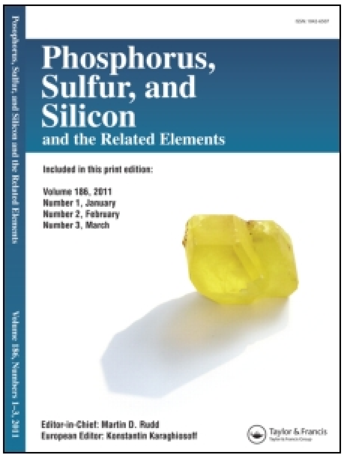

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THE MECHANISM AND STEREOCHEMISTRY OF WITTIG REACTIONS OF PHOSPHONIUM YLIDE-ANIONS.

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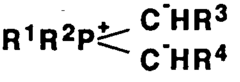
Schmidbaur's group have extensively investigated[1] the coordination properties of phosphonium 1,3-ylide-anions (1) in organometallic chemistry and more recently Cristau[2] has reported the potential usefulness of these compounds in synthetic organic chemistry. There have been a few studies[3] of specific phosphonium 1,1-ylide-anions (2), however their only use in the Wittig reaction appears to be that of (2a).[4] We have set out to study the stereochemistry and mechanism of Wittig reactions of (1) and (2) and to carry out some preliminary investigations on the arsenic analogues (3).



$R^1R^2\overset{+}{P}\begin{matrix}\overset{-}{C}HR^3\\ \overset{-}{C}HR^4\end{matrix}$

$Ph_3P^+C^-MR$

$R^1R^2\overset{+}{As}\begin{matrix}\overset{-}{C}HR\\ \overset{-}{C}HR\end{matrix}$

(1a) $R^3 = R^4 = H$
(1b) $R^3 = R^4 = CO_2Me$
(1c) $R^3 = R^4 = CN$
(1d) $R^3 = Ph$, $R^4 = CO_2Me$

(2a) R = H
(2b) R = Ph

(3a) R = H
(3b) R = Ph

Ylide-anions (1) have the potential to behave as enhanced Wittig reagents for several reasons. They should have increased nucleophilic reactivity compared to ylides due to their extra negative charge and an advantage over Horner-Wittig and Wadsworth-Emmons reagents in that they retain the strong driving force of P=O bond formation in the decomposition of the intermediate oxaphosphetanes. The reagents might also be expected to produce different alkene stereochemistries to those produced by normal ylides and have the potential to react with two carbonyl groups per molecule.

Investigations of the reactions of a wide range of ylide-anions with aldehydes and ketones confirmed our expectations. Ylide-anions derived from a variety of dibenylphosphonium salts reacted with one or two equivalents of benzaldehyde to give excellent yields of stilbene. Reactions with one equivalent of aldehyde usually led to increased E-selectivity compared to the reactions of the analogous ylides.[5]

Wittig reactions of methylene ylides often give low yields. Unfortunately Cristau has reported that the preferred reaction of ylide-anions with enolisable ketones is proton abstraction rather than olefination.[2a] In view of this our initial experiments with the ylide-anion (1a) derived from methylene ylide were carried out with the Ce(III) salt since it has been reported[6] that Ce(III) alkyls show reduced basicity while retaining nucleophilicity compared to the corresponding Lithium compounds. Although these reactions gave good yields of alkene, reactions of a variety of enolisable ketones with the corresponding *lithium* ylide-anion gave equally good results.

Stabilised ylides generally show low reactivity towards ketones. Wittig reactions of the reagents (1b), (1c), and (1d) derived from anionic activation gave much higher yields (40-95%) than those (0-6%) of the corresponding triphenylphosphonium ylide.[7] However, changing the ligands on phosphorus from triaryl to diarylalkyl also significantly improved the yields of Wittig reactions of the *ylides*. Wittig reactions of ylide-anions (e.g. 1d) carrying mixed ligands gave mixtures of alkenes and this has significant implcations for the mechanism of these reactions.

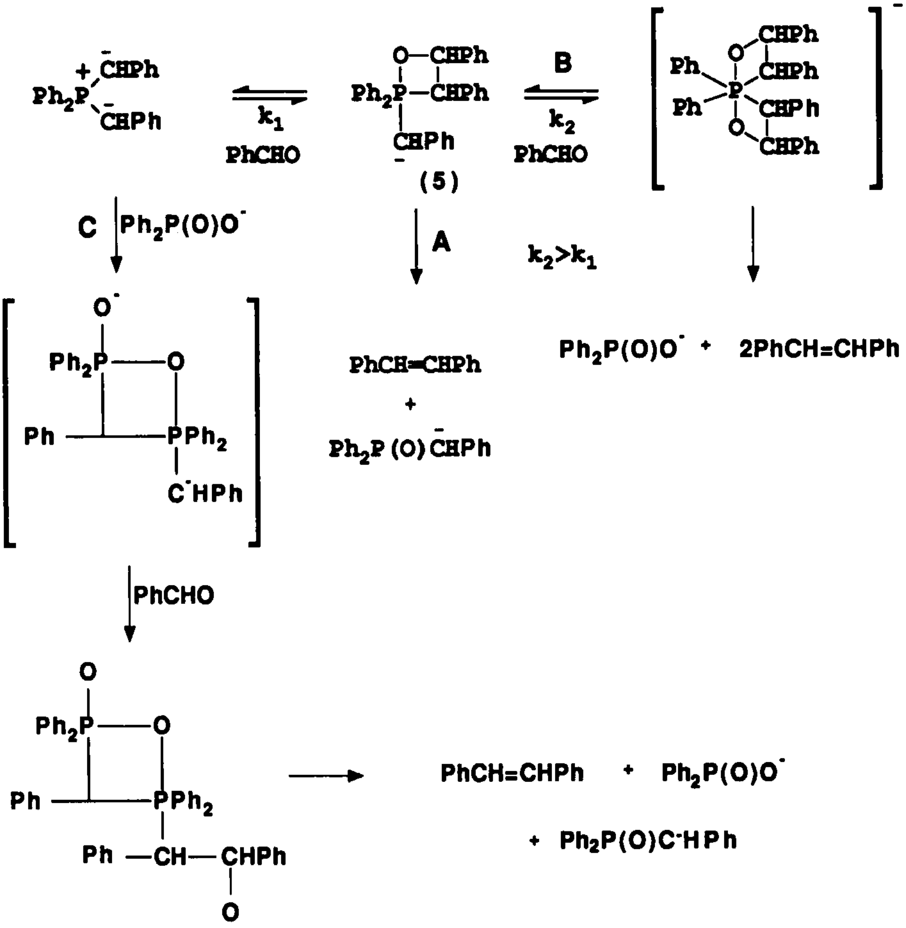
Mixtures of alkene and epoxide are frequently the products of reactions of arsonium ylides with carbonyl compounds. It can be argued that the use of the corresponding ylide-anions should enhance alkene formation in these reactions. Attempted Wittig reactions of ylide-anions (3a) derived from reactive arsonium ylides gave only epoxides, although in marginally better yields that reactions of the corresponding ylides. Analogous reactions at room temperature of (3b) derived from semi-stabilised arsonium ylides gave the Stevens rearrangement product; however, reactions at -98° gave moderate yields of alkene and epoxide mixtures.

The most obvious mechanisms for alkene formation from Wittig reactions of ylide-anions are those shown in Scheme1. Mechanism **A** is closely analogous to that of the Wittig reaction of ylides, while mechanism **B** involves further reaction of the initially formed oxaphosphetane anion (5) with carbonyl compound followed by step-wise or concerted collapse to phosphinic acid and alkene. Under the reaction conditions used in our ylide-anion reactions Horner-Wittig reactions provide at best low yields of alkene; it is clear from this that in reactions of ylide-anions with two equivalents of carbonyl compound the major mechanism operating is not that normally accepted for the Horner-Wittig reaction.

Clearly major factors controlling the extent to which each of mechanisms **A** and **B** operate will be the reactivity of the ylide-anion compared to that of (5) and the relative rate of decomposition of (5) to alkene and phosphine oxide anion. Our results are most easily interpreted by mechanism **B** operating in at least some cases; in the reaction of dibenzyldiphenylphonium ylide-anion with one mol equivalent of benzaldehyde the products are one mol of stilbene, half a mol of phosphinate anion and half a mol of unreacted ylide-anion.

Evidence obtained from quenching experiments suggests that a different mechanism becomes important in reactions involving a second mol equivalent of carbonyl compound. This may involve the formation of a complex (**scheme 1, C**) between unreacted ylide-anion and phosphinate anion produced by mechanism **B** . That such a complex is involved in alkene formation is supported by results from reactions of benzaldehyde with mixtures containing equimolar amounts of ylide-anion and phosphinate anion. The results obtained from reactions of benzaldehyde with the ylide-anion (1d) carrying two different anion groups can also be explained by this mechanism.

The reaction of benzyltriphenylphosphonium bromide with two mol equivalents of lithiumbutyl produces a dark red solution which reacts with benzaldehyde to give stilbene. On reaction with benzaldehyde the 1,1-ylide anion (2b) would be expected to form an intermediate analogous to Schlosser's 2-oxido ylide. 2-Oxido ylides derived from benzylphosphonium salts are not normally available since the betaine precursor decomposes to alkene before it can be reacted with a further mol of lithiumbutyl. All attempts to react this potential intermediate with alkylating agents led to the formation of *stilbene*.



Scheme 1

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