

Facile Ketene–Ketene and Ketene–Ketenimine Rearrangements: A Study of the 1,3-Migration of α -Substituents Interconverting α -Imidoylketenes and α -Oxoketenimines, a Pseudopericyclic Reaction

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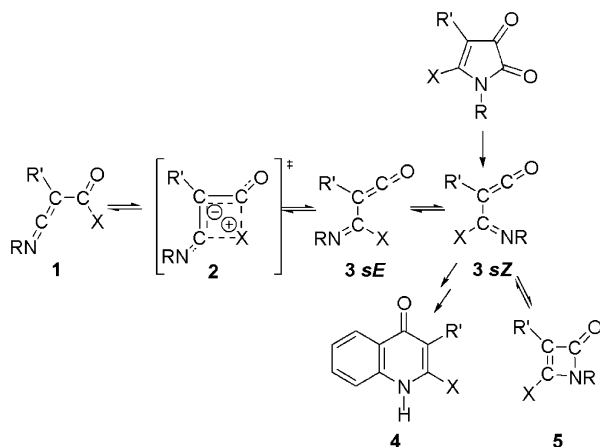
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Theoretical calculations (B3LYP/6-311+G(3df,2p)//B3LYP/6-31G*) of the 1,3 migration of NR_2 transforming α -oxoketenimines **1** to α -imidoylketenes **3** and vice versa indicate that this process is a pseudo-pericyclic reaction with a low activation energy (NH_2 97 kJ mol^{-1} , $\text{N}(\text{CH}_3)_2$ 62 kJ mol^{-1}). The oxoketenimines were found to be more stable (by 18–35 kJ mol^{-1}) which is in line with experimental observations. The hindered amine rotation in the amide and amidine moieties adjacent to the cumulenes are important in the migration of the NR_2 group, as one of the rotation transition states is close to the 1,3 migration pathway. This gives an interesting potential energy surface with a valley-ridge inflection (VRI) between the orthogonal hindered amine rotation and 1,3 migration transition states. The imidoylketene may also undergo ring closure to an azetinone **5**; however, this is metastable, and under the conditions that allow the 1,3-migration, the oxoketenimine **1** will be favored. The imine NH *E/Z*-interconversion of the ketenimine group takes place by inversion and has a low activation barrier (~ 40 kJ mol^{-1}). In all the amidines examined the *E/Z*-interconversion of the imine function was predicted to be by rotation with a high barrier (> 80 kJ mol^{-1}), in contrast to all other reported imine *E/Z*-interconversions which are by inversion.

Introduction

There has been considerable recent experimental interest in the chemistry of α -oxoketenimines **1** and α -imidoylketenes^{1,2} **3** and their interconversion via 1,3-substituent migration (Scheme 1).³ They have also been the objects of several theoretical studies.^{4–7} Although suprafacial thermal 1,3-migrations are formally “forbidden”,⁸ such migrations become possible in cumulenes.^{3a,5–7} For instance, we recently⁹ described the degenerate

SCHEME 1



- a X = R = R' = H
 b X = OCH₃; R = phenyl; R' = H
 c X = CH₃; R = 1'-adamantyl; R' = phenyl
 d X = NH₂; R = R' = H
 e X = N(CH₃)₂; R = R' = H

thermal 1,3 migration of the chloro-substituent of an α -oxoketene and determined the activation barrier, using

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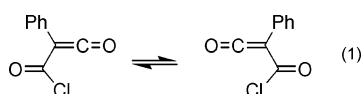
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TABLE 1. Calculated (B3LYP/6-311+G(3df,2p)//B3LYP/6-31G*) Energy Data²⁰ for the 1,3 Migration in α -Oxoketenes **6** Compared to the G2(MP2, SVP) Values (Difference Columns)⁹ (Calculated Energy Values Are for 298.15 K)

compd/substituent ^a	B3LYP			G2(MP2, SVP)	
	$\Delta H^\ddagger/\text{kJ mol}^{-1}$	$\Delta S^\ddagger/\text{JK}^{-1} \text{mol}^{-1}$	$\Delta G^\ddagger/\text{kJ mol}^{-1}$	$\Delta E/\text{kJ mol}^{-1}$	difference/ kJ mol^{-1}
6b /N(CH ₃) ₂ ^a	30.9	-20.6	37.0		-3.1
6b /N(CH ₃) ₂ ^b	36.3	-23.7	43.3	34	-9.5
6c /Br	25.5	-18.1	30.9	37	8.0
6d /SH	39.9	-20.4	46.0	51	5.5
6e /Cl	37.6	-16.3	42.5	53	10.2
6a /NH ₂	69.5	-11.8	73.1	70	-3.5
6f /F	78.7	-17.2	83.9	89	5.0
6g /OH	107.1	-14.2	111.4	114	3.1
6h /H	137.3	-10.1	140.3	143	2.4
6i /CH ₃	198.2	-11.6	201.7	206	4.3

^a In the N(CH₃)₂ case, the symmetric 1,3 migration structure was an intermediate. The migration therefore had two unsymmetric degenerate transition states either side of the intermediate. The results for both the intermediate (a) and the transition state (b) are reported.

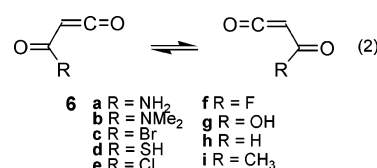
dynamic NMR (T_C -29 °C) or density functional theory (DFT) calculation, to be ~40 kJ mol⁻¹ (eq 1).



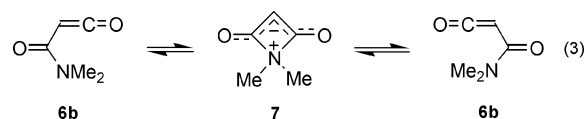
It is known that reactions producing methylthio-, dimethylamino-, or alkoxyimidoalkenes **3** can give rise to products derived from the corresponding 1,3-migration partner, the oxoketenimines **1**.¹⁰ The reverse process has also been demonstrated, e.g., the flash vacuum thermolysis (FVT) of **1b** affording the cyclization product of the corresponding α -imidoalkene, the 4-quinolone **4b** (94% yield by FVT at 800 °C).¹¹ While **1b** was the major heterocumulene product after FVT, with a 10-fold greater intensity of its cumulene band in the infrared region 2000–2200 cm⁻¹, a dynamic equilibrium must have existed to account for the high yield of **4b** (calculated intensity ratios for isomeric imidoalkenes and oxoketenimines are of the order 750:450 km mol⁻¹; representative data are given in the Supporting Information). In competition with the 1,3-migration there is a reversible electrocyclic ring closure of **3** to form **5**. This ring closure has been reported both experimentally¹² (**3c** to **5c**) and theoretically⁴ (**3a** to **5a**). The alternative ring closure to form an imino-oxetene has previously been calculated⁴ to be unstable and was not considered here. So far, only one ab initio study of the 1,3-migration process in oxoketenimines/imidoalkenes has been reported,^{5a} predicting a 1,3-migration barrier of 200 kJ mol⁻¹ for the hydrogen migration in the parent α -imidoalkene (at MP4(FC, SDQ)/6-31G* + ZPVE). In their study of the ring closure to **5a**, Nguyen and co-workers⁴ calculated an activation barrier of 102 kJ mol⁻¹ (MP4-(SDQ)/6-31G** + ZPVE), with the monocyclic **5a** being 41 kJ mol⁻¹ less stable than **3a**.

The migratory aptitude of a range of substituents was studied previously for the α -oxoketene system **6** (eq 2).^{6,9}

For ease of comparison with the present study, the migratory aptitudes of oxoketenes **6** have been recalculated at the DFT level used here, and the data are presented in Table 1.



The imidoalkene/oxoketenimine system can be expected to behave in a manner qualitatively similar to that of **6**. The amino and dimethylamino substituents have been found to be very good migrating groups in both experiment and calculations (calculated barriers for NH₂ 70 and for N(CH₃)₂ 34 kJ mol⁻¹ in **6**). Furthermore, the dimethylamino group migration in **6b** was uniquely found to present a shallow minimum for the four-membered cyclic zwitterionic intermediate **7** (eq 3).⁶



With amino migrating groups, three other conformational changes may impact on the migration. First, the amidine or amide group may rotate about the single bond to the heterocumulene (*sE*,¹³ *sZ*, *s90*, *s270*, rotation A, Scheme 2). Second, the amino group may undergo hindered rotation about the carbon–nitrogen bond (*A0*,¹³ *A90*, *A180*, rotation B, Scheme 2). The imine functions on the amidine may undergo rotation or inversion of the nitrogen substituent (imine *IZ*¹³ and *IE*, linear transition state *IL*, and rotation transition state *IR*, rotation/Inversion C, Scheme 2). Likewise, the ketenimine imine functions may undergo rotation or inversion of the nitrogen substituent (imine *kI90*¹³ and *kI270*, linear transition state *kIL*, and rotation transition state *kIR*, rotation/inversion D, Scheme 2).

In the previous study⁶ of the α -oxoketenes **10**, two minima were found for the α -amide group rotating about the single bond to the heterocumulene with both minima coplanar with the cumulene (*sE* and *sZ*). In that study, the relative energies between the two minima were -2 to +5 kJ mol⁻¹ with rotation barriers of 26–41 kJ mol⁻¹

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