Stereochemistry of a Wittig Olefin Synthesis in Alcoholic Solution

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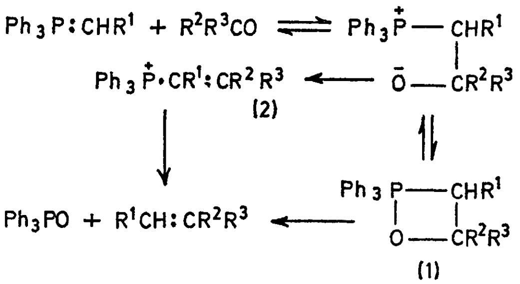
Summary (+)-Benzylethylmethylphenylphosphonium iodide and benzaldehyde in ethanolic sodium ethoxide give (+)-ethylmethylphenylphosphine oxide: the reaction therefore proceeds with retention of configuration at phosphorus and cannot involve a vinylphosphonium salt intermediate.

SCHWEIZER *et al.*[1] recently suggested that Wittig olefin syntheses in alcoholic solvents proceed, not *via* the usual oxaphosphetan intermediates (**1**), but *via* vinylphosphonium salts (**2**) when R^1, R^2, or R^3 is a substituent which will conjugate with the double bond. The vinylphosphonium salts would then undergo hydrolysis, utilising the water produced in their formation, to give the observed olefins and phosphine oxides. This mechanism implies that such olefin syntheses would proceed with inversion of configuration at phosphorus and casts doubt on stereochemical assignments[2] which have assumed that Wittig olefin syntheses in alcoholic solvents using optically active phosphonium salts involve retention at phosphorus. These reference olefin syntheses have used benzylphosphonium salts reacting in alcoholic alkoxide solution with benzaldehyde to give stilbene, and the purpose of this communication is to report that such an olefin synthesis does proceed with retention of configuration at phosphorus and cannot therefore involve a vinylphosphonium salt intermediate.



(+)-Benzylethylmethylphenylphosphonium iodide (**3**), $[\alpha]_{\mathrm{D}}^{25} + 23{\cdot}8 \pm 0{\cdot}2°$ (MeOH), lit.[3] $[\alpha]_{\mathrm{D}}^{25} + 25 \pm 1°$ (MeOH), with benzaldehyde in ethanolic sodium ethoxide (1 mol equivalent) at room temperature gave stilbene (> 70%; *cis*:*trans* 1:5·1) and (+)-ethylmethylphenylphosphine oxide (84%), $[\alpha]_{\mathrm{D}}^{25} + 18{\cdot}6 \pm 0{\cdot}2°$ (H_2O), lit.[3] $[\alpha]_{\mathrm{D}}^{25} + 21{\cdot}5 \pm 1°$ (H_2O). The same oxide was obtained from (**3**) in a similar olefin synthesis using phenyl-lithium,[3] while the enantiomer was obtained from (**3**) on alkaline hydrolysis.[3] The Wittig reaction between (**3**) and benzaldehyde in ethanolic ethoxide therefore proceeds with retention of configuration at phosphorus.

Schweizer has isolated some vinylphosphonium salts (**2**) from reactions in alcoholic solvents but not when R^1 = Ph. Routes *via* the oxaphosphetans (**1**) and the vinylphosphonium salts (**2**) are probably competitive: it is known in the case of arsenic betaines[4] and comparable intermediates in phosphonate olefin synthesis[5] that α-substituents capable of stabilising an adjacent carbanion increase the rate of olefin formation *via* four-membered intermediates and this may be so in phosphobetaines.

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[2] *E.g.*, N. J. De'ath and S. Trippett, *Chem. Comm.*, 1969, 172.

[3] W. E. McEwen, K. F. Kumli, A. Bladé-Font, M. Zanger, and C. A. VanderWerf, *J. Amer. Chem. Soc.*, 1964, **86**, 2378.

[4] S. Trippett and M. A. Walker, *J. Chem. Soc.* (*C*), 1971, 1114.

[5] E. J. Corey and G. T. Kwiatkowski, *J. Amer. Chem. Soc.*, 1968, **88**, 5655.