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Wittig vs. Corey–Chaykovsky Reaction. A Theoretical Study of the Reactivity of Phosphonium Methylide and Sulfonium Methylide with Formaldehyde

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Abstract: The factors which favor the Wittig reaction for a phosphonium ylide and the Corey–Chaykovsky reaction for a sulfonium ylide when they react with a carbonyl function are studied by means of ab initio calculations. Reaction paths for four model reactions which simulate salt-free conditions have been determined: $H_3P{=}CH_2 + H_2C{=}O \rightarrow H_3PO$ + ethylene (Wittig type); $H_3P{=}CH_2 + H_2C{=}O \rightarrow H_3P$ + ethylene oxide (Corey–Chaykovsky type); $H_2S{=}CH_2 + H_2C{=}O \rightarrow H_2SO$ + ethylene (Wittig type); $H_2S{=}CH_2 + H_2C{=}O \rightarrow H_2S$ + ethylene oxide (Corey–Chaykovsky type). For each model reaction, all the extrema were fully optimized by using an analytical gradient with the 4-31G* basis set at the SCF level. Single-point calculations were performed with the addition of diffuse orbitals on carbon and oxygen (4-31G^{*+} basis set). For the Wittig type reaction, only cyclic covalent four-membered rings were located as stable intermediates, and no betaine was found to be a stable species. In the case of phosphorus, two stable isomeric oxaphosphetanes were located, one with an apical oxygen center and the other one with an apical carbon center. The ring forming and ring opening of these two intermediates occur via a concerted $(2_s + 2_s)$ mechanism which is shown not to be forbidden. In the case of the sulfur, only one intermediate, with the apical oxygen center, is found to be stable. This fact is discussed in terms of the stability of sulfurane, depending on the electronegativity of the apical group. For the Corey–Chaykovsky reaction, no *trans*-betaine is found to be stable, and only one transition state is located on the reaction path. It is shown that both thermodynamic and kinetic factors cause the ylides to react differently. Formation of a phosphine oxide and an olefin is thermodynamically preferred to formation of an oxirane and a phosphine. Conversely, formation of an oxirane and a sulfide is thermodynamically preferred to that of a sulfoxide and an olefin. The activation energy is found to be smaller for the Wittig (5.2 kcal/mol) than for the Corey–Chaykovsky reaction (25 kcal/mol) in the case of a phosphonium ylide. The reverse order is obtained in the case of a sulfonium ylide (25 kcal/mol of activation energy for the Wittig reaction and 10.6 kcal/mol for the Corey–Chaykovsky reaction). It is shown that the step that kinetically differentiates the phosphorus from the sulfur in the Wittig reaction is the ring opening of the cyclic intermediate to yield the products. The capacity to undergo this crucial step is conditioned by the ease with which the oxygen can go from the apical to the equatorial site and exchange its position with the carbon. Such an interchange is calculated to be easy for the phosphorus and difficult for the sulfur. It is also shown that the ease for the reactants to undergo a Corey–Chaykovsky type reaction is controlled by the leaving-group ability of H_nX ($H_nX = H_3P$, H_2S), which is greater for the sulfide than for the phosphine.

Phosphonium and sulfonium ylides are two important reactants in synthetic organic chemistry. Although they are isoelectronic compounds and should therefore display many common properties, there are striking differences in their reactivity toward carbonyl groups. A phosphonium ylide reacts with carbonyl group to form an olefin and a phosphine oxide (Wittig reaction).[1] In contrast, a sulfonium ylide reacts with a carbonyl group to form an oxirane and a sulfide, as was discovered by Johnson[2] and by Corey and Chaykovsky.[3] The more stable oxosulfonium ylide (or derivatives) generally reacts like the sulfonium one and is usually preferred to the latter.[4]

Since the discovery of those reactions, a considerable amount of work has been devoted to the elucidation of the various facets of their mechanism. The Wittig reaction has been especially studied in great detail because of its importance in organic synthesis.[5] The crucial problem of this reaction is its stereoselectivity, namely, the fact that *cis*-olefin is preferentially obtained with nonstabilized ylide and *trans*-olefin with stabilized ylide.[6] In addition, there is a dramatic change in the syn/anti ratio in the resulting olefin when lithium cation is added to the reaction

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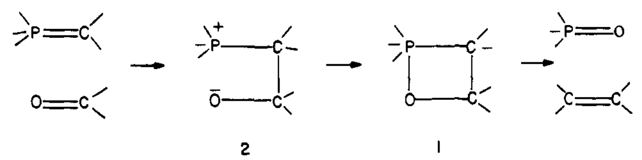
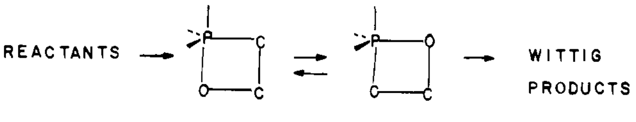
Scheme I



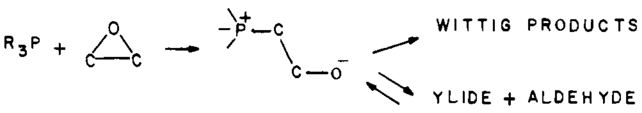
2 1

Scheme II



3 4

Scheme III



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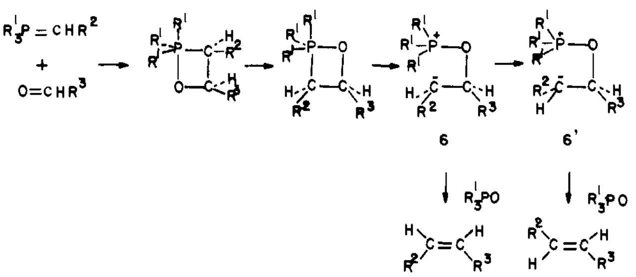
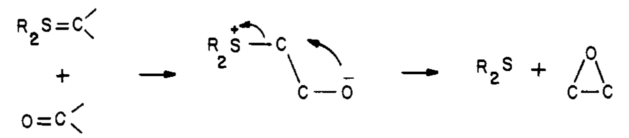
Scheme IV



6 6'

Scheme V



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mixture (salt effect).[6] With the understanding that stereoselectivity necessitates the knowledge of the various intermediates formed during the reaction so far, no general agreement has been reached concerning their nature. Wittig initially proposed the formation of a purely covalent intermediate (oxaphosphetane **1**) as the only intermediate.[1] This reaction scheme did not seem to be appropriate since taking into account only a nonionic covalent intermediate, which might not be very sensitive to the presence of ionic salts, could not explain the dramatic change in stereochemistry upon addition of ionic salts. Consequently, the formation of a second transient species **2** (betaine) was set forth, the zwitterionic nature of which provided a rationalization for the salt effect.[7] According to these hypotheses, one can describe the course of the reaction as in Scheme I.

Let us briefly summarize the available data supporting the existence of the two intermediates **1** and **2**. The oxaphosphetane has been first unambiguously spectroscopically characterized by Vedejs.[8] It was isolated and structurally characterized by X-ray diffraction.[9] It has been shown to decompose upon heating into either the Wittig products or an ylide and an aldehyde (retro-Wittig).[8,9c,10] In an elegant study, Bestmann et al. have shown that an intermediate is formed, in which the oxygen occupies the apical position of the pentacoordinated phosphorus, **3**, in agreement with the Muetterties apicophilicity rules. They have also shown that a pseudorotation is likely to exchange the position of the oxygen and carbon centers (**3** into **4**).[9c] The apical bonds being weaker than the equatorial ones in a trigonal-bipyramidal hypervalent phosphorus system,[11] the pseudorotation weakens the P–C apical bond and thus facilitates the formation of the olefin and phosphine oxide from the new oxaphosphetane **4**, which is in equilibrium with **3** (Scheme II). In contrast, the zwitterionic betaine **2** has never been isolated or spectroscopically characterized. Nevertheless, two experiments have substantiated the existence of such an intermediate. First, β-hydroxy phosphonium salts that could originate from the protonation of this betaine were characterized.[12,13] Second, olefin inversion reaction is coherent with the existence of a betaine, **5** (Scheme III).[12,14] The obtention of Wittig products from the addition of phosphine to oxirane necessitates the formation of a common intermediate that could be the betaine. However, recent stereochemical results by Vedejs and co-workers argue against the existence of a betaine as an intermediate in the salt-free Wittig reaction.[8b]

However, the consideration of the previously mentioned intermediates does not offer a straightforward interpretation of the observed stereochemistry. Namely, the preferential formation of the more unstable *cis*-olefin from the nonstabilized ylide is still somewhat a puzzling fact. The *erythro*-oxaphosphetane has recently been shown to be the most abundant isomeric intermediate[15] and to decompose mostly into the *cis*-olefin, although in some cases some stereochemical drift has been observed.[16] Various explanations for the preferential formation of the apparently more sterically unfavorable intermediate have been proposed.[17] Among these interpretations, symmetry rules were also used. If the formation of the oxaphosphetane intermediate is considered to be a concerted (2 + 2) cycloaddition, it should go through a supra–antara $(2_s + 2_a)$ transition state.[8a] However, the $(2_s + 2_a)$ hypothesis was withdrawn later on and was replaced by a cycloaddition rationale based on steric arguments.[8b]

The interconversion of the erythro and the threo intermediates seems to be one of the key steps for an elucidation of the stereochemistry. Bestmann proposed a mechanism in which a P–C bond is cleaved to give rise to a new type of betaine, **6** (Scheme IV).[5,18] This mechanism is supported by deuterium incorporation and is closely related to that proposed by Whangbo et al.[17d] On the other hand, Vedejs has shown that there is no detectable equilibration between the two isomeric intermediates when LiBr is added,[8b] which demonstrates that no zwitterionic intermediate is involved along the reaction path. In addition, Maryanoff has observed both *cis*- and *trans*-oxaphosphetanes equilibrated through the reactants and has interpreted the stereochemical drift by the reversibility of the reaction.[15,16]

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We have just highlighted here some of the important facts concerning the stereochemistry of the reaction, to which a large literature has been devoted and which is still said in 1984 to be badly understood.[19]

Finally, a completely different mechanism has been recently proposed by Olah and Krishnamurty.[20] They suggested a radical mechanism which would agree with the results obtained by Ashby et al. concerning the reduction of ketones by hydrides.[21]

In contrast to the Wittig reaction, the mechanism of the reaction of sulfonium ylide and a carbonyl group has apparently met a general agreement in the scientific community. Originally proposed by Johnson and co-workers,[2] it involves the nucleophilic addition of the sulfonium ylide to the carbonyl group to form a *trans*-betaine intermediate, 7 (Scheme V). This intermediate evolutes toward the oxirane by means of an intramolecular S_N2 reaction at the carbon, in which the oxygen acts as the nucleophile and the sulfide as the leaving group. This mechanism has been substantiated by independent synthesis of the conjugated acid of a betaine, which yields an oxirane after deprotonation.[22] The inverse reaction, ring opening of some oxiranes by sulfides which leads to the formation of stabilized sulfonium ylides and ketones, also supports the existence of a betaine intermediate.[23] However, as in the Wittig reaction, no betaine was detected as an intermediate of the reaction.

The same mechanism is supposed to apply to all sulfur ylide derivatives.[3] The various systems differ by their reactivities and the associated differences in regioselectivity and stereoselectivity of the CR_2 transfer.[24] The more reactive sulfonium ylide adds to deactivated ketones while oxosulfonium ylide remains inactive.[25] When reacting with α,β unsaturated enones, the oxosulfonium ylide adds exclusively to the C=C double bond, while the sulfonium ylide can form either the cyclopropane or the oxirane, depending on the nature of the substituents.[3] In a related manner, the preferred side of addition to cyclohexanone varies with the nature of the ylide. Sulfonium ylides enter on the axial side and oxosulfonium ylides on the equatorial side.[26] Since the reaction provides a convenient and versatile way to transfer any methylene-substituted group, numerous synthetic applications have beem made.[27]

To our knowledge, theoretical studies have been limited to the Wittig reaction. The first results have been published using CNDO[28] and MNDO[18b] semiempirical calculations. In both cases, it was found that the betaine-like structure was disfavored with respect to the neutral oxaphosphetane. As a result, the authors suggested the direct formation of the oxaphosphetane without prior involvement of a betaine, as proposed by Vedejs.[8] Concerning the stereochemistry of the formation of an oxaphosphetane, in both types of calculations, a supra–supra $(2_s + 2_s)$ approach was found to be favored relative to a supra–antara addition. An analogous work on the addition of phosphonium methylide to formaldehyde was performed by Höller and Lischka by means of ab initio calculations using various basis sets.[29] All minima were optimized by a gradient method, and transition structures were located after a partial optimization of coordinates orthogonal to the estimated reaction coordinate. In agreement with the semiempirical calculations, ab initio results confirm the direct formation of oxaphosphetane by a concerted $(2_s + 2_s)$ mechanism and the absence of a betaine intermediate. According to these authors, the apparent breakdown of the symmetry rules originates from the strong ionic character of the reactants and products. Two oxaphosphetanes were found to be intermediates on the reaction path, one with an apical oxygen atom and the other with an apical carbon atom. The first one was found to be hardly more stable (between 0 and 2.8 kcal/mol, depending on the basis set) than the second one, in agreement with the Muetterties rules of apicophilicity.[11] A very weak barrier (5 kcal/mol) was computed for the interconversion of the two isomers, the mechanism of interconversion being closer to a turnstile[30] than to a Berry rotation.[31] The suprisingly small energy difference between the two forms has been confirmed independently by Schleyer et al.[32] at the 4-31G (and 4-31G + d on phosphorus) level and has been found to be in agreement with ^{31}P NMR spectroscopic data, which attested to the facile equilibrium between the two isomers. Recent theoretical results by Streitwieser[33] on simpler models of substituted phosphoranes, H_4POH and H_4PCH_3, indicate a small preference (about 2.5 kcal/mol) at the 3-21G level for both OH and CH_3 groups to occupy the equatorial site, the preference being slightly higher for CH_3. Once again, this result supports the easy interchange between the two isomers, in agreement with the theoretical results of Höller and Lischka and of Schleyer.

The purpose of this work is to compare the reactivity of phosphonium ylide with that of sulfonium ylide vis-â-vis a carbonyl group. For each ylide, the methylene exchange (Wittig type reaction) and the methylene transfer (Corey–Chaykovsky type reaction) are studied. Our main goal is to locate the step(s) that differentiate(s) the reactivity of the two ylides. A preliminary presentation of these results has been communicated.[34]

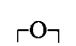
Theoretical Models and Procedure

We have chosen the simplest models for ylides and carbonyl groups, replacing all the substituents on the ylide and carbonyl group by hydrogen atoms. Two "Wittig" reactions were studied:

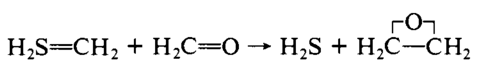
$$H_3P{=}CH_2 + H_2C{=}O \rightarrow H_2C{=}CH_2 + H_3P{=}O \qquad (1)$$

$$H_2S{=}CH_2 + H_2C{=}O \rightarrow H_2C{=}CH_2 + H_2S{=}O \qquad (2)$$

Likewise, the two "Corey–Chaykovsky" reactions that need to be compared are



$$H_3P{=}CH_2 + H_2C{=}O \rightarrow H_3P + H_2C\overset{O}{\frown}CH_2 \qquad (3)$$



$$H_2S{=}CH_2 + H_2C{=}O \rightarrow H_2S + H_2C\overset{O}{\frown}CH_2 \qquad (4)$$

Although none of these model ylides is stable, it is safe to assume that the intrinsic differences between the existing phosphonium and sulfonium ylides are present in these model compounds. The validity of this hypothesis will be verified by studying the influence of alkyl substitution on the thermochemistry of selected reactions. The effect of a lithium cation on the various extrema located on the potential energy surfaces has never been studied. Moreover, since all the substituents on the ylides have been replaced by hydrogen atoms, our results are only relevant to the reactivity of nonstabilized ylides in salt-free conditions.

All reactants, products, intermediates, and transition structures have been optimized by using the full analytical gradient proce-

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Table I. Optimized Structures (4-31G* Level) of Reactants and Products in Equations 1–4

compd	structural parameters[f]	ref for exptl structure
H_2CO	C–O, 1.182	*a*
	C–H, 1.092	
	H–C–H, 115.5	
H_3P	P–H, 1.409	*b*
	H–P–H, 92.8	
H_2S	S–H, 1.329	*c*
	H–S–H, 93.7	
$H_2C{=}CH_2$	C–C, 1.313	*d*
	C–H, 1.075	
	H–C–H, 116.3	
	C–C, 1.450	*e*
	C–O, 1.398	
	C–H, 1.076	
	O–C–X, 158.4	
	H–C–H, 115.2	
$H_3P{=}CH_2$	ref 33	
$H_2S{=}CH_2$	ref 33	
$H_3P{=}O$	P–O, 1.460	
	P–H, 1.398	
	H–P–O, 117.4	
$H_2S{=}O$	S–O, 1.480	
	S–H, 1.352	
	O–S–X, 116.3	
	H–S–H, 89.7	

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Table II. Enthalpies of Reaction for the Wittig and Corey–Chaykovsky Reactions Shown in Equations 1–4

equation	Δ*H*, kcal/mol[c]
$H_3P{=}CH_2 + H_2C{=}O \rightarrow H_3PO + H_2C{=}CH_2$	−49.7[a] −50.8[b]
$H_3P{=}CH_2 + H_2C{=}O \rightarrow H_3P + H_2\overset{\ulcorner O \urcorner}{C{-}C}H_2$	−35.1[a] −28.7[b]
$H_2S{=}CH_2 + H_2C{=}O \rightarrow H_2SO + H_2C{=}CH_2$	−24.1[a] −25.0[b]
$H_2S{=}CH_2 + H_2C{=}O \rightarrow H_2S + H_2\overset{\ulcorner O \urcorner}{C{-}C}H_2$	−63.2[a] −57.2[b]

[a] 4-31G* level. [b] 4-31G*+ level. [c] 1 kcal/mol = 4.18 kJ/mol.

dures of Monstergauss[35] and Gaussian80[35] with the 4-31G* basis set[36,37] after exploratory STO-3G*[38] optimizations, which will not be presented. Because a rather high electronic density was present on carbon and oxygen atoms in some of the optimized structures, we added a set of diffuse s and p orbitals[39] on these atoms (4-31G*+). This large basis set was exclusively used for single-point calculations using the structural parameters determined with the 4-31G* basis set, since the addition of such diffuse orbitals has little influence on the geometrical parameters.[40]

Energies were calculated at the SCF level. The role of electronic correlation on the thermochemistry of selected reactions was calculated by means of the Møller–Plesset perturbation theory[41] at the second and third level (MP2 and MP3).

Thermodynamic Study of the Wittig and Corey–Chaykovsky Reactions

All molecules but the ylides (already optimized at the 4-31G* level)[37] entering eq 1–4 have been optimized with the 4-31G* basis set. Structural information is reported in Table I along with the references to the experimental structural determinations. Since considerable work has already been devoted to each of these compounds and since discussion of these systems is not the main focus of our work, we will just briefly mention the points that are relevant to the rest of our study. Phosphonium and sulfonium ylides have been widely studied by means of semiempirical[42] and ab initio[37,43-46] methods. The P–C and S–C bond lengths have been shown to be very dependent on the basis set. Large basis sets with d orbitals on P and S are necessary to adequately describe the d_π/p_π conjugation, so as to obtain reasonable P–C and S–C bond lengths. As shown by Wolfe and co-workers,[37] the 4-31G* basis set is sufficiently large and flexible for that purpose, and their optimized structures agree well with those of known related phosphonium[47] and sulfonium[48] ylides. Two points, of interest to our study, concerning these molecules need to be mentioned here. First, while the rotation around the P–C bond is calculated to be almost free in $H_3P{=}CH_2$,[37,43a,45,46d] it is a hindered rotation in $H_2S{=}CH_2$,[37,45,46] with a calculated rotational barrier between 10 and 21 kcal/mol. In the preferred conformation, the carbon lone pair is perpendicular to the sulfur lone pair, in order to minimize the four-electron repulsion[37,45,46] and to maximize the two-electron stabilization with σ^*_{SH}.[37] A study of the tautomerization and the dissociation enthalpies of these ylides[37,44,45] has indicated that $H_2S{=}CH_2$ is intrinsically less stable than $H_3P{=}CH_2$.

The structures of phosphine oxide and sulfoxide are also given in Table I. As was the case for the ylides, the simplest parent

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(35) In Orsay we used MONSTERGAUSS (version 1976): Peterson, M.; Poirier, R., Department of Chemistry, University of Toronto. In Michigan and in Japan we used GAUSSIAN80: Binkley, J. S.; Whitehead, R. A.; Hariharan, P. C.; Seeger, R.; Defrees, D. J.; Schlegel, H. B.; Topiol, S.; Khan, L. R.; Pople, J. A.

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(38) Collins, J. B.; Schleyer, P. v. R.; Binkley, J. S.; Pople, J. A. *J. Chem. Phys.* **1976**, *64*, 5142.

(39) (a) Chandrasekhar, J.; Andrade, J. G.; Schleyer, P. v. R. *J. Am. Chem. Soc.* **1981**, *103*, 5609. (b) Clark, T.; Chandrasekhar, J.; Spinatzel, G. W.; Schleyer, P. v. R. *J. Comput. Chem.* **1983**, *4*, 294. (c) Spinatzel, G. W.; Clark, T.; Chandrasekhar, J.; Schleyer, P. v. R. *J. Comput. Chem.* **1982**, *3*, 363.

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(42) (a) Hoffmann, R.; Boyd, D. B.; Goldberg, S. Z. *J. Am. Chem. Soc.* **1970**, *92*, 3929. (b) Boyd, D. B.; Hoffmann, R. *J. Am. Chem. Soc.* **1971**, *93*, 1064. (c) Tatsumi, K.; Yoshioka, Y.; Yamaguchi, K.; Fueno, T. *Tetrahedron* **1976**, *32*, 1705. (d) Ostoja Starzewski, K.-H. A.; Bock, H. *J. Am. Chem. Soc.* **1976**, *98*, 8486. Ostoja Starzewski, K.-H. A.; Bock, H.; tom Dieck, H. *Angew. Chem., Int. Ed. Engl.* **1975**, *14*, 173. (e) Albright, T. A.; Gordon, M. D.; Freeman, W. J.; Schweizer, E. E. *J. Am. Chem. Soc.* **1976**, *98*, 6249. (f) Iwata, K.; Yoneda, S.; Yoshida, Z. *J. Am. Chem. Soc.* **1971**, *93*, 6745.

(43) (a) Absar, I.; Van Wazer, R. J. *J. Am. Chem. Soc.* **1972**, *94*, 2382. (b) Lischka, H. *J. Am. Chem. Soc.* **1977**, *99*, 353. (c) Strich, A. *Nouv. J. Chim.* **1979**, *3*, 105. (d) McDowell, R. S.; Streitwieser, A., Jr. *J. Am. Chem. Soc.* **1984**, *106*, 4047.

(44) (a) Trinquier, G.; Malrieu, J. P. *J. Am. Chem. Soc.* **1979**, *101*, 7169. (b) Yates, B. F.; Bouma, W. J.; Radom, L. *J. Am. Chem. Soc.* **1984**, *106*, 5805.

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compounds, H_3PO and H_2SO, are unstable, and no direct comparison between our optimized structures and experimental data is possible. We have satisfied ourselves with a partial comparison with the structure of substituted molecules. The calculated P-O bond length of 1.460 Å is encompassed between that in F_3PO (1.436 Å)[49] and in Me_3PO (1.479 Å).[49] In the same manner, the S-O bond length of 1.480 Å is close to that in F_2SO (1.413 Å)[49] and in Me_2SO (1.477 Å).[49] On the other hand, numerous theoretical calculations have been performed on these oxides,[29,49-53] and it has been shown that, as for the P-C and S-C bond lengths in the ylides, the P-O[29,49,51,53] and S-O[49,52,53] bond lengths are very sensitive to the basis set. The P-O bond length in H_3PO was found to be equal to 1.572,[29] 1.470,[51] and 1.469 Å,[53] and the S-O bond length in H_2SO was found to be equal to 1.48,[52b] 1.493,[52e] 1.510,[52e] and 1.515 Å.[53] Our results are therefore close to those obtained in previous theoretical studies.

We have reported in Table II the calculated enthalpies of reaction for eq 1-4. Both reactions (Wittig and Corey-Chaykovsky) are calculated to be exothermic for both ylides. However, large differences of exothermicity appear between the ylides. At the 4-31G* level, for phosphonium ylide, the formation of phosphine oxide and ethylene is more exothermic (-49.7 kcal/mol) than that of oxirane and phosphine hydride (-35.1 kcal/mol). The reverse thermodynamic preference is obtained for sulfonium ylide, since the formation of oxirane and hydrogen sulfide (-63.2 kcal/mol) is preferred over that of hydrogen sulfoxide and ethylene (-24.1 kcal/mol). *The thermodynamics of the reaction are in favor of the Wittig reaction for phosphonium ylide and in favor of the Corey-Chaykovsky reaction for the sulfonium ylide.* Thus, according to our calculations, the experimentally observed reactivity preference has some thermodynamic support.

Unfortunately, no direct comparison with experimental thermodynamic values is possible, since the enthalpies of formation of ylides have not been determined. In their theoretical study of the Wittig reaction, Höller and Lischka have found -48.3 kcal/mol[29] for reaction 1, which is very close to our -49.7 kcal/mol value.

On the other hand, some other thermodynamic results can be extracted from our calculations and compared with experimental data. It is widely admitted that a phosphine has a larger oxo affinity than a sulfide. This is well illustrated by the large enthalpy variation for the isodesmic reaction 5. ΔH_1 (53.7 kcal/mol) can

$$\mathrm{H_2S + H_3PO \rightarrow H_2SO + H_3P} \tag{5}$$

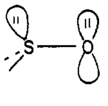
$$\Delta H_1 = 53.7\ \text{kcal/mol (calculated)}$$

$$\mathrm{Me_2S + Me_3PO \rightarrow Me_2SO + Me_3P} \tag{6}$$

$$\Delta H_2 = 52.5\ \text{kcal/mol (measured)}$$

be adequately compared with the experimental value, 52.5 kcal/mol, derived from the enthalpy of formation for methyl-substituted molecules[54] (eq 6). Wallmeier and Kutzelnigg estimated the bond energies for P-O and S-O to be respectively 108 and 54 kcal/mol.[53] The difference between these two values (54 kcal/mol) compares well with our calculated value for ΔH_1 and gives additional support to our results.

Let us discuss further this well-known difference in oxo affinity between phosphorus and sulfur. Wallmeier and Kutzelnigg[53] interpreted this fact in terms of increasing ionization potential and decreasing proton affinity going from H_3P to H_2S. According to these authors, the strength of the semipolar X^+-O^- bond in H_nX-O is in great part determined by the stability of the H_nX^+ moiety. In our opinion, another factor may also influence the relative stability of the X-O bond. It involves the interaction of one oxygen lone pair with the occupied orbitals of the H_nX moiety. In H_2SO, the lone pair localized on the sulfur interacts in a destabilizing way with one of the oxygen lone pairs as illustrated in **8**. This destabilization can be important since, as mentioned earlier, a similar one is responsible for the high rotation barrier in $H_2S{=}CH_2$ (calculated to be between 10 and 20 kcal/mol).[37,45,46] It is also responsible for the fact that the S and C lone pairs are perpendicular to each other in the more stable conformation of the ylide as shown in **9**. Thus the four-electron repulsion between the S and O lone pairs in H_2SO intrinsically destabilizes the S-O bond. On the contrary, this four-electron repulsion between the two lone pairs is replaced in H_3PO by a smaller four-electron repulsion between a lone pair and a P-H bond. This difference between the H_3P and H_2S moieties accounts simultaneously for the larger energy of the P-O bond with respect to the S-O bond and for the lower rotational barrier in the phosphonium ylide. Incidentally, the same argument provides an interpretation for the larger oxo affinity of Me_2SO compared with Me_2S.[55]



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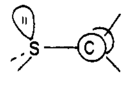

9

While the calculated enthalpy of reaction for the isodesmic eq 5 is in excellent agreement with the experimental value, the situation is not so good when comparing the enthalpies of the reactions describing the interconversion of products for each system (eq 7 and 8) with the available experimental values[54] (eq 9 and 10). The molecules that were selected for this comparison are

$$\mathrm{H_3PO + H_2C{=}CH_2 \rightarrow H_3P + H_2\overset{\ulcorner O \urcorner}{C{-}C}H_2} \tag{7}$$

$$\Delta H_3 = 14.6\ \text{kcal/mol (calculated)}$$

$$\mathrm{H_2SO + H_2C{=}CH_2 \rightarrow H_2S + H_2\overset{\ulcorner O \urcorner}{C{-}C}H_2} \tag{8}$$

$$\Delta H_4 = -39.1\ \text{kcal/mol (calculated)}$$

$$\mathrm{Me_3PO + H_2C{=}CH_2 \rightarrow Me_3P + H_2\overset{\ulcorner O \urcorner}{C{-}C}H_2} \tag{9}$$

$$\Delta H_5 = 54.6\ \text{kcal/mol (measured)}$$

$$\mathrm{Me_2SO + H_2C{=}CH_2 \rightarrow Me_2S + H_2\overset{\ulcorner O \urcorner}{C{-}C}H_2} \tag{10}$$

$$\Delta H_6 = 2.2\ \text{kcal/mol (measured)}$$

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(49) References quoted in: Pietro, W. J.; Francl, M. M.; Hehre, W. J.; DeFrees, D. J.; Pople, J. A.; Binkley, J. S. *J. Am. Chem. Soc.* **1982**, *104*, 5039.

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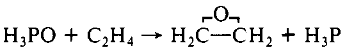
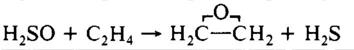
(55) The enthalpy of the following reaction, ΔH, is evaluated from experimental data.[54]

$$\mathrm{2Me_2SO \rightarrow Me_2S + Me_2SO_2}$$

$$\Delta H = -29.7\ \text{kcal/mol (measured)}$$

In Me_2SO the lone pair are on adjacent atoms, while in Me_2SO_2 the oxygen atoms that carry the lone pairs are further apart since they are separated by the sulfur atom. Four-electron destabilization is thus smaller in the later compound.

Table III. Relative Energies in kcal/mol of the Wittig and Corey–Chaykovsky Products at the 4-31G* Level

equation	SCF	MP2	MP3	exptl[a]
 $H_3PO + C_2H_4 \rightarrow H_2\overset{\ulcorner O \urcorner}{C{-}C}H_2 + H_3P$	14.6	16.0	12.4	54.6
 $H_2SO + C_2H_4 \rightarrow H_2\overset{\ulcorner O \urcorner}{C{-}C}H_2 + H_2S$	−39.1	−36.0	−37.8	2.2

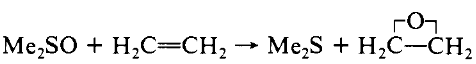
[a] The experimental values refer to eq 9 and 10.

as close as possible to our model systems; i.e., they bear CH_3 in place of H when the hydrogenated compound does not exist. In contrast to the excellent concordance between ΔH_1 and ΔH_2, there is approximately a 40 kcal/mol error between ΔH_3 and ΔH_5 on one side and between ΔH_4 and ΔH_6 on the other side. Since this discrepancy is directly connected with the thermodynamic control of the reactions we are studying, we need to understand the origin of these differences.

Two reasons may be at the origin of these discordances. First, we have neglected the correlation energy. Such an approximation is realistic when looking at an isodesmic reaction[56] in which the correlation energy does not dramatically change when going from reactants to products. In contrast, for eq 7 and 8, the compounds on each side of these chemical equations are very different in nature: a semipolar bond and a double bond on the left-hand side transform into the two σ bonds of a three-membered ring on the right-hand side. The second reason one can think of is related to the influence of the substituent on each of these molecules. An alkyl group may stabilize each of these compounds in a different manner. For instance, while H_2S and H_3P are experimentally well-characterized molecules, this is not the case for the corresponding oxides, which exist only in higher substituted forms.

In order to determine the reliability of our models, we have examined these two hypotheses. The correlation energy was estimated by using the Møller–Plesset perturbation theory to the second (MP2) and third order (MP3).[41] The results are shown in Table III. It is clear that the correlation effect on the enthalpy variations for these reactions is small (about 3 kcal/mol) and cannot account for the discrepancy of 40 kcal/mol between the experimental (substituted) and calculated (nonsubstituted) values. Since the correlation energy has only a minor influence on the thermodynamics of the reaction, it will be neglected from now on and the calculations will be pursued at the SCF level.

As could have been expected, substitution has a much more drastic influence. We exemplified our study with dimethyl sulfide (Me_2S) and dimethyl sulfoxide (Me_2SO) cases. Both molecules were optimized at the 4-31G* level. The structural parameters, reported in Table IV, compare well with the experimental structural values (in parentheses)[57,49] and theoretically optimized ones.[49,52c,58] The calculated enthalpy of reaction, ΔH_7, for eq 11 is calculated to be −20.3 kcal/mol, which can be compared with the experimental value of 2.2 kcal/mol (eq 10) and with the calculated −39.1 kcal/mol for the nonsubstituted systen (eq 8).

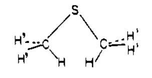
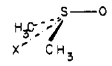


$$Me_2SO + H_2C{=}CH_2 \rightarrow Me_2S + H_2\overset{\ulcorner O \urcorner}{C{-}C}H_2 \qquad (11)$$

$$\Delta H_7 = -20.3 \text{ kcal/mol (calculated)}$$

Although ΔH_7 is still far from the experimental value, the improvement has been substantial and shows the important effect of alkyl-group substitution on the stability of the S–O bond. Methyl groups stabilize more the S–O bond than the sulfide group. Stabilization by alkyl groups of S–O and P–O bonds has already been discussed[50a,53,59] and attributed, for example, by Wallmeier and Kutzelnigg to the stabilization of the Me_2S^+ and Me_3P^+ moieties.[53] In order to better represent the semipolar bond, ΔH_7 was calculated within the 4-31G*+ basis set using the geometry found at the 4-31G* level. Its value is now −15.2 kcal/mol, which comes closer to the experimental one. This convergence of the calculated ΔH toward the experimental value clearly indicates that the present discrepancy essentially originates from the uncompleteness of the basis set.

Table IV. Optimized Structures (4-31G* Basis Set) of Dimethyl Sulfide and Dimethyl Sulfoxide[a]

compd	structural parameters[b]
	S–C, 1.807 (1.82) C–H, 1.082 C–S–C, 99.7 H–C–S, 107.5 H'–C–S, 111.3
	S–O, 1.487 (1.48) S–C, 1.800 (1.81) C–H, 1.082 (1.09) X–S–O, 114.7 C–S–C, 97.6 (96.4) H–C–S, 109.0 av (107.5 av)

[a] Experimental values are in parentheses: Me_2S ref 47; Me_2SO ref 40. [b] Bond angles are in degrees; bond lengths are in angstroms.

Despite the proved importance of substituents for a better estimate of the relative stability of products of both reactions, we will pursue our study of the nonsubstituted systems. Our purpose is to compare the reactivity of phosphonium ylide with that of sulfonium ylide, and we have seen that substituents favor the oxide formation by approximately the same amount for both ylides (see eq 7–10). This clearly shows that the experimental trends are well reproduced with the 4-31G* and the 4-31G*+ basis sets and that the origin of the difference in reactivity of phosphonium and sulfonium ylide is already present in the simplest models.

Before starting the presentation of the potential energy surfaces, let us summarize the results we have obtained about the thermodynamic control of these reactions. In the case of phosphonium ylides, there is a clear thermodynamic preference for the Wittig reaction, as shown by both the calculated and experimental values. The situation is not so clear in the sulfonium case. According to our calculations, there is a clear thermodynamic preference for oxirane formation. On the contrary, the experimental values suggest no thermodynamic preference for either product. This is a surprising fact since no traces of Wittig products have been reported with sulfonium ylides. This indicates the importance of the kinetic control in the reaction of sulfonium ylides.

Potential Energy Surfaces for the Wittig Type Reactions

The potential energy surfaces for reactions 1 and 2 are displayed respectively in Figures 1 and 5. In each figure we report the results obtained at the 4-31G*/4-31G* and 4-31G*+/4-31G* levels of calculations. Since the two basis sets give qualitatively equivalent results, we will discuss the results obtained with the larger basis set. The main structural features of the various extrema are reported in Figures 2 and 7. Full structural information is given in Tables VI and VII.

Phosphonium Ylide Reaction Pathway (Figures 1 and 2). The energy patterns found by Höller and Lischka and ourselves are collected in Table V. Let us first describe the general shape of the reaction scheme and then discuss in detail the structures of all extrema, minima, and transition structures.

As shown in Table V, the first intermediate, the oxaphosphetane P_{1O}, is formed with little activation energy (5.2 kcal/mol) by going through the transition structure P_{1TS}. This first oxaphosphetane, P_{1O}, with the oxygen at the apical position lies in a deep well (31.9 kcal/mol below the reactants). It undergoes a pseudorotation to form another oxaphosphetane P_{2O}, with the oxygen at the equatorial position, about 3 kcal/mol less stable than the first one. This last oxaphosphetane requires a somewhat large activation energy (26.3 kcal/mol) to go to the final products through the transition structure P_{2TS}. Since the energy of the second transition state is below that of the reactants, the system preferentially proceeds

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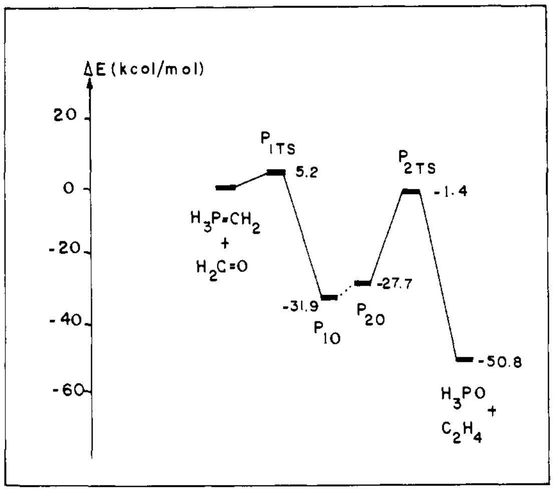

Figure 1. Energy profile for the Wittig reaction with phosphonium ylide. The energies are given for calculations at the 4-31G**/4-31G* level (1 kcal/mol = 4.18 kJ/mol).

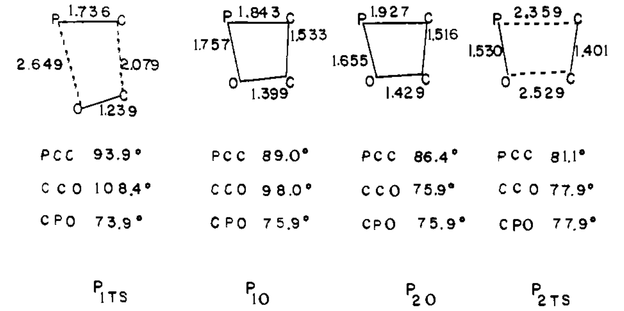

Figure 2. Main structural features of the P-C-C-O ring for the four located extrema of the Wittig reaction with phosphonium ylide. Additional structural information is given in Table VII.

Table V. Relative Energies in kcal/mol with Respect to the Reactants of the Extrema on the Potential Energy Surface of the Wittig Reaction with Phosphorus[a]

	P_{ITS}	P_{10}	P_{20}	P_{2TS}	products
ref 29	5.0	-34.0	-34.0	-9.6	-48.3
4-31G*	4.3	-36.2	-33.0	-4.5	-49.7
4-31G**+	5.2	-31.9	-27.7	-1.4	-50.8

[a] Structures have been optimized with the 4-31G* basis set and recalculated with the 4-31G**+ basis set.

to completion rather than return to the ylide and formaldehyde. As in the previous theoretical calculations,[18b,28,29] our results indicate the presence of two isomeric oxaphosphetanes and the direct formation and decomposition of these species without going through any additional zwitterionic intermediate. As indicated in the introduction, the absence of any zwitterionic intermediate (betaine) in salt-free conditions is supported by the experimental demonstration made by Vedejs.[8b] It should be recalled that no conclusion can be drawn for a reaction run in the presence of lithium salt. The localization of two isomeric oxaphosphetanes substantiates the hypothesis of a pseudorotation at the phosphorus made by Bestmann.[9c]

The oxaphosphetane P_{10} with an apical oxygen is found to be more stable by only 4.2 kcal/mol than P_{20} (Table V), which possesses the oxygen at the equatorial position. This very small energetical difference has been reproduced in previous ab initio calculations for either cyclic[29,32] or noncyclic systems.[33] Schleyer et al.[32] have found surprising that the two isomers were so close in energy, considering the difference in electronegativity between oxygen and carbon. They have attributed the reduced apicophilicity of the OR group to the π donating property of the oxygen lone pair.[11b] As recalled in the introduction, Streitwieser[33] has recently analyzed the apicophilicity of CH_3 and OH in phosphoranes at the 3-21G* level. He found that OH prefers to be equatorial by 2,7 kcal/mol in H_4POH and that CH_3 and OH have approximately the same energetical preference for the equatorial site. Consequently, assuming cumulative effects of substituents, the results of Streitwieser suggest that the two isomeric oxaphosphetanes should be almost isoenergetic. Since our results have been obtained after full optimization of geometry with a more adapted basis set, we believe them to be more reliable; i.e., P_{10} is slightly more stable than P_{20}. This preference is confirmed by the fact that all cyclic isolated oxaphosphetanes have an apical oxygen center.[9] Let us mention that the interconversion path exchanging the position of oxygen and carbon ($P_{10} \rightarrow P_{20}$) was not studied by ourselves. It was found to be an easy process via a turnstile rotation (approximately 5 kcal/mol of activation energy) by Höller and Lischka.[29] We have studied the various interconversion processes of acyclic model compounds $H_3P(OH)(CH_3)$ and confirmed their small interconversion activation energy.[60]

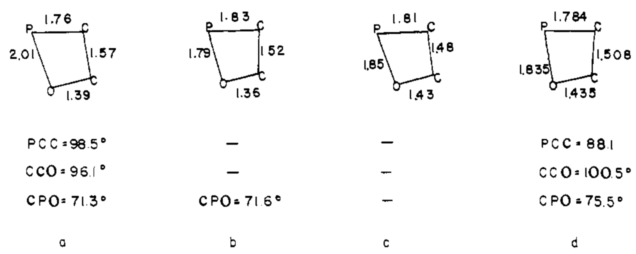

Figure 3. Main structural features of the P-C-C-O ring for experimental oxaphosphetanes. See ref 9a, 9b, 9c, and 9d for structures a, b, c, and d, respectively.

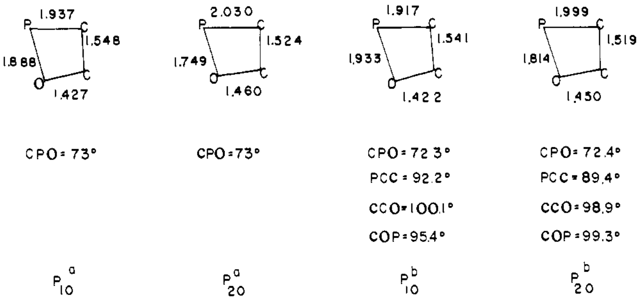

Figure 4. Main structural features of the P-C-C-O ring in previously calculated oxaphosphetanes; a and b refer respectively to ref 29 and 32.

We can now compare the calculated structures of oxaphosphetanes (Figure 2) with those of the experimentally observed ones.[9] The comparison is limited to P_{10} since, to our knowledge, no experimental equivalent to P_{20} has been isolated. Due to the large variety of substituents present in the experimental molecules, comparison is limited to the P-C-C-O four-membered ring. It is found to be planar like the experimental ones. The relevant experimental values (bond lengths and angles) are reported in Figure 3. The shape of the oxaphosphetane ring is well rendered in our calculations, and each bond length is reasonably close to the range of experimental values. The P-C bond length varies from 1.784 to 1,83 Å (calculated 1.843 Å), P-O varies from 1.79 to 1,85 Å (calculated 1.757 Å), C-C varies from 1.48 to 1.52 Å (calculated 1.533 Å), and C-O varies from 1.36 to 1.435 Å (calculated 1.399 Å). The O-P-C angle has been reported to be 71.3°, 71.6°, and 75.5°, which is close to our 75.9° value. The calculated P-O bond length is too short when compared with the experimental ones. Nevertheless, it should be noted that the substitution of an organic trans ligand by hydrogen on phosphorus may have a drastic effect on the P-O bond length by reinforcing the P-O bond in our case. Our set of results can also be confronted to the other theoretical results (Figure 4) by Höller and Lischka[29] and Bestmann and Schleyer.[32] In all cases, the two oxaphosphetanes have been found to be planar. In the previous calculations the lack of *d* functions on the phosphorus results in significantly too long P-C and P-O bond lengths. This clearly illustrates once

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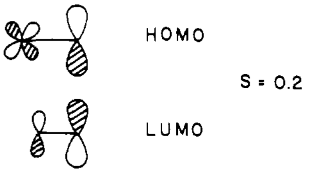
(60) Volatron, F.; Eisentein, O., to be published.

more the need of d orbitals for quantitatively reproducing the structure of molecules containing hypervalent phosphorus.

The first transition structure (P_{1TS} in our notation) located by Bestmann[18b] as well as the associated activation energy (20 kcal/mol) is quite different from ours (5.2 kcal/mol). This high activation energy seems to be in contradiction with the experimental fact that oxaphosphetane can be obtained at −78 °C,[8] and we believe that our value of 5.2 kcal/mol is more realistic. This discrepancy might be attributed to the well-known difficulty of semiempirical methods to calculate activation energies. On the opposite side, the energy pattern found by Höller and Lischka[29] agrees well with our present study (see Table V). However, note that the second transition state (P_{2TS}) is found to be slightly higher by ourselves (Table V). As mentioned earlier, the structures of our minima are closer to the available experimental data, which suggests that our energy pattern is also more reliable.

The two transition structures P_{1TS} and P_{2TS} are planar four-membered rings in which bonds are made or broken in the same extent. In P_{1TS} the oxygen occupies the pseudoapical site of a strongly distorted trigonal bipyramid ($O-P-H_1 = 132°$). Conversely, in P_{2TS} the carbon leaving the phosphorus occupies the apical site of a more regular trigonal bipyramid ($C-P-H_1 = 177°$). Since the weaker bond of a trigonal bipyramid is the apical one, the group that is coming in or leaving has to occupy an apical site. The planarity of the two rings characterizes two ($2_s + 2_s$) concerted processes, in apparent contradiction with the symmetry rules. Höller and Lischka have solved that contradiction by suggesting that the addition of the two components should proceed through a purely ionic mechanism.[29] This is not entirely satisfactory in our opinion since there is a good covalent character in the P–C bond.[43,45] Thus it is helpful to have a closer look at the shapes of the frontier orbitals of the two reactants (ylide and formaldehyde). In the addition of an ylide to formaldehyde, the two important frontier orbitals are the HOMO of the ylide and the LUMO of the formaldehyde, **10**.



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The HOMO of the ylide, mostly centered on the carbon, is the bonding combination of its p orbital with a phosphorus d orbital, and the LUMO of the formaldehyde is largely concentrated on the carbon center. As a consequence, the overlap between the two orbitals is not nil (0.2) as it would have been in the case of two ethylenes approaching in a ($2_s + 2_s$) fashion. This simple application of the frontier orbital control[61] clearly suggests that the ($2_s + 2_s$) cycloaddition of phosphonium ylide to formaldehyde is an allowed concerted process, in contrast to the supra-supra dimerization of ethylene. The same argument applies to the ring-opening ($2_s + 2_s$) cycloreversion of P_{2TS}.

In conclusion, the characteristic points concerning the Wittig reaction arising from our calculations are the following. (i) No zwitterionic betaine has been found as an intermediate in the overall reaction path. This implies the direct formation of the oxaphosphetane from the reactant through a concerted cycloaddition. (ii) Two isomeric oxaphosphetanes close in energy, P_{10} and P_{20}, have been located as the only intermediates. This result substantiates the hypothesis of a pseudorotation at the phosphorus during the reaction course. (iii) Ring forming and ring opening of the two oxaphosphetanes occur through a ($2_s + 2_s$) concerted mechanism. We have shown that this process does not violate the symmetry rules even if it does not involve an ionic mechanism.

Finally, note that starting from the oxaphosphetane, there is not a large difference in energy between going to the products (through P_{2TS}, 30.5 kcal/mol) and returning to the reactants (through P_{1TS}, 37.1 kcal/mol). Since we have shown that substitution may have noticeable influences on the energy scheme, it is understandable that the forward and the backward reactions may become competitive for a given substitution pattern. This would explain that the equilibration of *erythro*- and *threo*-oxaphosphetanes through the reactants may be highly substituent dependent, as shown by Maryanoff.[16,17]

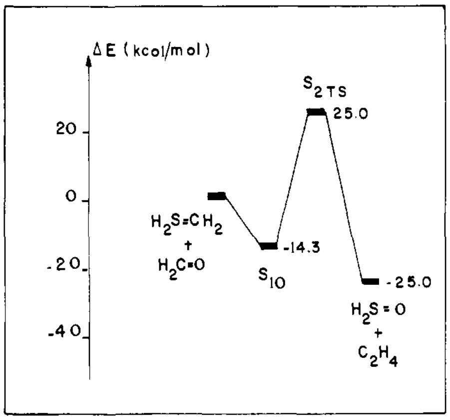

Figure 5. Energy profile for the Wittig reaction with sulfonium ylide. The energies are given for calculations at the 4-31G**+/4-31G* level.

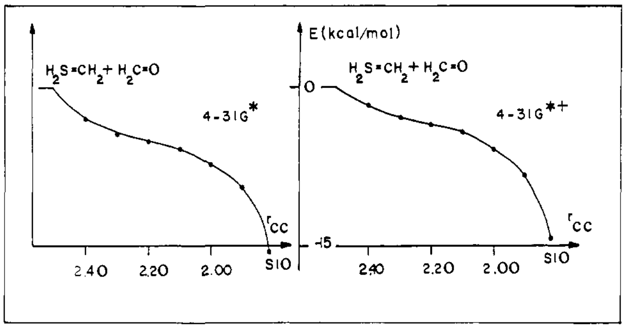

Figure 6. Energy profile of a linear path leading from the sulfonium ylide and formaldehyde to S_{10}.

Sulfonium Ylide Reaction Pathway. The shape of the potential energy surface reported in Figure 5 contrasts strongly with that of phosphonium ylide (Figure 1) and well illustrates the different behavior of the two ylides. Only one intermediate, S_{10}, was located on the potential energy surface. In this intermediate, the oxygen atom lies at the apical position of the sulfur pseudo trigonal bipyramid, the lone pair on sulfur occupying one equatorial site of the trigonal bipyramid. This intermediate is geometrically analogous with P_{10} found in the phosphorus case. It lies in a rather shallow well (−14.3 kcal/mol), is reached with no activation energy, and decomposes into the products with a high energy (39.4 kcal/mol) through the transition state S_{2TS}. Considerable effort was unsuccessfully spent in the search for two other extrema, the transition state between the reactants and S_{10} and another minimum between S_{10} and S_{2TS}, as was found in the phosphorus case. In order to prove the absence of an activation barrier between the reactants and S_{10}, we calculated a linear path between these two extrema (Figure 6). The energy decreases monotonically between the reactants and S_{10}, which proves that no transition state can be found for this cycloaddition. We did not find any S_{20} structure (equivalent to P_{20}) as a minimum on the reaction path; i.e., no oxathietane having the oxygen atom at the equatorial position and the carbon atom at the apical position could be located as a stable intermediate. As long as the whole potential energy surface is not fully calculated, it is impossible to assert that such a structure does not exist as a minimum. Nevertheless, calculations we performed on noncyclic model systems[60] made us confident that no stable hypervalent sulfurane, either cyclic or acyclic, could be stable without bearing strongly electronegative groups at the apical sites. Therefore, in contrast to the phosphorus case, the trans-

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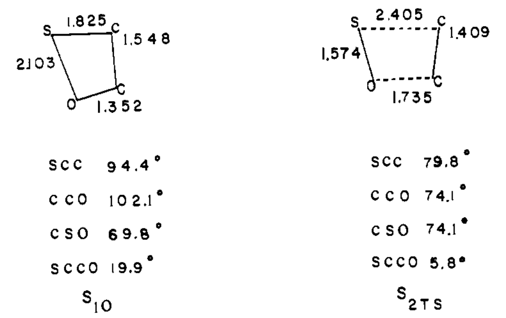

Figure 7. Main structural features of the S-C-C-O ring for the two located extrema of the Wittig reaction with sulfonium ylide. Additional structural information is given in Table VII.

formation of the reactants into the Wittig products proceeds via only one minimum and only one transition structure. The transformation of S_{10} into the Wittig products via S_{2TS} is difficult since it requires a high activation energy of 39.3 kcal/mol. According to our energy scheme, S_{10} would rather go back to the reactants, ylide and aldehyde (ΔE = 14.3 kcal/mol), than give the olefin and sulfoxide (ΔE = 39.3 kcal/mol).

The main geometrical features of the two extrema S_{10} and S_{2TS} are given in Figure 7. The oxathietane S_{10} is a monocyclic sulfurane with a slightly gauche ring. In this ring the sulfur has a distorted pseudo-trigonal-bipyramid structure with the lone pair and the carbon situated at the equatorial sites and the oxygen occupying one of the apical positions. Since, to the best of our knowledge, no oxathietane has been structurally characterized, we had to carefully compare our results with experimental data relative to sulfuranes. Sulfuranes form a class of (10-S-4)[62] molecules that present common features with our compounds, They have been synthesized and isolated with highly electronegative groups or atoms such as alkoxy, perfluoroalkoxy, chlorine, fluorine, or amide at the apical sites.[63] No sulfurane with less electronegative groups at the apical site has been reported (see Note Added in Proof). These experimental facts nicely account for the fact that S_{10} is calculated to be the only minimum and that no structure with an apical carbon center is found to be stable.

The comparison of the structure of S_{10} with sulfuranes presents some difficulties due to a peculiar behavior of the measured apical bond in the experimental structures. First, its length is especially sensitive to the nature of all other substituents present in the molecule, and it varies within a large range of values. Thus, for the S–O bond for instance, the shortest value is 1.66 Å[63l] and the longest one is 2.23 Å.[63l] Second, the two S–O apical bonds may have significantly different lengths even though the sulfurane is symmetrically substituted.[63c,63l] This deviation from symmetry has been explained in terms of the anisotropy of the environment of the sulfurane in the solid state due to an asymmetrical crystal packing. Both facts indicate a great sensitivity of the apical bonds in sulfurane to the presence of a perturbation,[63d,63m] and this deprives us of a good experimental reference value for apical bond lengths. This highly flexible geometry of the apical bonds in sulfurane suggests a weakly bonded situation along the apical axis, which has been analyzed by theoretical arguments.[64,65]

Although we are deprived of a good reference of experimental values to which our calculation could be confronted, we can be satisfied with our optimized S_{10} structure (Figure 7), quite well reproducing some of the characteristics of the sulfuranes. Our S–O 2.103 Å apical bond is encompassed between the experimental limits (1.66 and 2.23 Å), while the S–C equatorial bond length is very close to the upper limit of 1.82 Å.[63h] The θ_a angle between the two apical bonds is also very dependent on the nature of the apical atoms. Calculations have shown that the hypothetical SH_4 molecule is of C_{4v} symmetry with an H–S–H angle equal to 155°.[66] The other sulfuranes have a distorted trigonal-bipyramid structure with a θ_a angle varying from 167° to 180° and a θ_e angle between the two equatorial bonds ranging from 94° to 108°. Our calculated structure with hydrogens and heavier elements on the sulfur is intermediate between that of SH_4 and that of more substituted sulfuranes. However, it lies closer to the trigonal-bipyramid situation, with θ_a equal to 159.8° and θ_e equal to 105.6°, than to the square-pyramid structure.

The energetically high-lying S_{2TS} connecting S_{10} with the final products has the four heavy atoms S, C, C, and O almost coplanar (Figure 7). It is also a distorted pseudo-trigonal-bipyramid in which the S–C and C–O bonds have been elongated to a similar extent. Thus the rupture of the oxathietane occurs in a concerted manner. The important point about this transition structure is that the carbon occupies the apical position and the oxygen the equatorial one. This structure shows that a pseudorotation has finally occurred at the sulfur, but it only appears at the S_{2TS} point on the potential energy surface. The high energy barrier can now be easily understood: as in the case of the cleavage of the P–C bond in the oxaphosphetane, the cleavage of the S–C bond requires a pseudorotation at the sulfur, in order to bring the carbon to the apical site, Test calculations we made have shown that such a pseudorotation costs approximately 25 kcal/mol to the system.[60] Experimental data fully support the difficulty or impossibility for (10-S-4) (O_2, C_2)[63q] sulfuranes with oxygen atoms at the apical positions and carbon atoms at the equatorial ones to undergo a pseudorotation. Such a high value strongly differs from the 5 kcal/mol energy required to perform the pseudorotation in the phosphorus case ($P_{10} \rightarrow P_{20}$). Consequently, the cleavage of the X–C bond is much more energetic in oxathietane (X = S) than in oxaphosphetane (X = P).

Comparison of the Phosphonium Ylide and Sulfonium Ylide in the Wittig Reaction. The addition of the ylide to the formaldehyde to form the first intermediate is an easy process for both ylides. Its being even easier in the case of sulfur can be attributed to the intrinsic higher reactivity of the sulfonium ylide, related to its lower stability as previously mentioned.[37,44,45] Consequently, this first step does not differentiate the reactivity of the two ylides vis-à-vis a carbonyl group.

The two intermediates P_{10} and S_{10} exhibit the same geometrical features (oxygen at the apical site, carbon at the equatorial site), and they are both found to be more stable than the reactants. However, while the stability of P_{10} with respect to the reactants is large (−31.9 kcal/mol), that of S_{10} is much smaller (−14.3 kcal/mol). Substituents may modify the stability of P_{10} and S_{10} with respect to the corresponding reactants, since we have seen that substituents may have a large effect on the energetics of the

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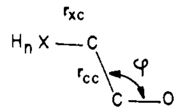
reactions. However, we have also seen that the intrinsic energy order found for the less-substituted phosphorus and sulfur derivatives was not reversed by the introduction of substituents (cf. eq 7–10). We thus believe that the relative order is correctly reproduced and that oxaphosphetanes are intrinsically more stable than oxathietanes. Experimental data on hypervalent pentacoordinated phosphorus and tetracoordinated sulfur support our results. Structures containing a pentacoordinated (10-P-5) phosphorus are much more numerous than structures containing a tetracoordinated (10-S-4) sulfur (the latter essentially belonging to the sulfurane class we described previously). In addition, while phosphoranes exist with a large variety of ligands, sulfuranes are much more demanding; i.e., highly electronegative apical ligands are needed to get a stable structure. This should indicate that tetracoordinated (10-S-4) sulfur compounds are intrinsically less stable than the isoelectronic (10-P-5) phosphorus compounds. It also suggests that it might be possible to synthesize an oxathietane, provided that enough σ-electron-withdrawing atoms or groups are introduced in a trans apical position with respect to the oxygen atom.

There is no structure corresponding to P_{20} in the sulfur case. An acyclic model for the hypothetical oxathietane S_{20}, with apical carbon and equatorial oxygen, calculated by freezing some of the structural parameters, was estimated to be 25 kcal/mol above the stable isomer. This is in sharp contrast with the 4.2 kcal/mol energy that separates the two isomers P_{10} and P_{20}. This is another aspect of the facts underlined in the previous paragraph, namely, that sulfur requires highly electronegative groups at the apical sites to become a hypervalent (10-S-4) species. A theoretical analysis in terms of valence-bond structures aimed at interpreting this point is under progress.

The activation energy to ring-open the cyclic intermediate is considerably higher in the case of sulfur (38.3 kcal/mol) than in the case of phosphorus (26.3 kcal/mol). *This is the step that differentiates the reactivity of the two ylides and prevents the sulfur ylide from undergoing a Wittig reaction.* The reasons for this difference are now quite clear. In P_{2TS} and S_{2TS} the carbon occupies the apical site in order to ease the cleavage of the P–C or S–C bonds. This situation is much more unfavorable for the sulfur system than for the phosphorus one. Whatever relative energies are required to cleave a S–C and a P–C bond in these four-membered rings, one should add to it the energy needed to bring the carbon to the apical site. Since this costs little in the case of phosphorus while it costs much more in the case of sulfur, the Wittig reaction is strongly disfavored with the sulfur. Experimental data support our analysis. Some cyclic four-membered rings with the S–C–C–O sequence have been reported to cleave in the Wittig type products (i.e., formation of an S=O and a C=C bond).[67] This result shows unambiguously that the S–C bond cleavage itself does not require too high an activation energy. The comparison of this fact with our preceeding results proves that the real limiting step of the Wittig reaction in the case of a sulfonium ylide is the ability of the oxathietane to undergo a pseudorotation at the sulfur. The fact that in one case an oxosulfonium ylide has been reported to undergo a Wittig reaction[67a] indicates that the pseudorotation at the sulfur in the associated (10-S-5) four-membered ring is easier than in the oxathietane. This point will be discussed in detail elsewhere.[60]

Corey–Chaykovsky Type Reaction. Formation of an Oxirane

As we have seen in the introduction, it is currently admitted that a *trans*-betaine, **5** (Scheme III), is the reaction intermediate for the formation of oxirane. Therefore, the reaction coordinate is essentially a combination of three variables, the C–C distance (r_{CC}), the C–C–O angle (ϕ), and the P–C or S–C distances (r_{XC}), as shown in **11**.



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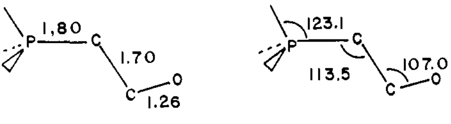
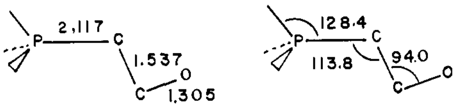
After some preliminary calculations, we found out that these three variables were not strongly coupled and that it was possible to define three regions, in which only one of these varibles was a good approximation of the reaction coordinate. The first region describes mostly the approach between the two reactants (r_{CC}). In the second region, H_nX starts to leave so that r_{XC} is significantly elongated, and in the third region, the oxirane completes its formation by closing the ϕ angle. Only one transition structure was located for each system on the potential energy surface. To provide additional insight on the shape of the potential energy surface, an approximate minimum energy path was determined by varying the main component of the reaction coordinate in each region and optimizing all the remaining variables. For each point, the first derivatives of the energy with respect to the main component of the reaction coordinate was calculated, in order to better follow the shape of the surface. At the junction between two regions, it is impossible to define one main component of the reaction coordinate since at least two of them are strongly coupled. A partial optimization process of all variables but one component of the reaction coordinate could then lead to erroneous results. An interpolation process was thus used, which allowed a smooth passage between the two regions. For both systems, in region 3, the energy falls constantly toward the final products. This part will thus not be discussed further and we will concentrate on regions 1 and 2.

The energy pattern for phosphonium ylide in regions 1 and 2 is shown in Figure 8 for two basis sets, 4-31G* (dashed line) and 4-31G*+ (solid line). The reaction starts with a slow increase in energy to reach a plateau where the energy keeps a constant value for a rather large spectrum of r_{CC} and r_{PC} values. As C–C diminishes, a very shallow well, only apparent with the 4-31G*+ basis set, precedes the energy raise leading to the transition structure. This transition structure corresponds to the departure of the phosphine in the intramolecular S_N2 reaction. After that transition state the energy falls constantly. The activation energy is found to be 24 kcal/mol, a rather high value which indicates that such reaction might not be easy. This illustrates the poor leaving-group ability of a phosphine group. The inverse reaction, the opening of oxirane by a phosphine in the absence of any electrophile, would also suffer a very high activation energy (52.7 kcal/mol). This is substantiated by the fact that ring opening of oxirane by phosphine is generally accomplished above 100 °C.[12]

The main point which results from the consideration of these two curves is the absence of an intermediate resembling a *trans*-betaine. The very shallow well obtained at the junction of regions 1 and 2 with the 4-31G*+ basis set can hardly be considered as an indication of a stable species. Furthermore, its structure, shown in **12**, does not fit very well our idea of a "realistic" intermediate since the C–C length (1.70 Å) is signif-



12



13

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[67] See, for instance: (a) Tamura, Y.; Miyamoto, T.; Kita, Y. *J. Chem. Soc., Chem. Commun.* **1974**, 531. (b) Jung, F.; Sharma, N. K.; Durst, T. *J. Am. Chem. Soc.* **1973**, *95*, 3420. (c) Durst, T.; Gimbarzevsky, B. P. *J. Chem. Soc., Chem. Commun.* **1975**, 724. (d) Gray, M. D. M.; Russel, D. R.; Smith, D. J. H.; Durst, T.; Gimbarzevsky, B. *J. Chem. Soc., Perkin Trans. 1* **1981**, 1826. (e) Burgess, E. M.; Pulcrano, M. C. *J. Am. Chem. Soc.* **1978**, *100*, 6538. (f) A cyclic intermediate derived from the addition of an oxysulfonium ylide to an aldehyde was isolated and characterized by X-ray diffraction: Okuma, K.; Tanaka, Y.; Ohta, H. *J. Am. Chem. Soc.* **1981**, *103*, 5976.

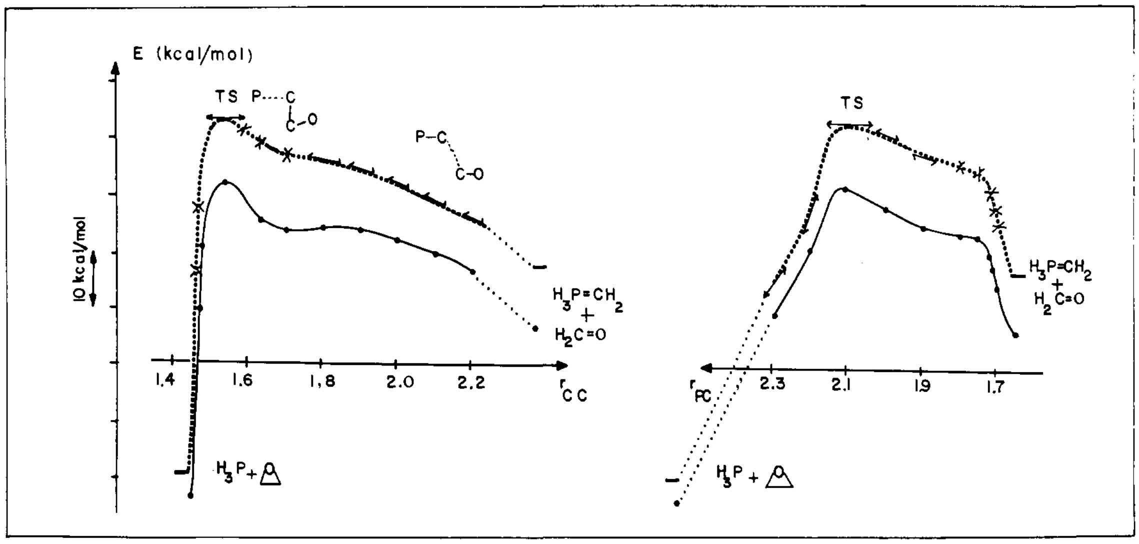


Figure 8. Energy profile (dashed line, 4-31G* level; solid line, 4-31G** level) for the Corey–Chaykovsky reaction with phosphonium ylide as a function of two main components, r_{CC} (left-hand side) and r_{PC} (right-hand side), of the reaction coordinate. The detailed structure of the transition state is given in Table VII.

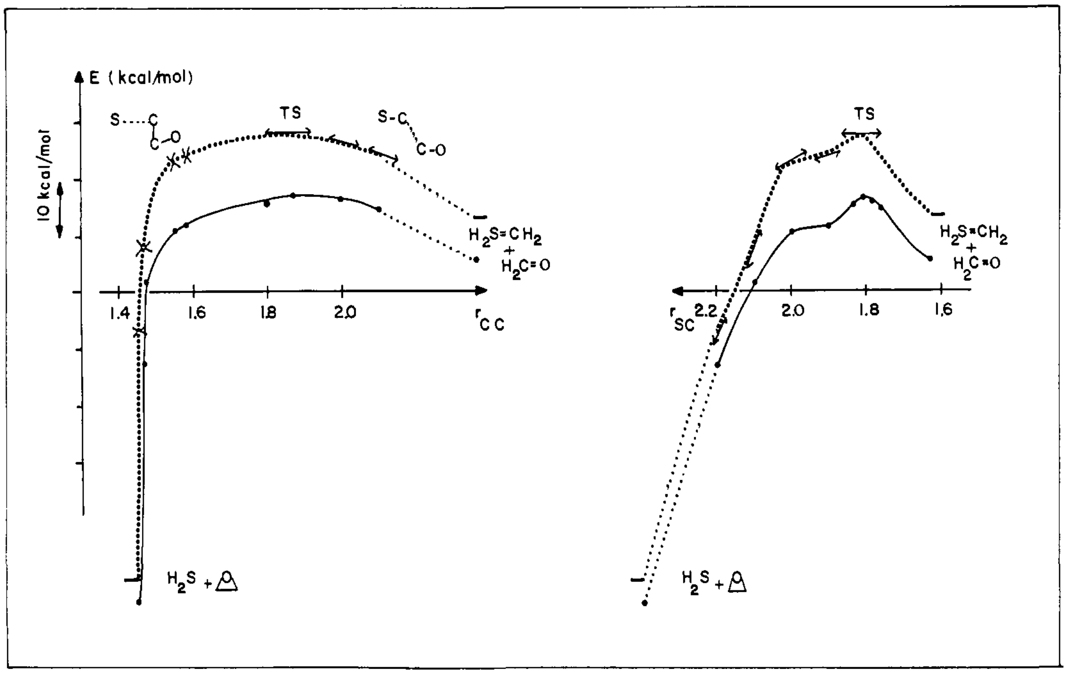


Figure 9. Energy profile (dashed line, 4-31G* level; solid line, 4-31G** level) for the Corey–Chaykovsky reaction with sulfonium ylide as a function of two main components, r_{CC} (left-hand side) and r_{SC} (right-hand side), of the reaction coordinate. The detailed structure of the transition state is given in Table VII.

icantly too long and the C–O length (1.26 Å) is significantly too short for a single bond. However, the other structural parameters correspond rather well to an open chain; the P–C bond of 1.80 Å is characteristic of a single bond, and all angles at the phosphorus and carbons are close to the tetrahedral value. This fact reemphasizes the conclusion concerning the absence of betaine in salt-free conditions that we have made previously. The absence of a *trans*-betaine as a stable intermediate disproves the interpretation concerning the stereoselectivity of the Wittig reaction involving such an intermediate.[17b] In this interpretation the stereochemical course of the reaction was determined by minimizing the steric interaction in the *trans*-betaine, which yields the more sterically hindered oxaphosphetane after rotation around the C–C bond. Such a control can only occur if the betaine is a stable intermediate. On the other hand, this result confirms our preceding conclusion concerning the nonexistence of a *cis*-betaine. If such a *cis*-betaine were a minimum on the potential energy surface, a small rotation barrier around the C–C single bond would transform it into another minimum. Our results are coherent since neither the *cis*- nor the *trans*-betaine are found to be stable intermediates.

The transition structure **12** well illustrates the intramolecular S_N2 mechanism. The four heavy atoms P, C, C, and O are coplanar. The P–C bond is significantly elongated, and the C–C–O angle of 94.0° places the oxygen 2.08 Å away from the attacked carbon.

The energy profiles for the sulfonium ylide in regions 1 and 2 are shown in Figure 9 for the same two bases. As in the case of phosphorus, there is only one transition structure, but in this case it occurs rather early, in region 1, and corresponds to the addition of the sulfonium ylide to formaldehyde. After this transition structure, the energy drops, reaches a small plateau, and then falls toward the products. There is no transition state corresponding to the departure of H_2S, which illustrates the better leaving-group ability of a sulfide compared with that of a phosphine. The activation energy for the whole reaction is small (10.6 kcal/mol) and, note, smaller than in the case of phosphorus. The reaction should proceed easily.

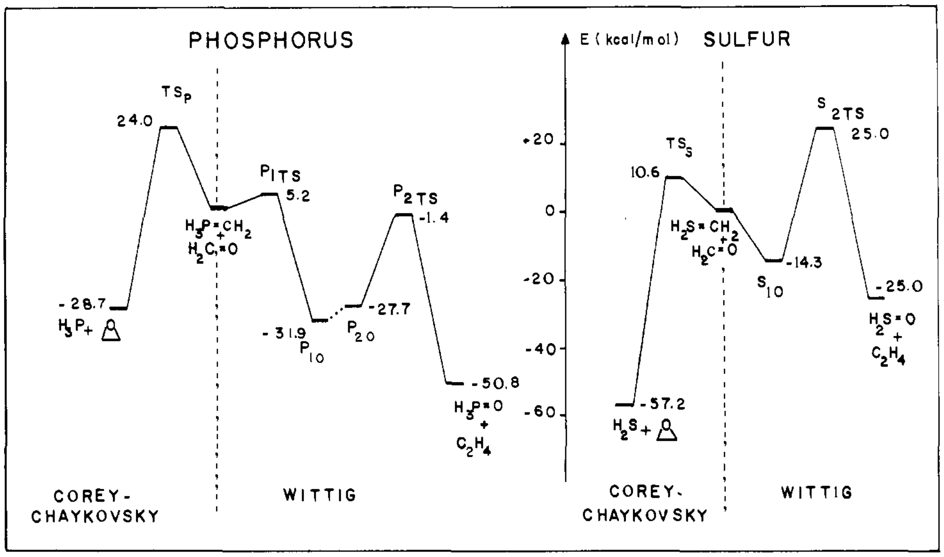
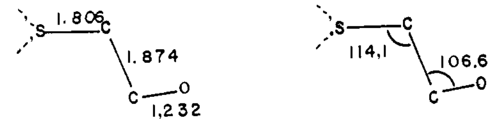


Figure 10. Energy profile of the Wittig (right-hand side of each part) and Corey–Chaykovsky reactions (left-hand side of each part) for phosphonium ylide (left-hand side) and sulfonium ylide (right-hand side).

As in the phosphorus case, the sulfur surface is characterized by the absence of a *trans*-betaine. Not even a small well appears on the surface at the 4-31G*+ level.

The transition structure in the case of sulfur is shown in **14**. It is typical of the transition structure of a nucleophile adding to a carbonyl group,[68] since the C–C–O angle is 106.6°, the C–C bond hardly formed, and the C–O bond weakly elongated. Let us note that the structure is slightly skewed (dihedral angle S–C–C–O = 2.3°).



14

It is of some interest to compare the activation energy of a trans addition leading to the open zwitterionic arrangement with that of a cis addition leading to the four-membered-ring intermediate. In both the phosphorus and sulfur cases, the trans addition is found to be more difficult than the cis addition. In the case of sulfur, there is no activation energy for the cis addition, while there is 10.6 kcal/mol for the trans addition. Similar considerations apply to the phosphorus, even though no transition state is found for the trans addition. Cis addition requires a 5.6 kcal/mol activation energy, while the energy cost in the case of the trans addition can be roughly estimated around 12.4 kcal/mol (energy needed to reach a P–C distance of 1.8 Å, equal to that found in the cis transition structure). This relative facility of the cis addition compared with the trans addition can be easily understood in terms of electrophilic assistance at the oxygen center. As seen before, if one considers the ylide as a purely covalent system, the (2_s + 2_s) cycloaddition to the carbonyl group is an allowed process. Nevertheless, the π system of $H_nX{=}CH_2$ in the ylide (H_nX = H_3P or H_2S) has a noticeable zwitterionic character (H_nX^+—CH_2^-). In the formation of the four-membered ring (cis addition), the H_nX moiety provides an electrophilic assistance to the oxygen center by polarizing the C–O bond and lowering the activation energy of the two methylene groups coupling. In contrast, no such phenomenon can occur in the trans addition, which accounts for its higher activation energy. Such an electrophilic assistance has been previously theoretically studied in the case of Li^+ cation by Lefour and Loupy,[69]

Table VI. Energy in kcal/mol of the Molecules and Extrema Optimized in This Work[a]

compd	4-31G*	4-31G*+
H_2S	−398.257 71	−398.257 71
H_3P	−342.090 26	−342.090 26
H_2CO	−113.757 06	−113.764 09
C_2H_4	−77.953 61	−77.959 26
ethylene oxide	−152.719 51	−152.725 87
$H_3P{=}CH_2$	−380.996 80	−381.006 27
$H_2S{=}CH_2$	−437.119 47	−437.128 25
H_3PO	−416.879 48	−416.892 03
H_2SO	−472.961 28	−472.972 96
Me_2S	−476.249 76	−476.254 41
Me_2SO	−550.982 63	−550.996 79
P_{10}	−494.811 54	−494.821 19
P_{20}	−494.806 52	−494.814 50
P_{1TS}	−494.747 03	−494.762 09
P_{2TS}	−494.761 03	−494.772 63
S_{10}	−550.901 29	−550.915 19
S_{2TS}	−550.840 80	−550.852 45
TS_P[b]	−494.714 64	−494.732 11
TS_S[c]	−550.858 70	−550.875 45

[a] The optimization of the structure was done at the 4-31G* level. Single-point calculations 4-31G*+/4-31G* (diffuse orbitals on C and O) were performed. Due to slight differences in the value of some internally defined constants between GAUSSIAN80 and MONSTERGAUSS, our energies may differ slightly from those presented in ref 34 and 37. [b] TS_P is the transition state for the Corey–Chaykovsky reaction with the phosphonium ylide. [c] TS_S is the transition state for the Corey–Chaykovsky reaction with the sulfonium ylide.

Finally, two reasons can be put forward to explain the relative ease of the two ylides to undergo the Corey–Chaykovsky reaction. First, the sulfonium ylide is more reactive than the phosphonium ylide, which favors the addition step for sulfur (activation energy found to be 10.6 kcal/mol in the case of sulfur and estimated to be 12.4 kcal/mol in the case of phosphorus). Second, the leaving-group ability of a sulfide is larger than that of a phosphine, which makes the internal S_N2 reaction easier for the sulfur (relative to the plateau no activation energy is found in the case of sulfur while an activation energy of 7.6 kcal/mol is obtained in the case of phosphorus).

Conclusions

Compared Reactivity of the Two Ylides. The energy profiles for the two reactions in the case of the two ylides are represented side by side in Figure 10, in order to facilitate comparison. It does very well illustrate the experimental preferences. Both thermodynamic and kinetic factors are responsible for the reactivity preferences. Sulfonium ylide is more reactive than

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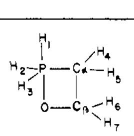
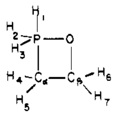
(68) Bürgi, H.-B.; Lehn, J. M.; Wipff, G. *J. Am. Chem. Soc.* **1974**, *96*, 1956. Bürgi, H.-B.; Dunitz, J. D.; Lehn, J. M.; Wipff, G. *Tetrahedron* **1974**, *30*, 1563.

(69) Lefour, J.-M.; Loupy, A. *Tetrahedron* **1978**, *34*, 2597.

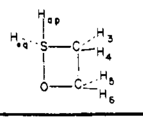
Table VII. Geometrical Parameters of All the Extrema Located on the Potential Energy Surface for the Wittig and Corey-Chaykovsky Reactions for Both Ylides[a]

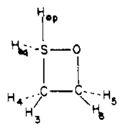


	P_{10}	P_{1TS}		P_{10}	P_{1TS}
$P{-}C_{\alpha}$	1.843	1.736	$H_2{-}P{-}C_{\alpha}$	123.4	112.8
$C_{\alpha}{-}C_{\beta}$	1.533	2.079	$H_2{-}P{-}C_{\alpha}{-}C_{\beta}$	83.0	60.0
$C_{\beta}{-}O$	1.399	1.239	$C_{\alpha}{-}H_4$	1.079	1.077
$P{-}C_{\alpha}{-}C_{\beta}$	89.0	93.9	$C_{\beta}{-}H_6$	1.080	1.085
$C_{\alpha}{-}C_{\beta}{-}O$	98.1	108.4	$H_4{-}C_{\alpha}{-}P$	112.7	111.6
$P{-}H_1$	1.438	1.398	$H_6{-}C_{\beta}{-}O$	111.9	120.8
$P{-}H_2$	1.389	1.378	$H_4{-}C_{\alpha}{-}P{-}H_1$	61.6	62.5
$H_1{-}P{-}C_{\alpha}$	97.4	119.4	$H_6{-}C_{\beta}{-}O{-}P$	119.1	105.4

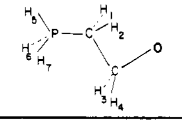


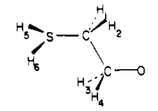
	P_{20}	P_{2TS}		P_{20}	P_{2TS}
$P{-}C_{\alpha}$	1.924	2.359	$H_2{-}P{-}O$	128.4	123.6
$C_{\alpha}{-}C_{\beta}$	1.516	1.401	$H_2{-}P{-}O{-}C_{\alpha}$	88.2	74.6
$P{-}O$	1.655	1.530	$C_{\alpha}{-}H_4$	1.078	1.072
$P{-}C_{\alpha}{-}C_{\beta}$	86.4	81.1	$C_{\beta}{-}H_6$	1.077	1.068
$O{-}P{-}C_{\alpha}$	75.9	77.9	$H_4{-}C_{\alpha}{-}C_{\beta}$	115.0	117.7
$P{-}H_1$	1.420	1.403	$H_6{-}C_{\beta}{-}C_{\alpha}$	115.2	120.8
$P{-}H_2$	1.402	1.383	$H_4{-}C_{\alpha}{-}C_{\beta}{-}P$	116.0	107.9
$H_1{-}P{-}O$	87.2	99.3	$H_6{-}C_{\beta}{-}C_{\alpha}{-}P$	115.8	103.0





	S_{10}		S_{10}		S_{2TS}		S_{2TS}
$S{-}C_{\alpha}$	1.825	$H_{eq}{-}S{-}C_{\alpha}$	105.6	$S{-}C_{\alpha}$	2.405	$H_{ap}{-}S{-}O$	89.7
$C_{\alpha}{-}C_{\beta}$	1.548	$H_3{-}C_{\alpha}{-}C_{\beta}$	114.1	$C_{\alpha}{-}C_{\beta}$	1.409	$H_3{-}C_{\alpha}{-}C_{\beta}$	118.1
$C_{\beta}{-}O$	1.352	$H_4{-}C_{\alpha}{-}C_{\beta}$	119.8	$S{-}O$	1.574	$H_4{-}C_{\alpha}{-}C_{\beta}$	117.9
$S{-}H_{ap}$	1.367	$H_5{-}C_{\beta}{-}C_{\alpha}$	109.4	$S{-}H_{eq}$	1.329	$H_5{-}C_{\beta}{-}C_{\alpha}$	120.1
$S{-}H_{eq}$	1.316	$H_6{-}C_{\beta}{-}C_{\alpha}$	109.0	$S{-}H_{ap}$	1.356	$H_6{-}C_{\beta}{-}C_{\alpha}$	119.5
$C_{\alpha}{-}H_3$	1.076	$O{-}C_{\beta}{-}C_{\alpha}{-}S$	−19.9	$C_{\alpha}{-}H_3$	1.071	$O{-}S{-}C_{\alpha}{-}C_{\beta}$	−5.8
$C_{\alpha}{-}H_4$	1.079	$H_{ap}{-}S{-}C_{\alpha}{-}C_{\beta}$	179.0	$C_{\alpha}{-}H_4$	1.073	$H_{ap}{-}S{-}O{-}C_{\alpha}$	81.0
$C_{\beta}{-}H_5$	1.088	$H_{eq}{-}S{-}C_{\alpha}{-}C_{\beta}$	85.8	$C_{\beta}{-}H_5$	1.070	$H_{eq}{-}S{-}O{-}C_{\alpha}$	172.4
$C_{\beta}{-}H_6$	1.090	$H_3{-}C_{\alpha}{-}C_{\beta}{-}O$	92.3	$C_{\beta}{-}H_6$	1.070	$H_3{-}C_{\alpha}{-}C_{\beta}{-}S$	104.5
$S{-}C_{\alpha}{-}C_{\beta}$	94.4	$H_4{-}C_{\alpha}{-}C_{\beta}{-}O$	−135.0	$S{-}C_{\alpha}{-}C_{\beta}$	79.8	$H_4{-}C_{\alpha}{-}C_{\beta}{-}S$	−110.2
$O{-}C_{\beta}{-}C_{\alpha}$	102.1	$H_5{-}C_{\beta}{-}C_{\alpha}{-}S$	−142.0	$O{-}S{-}C_{\alpha}$	74.1	$H_5{-}C_{\beta}{-}C_{\alpha}{-}S$	110.5
$H_{ap}{-}S{-}C_{\alpha}$	95.4	$H_6{-}C_{\beta}{-}C_{\alpha}{-}S$	101.5	$H_{eq}{-}S{-}O$	108.5	$H_6{-}C_{\beta}{-}C_{\alpha}{-}S$	−102.2





	TS_P		TS_P		TS_S		TS_S
$C_{\alpha}{-}C_{\beta}$	1.537	$H_6{-}P{-}C_{\alpha}$	111.5	$C_{\alpha}{-}C_{\beta}$	1.874	$H_2{-}C_{\alpha}{-}C_{\beta}$	104.6
$C_{\beta}{-}O$	1.305	$H_1{-}C_{\alpha}{-}C_{\beta}{-}O$	65.3	$C_{\beta}{-}O$	1.232	$H_3{-}C_{\beta}{-}C_{\alpha}$	96.0
$P{-}C_{\alpha}$	2.117	$H_3{-}C_{\beta}{-}C_{\alpha}{-}O$	121.8	$S{-}C_{\alpha}$	1.806	$H_4{-}C_{\beta}{-}C_{\alpha}$	99.2
$C_{\alpha}{-}H_1$	1.074	$H_6{-}P{-}C_{\alpha}{-}C_{\beta}$	55.8	$C_{\alpha}{-}H_1$	1.078	$H_5{-}S{-}C_{\alpha}$	110.9
$C_{\beta}{-}H_3$	1.105			$C_{\alpha}{-}H_2$	1.077	$H_6{-}S{-}C_{\alpha}$	99.6
$P{-}H_5$	1.400			$C_{\beta}{-}H_3$	1.110	$S{-}C_{\alpha}{-}C_{\beta}{-}O$	182.3
$P{-}H_6$	1.392			$C_{\beta}{-}H_4$	1.103	$H_1{-}C_{\alpha}{-}C_{\beta}{-}O$	62.8
$C_{\alpha}{-}C_{\beta}{-}O$	94.0			$S{-}H_5$	1.336	$H_2{-}C_{\alpha}{-}C_{\beta}{-}O$	−57.9
$P{-}C_{\alpha}{-}C_{\beta}$	113.8			$S{-}H_6$	1.334	$H_3{-}C_{\beta}{-}C_{\alpha}{-}O$	124.3
$H_1{-}C_{\alpha}{-}C_{\beta}$	113.0			$C_{\alpha}{-}C_{\beta}{-}O$	106.6	$H_4{-}C_{\beta}{-}C_{\alpha}{-}O$	−125.8
$H_3{-}C_{\beta}{-}C_{\alpha}$	109.7			$S{-}C_{\alpha}{-}C_{\beta}$	114.1	$H_5{-}S{-}C_{\alpha}{-}C_{\beta}$	133.3
$H_5{-}P{-}C_{\alpha}$	128.4			$H_1{-}C_{\alpha}{-}C_{\beta}$	110.3	$H_6{-}S{-}C_{\alpha}{-}C_{\beta}$	35.4

[a] Bond angles are in degrees; bond lengths are in angstroms. All the structures involving phosphorus belong to the C_S symmetry point group.

phosphonium ylide and therefore adds more easily to formaldehyde in the two types of reactions. Nevertheless, *the addition step is never found to be the determining step that explains the different behavior of the two ylides.*

The activation energy (from the reactants) is 5.2 kcal/mol for the Wittig reaction and 25 kcal/mol for the Corey-Chaykovsky reaction in the case of the phosphonium ylide. The first reaction is thus preferred. In contrast, the corresponding activation energies in the case of the sulfonium ylide are 25 (Wittig) and 10.6 kcal/mol (Corey-Chaykovsky). The second one is thus preferred.

The formation of phosphine oxide and olefin is thermodynamically preferred to the formation of oxirane and phosphine. Conversely, formation of oxirane and sulfide is thermodynamically preferred to that of sulfoxide and olefin. This reversal in the thermodynamic preferences is attributed to the smaller oxo affinity of H_2S compared with H_3P, which in turn may be partly attributed to a four-electron destabilization involving the sulfur and oxygen lone pairs.

As expected, the kinetic preference for the Corey–Chaykovsky reaction is controlled by the leaving-group ability of the group next to the ylide, which is greater for the sulfide. Less obviously, *the step that kinetically differentiates the phosphorus from the sulfur in the Wittig reaction is the ring-opening of the cyclic intermediates to yield the products.* The capacity to undergo this crucial step is conditioned by the ease with which the oxygen can reach the equatorial site and the carbon the apical site and not by the fact that the S–C bond is intrinsically difficult to cleave. This interchange of groups is easy in the case of phosphorus and very difficult in the case of sulfur.

We have now at hand a convenient way to estimate the ability of a given ylide to undergo the Wittig reaction. The smaller the energy difference between the two isomers of the four-membered-ring intermediate, the easier the Wittig reaction is. As mentioned previously, the oxosulfonium ylide may fulfill this requirement since it has been shown in one case to undergo a Wittig reaction.[67a] The case of arsonium ylide, the reactivity of which is very sensitive to the nature of substituents, could be approached in that manner.

Let us conclude this study by pointing out that our calculations and results cannot be applied, at least in a straightforward manner, when lithium salt is added to the reaction mixture, since they simulate salt-free conditions. In particular, *cis*- or *trans*-betaine, which has been found to be a nonstable intermediate in our calculations, may become strongly stabilized when lithium cation is present in the reactive media.

Acknowledgment. This work has greatly beneficiated from helpful discussions with Profs. K. Morokuma and E. Vedejs and Drs. Y. Jean, J. M. Lefour, and J. Seyden-Penne. This work beneficiated from a generous donation from the computer centers of the University of Michigan (USA) and of the Institute of Molecular Science at Okasaki (Japan). In France, the calculations were done at the CIRCE (CNRS) and CRAY1 (CCVR, ATP n° 3655 and 3070). We thank these four computer centers for computational facilities and generous donation in computing time. O. E. thanks Prof. K. Morokuma for having invited her to Japan. Her stay in Japan was financially supported by the Rackham Research and Fellowship Grant from the University of Michigan. O. E. thanks the donors of the Petroleum Research Fund, administered by the American Chemical Society, for partial financial support of this work.

Note Added in Proof. Akiba et al. (Akiba, K.-Y.; Takee, K.; Shimizu, Y.; Ohkata, K. *J. Am. Chem. Soc.* **1986**, *108*, 6320) have recently structurally characterized a strongly distorted sulfurane with an apical methyl group. However, this structure can still be viewed as a distorted episulfonium cation in weak interaction with an incoming nucleophile. Note that replacing the alkyl group by other more electronegative atoms or groups makes the sulfurane closer to a TBP structure.

Registry No. $H_3P{=}CH_2$, 36429-11-5; $H_2S{=}CH_2$, 59301-38-1; H_2CO, 50-00-0; H_2S, 7783-06-4; C_2H_4, 74-85-1; $\overline{PH_3OCH_2CH_2}$, 40110-50-7; $\overline{SH_2OCH_2CH_2}$, 104994-70-9; H_3P, 7803-51-2; ethylene oxide, 75-21-8.

Theoretical Studies of Conformations of Acrolein, Acrylic Acid, Methyl Acrylate, and Their Lewis Acid Complexes

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Contribution from the Department of Chemistry, University of Pittsburgh, Pittsburgh, Pennsylvania 15260, and Department of Chemistry and Biochemistry, University of California, Los Angeles, California 90024. Received June 17, 1986

Abstract: Ab initio calculations have been performed on the conformations of acrolein, acrylic acid, methyl acrylate, and complexes of these species with Lewis acids, H^+, Li^+, and BH_3. Acrylic acid and methyl acrylate have small preferences for s-cis conformations, but the Lewis acid complexed acrylates prefer the s-trans conformations. Both acrolein and Lewis acid complexed acrolein prefer the s-trans conformation. These calculations confirm conformational hypotheses made to rationalize the stereoselectivities of catalyzed Diels–Alder reactions of chiral acrylates.

The regioselectivities, stereoselectivities, and rates of Diels–Alder reactions are profoundly influenced by Lewis acid catalysts.[1–5] For example, the degree of asymmetric induction observed in Diels–Alder cycloadditions to chiral acrylates is large only when the reactions are catalyzed by Lewis acids, while the corresponding thermal reactions occur with very modest stereoselectivities, at best. We have undertaken a theoretical investigation of the influence of Lewis acids upon the conformations of acrylic esters, which are perhaps the most common dienophiles in Diels–Alder cycloadditions with electron-rich dienes. The simpler molecules, acrolein and acrylic acid, were studied for comparison. We first describe the experimental results which show that stereoselectivities of asymmetric Diels–Alder reactions vary upon catalysis, suggesting that acrylate conformations are influenced by Lewis acid complexation. We then describe the theoretical results which provide a partial explanation for these phenomena.

Asymmetric Diels–Alder Reactions. Table I shows a few examples of asymmetric Diels–Alder reactions. The catalyzed reactions of three acrylic esters all exhibit a high degree of asymmetric induction. For each of the dienophiles listed, the conformation shown predicts the experimentally observed product, by endo addition to the sterically less hindered side of the dienophile.

Cycloadditions of cyclopentadiene with (−)-menthyl acrylate[6a–d] and of butadiene[7] and cyclopentadiene with di-(−)-menthyl fu-

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