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Imidoylketene: An *ab Initio* Study of Its Conformations and Reactions

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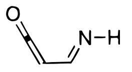
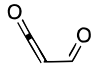
MP4(SDQ)/6-31G**//MP2/6-31G** calculations on the conformations of imidoylketene (**1**) as well as transition structures for several of its reactions are reported. Anti-*Z*-**1** and anti-*E*-**1** are of equal energy, while syn-*Z*-**1** and syn-*E*-**1** are respectively 2.0 and 0.5 kcal/mol higher. As the nitrogen analog of formylketene (**2**), the reactivity of **1** is modified from that of **2**. While the nitrogen in **1** is more basic and nucleophilic than the oxygen in **2**, greater resonance donation from the nitrogen decreases the electrophilicity of the ketene carbon in **1** relative to **2**. Thus the barriers for the addition of water (6.3 kcal/mol) and of formaldehyde (10.6 kcal/mol) to **1** are very similar to those previously calculated for their respective additions to **2**. Transition structures for the 1,3-hydrogen shifts of 3-amino-1,2-propadien-1-one (**5a**) and formylketene imine (**6a**) to give **1** were also located. The barriers to these reactions, (41.0 and 48.6 kcal/mol, respectively) are higher than those of the analogous reactions to form **2**; reasons for these trends are discussed. The transition structures for these reactions are all planar or nearly so, reflecting the pseudopericyclic orbital topology which makes all the reactions allowed.

Introduction

Imidoylketene (**1**) is closely related to formylketene (**2**); the substituents in both possess a π-bond in conjugation with the ketene as well as an in-plane lone pair. Although substituted imidoylketenes[1] have been less widely studied than α-oxoketenes,[2] they undergo a rich variety of reactions. We have been interested in the mechanisms of various reactions of conjugated ketenes[3] and have shown that when an in-plane lone pair participates in a given reaction, there may be a disconnection in the cyclic orbital overlap. This orbital topology has been termed pseudopericyclic[4] and in many cases leads to planar transition states and most remarkably to situations in which reactions are allowed regardless of the number of electrons involved.[3d] In view of the electronic similarities between the two systems, and to explore the effects of the greater basicity/nucleophilicity of the nitrogen in imidoylketene, we undertook this *ab initio* study of the conformations of imidoylketene and of several of its reactions as illustrated in Scheme 1. These reactions, the additions of water and formaldehyde to **1** to form **3a** and **4a** and the 1,3-hydrogen shifts to give **5a** and **6a**, are compared to those previously studied in the formylketene system.[3c,d]

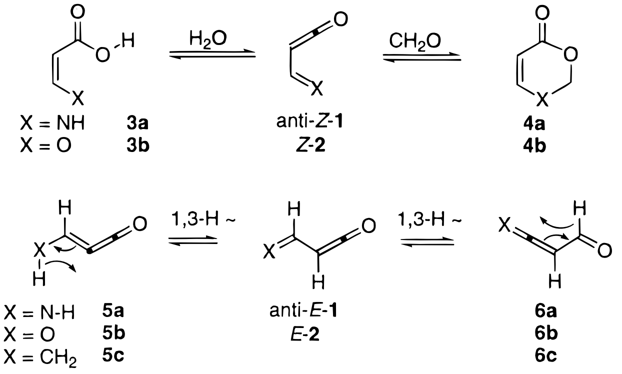


anti-*Z*-**1**



Z-**2**

Scheme 1



Background

The preparation and reactions of imidoylketenes have recently been reviewed by Tidwell.[2c] The intermediacy of an imidoylketene (e.g., **8**) in the Conrad−Limpach reaction[5] was first proposed in 1964[1] (eq 1). Most recent studies of imidoylketenes have focused on the prepara-

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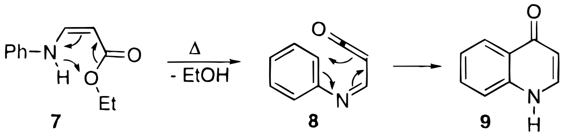
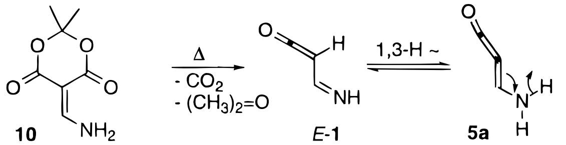
tion[1f–i,l,m] and matrix isolation spectroscopy[1d,e,j,k,q] of these reactive intermediates. In addition to the elimination of alcohols from enamino esters **7** as in eq 1, imidoylketenes have been directly prepared by thermal decarbonylations of pyrole-2,3-diones[1d,h,j,11] and indirectly by fragmentation of Meldrum acid derivatives (e.g., **10**) presumably via a 1,3-hydrogen shift of the initially formed 3-amino-1,2-propadien-1-ones (e.g., **5a**) (eq 2).[1d–f,i,j,n,6]

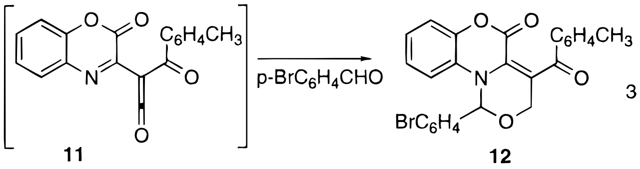


1



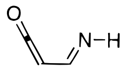
2

Imidoylketenes and oxoketene imines (e.g., **6a**) equilibrate through 1,3-shifts, as illustrated in Scheme 1.[1e,1i–k,m,n,q] Although 1,3-hydrogen shifts in hydrocarbons are orbital symmetry forbidden,[7] they become allowed when there is a pseudopericyclic orbital topology.[3d,8] There are a few reports of deliberate bimolecular reactions of imidoylketenes. They will dimerize if they cannot rearrange,[1c] and there are occasional reports of trapping with alcohols.[1i,r] Interestingly, there is only one report of trapping with an aldehyde; in **11** the imidoylketene was more reactive than the α-oxoketene moiety (eq 3).[11]

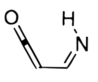


3

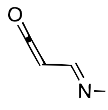
We are aware of only two previous *ab initio* calculations on imidoylketenes. At the RHF/6-31G** level, Nguyen, Ha, and More-O'Ferrall found that the energies of two of the possible conformations of the parent system (anti-*Z*-**1** and anti-*E*-**1**) were within 0.2 kcal/mol.[9] Eisenberg, Kurth, and Fink [1p] have reported calculations on the elimination of acetone from **13** yielding (methylimidoyl)ketene (**14**) (eq 4). They also reported RHF/6-31G* calculations on the elimination of formaldehyde from 4*H*-1,3-dioxin-4-one (**4b**) to give formylketene (**2**) which confirm our previous and higher level (MP2/6-31G*) calculations on this system.[3c] The transition states for both reactions are approximately planar, because the pseudopericyclic orbital topology avoids the electron–electron repulsion inherent in a pericyclic reaction.[3c,e,10]



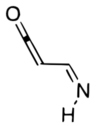
anti-*Z*-**1**



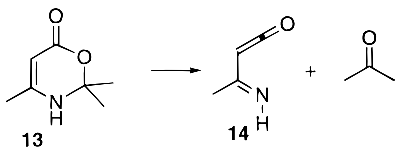
syn-*Z*-**1**



anti-*E*-**1**



syn-*E*-**1**



4

The calculations reported herein begin with a more detailed analysis of the conformations of imidoylketene (**1**). The transition states for the addition of water and formaldehyde to imidoylketene were anticipated to provide insight into the similarities and differences in reactivities between imidoylketene and formylketene as well as for the synthetic application of these reactions. Similarly, transition structures were located for the 1,3-hydrogen shifts of **1** represented in Scheme 1.

Computational Methods

The *ab initio* molecular orbital calculations were carried out using Gaussian 92.[11] Geometry optimizations were performed first at the RHF/6-31G* level and then at the MP2(FC)/6-31G** level; the latter structures are shown in Figure 1. Single-determinant wave functions such as RHF/6-31G* calculations usually qualitatively reproduce transition structures while MP2 optimizations give reasonable agreement with MCSCF geometries for orbital symmetry allowed (but not forbidden) pericyclic reactions.[12] Frequency calculations verified the identity of each stationary point as a minimum or transition state. Single-point energies of each structure were obtained at the MP4(FC, SDQ)/6-31G** level. The zero-point vibrational energy (ZPE) corrections were obtained by scaling the MP2/6-31G* ZPE by 0.9646, as recommended by Pople *et al.*[13] Unless otherwise indicated, all energies discussed in the text are MP4(SDQ, FC)/6-31G** with the ZPE correction. Absolute energies are reported in the supporting information. Relative energies, entropies, dipole moments, and the lowest or imaginary frequencies for all structures are reported in Table 1. To aid in experimental identifications, the ketene and imine frequencies (scaled by 0.960[14] and 0.9427,[13] respectively) for the conformations of **1** and for **5a** and **6a** are given in Table 2. Selected data for optimized geometries are shown in Figure 1 and in Tables 3 and 4; full geometries and vibrational frequencies are available in the supporting information. Atom numbering is as shown in Figure 1 for **16**, **18**, **19**, and **20**.

The 6-31G** basis set, which provides polarization functions on the hydrogens, was chosen because of the hydrogen transfers involved. Although inclusion of triple excitations in the MP4 procedure does lower the absolute energies calculated, in our experience it does not alter the relative energies of ketenes.[3d,e] For computational economy then, the energies were calculated at the MP4(SDQ) level.

Results and Discussion

Conformations of Imidoylketene. Although Nguyen *et al.*[9] only calculated two conformers of **1**, *Z* and *E*

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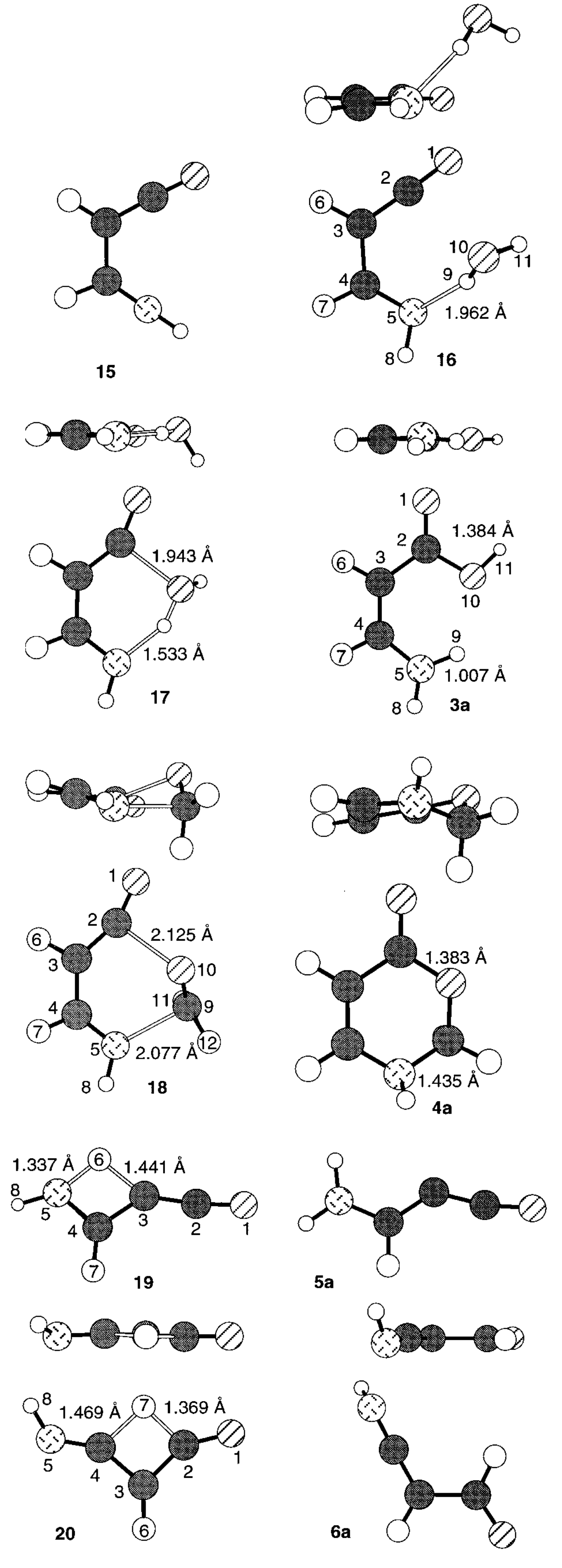

Figure 1. MP2/6-31G*-optimized geometries of selected structures. Partial bonds are unfilled. Side views of nonplanar structures are provided. Carbons atoms are shaded, oxygens are striped, nitrogens are hashed, and hydrogens are open circles. Additional geometrical information is available in Tables 3 and 4 and in the supporting information.

around the C–C bond, there are in fact four, due to the possibility of syn and anti conformations of the imine hydrogen. The two anti conformations are calculated here to be of equal energy, although the previous RHF/6-31G** optimization placed the *E* conformation 0.3 kcal/mol below the *Z*. The syn-*Z* conformation is 2.0 kcal/mol above the anti ones. These trends in energies are not explained simply on the basis of the dipole moments,[3a,b,d,15] for anti-*Z*-**1** and anti-*E*-**1** have the largest and smallest dipole moments, respectively, yet are of equal stability. While the stability of anti-*E*-**1** is certainly related to its small dipole moment, anti-*Z*-**1** is stabilized by an electrostatic attraction between the partially positive ketene carbon and the lone pair on the nitrogen.[16] The syn-*Z*-**1** conformation is likewise destabilized by electrostatic and steric repulsions between the partially positive ketene carbon and the partially positive hydrogen on the nitrogen. The barrier for the in-plane isomerization of anti-*Z*-**1** to syn-*Z*-**1** via **15** is calculated to be 29.5 kcal/mol. Although significant, this barrier would be surmountable under the FVP conditions under which imidoylketenes are commonly generated.

Infrared Spectra. Experimentally, imidoylketene (**1**) is reported to absorb at 2130 cm^{-1}, while formylketene imine (**6a**) absorbs at 2080 cm^{-1}.[1e] These are reasonably reproduced by the calculations, 2139.6–2126.9 cm^{-1} and 2042.5 cm^{-1}, respectively.[18] However, the various conformers of **1** have not been distinguished. The spectra reported here (Table 2 and supporting information) may prove useful for this identification. Only 12.7 cm^{-1} separate the calculated ketene stretches of the four conformations of **1**; this close spacing means that it will not be possible to resolve them in solution. Since they are equally stable, both anti-*Z*-**1** and anti-*E*-**1** are expected to be present in a matrix. The C=N and C=C=O stretches of anti-*E*-**1** are predicted to be more closely spaced (539.4 cm^{-1} apart) than those of anti-*Z*-**1** (553.2 cm^{-1} apart). This trend may persist with more highly substituted derivatives.[14] Syn-*E*-**1** may be more difficult to identify, because the C=N peak is close to that of anti-*Z*-**1**, while the C=C=O peak is close to that of anti-*E*-**1**. Although this conformation is likely to be present in a matrix sample of **1**, replacement of the imine hydrogen by a larger group would disfavor this conformation. The peaks due to syn-*Z*-**1** should be readily distinguished because they are at significantly lower frequencies. However the higher energy of this conformation predicts it will be difficult to observe.

Addition of Water to Imidoylketene. Enamino esters reversibly eliminate alcohols giving imidoylketenes (eq 1); water is a reasonable model for an alcohol. As was the case for the addition of water to formylketene,[3c,19] there was no barrier to the addition of water to imidoylketene at the RHF/3–21G level (eq 5). However, a transition structure was located at both the RHF/6-31G* and MP2/6-31G** levels (Figure 1).[20]

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[16] The O_1–C_2–C_3 bond angle of 180° in anti-*Z*-**1** is inconsistent with a bonding interaction between N_5 and C_2. We note that for the 1,3-migration of the NH_2 group in carboxamidoketene Wentrup and Wong have argued that the favorable interaction of the nitrogen lone pair with the ketene LUMO leads to a low barrier and a stable intermediate in the rearrangement.[17]

[17] Wong, M. W.; Wentrup, C. *J. Org. Chem.* **1994**, *59*, 5279–5285.

[18] Substituted derivatives absorb in the same region.[1e,k,m,q]

Table 1. Relative Energies (kcal/mol), Entropies, Dipole Moments, and Low or Imaginary Frequencies of Structures Related to 1, Optimized at the MP2/6-31G Level**

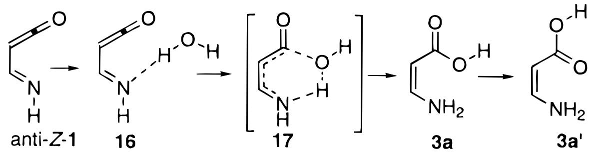
structure	MP2/6-31G** [a]	MP3/6-31G** [a]	MP4(SDQ)/6-31G** [a]	MP4[a] + ZPE[b]	S (cal/mol·K)	μ (D)[c]	low freq (cm^{-1})
			Addition of Water to Anti-*Z*-1				
anti-**Z-1** + H_2O	8.3	7.3	7.3	5.3			
16	0.0	0.0	0.0	0.0	88.2	4.08	56.6
17	2.6	6.3	5.8	6.3	76.7	3.63	208.5i
3a	−33.1	−35.4	−33.3	−30.1	77.4	4.72	90.5
3a′	−36.5	−38.8	−36.5	−33.2	77.3	2.75	116.1
			Addition of Formaldehyde to Anti-*Z*-**1**				
anti-**Z-1** + CH_2O	0.0	0.0	0.0	0.0			
18	3.7	8.8	8.0	10.6	82.5	4.50	331.1i
4a	−45.0	−47.7	−43.1	−36.4	75.4	6.00	148.9
			C_3H_3NO Isomers				
anti-*Z*-**1**	0.0	0.2	0.0	0.0	71.8	3.56	149.5
syn-*Z*-**1**	2.2	1.2	2.1	2.0	72.7	2.90	107.7
anti-*E*-**1**	0.2	0.0	0.0	0.0	71.4	1.23	132.7
syn-*E*-**1**	0.7	0.7	0.5	0.5	71.7	2.23	123.5
15	31.2	31.7	31.4	29.5	72.5	1.37	1222.8i
5a	7.4	12.0	12.3	12.9	72.9	6.00	134.7
19	50.6	59.1	58.0	54.8	72.1	4.22	1940.1i
6a	6.0	4.9	5.4	4.8	71.5	4.18	147.3
6a′	16.6	17.2	17.8	17.0	71.0	6.67	805.3i
20	50.5	59.9	57.0	53.4	69.8	2.75	1047.1i

[a] Calculated using the frozen core approximation. [b] Zero-point vibrational energy correlation from MP2/6-31G** frequencies and scaled by 0.9646 (ref 13). [c] From the RHF/6-31G** electron distribution, at the MP2/6-31G** geometry.

Table 2. Predicted Infrared Absorptions for Isomers of 1, at the MP2/6-31G Level**

structure	C═N[a]	intensity[b]	C═C═O[c]	intensity[b]
anti-*Z*-**1**	1586.4	116.6	2139.6	552.4
syn-*Z*-**1**	1571.3	94.1	2126.9	515.3
anti-*E*-**1**	1594.3	162.9	2133.7	643.4
syn-*E*-**1**	1584.6	158.5	2132.3	642.5
5a	1684.4[d]	412.0	2150.6	1369.8
6a	1656.2[e]	266.5	2042.5[f]	461.3

[a] In cm^{-1}. Scaled by 0.9427 (ref 13). [b] km/mol. [c] In cm^{-1}. Scaled by 0.960 (ref 14). [d] C═C stretch. [e] C═O stretch. [f] C═C═N stretch.



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The asynchronicity of the transition structure provides useful insight into the expected reactivity patterns (Table 5). Asynchronicity may be evaluated either on the basis of either partial bond orders or bond lengths; we chose the latter. We first define the bond extension by comparing the lengths of the partially formed bonds at the transition structure to those of the fully formed bonds. The asynchronicity is then the difference of the two bond extensions. A positive value indicates that the C_2−O_{10} bond is longer (i.e., less formed) than the N_5−H_9(C_9) bond in the transition structure. In **17**, for the addition of water to anti-*Z*-**1**, the asynchronicity is 0.033 Å. Thus, it is the basicity of the nitrogen which leads the reaction of anti-*Z*-**1** with water, while the nucleophilic addition of the water to the ketene lags slightly. This suggests that substituents which increase the basicity of the nitrogen would accelerate the reaction. In contrast, for the addition of water to formylketene (*Z*-**2**), the value of −0.089 Å for the asynchronicity indicates that nucleophilic addition of the water oxygen leads the reaction.[3c]

Interestingly, at the RHF/6-31G* level, the sense of asynchronicity (−0.194 Å) is reversed and exaggerated in the reaction of anti-*Z*-**1** with water, with the proton transfer lagging significantly behind the C−O bond formation in **17**. This indicates that any interpretations of asynchronicity, which are based on RHF/6-31G* geometries, should be undertaken with caution.

As expected for a pseudopericyclic reaction, but in contrast to conventional pericyclic ones, this transition structure was essentially planar. The spectator water

Table 3. Selected Geometrical Parameters for Imidoylketene (1) and Related Structures[a]

	anti-*Z*-**1**	syn-*Z*-**1**	anti-*E*-**1**	syn-*E*-**1**	**15**	**5a**	**19**	**6a**	**6a′**	**20**
O_1−C_2	1.173	1.177	1.178	1.176	1.176	1.190	1.185	1.228	1.231	1.200
C_2−C_3	1.334	1.332	1.331	1.333	1.331	1.305	1.308	1.462	1.446	1.392
C_3−C_4	1.457	1.468	1.453	1.461	1.483	1.355	1.396	1.331	1.347	1.400
C_4−N_5	1.290	1.288	1.288	1.286	1.247	1.348	1.321	1.228	1.189	1.237
C_4−H_7	1.097	1.088	1.094	1.090	1.104	1.090	1.086	2.597	2.578	1.469
N5−H8	1.023	1.025	1.021	1.023	0.987	1.004	1.017	1.018	0.993	1.008
C_3−H_6	1.083	1.079	1.081	1.080	1.079	2.593	1.441	1.080	1.079	1.079
C_2−H_7	3.352	3.360	2.632	2.627	3.341			1.105	1.108	1.369
N_5H_6	3.380	3.438	2.650	2.813	3.393	1.007	1.337			
$\angle O_1C_2C_3$	180.0	178.2	180.0	179.0	177.8	167.7	172.9	123.6	124.6	149.2
$\angle C_2C_3C_4$	119.0	121.5	121.5	120.8	118.3	132.5	137.5	119.9	119.5	94.4
$\angle C_3C_4N_5$	121.4	130.0	120.0	127.3	126.0	123.2	105.4	172.8	178.6	148.4
$\angle C_4N_5H_8$	109.9	110.8	109.0	109.8	179.6	121.9	122.6	118.3	180.0	126.6
$\angle C_3C_4N_5H_8$	180.0	0.3	180.0	0.0		180.0	0.0	167.4[b]	*c*	162.8
$\angle C_2C_3C_4N_5$	0.0	0.0	180.0	180.0	0.0	180.0	0.0	−77.7[d]	*e*	170.3

[a] Distances in ångstroms, angles in degrees. [b] C_2−C_3−N_5−H_8 = 91.0°. [c] C_2−C_3−N_5−H_8 = 0.0° (fixed). [d] O_1−C_2−C_3−C_4 = −178.8°. [e] O_1−C_2−C_3−C_4 = 180.0° (fixed).

Table 4. MP2/6-31G-Optimized Geometries of Intermediates, Transition Structures, and Products in the Addition of Water and Formaldehyde to Imidoylketene**[a]

	16	**17**	**3a**	**3a′**	**18**	**4a**
$O_1{-}C_2$	1.171	1.185	1.223	1.236	1.176	1.217
$C_2{-}C_3$	1.337	1.369	1.451	1.444	1.359	1.470
$C_3{-}C_4$	1.448	1.425	1.360	1.363	1.430	1.355
$C_4{-}N_5$	1.293	1.303	1.360	1.352	1.298	1.383
$C_3{-}H_6$	1.078	1.081	1.077	1.077	1.082	1.078
$C_4{-}H_7$	1.091	1.090	1.084	1.084	1.090	1.083
$N_5{-}H_8$	1.018	1.014	1.003	1.003	1.018	1.011
$N_5{-}H_9$ (C_9)	1.962	1.533	1.007	1.011	2.077	1.435
H_9 (C_9)$-O_{10}$	0.972	1.032	2.034	3.908	1.245	1.434
$O_{10}{-}H_{11}$	0.961	0.967	0.971	0.971		
$C_9{-}H_{11}$					1.095	1.093
$C_9{-}H_{12}$					1.095	1.085
$C_2{-}O_{10}$	3.011	1.943	1.384	1.364	2.125	1.383
$\angle O_1{-}C_2{-}C_3$	176.6	149.4	126.0	126.3	156.9	124.7
$\angle C_2{-}C_3{-}C_4$	121.5	129.7	126.7	120.8	131.7	120.0
$\angle C_3{-}C_4{-}N_5$	123.0	126.3	128.5	125.8	127.2	120.2
$\angle C_4{-}N_5{-}H_9$ (C_9)	113.0	103.9	118.0	117.2	112.0	112.6
$\angle N_5{-}H_9$ (C_9)$-O_{10}$	161.5	152.0	123.0	127.6	103.8	113.6
$\angle C_3{-}C_2{-}O_{10}$	101.5	104.0	113.4	112.8	99.5	115.2
$\angle C_2{-}C_3{-}C_4{-}N_5$	6.9	0.3	4.0	−3.3	−12.0	−21.9
$\angle C_3{-}C_4{-}N_5{-}H_9$ (C_9)	38.5	3.6	−12.0	7.4	18.2	−8.9
$\angle C_3{-}C_4{-}N_5{-}H_8$	−179.0	180.0	−164.0	169.0	177.4	132.4
$\angle C_3{-}C_2{-}O_{10}{-}H_9$ (C_9)	48.0	8.3	−1.0		65.0	25.3
$\angle N_5{-}H_9$ (C_9)$-O_{10}{-}C_2$	34.4	−9.3	−9.5		−57.9	−56.9
$\angle N_5{-}H_9{-}O_{10}{-}H_{11}$	−121.6	−119.0	−9.5			
$\angle C_2{-}O_{10}{-}C_9{-}H_{11}$					40.0	62.3
$\angle C_2{-}O_{10}{-}C_9{-}H_{12}$					−160.0	−178.9

[a] Distances in ångstoms, angles in degrees.

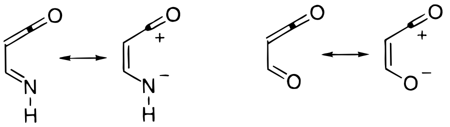
Table 5. Calculated Asynchronicity of Addition Transition Structures[a]

	RHF/6-31G*			MP2/6-31G**		
	bond extension			bond extension		
structure	$C_2{-}O_{10}$	$N_5(O_5){-}C_9(H_9)$	asynchr	$C_2{-}O_{10}$	$N_5(O_5){-}C_9(H_9)$	asynchr
17	0.348	0.542	−0.194	0.559	0.526	0.033
Z-**2** + H_2O[b]	0.334	0.553	−0.219	0.481	0.560	−0.089
18	0.793	0.478	0.315	0.742	0.642	0.100
Z-**2** + CH_2O[b]				0.626	0.668	−0.042

[a] In ångstroms. See text for a definition of asynchronicity. [b] From ref 3c.

hydrogen is slightly out of plane, because it is one of the lone pairs of the water which adds to the ketene. However, the deviation from planarity is smaller than that in the formylketene case, which is consistent with the earlier formation of the N−H bond and the delayed formation of the C−O bond. The other aspects of the geometry of **17** are similar to those previously discussed for formylketene.[3c] Note that this planar transition structure lacks the cyclic orbital overlap required[3a,c-e,10] for it to be aromatic.[12c,d,21] Since this lacks the electron−electron repulsions enforced by cyclic overlap, the reaction can, and does, have a very low barrier, as discussed below.

A hydrogen-bonded complex (**16**) between water and **1** was also located. Although there are likely to be other hydrogen-bonded complexes, this one is 5.3 kcal/mol below the isolated reactants and 6.3 kcal/mol below the transition structure **17**. Note that without calculating **16**, the activation energy from isolated reactants would be seriously underestimated at only 1.0 kcal/mol. While an experimental activation energy is not available, Wentrup has observed the addition of ethanol to an imidoylketene below −120 °C; clearly it has a low barrier.[1i] This calculated activation energy is fortuitously close to the 6.5 kcal/mol barrier calculated for the addition of water to formylketene at the MP4(SDQ)/6-31G* level.[22] Although a direct comparison is inappropriate because of the difference in basis sets, the barriers are undoubtedly similar. It would appear that although the nitrogen in **1** is more basic, the ketene is less susceptible to nucleophilic attack than in formylketene (**2**) because of the relative importance of the resonance structures below. Indeed, the Mulliken charges on C_2 support this; at the RHF/6-31G** level, this charge is 0.605 esu in anti-*Z*-**1** while the RHF/6-31G* charge on the same carbon in (*Z*)-formylketene is 0.645 esu.[3c]



The barrier for the elimination of water from the more stable conformer of 3-aminopropenoic acid (**3a′**) to form anti-*Z*-**1** is calculated to be 39.5 kcal/mol. The reactive conformer **3a** is 3.1 kcal/mol higher in energy than **3a′**. This barrier is higher than the 30.9 kcal/mol calculated for the analogous loss of water from 3-hydroxypropenoic

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(19) Allen, A. D.; McAllister, M. A.; Tidwell, T. T. *Tetrahedron Lett.* **1993**, *34*, 1095−1098.

(20) Some pseudopericyclic reactions apparently occur with no barrier.[3d]

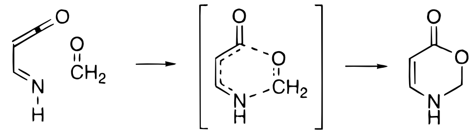
(21) Bernardi, F.; Celani, P.; Olivucci, M.; Robb, M. A.; Suzzi-Valli, G. *J. Am. Chem. Soc.* **1995**, *117*, 10531−10536.

(22) Based on the data in reference,[3c] but with the ZPE scaling of 0.9646 as used here.

acid (**3b′**) to form formylketene (**2**).[3c,23] This barrier appears to be reasonable in view of the fact that the elimination of ethanol occurs under flash vacuum pyrolysis conditions below 400 °C.[1i] A direct comparison awaits an experimental determination of an activation energy. It may also be that the actual barriers are indeed lower than that calculated here, because in all the experimental systems the nitrogen bears a substituent. This would increase the basicity of the nitrogen, which would be expected lower the barrier from this model system (*vide supra*).

We note that the amine group (N_5) is slightly pyramidalized in both conformers of 3-aminopropenoic acid; the $C_3H_4N_5H_8$ angle is 164.0° in **3a** (Figure 1) and 169.0° in **3a′**. As a vinylogous carbamate, it might have been expected to be planar. Although this slight pyramidalization would not seriously interfere with conjugation, apparently the resonance stabilization in this vinylogous system is insufficient to enforce planarity of the nitrogen. Vinylogous carbamates often show similar small deviations from planarity in X-ray structures, although they are usually described in the same literature as planar.[24] However, vinylogous amides are indeed essentially planar in crystal structures.[25] The nitrogens in urea are similarly calculated to be non-planar,[26] and it has been suggested that pyramidalization of amides occurs in proteins.[27]

Addition of Formaldehyde to Imidoylketene. Transition structure **18** for this addition (eq 6) was located at both the RHF/6-31G* and MP2/6-31G** levels. Both structures were qualitatively similar and resembled that which we previously calculated for the addition of formaldehyde to formylketene.[3c] At both levels, transition structure **18** was close to planar, with the formaldehyde oxygen twisted slightly out of the plane of the imidoylketene, to accommodate the attack by of one of its lone pairs on C_2 (see Figure 1). The MP2/6-31G** calculation predicts a smaller degree of asynchronicity (0.100 Å) than the RHF/6-31G* one (0.315 Å), but both predict that the N_5-C_9 bond is more formed in the transition structure.[28]



anti-*Z*-**1** **18** **4a** 6

Furthermore, the sense of asynchronicity is opposite to that calculated for the addition of formaldehyde to formylketene (**2**, −0.042 Å). Thus the more nucleophilic nitrogen combined with the reduced electrophilicity of the ketene in **1** has reversed the asynchronicity of the reaction. This has obvious consequences for the selectivity of the two systems toward various carbonyl reactants. For example, it predicts that aldehydes should be more reactive than ketones in additions to **1**, but the opposite trend should be observed in reactions of **2** since ketones are more basic than aldehydes. Note that the opposite selectivity is predicted from the RHF/3−21G results of Eisenberg *et al.*[1p]

The barrier for the addition of formaldehyde to **1** is calculated to be 10.6 kcal/mol, which suggests that the addition of aldehydes and ketones to imidoylketene may be a general and synthetically useful reaction, despite the paucity of experimental examples to date. This barrier height is again quite close to that calculated for the analogous reaction with formylketene (**2**) (10.9 kcal/mol).[22] This small difference in activation energy is insufficient to explain the preference for an aldehyde to react with an imidoylketene in preference to an α-oxoketene implied by eq 3.[11] However, it may be that steric congestion in **11** prevents the α-oxoketene moiety from achieving planarity, thus disfavoring its reaction with *p*-bromobenzaldehyde. The similar reactivities of **1** and **2** toward formaldehyde again reflect the opposing effects of the nitrogen versus oxygen substitution. The greater in-plane nucleophilicity of the nitrogen is offset by the out-of-plane resonance donation, which decreases the electrophilicity of the ketene carbon (C_2) as described above.

Finally, the 4.3 kcal/mol higher barrier for the 3.2 kcal/mol more exothermic addition of formaldehyde to imidoylketene **1**, as compared to water, is not as expected from the Hammond postulate.[29] The difference in exothermicity reflects the greater strength of the O−H σ-bond as compared to the C═O π-bond, while the higher barrier for addition of formaldehyde may be due to its differences in electrophilicity and nucleophilicity as compared to water. Nevertheless, the barriers imply that there should be synthetically useful selectivity between alcohols and carbonyl compounds. This also suggests that the fragmentation of enamino esters is not likely to be preparatively useful, because the product alcohol would react with the ketene faster than would a carbonyl compound. Preliminary experiments in this laboratory are in accord with these predictions.

1,3-Hydrogen Shifts. Although forbidden in hydrocarbons,[7] 1,3-hydrogen shifts with a pseudopericyclic orbital topology are allowed.[3d,8] To explain the observed formation of 3-amino-1,2-propadien-1-one (**5a**) from pyrolysis of the Meldrum acid derivative **10**, a 1,3-hydrogen shift from **1** has been proposed (eq 2).[1e] Cumulene **5a** is calculated to be planar but strongly kinked, as is the hydroxy compound **5b**.[30] Transition structure **19** for the hydrogen shift is also planar, and similar to that found for the oxygen analog. Formation of **2** from **5b** is more exothermic (23.8 kcal/mol, MP4(SDQ)/D95**//MP2/6-31G* + ZPE) than is formation of **1** from **5a** (12.9 kcal/mol) presumably due to the greater stability of the C═O

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[23] This may reflect the importance of the extra polarization functions on hydrogens used in this work (6-31G**) as compared to previous work (6-31G*).[3c]

[24] (a) Heslin, J. C.; Moody, C. J.; Slawin, A. M. Z.; Williams, D. J. *Tetrahedron Lett.* **1986**, *27*, 1403. (b) Balogh, M.; Lazlo, P.; Simon, K. *J. Org. Chem.* **1987**, *52*, 2026. (c) Vainiotalo, P.; Savolainen, P.-L.; Ahlgren, M.; Malkonen, P. J.; Vepsalainen, J. *J. Chem. Soc., Perkin Trans. 2* **1991**, 735.

[25] (a) Bernth, N.; Larsen, E.; Larsen, S. *Tetrahedron* **1981**, *37*, 2477−2484. (b) Goti, A.; Brandi, A.; Danza, G.; Guarna, A.; Donati, D.; DeSarlo, F. *J. Chem. Soc., Perkin Trans. 1* **1989**, 1253−1258. (c) Fernandez-G., J. N.; Enriquez, R. G.; Tobon-Cervantes, A.; Bernal-Uruchurtu, M. I.; Villena-I., R.; Reynolds, W. F.; Yang, J.-P. *Can. J. Chem.* **1993**, *71*, 358−363. (d) Bailey, N. A.; Fenton, D. E.; Gayda, S. E.; Phillips, C. A. *J. Chem. Soc., Dalton Trans.* **1984**, 2289−2292. (e) Bresciani-Pahor, N.; Calligaris, M.; Nardin, B.; Randaccia, L.; Viterbo, D. *Acta Crystallogr.* **1979**, *B35*, 2776−2778.

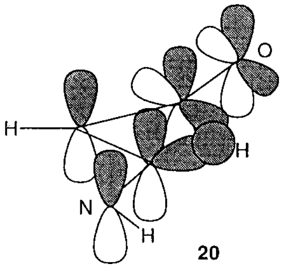
[26] Rasul, G.; Prakash, G. K. S.; Olah, G. A. *J. Org. Chem.* **1994**, *59*, 2552.

[27] Sulzbach, H. M.; Schleyer, P. v. R.; Schaefer, H. F., III. *J. Am. Chem. Soc.* **1995**, *117*, 2632−2637.

[28] We note, however, that the RHF/3-21G-optimized geometry of Eisenberg *et al.*[1p] predicts that the asynchronicity in the bond formation is opposite to that obtained from the RHF/6-31G* and MP2/6-31G** optimizations. This could be due to the lower electrophilicity of acetone as compared to that of formaldehyde or to a limitation of the level of theory.

[29] Hammond, G. S. J. *J. Am. Chem. Soc.* **1955**, *77*, 334.

[30] The origins of this bend have been previously discussed.[3d]



20

Figure 2. Orbital interactions for the 1,3-hydrogen shift transition structure **20**. Note that the extended out-of-plane π-system does not overlap with the in-plane breaking and forming bonds.

bond in **2** as compared to the C═N bond in **1**. As expected on the basis of the Hammond Postulate,[29] the rearrangement of **5a** has a higher barrier (41.9 kcal/mol) than that of the oxygen analog **5b** (33.1 kcal/mol). This barrier for the 1,3-hydrogen shift from **5a** to **1**, although substantial, is surmountable under the FVP conditions (>400 °C) for the decomposition of **10**.[31]

The 1,3-hydrogen shift of **6a** to **1** has also been proposed.[1i] The NH bond in **6a** is twisted out-of-plane, as expected for an ketene imine, because the C═N π-bond is in the plane of the molecule. However, at the transition structure **20**, this hydrogen is almost completely in the plane of the molecule as is the hydrogen which is being transferred. The barrier for this rearrangement is substantial (48.6 kcal/mol). It is instructive to compare this barrier with those found for formylketene (**2**) and formylallene (**6c**). The degenerate, thermoneutral 1,3-shift in **2** has a barrier of only 33.8 kcal/mol (MP4(SDQ)/D95**//MP2/6-31G* + ZPE).[3d] The barrier to the rearrangement of **6a** is substantially higher, although it is modestly (4.8 kcal/mol) exothermic. The 1,3-shift in formylallene to form vinylketene is the most exothermic of the three (10.3 kcal/mol, QCISD(T)/6−311+G(2d,p)//MP2/6-31G* + ZPE) and yet also has the highest barrier of 54.9 kcal/mol.[32] This trend, opposite to the prediction of the Hammond postulate,[29] can be rationalized in terms of orbital topologies.[33] The shift in **2** is fully pseudopericyclic; the hydrogen is transferred in the plane, and those orbitals never overlap with the π-system. Since **6a** is nonplanar, the p orbital on the nitrogen must switch from in-plane in **6a** to out-of-plane in **1**. Thus there is not a complete pseudopericyclic array of orbitals until the molecule becomes planar as it is in the transition structure (see Figure 2). Structure **6a′** was constrained to planarity and optimized to a linear structure; it is 12.2 kcal/mol higher in energy than **6a**.[34] The hypothetical rearrangement from **6a′** to **1** would therefore be 17.0 kcal/mol exothermic and have a barrier of 36.4 kcal/mol. Although this does not account for the entire difference between the rearrangements of **2** and **6a**, the necessity for planarity is a significant contribution to the barrier height. In the rearrangement of formylallene (**6c**) to vinylketene, a pseudopericyclic orbital topology would first require twisting of the CH_2 group into the plane of the molecule. Since this involves breaking the C═C π-bond, it is even more difficult than rehybridizing the nitrogen in **6a**, thus **6c** has the highest barrier.[36]

Conclusions

MP2/6-31G**-optimized structures were obtained for all four conformations of imidoylketene. The relative energies reflect the overall dipole moments of the molecules and also electrostatic interactions with the central ketene carbon. Approximately planar, pseudopericyclic transition structures for two 1,3-hydrogen shifts (**19** and **20**) were obtained at the same level. The barriers for these reactions were higher than those for the analogous reactions of **2** with oxygen replacing the nitrogen of **1**. In the case of **19** the barriers reflect the more modest exothermicity of the reaction, but not in the case of **20**. Transition structures for the additions of both water (**17**) and formaldehyde (**18**) to imidoylketene were also approximately planar and pseudopericyclic. MP2/6-31G** and RHF/6-31G* optimizations give a different sense of asynchronicity as compared to RHF/3−21G optimization for the addition of water. The nitrogen in imidoylketene (**1**) is more basic and/or nucleophilic than the oxygen in formylketene (**2**), but the ketene (C_2) is less electrophilic in **1** than **2**. These results suggest that aldehydes are slightly more reactive than ketones toward imidoylketenes and that alcohols are much more so than either. Work is underway in these laboratories to explore these and other predictions made herein.

Acknowledgment. This work was supported by a grant from the Robert A. Welch Foundation. We thank Curt Wentrup for helpful discussions.

Supporting Information Available: MP2/6-31G**-optimized Cartesian coordinates and vibrational frequencies for all stationary points and a table of absolute energies calculated for all stationary points (9 pages). This material is contained in libraries on microfiche, immediately following 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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[31] Wentrup originally postulated an alternative mechanism for this rearrangement, involving a 1,5-hydrogen shift to a hydroxyalkyne followed by a 1,3-hydrogen shift to give **1**.[1e]

[32] Bibas, H.; Wong, M. W.; Wentrup, C. *J. Am. Chem. Soc.* **1995**, *117*, 9582−9583.

[33] The barrier heights also correlate with the acidity of the center from which the hydrogen is transferred.

[34] A stable linear keteneimine has been made.[35] Both strain and electron-withdrawing groups contribute to its linearity.

[35] Wolf, R.; Wong, M. W.; Kennard, C. H. L.; Wentrup, C. *J. Am. Chem. Soc.* **1995**, *117*, 6789−6790.

[36] Alternatively, Wentrup and Wong have suggested that the relative ease of the 1,3-shifts is due to the energy ordering of the ketene LUMOs in **1**, **2**, and vinylketene.[32] While this is certainly true (the LUMO of **1** is 0.13150 while that of **2** is 0.09339), the observation that the HOMO−LUMO gap is slightly smaller in **1** than in **2** (0.46349 vs 0.47934)[3c] suggests to us that another factor (specifically the orbital overlap, or lack thereof) is also important in determining the barrier heights.