formation of a bond between C-4 and C-17, followed by H migration. The resulting two cation intermediates I and II are in equimolar equilibrium and open with aqueous acid to give equal amounts of the 4- and the 17-hydroxy phane (*syn*-**2** and **3**). An alternative mechanism involves intramolecular diazo coupling to form a nonionic azo intermediate (III), which could undergo ring protonation on either ring with loss of N_2 and addition of H_2O to give equal amounts of *syn*-**2** and **3**. This mechanism does not involve the transannular H migration. In order to make a choice between these possible explanations, a further study is in progress.

Failure To Confirm Our Observations of Reactivity of Triose-P Isomerase, Methylglyoxal Synthase, and Ferricyanide with Triose-P Enediol

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It has been reported[1] that the enzymes methylglyoxal synthase and triose-P isomerase make use of different stereoisomers of enediol-3-P. This conclusion was based on the finding that as the *cis*- and *trans*-enediol-Ps were generated in dilute alkaline solution from L-glyceraldehyde 3-phosphate one of them could be diverted from its rapid β-elimination to P_i and methylglyoxal by added triose-P isomerase and the other isomer by oxidation with 1 mM $K_3Fe(CN)_6$. It was reported that methylglyoxal synthase, an enzyme that normally converts dihydroxyacetonephosphate to P_i and methylglyoxal, restored the β-elimination reaction in competition with the ferricyanide but not the isomerase.

These observations cannot be reproduced: no effect of 2 μM triose-P isomerase on the rate of P_i formation from L-glyceraldehyde 3-phosphate can be shown. Furthermore, the effect of ferricyanide is now found to be much less than was reported. Table I compares the earlier and present results.

Evidence that the P_i is formed by β-elimination of -OPO_3^{2-} from enediol-P derives from the observation (Table I) of the complete diversion of the intermediate to an alkaline-stable species by I_2. The failure of isomerase to trap any of the intermediate was surprising in view of our earlier reports that fresh isomerase can trap an intermediate generated by acid denaturation of an isomerase–DHAP equilibrium mixture.[2,3] However, recent experiments have failed to confirm these observations. Ferricyanide was expected to oxidize the enediol-P by analogy with its oxidation of dihydroxyacetone phosphate to phosphopyruvaldehyde with aldolase of yeast.[4] Evidently, unlike I_2, ferricyanide does not compete well with the β-elimination reaction. Moreover, since we are unable to confirm the high equilibrium concentration of enzyme-bound D-glyceraldehyde 3-phosphate, reported earlier,[2,3] a second paper[5] purporting to explain a D_2O effect on the partition of this bound substrate must also be retracted. A separate report indicating our inability to reproduce observations on complexes present on triose-P isomerase is to appear elsewhere.[6]

I deeply regret the misinformation resulting from these reports.

Table I. Trapping of Triose-P Enediol, Failure To Substantiate Our Earlier Report

	$[^{32}P]P_i$, % of total ^{32}P			
	Iyengar and Rose[1]	current expts		
addn				
none	62[a]	19.4[b]	41[c]	53[d]
TIM	24	19.1	39	
TIM + $K_3Fe(CN)_6$	8.4	14.1		
$K_3Fe(CN)_6$			28	49
I_2 (1.5 mM), KI (12 mM)				0

[a] From Table II of Iyengar and Rose.[1] The incubation mixture contained in 0.5 mL: Gly·NaOH (80 mM, pH 9.5), $[^{32}P]$-L-G3P (~5 pm, 4.5 × 10^5 cpm), NADH (0.4 mM), α-glycerol-phosphate dehydrogenase (7 units), noted additions of triose-P isomerase, TIM (2 μM), and $K_3Fe(CN)_6$ (0.8 mM). After 1 h at 25 °C the $[^{32}P_i]P_i$ formed was determined as the molybdate complex extracted into 2-butanol. [b] Same as *a*. [c] L-G3P increased to 0.1 mM, α-glycerol-phosphate dehydrogenase only present with TIM. [d] Same as *c*. With I_2/KI present the $[^{32}P]$-L-glyceraldehyde 3-phosphate disappeared as expected from the formation of P_i in the control.

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Theoretical Study of the Reactivity of Phosphonium and Sulfonium Ylides with Carbonyl Groups

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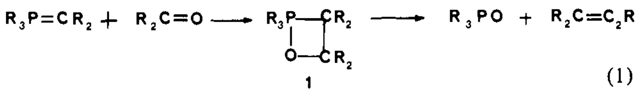
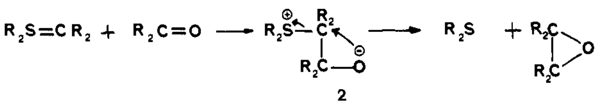
The ylides form a class of nucleophilic reactants that have been extensively used in organic synthesis. The nature of the atom linked to the nucleophilic carbon is important in determining the course of the reaction. Phosphonium,[1] sulfonium,[2] and oxosulfonium[3] ylides react differently with carbonyl groups. While in the Wittig reaction an olefin and a phosphine oxide are the products of the reaction,[1] oxirane is exclusively formed in the reaction of sulfur ylides, as shown primarily by Corey and Chaykovsky.[2-4] Different mechanisms have been proposed to account for the different products: (a) a phosphonium ylide adds to the carbonyl group to form a four-membered ring, oxaphosphetane **1**, which decomposes into an olefin and a phosphine oxide (eq 1); (b) a sulfonium ylide adds to the carbonyl group to give



(1)



(2)

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0002-7863/84/1506-6117$01.50/0

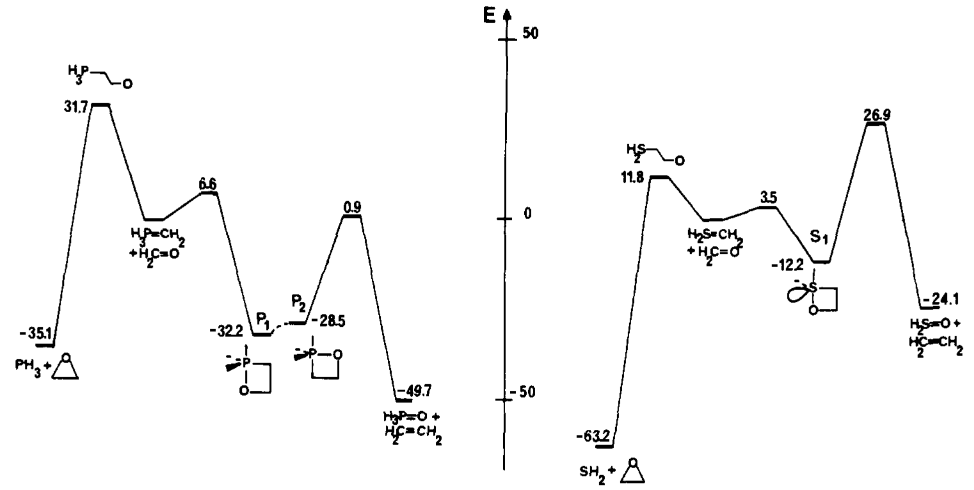

Figure 1. Energy profiles (in kcal/mol) for the reaction of formaldehyde with $H_2S{=}CH_2$ (right-hand side) and $H_3P{=}CH_2$ (left-hand side). All points are optimized at the 4-31G* level except the two transition structures connecting the reactants to the oxirane and the transition structure connecting $H_2S{=}CH_2$ + $H_2C{=}O$ to S_1.

a trans betaine **2**, which undergoes an intramolecular S_N2 reaction in which the oxygen atom displaces a sulfide to form the oxirane (eq 2). A similar mechanism applies to oxosulfonium ylides.

The reasons for these different mechanisms are not yet fully understood. Theoretical calculations have exclusively been undertaken on the Wittig reaction. The reaction path has been studied with ab initio[5] and MNDO[6] calculations. The pseudorotational barrier of the oxaphosphetane **1** intermediate has been shown to be low with ab initio calculations.[7] The stereochemistry of the reaction was also discussed.[6,8]

In this communication we present a determination of the fully optimized transition states and intermediates in the model Wittig reaction $H_3P{=}CH_2 + H_2CO \rightarrow H_3PO + H_2C{=}CH_2$ as well as in the hypothetical analogous reaction $H_2S{=}CH_2 + H_2CO \rightarrow H_2SO + H_2C{=}CH_2$. We also present preliminary results for the model Corey–Chaykovsky reaction $H_2S{=}CH_2 + H_2CO \rightarrow H_2S + \overline{CH_2OCH_2}$ as well as in the hypothetical analogous reaction $H_3P{=}CH_2 + H_2CO \rightarrow H_3P + \overline{CH_2OCH_2}$.

All stationary points were located with an analytical gradient.[9] Full optimization was done for all minima and most of the transition structures at the 4-31G* level.[10] Preliminary results (4-31G* single-point calculations on a STO-3G*[11] optimized geometry) are presented for three transition structures.[12] The results are summarized in Figure 1.

Wittig-Type Reaction. For the phosphorus ylide, the activation energy to form the first intermediate P_1 is 6.6 kcal/mol. This oxaphosphetane, P_1, in which the oxygen atom occupies an axial position of the trigonal-bipyramidal phosphorus, is 32.2 kcal/mol more stable than the reactants. A pseudorotation at the phosphorus center interchanges the position of the oxygen and the carbon atoms. This motion is necessary in order to weaken to P–C bond. Test calculations by us on more simple models as well as the results of Höller and Lischka[5] show that a very small activation energy is involved in this pseudorotation. The second intermediate oxaphosphetane P_2 with an axial carbon is 3.7 kcal/mol less stable than P_1. These results agree with the Muetterties rules: the more electronegative atom prefers the axial position in a trigonal bipyramid.[13] The activation energy for the decomposition of P_2 toward the olefin production is 29.4 kcal/mol, markedly lower than the activation energy (38.8 kcal/mol) of the reverse reaction ($P_1 \rightarrow$ ylide + formaldehyde). The structures of the two transition states indicate that the formation and the decomposition of the oxaphosphetane are concerted (supra, supra) in a geometrical sense, the four heavy atoms being coplanar. Our overall pathway agrees with the results of Höller and Lischka[5] and those of Bestmann, Schleyer, and co-workers.[6,7]

For the sulfur ylide, the activation energy to form the cyclic intermediate oxathietane is 3.5 kcal/mol. Note that the transition state has been difficult to locate because of soft coupled motions involving the SH_2 group. Therefore, only the STO-3G* basis set was used for the search. Then a single point, at the 4-31G* level, calculation using the STO-3G* structure was done.

This oxathietane, S_1, in which the oxygen atom occupies an axial position is 12.2 kcal/mol more stable than the reactants.[14] No stable isomeric oxathietane with an equatorial oxygen atom has been found. S_1 decomposes toward the olefin formation with an activation energy of 39.1 kcal/mol. This high activation energy is due to the attempt to cleave an equatorial S–C bond.[15] In this case the activation energy for the reverse decomposition of the oxathietane is much lower (15.7 kcal/mol). The structures of the transition states, which are only slightly puckered, suggest a (supra, supra) concerted process.

The comparison between the above reaction paths can be summarized in the following way: (i) in both cases the formation of the cyclic intermediate (P_1, S_1) is easy and therefore cannot differentiate the reactivity of both ylides, (ii) the difference arises in the possibility of axial–equatorial exchange between the substituents. In the case of phosphorus, the carbon atom can easily occupy the equatorial position weakening the P–C bond. Consequently, the cleavage of the oxaphosphetane to form the olefin requires only 29.4 kcal/mol. In the case of sulfur, the exchange is not possible, the S–C bond remains strong and the cleavage of

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the oxathietane to form the olefin requires a much higher activation energy (39.1 kcal/mol).

Another relevant point concerns the relative stability of the various oxygenated compounds. The formation of cyclic intermediates and final products are much more exothermic for phosphorus than for sulfur. This fact is probably related to the larger oxygen affinity for phosphorus than for sulfur.

Corey–Chaykovsky-Type Reaction. Preliminary results are given on Figure 1. Transition states for the oxirane formation have been located at the STO-3G* level and recalculated with the 4-31G* basis. Both structures can be viewed as intramolecular S_N2 transition states.[16] No minima have been located around these saddle points. This suggests that the trans betaines are transition structures (at least in the absence of solvent effects) and not intermediates as often proposed.

The activation energy for the sulfur is found lower than for the phosphorus. This can be understood in term of a better leaving group ability for the sulfide than for the phosphine.

Finally, our description does not support some aspects of the conventional representations of the Wittig and Corey–Chaykovsky reactions. In the Wittig-type reactions, no zwitterionic structures (cis betaines) have been located on the reaction path. In the Corey–Chaykovsky-type reactions, the open structures look like trans betaines but correspond to saddle points and not minima on the potential energy surface.

Full details of the calculations will be given in a forthcoming paper.

Acknowledgments. The calculations were done at the computer centers of Orsay (CIRCE), Palaiseau (CCVR) (France), the University of Michigan, and the Institute of Molecular Science at Okazaki (Japan). We thank these computer centers for a generous allocation of computing time. We are grateful to Professor Nguyen Trong Anh, K. Morokuma, and Dr. F. Delbecq for their suggestions and stimulating discussions. O. Eisenstein thanks the donors of the Petroleum Research Fund, administered by the American Chemical Society, for their financial support. The stay in Japan was made possible by a Rackham Research and Fellowship Grant (O.E.).

Registry No. $H_3P{=}CH_2$, 36429-11-5; $H_2S{=}CH_2$, 63933-47-1; H_2CO, 50-00-0.

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[16] The ∠CCO angle is 91.6° in the case of phosphorus and 96.7° in the case of sulfur. The ∠PCC angle is 121°, and the ∠SCC angle is 130°.

Additions and Corrections

^{13}C–^{1}H Coupling Constants in Carbocations. 4. Conformations of Internal Cyclopropylcarbinyl Cations (Benzobicyclo[4.1.0]heptyl Cations) and Their Rearrangements to Naphthalenium Cations [*J. Am. Chem. Soc.* **1984**, *106*, 687]. David P. Kelly,* D. Ralph Leslie, and Bradley D. Smith

Page 693: The ^{13}C NMR assignments for compound **29** refer to a numbering scheme different from that given on structure **29** (p 692). The entry under **29** should read as follows: ^{13}C NMR δ 10.2 (t, J = 164 Hz, C_7), 26.6 (d, J = 169 Hz, C_1), 27.2 (q, J = 126 Hz, CH_3), 28.7 (d, d, J(av) = 121 Hz, C_4), 30.0 (q, J = 124 Hz, CH_3), 30.4 (d, J = 164 Hz, C_6), 30.4 (t, J = 127 Hz, C_3), 33.2 (s, C_5), 209.0 (s, C_2); etc.

Stepwise Metal-Assisted Oxidative Decarboxylation of Vanadium(V) Ethylenebis((*o*-hydroxyphenyl)glycine). Isolation of a Possible Intermediate [*J. Am. Chem. Soc.* **1984**, *106*, 3360]. Vincent L. Pecoraro, Joseph A. Bonadies, Carl A. Marrese, and Carl J. Carrano*

Page 3361, line 16 should read: ...electrons, with the concomitant....

Page 3361, Scheme I: compound **5** should have no oxo group.

Electronic Structure and Bonding of $Hg(CH_3)_2$, $Hg(CN)_2$, $Hg(CH_3)(CN)$, $Hg(CCCH_3)_2$, and $Au(PMe_3)(CH_3)$ [*J. Am. Chem. Soc.* **1984**, *106*, 3387]. Roger L. DeKock,* Evert Jan Baerends, Paul M. Boerrigter, and Rudy Hengelmolen

Pages 3387 and 3395: We refer to the $Hg–CH_3$ bonds in $Hg(CH_3)_2$ as 3c–2e bonds. It is clear from the discussion and from Figure 8 that we were emphasizing that two electrons are *bonding* and two are mainly nonbonding. In that sense the bonding is not unlike that in HF_2^-, I_3^-, or XeF_2. In the usual inorganic parlance such a bond is described as 3c–4e. We apologize for any confusion this may have caused.

Comparative Photophysics of Platinium(II) and Platinum(IV) Porphyrins [*J. Am. Chem. Soc.* **1984**, *106*, 4015–4017]. Dongho Kim, Dewey Holten,* Martin Gouterman, and Johann W. Buchler

Page 4015, abstract, line 5: $[a_{2u}(\pi), d_{x^2-y^2}]$ should read $[a_{2u}(\pi), d_{z^2}]$.

Page 4016, column 2, fifth line from the bottom: again $[a_{2u}(\pi), d_{x^2-y^2}]$ should read $[a_{2u}(\pi), d_{z^2}]$.