Hydrogen Shifts in Formyl- and Diformylphosphine

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The energetics of the [1,3]-hydrogen shift in formyl and diformylphosphine are determined at MP4SDQ/6-31G**//MP2/6-31G** + ZPE(HF/6-31G**). These results are compared to the [1,3]-hydrogen shift in acetaldehyde and malonaldehyde. The keto forms of formylphosphine and acetaldehyde are more stable than the corresponding enol forms, by 7.01 and 14.93 kcal mol^{-1}, respectively. The activation energy for the antarafacial TS for the phosphine systems is approximately 20 kcal mol^{-1} lower than the carbon systems. The enol form of diformylphoshine having an intramolecular hydrogen bond is 0.79 kcal mol^{-1} more stable than the diketo form. The activation barrier for the [1,5]-hydrogen shift in the intramolecular hydrogen-bonded enol form of diformylphosphine is 1.5 kcal mol^{-1} lower than in malonaldehyde. Conformational analysis shows the intramolecular hydrogen bonded enol for diformylphosphine and malonaldehyde to be at least 6 kcal mol^{-1} more stable than the other conformers.

Introduction

Keto–enol tautomerization is known to occur in many simple aldehydes and ketones, with the equilibrium shifted heavily in favor of the keto form.[1,2] Nevertheless, the enol forms can be experimentally observed, especially if there is an internal stabilization. For instance, 1,3-diketones in their enol forms can have an internal hydrogen bond. Due to the stabilization of this hydrogen bond, the equilibrium can be shifted toward the enol.[2] Analogous to the 1,3-diketones, tautomerization has been observed in diacylphosphines by Becker[3] as early as 1972 (Scheme 1), but only for a few specific cases. In 1986, Märkl and Sejpka[4] observed the tautomerization of three diacylphosphines (R = Me, CMe_3, and C_6H_5) that showed the enol form to exist in anywhere from 40–90%, depending upon the polarity of the solvent. Later, Becker[5] reported a general procedure for synthesizing diacylphosphines with various types of substituent groups. He also reported X-ray crystal analysis and an NMR variable temperature study which suggests the enol form of diacylphosphines to be the preferred tautomer. This was not conclusive, however, since the thermodynamics of the solvent were not known and the tautomerization study was not done for all diacylphosphines prepared. Therefore, it is difficult to say in general which direction the equilibrium lies, whether toward the keto form or the internal hydrogen-bonded enol form.

In this paper, we examine the keto–enol tautomerizations in formyl- and diformylphoshine and compare them with the hydrocarbon analogues acetaldehyde and malonaldehyde (Scheme 2). The enol form in the phosphines demands the formation of the weak P=C double bond, and we wish to determine the factors that might lead to stabilizing this species.

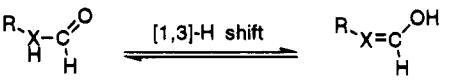
[1,3]-Hydrogen shifts are not known to take place with considerable ease[1,6] because a four-electron [1,3]-sigmatropic rearrangement is symmetry allowed only via an antarafacial path. For an antarafacial [1,3]-hydrogen shift, the hydrogen must maintain contact with opposite sides of the π system; see Scheme 3. In the suprafacial pathway, the hydrogen simply migrates across one face of the π system, but since it is symmetry forbidden, it is highly unlikely. Will these symmetry arguments apply to the phosphine cases?

Finally, a [1,5]-intramolecular hydrogen shift between equivalent hydrogen-bonded enol forms has been observed for malonaldehyde.[7–17] Therefore, we also exam-

Scheme 1

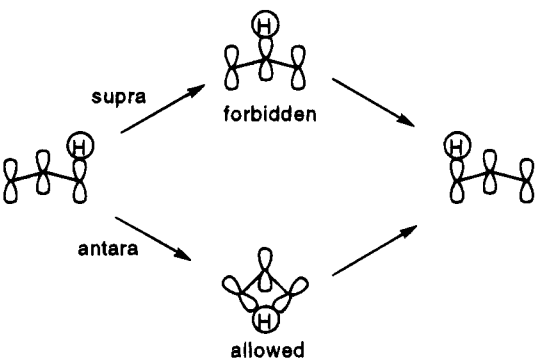
R = cyclo-hexyl or adamant-1-yl[3]

Scheme 2



Reactions
1: X=CH, R=H
2: X=P, R=H
3: X=CH, R=CHO
4: X=P, R=CHO

Scheme 3



[⊗] Abstract published in *Advance ACS Abstracts,* October 15, 1995.

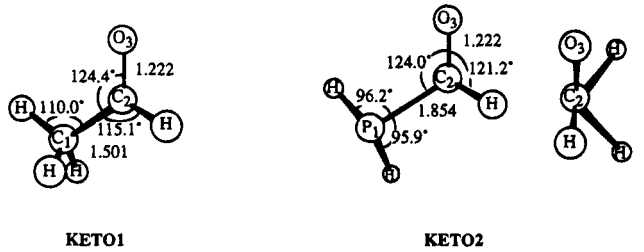
(1) Hart, H. *Chem. Rev.* **1979**, *79*, 515–528.
(2) Solomons, T. W. G. *Organic Chemistry*, 5th ed.; John Wiley & Sons, Inc.: New York, 1992.
(3) Becker, G. *Allg. Prakt. Chem.* **1972**, *23*, 71.
(4) Märkl, G.; Sejpka, H. *Tetrahedron Lett.* **1986**, *27*, 1771–1774.
(5) Becker, G.; Schmidt, M.; Schwarz, W.; Westerhausen, M. *Z. Anorg. Allg. Chem.* **1992**, *608*, 33–42.
(6) Spangler, C. W. *Chem. Rev.* **1976**, *76*, 187–217.
(7) Luth, K.; Scheiner, S. *J. Phys. Chem.* **1994**, *98*, 3582–3587.
(8) Latajka, Z.; Scheiner, S. *J. Phys. Chem.* **1992**, *96*, 9764–9767.

0022-3263/95/1960-7110$09.00/0

Table 1. Structural Parameters at MP2/6-31G. Distances are in Angstroms, and Angles are in Degrees**

parameter	ENOL 3	exptl[a]	ENOL 4	exptl[b]	ENOL 3B	ENOL 4B	TS3-(1,5)	TS4-(1,5)
O···O	2.589	2.553	2.547	2.447	2.810	2.744	2.383	2.383
O–H	0.994	0.969	1.000	1.2	0.964	0.967	1.204	1.195
O···H	1.694	1.68	1.604	1.3			1.204	1.195
C–C	1.439	1.454			1.463		1.396	
(C–P)			1.829	1.798		1.863		1.770
C=C	1.362	1.348			1.348		1.396	
(C=P)			1.721	1.789		1.699		1.770
C–O	1.328	1.320	1.320	1.297	1.351	1.346	1.285	1.279
C=O	1.248	1.234	1.245	1.286	1.228	1.223	1.285	1.279
C–C=C	119.5	119.4			125.1		116.0	
(C–P=C)			97.4			102.1		95.0
C=C–O	124.5	124.5	130.0		123.4	128.7	121.9	
(P=C–O)								126.9
C–C=O	123.5	123.0	127.1		125.6	128.1	121.9	
(P–C=O)								126.9
C–O–H	105.4	106.3	106.5		108.6	108.9	101.2	104.2
C=O···H	99.5		103.9				101.2	104.2
O···H–O	147.6	147.6	155.1				157.9	160.5

[a] See ref 13. [b] Values for diadamant-1-ylphosphine, see ref 5.



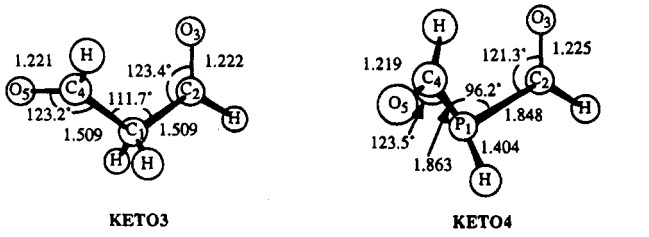
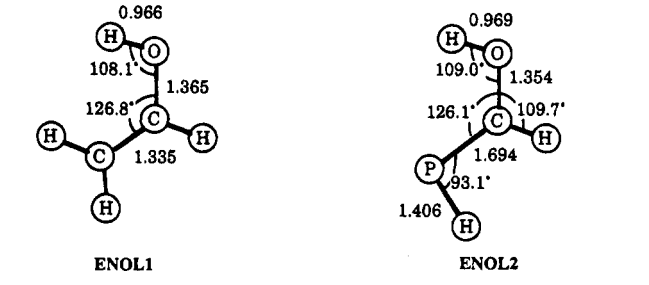


Figure 1. MP2/6-31G**-optimized keto structures. Distances are in angstroms, and angles are in degrees.



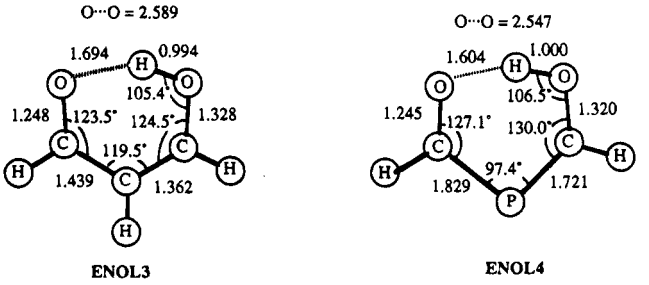


Figure 2. MP2/6-31G**-optimized enol structures, all with C_s symmetry. Distances are in angstroms, and angles are in degrees.

ine here the [1,5]-hydrogen shift for malonaldehyde and diformylphosphine, comparing the activation energies and strucutres of the transition states.

Computational Methods

Full geometry optimizations for all structures were performed using GAUSSIAN 92.[18] Initial optimizations were performed at HF/6-31G** to obtain analytical frequencies in order to properly identify the structures and obtain zero-point energies. Frisch, Scheiner, Schaefer, and Binkley noted that the HF geometries were not adequate enough to accurately define the O–H, O···O, or H···O distances in the enol form of malonaldehyde and that electron correlation was necessary to obtain a good structure.[10] Therefore, all compounds were fully reoptimized at MP2=full/6-31G**. These structures are drawn in Figures 1–3, with some geometric parameters listed in Table 1 and Table 4 (supporting information). Single-point energy calculations at MP4SDQ/6-31G** using the MP2/6-31G** geometries were performed to obtain a better accounting of electron correlation.

We searched for both the antarafacial and suprafacial TSs for the [1,3]-hydrogen shift in acetaldehyde and formylphosphine. Locating the antarafacial TS posed no difficulties. However, despite reports of finding a suprafacial TS for similar

(9) Shida, N.; Almlöf, J.; Barbara, P. F. *J. Phys. Chem.* **1991**, *95*, 10457–10464.
(10) Frisch, M. J.; Scheiner, A. C.; Schaefer, H. F., III; Binkley, J. S. *J. Chem. Phys.* **1985**, *82*, 4194–4198.
(11) Baughcum, S. L.; Smith, Z.; Wilson, E. B.; Duerst, R. W. *J. Am. Chem. Soc.* **1984**, *106*, 2260–2265.
(12) Bicerano, J.; Schaefer, H. F., III; Miller, W. H. *J. Am. Chem. Soc.* **1983**, *105*, 2550–2553.
(13) Baughcum, S. L.; Duerst, R. W.; Rowe, W. F.; Smith, Z.; Wilson, E. B. *J. Am. Chem. Soc.* **1981**, *103*, 6296–6303.
(14) Fluder, E. M.; de la Vega, J. R. *J. Am. Chem. Soc.* **1978**, *100*, 5265–5267.
(15) Rowe, W.; Duerst, R. W.; Wilson, E. B. *J. Am. Chem. Soc.* **1976**, *98*, 4021–4023.
(16) Karlström, G.; Wennerström, H.; Jönsson, B.; Forsén, S.; Almlöf, J.; Roos, B. *J. Am. Chem. Soc.* **1975**, *97*, 4188–4192.
(17) Isaacson, A. D.; Morokuma, K. *J. Am. Chem. Soc.* **1975**, *97*, 4453–4457.
(18) Frisch, M. J.; Trucks, G. W.; Head-Gordon, M.; Gill, P. M. W.; Wong, M. W.; Foresman, J. B.; Jouhnson, B. G.; Schlegel, H. B.; Robb, M. A.; Replonge, E. S.; Gomperts, R.; Andres, J. L.; Raghavachari, K.; Binkley, J. S.; Gonzales, C.; Martin, R. L.; Fox, D. L.; Defrees, D. J.; Baker, J.; Stewart, J. J. P.; Pople, J. A. Gaussian, Inc.: Pittsburgh, PA, 1992.

Table 2. Activation and Reaction Energies (kcal mol^{-1}) for the [1,3]-H Shift in Reactions 1−4. All Energies Have Been Corrected for ZPE (HF Scaled by 0.89)

	HF/6-31G**		MP2/6-31G**		MP4SDQ/6-31G** [a]	
reaction	E_{act}	ΔE_{rxn}	E_{act}	ΔE_{rxn}	E_{act}	ΔE_{rxn}
KETO1 → ENOL1	84.45	14.36	70.71	15.15	74.49	14.93
KETO2 → ENOL2	61.99	11.02	47.54	6.04	51.46	7.01
KETO3 → ENOL3 cisoid TS	72.90	0.26	60.02	−2.12	64.54	0.50
KETO3 → ENOL3 transoid TS	76.37	0.26	61.88	−2.12	66.75	0.50
KETO4 → ENOL4 cisoid TS	58.89	3.22	45.50	−3.40	49.54	−0.79
KETO4 → ENOL4 transoid TS	61.71	3.22	46.10	−3.40	50.57	−0.79

[a] MP4SDQ/6-31G**//MP2/6-31G**.

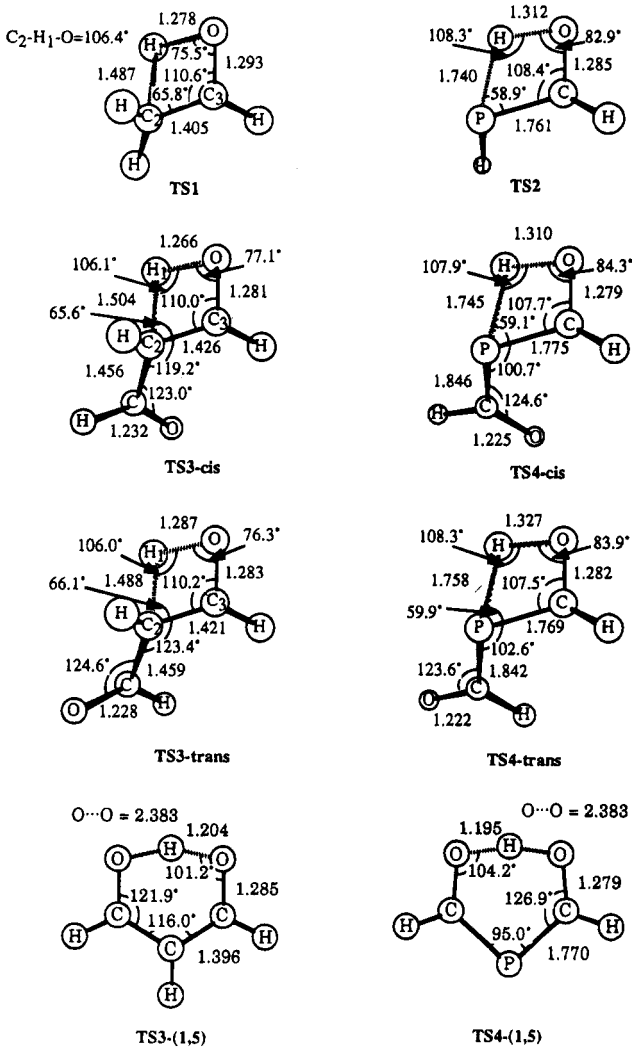


Figure 3. MP2/6-31G**-optimized transition structures for the [1,3]- and [1,5]-hydrogen shifts. Distances are in angstroms, and angles are in degrees.

systems,[19] a suprafacial TS for acetaldehyde and formylphosphine could not be located. A structure that resembles what the suprafacial TS should look like was located at HF/6-31G**, but upon closer analysis, it did not correspond to a [1,3]-hydrogen shift, but rather a [1,2]-hydrogen shift. This observation of a [1,2]-hydrogen shift has also been suggested by others in the tautomerization of acetaldehyde.[20] Furthermore, optimizing the TS for the [1,2]-hydrogen shift at MP2 resulted in the collapse to the antarafacial TS. Thus, only the antarafacial transition structures and energies will be discussed for the four reactions. Reaction energies and activation barriers for the [1,3]- and [1,5]-shifts are listed in Tables 2 and 3. The conformational studies of the enol forms of the β-dicarbonyl systems is presented in terms of whether the double bond is cis or trans, if the C=O is syn or anti to the double bond, and if the O−H is syn or anti to the double bond. The geometries and relative energies of these conformers are found in Table 5 (supporting information) and Figure 4.

Table 3. Activation Barriers (kcal mol^{-1}) for the [1,5]-H Shift for Malonaldehyde ENOL3 and Diformylphosphine ENOL4. All Energies Have Been Corrected for ZPE (HF Scaled by 0.89)

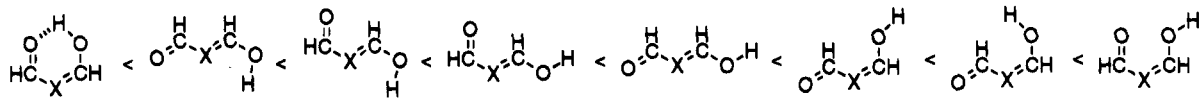
molecule	HF/6-31G**	MP2/6-31G**	MP4SDQ/6-31G** [a]
ENOL3	7.63	0.98	3.11
ENOL4	4.35	0.06	1.60

[a] MP4SDQ/6-31G**//MP2/6-31G**.

Results

Geometries. The keto structures, drawn in Figure 1, all have C_1 symmetry. Acetaldehyde, **KETO1**, has a methyl hydrogen nearly eclipsed with the C=O. Formylphosphine, **KETO2**, optimized to a structure that has P lone pair perpendicular to the P−C−O plane. While this may suggest some conjugation between the lone pair and the C−O π bond, keep in mind that phosphorus is pyramidal which points the lone pair away from the carbonyl group. This type of structure is in agreement with experimental results of similar acylphosphines[21] and with previous theoretical studies of formylphosphine.[22,23] The lowest energy conformation for malonaldehyde in its keto form, **KETO3**, has the two carbonyl groups nearly perpendicular to one another. One carbonyl nearly eclipses the methylene hydrogen. All attempts to optimize the keto form of malonaldehyde constrained to any point group (C_s, C_2, or C_{2v}) resulted in higher energy conformers that were not always ground states. The keto form of diformylphosphine, **KETO4**, is similar to **KETO3** in that the carbonyls are perpendicular. As in **KETO2**, the P lone pair tries to be perpendicular to both P−C−O planes. However, the bond distances are somewhat different in the two molecules. In **KETO4**, one P−C bond is longer (1.863 Å) and one is shorter (1.848 Å) than the P−C bond in **KETO2** (1.854 Å). The C−O distances also

(19) Nguyen, M. T.; Landuyt, L.; Vanquickenborne, L. G. *Chem. Phys. Lett.* **1993**, *212*, 543−546.
(20) Bouma, W. J.; Poppinger, D.; Radom, L. *J. Am. Chem. Soc.* **1977**, *99*, 6443−6444.
(21) Khaikin, L. S.; Andrutskaya, L. G.; Grikina, O. E.; Vilkov, L. V.; El'natanov, Y. I.; Kostyanovskii, R. G. *J. Mol. Struct.* **1977**, *37*, 237−250.
(22) Damewood, J. R.; Mislow, K. *Monatsh. Chem.* **1980**, *111*, 213−220.
(23) Xie, Y.; Boggs, J. E.; Khaikin, L. S. *THEOCHEM* **1986**, *32*, 255−265.



	css	tas	tss	tsa	taa	caa	cas	csa
X=CH	0.0	6.09	6.78	7.80	7.87	8.76	8.78	11.90
X=P	0.0	6.68	6.71	8.61	9.21	9.88	10.19	13.15

Figure 4. Cis and trans conformers of the enol forms of diformylphosphine and malonaldehyde. Relative energies are in kcal mol^{-1}.

differentiate in terms of distance, with the carbonyl adjacent to the longer P–C bond shorter than the other carbonyl bond.

The enol tautomers all optimized to minima having C_s symmetry, as seen in Figure 2. For all enols, having the hydroxy group syn to the double bond gave the lowest energy. The distances and angles in the MP2-optimized structure of **ENOL1** are very close to those determined by microwave spectroscopy: O–H = 0.956 Å, C–O = 1.373 Å, C=C = 1.332 Å, C=C–O = 126.0°, C–O–H = 108.5°.[24,25] The biggest discrepancy is the experimental C–O distance of 1.373 Å with our calculated value of 1.365 Å. However, the experimental C–O distance was an assumed distance.[25] The isomer of vinyl alcohol with an anti hydroxy group **ENOL1B** was located at higher energy (see Figure 5, supporting information); the biggest difference between it and **ENOL1** is the much wider C–C–O angle in the latter. **ENOL2** would only optimize if the hydroxy group was syn to the P=C; every attempt to optimize the anti conformer led to dissociation. Besides rotating the O–H group 180°, the P–H group could also be rotated. Interestingly, we did locate another minima, **ENOL2B** (see Figure 5, supporting information), which still has the O–H group positioned in a syn fashion to the P=C but the P–H group rotated 180°.

For **ENOL3** and **4**, the carbonyl and hydroxy groups must be *cis* about the C=C or P=C so that internal hydrogen bonding can occur. The structure of **ENOL3** is in close agreement with previous calculated[10] and experimental structures.[13,15] Of particular interest are the O···O, O···H, and O–H distances of 2.589, 1.694, and 0.994 Å. The O–H and O···H distances are slightly longer than reported experimentally, and the O···O distance is very close to the experimental range of 2.55–2.58 Å.[13]

Becker has reported the X-ray crystal structure of the bisadamantyl derivative that corresponds to **ENOL4**,[5] with pertinent results listed in Table 1. The calculated structure is not as symmetric as the crystal structure, no doubt due to the difficulty in locating the bridging hydrogen. Nevertheless, considering the differences in phase and substitution, the calculated and experimental geometries are in reasonable agreement. In particular, we note that the nonbonding O···O distance is 2.547 Å in **ENOL4** and 2.447 Å in the crystal structure. The shorter distance in the experimental structure may be due to steric congestion from the bulky adamantyl groups.

Comparing **ENOL4** to **ENOL3** shows that the smaller angle about phosphorus does not have as much effect on the O···O distance as one might suspect. The C–C–C angle in **ENOL3** is 119.5°, and the analogous C–P–C angle in **ENOL4** is 97.4°. The effect that this 22.1° decrease has on the O···O distances is practicably negligible (0.042 Å shorter in **ENOL4**) due to the longer P–C and P=C bonds in **ENOL4** relative to the C–C and C=C bonds in **ENOL3**. In **ENOL4**, the O···H distance of 1.604 Å is 0.090 Å shorter than in **ENOL3**, indicating a stronger hydrogen bond in diformylphosphine.

The [1,3]-hydrogen shift occurring in the reaction of acetaldehyde to vinyl alcohol is the simplest example of a keto–enol tautomerization. Due to their small size, the tautomerization of acetaldehyde and vinyl alcohol has been the subject of many theoretical studies.[20,26,27] In **TS1**, the C_2–C_3 bond length of 1.405 Å is in between typical C–C and C=C bond lengths, and the C–O bond length of 1.293 Å is also intermediate C–O and C=O bond lengths. The C–H and O–H partial bonds have distances of 1.487 Å and 1.278 Å, respectively. The bridging hydrogen lies approximately 10° out of the plane formed by the heavy atoms.

The P–C and C–O bond lengths in **TS2** display partial bond character, being between typical single and double bond distances. The major difference between **TS2** and **TS1** is that phosphorus can accommodate a much smaller ring angle (58.9°) than about the carbon in **TS1** (65.6°). As a result of this smaller angle, the H–O–C angle is widened from 75.5° in **TS1** to 82.9° in **TS2**. The cyclic TS is puckered in **TS2** as in **TS1**, where H_1 again is about 10° out of the heavy atom plane.

For the β-dicarbonyl systems, there are two possible transition structures for the [1,3]-H shift, distinguished by the arrangement of the β-carbonyl group not involved in the hydrogen shift, relative to the C–C bond that is in the cyclic TS. This carbonyl is arranged in a cisoid **TS3-*cis*** or transoid **TS3-*trans*** fashion relative to the double bond. Comparing the two structures, we see that the C–C and C–O bonds are nearly identical. However, differences are seen in the C_2–H and O–H distances. In **TS3-*cis***, the O–H distance is 0.021 Å shorter than in **TS3-*trans***, whereas C_2–H_1 is 0.016 Å longer in **TS3-*cis*** than in **TS3-*trans***. Therefore, for the keto–enol tautomerization of malonaldehyde, **TS3-*cis*** is later than **TS3-*trans***.

Similar trends are seen in the case of the TSs for the [1,3]-hydrogen shift in diformylphosphine. The C–O and C–P distances are nearly identical in **TS4-*cis*** and **TS4-*trans***. The O–H distance is shorter (by 0.17 Å) in the *cisoid* TS, but the P–H distance is also shorter in the *cisoid* TS, suggesting that **TS4-*cis*** is a tighter TS than **TS4-*trans***. As with the monocarbonyl systems, the ability of phosphorus to accommodate small internal angles allows the angles about oxygen to widen in **TS4** relative to in **TS3**.

(24) Samdal, S.; Seip, H. M. *J. Mol. Struct.* **1975**, *28*, 193.
(25) Saito, S. *Chem. Phys. Lett.* **1976**, *42*, 399–402.
(26) Poirier, R. A.; Majlessi, D.; Zielinski, T. J. *J. Comput. Chem.* **1986**, *7*, 464–475.
(27) Ventura, O. N.; Lledós, A.; Bonaccorsi, R.; Bertrán, J.; Tomasi, J. *Theor. Chim. Acta* **1987**, *72*, 175–195.

The enol form of malonaldehyde has been the subject of numerous [1,5]-hydrogen shift studies.[7-17] **TS3-(1,5)** corresponds to the [1,5]-hydrogen shift transition structure between two equivalent forms of **ENOL3**. This structure has C_{2v} symmetry. The important parameters are the O−H distance and the O···O distance, which are 1.204 and 2.383 Å, respectively. These values match those previously reported by Frisch, Scheiner, Schaefer, and Binkley.[10] **TS4-(1,5)** is the C_{2v} TS for the [1,5]-hydrogen migration in diformylphosphine. The O···O distance in **TS4-(1,5)** is almost identical to that in **TS3-(1,5)**, despite the fact that the internal C−P−C angle is 21° smaller than the C−C−C internal angle in **TS3-(1,5)**. The O−H distance in **TS4-(1,5)** is 0.009 Å shorter than in **TS3-(1,5)**.

We also determined the structures for all the possible conformations of the enols of malonaldehyde and diformylphosphine. The geometric parameters for these various enols are presented in Table 5 (supporting information). We are not so interested in the structures of these as we are of their relative energies. However, it is interesting to note that once the internal hydrogen bonding, present only in **ENOL3** and **ENOL4**, cannot occur, the O−H bond is shortened significantly, the single bonds (C−C, C−P, and C−O) are lengthened, and the double bonds (C=C, C=P, and C=O) are shortened. Without the internal hydrogen bonding, the bond lengths are closer to typical values.

Energies. The MP2=full/6-31G** level used for the geometry optimizations is not sufficient for the energy calculations because MP2 energies tend to underestimate the activation barriers for similar reactions.[28] Therefore, we performed MP4SDQ=full/6-31G** energy calculations with the optimized MP2/6-31G** geometries, and these energies will be used in the discussions that follow.

For the first two systems, it is well known that the keto form is thermodynamically more stable than the enol form, which is also indicated by our results in Table 2. The reaction energy of 14.93 kcal mol^{-1} for acetaldehyde to vinyl alcohol is close to an estimated experimental gas phase value of 13.2 kcal mol^{-1}.[29] The reaction energy for the conversion of **KETO2** into **ENOL2** is 7.01 kcal mol^{-1}, which indicates that the preference is not as strong in formylphosphine for the keto form as it is for acetaldehyde. The activation barrier is 74.49 kcal mol^{-1} for reaction 1 and 51.46 kcal mol^{-1} for reaction 2. These energies can also be compared to the nitrogen analogue, the tautomerization of hydroxamic acid to hydroximic acid, which Yuanqi and Wengui reported in 1992.[30] For the antarafacial [1,3]-hydrogen shift of hydroxamic acid at MP4/4−31G**//RHF/4−31G** + ZPE, the activation energy is 36.17 kcal mol^{-1}, substantially lower than the carbon and the phosphorus analogues. Also, the reaction energy (9.72 kcal mol^{-1}) for the nitrogen analogue is less endothermic than for acetaldehyde but more endothermic than formylphosphine.[30] It appears that the inclusion of a P or N in the 2-position of these systems lowers the activation barrier and will slightly effect the distribution of tautomers. The lowering of the activation barrier for the phosphine is not surprising since phosphorus can accommodate a much smaller angle than a carbon can and the strain in the cyclic TS would be lessened.

The energetics for the keto−enol tautomerization of the β-dicarbonyls are different than the monocarbonyls in that the enol form is stabilized by the internal hydrogen bond. The energy for reaction 3 is +0.50 kcal mol^{-1} and −0.79 kcal mol^{-1} for reaction 2. Solution thermodynamics suggests that the enolization of the carbon dicarbonyls are 1−2 kcal mol^{-1} more favorable than the phosphorus analogues.[5] However, the experiments were performed in solution with substituted systems, so direct comparison is not possible.

There are two possible transition structures for the [1,3]-hydrogen shift in the β-dicarbonyl systems, one cisoid and the other transoid. For both reactions 3 and 4, the cisoid conformation gives the lower activation barrier and therefore the more favorable TS. **TS3-*cis*** is favored by 2.21 kcal mol^{-1} over **TS3-*trans***. For the phosphine system, **TS4-*cis*** is 1.03 kcal mol^{-1} lower than **TS4-*trans***. The activation energy for the [1,3] shift in malonaldehyde is 15.0 kcal mol^{-1} greater than for diformylphosphine. Phosphorus stabilizes the TS for this [1,3]-hydrogen shift, presumably due to the reduction in strain in the cyclic TS, but the difference in activation energies is less for the dicarbonyl systems than in the monocarbonyls.

Comparing activation barriers of reaction 1 with 3 and reaction 2 with 4 shows that the addition of a second carbonyl group lowers the activation barriers for the [1,3]-H shift. This is especially true in the carbon system, where we see an 8−10 kcal mol^{-1} reduction of the barrier as we go from reaction 1 to reaction 3. However, the effect is much smaller for the phosphine system, where the β-carbonyl only lowers the activation barrier by 1−2 kcal mol^{-1}.

The energetics of the [1,5]-H shift for malonaldehyde have been thoroughly studied by many.[7-13] Our MP4SDQ results indicate a 3.11 kcal mol^{-1} activation barrier for the [1,5]-H shift for **ENOL3**, which is close to the 4.0−5.0 kcal mol^{-1} range found for the deuterium-labeled compound.[11] The barrier for the [1,5]-hydrogen shift in **ENOL4** is 1.60 kcal mol^{-1}. Thus, replacement of the methylene carbon by phosphorus reduces the barrier by 1.5 kcal mol^{-1}.

All of the cis and trans conformers of enol forms of malonaldehyde and diformylphosphine were optimized at MP2/6-31G**. The MP4SDQ/6-31G** energies, with the inclusion of ZPE, for all the conformers are shown in Figure 4. While the relative energies of the various conformers are different for malonaldehyde and diformylphosphine, the ordering of the isomers is identical. The *css* (*c*is double bond, *s*yn relationship of the oxygens, *s*yn O−H bond to the double bond) conformers (**ENOL3** and **ENOL4**), which are stabilized by intramolecular hydrogen bonding, are more than 6 kcal mol^{-1} lower in energy than any of the other conformers. The lowest energy conformer not containing the hydrogen bond is the *tas* conformer which has maximum separation of the oxygen atoms. Rotating 180° about the C−O single bond from *css* leads to an increase in energy of over 11 kcal mol^{-1}, due to the loss of hydrogen bonding moderating the repulsion between the negatively charged oxygens.

Discussion

We were initially intrigued by the reports of the keto−enol tautomerization of diacylphoshines because the enol

(28) Adeney, P. D.; Bouma, W. J.; Radom, L.; Rodwell, W. R. *J. Am. Chem. Soc.* **1980**, *102*, 4069.
(29) Holmes, J. L.; Terlouw, J. K.; Lossing, F. P. *J. Phys. Chem.* **1976**, *80*, 2860.
(30) Yuanqi, T.; Wengui, D. *Int. J. Quant. Chem.* **1992**, *44*, 319−325.

form contains the relatively weak C=P double bond. However, **KETO2** is only 7.0 kcal mol^{-1} more stable than **ENOL2**, while the difference in the keto and enol forms of acetaldehyde is 14.9 kcal mol^{-1}. If the formation of the weak C=P was the dominant factor, enolization of formylphosphine should be more *endothermic* than for acetaldehyde, not less. However, enolization of an acylphosphine requires breaking a weak P–H bond, while enolization of an aldehyde requires cleavage of the strong C–H bond. Using standard bond energies, enolization of formylphosphine and acetaldehyde should be identical.

What then causes the reduction in endothermicity of the enolization of formylphosphine? We believe the answer lies in the stability of formylphosphine in the keto form. The carbon of a carbonyl is quite positively charged. We have noted that the C–P bond is strongly polarized with the phosphorus carrying a positive charge.[31] Therefore, in formylphosphine two positively charged atoms are placed in adjacent postitions. Further, the fact that phosphorus is pyramidal reduces the ability of the lone pair to donate to the carbon, the primary means of stabilization in acetamide.[32]

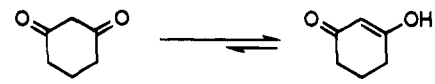
This relative destabilization of formylphosphine also accounts for why the enolization of diformylphoshine is more exothermic than the enolization of malonaldehyde. While we predict an opposite relative enolization energy than experiment, which is likely due to differences in phase and substituents used in the experiment and our calculations, the calculations clearly indicate the enol tautomer to be the favored form of diacylphosphines.

[1,3]-Hydrogen shifts do not typically proceed through a unimolecular process. We find activation energy for this shift is 74.5 kcal mol^{-1} for acetaldehyde. However, the barrier in formylphsophine is lower by 23.0 kcal mol^{-1}. This substantial reduction is likely due to the reduced ring strain in the cyclic TS when phosphorus replaces a carbon in the ring. We were unable to locate any suprafacial TSs, finding only the orbital symmetry allowed anatrafacial TS.

The [1,3]-hydrogen shift is more facile in the β-dicarbonyl systems. In malonaldehyde, the activation energy is 64.5 kcal mol^{-1}, a reduction of 10 kcal mol^{-1} from the monocarbonyl system. This reduction is likely due to the incipient conjugation between the carbonyl and the forming C=C double bond. The stabilization by the second carbonyl of the TS in the phosphorus system is only 2 kcal mol^{-1}. The second carbonyl is positioned farther from the incipient C–P double bond, reducing its ability to stabilize the TS. Neverthless, the barrier for the [1,3] shift in diformylphosphine is 15 kcal mol^{-1} lower than in malonaldehyde; again, the ability of phosphorus to readily accommodate a small ring reduces the ring strain in the cyclic TS relative to the hydocarbon system.

The barrier for the [1,5]-hydrogen shift in the enol tautomer of diformylphosphine is estimated to be only 1.60 kcal mol^{-1}, about 1.5 kcal mol^{-1} less than in malonaldehyde. The hydrogen has to migrate a shorter distance from the enol to the TS in the phosphorus case, thereby leading to the lower barrier. This shift should therefore be quite rapid in diacylphosphines. Since there has been much debate on the malonaldehyde system tunneling effect, due to the low [1,5]-hydrogen shift barrier, one would expect that with the phosphine system having a lower activation barrier, tunneling would occur to a much greater extent.

Scheme 4



We next turn to understanding the reasons for the stabilization of the enol form of the β-discarbonyl compounds. **ENOL1** is 15 kcal mol^{-1} less stable than **KETO1**, while **ENOL3** is only 0.5 kcal mol^{-1} less stable than **KETO3**. **ENOL3** can be stabilized (relative to the monocarbonyl **ENOL1**) by the intramolecular hydrogen bond and conjugation between the carbonyl and the C=C double bond. The *tas* conformer of the enol form of malonaldehyde contains no intramolecular hydrogen bond but does have conjugation and is only 6.6 kcal mol^{-1} less stable than **KETO3**. Thus, the reduction in enolization energy of 15 kcal mol^{-1} for acetaldehyde to 6.6 kcal mol^{-1} for malonaldehyde (to the *tas* conformer) can be attributed to delocalization energy in the *tas* conformer and the destabilization caused by the repulsions between the two carbonyls in **KETO3**. Further, this suggests that the intramolecular hydrogen bond in **ENOL3** is worth about 6 kcal mol^{-1}.

The enolization energy of formyl phosphine (7.0 kcal mol^{-1}) is only 1.1 kcal mol^{-1} greater than the enolization energy of diformylphosphine to the *tas* conformer (5.9 kcal mol^{-1}). Conjugation with the C=P double bond is expected to be less extensive than with C=C double bonds due to poorer orbital overlap, and the electrostatic repulsion between the two carbonyls will be less in **KETO4** than **KETO3** due to their larger separation in the former. Nevertheless, the strength of the hydrogen bond in **ENOL4** is estimated to be about 6 kcal mol^{-1}, essentially identical to that in **ENOL3**. The similar O···O and O–H distances in the two enols supports similar hydrogen bond strengths.

The ordering of the enol conformers is of interest for understanding the keto–enol tautomerism of 1,3-cyclohexanedione (Scheme 4). Recent experimental studies find that 1,3-cyclohexanedione exists primarily in its enol form.[33] This enol must have a trans C=C double bond with the carbonyl anti to the C=C double bond. According to our calculations on malonaldehyde, the lowest trans-anti conformer has a syn hydroxy group, *tas*, which is 6.09 kcal mol^{-1} higher in energy than the hydrogen-bonded form, suggesting that the keto structure should be the thermodynamic choice.

We calculated the lowest energy conformations of the keto and enol form of 1,3-cyclohexanedione at MP4SDQ = fc/6-31G**//MP2/6-31G** + ZPE/HF. The keto form optimized with C_s symmetry and the enol form with C_1 symmetry. Our highest level results indicates that the enolization energy of 1,3-cyclohexanedione is +6.92 kcal mol^{-1}. In the absence of any intermolecular effects, the keto form of 1,3-cyclohexanedione should predominate. The enol form of 1,3-cyclohexanedione has one carbonyl and one hydroxy group, so each molecule can participate in at least two intermolecular hydrogen bonding interactions. In solution, intermolecular hydrogen bonding shifts the equilibrium in favor of the enol structure.

(31) Bachrach, S. M. *J. Comput. Chem.* **1989**, *10*, 392–406.
(32) Wiberg, K. B.; Breneman, C. M. *J. Am. Chem. Soc.* **1992**, *114*, 831–840.
(33) Bordwell, F. G.; Satish, A. V. *J. Am. Chem. Soc.* **1994**, *116*, 8885–8889.

Conclusions

The keto–enol tautomerization of diformylphosphine in the gas phase is exothermic by 0.80 kcal mol^{-1}, due to an intramolecular hydrogen bond stabilizing the enol form. The phosphine system is slightly more exothermic (1.2 kcal mol^{-1}) than the tautomerization of malonaldehyde. When the β-carbonyl is not present, intramolecular hydrogen bonding cannot take place, and the tautomerization is an endothermic process. Our results indicate the tautomerization of formylphosphine is less endothermic (by 8 kcal mol^{-1}) than the tautomerization of acetaldehyde. The observation that the tautomerization of formylphosphine is less endothermic than for acetaldehyde, but that diformylphosphine is more exothermic than for malonaldehyde, is due to the destabilization of the keto form of the formylphosphines. The weak P–H bond and the adjacent postively charge phosphorus and carbonyl carbon destabilize the keto form of phosphines relative to keto tautomers of the aldehydes. Of course, enolization of acylphosphines in solution will further shift the equilibrium in favor of the enol form.

For the symmetry-allowed antarafacial [1,3]-hydrogen shift, the replacement of the carbon with a phosphorus substantially lowers the activation barrier. Phosphorus can more readily accommodate small internal angles and thereby reduce the ring strain in the cyclic TS. The addition of a β-carbonyl group also has the effect of lowering the activation barrier along with shifting the keto–enol tautomerization toward the enol. The second carbonyl stabilizes the TS and enol by conjugation.

The [1,5]-shift in diformylphosphine has a very small barrier of only 1.6 kcal mol^{-1}. The distance that hydrogen must move in progressing from **ENOL4** to the TS is quite small. Tunneling between the two equivalent forms of **ENOL4** should therefore be significant.

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Supporting Information Available: Tables 4 and 5 and Figure 5 (4 pages). This material is contained in libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.

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