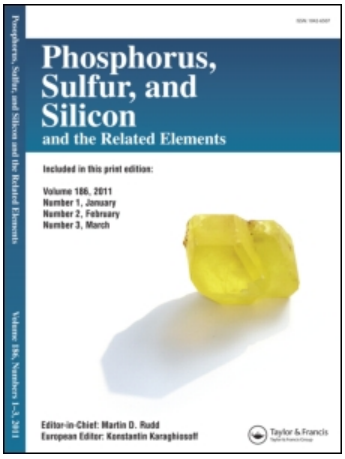

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Synthesis and Unexpected Rearrangement of a Hydroxyphostone (1)

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SYNTHESIS AND UNEXPECTED REARRANGEMENT OF A HYDROXYPHOSTONE (1)

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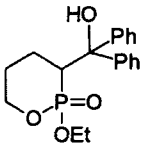
During our investigations on the wide range of stereoselective alkylations of 6-membered ring phostones,[1] we uncovered a novel rearrangement of 3-(diphenylhydroxymethyl)-2-ethoxy-2-oxo-1,2-oxaphosphorinane (**1**). The *cis/trans* diastereomers of **1** were prepared by the reaction of benzophenone with the appropriate ylide of the parent phostone (**3**).[2] When *trans*-**1** was left unattended at rt in CH_2Cl_2 a new compound, **2**, was isolated which showed a significant downfield ^{31}P 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, ^{1}H, ^{13}C, ^{31}P, 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 CH_2Cl_2/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 HPF_6; only **5** was produced. The stereochemistry and mechanisms of these transformations are presented.



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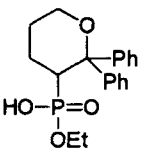

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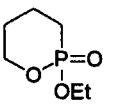

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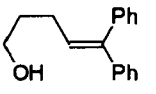

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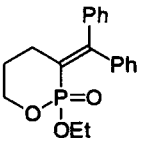

5

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).