Stereo- and Regio-selectivity in Diene Synthesis using Diphenylphosphinoyl as a Migrating Functional Group

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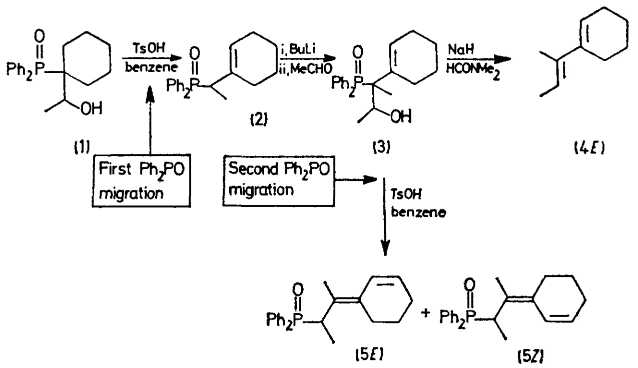
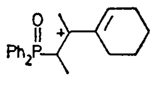
Summary Diphenylphosphinoyl migration from an unsymmetrical migration origin gives largely the *E* isomer of the more substituted allyl phosphine oxide.

We have recently described[1] a synthesis of dienes (*e.g.* **4***E*) by a Wittig Horner reaction on allyl phosphine oxides (*e.g.* **2**). The intermediate alcohols (**3**) are highly crystalline and can be easily separated into diastereoisomers each giving a single geometrical isomer of the diene. The allyl phosphine oxides (**2**) were made by diphenylphosphinoyl migration in a suitably substituted alcohol (**1**). We now report that the Wittig–Horner intermediates (**3**), being alcohols with the same substitution pattern, undergo a second diphenylphosphinoyl migration. Either diastereoisomer of (**3**) gives a mixture of (**5***E*) and (**5***Z*) on treatment with toluene-*p*-sulphonic acid in refluxing benzene suggesting that the rearranged allyl cation (**6**) is an intermediate.

All the rearrangements we have previously described[1] have started with alcohols with symmetrical migration origins (*e.g.* **1** or **8**, R=H), but the second diphenylphosphinoyl migration (**3**)→(**5**) is regiospecific in that none of the *exo*-methylene compound (**7**) is formed. We have therefore studied rearrangements in alcohols with unsymmetrical migration origins (**8**) and found that the reaction is

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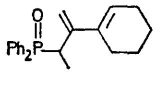
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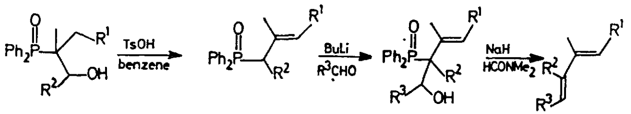
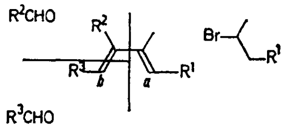


(8) (9)

R^1 = Me, Bu^n, R^2,R^3 = Me, Ph.



(10)

again regiospecific, giving only the allyl phosphine oxide with the more substituted double bond. It is also very stereoselective, giving a ($9E$:$9Z$) ratio of 8:1 (R^1=Me) or 6:1 (R^1=Bu^n).

The new allyl phosphine oxides (**9**) may in turn be converted into dienes by the Wittig–Horner procedure giving again single geometrical isomers. Our diene synthesis[1] is therefore more general than we have previously reported, giving dienes of the general structure (**10**) where the origin of each part of the diene structure is shown. Double bond *b* can be *E* or *Z* at will, but double bond *a* must be *E*. The restriction that double bond *a* can be only the more substituted alternative can be removed by using the trimethylsilyl group as described in the following communication.[2]

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[1] A. H. Davidson and S. Warren, *J.C.S. Chem. Comm.*, 1975, 148; *J.C.S. Perkin I*, 1976, in press; A. H. Davidson, P. K. G. Hodgson, D. Howells, and S. Warren, *Chem. and Ind.*, 1975, 455.

[2] I. Fleming, A. Pearce, and R. L. Snowden, following communication.