J. Am. Chem. Soc. **1992**, *114*, 813-821

A Theoretical Study of the Wittig Olefination Reaction: MNDO-PM3 Treatment of the Wittig Half-Reaction of Unstabilized Ylides with Aldehydes[1]

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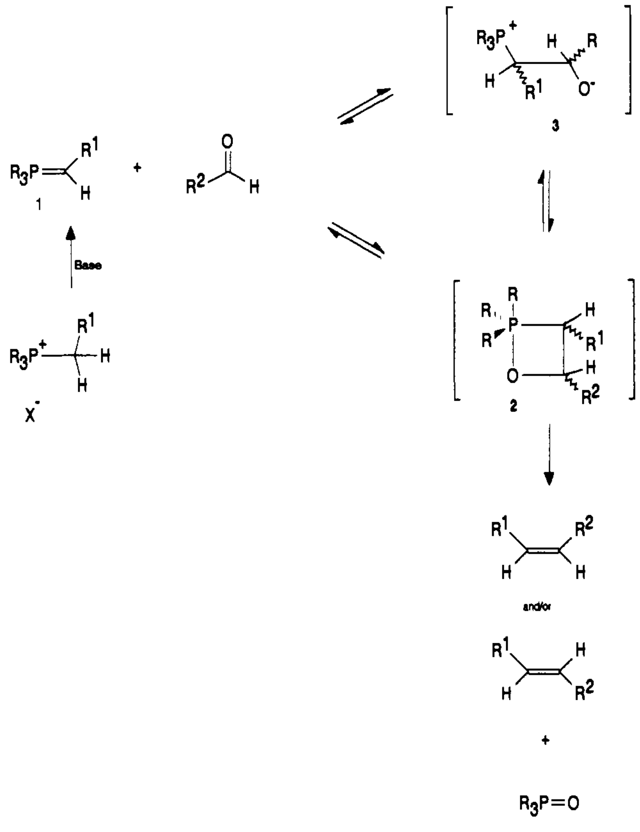
Abstract: As with our previous report (Mari, F.; Lahti, P. M.; McEwen, W. E. *Heteroatom Chem.* **1991**, *2*, 265) on the mythical Wittig half-reaction ($H_3P{=}CH_2 + CH_2O \rightarrow$ the oxaphosphetane), use of the MNDO-PM3 molecular orbital method on the reaction of $(C_6H_5)_3P{=}CHCH_3$ and the mythical analogue $H_3P{=}CHCH_3$ with aldehydes (acetaldehyde, propargylaldehyde, and glyoxylonitrile) to give the respective *Z*- and *E*-diastereomeric oxaphosphetanes has provided evidence that the mechanisms are best described as very asynchronous cycloadditions (borderline two-step mechanisms). The geometries of the transition states of these model reaction are such that the P, C, C, and O atoms that interact in the bond-breaking–forming process lie in the same plane. The C–C distance in the transition state varies from 1.96 Å to 2.14 Å, whereas the P–O distance varies from 2.48 Å to 2.94 Å. Analysis of the evolution of the bond orders of these reactions shows that each C–C bond is about 30–50% formed in the respective transition states, whereas no P–O bond has been formed to any significant degree. An analysis of localized molecular orbitals througout each reaction leads to the same conclusions. For the formation of the *Z* oxaphosphetanes, the enthalpies of activation $\Delta H^{\ddagger}$ were calculated to be 1.5 to 3.5 kcal/mol higher than the $\Delta H^{\ddagger}$ for the formation of the *E* oxaphosphetanes. The enthalpies of reaction, ΔH_r, were calculated to be 1.5 kcal/mol less negative for the formation of the *Z* oxaphosphetanes when compared to the formation of *E* oxaphosphetanes. In addition, values of $\Delta H^{\ddagger}$ are about 10 kcal/mol less and the values of ΔH_r 5–8 kcal/mol less negative for reactions with $H_3P{=}CHCH_3$ than for the respective ones of $(C_6H_5)_3P{=}CHCH_3$ with the same aldehydes. Thus, the presence of the phenyl groups bonded to phosphorus makes an important contribution to the steric strain of formation of each oxaphosphetane and to the transition state leading to it. The calculated $\Delta H^{\ddagger}$ decreases as the electrophilicity of the aldehydes is increased, which is in good agreement with experimental evidence. The nature of the transition states suggests that along the reaction coordinate for real Wittig reactions carried out in polar solvents or in the presence of metal ions, the reactants do not have to be restricted to the "syn" approach. An "anti" approach of the reactants is considered as a possibility to explain *Z* stereoselectivity of some Wittig reactions.

Introduction

The unusual *Z* stereoselectivity of alkene formation is perhaps the most striking mechanistic feature of the salt-free Wittig reactions of certain phosphorus ylides[2] (Scheme I). The stereoselectivity, which also largely determines its synthetic value, is highly dependent on the substituents bonded to the ylidic carbon (R^1) and to the phosphorus atom. According to the nature of these substituents, the Wittig reaction has been shown to yield preferentially *Z* alkenes for unstabilized ylides where R^1 = alkyl and R = phenyl (the most common case), mixtures of the *Z* and *E* alkenes for semistabilized ylides (R^1 = phenyl, vinyl, propargyl, –F), and mainly *E*-alkenes for stabilized ylides ($R^1 = -COOCH_3$, –CN). There is no general mechanism that presently provides sufficient hard evidence to accommodate all of these observations.

Scheme I



Oxaphosphetanes, **2**, were early recognized to be likely intermediates in the Wittig reaction,[3] since a syn elimination of the phosphine oxide from an oxaphosphetane would generate the desired alkene (Scheme I). This hypothesis was confirmed by the use of ylides derived from optically active phosphonium salts, which had been shown to undergo the Wittig reaction with retention of the configuration at the phosphorus atom, an event which gave evidence against a possible anti elimination.[4] Further evidence was found by the isolation and characterization (NMR spectroscopy and X-ray crystallography) of unusually stable oxaphosphetanes that could be induced to give Wittig products under more drastic conditions.[5] Later, it was confirmed by ^{31}P NMR spectroscopy that the oxaphosphetanes were indeed formed as intermediates in Wittig reactions of unstabilized ylides.[6] However, the detection of the oxaphosphetanes as intermediates of the Wittig reaction cannot explain the *Z* stereoselectivity for the reactions of unstabilized ylides. In fact, it would be expected on the basis

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[1] (a) Molecular Modeling of the Wittig Reaction. 3. (b) Previous paper in this series: Mari, F.; Lahti, P. M.; McEwen, W. E. *Heteroatom Chem.* **1991**, *2*, 265.

[2] For a recent review of the Wittig reaction, see: Maryanoff, B.; Reitz, A. E. *Chem. Rev.* **1989**, *89*, 863.

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[4] (a) McEwen, W. E.; Kumli, K. F.; Blade-Font, A.; Zanger, M.; VanderWerf, C. A. *J. Am. Chem. Soc.* **1964**, *86*, 2373. (b) Jones, E.; Trippett, S. *J. Chem. Soc. C* **1966**, 1090.

[5] (a) Birum, G. H.; Matthews, C. N. *Chem. Commun.* **1967**, 137. (b) Chiccola, G.; Daly, J. J. *J. Chem. Soc. A* **1968**, 568. (c) Ul-Haque, M.; Caughlan, C. N.; Ramirez, F.; Pilot, J. F.; Smith, J. P. *J. Am. Chem. Soc.* **1971**, *93*, 5229.

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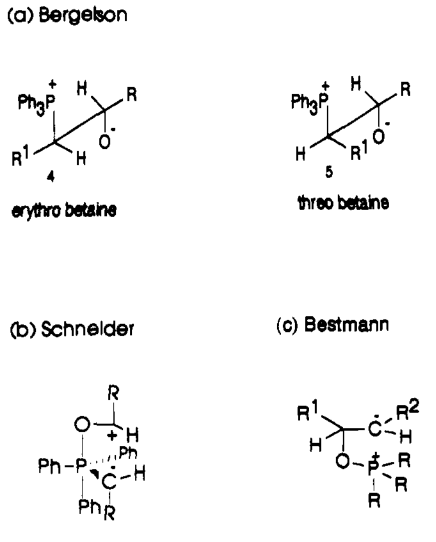
Scheme II

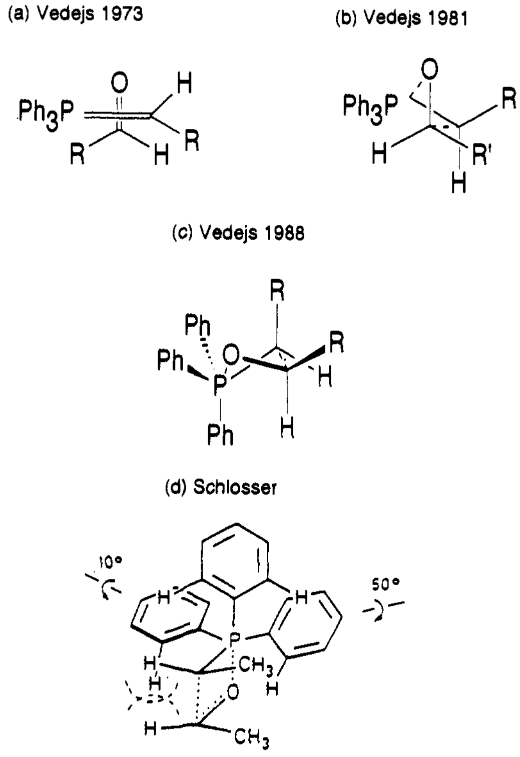


of steric considerations that the *E* oxaphosphetanes would form faster and would be more stable than their *Z* counterparts. Thus, the outcome of the reaction would be mainly formation of the *E* alkene. Although it was necessary to invoke the formation of oxaphosphetanes as intermediates to explain the observed products, it is clear that an unambiguous explanation is still lacking for the unusual stereoselectivity observed.

Two general types of mechanisms for the Wittig reaction have been proposed: (i) a stepwise ionic type of mechanism and (ii) a direct cycloaddition mechanism. The ionic stepwise mechanism was the first proposed. Wittig himself suggested a betaine (**3**) as a possible intermediate in the reaction, which would subsequently undergo ring closure to give the four-membered ring oxaphosphetane, then undergo syn elimination to give the products[3] (Scheme I). Later, Bergelson et al. proposed a hypothesis in which the formation of the betaine (Scheme IIa) is the step that determines the stereoselectivity of the reaction.[7] According to Bergelson et al., different approaches of the reactants could generate both an erythro stereoisomer **4** (*Z*-generator) and a threo isomer **5** (*E*-generator). An evaluation of the relative stabilities of these two isomers led them to consider that the erythro isomer is more stable and that it would be formed at the faster rate; this in turn would lead to preferential formation of the *Z* oxaphosphetane and subsequently the *Z* alkene in the reaction of an unstabilized ylide with an aldehyde.

Actually, betaines have not been observed spectroscopically as transient intermediates in salt-free Wittig reactions, and their involvement in the Wittig reaction has been questioned even by the use of theoretical methods.[8] Other ionic intermediates, involving prior P–O bond formation, have been proposed by Schneider[9] (Scheme IIb) and by Bestmann[10] (Scheme IIc) in order to account for the unusual *Z* stereoselectivity; in the former case, steric reasons were invoked to justify the observed stereoselectivity. Another type of stepwise mechanism of the Wittig reaction, involving an electron transfer from the ylide to the aldehyde, has been proposed by Olah;[11] however, not enough evidence has been collected to support this proposal.

Scheme III



Other general mechanistic considerations to rationalize the puzzling *Z* stereoselectivity of the salt-free Wittig reaction of unstabilized ylides have been based on the assumption of a one-step direct cycloaddition of the ylide to an aldehyde to form the oxaphosphetane. In order to explain the stereoselectivity, Vedejs initially regarded the reaction to be a synchronous symmetry controlled $_{\pi}2_{a} + _{\pi}2_{s}$ cycloaddition process,[6] a crisscrossed approach of the reactants being necessary for the proper orbital overlap (Scheme IIIa). Later, Vedejs modified his previous hypothesis to advocate the same crisscrossed geometry, but giving steric reasons for the stereoselectivity of the reaction[12] (Scheme IIIb). More recently, Vedejs has modified this view again, invoking an asynchronous cycloaddition with a four-center puckered transition state, in which steric arguments and the hybridization states of the phosphorus atom are responsible for the *Z* stereoselectivity[13] (Scheme IIIc). Also, in the concerted cycloaddition category, Schlosser has proposed a one-step mechanism in which a leeward approach of the reagents, with a planar transition state, would be responsible for the stereoselectivity;[14] in this case the interaction of the groups on the aldehyde with the groups on the phosphorus play the key factor in determining the stability of the transition state (Scheme IIId).

Even though all the mechanisms proposed for the Wittig reaction represent attempts to accommodate the experimental evidence, all remain essentially unsubstantiated. Furthermore, they are all based on the subjective evaluation of how the steric strain in the *Z*-generating transition-state structure compares with that of its *E*-generating counterpart. The experimental evidence indicates that, within the Wittig reaction path, the step that yields the oxaphosphetane seems to be the one that determines the stereoselectivity of the reaction.[15] (For convenience, we have

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(7) (a) Bergelson, L. D.; Shemyakin, M. M. *Tetrahedron* **1963**, *19*, 149. (b) Bergelson, L. D.; Shemyakin, M. M. *Angew. Chem., Int. Ed. Engl.* **1964**, *3*, 250. (c) Bergelson, L. D.; Vaver, V. A.; Barsukov, L. I.; Shemyakin, M. M. *Tetrahedron Lett.* **1964**, *38*, 2669. (d) Bergelson, L. D.; Barsukov, L. I.; Shemyakin, M. M. *Tetrahedron* **1967**, *23*, 2709.

(8) (a) Höller, R.; Lischka, H. *J. Am. Chem. Soc.* **1980**, *102*, 4632. (b) Volatron, F.; Eisenstein, O. *J. Am. Chem. Soc.* **1987**, *109*, 1.

(9) Schneider, W. P. *Chem. Commun.* **1969**, 785.

(10) (a) Bestmann, H. J. *Pure Appl. Chem.* **1980**, *52*, 771. (b) Bestmann, H. J.; Vostrowsky, O. *Top. Curr. Chem.* **1983**, *109*, 85. This intermediate was postulated to be formed in the conversion of the oxaphosphetane to final products.

(11) Olah, G. A.; Krishnamurthy, V. V. *J. Am. Chem. Soc.* **1982**, *104*, 3987.

(12) Vedejs, E.; Meier, G. P.; Snoble, K. A. *J. Am. Chem. Soc.* **1981**, *103*, 2823.

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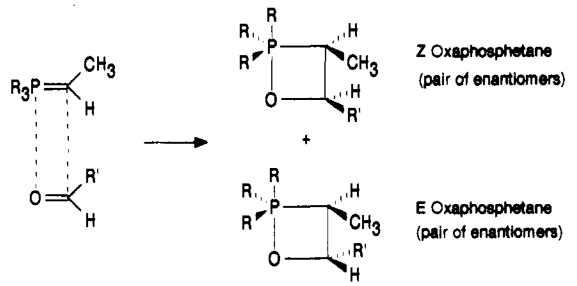
(14) (a) Schlosser, M.; Schaub, B. *J. Am. Chem. Soc.* **1982**, *104*, 3989. (b) Schlosser, M.; Oi, R.; Schaub, B. *Phosphorus Sulfur* **1983**, *18*, 171.

(15) Maryanoff, B. E.; Reitz, A. B.; Mutter, M. S.; Inners, M. S.; Almond, R. R. H.; Whittle, R.; Olofson, R. R. *J. Am. Chem. Soc.* **1986**, *108*, 7664. Complications of "stereochemical drift" and "diastereomeric synergism" have been described by Maryanoff et al. in this and earlier publications, but these are not general phenomena.

Scheme IV



Reaction/ TS	R	R'	Reaction/ TS	R	R'
1a/6a(Z)	H	CH_3	**4a/9a(Z)**	C_6H_5	CH_3
1b/6b(E)	H	CH_3	**4b/9b(E)**	C_6H_5	CH_3
2a/7a(Z)	H	$C{\equiv}CH$	**5a/10a(Z)**	C_6H_5	$C{\equiv}CH$
2b/7b(E)	H	$C{\equiv}CH$	**5b/10b(E)**	C_6H_5	$C{\equiv}CH$
3a/8a(Z)	H	$C{\equiv}N$	**6a/11a(Z)**	C_6H_5	$C{\equiv}N$
3b/8b(E)	H	$C{\equiv}N$	**6b/11b(E)**	C_6H_5	$C{\equiv}N$

referred to this step as the Wittig half-reaction.[1]) However, it must be emphasized that there is no direct experimental evidence that indicates what is the most likely nature of the transition state involved in the Wittig half-reaction. Furthermore, the failure to detect spectroscopically possible transient intermediates, such as betaines, spin-paired diradicals,[16] or charge-transfer complexes,[11,17] cannot rule out their possible involvement in the Wittig reaction.

Since there seems to be at present no experimental method to permit the evaluation of the geometries and relative stabilities of possible transition states under the conditions of the Wittig reaction, the use of theoretical methods offers an alternative, objective means for such evaluation. We have taken advantage of recent advances in theoretical chemistry and computational resources to evaluate complex systems such as those found in the Wittig reaction. In particular, we have shown that the MNDO-PM3 semiempirical molecular orbital method[18] is capable of yielding calculated structures of oxaphosphetanes and ylides that are comparable with the experimentally known structures.[1] Also, the MNDO-PM3 method reproduces the geometric and thermodynamic parameters, previously calculated using a more elaborate and costly ab initio molecular orbital approach (4-31G* level), of the "mythical Witting half-reaction" ($H_3P{=}CH_2$ + CH_2O → the oxaphosphetane).[8b] We found that the mythical Wittig half-reaction is best described as a very asynchronous cycloaddition (a borderline two-step mechanism) with a planar geometry in the transition state, composed of a multicentered P–C–C–O bond orbital, and with the phosphorus and the oxygen atoms sharing a strong attractive charge interaction, which denotes an important zwitterionic character.[1] In this paper we use the same semiempirical MNDO-PM3 molecular orbital methodology to investigate the Wittig half-reaction of the unstabilized ylides $H_3P{=}CH{-}CH_3$ (mythical) and $(C_6H_5)_3P{=}CH{-}CH_3$ (real) with aldehydes, thus evaluating the feasibility of the one-step cycloaddition mechanisms proposed by Schlosser and Vedejs.

Methodology

The model reactions selected for the present study are those of the unstabilized ylides ethylidenephosphorane (R = H) and ethylidenetriphenylphosphorane (R = C_6H_5) with acetaldehyde, propargylaldehyde, and glyoxylonitrile, to form the respective *Z* and *E* oxaphosphetanes (Scheme IV). We have already justified the use of such Wittig half-reactions as models to attempt to explain mechanistically the observed stereoselectivity.[1] The model reactions used for this study are based on the assumption that the ylide and aldehyde are aligned in the proper geometry for a one-step cycloaddition reaction; i.e., the ylide and the aldehyde approach in the appropriate manner so as to form in a concerted fashion each expected oxaphosphetane.

The MOPAC[19] (Version 5.0) molecular orbital package utilizing the MNDO-PM3 Hamiltonian[18] was used for the semiempirical MO calculations. Input files were generated using the graphics interface of PCMODEL-PI (v3.0) (Serena Software, Bloomington, IN). The starting geometries for all of these semiempirical calculations were the minimized geometries of the MMX89[20] force field. The presence of phenyl rings attached to the phosphorus in some of our model reactions presents the possibility of different conformations by rotation about the P–C bonds; thus, the global minimum among these possible conformations was obtained by a multitorsional global optimization of dihedrals with a Monte Carlo–Metropolis approach to simulated annealing, a routine implemented in the MMX89 program. The calculations were carried out on DEC VAX-6210 computers at the University of Massachusetts University Computer Center, or on the IBM 3090 supercomputer at the Cornell National Supercomputer Facility.

The transition states for each "Wittig half-reaction" were located using the SADDLE[21] routine implemented in MOPAC. No arbitrary assumptions were imposed on finding the most likely geometries for the transition state in each case. Further refinement of some transition state geometries was carried out with the use of the NLLSQ algorithm.[22] The systems were characterized as transition states by the presence of one and only one negative force constant in the Hessian matrix of a force calculation.[23] Bond orders were calculated as the sum of the squares of the density matrix elements connecting two atoms by the BONDS routine implemented in MOPAC.[24] Another bond order analysis was carried out by the use of the relative variation of bond orders at the transition state of particular bonds *i*, δB_i,[25] a parameter which is defined in

$$\delta B_i = (B_i^{TS} - B_i^{R})/(B_i^{P} - B_i^{R}) \qquad (1)$$

where TS, R, and P refers to the transition state, reactant, and product stages, respectively. An average value of these relative bond orders (δB_{av}) can be used as a measure of the degree of advancement of the transition state along a reaction path.[25] The localized molecular orbitals (LMOs) for the reactants, products, and transition states were found using the Perkins–Stewart method implemented in the same program.[26]

Results and Discussion

The "cycloaddition-like" approaches of the ylides to the aldehydes that we considered in our model reactions led to reaction paths in which we found only one transition state. Other possible paths were investigated by the use of the SADDLE routine and appropriate reaction coordinate analysis; however, the parallel approach of planes that contain each reactant (the plane defined

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(16) (a) McEwen, W. E.; Beaver, B. D.; Cooney, J. V. *Phosphorus Sulfur* **1985**, *25*, 255. (b) Ward, W. J.; McEwen, W. E. *Phosphorus Sulfur* **1989**, *41*, 393. (c) Ward, W. J.; McEwen, W. E. *J. Org. Chem.* **1990**, *55*, 493.

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(20) Available from Serena Software through Professor K. Steliou, University of Montreal, Quebec, Canada.

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Table I. Energetics and Geometric Parameters Calculated Using the MNDO-PM3 Method for the Set of Reactions Described in Scheme IV[a]

reaction/TS	R	R′	ΔH_r, kcal/mol	$\Delta H^{\ddagger}$, kcal/mol	C–C, Å	P–O, Å	∠PCCO, deg
1a/**6a** (*Z*)	H	CH_3	−20.45	15.3	2.14	2.48	0.00
1b/**6b** (*E*)	H	CH_3	−21.97	13.94	2.11	2.57	13.00
2a/**7a** (*Z*)	H	C≡CH	−21.80	14.65	2.12	2.67	6.53
2b/**7b** (*E*)	H	C≡CH	−23.30	12.62	2.10	2.71	3.47
3a/**8a** (*Z*)	H	C≡N	−26.95	8.92	2.09	2.93	17.45
3b/**8b** (*E*)	H	C≡N	−28.46	6.76	2.09	2.94	12.7
4a/**9a** (*Z*)	C_6H_5	CH_3	−13.56	26.78	1.96	2.63	2.11
4b/**9b** (*E*)	C_6H_5	CH_3	−18.24	22.92	2.00	2.73	1.54
5a/**10a** (*Z*)	C_6H_5	C≡CH	−16.16	25.65	1.96	2.77	11.33
5b/**10b** (*E*)	C_6H_5	C≡CH	−17.90	21.27	1.97	2.85	2.30
6a/**11a** (*Z*)	C_6H_5	C≡N	−20.54	19.31	1.98	2.86	9.96
6b/**11b** (*E*)	C_6H_5	C≡N	−22.06	15.64	2.00	2.93	14.37

[a] The bond distances and bond angles are given for the structures of the calculated transition states. The P–C–C–O angles provide a measure of the puckering in these transition states.

by the P–C–C bonds in the case of the ylide and defined by the O–C–H bonds in the case of the aldehyde) showed this path to be the most favorable for the reaction to take place. The following discussion is in reference to the analysis of the reaction paths of the different model sets and the effects of the different substituents on these reaction paths.

Table I shows the calculated enthalpies of formation and activation (ΔH_r and $\Delta H^{\ddagger}$, respectively) of the Wittig half-reaction of the mythical unstabilized ylides $H_3P{=}CHCH_3$ and of $(C_6H_5)_3P{=}CHCH_3$ with acetaldehyde, propargylaldehyde, and glyoxylonitrile. In all these cases, the $\Delta H^{\ddagger}$ of model Wittig half-reactions that lead to the formation of the *Z* oxaphosphetane are ~1.5 kcal/mol more positive than their *E*-generating counterparts. The same energy differences are found between the *Z* oxaphosphetanes and the *E* oxaphosphetanes, confirming our previous expectations and findings, using a MNDO approach,[27] that *E* oxaphosphetanes are more stable than their *Z* counterparts.

In general, the model Wittig half-reactions herein studied showed good agreement with the principles of the Hammond postulate,[28] since the transition states of lower energy correspond to the formation of the most stable stereoisomer in each component of a given series, i.e., in either the *Z* versus *E* case or when the electrophilicity of the aldehyde is considered. Also, according to our calculations, the greater thermodynamic stability of the *E* oxaphosphetanes contradicts the hypothesis that thermodynamic control of the Wittig half-reaction by the oxaphosphetane is responsible for the unusual experimentally observed *Z* stereoselectivity.[14]

Figure 1 shows the geometries of the *Z* transition states **6a** and **9a** and their respective *E* counterparts, **6b** and **9b**. Little variation in the C–C distances at the transition state is found in all our model Wittig half-reactions, ranging from 1.96 Å to 2.14 Å, whereas, the P–O distances at the transition state range from 2.48 Å to 2.93 Å. The phosphorus–oxygen distances in the transition states are found to increase along with the electrophilicity of the aldehyde (acetaldehyde < propargylaldehyde < glyoxylonitrile), varying from 2.48 Å to 2.94 Å for the reactions of $H_3P{=}CHCH_3$ along this series and from 2.63 Å to 2.93 Å for the reactions of $(C_6H_5)_3P{=}CHCH_3$. This result suggests that the model Wittig half-reactions become more asynchronous as the electrophilicity of the aldehyde increases. Also, as ΔH_r values of the respective oxaphosphetanes become more negative and their associated $\Delta H^{\ddagger}$ become lower, these model reactions become less synchronous.

The planarity of the transition state (measured in terms of the P–C–C–O dihedral angle) does not seem to be associated with steric factors, since in the most crowded transition states (entries 1 and 4), one might expect to find the least planar orientation. Contrary to this, the *Z* transition states, **6a** and **9a**, were shown to be completely planar, whereas a less crowded *E* counterpart, **6b**, shows some degree of puckering. The largest degree of puckering in the transition state was found to be in the reactions of the glyoxylonitrile (entries **3** and **6** in Table I).

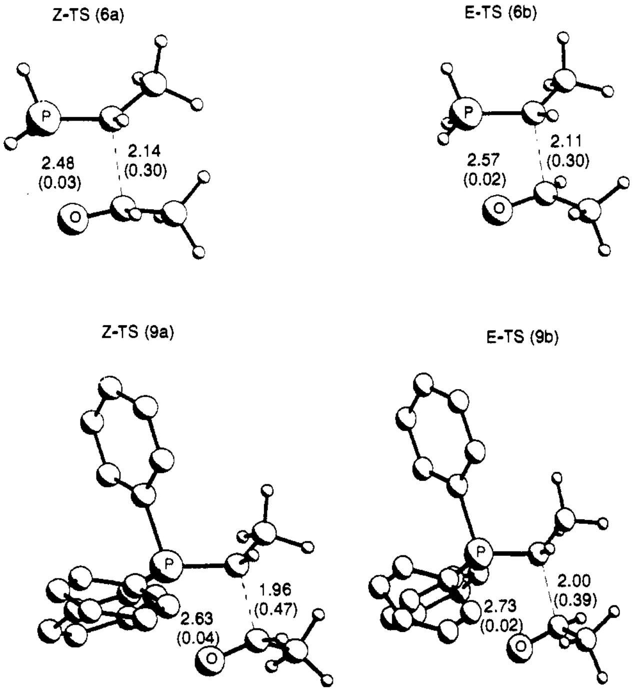

Figure 1. Transition states of model Wittig half-reactions **1** and **4**. These views are referred to those representations where the plane of the figure contains the P–C–C–O atoms. The bond distances are given in å units, whereas the quantities in parentheses are the absolute bond orders (see text below and Table II for the discussion of the relevance of the bond orders).

The inclusion of phenyl groups, which increases the steric repulsion in the systems, causes an increase of 10 kcal/mol in the $\Delta H^{\ddagger}$ (Table I, entries **4**–**6**), in comparison with the cases where hydrogens are attached to the phosphorus atom. Likewise, the model reactions with phenyl groups on the phosphorus were shown to have ΔH_r 5–8 kcal/mol less negative than the previous cases. Therefore, the presence of the phenyl groups makes an important contribution to the steric strain of both the formation of the oxaphosphetanes and the formation of the transition states that lead to these oxaphosphetanes. Associated with these energy changes, the P–O distances in the transition states of this set (reactions **4**–**6**) are 0.10 and 0.20 Å longer than those of the previous set (reactions **1**–**3**). For all the model reactions (**1**–**6**), the C–C distances at the transition state remained essentially constant as the electrophilicities of the aldehydes are increased, whereas the P–O distances increase with the same change.

The results of the model reactions of $(C_6H_5)_3P{=}CHCH_3$ with aldehydes represent a crucial test for mechanistic proposals that invoke a one-step cycloaddition of the ylide to the aldehyde, since the presence of the phenyl groups on the phosphorus atom is an experimental requirement for the unusual *Z* stereoselectivity. In this set of model reactions, the transition states that generate the *Z* oxaphosphetanes are about 4 kcal/mol higher in energy than

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(27) Marí, F.; Lahti, P. M.; McEwen, W. E. *Heteroatom Chem.* **1990**, *1*, 255.

(28) Hammond, G. S. *J. Am. Chem. Soc.* **1955**, *77*, 334.

those of the reactions in which the *E* isomer is formed. A parallel situation is found for the respective oxaphosphetanes: the *E* oxaphosphetanes are 1.5 to 4.5 kcal/mol more stable than the *Z* oxaphosphetanes. The above results indicate that the one-step cycloaddition hypothesis to explain the *Z* stereoselectivity is by itself not adequate. Vedejs[6,12,13] who has advocated one of these one-step cycloaddition mechanisms, has invoked partial support for this mechanistic proposal based on the interferences made by Volatron and Eisenstein in their ab initio work.[8b] According to them, the mythical Wittig half-reaction proceeds by a concerted, symmetry-controlled cycloaddition that has a planar transition state. Vedejs' arguments involve the same type of mechanism, but this hypothesis includes the effects of substituents on the phosphorus atom, ylidic carbon, and the aldehyde, which, by virtue of the steric strain that they exert on the transition state and the role that they play in the phosphorus atom hybridization throughout the reaction, are thought to perturb the transition state in such a way that it is no longer planar, but rather puckered.[13] Then, a subjective evaluation of these puckered transition states is used to justify the unusual *Z* stereoselectivity. However, it had already been pointed out by Volatron and Eisenstein that the lack of substituents in the mythical Wittig half-reaction has an important effect on the energetics of the reaction, and large discrepancies can be found in comparison with experimental results.[8b] Moreover, based on their geometrical assessment of the transition state of the mythical Wittig half-reaction, Volatron and Eisenstein *hypothesized* that a $2_s + 2_s$ cycloaddition that calls for the use of the d orbitals and frontier orbital control[29] would justify a concerted cycloaddition without violating the Woodward–Hoffmann symmetry rules. However, our semiempirical results suggest that this is not the case; instead, the Wittig half-reaction proceeds through a nonsymmetry-controlled one-step but, nevertheless, very asynchronous cycloaddition.[1] In addition, we have carried out 4-31G* ab initio fixed geometry calculations using the Volatron and Eisenstein transition-state geometry for oxaphosphetane formation, and we find no significant degree of covalent bonding interaction between phosphorus and oxygen in the bond order analysis. Our present calculations, which include substituents at the phosphorus atom, the ylidic carbon, and the aldehyde, show dramatic energy and geometric changes when compared to the mythical case. For instance, the $\Delta H_f°$ values of the oxaphosphetanes become less negative by up to 15 kcal/mol, and $\Delta H^{\ddagger}$s are increased by up to 18 kcal/mol by the presence of these substituents, when the entries in Table I are compared to the mythical Wittig half-reaction ($H_3P{=}CH_2 + CH_2O \rightarrow$ the oxaphosphetane).[1] Geometrically, the transition states are those that correspond to an even more asynchronous process, since longer P–O distances are found. This interpretation is also confirmed by the bond order and localized MO analyses, as shown later. Also, we found that the transition states in these reactions are very slightly puckered, but not for the reason that Vedejs previously proposed. Instead, the puckering seems to be associated mainly with the electrophilicity of the aldehyde.

Thus, the one-step cycloaddition with a puckered transition state, proposed by Vedejs to explain the *Z* stereoselectivity of the Wittig reaction,[13] is not only inconsistent with our present computational modeling, but also presumes P–O covalent bonding in the transition state within the context of a symmetry-controlled cycloaddition.[8b] Our theoretical methodology suggests that this mechanistic hypothesis is not likely.[1]

The other one-step cycloaddition mechanism, proposed by Schlosser,[14] is at first glance more consistent with our results, since it considers the geometry of the transition state to be essentially planar, with a propeller-like orientation assumed by the phenyl substituents around the phosphorus atom. Figure 2 shows the CPK space-filling representation of the transition states, **9a** and **9b**, of reactions **4a** and **4b** calculated using the MNDO-PM3 approach and some of the possible steric interactions of importance in such a system. These transition states indeed show a propeller-like orientation of the phenyl rings, but with a different orientation than that proposed by Schlosser, and, as it was shown previously, the *Z* transition state, **9a**, has a higher energy content that its *E* counterpart, **9b** (Table I). Even though the Schlosser geometry and steric interaction analysis is qualitatively the same as we noted in the transition states of reactions **4a** and **4b**, the relative weights of such interactions were quantitatively different from our analysis, in which the methyl–methyl interaction in the *Z* stereoisomer seems to be by far the most important contribution to the steric strain of the system. Thus, this one-step cycloaddition model also does not unequivocally explain the unusual stereoselectivity.

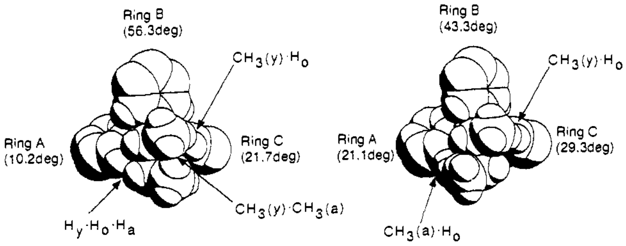

Figure 2. Transition states of reactions **4a** (*Z*) and **4b** (*E*) calculated using the MNDO-PM3 methodology. The numbers in parentheses indicate the angle of rotation of the phenyl ring.

Under salt-free conditions, Wittig reactions of unstabilized ylides that bear alkyl substituents on the phosphorus atom do not experimentally show the unusual *Z* stereoselectivity shown[30] by ylides with phenyl substituents on the phosphorus atom, a phenomenon at least partially attributable to the greater tendency of the former systems to undergo stereochemical drift.[2,15] Also, regardless of the substituents on the phosphorus atom, the more electrophilic aldehydes tend to yield more of the *E* alkene isomer.[31] Both of these situations might have a further justification based upon the results of our calculations. The model reactions **1–3**, may resemble those of phosphorus ylides having substituents on the phosphorus. The *E* stereoselectivity in our model reactions may be explainable in terms of the steric strain exerted by the methyl groups. By contrast, the presence of the bulky phenyl groups on the phosphorus not only enhances the already marked relative stabilities of the *E*-generating transition states as against the *Z*-generating ones, but also makes kinetic control of the reactions more likely because of the significant increase in the enthalpies of activation caused by the increase of steric strain in the transition states. This effect is counterbalanced, however, by the use of more electrophilic aldehydes. In these reactions, there is a decrease in activation energy, to the point where the enthalpies of activation of reaction **6** are comparable to those shown in Table I (reactions **1–3**, R = H). In any case, there is the possibility that the *E* product formed in Wittig reactions of unstabilized ylides may be viewed as occurring by a one-step cycloaddition pathway, since our calculations do predict *E* stereoselectivity in such cases. Therefore, a further analysis of the nature of the transition states will now be assessed in terms of calculated bond orders and the localized molecular orbitals (LMOs) of the reaction paths.

An examination of the geometries of the transition states of the model reactions, where C–C distances range from 1.96 Å to 2.14 Å and P–O distances from 2.48 Å to 2.94 Å, could be interpreted as an indication that these reactions proceed by a synchronous process. However, the evaluation of bond-breaking–forming processes in transient species, where bond distances are significantly longer than those of known ground-state species, could be misleading.[25] The use of the bond orders, which are an approximate measure of the bond strength, is a more objective method for such an evaluation.

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(31) Gosney, I.; Rowley, A. G. In *Organophosphorus Reagents in Organic Chemistry*; Cadogan, J. I. G., Ed.; Academic Press: New York, 1979; pp 15–253 and references therein.

Table II. Bond Orders of Relevant Atom Pairs in the Model Wittig Half-Reactions and Relative Variation of the Bond Order at the Transition State (δB_i) with Its Respective Average (δB_{av})[a]

bonds		R	R′	reactants: $R_3P{=}CHCH_3$ + R′CHO	transition state	product: oxaphosphetane	δB_i	δB_{av}
P–C	**1**	H	CH_3	1.13	0.97 (0.97)	0.67 (0.66)	0.35 (0.34)	0.28 (0.27)
C–C					0.30 (0.30)	0.96 (0.96)	0.31 (0.31)	
C–O				1.92	1.56 (1.57)	1.00 (1.00)	0.39 (0.38)	
P–O					0.03 (0.02)	0.53 (0.53)	0.06 (0.04)	
P–C	**2**	H	C≡CH	1.13	0.98 (0.98)	0.67 (0.67)	0.33 (0.33)	0.27 (0.27)
C–C					0.31 (0.32)	0.95 (0.95)	0.33 (0.34)	
C–O				1.95	1.59 (1.58)	1.00 (1.00)	0.39 (0.39)	
P–O					0.01 (0.01)	0.52 (0.52)	0.02 (0.02)	
P–C	**3**	H	C≡N	1.13	0.98 (0.98)	0.67 (0.66)	0.33 (0.32)	0.27 (0.26)
C–C					0.34 (0.34)	0.95 (0.95)	0.36 (0.36)	
C–O				1.99	1.63 (1.63)	1.01 (1.02)	0.37 (0.37)	
P–O					0.00 (0.00)	0.49 (0.50)	0.00 (0.00)	
P–C	**4**	C_6H_5	CH_3	1.21	0.91 (0.94)	0.69 (0.70)	0.58 (0.53)	0.41 (0.35)
C–C					0.47 (0.39)	0.95 (0.95)	0.49 (0.41)	
C–O				1.92	1.45 (1.52)	1.00 (1.00)	0.51 (0.43)	
P–O					0.04 (0.02)	0.57 (0.57)	0.07 (0.04)	
P–C	**5**	C_6H_5	C≡CH	1.21	0.94 (0.92)	0.69 (0.69)	0.52 (0.56)	0.36 (0.39)
C–C					0.43 (0.46)	0.94 (0.94)	0.46 (0.49)	
C–O				1.95	1.52 (1.49)	1.00 (1.00)	0.45 (0.48)	
P–O					0.01 (0.02)	0.56 (0.56)	0.07 (0.04)	
P–C	**6**	C_6H_5	C≡N	1.21	0.92 (0.94)	0.69 (0.69)	0.56 (0.52)	0.40 (0.35)
C–C					0.46 (0.42)	0.95 (0.95)	0.48 (0.44)	
C–O				1.99	1.49 (1.59)	1.02 (1.02)	0.52 (0.41)	
P–O					0.02 (0.01)	0.53 (0.53)	0.04 (0.02)	

[a] The numbers in parentheses indicate the bond orders of the respective reactions in which the *E* stereoisomer is formed.

Table II shows the bond orders throughout the reaction paths of the model reactions used in this study. In all cases, the C–C bond is more than 30% formed in the transition state, whereas the P–O bonds are not formed to any significant degree at this stage. These results indicate that the Wittig half-reaction of unstabilized ylides is a highly asynchronous process regardless of the substituents on the phosphorus atom or the aldehyde. However, the results of bond order calculations (absolute, relative, or average) of reactions that bear H substituents on the phosphorus atom as compared with those of the reactions of ylides that bear phenyl substituents on phosphorus, show that the latter reactions are more advanced (i.e., have a later transition state), with C–C bond formation ~50% in reactions **4**–**6** versus ~33% in reactions **1**–**3**.

No significant differences at any stage of the reaction paths were detected between the bond orders of reactions that generate the *Z* stereoisomers and those that generate the *E* stereoisomers. Thus, within a one-step cycloaddition mechanistic scheme, both types of reaction (*Z*-generating and *E*-generating) have the same degree of synchrousness in the transition states. These results confirm the geometrical finding shown above; i.e., no significant differences were found between the distances of relevant atom pairs of *Z* transition states as against those of their *E* counterparts. Surprisingly, the bond order results do not show any trend relative to the electrophilicity of the aldehyde in any comparison of the two sets of reactions. We have shown above that there seems to be a correlation of the P–O distances and slight puckering of the transition states with the electrophilicity of the aldehyde; however, the bond orders are apparently insensitive to such a change. Also, the bond order analysis reveals the development of the bond strength within individual atom pairs throughout the reaction path of these model Wittig half-reactions. Thus, the P–C and C–O bond strengths decrease as the reaction proceeds, whereas the C–C bond strengths increase. On the other hand, the P–O bond is formed only very late in the oxaphosphetane-yielding process.

In addition to the bond order analysis, we have shown that the use of the localized molecular orbitals (LMOs) can yield valuable information about the asynchronousness of the Wittig half-reaction and the nature of the transition state.[1]

Figures 3 and 4 show the energy correlation of the LMOs of reaction **1a**; other model reactions of this set show very similar LMO diagrams. The average displacement of the electron densities during the Wittig half-reaction may be described by the changes in the LMOs as follows: the π_{P-C}, the bond orbital of the highest energy content of the system, is transformed into a lower energy multicentered m_{PCCO} bond orbital at the transition state, which in turn is transformed into an even lower σ_{C-C} bond orbital at the oxaphosphetane stage. The transformation of the π_{P-C} into the σ_{C-C} bond orbital represents the largest energy and orbital symmetry change throughout the entire reaction path, and it can be considered a stabilizing contribution to the transition

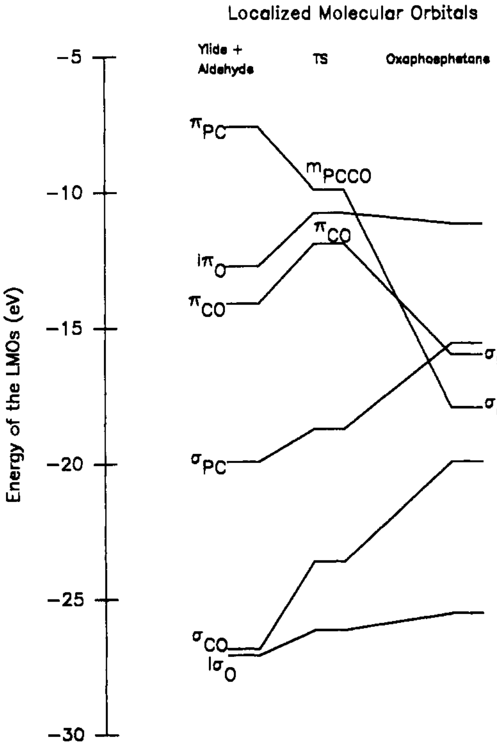

Figure 3. Energy correlation diagram of the localized molecular orbitals (LMOs) of the bond orbitals that intervene in the bond-forming–breaking process in reaction **1**. The orbitals have been labeled with the following criteria: Is and Ip refer to the localized monocentric orbitals, σ and π refer to bicentric localized orbitals, and the multicentered P–C–C–O localized orbital was designated m_{PCCO}.

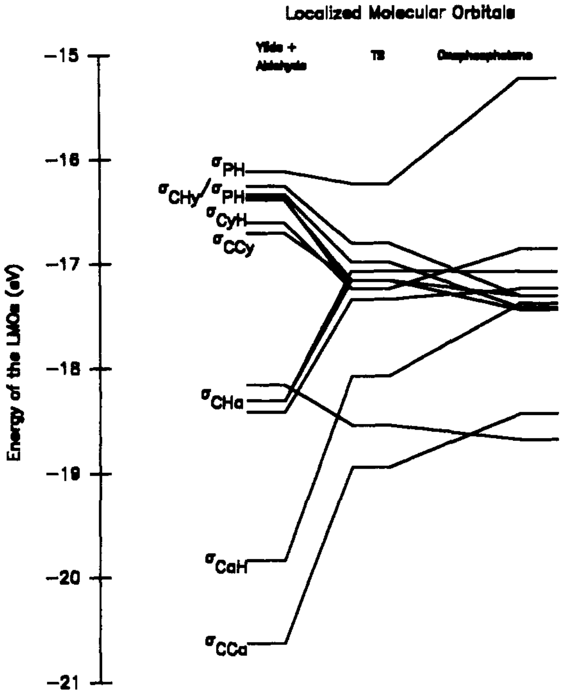

Figure 4. Energy correlation diagram of the localized molecular orbitals (LMOs) of the bond orbitals that do not intervene directly in the bond-forming–breaking process in reaction 1.

state and to the product,[32] since this transformation is associated with the bond-forming process of the Wittig half-reaction. On the other hand, the bond-breaking process of the reaction can be followed by the observed transformation of the π_{C-O} bond orbital, which, without changing its symmetry, increases in energy at the transition state and then transforms into the σ_{P-O} at the oxaphosphetane stage. The increase in energy from the reactant to the TS stage indicates that this transformation would be a destabilizing contribution to the TS, and it can be viewed as the energy cost to break the C═O bond to reach the TS. The results in the LMOs analysis indicate that no P–O bond formation has occurred at the transition-state stage, since there is no phoshorus participation in the bond orbital associated with the oxygen atom. Instead, the electron population analysis indicates that, at the transition state, the π_{C-O} bond orbital is distinctly more polarized, with more negative charge density at the oxygen atom in the transition-state stage than at the reactant stage. Even though this bonding orbital does not become transformed into a monocentric localized orbital at the transition state (an apparent requirement for the reaction to proceed by an ionic pathway[25]), the transition state, nevertheless, has a very significant zwitterionic character as shown by the charge distribution.

As indicated by the bond order analysis, the driving force for the formation of the TS is the C–C bond formation, which, as the LMOs analysis reveals, involves the formation of the m_{PCCO} bond orbital for the reaction of the phosphorane with aldehydes. In the case of the triphenylphosphorane, a m_{PCC} bond orbital is found at the transition state. These multicentered orbitals are dominated by the C–C part, with a heavy negative charge polarization toward the ylidic carbon. The relative degree of asynchronousness of the Wittig half-reaction should be reflected by changes in the nature of the multicentered bonding LMOs. Therefore, an analysis of the relative levels of energy of this bonding orbital might yield information about the asynchronousness of the reaction. Figure 5 shows the correlation diagram of the transformation of the π_{P-C} into the σ_{C-C} bonding orbitals for reactions **1** to **6**. In the phosphorane cases, the m_{PCCO} bond orbital tends to lie more toward the reactants, indicating an early transition state. However, as the electrophilicity of the aldehyde increases, this orbital tends to be more stabilized at the transition state, thus becoming more advanced with such a change. In the triphenylphosphorane cases, the m_{PCC} bond orbital still lies closer to the reactants than to the product; however, it is more stabilized than any of the m_{PCCO} bond orbitals of the previous set. Consequently, a less reactant-like transition state is indicated in this case. These events correlate directly with the bond order results, where the C–C bond formation of the second set was shown to be greater than that of the first. Thus, the stability of the multicentered bond orbital does reflect differences in asynchronousness or advancement of the transition state. Small changes in the energies of the m_{PCC} and m_{PCCO} bond orbitals are observed (only up to 1 eV) within each series, a difference in asynchronousness that could not be detected by the bond order analysis. On the other hand, larger differences in asynchronousness between the two sets, observed even by the bond order analysis, are accompanied by larger LMO energy differences of up to 3 eV. Even the difference in the nature of the multicentered bond orbital seems to be indicative of the asynchronousness of the reaction, since the more advanced reaction set does not show residual C═O bonding in the multicentered bond orbital. Thus, the reactions become more asynchronous as phenyl groups are included in the reaction scheme.

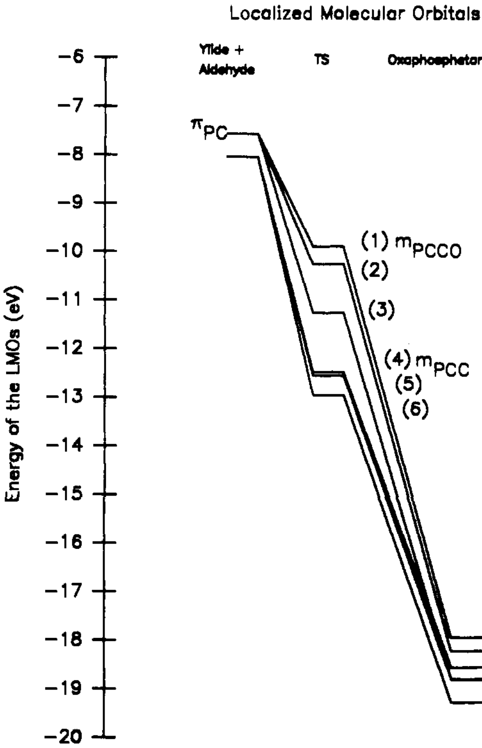

Figure 5. Energy correlation diagram of the localized molecular orbitals (LMOs) of the bond orbitals that intervene in the transformation of the πP–C into the σC–C bonding orbitals for reactions **1** to **6**.

The analysis of the LMOs given above confirms the trends in asynchronousness provided by the examination of the geometries of the transition states, where the more electrophilic aldehydes in reactions with the ylide having phenyl substituents on the phosphorus atom tend to result in longer P–O distances in the transition state, indicating a shift of the asynchronousness of the model Wittig half-reaction with these changes.

The lack of P–O covalent bonding at the transition state of all our model Wittig half-reactions is confirmed separately by the bond order analysis and the analysis of the LMOs. Therefore, according to the events described above, the mechanism of the Wittig half-reaction may be represented in terms of the curved arrows depicted in Scheme V, where the partial bonding between the P–C and C–O in the transition state is very weak, while a highly polarized C–O bond denotes important zwitterionic character.

The origin of the *Z* stereoselectivity of olefin formation in

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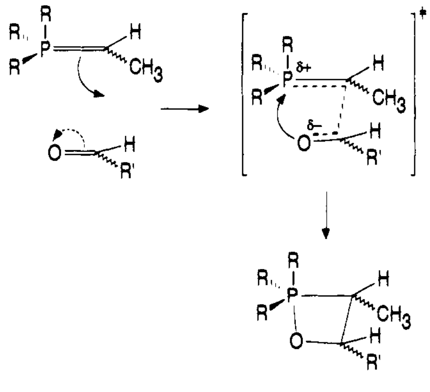
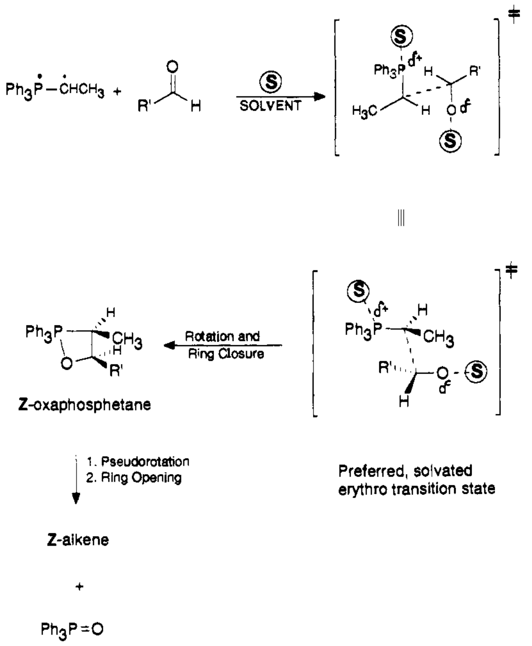
(32) Moyano, A.; Pericàs, M. A.; Serratosa, F.; Valenti, E. *J. Org. Chem.* **1987**, *52*, 5532.

Scheme V



Scheme VI. Possible Mechanism for the Preferred Formation of the *Z* Oxaphosphetane in Solution



salt-free reactions of unstabilized ylides having phenyl groups bonded to the phosphorus atom with aldehydes remains an intriguing phenomenon. Even though our computational modeling appears not to accord with the proposed explanations of Vedejs[13] and of Schlosser,[14] our results suggest a possible resolution of the problem. The highly evolved C–C bond formation at the transition state of the Wittig half-reaction involving a "syn" approach of the reactants to form the oxaphosphetane is a result of our computations with respect to a mythical gas-phase reaction at 0 K. This concept very likely requires modifications when applied to the real world of Wittig reactions carried out in a solvent such as tetrahydrofuran,[2] which is moderately polar. The consideration of factors such as solvation, formation of aggregates of reactants by intermolecular interactions, or the presence of other ionic species in the reaction environment, might make an "anti" approach conceivable.[7] On the assumption that this is a transition-state phenomenon, as in the case of our computations for a mythical gas-phase reaction, there is no necessity for the formation of a discrete intermediate, such as a solvated betaine.[33]

A mechanism which is reminiscent of the classical ionic mechanism is suggested in Scheme VI, except that the critical action that determines the predominant stereochemistry occurs in the formation of the transition state and its subsequent decay to the oxaphosphetane product. Our MNDO-PM3 approach has indicated that under a cycloaddition-type of mechanism with a "syn" approach of the reactants, this type of transition state with partial C–C bond formation and no evidence of P–O bond formation is occurring. In the presence of other elements in the media, an "anti" approach of the reactants that leads to an "anti" transition state is feasible.

We, like others have noted that the "anti" approach in our model does not lead to a stable "anti" betaine.[8,10a] Dipolar solvation effects might alter this-gas phase finding, but at present it is not readily modeled (vide infra). The "syn" geometries found for the transition states of the model Wittig half-reactions in the present study are forced by the attractive electrostatic interaction between the phosphorus atom and the oxygen atom, which is a consequence of the approximations made in our modeling approach. Fortunately, our results, in this and previous work, indicate that semiempirical MO methods are already capable of successfully modeling a large variety of experimentally verifiable effects for experimentally realistic molecules in Wittig reaction chemistry. Bearing in mind the unavoidable potential pitfalls when a theoretical prediction is compared with the experimental findings, we summarize the following conclusions of our study. (1) The Wittig half-reactions of unstabilized ylides with aldehydes to form oxaphosphetanes may be described as a highly asynchronous process, a borderline two-step cycloaddition, with little (if any) P–O covalent bonding in the transition state. (2) Phenyl group substitution on the phosphorus in this process appears to have an essentially steric effect on the reaction, raising the activation enthalpy and lowering the overall reaction enthalpy relative to the mythical model systems with hydrogen substituents upon the phosphorus. (3) The half-reaction activation enthalpy decreases with increasing aldehyde electrophilicity, in accord with experimental observations.[7a] (4) *Z* stereoselectivity is not predicted in any of our model reactions, but rather steric effects lead to Hammond-type production of the most stable *E* isomers.

Clearly computational modeling studies will require further refinement in order to predict unambiguously experimental results in this fascinating reaction. We feel that inclusion of solvent effects may be critical to the solution of point 4 above. However, an example of the sort of important problem to be faced is the question of solvent reorganization in the transition state; i.e., what solvent cavity size and shape are appropriate in going from two isolated reactants to a single transition state in a bimolecular reaction?[35] The resolution of these types of problems is beyond

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(33) Ward and McEwen have demonstrated that (*Z*)-stilbene is the major alkene formed in the reaction of benzylidenemethyldiphenylphosphorane with benzaldehyde at −78 °C in tetrahydrofuran in the presence of a soluble lithium salt. The same holds true when a soluble sodium salt is present. In the absence of a soluble metal salt, (*E*)-stilbene is the major alkene formed. The same holds true for many additional reactions involving aldehydes (both aromatic and aliphatic) other than benzaldehyde. On the basis that a phenyl group will preferentially occupy an apical position of the trigonal bipyramidal phosphorus of each of the oxaphosphetanes that can actually be formed by reaction of benzylidenetriphenylphosphorane with benzaldehyde, eight stereoisomeric oxaphosphetanes are possible (four pairs of enantiomers). Four of the stereoisomers having *Z* configurations would result from erythro metalated betaines that arise by the Bergelson mechanism, and four stereoisomers having the *E* configuration would arise from threo metalated betaines. Of course, the *Z* oxaphosphetanes would eventually give rise to (*Z*)-stilbene, the major alkene, and the *E* oxaphosphetanes would give (*E*)-stilbene, the minor alkene. Mari, Lahti, and McEwen[34] have carried out molecular modelling studies of these reactions with the aid of the MMX89 force field and by an analysis that included a multitorsional global optimization of dihedrals, and it was found that all of the metalated erythro betaines (the (*Z*)-stilbene generators) have lower total MMX energies that the metalated threo betaines (the (*E*)-stilbene generators). This and related work will be presented in detail in a forthcoming paper.

(34) Mari, F.; Lahti, P. M.; McEwen, W. E. 199th National Meeting of the American Chemical Society, Division of Organic Chemistry, Boston, MA, April 22–27, 1990, Paper 413.

(35) The use of self-consistent reaction field theory has been recently described in the literature.[36] This methodology has been successfully utilized to predict the relative stabilities of tautomeric substituted pyridines,[36b] five-membered ring heterocycles with two heteroatoms,[36c] nucleic acid pyrimidines, and purine bases[36d] and to model the solvation of amino acids.[36e] To our knowledge, the use of such methodology to study bimolecular chemical reactions has not been effected. The self-consistent reaction field theory uses solvation cavities to describe the effect of the solvent on the solute; thus the cavity sizes become another important variable, which might not be adequate to describe the solvent reorganization in chemical reactions.

the scope of the present work. Further development in theoretical methodology to treat the solvent effects in order to model chemical reactions more realistically must be awaited. As a result, the hypothesis presented in Scheme V can only be tested when such a methodology becomes available.

Acknowledgment. This work was supported in part by the National Science Foundation (CHE 8712389). The University of Massachusetts Computer Services made a generous grant of computer time to enable part of this work. Some of the calculations were conducted on the Cornell National Supercomputer Facility, a resource of the Center for Theory and Simulation in Science and Engineering (Theory Center), which receives major funding from the National Science Foundation and IBM Corporation, with additional support from New York State and members of the Corporate Research Institute.

Supplementary Material Available: The *Z* matrix data of the optimized molecular structures can be obtained from the authors. Contact the authors for a suitable media for data transfer.

Registry No. 1 (R = H; R^1 = Me), 31918-07-7; **1** (R = C_6H_5; R^1 = Me), 1754-88-7; *cis*-**2** (R = H; R^1 = R^2 = Me), 137895-07-9; *trans*-**2** (R = H; R^1 = R^2 = Me), 137895-08-0; *cis*-**2** (R = H; R^1 = Me, R^2 = C≡CH), 137895-09-1; *trans*-**2** (R = H; R^1 = Me, R^2 = C≡CH), 137895-10-4; *cis*-**2** (R = H; R^1 = Me, R^2 = CN), 137895-11-5; *trans*-**2** (R = H; R^1 = Me, R^2 = CN), 137895-12-6; *cis*-**2** (R = C_6H_5; R^1 = R^2 = Me), 137895-13-7; *trans*-**2** (R = C_6H_5; R^1 = R^2 = Me), 137895-14-8; *cis*-**2** (R = C_6H_5; R^1 = Me, R^2 = C≡CH), 137895-15-9; *trans*-**2** (R = C_6H_5; R^1 = Me, R^2 = C≡CH), 137895-16-0; *cis*-**2** (R = C_6H_5; R^1 = Me, R^2 = CN), 137895-17-1; *trans*-**2** (R = C_6H_5; R^1 = Me, R^2 = CN), 137895-18-2; CH_3CHO, 75-07-0; CH≡CCHO, 624-67-9; NCCHO, 4471-47-0.

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An ab Initio Study of the Structure of Monomeric, Unsolvated Benzyllithium. Is Covalency of the Carbon–Lithium Bond Important?

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Abstract: Ab initio calculations at the 3-21G level reveal the existence of two minima on the potential energy surface of isolated benzyllithium, the classic η^3 structure and an η^5 haptomer with lithium located over the aromatic ring. A third haptomer with lithium positioned over the C_{ipso}–C_α bond (η^2) was shown to be a transition state for racemization of the η^3 haptomer. The influence of the basis set, electron correlation effects, and zero point energies on the relative stabilities of the haptomers in question was tested. At the MP2/6-311G** with ZPE correction level, η^3 is more stable than η^5 by 1.69 kcal/mol. When purely ionic C–Li bonding was modeled, geometry optimization led to a distinctly different η^1 structure as the global minimum, demonstrating the importance of the partial covalency of carbon–lithium bonding in benzyllithium.

To date, the results of three independent X-ray structure determinations of benzyllithium (**1**) have been published[1-3] reflecting an interest in the structure of organolithium compounds in general and an interest in benzylic anions in particular. In the classic study by Stucky et al.[1] the lithium atom, additionally coordinated by two triethylenediamine molecules, was found to be in bonding distance with three carbon atoms: C_α, C_{ipso}, and C_{ortho} (2.21, 2.39, and 2.59 Å, respectively). The η^3 arrangement was rationalized on the basis of the interactions of the benzyl carbanion's HOMO with the 2s and 2p orbitals of the lithium cation.[1,4] The subsequent structure determination of **1**–diethyl ether complex by Power et al.[2] revealed an infinite chain of alternating benzyl and lithium ions with the lithium also coordinated to Et_2O. In this case lithium was located approximately over the C_{ipso}–C_α bond with distances in the range 2.40–2.88 Å (C_{ipso}) and 2.19–2.23 Å (C_α), and therefore in the η^2 arrangement.[2] Finally Boche et al.[3] determined the structure of **1**·THF·TMEDA complex and found the lithium atom to be located over C_α with the C–Li distance of 2.21 Å and the Li–C_α–C_{ipso} angle equal to 94°; i.e., the η^1 haptomer. The distinctly different locations of the lithium cation with respect to the benzyl anion demonstrate the shallowness of the potential energy surface around the lowest energy arrangement as well as the importance of lithium coordination and/or crystal packing forces in this system.

Some theoretical efforts have been made to understand the structure of benzyllithium. Despite the emphasized importance of intermolecular interactions, such studies must start with consideration of the isolated molecule only. On the basis of an electrostatic model, the η^3 structure analogous to the classic structure was found to be most stable when either HMO or CNDO atomic charges were employed. However, the position of the lithium cation over the benzene ring (η^6 haptomer) was favored when STO-3G charges were used.[5] Semiempirical MNDO calculations for isolated **1** locate two minima on the potential energy surface, η^3 and η^6, with the latter being the global minimum.[3,4,6] On the other hand, when solvation is included in

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