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Imidoylketene-α-oxoketenimine and α-oxoketene–α-oxoketene rearrangements. 1,3-Shifts of substituted phenyl groups†

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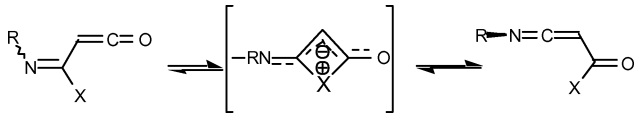
1,3-Phenyl shifts interconvert imidoylketenes **1** and α-oxoketenimines **2** and, likewise, α-oxoketenes **3** automerize by this 1,3-shift. These rearrangements usually take place in the gas phase under conditions of flash vacuum thermolysis. Energy profiles calculated at the B3LYP/6-31G(d,p) and B3LYP/6311 + G(3df,2p)//B3LYP/6-31G(d,p) levels demonstrate that electron donating substituents (D) in the migrating phenyl group and electron withdrawing ones (W) in the non-migrating phenyl group, can stabilise the transition states **TS1** and **TS2** to the extent that activation barriers of *ca.* 100 kJ mol^{-1} or less are obtained; *i.e.* enough to make these reactions potentially observable in solution at ordinary temperatures. The calculated transition state energies ΔG(**TS1**) show an excellent correlation with the Hammett constants σ_p(W) and σ_p^+(D).

Introduction

Although few ketenes are stable at room temperature, both ketenes[1] and ketenimines[2] are highly useful synthetic intermediates. Furthermore, their many and varied reaction types continue to attract the attention of theoretical chemists.[3]

It is known that α-imidoylketenes and α-oxoketenimines can interconvert by a 1,3-shift of the α-substituent X (eqn. 1).[4] This reaction is analogous to the α-oxoketene–α-oxoketene intercon-



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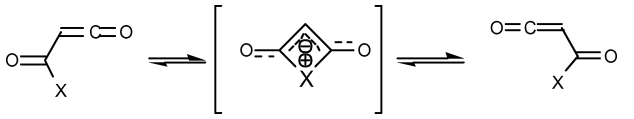


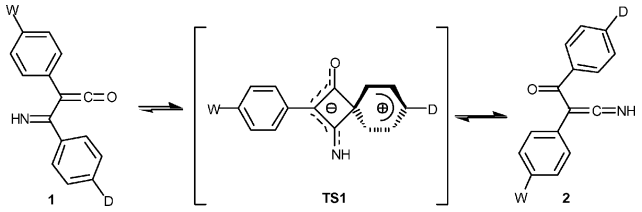
(2)

version (eqn. 2)[5,6] and is particularly facile in both cases when X is an electron donating group which can interact favourable with the low-lying ketene LUMO (NR_2, OR, SR and halogens).[5,7] The dimethylamino group has the highest migratory aptitude and the calculated activation barrier is 62 kJ mol^{-1} (eqn. 1; X = NMe_2, R = H).[8] Thus, this reaction will take place below room temperature.[8] However, phenyl groups also undergo the 1,3-shift, but so far only in the gas phase under FVT conditions at temperatures around 970–1020 K in a high vacuum and with short contact times.[9] Phenyl groups do *not* undergo the 1,3-shift in solution in dibenzoylketene at temperatures up to 145 °C, or in 1-benzoyl-2-phenylimidoylketene up to 250 °C.[10]

Calculations of the energy profiles for the rearrangements of the unsubstituted imidoylketene afforded an activation barrier for the 1,3-H shift of 180 kJ mol^{-1}.[11,12] The calculated 1,3-shift barrier for a phenyl group in the otherwise unsubstituted imidoylketene is 186 kJ mol^{-1}[8b] and the 1,3-shift of a phenyl group interconverting the diphenylimidoylketene **1a** and diphenyloxoketenimine **2a** is 149 kJ mol^{-1}.[11] Similarly, the 1,3-shift barrier for a phenyl group in benzoylketene, PhCO–CH=C=O, is 151 kJ mol^{-1} and, as shown in this paper, for the diphenyl analog, PhCO–C(Ph)=C=O, it is *ca.* 120 kJ mol^{-1}. Thus, there is a significant effect of the second phenyl group, although all these reactions still have high activation barriers, so that they are most likely to be observed under conditions of FVT. We have now calculated the effects on **TS1** of electron donating substituents (D) in the migrating phenyl group and electron-withdrawing ones (W) in the non-migrating phenyl group in the imidoylketenes **1**–oxoketenimines **2** rearrangement (eqn. 3), as well as the corresponding **TS2** in the oxoketene–oxoketene **3** rearrangement (eqn. 4).

Results and discussion

The computational results for the two 1,3-shift rearrangements depicted in eqn. (3) and eqn. (4) are shown in Table 1 and Fig. 1 and Fig. 2. It is readily seen that electronegative substituents (W; *i.e.* F, CHO, CN, NO_2, SO_2CN) on the non-migrating phenyl group lowers the transition state energy, although the effect is not large. The C_6F_6 group is surprising in that the activation energy is actuallyincreased. Electron-donating substituents (D;



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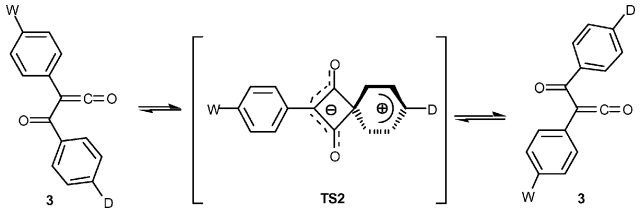

(4)

i.e. OH, NMe_2, NHMe) on the migrating ring have a much more pronounced effect and the best results are obtained by a combination of the D and W groups. This 'push-pull' or 'captodative' effect is larger than the sum of the individual components for single substitution. Thus, the activation barriers may be reduced by some 45 and 40 kJ mol^{-1} for imidoylketenes and oxoketenes, respectively; *i.e.* enough to make these reactions potentially observable under ordinary reaction conditions.

† Electronic supplementary information (ESI) available: computational data for the ground and transition states shown in Table 1 and for benzoylketene PhCOCHCO. See http://dx.doi.org/10.1039/b504260g

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Table 1 Activation barriers for the 1,3-phenyl shifts in imidoylketenes **1** to oxoketenimines **2** *via* **TS1** and for automerization of oxoketenes **3** *via* **TS2**[a]

Diphenylimidoylketene 1

1	Substituents D on migrating phenyl group in **1**	Substituents W on nonmigrating phenyl group in **1**	Oxoketenimine **2** energy relative to ketene **1** kJ mol^{-1}	**TS1** energy relative to ketene **1** kJ mol^{-1}	ΔG(**TS1**) relative to ketene **1** kJ mol^{-1}
a	–H	–H	2.7	149.3	150.6
a[b]			4.7	151.9	153.2
b	–H	–C_6F_5	4.3	158.2	160.4
c	–H	–F	2.6	148.7	149.1
d	–H	–CHO	2.6	145.2	149.3
e	–H	–CN	2.6	144.3	148.2
f	–H	–NO_2	2.8	143.1	147.7
g	–OH	–H	0.2	134.3	136.7
h	–NMe_2	–H	−0.5	117.6	121.8
i	–OH	–CN	−0.1	127.6	132.0
j	–NMe_2	–CHO	0.4	111.7	116.0
k	–NMe_2	–CN	0.4	110.2	114.4
m	–NMe_2	–NO_2	0.6	108.0	112.3
m[b]			−0.5	104.7	109.0
n	–NHMe	–SO_2CN	0.1	105.1	108.4
n[b]			−0.1	104.1	107.4

Diphenyloxoketene 3

3	Substituents D on migrating phenyl group in **3**	Substituents W on nonmigrating phenyl group in **3**	—	**TS2** energy relative to oxoketene **3**	ΔG(**TS2**) relative to oxoketene **3**
a	–H	–H	—	117.2	120.8
a[b]				121.2	124.8
m	–NMe_2	–NO_2	—	80.6	86.6
m[b]				81.0	87.0
n	–NHMe	–SO_2CN	—	78.6	84.6
n[b]				79.8	85.8

[a] Calculations at the B3LYP/6-31G(d,p) level unless indicated otherwise ([b]). The absolute energies of **1a** and **3a** are −707.898328 and −727.850564 Hartree, respectively. All energies are ZPVE corrected. All transition states are confirmed by IRC calculations. [b] Calculations using the B3LYP/6311 + G(3df,2p)//B3LYP/6-31G(d,p) basis set.

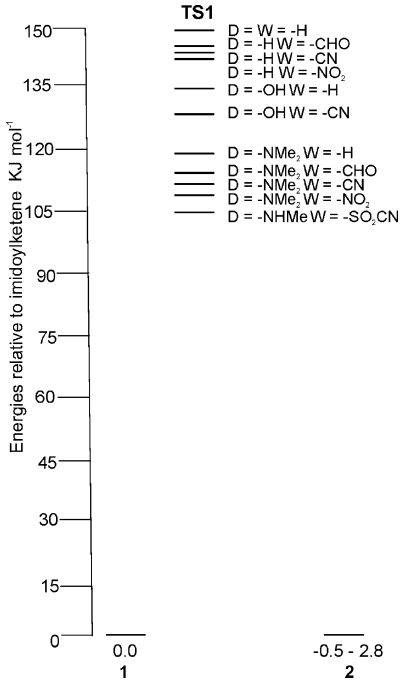

Fig. 1 Energy profiles for the imidoylketene **1**–oxoketenimine **2** rearrangements (B3LYP/6-31G(d,p)).

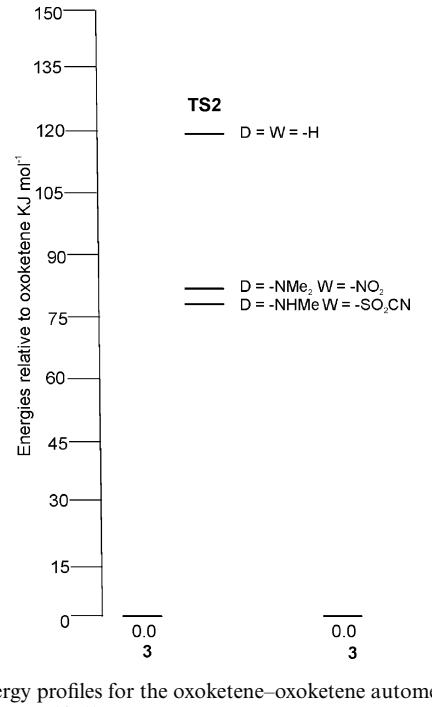

Fig. 2 Energy profiles for the oxoketene–oxoketene automerization of **3** (B3LYP/6-31G(d,p)).

A referee has pointed out that our calculated activation energies can be correlated by the Hammett equation. This is the reason that we calculated the SO_2CN/NHMe combination, which gives particularly high values of the Hammett σ_p and σ_p^- constants[13] for W and a low value of the σ_p^+ constant for D. As seen in Fig. 3, there is in fact an excellent correlation between σ_p^+(D) and σ_p(W) of the form ΔG(**TS1**) = −18.45 [0.5 × σ_p(W) − σ_p^+(D)] + 152.66 (R = 0.9943). This confirms the statement above, that the effect of the donor D is much

stronger (in fact twice as strong) than that of the withdrawer W. A slightly inferior correlation is obtained if σ_p^-(W) is used ($R = 0.9811$). A significantly poorer correlation is obtained if D and W are given equal weight, *i.e.* a plot of ΔG(**TS1**) *vs.* [σ_p(W) − σ_p^+(D)] gives $R = 0.9212$. A further lowering of the activation barrier may be possible using charged substituents, although the requisite ketenes and ketenimines will be difficult to access experimentally. If the Hammett correlation remains valid for charged species, extrapolation predicts activation energies as low as *ca.* 65 and 55 kJ mol^{-1} for the NMe_3^+/O^- and N_2^+/O^- combinations, respectively, for the imidoylketene–oxoketenimine rearrangement.

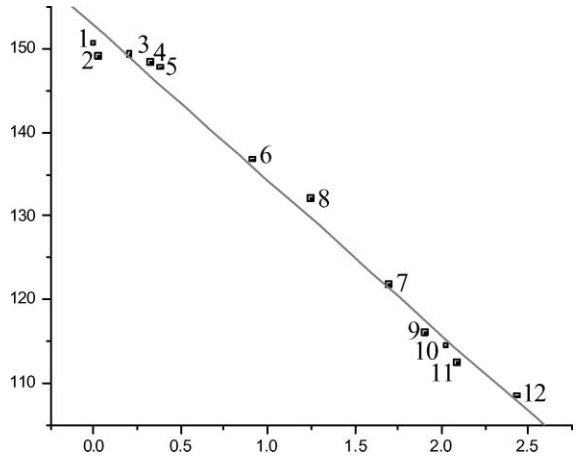

Fig. 3 . Hammett correlation of calculated activation energies (ΔG(TS), kJ mol^{-1}, ordinate) with [0.5 × σ_p(W) − σ_p^+(D)] (abscissa) for the imidoylketene **1**–oxoketenimine **2** rearrangements (eqn. 3) of the form ΔG(**TS1**) = −18.45 [0.5 × σ_p(W) − σ_p^+(D)] + 152.66 (R = 0.9943). The D/W combinations are: 1: H/H, 2: H/F, 3: H/CHO, 4: H/CN, 5: H/NO_2, 6: OH/H, 7: NMe_2/H, 8: OH/CN, 9: NMe_2/CHO, 10: NMe_2/CN, 11: NMe_2/NO_2 and 12: NHMe/SO_2CN.

Conclusion

The activation barrier for the 1,3-phenyl group shift in imidoylketenes **1** to afford the oxoketenimine **2** *via* **TS1** as well as the corresponding barrier for the oxoketene–oxoketene rearrangement of **3** *via* **TS2** can be lowered by *ca.* 40 kJ mol^{-1} by suitable choice of substituents, the most effective combinations of neutral substituents being NMe_2 or NHMe (D on migrating group, eqn. 3 and eqn. 4) and NO_2 or SO_2CN (W on non-migrating group, eqn. 3 and eqn. 4). This lowers the free energies of activation for the phenyl shifts to below 100 kJ mol^{-1} for imidoylketenes and oxoketenes. Therefore, these rearrangements may take place at ambient temperatures.

Experimental

Calculations were carried out at the B3LYP/6-31G(d,p) level of theory using the Gaussian 03 suite of programs.[14] The energies of some of the species and transition states were also computed at the B3LYP/6-311 + G(3df,2p)//B3LYP/6-31G(d,p) level (see Table 1). Transition states were verified by intrinsic reaction coordinate calculations. Imaginary vibrational frequencies are listed in the ESI material.† All ΔG values are for 298.15 K. The entropy contributions are taken from the lower level harmonic frequency calculations (B3LYP/6-31G(d,p)). All energies are corrected for unscaled zero point vibrational energies (ZPVE).

Acknowledgements

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