

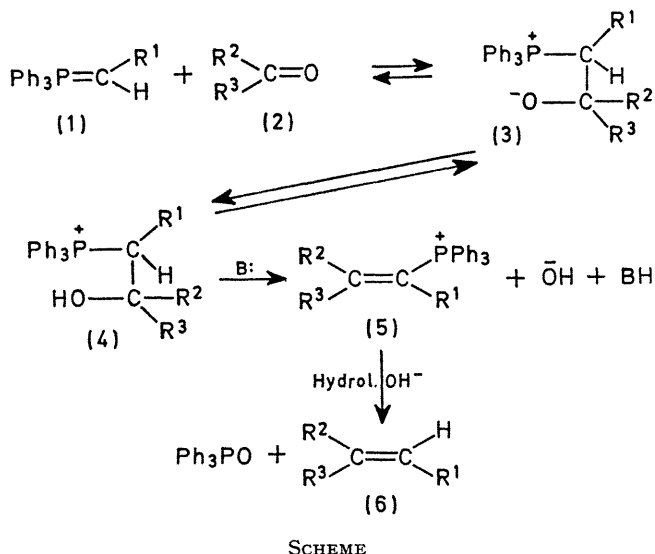
## Reactions of Phosphorus Compounds: Reaction of Phosphoranes with Carbonyl Reagents to produce Olefins *via* Vinylphosphonium Salt Intermediates

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**Summary** The preparation of olefins from phosphoranes ( $\text{Ph}_3\text{P}=\text{CHR}^1$ ), with one  $\alpha$ -proton, and carbonyl ( $\text{R}^2\text{R}^3\text{-C}=\text{O}$ ) reagents is accomplished *via* vinylphosphonium salts when the reaction is run in alcoholic solvent.

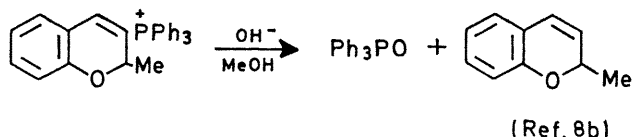
We suggest an alternative (Scheme) to the Wittig and Schollkopf mechanism<sup>1,2</sup> for the formation of olefins from phosphoranes and carbonyl reagents in alcoholic (protonic) media.



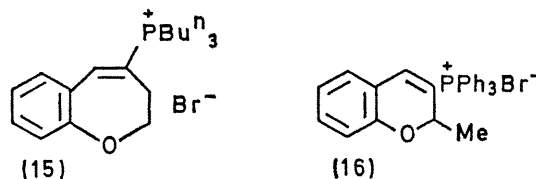
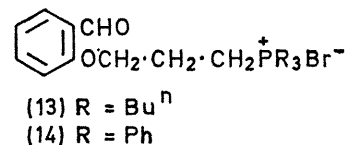
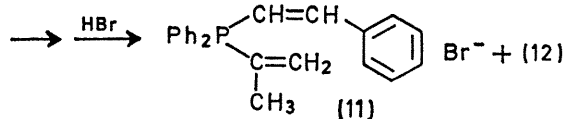
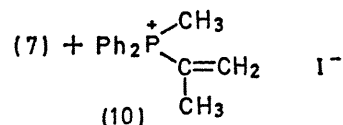
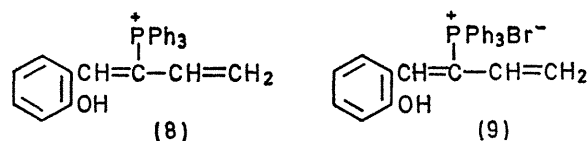
The *sine qua non* of this reaction pathway is the presence in the system of protic solvents which may protonate the intermediate betaine (3) (preventing the formation of an oxaphosphetan) thus forming the  $\beta$ -hydroxyphosphonium species, (4). There must also be a proton  $\alpha$  to the phosphonium moiety in (4), and one of the substituents (R) must be a  $\pi$ -bonded system in order to produce the vinyl salt (5) by loss of water.

We suggest that phosphoranes and carbonyl reagents in protonic solvents initially form vinylphosphonium salts (prior to hydrolysis) when the double bond produced is in conjunction with groups such as phenyl, double bonds, or electrophilic moieties (*i.e.* CN, COR). Phosphoranes obviously do not react with carbonyl reagents to form simple  $\alpha$ - and  $\beta$ -alkyl substituted vinylphosphonium salts when no conjugation is present. These  $\alpha$ - and  $\beta$ -alkyl substituted vinylphosphonium salts, when formed by other means, give  $\alpha$ - and  $\beta$ -alkyl substituted phosphine oxides on alkaline hydrolysis;<sup>3,4</sup> thus they are excluded from the reaction (Scheme). It has also been shown that phenyl migration occurs, when  $\text{R}^1 = \text{R}^2 = \text{H}$ ,  $\text{R}^3 = \text{acyl}$  or phenyl, under alkaline hydrolysis<sup>5</sup> or normal "Wittig conditions" using

alcoholic ethoxide.<sup>6</sup> It is evident, however, that  $\alpha$ -substituted conjugated vinylphosphonium salts do not give phenyl migration, but give olefins on hydrolysis, whether the  $\alpha$ -substituent is phenyl or alkyl.<sup>3,7-9</sup> We suggest that



the scope of the mechanism encompasses compounds of formula (1) where  $\text{R}^1$  is not H, and either  $\text{R}^1$ ,  $\text{R}^2$ , or  $\text{R}^3$  (in compounds 1 and 2) is a phenyl, double bond, or an electrophilic species (all  $\pi$ -bonded systems) which will conjugate with the vinyl bond formed.



Under the conditions used in most normal Wittig reactions in alcoholic solvents, the vinyl intermediates (5) could never be isolated because of the presence of the hydroxide which would immediately hydrolyse the salt (5)

to the olefin (6). However, vinylphosphonium salts<sup>†</sup> have been isolated under certain conditions. In the reaction of the sodium salt of salicylaldehyde (7) with allyltriphenylphosphonium bromide in ethanol, the phenolic group in the intermediate (8) consumes the base (OH<sup>-</sup>) which would normally attack the triphenylphosphonium moiety thus allowing for the isolation<sup>10</sup> of salt (9) (after acidification).

Methyl isopropenyl diphenylphosphonium iodide (10), on reaction with (7), similarly gives (11) as well as the expected 3-methyl-2H-1-benzopyran (12).<sup>8a</sup>

The salts (15) and (16) may be isolated in good yields on treatment of (13) and (14), respectively, with 10% alcoholic

base. With 1 equiv. of base, olefins are produced from (13) and (14), and little of the vinyl salts (15) and (16) is produced.<sup>8b</sup>

Thus the weight of evidence suggests that certain phosphoranes and carbonyl reagents in alcoholic solvents (*i.e.*, relatively acidic media) react *via* a pathway dissimilar to that originally suggested for the well known Wittig reaction to form olefins and triphenylphosphine oxide.

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† The vinylphosphonium salts isolated were stable white solids with high melting points. They were characterized by elemental analyses and spectra (*i.r.*, *n.m.r.*, mass spectra) which were consistent with the structures assigned.

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<sup>6</sup> (a) S. Trippett and B. J. Walker, *J. Chem. Soc. (C)*, 1966, 887; (b) E. M. Richards and J. C. Tebby, *Chem. Comm.*, 1969, 494.

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<sup>9</sup> E. M. Richards and J. C. Tebby, *J. Chem. Soc. (C)*, 1971, 1059, give an example where olefin formation and phenyl migration are both observed.

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