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

addn	$[^{32}P]P_i$, % of total ^{32}P			
	Iyengar and Rose[1]	current expts		
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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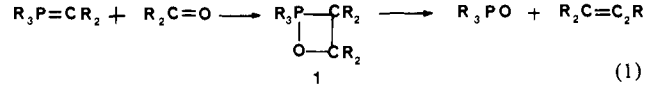
The ylides form a class of nucleophilic reactants that have been extensively used in organic synthesis. The nature of the atom linked to the nucleophilic carbon is important in determining the course of the reaction. Phosphonium,[1] sulfonium,[2] and oxosulfonium[3] ylides react differently with carbonyl 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



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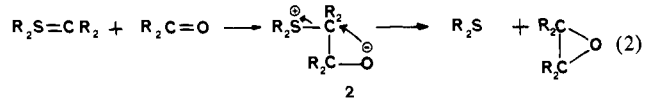

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