# Oxoketene–oxoketene, imidoylketene–imidoylketene and oxoketenimine–imidoylketene rearrangements. 1,3-Shifts of phenyl groups†

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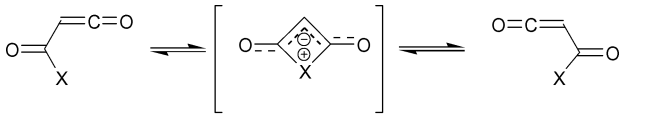
Dibenzoylketene **5** undergoes degenerate 1,3-shifts of the phenyl group between acyl and ketene carbon atoms, thus interconverting it with **6** and **7**. This 1,3-shift takes place in the gas phase under flash vacuum thermolysis (FVT) conditions, but not in solution at 110–145 °C. Imidoyl(benzoyl)ketene **13** undergoes degenerate 1,3-shift of the phenyl group on FVT, thus interconverting it with **14**, but the ketenimine isomer **15** is not formed, and none of these shifts take place in the solid state at 250 °C. Imidoyl(*p*-toluoyl)ketene **21** undergoes a 1,3-*p*-tolyl shift, interconverting it with ketene **22** but not with ketenimine **23**. The imidoyl(*p*-toluoyl)ketene rotamer **25** cyclizes to 4-toluoyloxyquinoline **28** and 4-quinolone **29**. The cyclization of imidoyl(benzoyl)ketene **13** to 4-benzoyloxyquinoline **18**, and of **25** to **28** involves 1,3-*C*-to-*O* shifts of benzoyl (toluoyl) groups. Calculations of the transition states for the transformations at the B3LYP/6-31G** level of theory are in agreement with the observed reaction preferences.

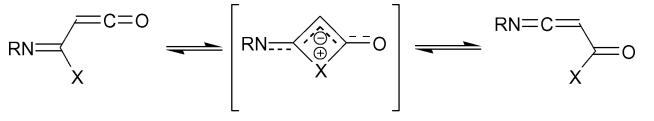
## Introduction

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

α-Oxoketenes **1** undergo a degenerate interconversion, *viz*. the α-oxoketene−α-oxoketene rearrangement (eqn. (1)).[5] Likewise, imidoylketenes **2** and α-oxoketenimines **3** can interconvert by a 1,3-shift of the α-substituent X (eqn. (2)).[6]



(1)



(2)

The dimethylamino group has the highest migratory aptitude, and this reaction takes place well below room temperature. Also phenyl groups undergo the 1,3-shift, typically under FVT conditions at temperatures around 970–1020 K in our apparatus,[3d,5a,7] and the activation barrier for this shift can be lowered dramatically by proper choice of electron-withdrawing substituents in the non-migrating, and electron-donating substituents in the migrating, phenyl group.[8]

The 1,3-migrations described in eqn. (1) have the characteristics of pseudopericyclic reactions,[3,5a] where the donor substituent X migrates in the plane of the molecule, and the reaction is facilitated when X is an electron donating group which can interact favourably with the low-lying ketene LUMO ($NR_2$, OR, SR, and halogens).[5–9] Calculations of the activation barriers for the 1,3-X shifts indicated that they are 0–32 kJ $mol^{-1}$ lower in the oxoketenes (eqn. (1)) than in the imidoylketenes.[8,10] The calculated free energies of activation, $\Delta G_{298}$, for the 1,3-shift of a phenyl group were 151 kJ $mol^{-1}$ for the α-oxoketene Ph–CO–CH=C=O, 182 kJ $mol^{-1}$ for the α-imidoylketene Ph–C(NH)–CH=C=O, and 175 kJ $mol^{-1}$ for the α-oxoketenimine Ph–CO–CH=C=NH at the B3LYP/6-311 + G(3df,2p)//B3LYP/6-31G(d) level.[8]

The benzoyl(phenylimidoyl)ketene **13** is a very attractive molecule for the purpose of a detailed understanding of the potential energy surface, since it allows us to put all energies for the various rearrangements on the same scale. Here we report experimental and computational evidence that, when both shifts are possible within the same molecule, only the oxoketene–oxoketene interconversion takes place, not the imidoylketene–oxoketenimine interconversion. Furthermore, the oxoketene–oxoketene rearrangement of the unsubstituted phenyl group takes place only in the gas phase under FVT conditions, not in solution.

## Results and discussion

### Dibenzoylketene 5 from 4-benzoyl-5-phenyl-furan-2,3-dione 4

Demonstration of the degenerate 1,3-shift in oxoketenes (eqn. (1)) by IR spectroscopy requires $^{13}C$-labelling. Furan-2,3-diones, thiophen-2,3-diones and pyrrol-2,3-diones have been used as efficient precursors of acyl-, thioacyl-, and imidoylketenes.[1,3d,6c,7,11,12]

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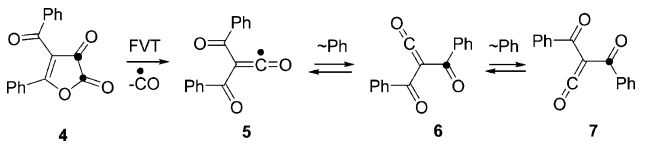
† Electronic supplementary information (ESI) available: Computational data for all calculated species. See DOI: 10.1039/b515917b

The $^{13}$C-labelled furan-2,3-dione **4** (2 × 90 at% $^{13}$C) was synthesised from [1,2-$^{13}$C]oxalic acid dichloride, which itself was prepared from commercial [1,2-$^{13}$C]oxalic acid. A cyclocondensation reaction of dibenzoylmethane and [1,2-$^{13}$C] oxalic acid dichloride afforded pure [2,3-$^{13}$C]-4-benzoyl-5-phenylfuran-2,3-dione **4** in 47% yield.

FVT reactions were carried out in the range 250–700 °C with isolation of the thermolysis products on a KBr disk in a liquid nitrogen-cooled cryostat (*ca.* −190 °C) for IR spectroscopy. The unlabelled dibenzoylketene absorbs strongly at 2130 cm$^{-1}$. A Hooke's law calculation predicts a value of 2083 cm$^{-1}$ for the labelled ketene. The labelled dibenzoylketene **5**, obtained by FVT of **4** at 260 °C (Scheme 1), shows a major absorption at 2080 cm$^{-1}$ and a minor one at 2130 cm$^{-1}$. The ratio of the two peaks was 8 : 1 (88 : 12). In other words, the degree of labelling on C3 of the furandione is retained virtually completely on the ketene carbon of **5**, *i.e.*, there is no ketene–ketene rearrangement at this temperature. In contrast, FVT at 700 °C affords two peaks at 2130 and 2080 cm$^{-1}$ in the ratio 2 : 1, thus demonstrating that the 1,3-phenyl shift interconverting the three dibenzoylketene molecules **5–7** is complete at this temperature. The ketene is stable on warm-up until *ca.* −100 °C, where the two ketene signals in the IR spectrum disappear with the same rate.

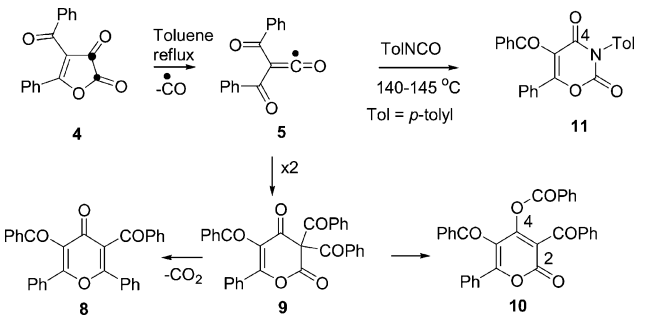



**Scheme 1**

The reaction products of ketene **5** have been described. Dry heating at 120 °C causes loss of CO and $CO_2$, and the γ-pyrone **8** is obtained exclusively.[13] Reflux in toluene causes dimerization of the initially generated dibenzoylketene to dihydropyronedione **9** and subsequent 1,3-*C*-to-*O*-benzoyl migration to afford the α-pyrone **10**.[12] By using the labelled furandione **4** (2 × 90 at% $^{13}$C), refluxing in toluene (110 °C) for 48 h afforded the [2,4-$^{13}$C]-α-pyrone **10**, the labelled carbons being identified by their high signal intensities in the $^{13}$C NMR spectrum (C2, $\delta$ 160.7 ppm; C4, 159.5 ppm). The presence of only *two* labelled carbons indicates that no 1,3-phenyl migration has taken place. The *in situ* generation of dibenzoylketene was also demonstrated by several trapping reactions of the hetero-Diels–Alder type.[14] In order to examine whether increased temperature and/or change of solvent polarity could enforce any 1,3-phenyl migration, the labelled furandione **4** was also allowed to decompose to dibenzoylketene in hot *p*-tolyl isocyanate (140–145 °C). The resulting 1,3-oxazin-2,4-dione derivative **11** was isolated in 69% yield and exhibited only *one* labelled carbon atom in the $^{13}$C NMR spectrum (C4, $\delta$ 160.5 ppm), again making evident the absence of any 1,3-phenyl migration in solution Scheme 2.

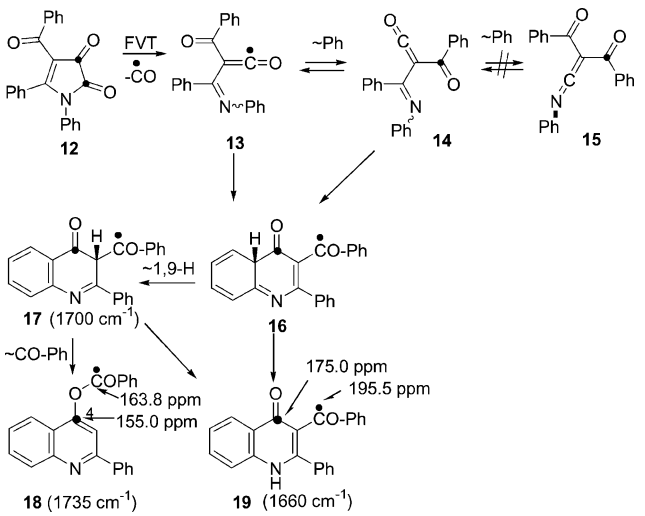
### Benzoyl(phenylimidoyl)ketene 13 from 4-benzoyl-1,5-diphenyl-pyrrole-2,3-dione 12

[2,3-$^{13}$C]Pyrrol-2,3-dione **12** (2 × **13** at% $^{13}$C) was obtained in 88% yield from the reaction between β-anilinochalcone and the labelled oxalic acid dichloride. The unlabelled benzoyl(imidoyl)ketene **13** obtained by FVT of unlabelled **12** at 510 °C absorbs strongly at 2120 in the IR spectrum.[15] The corresponding product obtained




**Scheme 2** When using $^{13}$C labelling, compound **11** is labelled on C4 only. Compound **10** is labelled on both C2 and C4.

from labelled **12** shows a strong absorption at 2120 cm$^{-1}$ and a minor peak with *ca.* 13% relative intensity at 2070 cm$^{-1}$ due to the labelled ketene **13** with *ca.* 13 at% labelling on the ketene carbon. A Hooke's law calculation predicts 2075 cm$^{-1}$ for the labelled ketene. Repetition of this thermolysis at 700 °C causes a reduction by *ca.* 50% in the intensity of the minor peak at 2070 cm$^{-1}$, thereby indicating that the ketene–ketene rearrangement **13** → **14** takes place (Scheme 3). There was no evidence for formation of the ketenimine **15** in the IR spectrum (expected in the range 2000–2050 cm$^{-1}$) but this experiment does not in itself rule out the potentially reversible formation of **15**. However, the experiment with the *p*-tolyl derivative **20** reported below rules it out.

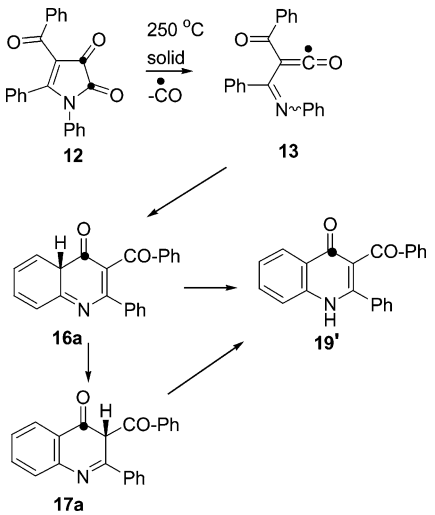



**Scheme 3** In compounds **16**–**19** the $^{13}$C labels are in either one of the two positions indicated.

Two products are formed in the preparative FVT of **12** at 650 °C, 4-benzoyloxyquinoline **18** (60%), and 4-quinolone **19** (30%). The initial (gas phase) electrocyclization of ketene **13** would lead to the intermediate **16**. A 1,5(1,9)–H shift in **16** affords a new intermediate **17**, which rearranges already in the gas phase by a 1,3-*C*-to-*O* benzoyl shift[12,16] to afford **18** (1740 cm$^{-1}$, present in the cold thermolysate at −196 °C). Intermediate **17** can be detected at 1700 cm$^{-1}$ by IR spectroscopy of the cold thermolysate (−190 °C), its intensity growing steadily with the FVT temperature from 510 to 700 °C. This peak starts being replaced by a new peak at 1670 cm$^{-1}$ due to **19** on warm-up above −45 °C, but the 1700 cm$^{-1}$ peak it is still observable at room temperature (due to the low

(13%) degree of $^{13}C$ labelling, these wavenumbers are for the $^{12}C$ isotopomers). Intermolecular H-transfer in **17** in the condensed state is a likely means of forming quinolone **19**. Compounds **18** and **19** were isolated and fully characterized. The $^{13}C$ NMR spectra reveal *two* $^{13}C$-labelled carbons in each (see data in Scheme 3), thereby confirming the interconversion of ketenes **13** and **14** by a 1,3-phenyl shift at 650 °C. However, the interconversion is not complete under these conditions. The intensity ratio of the peaks at $\delta$ 155.0 and 163.8 is *ca.* 3 : 1, and so it is for the peaks at $\delta$ 175.0 and 195.5, whereas in the unlabelled compounds these two sets have intensity ratios of *ca.* 1 : 1. Thus, there is *ca.* 50% rearrangement at 650 °C. At 510 °C there was *ca.* 20% rearrangement.

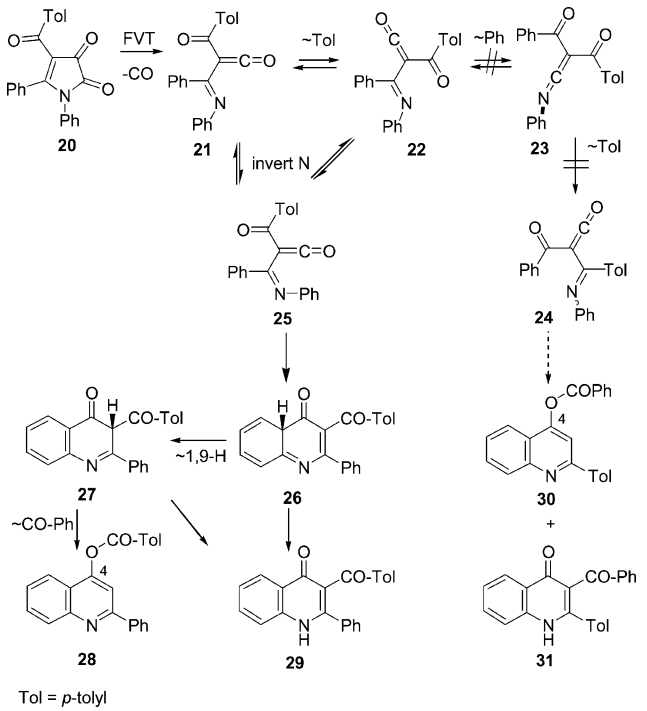
Thermolysis of **12** in the solid state at 250 °C is much simpler. Only the quinolone **19** was obtained. In the $^{13}C$ NMR spectrum of **19** only *one* labelled carbon atom was detected under these conditions (**19′**, C-4, 175.0 ppm). This is the carbon corresponding to the original ketene **13**. Thus, there is *no* ketene–ketene rearrangement by 1,3-phenyl migration in the solid state at 250 °C (Scheme 4).




**Scheme 4** Quinolone **19′** is labelled exclusively on C4.

### Toluoyl(phenylimidoyl)ketene 21 from 4-toluoyl-1,5-diphenyl-pyrrole-2,3-dione 20

FVT of pyroledione **20** allows the conclusion that ketenes **21** and **22** interconvert, but there is no further interconversion with ketenimine **23**, which would have resulted in formation of the isomeric ketene **24** (Scheme 5). FVT of **20** with IR observation at −190 °C resulted in a ketene absorbing at 2130 $cm^{-1}$ together with carbonyl absorptions at 1735 and 1660 $cm^{-1}$. The latter two absorptions correspond to two products, **28** and **29**, which were isolated from the preparative FVT of **20** at 650 °C. The isomeric products **30** and **31** which would have resulted from ketene **24**, were *not* present. Thus, it appears that the ketene–ketene interconversion, **21** → **22** is much preferred over the ketene–ketenimine interconversion **22** → **23**. This is due to a *ca.* 25 kJ $mol^{-1}$ higher activation barrier for the latter, as predicted by theoretical calculations reported below. The formation of the quinolones suggest the population of the imidoylketene conformer **25**, formed by imine group inversion.[6e] Cyclization of **25** affords the




**Scheme 5**

4a*H*-quinolone **26**, from which **27–29** can be formed by hydrogen and benzoyl group shifts (Scheme 5).

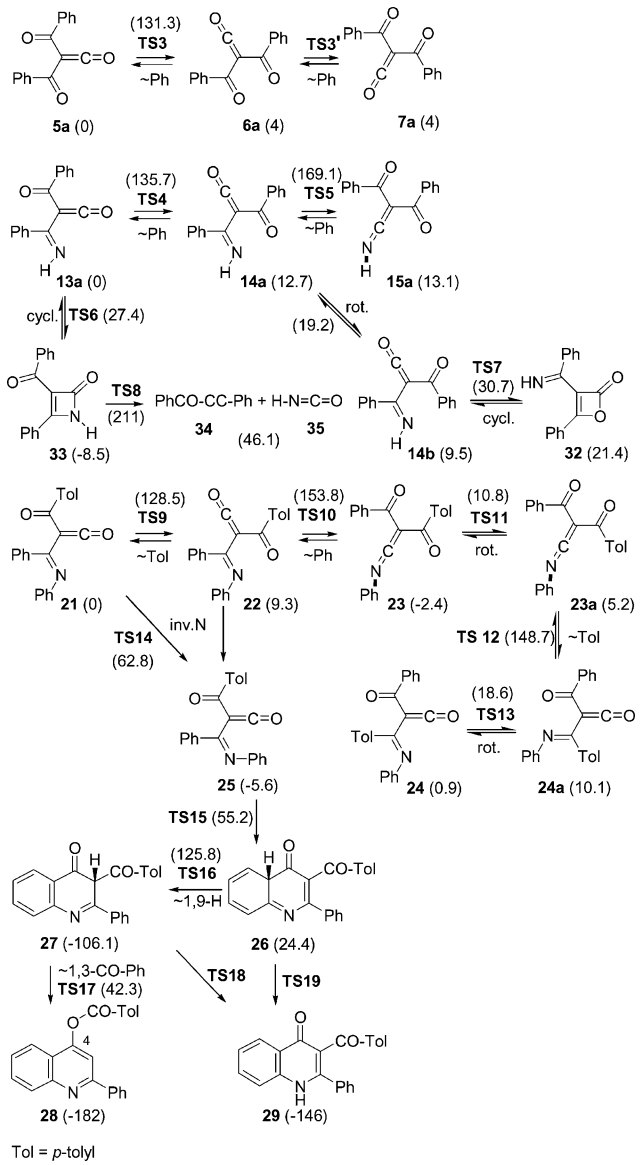
### Calculations

Calculations were carried out at the B3LYP/6-31G** level of theory using the Gaussian 03 suite of programs.[17] Transition states were verified by intrinsic reaction coordinate calculations. Imaginary vibrational frequencies are listed in the electronic supplementary information (ESI)†.

Relevant energies of ground and transition states are indicated in Scheme 6. The activation barrier for the 1,3-phenyl shift in dibenzoylketene **5a** (**TS3**) is 131 kJ $mol^{-1}$, significantly less than for the mono-benzoylketene (151 kJ $mol^{-1}$).[8] This can be ascribed to the stabilizing effect of electron-withdrawing groups, which can delocalize negative charge in the 4-membered transition state **TS1** (eqn. (1)).[8] The barrier for conversion of benzoyl(imidoyl)ketene **13a** to **14a** is, as expected, similar to that of **5a** (**TS4** = 136 kJ $mol^{-1}$), but the barrier to the ketenimine **15a** is significantly larger (**TS5** = 169 kJ $mol^{-1}$) in accord with the fact that this reaction is not observed experimentally. Ketene **13a** could also in principle cyclize to azetinone **33** and *via* **TS6** (27.4 kJ $mol^{-1}$), and ketene **14a** can undergo single-bond rotation to **14b** and then cyclize to oxetone **32** *via* **TS7** (30.7 kJ $mol^{-1}$). The oxetone has a higher energy than the ketenes and ketenimine (21.4 kJ $mol^{-1}$), but the azetinone (−8.5 kJ $mol^{-1}$) could act as a thermodynamic sink, helping to prevent the rearrangement to ketenimine **15a** *via* **TS5**. Cyclizations of this type have been considered for other oxo- and imidoylketenes,[3d,8,18] as has their fragmentations, in this case of the azetinone *via* **TS8** (211 kJ $mol^{-1}$) to benzoyl(phenyl)acetylene **34** and isocyanic acid **35**.

In the *p*-tolyl-substituted case, imidoylketene **21** has a barrier of 128.5 kJ $mol^{-1}$ (**TS9**) for the 1,3-tolyl shifts, which generates the conformer **22**. The barrier from imidoylketene **22** to the ketenimine

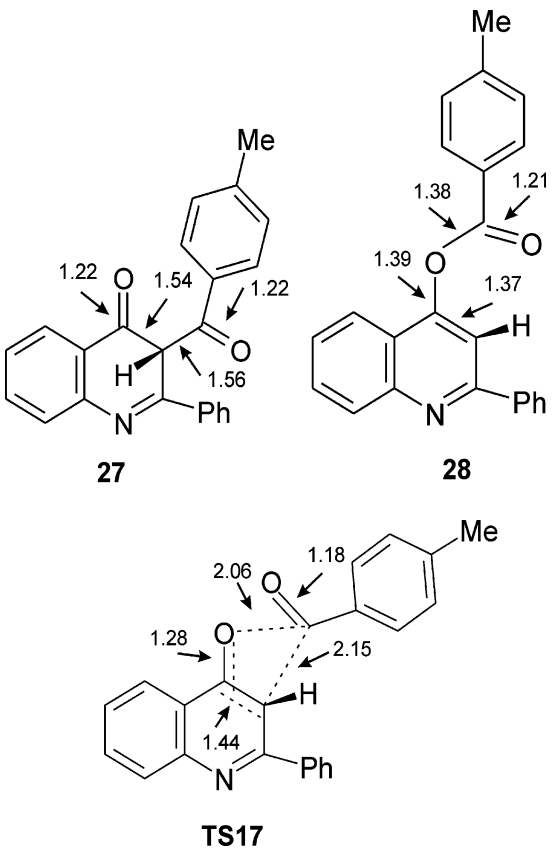



**Scheme 6** Energies relative to **5a**, **13a**, and **21** at the B3LYP/6-31G** level (ZPVE corrected) in kJ mol$^{-1}$ in parentheses. Compounds **5a–15a** are the unlabelled analogs of the $^{13}$C-labelled compounds **5–15**.

**23** is higher (**TS10** = 153.8 kJ mol$^{-1}$), thereby explaining the non-formation of **23** when other reaction channels are available to the ketenes. If ketenimine **23** had been formed, it would have been able to undergo single-bond rotation to the conformer **23a**, and 1,3-shift of the tolyl group to give imidoylketene **24a** (**TS12** = 149 kJ mol$^{-1}$). **TS11** and **TS13** are rotational transition states.

Imidoylketene **21** can undergo imine group inversion[6e] to give the conformer **25** *via* **TS14** (62.8 kJ mol$^{-1}$). **25** has the correct orientation for 6-π-electron electrocyclization to the 4a*H*-quinolone **26** with an activation barrier of only 60 kJ mol$^{-1}$ (**TS15** = 55.2 kJ mol$^{-1}$). Since **26** has lost all aromaticity, this cyclization is endothermic by 30 kJ mol$^{-1}$. A 1,9(1,5)-H shift in **26** affords the 3*H*-quinolone **27**. This reaction has an activation barrier of *ca.* 100 kJ mol$^{-1}$ (**TS16** = 125.8 kJ mol$^{-1}$) and is highly exothermic (130.5 kJ mol$^{-1}$).

The 1,3-*C*-to-*O* acyl shift from **27** to **28** has a barrier of *ca.* 148 kJ mol$^{-1}$ (**TS17** = 42 kJ mol$^{-1}$), and the reaction is exothermic by 76 kJ mol$^{-1}$. There has been much discussion of the mechanism(s) of thermal 1,3-acyl migrations in the literature, and both free radical and ion pair mechanisms have been proposed.[16b,c] 1,3-Shifts of H and alkyl are "forbidden" by the rules of orbital symmetry, but π-bonded substituents are allowed to undergo 1,3-shifts with inversion at the migrating atom.[19] In the case of the planar acyl group, inversion cannot be determined experimentally. The inversion utilising a p orbital corresponds to the introduction of a disconnection in the loop of orbitals. This is also the case in pseudopericyclic reactions, where an orthogonal lone pair takes the role of a p orbital with the wrong symmetry, thereby making the reaction symmetry allowed.[3a,20] We have described another case of a pseudopericyclic reaction where a lone pair on a carbonyl oxygen is involved.[20b] Similarly, the disconnection arising from two orthogonal p orbitals makes the 1,3-shifts to the central carbon atom in ketenes allowed.[5a] The 1,3-acyl shift *via* **TS17** can be understood in this light, *viz.* as an inversion at the site of the p orbital on the carbon of the migrating C=O group, and this is caused by a pseudopericyclic interaction between a lone pair on oxygen at C-4 and the unoccupied π* orbital of the migrating C=O group. In **TS17** the carbonyl oxygen at C4 of the quinolone ring has attacked the carbon atom of the migrating C=O group. The attacking C=O bond has been lengthened only marginally from 1.22 to 1.28 Å and is still far from the single-bond value in **28** (1.39 Å). In contrast, the C–C bond in **27** has lengthened dramatically, from 1.56 to 2.15 Å. These bond lengths suggest that it is indeed the




**Scheme 7** Structures **27**, **28**, and the transition state for the 1,3-*C*-to-*O* acyl shift **TS17** showing essential bond lengths in Å.

oxygen lone pair at O(C4) that is attacking and forming a bond to the migrating C=O group, and C(4)=O is still largely double-bonded. The forming C–O bond to the migrating group is 2.06 Å, and the breaking C–C bond is 2.15 Å. The structures of **27**, **28**, and **TS17** with relevant bond lengths are shown in Scheme 7.

The deep minimum in which **27** resides explains the observation of the analog **17** at 1700 $cm^{-1}$ in the solid-state IR spectrum (see Scheme 3). The conversion of either the 4a*H*- or 3*H*-quinolones **26** or **27** to the 1*H*-quinolone **29** formally involves 1,3-H shifts, which are expected to have very high activation barriers, and in fact neither of these transition states, **TS18** and **TS19**, was located computationally. These reactions are likely to take place by intermolecular *C*-to-*N* H-transfer in the solid state.

## Conclusion

Mild FVT of furandione **4** generates dibenzoylketene **5**. $^{13}C$-labelling demonstrates that **5** undergoes rapid, degenerate 1,3-shifts of the phenyl group, thereby interconverting it with the isotopomeric ketenes **6** and **7**, which were observed directly by low temperature IR spectroscopy. However, product studies demonstrate that this 1,3-phenyl shift does not take place in solution at 110–145 °C, presumably because formation of the products (**8**, **10**, and **11**) is faster. Imidoyl(benzoyl)ketene **13** undergoes degenerate 1,3-shift of the phenyl group on FVT, thus interconverting it with **14**, but the ketenimine isomer **15** is not formed, or if it is, the reaction is reversible and lies entirely on the side of **14**. Calculations agree that the barrier for **14** → **15** (**TS5**, 169 kJ $mol^{-1}$) is significantly higher than that for **13** → **14** (**TS4**, 136 kJ $mol^{-1}$). The reaction products from **13** are the 4-benzoyloxyquinoline **18** and the 4-quinolone **19**. None of these 1,3-shifts take place in the solid state at 250 °C, where the uniquely labelled 4-quinolone **19′** is formed. Imidoyl(*p*-toluoyl)ketene **21** undergoes a 1,3-*p*-tolyl shift, interconverting it with the identical imidoyl(*p*-toluoyl)ketene **22** but not with ketenimine **23**. Had **23** been formed, it should have been able to to undergo a 1,3-phenyl shift to give imidoyl(benzoyl)ketene **24**, products from which were not observed. The calculated energy of transition state **TS10** for **22** → **23** is significantly higher than that of **TS9** for **21** → **22** (153.8 *vs.* 128.5 kJ $mol^{-1}$). The imidoyl(*p*-toluoyl)ketene rotamer **25** cyclizes to 4-toluoyloxyquinoline **28** and 4-quinolone **29**. The cyclization of imidoyl(benzoyl)ketene **13** to 4-benzoyloxyquinoline **18**, and of **25** to **28** involves 1,3-*C*-to-*O* shifts of benzoyl (toluoyl) groups with a calculated barrier of *ca.* 148 kJ $mol^{-1}$ (*e.g.* **17** → **18** and **27** → **28** *via* **TS17**).

## Experimental

The apparatus and procedures used for flash vacuum thermolysis (FVT) and low temperature IR spectroscopy were as described earlier.[15] Preparative FVT was carried out in unfilled quartz tubes (2 cm Ø) in a 25 cm tubular oven at $10^{-3}$–$10^{-4}$ mbar, and the products were isolated in a U-tube cooled in liquid nitrogen.

### [1,2-$^{13}C_2$]Oxalic acid dichloride

[1,2-$^{13}C_2$]Oxalic acid dihydrate (0.25 g, 2 × 90 at% $^{13}C$, from Stohler, Switzerland) was dehydrated at 70–75 °C (12 mbar) for 48 h. Phosphorous pentachloride (6.5 g) was then added, and the solid reaction mixture, protected from moisture by a $CaCl_2$ tube, was allowed to stand for 72 h at rt.[21] The liquid formed was separated from the solid residue by pipetting and distilled with the aid of a microdistillation apparatus. The fraction boiling at 60–65 °C contains the oxalic acid dichloride (1.08 g, 50%), which was used without further purification.

**[2,3-$^{13}C_2$]-4-Benzoyl-5-phenylfuran-2,3-dione 4.** (2 × 90 at% $^{13}C$), was prepared following the procedure for the unlabelled compound.[13] 0.45 g (3.6 mmol) of [1,2-$^{13}C$]$_2$oxalic acid dichloride are added with the aid of a syringe to a solution of 0.7 g (3.1 mmol) of dibenzoylmethane (purchased from Sigma-Aldrich) in dry ether (4 mL) at rt. After 3–5 h yellow needles precipitate, which after careful washing with dry ether to completely remove sticking oxalic acid dichloride are obtained as bright yellow needles (0.41 g, 47%); mp: 120 °C (decomp). IR-, $^1H$- and $^{13}C$ NMR spectroscopic data of unlabelled **4** see ref.[13,22] In the $^{13}C$ NMR spectrum of [2,3-$^{13}C_2$]-**4** the signals at $\delta$ 153.3 ppm (C-2) and 175.7 ppm (C-3) show strongly enhanced intensities. Exact assignments of all carbon atoms in furan-2,3-dione **4** and pyrrol-2,3-dione **12** have been made on the basis of long-range coupled $^{13}C$ NMR spectra.[19] Therefore, the positions of the labelled carbons could be located unequivocally from their high intensities as indicated in Chart 1.

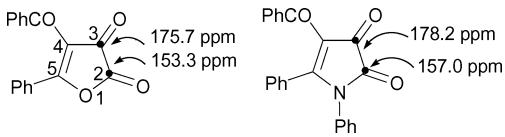



**Chart 1**

**FVT of 4.** FVT of [2,3-$^{13}C_2$]-**4** (2 × 90 at% $^{13}C$) with IR detection of the neat thermolysates at −196 °C was carried out in the range 250–700 °C. Details are described in the main text. IR: unlabelled dibenzoylketene **5a** 2130 $cm^{-1}$; $^{13}C$-labelled dibenzoylketene **5** 2080 $cm^{-1}$. CO does not appear in the spectrum at this temperature. The neat ketene is stable on warm-up until *ca.* −100 °C.

**Thermolysis of [2,3-$^{13}C_2$]-4 in toluene.** A portion of [2,3-$^{13}C_2$]-**4** (0.11 g; 0.4 mmol; 2 × 13.4 at% $^{13}C$) was refluxed in dry toluene (3 mL) for 90 min. The solution is then allowed to stand for 48 h at rt. After filtration from a tiny amount of pyrone **8**, the toluene is evaporated and the oily residue crystallizes from triturating with ethanol to give 44 mg (44%) of [2,4-$^{13}C_2$]-**10**. For analytical and spectroscopic data of unlabeled **10** see ref.[12,13,14a] $^{13}C$ NMR ($CDCl_3$): $\delta$ 190.5, 189.3 (benzoyl-C), 163.8 (OCOPh), 162.4 (C-6), 160.7 (C-2, labelled), 159.5 (C-4, labelled), 116.0, 115.0 (C-3, C-5).

**[4-$^{13}C$]-5-Benzoyl-6-phenyl-3-*p*-tolyl-1,3-oxazin-2,4-dione 11.** A portion of [2,3-$^{13}C_2$]-**4** (40 mg; 0.14 mmol; 2 × 13.4 at% $^{13}C$) was added to *p*-tolyl isocyanate (0.15 mL) kept at 140–145 °C. After the evolution of carbon monoxide is finished, the reaction product starts to precipitate. After cooling to rt the solid formed is isolated by suction filtration, washed with dry ether and recrystallized from acetic acid to afford 38 mg (69%) of [4-$^{13}C$]-**11**. For analytical and spectroscopic data of **11** see ref. 14*a*. $^{13}C$ NMR (ring carbons, $d_6$-DMSO): $\delta$ 190.5 (benzoyl-C), 160.5 (C-4, labelled), 159.5 (C-2), 147.5 (C-6), 113.2 (C-5).

**[2,3-$^{13}C_2$]-4-Benzoyl-1,5-diphenyl-1H.-pyrrol-2,3-dione 12.** (2 × 13.4 at% $^{13}C$) was prepared following the procedure for the unlabelled compound.[14a] 70 mg of [1,2-$^{13}C_2$] oxalic acid dichloride, dissolved in dry ether (0.5 mL), was added to a solution of 0.1 g (0.28 mmol) β-anilinochalcone[23] in dry ether (2 mL). The solution turns red and the pyrroldione crystallizes from scratching. After suction, the deeply red coloured product is carefully washed with dry ether to give 0.104 g (88%) of [2,3-$^{13}C_2$] **2**. Analytical and spectrscopic data see ref. 14*a*. $^{13}C$ NMR (ring carbons, $CDCl_3$): $\delta$ 187.8 (benzoyl-C), 178.2 (C-3, labelled), 173.2 (C-5), 157.0 (C-2, labelled), 112.6 (C-4) (see Chart 1 for labelled atoms).

**FVT of 12.** [2,3-$^{13}C$]Pyrrol-2,3-dione **12** (2 × 13 atom-% $^{13}C$) was subjected to FVT at 510 and 700 °C with IR detection at −196 °C. IR: unlabelled benzoyl(imidoyl)ketene **13a**: 2120 $cm^{-1}$; $^{13}C$-labelled **13**: 2070 $cm^{-1}$. The neat ketene is stable until −70 °C on warm-up. Further details are given in the main text.

[2,3-$^{13}C$]Pyrrol-2,3-dione **12** (200 mg; 2 × 13 atom-% $^{13}C$) was also subjected to preparative FVT at 650 °C (sublimation temperature 175 °C; 1.5 h). The products were collected in a U-tube cooled in liq. $N_2$ and after the end of the reaction taken up in $CH_2Cl_2$. Evaporation afforded 182 mg yellow crude product, which was separated into two substances by preparative thin layer chromatography on alumina/$CH_2Cl_2$, *viz.* 4-benzoyloxyquinoline **18**, $R_f = 0.5$; 60% yield, and 4-quinolone **19**, $R_f = 0$; 30% yield.

**4-Benzoyloxyquinoline 18.** Recrystallization from petroleum ether yielded 100 mg (60%) white needles, mp 96 °C (lit.[24] 90–91 °C). The compound exists in two modifications. After melting and resolidifying, the substance remelted at 110–111 °C (white rhombs); $^{13}C$ NMR (DMSO-$d_6$, 400 MHz) $\delta$ 157.0 (C2), 111.2 (C3), 155.0 (C4), 121.1 (C4a), 129.2 (C5), 127.0 (C6), 130.5 (C7), 121.1 (C8), 149.1 (C8a), 163.8 (benzoyl-CO), 138.0 (C1′ (phenyl ring at C2)), 127.1 (C2′), 129.0 or 128.7 (C3′), 129.8 (C4′), 128.1 (C1″ (benzoyloxy group at C4)), 130.0 (C2″), 128.7 or 129.0 (CC3″), 134.4 (C4″); assignments are based on the $^1H$-coupled spectrum. The two carbons at $\delta$ 155.0 and 163.8 ppm showed enhanced intensity due to the $^{13}C$ labelling, with an intensity ratio of *ca.* 3 : 1 (*ca.* 1 : 1 for the unlabelled compound); MS *m/z* 325 ($M^+$, 15%), 106 (9), 105 (100), 77 (33).

Anal. Calcd for $C_{22}H_{15}NO_2$: C, 81.21; H, 4.65; N, 4.30. Found C, 81.39; H, 4.71; N, 4.46.

Standing in an aqueous methanolic solution for several days caused solvolysis to 2-phenylquinolin-4-one, mp 251 °C (lit.[25] 254 °C), identified by direct comparison with an authentic[23] sample; $^{13}C$ NMR (DMSO-$d_6$, 400 MHz) $\delta$ 176.9 (C4), 149.9 (C2), 140.5 (C1′), 134.2 (C8a), 131.6 (C7), 130.2 (C4′), 128.8 (C3′ or C2′), 127.3 (C2′ or C3′), 124.8 (C4a), 124.6 (C5), 123.1 (C6), 118.6 (C8), 107.3 (C3). Assignments are based on the $^1H$-coupled spectrum.

**3-Benzoyl-2-phenylquinolin-4-one 19.** Recrystallization from ethanol afforded 54 mg (30%) white leaves, mp 293–295 °C. An authentic sample[26] had mp and mixed mp 295 °C. $^{13}C$ NMR (DMSO-$d_6$, 400 MHz) $\delta$ 195.5 (benzoyl-CO), 175.0 (C4), 149.3 (C2), 139.8 (C1′ phenyl ring at C2)), 137.9 (C1″ (benzoyl group)), 133.5 (C8a), 132.8 (C4″), 132.2 (C7), 129.8 (C4′), 128.8, 128.5, 128.4, 128.3 (C2′, C2″, C3′, C3″), 124.73 (C5), 124.69 (C4a), 123.8 (C6), 120.2 (C3), 118.7 (C8); assignments are based on the $^1H$-coupled spectrum. The two carbons at $\delta$ 175.0 and 195.5 ppm showed enhanced intensity due to the $^{13}C$ labelling, with an intensity ratio of *ca.* 3 : 1. At 510 °C this ratio was *ca.* 5.5 : 1. In the the unlabelled compound this ratio was *ca.* 1 : 1. MS *m/z* 326 (16), 325 ($M^+$, 74), 324 (25), 297 (22), 296 (100), 248 (38), 165 (10), 163 (12), 105 (16), 77 (36).

**Thermolysis of neat 12.** A sample of [2,3-$^{13}C_2$]-**12** (50 mg; 0.14 mmol) was heated to 250 °C until the evolution of CO had ceased. After cooling to rt, the residue was triturated with ether, and the resulting crude product was recrystallized from acetic acid to give 26 mg (58%) [4-$^{13}C$]-3-Benzoyl-2-phenylquionlin-4-one **19′** labelled only on C4. For analytical and spectroscopic data see refs.14*a*, 24. $^{13}C$ NMR (DMSO-$d_6$) $\delta$ 195.5 (benzoyl-CO; unlabelled), 175.0 (C-4, $^{13}C$-labelled).

**1,5-Diphenyl-4-(*p*-toluoyl)pyrrol-2,3-dione 20.** was prepared using a procedure analogous to that for **12**;[14a,15] mp 171–173 °C, $^1H$ NMR ($CDCl_3$) 2.38 (s, 3H), 7.02–7.05 (2 H, tolyl-*meta*), 7.19–7.22 (6 H, phenyl), 7.30–7.34 (4 H, phenyl), 7.72 (*d*, $J = 8.1$ Hz, 2 H, tolyl-*ortho*); $^{13}C$ NMR ($CDCl_3$) 187.4 (CO), 178.5 (C3), 172.5 (C5), 157.0 (C2), 112.9 (C4), 21.2, 123.7–144.0 (aromatic signals).

**FVT of 20**

**1,5-Diphenyl-4-(*p*-toluoyl)pyrrol-2,3-dione 20.** (200 mg) was subjected to preparative FVT at 650 °C (sublimation temperature 180 °C; 2 h). The products were collected in a U-tube cooled in liq. $N_2$ and after the end of the reaction taken up in $CH_2Cl_2$. Filtration afforded 20 mg (10%) of almost insoluble quinolone **29**, and evaporation of the filtrate and recrystallization from petroleum ether afforded 80 mg (43%) of 2-phenyl-4-(*p*-toluoyloxy)quinoline **28**. A $^1H$ NMR spectrum of the crude FVT product demonstrated that **28** and **29** accounted for *ca.* 90% of the material in a ratio of 30 : 70. The mass spectra of **28** and **29** clearly show that no interchange of phenyl and tolyl groups had taken place: the toluoyl group gives rise to characteristic peaks at *m/z* 119; the corresponding benzoyl peaks in **18** and **19** are at *m/z* 105. There were no detectable *m/z* 105 peaks in the mass spectra of **28** and **29**.

**2-Phenyl-4-(*p*-toluoyloxy)quinoline 28.** $R_f = 0.5$ (alumina/$CH_2Cl_2$); mp 116–117 °C; $^1H$ NMR (DMSO-$d_6$, 400 MHz) δ 2.46 (s, $CH_3$), 7.49 (d, 2 H, *J* 8.0 Hz), 7.52–7.59 (m, 3 H), 7.61–7.65 (m, 1 H), 7.83–7.88 (m, 1 H), 7.96 (d, 1 H, *J* 8.3 Hz), 8.17 (d, 1 H, *J* 7.5 Hz), 8.19 (d, 2 H, *J* 8.0 Hz), 8.25 (s, 1 H), 8.29–8.32 (m, 2 H); MS *m/z* 339 ($M^+$, 9%), 120 (9), 119 (100), 91 (20).

A sample of **28** was solvolysed with aq. methanol as described for **18** above to afford 2-phenylquinolin-4-one, mp 251 °C, identified by direct spectral comparison with the sample described above.

**2-Phenyl-3-(*p*-toluoyl)quinolin-4-one 29.** mp 331 °C; $^1H$ NMR (DMSO-$d_6$, 400 MHz) $\delta$ 2.33 (s, $CH_3$), 7.22 (d, 2 H, *J* 8.0 Hz), 7.39–7.47 (m, 6 H), 7.67 (d, 2 H, *J* 8.0 Hz), 7.74–7.75 (m, 2 H), 8.09 (d, 1 H, *J* 7.9 Hz), 12.09 (s, 1 H); MS *m/z* 340 (18), 339 ($M^+$, 71), 338 (24), 311 (25), 310 (100), 248 (36), 165 (10), 119 (27), 91 (42), 65 (13). The identity of this compound follows from the analogy with **19**.

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