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Theoretical Study on the Transition State of Oxaphosphetane Formation between Ethylidenetriphenylphosphorane and Acetaldehyde

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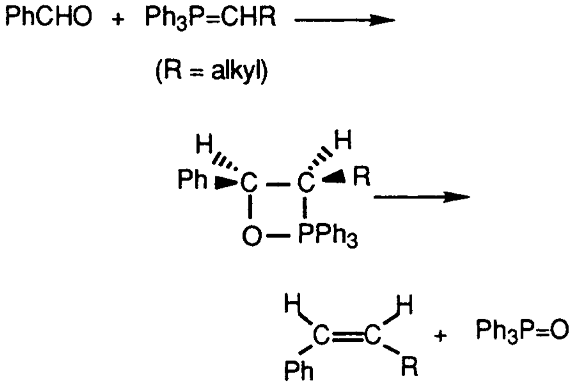
ABSTRACT

The MNDO MO calculations were carried out for the formation of oxaphosphetanes from substituted ylides and aldehydes (Equations 2–4). It was found that the reactions proceed through a nearly planar cyclic four-membered ring transition state (TS) in all cases studied and that phenyl substitution on phosphorus has little effect on the TS geometry. This finding is not in line with the TS models that have been proposed to explain the experimentally observed cis-selectivity.

INTRODUCTION

The Wittig reaction of a nonstabilized ylide with an aldehyde yields the corresponding Z-alkene stereoselectivity under Li salt-free conditions (Equation 1) [1], and the reaction has been shown to proceed via an oxaphosphetane as the only detectable intermediate by means of ^{31}P NMR spectroscopy [2–4]. Since the oxaphosphetane is known to retain its stereochemistry during its decomposition to the alkene, the current mechanistic interest has been focused on the origin of the stereoselective formation of the *cis*-oxaphosphetane [5]. Several transition-state (TS) models have been proposed to explain this cis selectivity [2a, 6, 7].



(1)

In 1982, Schlosser claimed that the three phenyl groups on phosphorus adopt a special propeller-like conformation and make the *cis*-TS sterically more favorable than the *trans*-TS as shown in Figure 1a [6]. More recently, Vedejs proposed that cis-selective nonstabilized ylides react via an early reactant-like TS while stabilized ylides react via a late oxaphosphetane-like TS to yield trans product [7]; the TS for nonstabilized ylides was considered to have a nonplanar puckered structure (Figure 1b) as a

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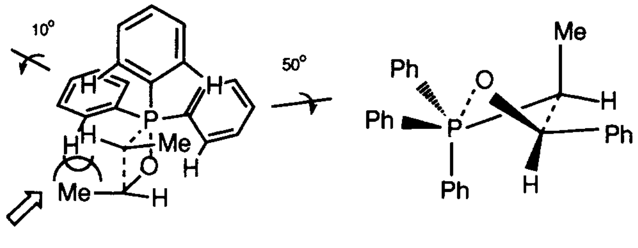


(a) (b)

FIGURE 1 (a) Leeward *trans*-TS model (Schlosser). (b) Puckered TS model (Vedejs).

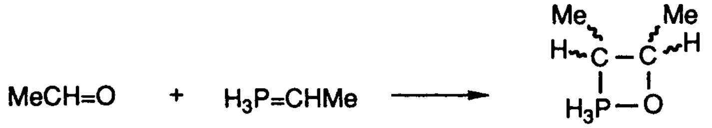
result of a compromise between steric repulsion and π overlap attraction, favoring the *cis*-TS. Although previous MO calculations showed that such a concerted cyclic TS should have a planar four-membered ring geometry [8], Vedejs argued that these MO results may not have realilty because the steric effects of large substituents on phosphorus were completely neglected in these calculations. Thus, it is important to investigate the effect of substituents on phosphorus on the structure of the TS and compare the results with experiment. For this purpose, we have undertaken MO calculations on three reactions leading to oxaphosphetanes and examined how the TS structure as well as the relative (cis vs. trans) barrier height of each reaction is affected by substituents on the ylide and the aldehyde.

RESULTS AND DISCUSSION

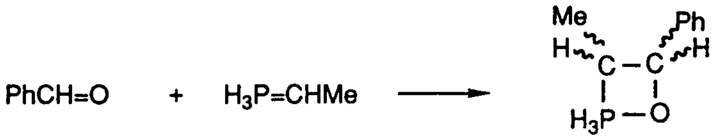
The reactions considered in the present study are shown in Equations 2–4 [9]. In all cases, both cis and trans TS structures were fully optimized by the MNDO method. For reaction 2, HF/3-21G optimization was also carried out and the results were compared with those obtained by the MNDO method. Although it has been reported that the reaction energy computed at the MNDO level of theory is not highly reliable [8a], the structure of the unsubstituted (mythical) oxaphosphetane computed by MNDO was found to be similar to that obtained by the ab initio method [10] (Figure 2). We determined that cyclic four-membered ring TS structures but no betaines were obtained for our systems, as in the previous ab initio calculations for the formation of the unsubstituted oxaphosphetane [8]. Figure 3 shows four TS structures for reaction 2, two by MNDO and two by HF/3-21G. It should be noted that the important TS characteristics are similar for both computations, i.e., the transition states have nearly planar four-centered structures. Furthermore, the energy differences between the cis and trans transition states are almost the same for both methods; the *trans*-TS is 1.1 (HF/6-31G*//HF/3-21G) and 1.0 (MNDO) kcal/mol more stable than the *cis*-TS [11]. These results suggest that the MNDO calculations are applicable at least in a qualitative sense to determine the transition states for related reactions.

The same characteristics were found for the reaction of benzaldehyde with $H_3P{=}CHMe$ (Equation 3), having nearly planar four-membered ring transition states and the *trans*-TS being 1.5 (MNDO) kcal/mol more stable than the *cis*-TS (Figure 3).

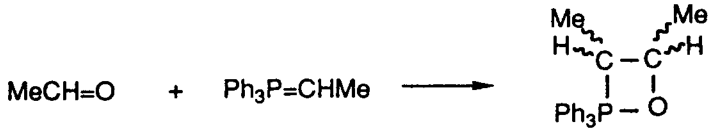
The reaction of ethylidenetriphenylphosphorane with acetaldehyde (Equation 4) is of particular interest since the ylide has three phenyl groups bonded to phosphorus and thus the TS structures can be compared directly with the proposals by Schlosser and Vedejs. The *cis*- and *trans*-TS structures at the MNDO level are illustrated in Figure 4. It can be seen in Figure 4 that the four-membered P–C–C–O rings are almost planar, as in the cases of reactions 2 and 3. The four-membered ring structures are basically unchanged by the changes of


$MeCH{=}O + H_3P{=}CHMe \longrightarrow$

(2)


$PhCH{=}O + H_3P{=}CHMe \longrightarrow$

(3)


$MeCH{=}O + Ph_3P{=}CHMe \longrightarrow$

(4)

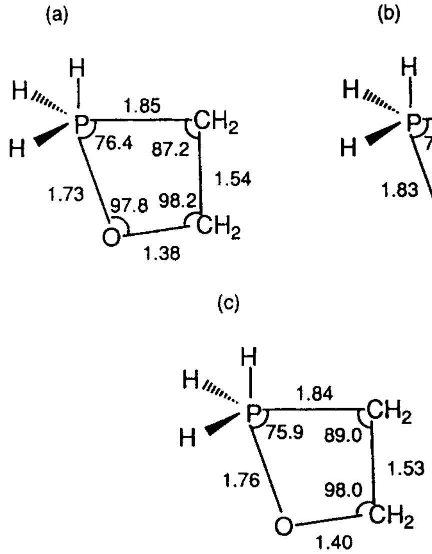


FIGURE 2 The computed structures of oxaphosphetane at various levels of theory. Bond lengths are in Å and bond angles in degrees. (a) MNDO, data taken from [10], (b) HF/3-21G, this work, and (c) HF/4-31G*, data taken from [8b].

substituents on phosphorus from H to Ph (from reaction 2 to 4), although the comparison of the bond lengths in Figure 3 and 4 revealed that the P–O bond formation is less advanced in the triphenyl-substituted transition states. This difference may arise from the large steric hindrance of the three phenyl groups, which makes the P–O bond formation difficult.

The observed similarity in the TS structures for reactions 2 and 4 is not in line with the argument that the three phenyl substituents on phosphorus have a crucial effect on the TS structure and hence on the stereochemistry of the oxaphosphetane-formation step. It was assumed in Vedejs' model that the reaction has an early TS and that because of the three phenyl groups on phosphorus the TS structure is puckered favoring *cis*-oxaphosphetane formation. The present calculations indeed suggest an early TS for reaction 4, but the TS has a planar geometry. There is no consistency between the MNDO-calculated TS geometry with Vedejs' model. Furthermore, as expected from the geometries of the transition states, the TS leading to the *trans*-oxaphosphetane is sterically less hindered and hence has a lower energy (1.6 kcal/mol at the MNDO level) than that of the *cis*-TS.

It is also apparent in Figure 4 that the conformation of the three phenyl groups on phosphorus is different from that proposed by Schlosser to explain the cis-selectivity. Thus, the MNDO-calculated TS geometry is also not consistent with Schlosser's explanation.

In summary, the present MNDO calculations suggest that the experimental cis-selectivity observed for the Wittig reaction of ethylidenetriphenylphosphorane with an aldehyde is not rationalized by the direct [2+2] cycloaddition model. Another mechanism, which includes a transient intermediate such as a radical-ion pair (via electron transfer) or a spin-paired diradical en route to the oxaphosphetane, may be considered to explain the experimental stereoselectivity [12].

ACKNOWLEDGMENT

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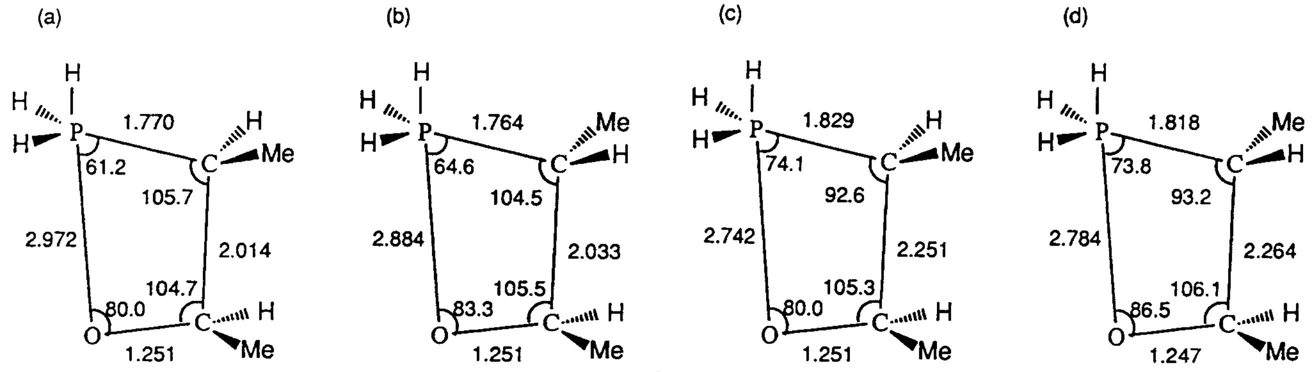
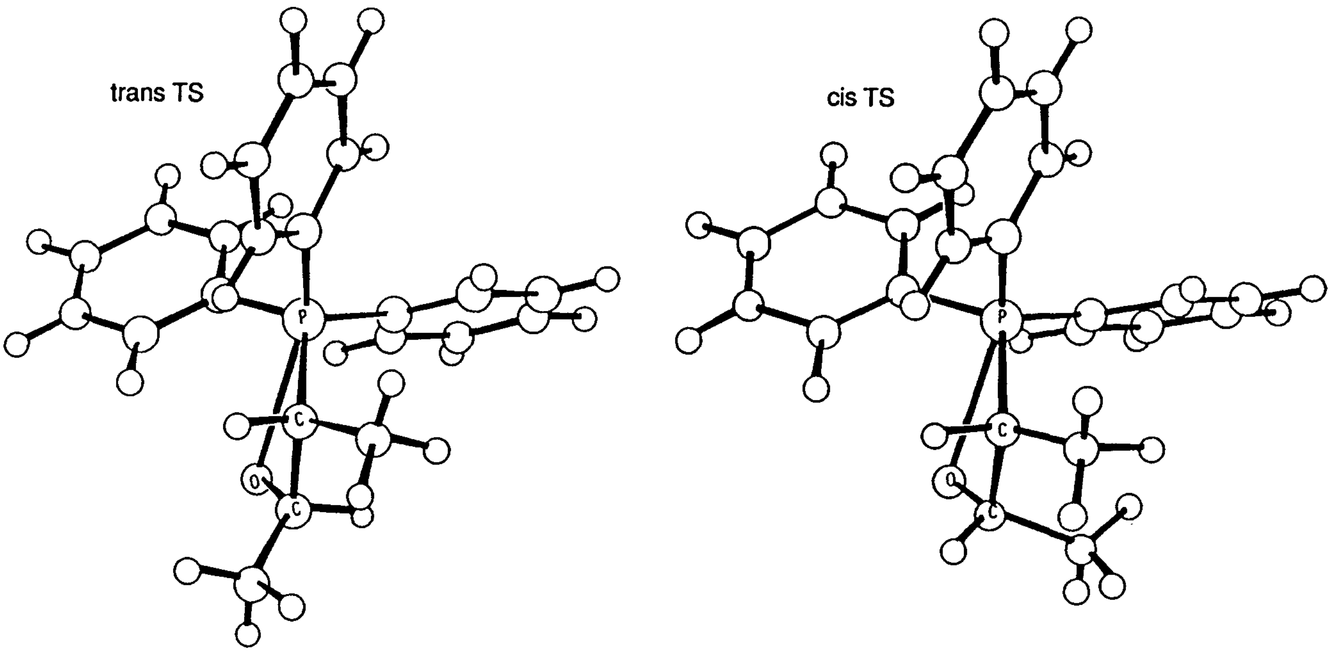


FIGURE 3 TS structures for reaction 2. Bond lengths are in Å and bond angles in degrees. (a) *cis*-TS by MNDO, (b) *trans*-TS by MNDO, (c) *cis*-TS by HF/3-21G, and (d) *trans*-TS by HF/3-21G.



trans TS			
$r_{P\text{-}O}$	3.248 Å	<OPC	55.3°
$r_{P\text{-}C}$	1.934 Å	<PCC	114.4°
$r_{C\text{-}C}$	2.035 Å	<CCO	106.4°
$r_{O\text{-}C}$	1.248 Å	<COP	79.2°

cis TS			
$r_{P\text{-}O}$	3.229 Å	<OPC	56.6°
$r_{P\text{-}C}$	1.821 Å	<PCC	112.3°
$r_{C\text{-}C}$	2.056 Å	<CCO	106.8°
$r_{O\text{-}C}$	1.248 Å	<COP	78.5°

FIGURE 4 *Cis* and *trans* MNDO transition states for reaction 4.

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