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# Ketene−Ketenimine Rearrangements in the Gas Phase and in Polar Media. 1,3-Migration Intermediates and Sequential Transition States

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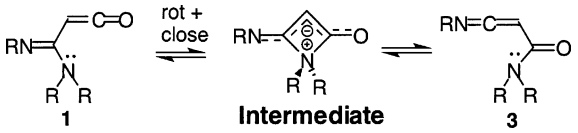


Calculations of the activation barrier for the 1,3-shifts of substituents X in α-imidoylketenes **1** (HN=C(X)−CH=C=O), which interconverts them with α-oxoketenimines **3** (HN=C=CH−C(X)=O) via a four-membered cyclic transition state **TS2** have been performed at the B3LYP/6-311+G(3df,2p)//B3LYP/6-31G* level. Substituents with accessible lone pairs have the lowest activation barriers for the 1,3-shift (halogens, OR, $NR_2$). The corresponding activation barriers for the α-oxoketene−α-oxoketene rearrangement of **4** via **TS5** are generally lower by 1−30 kJ/mol. A polar medium (acetonitrile, $\epsilon = 36.64$) was simulated using the polarizable continuum (PCM) solvation model. The effect of the solvent field is a reduction of the activation barrier by an average of 12 kJ/mol. In the cases of 1,3-shifts of amino and dimethylamino groups, the stabilization of the transition state **TS2** in a solvent field is so large that it becomes an *intermediate*, **Int2**, flanked by transition states (**TS2′** and **TS2″**) that are due primarily to internal rotation of the amine functions, and secondarily to the 1,3-bonding interaction. In the case of the α-oxoketene−α-oxoketene rearrangement of **4**, there is a corresponding intermediate **Int5** for the 1,3-amine shift already in the gas phase.

## Introduction

Ketenes and ketenimines are highly useful synthetic intermediates, and their reactions continue to attract the attention of theoretical chemists.[1,2] Computational studies have established the pseudopericyclic nature of several nucleophilic addition, cycloaddition, and electrocyclic reactions of ketenes.[3,4]

It is known that α-imidoylketenes **1** and α-oxoketenimines **3** can interconvert by a 1,3-shift of the α-substituent X (eq 1; the compounds are usually substituted on N).[5] The analogous and degenerate α-oxoketene−α-oxoketene interconversion of **4** is also known (eq 1; computational data for this reaction are compiled in Table S1, Supporting Information).[6] The dimethylamino group has the highest migratory aptitude, and the calculated activation barrier for **1** → **3** (X = $NMe_2$, Y = NH) is 62 kJ $mol^{-1}$.[7] Thus, this reaction will take place below room temperature. Phenyl groups also undergo the

(1) Ketenes: (a) Tidwell, T. T. *Ketenes*; Wiley: Chichester, 1995. (b) Hyatt, J.; Raynolds, P. *Org. React.* **1994**, *45*, 159−646. (c) Wentrup, C.; Heilmayer, W.; Kollenz, G. *Synthesis* **1994**, 1219−1248.

(2) Ketenimines: Perst, H. In *Houben-Weyl, Methoden der Organischen Chemie*; Thieme Verlag: Stuttgart, Germany, 1993; Vol. E15/3, pp 2531−2710.

(3) Oxoketenes: (a) Birney, D. M.; Wagenseller, P. E. *J. Am. Chem. Soc.* **1994**, *116*, 6262−6270. (b) Birney, D. M. *J. Org. Chem.* **1996**, *61*, 243−251. Imidoylketenes: (c) Zhou, C.; Birney, D. M. *J. Org. Chem.* **2004**, *69*, 86−94. (d) George, L.; Netsch, K.-P.; Bernhardt, P. V.; Wentrup, C. *Org. Biomol. Chem.* **2004**, *2*, 3518−3523.

(4) (a) *N*-Acylimidoylketene to 1,3-oxazin-6-one: Alajarín, M.; Sánchez-Andrada, P.; Cossio, F. P.; Arrieta, A. *J. Org. Chem.* **2001**, *66*, 8370−8477. (b) *N*-Acylvinylketenimine cyclizations: Alajarín, M.; Sánchez-Andrada, P.; Vidal, A.; Tovar, F. *J. Org. Chem.* **2005**, *70*, 1340−1349. (c) Oxovinylketenes to α-pyrones and analogous hetero-1,2,4,6-heptatetraene cyclizations: Rodriguez-Otero, J.; Cabaleiro-Lago, E. M. *Chem. Eur. J.* **2003**, *9*, 1837−1843. (d) Zora, M. *J. Org. Chem.* **2004**, *69*, 1940−1947.

(5) (a) Fulloon, B.; Wentrup, C. *J. Org. Chem.* **1996**, *61*, *1* (4), 1363−1368. (b) Rao, V. V. R.; Wentrup, C. *J. Chem. Soc., Perkin Trans. 1* **1998**, 2583−2586. (c) Wentrup, C.; Rao, V. V. R.; Frank, W.; Fulloon, B. E.; Moloney, D. W. J.; Mosandl, T. *J. Org. Chem.* **1999**, *64*, 3608−3619. (d) Rao, V. V. R.; Wentrup, C. *J. Chem. Soc., Perkin Trans. 1* **2002**, 1332−1335. (e) Bornemann, H.; Wentrup, C. *J. Org. Chem.* **2005**, *70*, 5862−5868. (f) George, L.; Wentrup, C. *Org. Biomol. Chem.* **2005**, *3*, 2998−3000.

(6) (a) Wong, M. W.; Wentrup, C. *J. Org. Chem.* **1994**, *59*, 5279−5285. (b) Finnerty, J.; Andraos, J.; Yamamoto, Y.; Wong, M. W.; Wentrup, C. *J. Am. Chem. Soc.* **1998**, *120*, 1701−1704.

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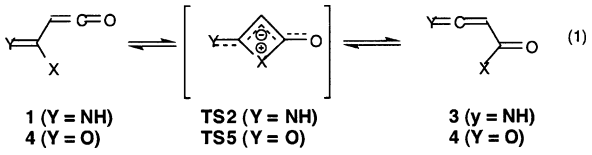
1,3-shift, typically under FVT conditions at temperatures around 970−1020 K in our apparatus,[3d,5,8] but a judicious choice of electron-donating substituents on the migrating and electron-withdrawing substituents on the nonmigrating phenyl group can stabilize the transition state so much that aryl group migrations become feasible at room temperature.[5f]




The 1,3-migrations described in eq 1 have the characteristics of pseudopericyclic reactions,[7] i.e., the substituent X migrates in the plane of the molecule, and the reaction is facilitated when X is an electron-donating group which can interact favorably with the low-lying ketene LUMO ($NR_2$,[7] OR,[5e] SR,[5a,c] and halogens[6b]). We made the interesting observation that the activation barrier for the 1,3-amino group migration in **1/3** can be viewed as a composite of the rotational barrier of the amino group, with the actual 1,3-shift barrier added on top of the rotational barrier.[7] If, however, the 1,3-shift structure is stabilized sufficiently to bring it below the rotational and migratory barriers, then the transition state **TS2** will become an *intermediate*.[6a,7]

To gain further insight into the nature of the 1,3-shifts and to facilitate comparison with experimental results,[3d,5,8] we now report computational studies of the activation barriers for the 1,3-shifts of a wide range of α-substituents X in α-imidoylketenes and α-oxoketenimines.[9]

## Results and Discussion

The transition states **TS2**, the *sE*, *sZ* and *iE*, *iZ* configurations[10] of α-imidoylketenes **1**, and the *sE* and *sZ* configurations of α-oxoketenimine **3** were calculated for the vacuum ($\epsilon = 0$). The data are presented graphically in Figure 1. A larger scale of this figure and a table with the numerical data (Table S2) are provided in the Supporting Information. Analogous calculations for reaction in simulated acetonitrile ($\epsilon = 36.64$) were carried out using the polarizable continuum (PCM) solvation model[11] (see Table S3, Supporting Information). The change in activation energy from α-imidoylketenes **1** to the transition states **TS2** and from α-oxo-ketenimines **3** to the transition states **TS2** as the medium is changed from the gas phase to acetonitrile is summarized in Table 1.

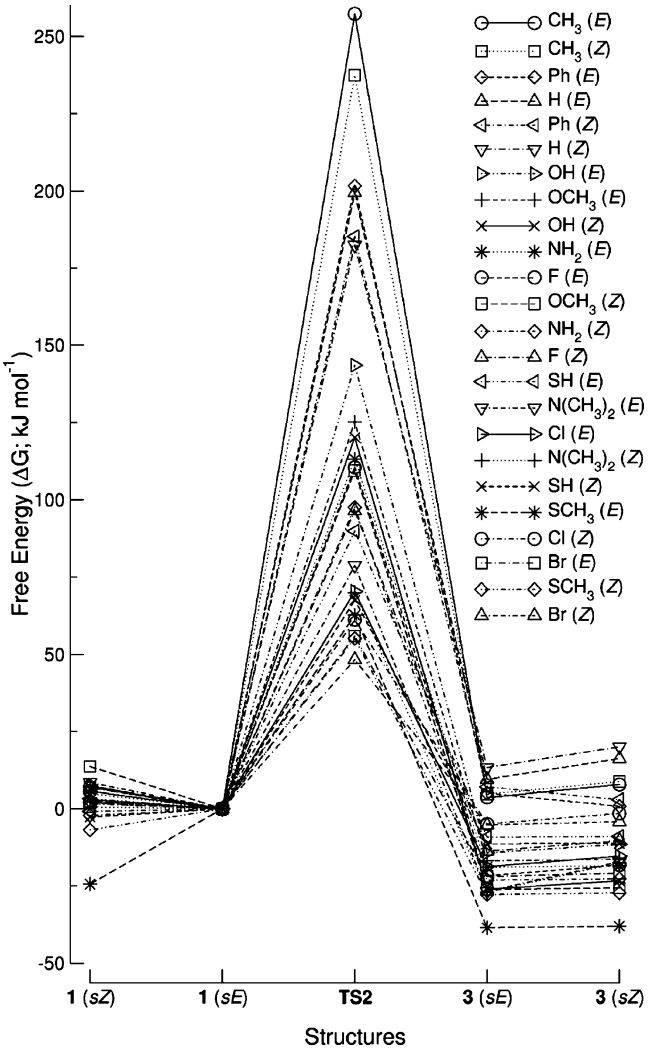



**FIGURE 1.** Potential energy paths for the 1,3-migrations of groups in the reaction **1** → **3** (calculations for the gas phase, $\epsilon = 0$).

The activation barriers for the 1,3-migration of the various groups in imidoylketenes **1** in a vacuum (Figure 1) are in accord with the results for α-oxoketenes **4** reported earlier (Table S1),[6a] although they are on average ~20 kJ mol$^{-1}$ higher for the imidoylketenes. The barriers for F, Cl, Br, and OH are 1−15 kJ mol$^{-1}$ higher, and those for H, $CH_3$, $NH_2$, and $N(CH_3)_2$ are 27−30 kJ mol$^{-1}$ higher for **1**. This is not surprising, as ketenes are more electrophilic than ketenimines, and oxoketenes are more electrophilic than imidoylketenes, i.e., they have lower LUMO energies. The estimated error for the computational theory level used is ±12 kJ mol$^{-1}$ (vide infra), which means that the calculated differences in ground-state energy between the ketenes **1** and ketenimines **3** are not statistically significant, although in most cases the ketenimines **3** are calculated to be more stable than the ketenes **1**, particularly in the solvent field. This is in accord with experiment, where ketenimines are usually, but not always, observed as the more stable species[5,8]

The move to a polar solvent has a more stabilizing effect on the ketenimines **3** and transition states **TS2** than on the ketenes **1**. This has the effect of decreasing

(8) (a) Kappe, C. O.; Kollenz, G.; Wentrup, C. *Chem. Commun.* **1992**, 485−486. (b) Kappe, C. O.; Kollenz, G.; Leung-Toung, R.; Wentrup, C. *Chem. Commun.* **1992**, 487−488. (c) Kappe, C. O.; Kollenz, G.; Netsch, K.-P.; Leung-Toung, R.; Wentrup, C. *Chem. Commun.* **1992**, 489−490.

(9) Finnerty, J. J.; Wentrup, C. Abstracts. *3rd Heron Island Conference on Reactive Intermediates and Unusual Molecules*; Heron Island, Queensland, Australia, July 17−23, 2004.

(10) The orientation of the acyl or imine group X−C=O or X−C=NH with respect to the cumulene function is denoted by *sZ* and *sE*. The configurations of the imine hydrogens are denoted by *iE* and *iZ*. For further details, see ref 7.

(11) Cancès, M. T.; Mennucci, B.; Tomasi, J. *J. Chem. Phys.* **1997**, *107*, 3032. Cossi, M.; Barone, V.; Mennucci, B.; Tomasi, J. *Chem. Phys. Lett.* **1998**, *286*, 253. Mennucci, B.; Tomasi, J. *J. Chem. Phys.* **1997**, *106*, 5151.

**TABLE 1. Difference in Free Energy of Reaction (ΔΔ*G*; kJ mol$^{-1}$) between a Polar Medium (Acetonitrile; $\epsilon$ = 36.64) and Vacuum ($\epsilon$ = 0) for 1,3-Migration of Substituents from Imidoylketenes 1 (Column 1) and Oxoketenimines 3 (Column 2) to the Transition State TS2[a]**

| substituent | ΔΔ*G* **1 → TS2** | ΔΔ*G* **3 → TS2** | ΔΔ*G* **1 → 3** |
|---|---|---|---|
| $CH_3$ *iE* | −4 | 13 | −17 |
| $CH_3$ *iZ* | 9 | 28 | −19 |
| Ph *iE* | −22 | −5 | −16 |
| Ph *iZ* | −17 | 2 | −19 |
| H *iE* | 13 | 27 | −14 |
| H *iZ* | 12 | 29 | −17 |
| OH *iE* | −17 | 3 | −20 |
| OH *iZ* | −5 | 7 | −12 |
| $OCH_3$ *iE* | −11 | 5 | −15 |
| $OCH_3$ *iZ* | −9 | 7 | −16 |
| $NH_2$ *iE* | −18 | 1 | −20 |
| $NH_2$ *iZ* | −19 | −1 | −18 |
| F *iE* | −11 | 0 | −10 |
| F *iZ* | −10 | 8 | −18 |
| $N(CH_3)_2$ *iE* | −15 | −7 | −7 |
| $N(CH_3)_2$ *iZ* | −25 | −10 | −15 |
| SH *iE* | −16 | 2 | −19 |
| SH *iZ* | −13 | 4 | −18 |
| Cl *iE* | −27 | −16 | −11 |
| Cl *iZ* | −30 | −11 | −19 |
| $SCH_3$ *iE* | −7 | 1 | −8 |
| $SCH_3$ *iZ* | −13 | 3 | −15 |
| Br *iE* | −26 | −14 | −12 |
| Br *iZ* | −24 | −5 | −19 |
| Average | −13 | 3 | −16 |

[a] The change in free energy of reaction on going from **1** to **3** is shown in column 3. The *E* and *Z* configurations of the imine groups in **1** are denoted *iE* and *iZ*.[10]

the activation barrier by an average of 12 kJ mol$^{-1}$ and decreasing the free energy of reaction by an average of 16 kJ mol$^{-1}$ (see Table 1). Inspection of the changes in the free energy of the transition states and of reaction (Table 1) does not reveal any systematic substituent effect.[12]

The most important effect of going to a polar medium is to produce an *intermediate* **Int2** in the 1,3-migration of amino groups from **1** to **3** (Table 2, Scheme 1b and Figure 2). In the case of 1,3-migration of amino groups in oxoketenes **4** via **TS5** (Scheme 1c), an intermediate **Int5** is predicted for the amino group shift already in the gas phase (Scheme 1d).[6a] The polar medium increases the stability of **Int5** further (Table 3).

In a previous paper,[7] we identified an inflection on the 1,3-migration path of $NH_2$ and $NMe_2$ which coincides with the transition state for rotation of the amine function. That is, in order that ketene **1** or ketenimine **3** in Scheme 1 can undergo cyclization to **TS2** or **Int2**, the amino group first has to rotate 90° to bring it into the plane of the imidoylketene or oxoketenimine moiety. The

(12) There are two apparently significant changes in the activation barrier, namely for H migration (disfavored by 33 kJ mol$^{-1}$) and $CH_3$ *iZ* migration (disfavoured by 35 kJ mol$^{-1}$). The results presented are the correct results obtained from the calculations but appear to be anomalous. It has not been determined whether the anomaly is real or a limitation of the computational methods used. The limitation in the $CH_3$ case was the difficulty in obtaining a TS, where we may have missed the minimum energy path. For the H case the limitation was the need to treat the migrating H differently from all the other migrating groups in the solvent model, where it was necessary to explicitly specify a cavity sphere on the migrating H in the transition state calculation.

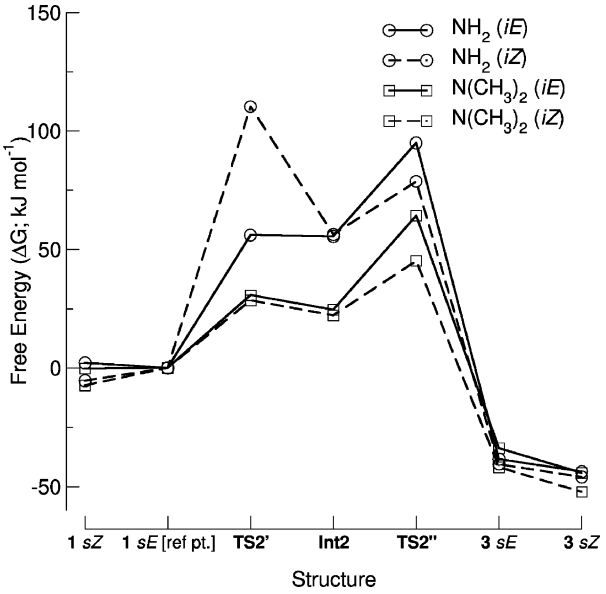



**FIGURE 2.** Potential energy paths for the 1,3-migrations of amino groups in the reaction **1** → **3** in a polar medium (acetonitrile, $\epsilon$ = 36.64).

**TABLE 2. Free Energies (Δ*G*; kJ mol$^{-1}$) of Intermediates Int2 Present in the 1,3-Migration of Amino Groups from 1 to 3 in a Polar Medium (Acetonitrile, $\epsilon$ = 36.64) via Transition States TS2′ and TS2″ (cf. Scheme 1b)[10]**

| | $NH_2$ | | $N(CH_3)_2$ | |
|---|---|---|---|---|
| | *iE* | *iZ* | *iE* | *iZ* |
| **1** *sZ* | 2.15 | −5.40 | −0.23 | −7.38 |
| **1** *sE* | 0.00 | 0.00 | 0.00 | 0.00 |
| **TS2′** | 56.10 | 110.20 | 30.69 | 28.47 |
| **Int2** | 55.52 | 56.33 | 24.53 | 22.22 |
| **TS2″** | 94.98 | 78.67 | 64.24 | 45.19 |
| **3** *sE* | −38.47 | −40.65 | −33.81 | −41.84 |
| **3** sZ | −43.79 | −45.96 | −44.22 | −52.25 |

amino groups are now in the correct orientation for the 1,3-bonding to occur via **TS2′** or **TS2″**. In the same way, the amino groups in oxoketenes **4** have to rotate 90° to the rotational transition state in order that the reaction can proceed to **TS5′**. In other words, we have reactions with sequential transition states: first the amino and dimethylamino groups undergo rotation about single bonds with activation barriers of 18−30 kJ/mol (18 kJ/mol for the $NMe_2$ group in the IZ conformation in **1** and **3**).[7] Then, after an additional 44 kJ/mol, the second transition state (**TS2**) is reached (see Figure 3). The activation barriers for the amino group migrations in the polar solvent are illustrated in Figure 2. The rotational transition structures, the 1,3-migration transition structures (**TS2**, **TS2′**, and **TS2″**) calculated for the gas phase and for the polar medium, and the intermediate (**Int2**) are illustrated in Figure 3 for the case of the $NMe_2$ *iZ* conformer.[10] The rotational TSs were characterized previously.[7] Data for all the 1,3-migration TSs are given in the Supporting Information. In the case of Figure 3, only ca. 10 kJ/mol additional energy is needed after reaching the rotational transition state (calculated for the gas phase) in order to reach the 1,3-migration transition state **TS2′** (calculated for the polar medium). The rotational transition state (18 kJ/mol) is only slightly below the

**SCHEME 1**

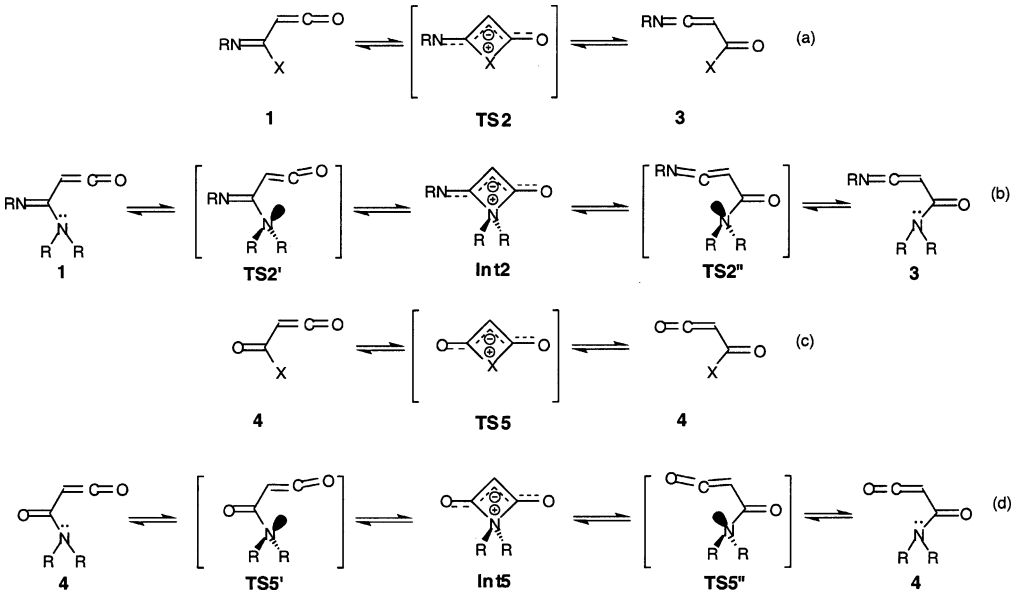



**TABLE 3. Free Energies (Δ*G*; kJ mol$^{-1}$) of Transition States TS5′ and Intermediates Int5 in the 1,3-Migration of the Dimethylamino Group in the α-Dimethylamino-α-oxoketene 4 in Vacuum and in a Polar Medium (ϵ = 36.64) Relative to the *sE* Ground State (cf. Scheme 1d)**

| medium | **TS5′** | intermediate **Int5** |
|---|---|---|
| vacuum | 43.5 | 37.1 |
| acetonitrile | 47.0 | 34.0 |

energy of the intermediate, **Int2** (22 kJ/mol). In the analogous case of the *iE* conformer of **1** (X = $NMe_2$) there is only an 8 kJ/mol difference between the rotational transition state calculated for the gas phase and the 1,3-migration transition state in the polar medium (23 and 31 kJ/mol, respectively); the rotational transition state and the intermediate **Int2** have almost the same energy (23 and 24.5 kJ/mol, respectively). While the rotational barriers may be slightly different in polar media, the general picture is clear: after rotating the amino groups 90°, which does not affect the structures of the ketene or ketenimine moieties, they stay in this position while the ketene function in **1** undergoes a bending of ca. 20°, allowing the central ketene C atom to approach the amine N atom and reach **TS2′** for cyclization. The general aspect of these energy surfaces with connecting, orthogonal rotational and cyclization transition states is shown schematically in Figure 4.

Since both the rotational and the 1,3-migration transition states have been characterized as proper TSs, and since no energy minimum has been found between them, they have to be sequential TSs. Therefore, there has to be a bifurcation point (valley-ridge inflection, VRI) between them.[13]

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Figures showing the rotational transition structures for dimethylamino-oxoketenes **4**, the 1,3-migration transition structures and intermediate (**TS5**, **TS5′**, **TS5″**, and **Int5**), and 1,3-migration transition states **TS2** for all the

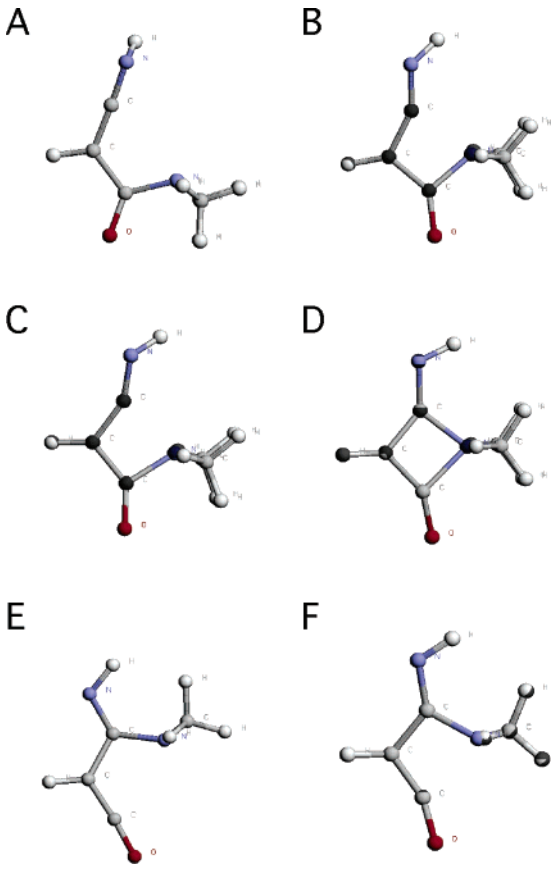


**FIGURE 3.** Calculated $NMe_2$ migration for *iZ* conformers of **1** and **3**. A, C, and E for the gas phase (ϵ = 0); B, D, and F for simulated acetonitrile (ϵ = 36.64). A and E: transition structures for rotation of the $NMe_2$ groups (18 kJ/mol above ground states of **1** or **3**). C: **TS2**, 62 kJ/mol. D: **Int2**, 22.2 kJ/mol. B: **TS2″**, 45.2 kJ/mol. F: **TS2′**, 28.5 kJ/mol.

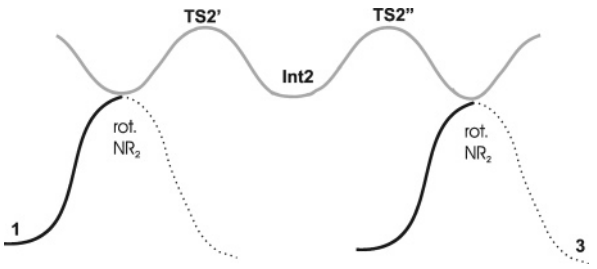


**FIGURE 4.** Schematic energy profile for amino group rotation in ketenes **1** (**4**) and ketenimines **3**, 1,3-migration via transition states **TS2′** and **TS2″**, and the 1,3-migration intermediate, **Int2**.

substituents for the reactions in the gas phase and in the polar medium are provided in the Supporting Information.

The effect of the polar solvent may be understood in terms of the zwitterionic 1,3-migration structures (**Int2**, **Int5**) being stabilized by the polar medium, whereas the transition states for rotation and migration of the amino groups (**TS2**, **TS2′**, **TS2″**, **TS5**, **TS5′** in Scheme 1) are much less so. An intermediate cannot be expected in all cases; it can only be expected when either the intermediate is selectively stabilized, or the rotational barriers flanking it are sufficiently high, or both. The case of RO migration has been discussed previously.[5e] The case of amino group migration in imidoylthioketenes, where 1,3-migration intermediates are also found, will be described elsewhere.[14]

## Computational Methods

Standard DFT molecular orbital calculations[15] were carried out using the GAUSSIAN 03[16] system of programs. All geometry optimizations have been performed with the standard polarized split-valence 6-31G* basis set[14] at the B3LYP level.[17] Wave function stability and harmonic vibrations have been calculated at this level in order to characterize the stationary points as minima or saddle points and to evaluate zero-point vibrational energies (ZPVEs). Improved relative energies have been obtained using the expanded basis set 6-311+G(3df,2p) and the B3LYP method on the previously optimized 6-31G* geometries, the aggregate method being B3LYP/6-311+G(3df,2p)// B3LYP/6-31G*. The enthalpy ($\Delta H$) for the processes was calculated using energy values from the higher level and an unscaled correction from the vibration calculation at the lower level. The entropy ($\Delta S$) was taken directly from the harmonic vibration calculation at the lower level. The free energy ($\Delta G$) was then calculated from these two values. The temperature used in the harmonic vibration calculation, and hence, the thermochemistry was 298.15 K. The thermochemistry presented here includes an (unscaled) correction for ZPVE. A scaling factor of 0.9804[18] has been recommended for ZPVE/thermal energy calculated using the B3LYP/6-31G* method but was not applied here, as the difference in ZPVE between two compounds or conformers was found to be small (<10 kJ mol$^{-1}$). The corresponding correction for scaling the ZPVE/thermal energy is estimated as less than ~0.2 kJ mol$^{-1}$, a value significantly less than the presumed accuracy of the method. The chosen method can be presumed to have an accuracy between B3LYP/6-311+G(2d,p)//B3LYP/6-31G* and B3LYP/6-311+G(3df,2df,2p)//B3LYP/6-31G*. A comparison[19] of these two methods with the experimental data from the GAUSSIAN G2 molecule set had, respectively, mean absolute deviations (standard deviations) of <13(12.5) and <11(11) kJ mol$^{-1}$. While the chosen method's overall mean absolute deviation (or accuracy) for predicting energy is estimated at <13 kJ mol$^{-1}$, the error for closely related compounds would be expected to be smaller. A comparison of the migratory aptitudes of groups in α-oxoketenes **4** calculated using the ab initio G2(MP2, SVP) method[6] with those derived from the DFT method indicated that the latter method[6a] overestimates the 1,3-migration barrier for amino groups by only ~3−4 kJ mol$^{-1}$.[7]

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**Supporting Information Available:** Table S1 of calculated 1,3-migration activation barriers for various substituents in α-oxoketenes **4** (B3LYP/6-311+G(3df,2p)//B3LYP/6-31G* and G2(PM2,SVP) data) from refs 6a and 7. Table S2 of the relative free energies for 1,3-migration of substituents from imidoylketene **1** via four-membered ring transition state **TS2** to oxoketenimine **3**. Table S3 of the relative free energies for 1,3 migration of substituents in polar medium (acetonitrile; $\epsilon$ = 36.64) from imidoylketene **1** via four-membered transition state **TS2** to oxoketenimine **3**. Figure S1 is a full-page version of Figure 1. Figures S2−S15 show transition structures **TS2** (**TS2′**, **TS2″**, **Int2**) for all of the substituents in Tables 1 and 2 and **TS5′** and **Int5** for the 1,3-shift of $NMe_2$ in oxoketene **4** in the gas phase and in simulated acetonitrile. Summary information is provided for each calculation performed, including Hartree−Fock energy, optimized geometry, calculated harmonic frequencies, and imaginary frequencies for transition states. This material is available free of charge via the Internet at http://pubs.acs.org.

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