Imidoylketene dimerization and rearrangement†

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FVT of pyrroledione **10** affords the *NH*-imidoylketene **11**, which is characterized by its matrix isolation IR spectrum (2117 cm^{-1}). On warming above 170 K, **11** dimerizes to the oxazinone **13**, the X-ray crystal structure of which is reported. Imidoylketene **11** also undergoes a (reversible) 1,3-phenyl shift to afford the detectable α-oxoketenimine **16** (2062 cm^{-1}) which at FVT temperatures above 400 °C, isomerizes to 2-cyano-2-phenylacetophenone **18** (optimally at 700 °C). Moreover, imidoylketene **11** can cyclize to azetinone **19**, detectable at FVT temperatures up to 570 °C, which undergoes cycloreversion to diphenylacetylene **20** and isocyanic acid (HNCO) **21**. Energy profiles calculated at the B3LYP/6-31G** level for the unsubstituted imidoylketene, the diphenylimidoylketene **11** and the *N-tert*-butylimidoylketene are also reported.

Introduction

Ketenes are highly useful synthetic intermediates.[1,2] Few ketenes are stable at room temperature, and in the absence of another reaction partner, they will dimerize. The dimers can be useful synthetic intermediates too, sometimes as reservoirs for the ketenes themselves *via* thermal dedimerization reactions.[2,3] α-Oxoketenes **1** usually dimerize to form pyrones **2**, formally in a [2+4] cycloaddition reaction involving a ketene C=C bond as dienophile. Computational studies by Birney *et al.* have established the pseudopericyclic nature of related [2+4] cycloaddition reactions of ketenes.[4] A second mode of dimerization of α-oxoketenes involves the ketene C=O bond as dienophile and appears to be favoured under conditions of steric hindrance of the C=C=O function. Thus, dipivaloylketene **1a** dimerizes at room temperature to the 1,3-dioxinone **3a**. Depending on reaction conditions, another mode of dimerization of **1a**, involving a straightforward addition of one molecule of the oxoketene to a pivaloyl C=O group in the other, is also possible. Both dimers dedimerize on flash vacuum thermolysis (FVT) and thus can serve as reservoirs for ketene **1**.[2,3] Methoxycarbonyl(pivaloyl)ketene **1b** undergoes analogous dimerization across the ketene C=O group to afford **3b** (Scheme 1).[5]

Considerably less is known about the chemistry of imidoylketenes, largely because of the occurrence of facile isomerizations. Alkylimidoylketenes **4** carrying an α-hydrogen atom undergo a 1,5-H shift to afford iminoacroleins **5**, which may isomerise further.[6] Imidoylketenes may also undergo 1,3-shifts of the α-substituents X to generate α-oxoketenimines,[7] as discussed below (eqn. (1)). Moreover, *N*-arylimidoylketenes **4** undergo a facile and preparatively useful cyclization to afford quinolones **6**, often in high yields.[8]

However, Chuche and coworkers achieved the isolation of the imidoylketene dimer **8a** from **7a**.[9] This corresponds to the normal behaviour of the ketene C=C bond acting as the dienophile. Very recently, Zhou and Birney have shown that the *N*-propyl analogue **7b** undergoes C=C addition to give **3b** in *ca.* 15% yield, whereas the *N*-unsubstituted imidoylketene **7c** affords the ketene C=O adduct **9** in *ca.* 7% yield.[10] Smalley and coworkers similarly reported the formation of 3-(2-aminophenyl)benzo[*d*][1,3]oxazin-1-one from the putative
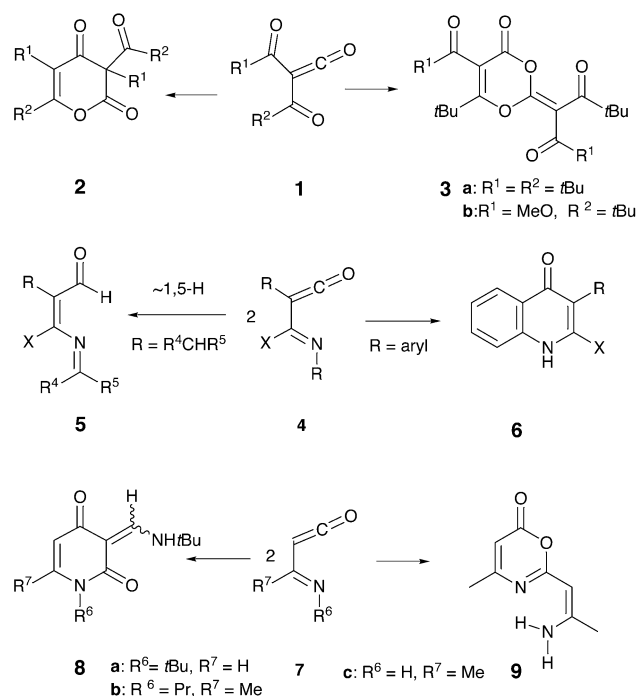
imidoylketene by ring opening of benzazetinone.[11] Detailed calculations of the transition structures for the two types of dimerization, involving addition to C=C and C=O bonds, respectively, demonstrated that both followed the minimum energy paths, and both were rationalized as pseudopericyclic reactions with planar transition states.[10]

Here we report the first direct observation of an *NH*-imidoylketene (**11**), its dimerization involving the ketene C=O bond as dienophile, its isomerization to the oxoketenimine, **16** and its cyclization to azetinone and cleavage of the latter.

Results and discussion

Observation and dimerization of the imidoylketene

FVT of the pyrrole-2,3-dione **10** at temperatures above 325 °C resulted in the loss of CO (absorbing at 2138 and 2149 cm^{-1}) and formation of the imidoylketene **11**, characterized by an intense absorption at 2117 cm^{-1} in the IR spectrum (Ar matrix, 10 K, Fig. 1) or at 2112 cm^{-1} as a neat solid at 77 K. This absorption is
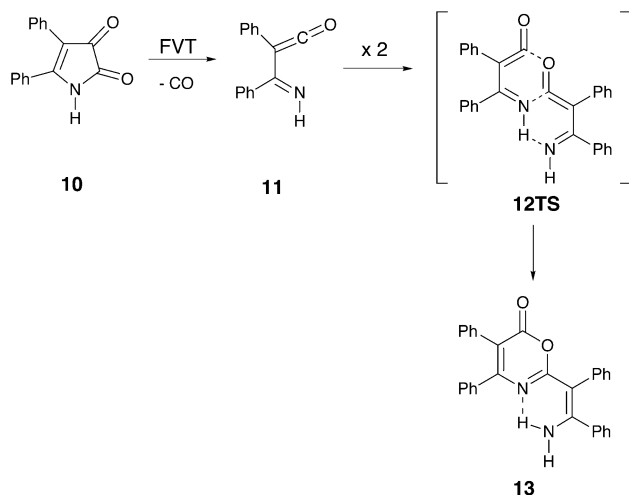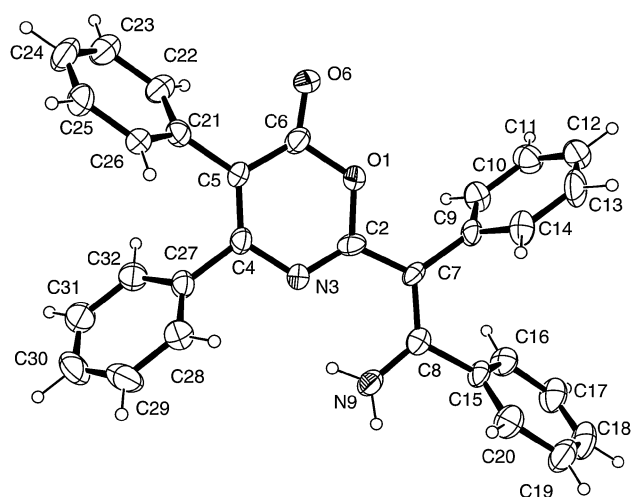
Scheme 1
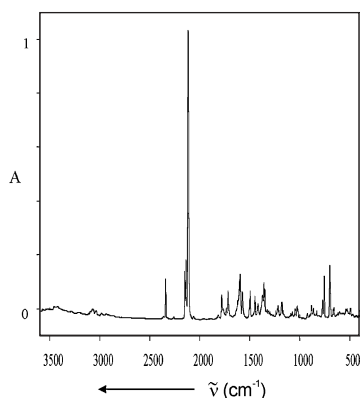
Fig. 1 FTIR spectrum of imidoylketene **11** (Ar matrix, 10 K). The strongest absorption of **11** is at 2117 cm^{-1}. Weaker bands at 2139 and 2149 cm^{-1} are due to CO. When **11** is isolated without Ar at 70 K, its main absorption is at 2112 cm^{-1}, and the CO bands are missing. The band at 2340–2345 cm^{-1} is due to a minor amount of CO_2. Absorbance (*A*) in arbitrary units.

Fig. 2 ORTEP drawing of the crystal structure of **13**.

in good agreement with that computed at the B3LYP/6-31G** level, where the ketene stretch is the only calculated strong band (2119 cm^{-1}, 904 km mol^{-1}). It is noteworthy that the calculated intensity of the NH band is very small (3330 cm^{-1}, 1 km mol^{-1}), indeed this band is barely visible in the experimental spectrum. For further details of the calculated spectrum, see the electronic supplementary information.† Doubling of several bands in the experimental IR spectrum is probably due to the presence of more than one conformer of **11** in the matrix (see the calculated energy profile in Fig. 4 below).

The disappearance of the starting material **10** was complete at an FVT temperature of *ca.* 570 °C. The ketene remained observable in the IR spectrum of the neat solid on warm-up till above 190 K, but its intensity decreased rapidly above 170 K due to dimerization. The dimer was isolated as lemon-yellow rhombohedral crystals in a preparative FVT experiment under the same conditions. The IR spectrum of the matrix-isolated dimer confirmed that this compound was formed on dimerization of the ketene above 170 K. The ^{13}C NMR spectrum of the dimer indicated C1 symmetry. The elemental analysis and strong carbonyl absorption at 1700 cm^{-1} are consistent with a 1,3-oxazinone structure **13** (Scheme 2). Notably, the two NH protons appear at widely different chemical shifts, 5.3 and 10.4 ppm (both broad), which can be ascribed to one of them being engaged in a strong hydrogen bond to the oxazine nitrogen N3 in **13**. This structure was confirmed by an X-ray crystal analysis (Fig. 2). The molecular backbone is virtually

planar, and the length of the intramolecular hydrogen bond is 1.99 Å. The other hydrogen atom of the amino group is involved in intermolecular H-bonding with the C=O group (O6) in a neighbouring molecule (see the ESI document).† The formation of **13** is depicted in Scheme 2 as occurring *via* a [2+4] cycloaddition of one ketene molecule to the ketene C=O group of another *via* the transition state **12TS**. The calculations by Zhou and Birney demonstrate that this mode of dimerization is favoured in *NH*-imidoylketenes due to a stabilization of the transition state by hydrogen bonding.[11]

FVT of the dimer **13** at 710 °C generated a small amount of a ketene absorbing at 2117 and 1659 cm^{-1}. This is probably not ketene **11**, but a new ketene formed by electrocyclic opening of the oxazinone ring in **13**. We have investigated similar ring opening reactions of oxazinones[12] and will publish them in a separate paper.

Rearrangement

It is known that α-imidoylketenes **14** and α-oxoketenimines **15** can interconvert by a 1,3-shift of the α-substituent, X (eqn. (1)).[7]
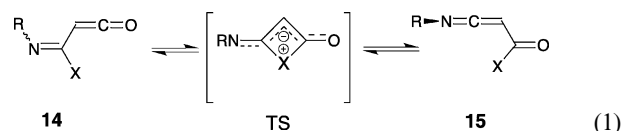
This reaction, analogous to the α-oxoketene–α-oxoketene interconversion,[13] is particularly facile when X is an electron donating group which can interact favourably with the low-lying ketene LUMO (NR$_2$, OR, SR, and halogens).[7,13,14] The dimethylamino group has the highest migratory aptitude, and the calculated activation barrier for **14** → **15** (X = NMe$_2$, R = R′ = H) is 62 kJ mol^{-1}.[7b] Thus, this reaction will take place below room temperature.[8] However, phenyl groups also undergo the 1,3-shift, typically under FVT conditions at temperatures around 970–1020 K in our apparatus.[14] Further computational studies of the activation barriers for 1,3-shifts of a wide range of α-substituents in α-oxoketenes, α-imidoylketenes and α-oxoketenimines will be published.[15]

Further FVT experiments with matrix isolation, as well as GC-MS of the products, revealed that the intensity of the imidoylketene **11** diminished above 600 °C, although it was still easily detectable at 850 °C. The isomeric nitrile **18** was formed in its place. GC-MS analysis established the optimal temperature for formation of **18** as 700 °C. Compound **18** was also identified by direct comparison of IR and NMR spectra with authentic material.[16] A 1,5-hydrogen shift in ketenimine **16** generates hydroxynitrile **17**, which is a tautomer of **18**. The

Scheme 2

existence of a solvent dependent mixture of two *Z*/*E* isomers of enol **17** (**17a** and **17b**) and ketone **18** has been reported,[16b,c] and our own NMR measurements support a ratio of 80 : 8 : 12 of the two isomers of enol **17** and ketone **18** (DMSO-d_6 solution).

The ketenimine **16** was itself observable as a weak peak at 2062 cm^{-1} in the matrix IR spectra at very mild FVT temperatures, 350–500 °C; the imidoylketene peak at 2117 cm^{-1} always remained the strongest peak. The reason for this is easily understood: although more ketenimine **16** should be formed in equilibrium with ketene **11** at higher temperatures, **16** is removed by isomerization to the nitrile **18**. *N*-Unsubstituted ketenimines always tautomerize very easily to nitriles under FVT conditions, probably due to wall-catalyzed reactions.[17] An analogous reaction is known: generation of the ketenimine **7a** above 700 °C results in elimination of isobutene and rearrangement to the corresponding ketenimine, which isomerizes to the tautomeric mixture of 3-oxopropionitrile and 3-hydroxyacrylonitrile.[6a]

Furthermore, a second isomerization pathway with a lower activation energy also removes imidoylketene **11** and therefore also hinders any build-up of ketenimine **16**: the cyclization of **11** to azetinone **19**. The latter compound is observable by means of a weak peak at 1814 cm^{-1} in the matrix IR spectra only at the mildest FVT temperatures, 325–400 °C. The weakness of this peak can be ascribed to a fragmentation to diphenylacetylene **20** and HNCO **21** (Scheme 3 and Fig. 4). Diphenylacetylene **20** was identified by GC-MS comparison with authentic material, its yield increasing with the temperature, and HNCO was identified by its characteristic matrix IR spectrum (2259 cm^{-1}). The rearrangement and fragmentation modes leading to **18** and **20** became major reactions above 700 °C. In addition, benzonitrile was always formed as a by-product in the high temperature range. The mechanism of formation of benzonitrile is not known.

We have calculated the energy profiles for the relevant rearrangements of the unsubstituted imidoylketene **11a** (Fig. 3), the diphenylimidoylketene **11** (Fig. 4), and the *N*-*tert*-butyl-phenylmethylimidoylketene **11b** (Fig. 5) at the B3LYP/6-31G** level of theory. The energies of some of the species and transition states (TS2) were also computed at the 6-311+G(3df,2p)//B3LYP/6-31G* level. Transition states were verified by intrinsic reaction coordinate calculations and imaginary vibrational frequencies (listed in the electronic supplementary information).† Part of the energy profile of the unsubstituted compounds, including ketene **11a**, ketenimine **16a** and azetinone **19a** has been calculated previously at
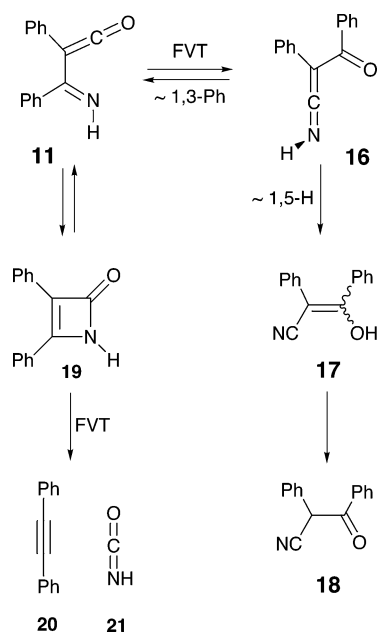
the MP4(SDQ)/6-31G**//MP2/6-31G** level.[18] Our results (Fig. 3) are in good accord. The *N*-*tert*-butyl derivative in Fig. 5 is a model for the corresponding *N*-adamantyl-phenylmethyl derivative, which has been the subject of a previous investigation, where the thermal conversion of the *N*-adamantylimidoylketene to the *N*-adamantyloxoketenimine, the cyclization of *N*-adamantylimidoylketene to the *N*-adamantylazetinone (observed at 1814 and 1819 cm^{-1} in the Ar matrix IR spectrum), and the fragmentation of the latter to 1-phenyl-1-propyne and adamantyl isocyanate on FVT above 450 °C were observed.[14c]

The energy profiles in Figs. 4 and 5 reveal that the activation barrier for the 1,3-phenyl shift interconverting imidoylketenes and oxoketenimines, *ca.* 150 kJ mol^{-1}, is well within the expectations for FVT reactions. The calculated 1,3-shift barrier for a phenyl group in the otherwise unsubstituted imidoylketene is 186 kJ mol^{-1}.[14] Thus, the two phenyl groups in **11** have a significant stabilizing effect on TS2 (Fig. 4). We have found that electron donating substituents (D) in the migrating phenyl group, and electron-withdrawing ones (W) in the other can lower this 1,3-phenyl migration barrier (**TS2**) in α-oxoketenes (Z = O)
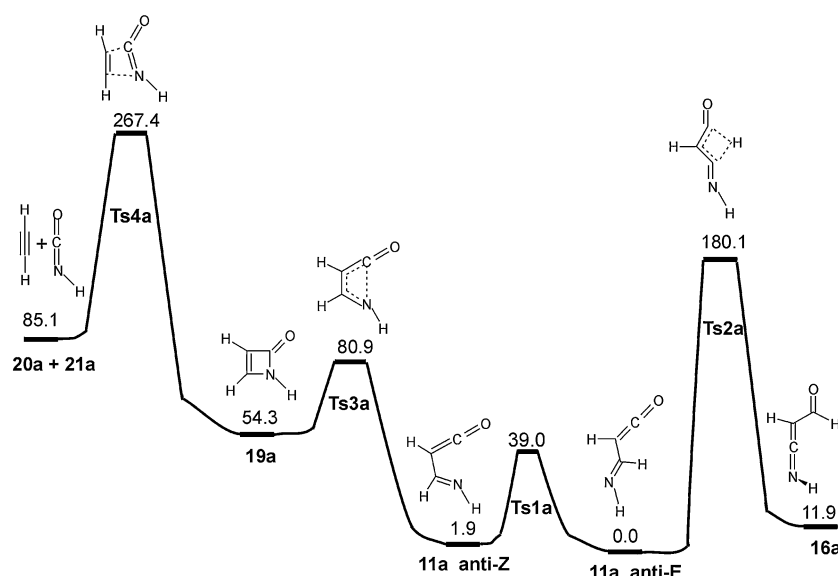

Scheme 3

Fig. 3 Calculated energy profile for the rearrangements of the unsubstituted imidoylketene **11a** at the B3LYP/6-31G** level of theory, corrected for zero-point vibrational energies (ZPVE).
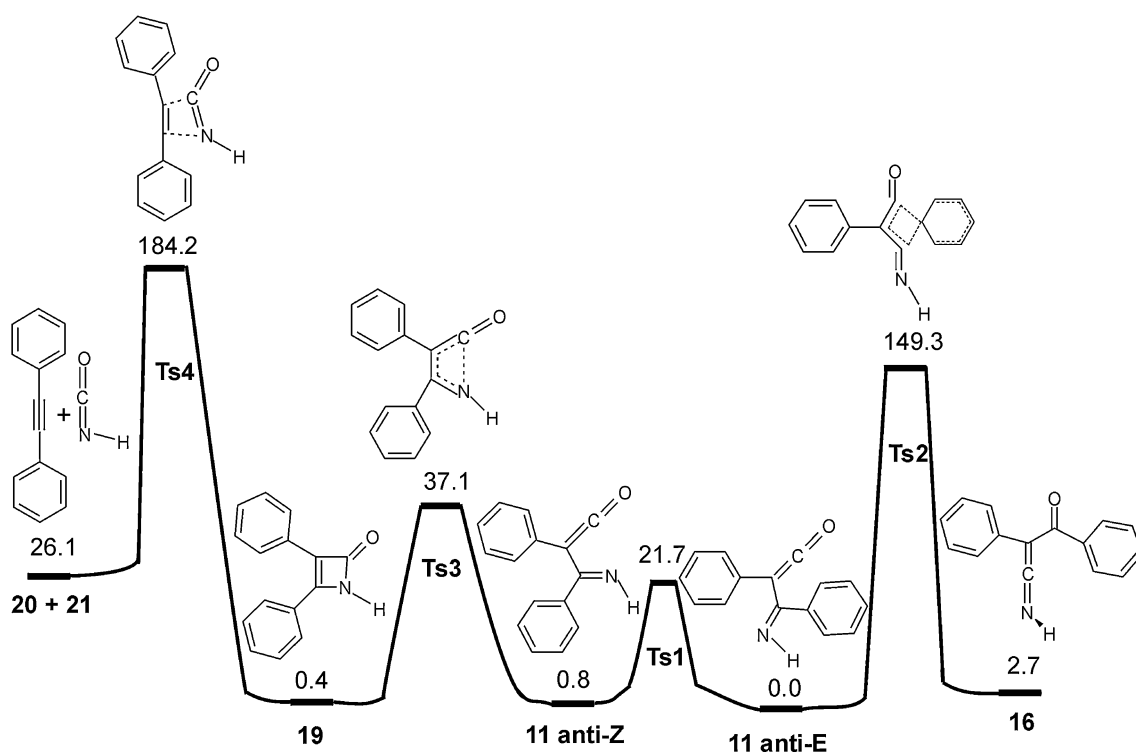
Fig. 4 Calculated energy profile for the rearrangements of the diphenylimidoylketene **11** at the B3LYP/6-31G** level of theory, corrected for ZPVE.
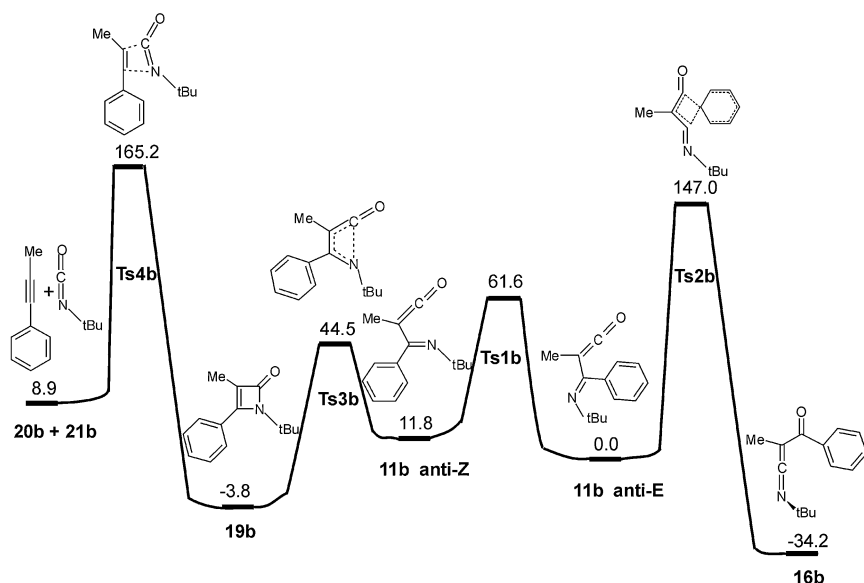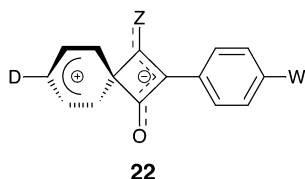

Fig. 5 Calculated energy profile for the rearrangements of the *N-tert*-butyl-phenylmethylimidoylketene **11b** at the B3LYP/6-31G** level of theory, corrected for ZPVE.

and imidoylketenes (Z = NR) further still.

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Comparison of the three energy profiles also reveals that an *N-tert*-butyl group significantly destabilizes the ketene **11**, probably due to steric strain, and conversely stabilizes the ketenimine isomer **16a**, in agreement with the observation that the analogous *N*-adamantylimidoylketene, underwent isomerization to the isolable *N*-adamantyloxoketenimine on FVT above 600 °C.[14c] The phenyl substitution lowers the energy of the azetinone **19**

(Fig. 4) very significantly, compared with the unsubstituted case (Fig. 3), and the *N-tert*-butyl group lowers this energy even further (Fig. 5) relative to the ketene **11**. This is in accord with the finding that the *N*-adamantyl case was the only one where significant amounts of the azetinone could be matrix isolated.[14c] In the case of the diphenyl derivative, Fig. 4, **19**, **11** and **16** all have very similar calculated energies, and only a trace of the azetinone **19** is observable under FVT conditions. As mentioned above, this can be ascribed to the cleavage to diphenylacetylene **20** and HNCO **21** as well as the isomerization of the easily formed ketenimine **16** to nitrile **18**.

Conclusion

The *NH*-imidoylketene **11** is stable in the gas phase under conditions of FVT at moderate temperatures. It is also stable

in the solid phase till *ca.* −100 °C, when it dimerizes to the 1,3-oxazinone **13**. At FVT temperatures above 700 °C, **11** undergoes a 1,3-phenyl shift to afford the *NH*-ketenimine **16**, which tautomerizes to nitrile **18**. Imidoylketene **11** also cyclizes to azetinone **19**, which fragments to diphenylacetylene and HNCO. All the processes are summarized in Scheme 4.

Scheme 4
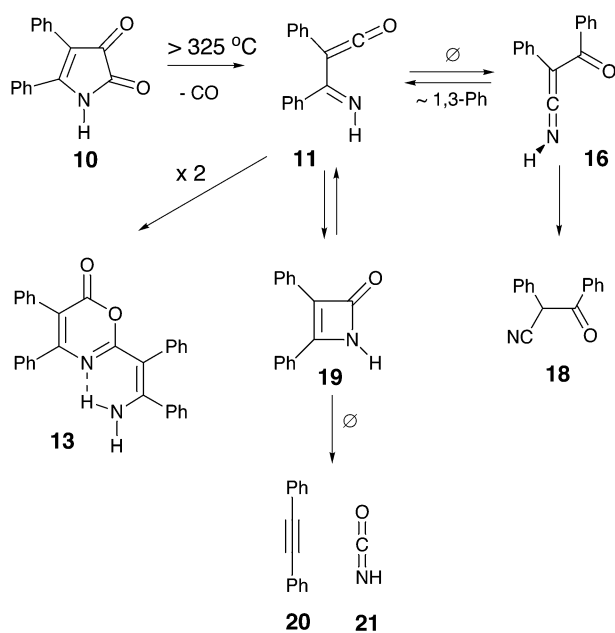
Experimental

The apparatus for FVT and matrix isolation was as previously reported.[19] For GC-MS conditions see ref. 20. The pyrroledione **10** was prepared according to the literature,[21] mp 189–191 °C; IR (KBr) 3270 m, 1735 vs, 1700 vs, 1615 m cm^{-1}; ^{13}C NMR (DMSO-d_6) δ 159.9 (C2), 183.3 (C3), 110.4 (C4), 163.6 (C5), 127.1, 128.3, 128.5, 128.6, 128.7, 129.1, 130.0, 132.3. 2-Cyano-2-phenylacetophenone **18** was prepared according to the literature;[22] ^{1}H NMR (DMSO-d_6): the spectrum scanned till 15 ppm showed peaks at δ 12.0 (OH), 11.6 (OH) and 6.6 (CH) in the integrated ratio 80 : 8 : 12 corresponding to enol **17a** : enol **17b** : ketone **18**, together with phenyl signals at δ 8.0 to 7.0; ^{13}C NMR (DMSO-d_6) δ 167.9 (CO of main enol **17**), 120.0 (CN of main enol **17a**), 88.0 (CH of main enol**17a**), 87.8 (CH of isomeric enol **17b**), 45.9 (CH of ketone **18**). The eight phenyl group signals of the major tautomer **17a** are at 135.9, 132.9, 130.4, 128.4, 128.3 (two signals), 127.3, and 126.7 (*cf.* ref. 16*c*). The assignment of the ^{13}C NMR data was supported by a DEPT spectrum.

Crystallography

Cell constants were determined by least-squares fits to the setting parameters of 25 independent reflections measured on an Enraf–Nonius CAD4 four-circle diffractometer employing graphite-monochromated Mo Kα radiation (0.71073 Å) and operating in the ω-2θ scan mode. Data reduction was performed with the WinGX package.[23] The structure of compound **13** was solved by direct methods with SHELXS and refined by full-matrix least-squares analysis with SHELXL-97.[24] All non-H atoms were refined with anisotropic thermal parameters. H-atoms attached to carbon were included in estimated positions using a riding model whereas and those attached to nitrogen were located from difference maps in the first instance then restrained also using a riding model. The drawing of the molecule (Fig. 2) was produced with ORTEP.[25]

FVT and matrix isolation

Pyrroledione **10** was sublimed into the FVT tube in a stream of Ar at 100 °C and thermolysed at temperatures ranging from 300–800 °C. No reaction took place at 250 °C. The products were isolated in an Ar matrix at 20 K, and FTIR spectra were recorded at *ca.* 10 K. A typical IR spectrum is shown in Fig. 2. Bands due to imidoylketene **11** are at 3456 vw, 3071 vw, 2117 vs, 1595 m, 1575 m, 1498 m, 1361 m, 1351 m, 1180 w, 1046 884 w, 862 w, 775 w, 756 m, 699 m, 655 w cm^{-1}. Bands at 2138 and 2149 cm^{-1} are due to CO. The band at 2340–2345 cm^{-1} is due to a minor amount of CO$_2$. Similar FVT of **10** using Ar as a carrier gas but with isolation at 70 K (*i.e.* without Ar and CO condensing), afforded **11** with its main absorption at 2112 cm^{-1}, and the CO bands were missing under these conditions.

FVT temperatures above 700 °C caused formation of nitrile **18** in amounts increasing with the temperature and identified by GC-MS, IR and NMR comparison of the isolated product with the spectra of authentic material. Benzonitrile (identified by GC-MS and IR comparison with authentic material), diphenyl-lacetylene (identified by GC-MS comparison with authentic material), and isocyanic acid HNCO (identified by its Ar matrix IR absorption at 2259 cm^{-1}) were formed at the same time. GC retention times in min (relative peak abundance in %) for the products formed at 700 °C: benzonitrile 2.95 (100), diphenylacetylene 9.4 (60), 2-cyano-2-phenylacetophenone **18** 11.6 (75).

4,5-Diphenyl-2-(1,2-diphenyl-2-aminoethenyl)-1,3-ozaxin-6-one 13

Pyrroledione **10** (300 mg; 1.20 mmol) was sublimed into the FVT apparatus at 110 °C and thermolysed at 570 °C in the course of 2.5 h. The product was collected in a liquid nitrogen-cooled U-tube and after the end of the experiment dissolved in acetone–methanol. Preparative thin layer chromatography on SiO$_2$, eluting with methylene chloride, afforded a yellow solid (80 mg; 30%), which crystallized as lemon-yellow rhombohedra from ethanol; mp 296 °C; ^{1}H NMR (CDCl$_3$, 400 MHz) δ 5.6 (br, 1H), 7.05–7.40 (m, 20 H), 10.4 (br, 1H); ^{13}C NMR (CD$_2$Cl$_2$, 100 MHz; relative intensities in parentheses) δ 99.9 (1.7), 113.7 (1.7), 126.8 (5.8), 127.8 (6.5), 128.1 (11.5), 128.4 (13.5), 128.5 (22.6), 128.9 (12.4), 129.3 (6.4), 129.7 (6.3), 129.8 (10.9), 131.5 (12.1), 133.5 (10.9), 134.2 (2.8), 136.7 (3.4), 138.4 (2.8), 138.8 (2.8), 160.2 (2.1), 160.9 (1.9), 162.2 (3.4), 165.1 (2.0); IR (KBr) 3325 (s, br) 1700 (vs, br) 1610 m, 1595 m, 1560 m, 1540 m, 1500 s, 1460 vs, 1435 s, 1410 s, 1290 s, 1270 (s, br) cm^{-1}; MS *m/z* 443 ([M$^+$ + 1], 9%), 442 ([M$^+$], 28%); HRMS calcd. for ^{12}C$_{30}$H$_{22}$N$_2$O$_2$ *m/z* 442.1681; found 442.1686.

Crystal data

C$_{30}$H$_{22}$N$_2$O$_2$, M = 442.50, monoclinic, space group *Pc*, a = 11.209(3), b = 6.6731(8), c = 16.500(4) Å, β = 108.47(2)°, U = 1170.6(4) Å^3, Z = 2, D_c = 1.255 g cm^{-3}, μ = 0.79 cm^{-1}, 2165 unique reflections (R_{int} = 0.000), R_1 = 0.0409 (for 927 observed data, $I > 2\sigma$), wR_2 = 0.1210 (all data).‡

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