Imidoylketene–Azetin-2-one–Oxoketenimine Rearrangement

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N-Adamantylimidoylketene **2** produced from pyrroledione **1** is in thermal equilibrium with azetin-2-one **4**; **2** also thermally rearranges to oxoketenimine **3**; azetin-2-one **4** is photolytically converted into imidoylketene **2**, and thermally cleaved to adamantyl isocyanate **5** and 1-phenylpropyne **6**.

Azetin-2-ones are rather elusive compounds requiring sterically protecting groups such as adamantyl or *tert*-butyl for stabilization under ordinary reaction conditions.[1–3] Although several syntheses of monocyclic azetin-2-ones have been claimed, none has been substantiated.[2] Here, we report the formation of such an azetinone **4** in thermal equilibrium with an imidoylketene **2**, as well as the clean photochemical conversion of **4** into **2**, and the thermal cleavage of **4** into adamantyl isocyanate **5** and 1-phenylpropyne **6**.

Flash vacuum pyrolysis (FVP) of 1-adamantyl-4-methyl-5-

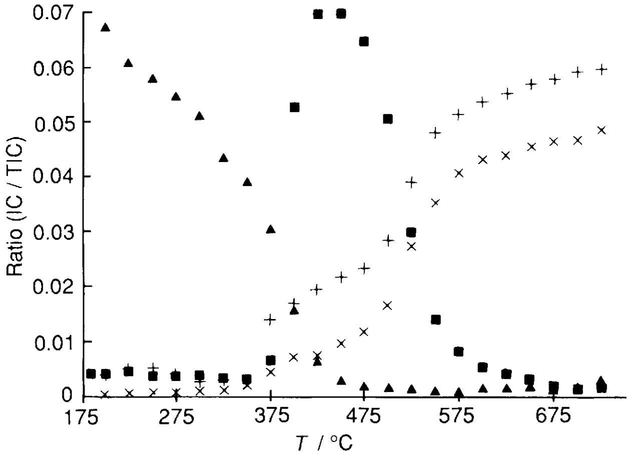


Fig. 1 FVP–MS monitoring of the decomposition of **1**. Ion current *vs.* total ion current (TIC) as a function of temperature (°C). ▲: *m/z* 321 × 5; ■: *m/z* 293; ×: *m/z* 177; +: *m/z* 116.

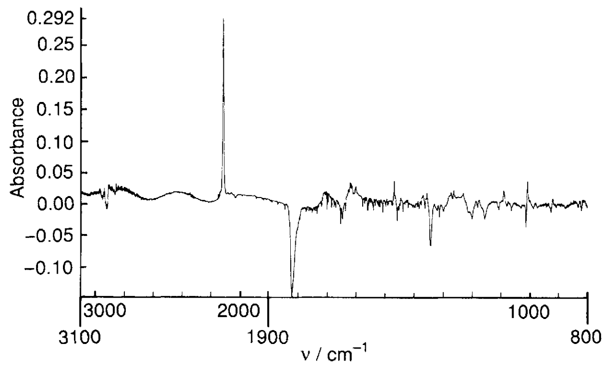


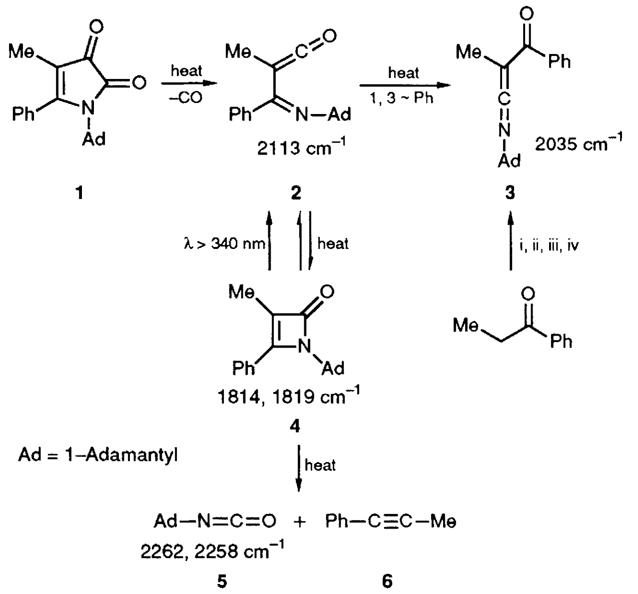
Fig. 2 Difference IR spectrum (Ar, 18 K), showing the formation of **2** (positive peaks) on photolysis of **4** (negative peaks) at λ > 430 nm for 15 min

phenyl-2,3-dihydropyrrole-2,3-dione **1** in the temperature range 400–750 °C (*ca.* 10^{-5} mbar) was monitored by direct on-line mass spectrometry[4] and by IR spectroscopy in Ar matrix at 18 K or as neat solids at 77 K.

The mass spectra (Fig. 1) clearly demonstrate the formation of an intermediate or intermediates with *m/z* 293, corresponding to loss of CO from **1**, which at temperatures above 450 °C is again destroyed to give masses corresponding to adamantyl isocyanate **5** and 1-phenylpropyne **6**.†

The IR investigation revealed that no less than three different species corresponding to the *m/z* 293 intermediate were formed. At the lowest practicable pyrolysis temperature of 400 °C, the major new absorptions were at 1803 (neat) or 1814, 1819 cm^{-1} (Ar matrix) and are assigned to the azetinone **4** as elaborated below. At higher pyrolysis temperatures, **4** ring opens to the imidoylketene **2** (2113 cm^{-1} in Ar matrix: 2103 cm^{-1} neat solid) and at *ca.* 600 °C and above, **2** is removed from the equilibrium by an imidoylketene–oxoketenimine rearrangement[4] involving a 1,3-shift of a phenyl group, leading to **3**. At the same time, **4** is also removed by irreversible fragmentation into **5** and **6**. An analogous fragmentation of thiet-2-ones to acetylenes and OCS has been reported.[5]

Compound **5** was identified by its IR spectrum, GC–MS, and hydrolysis in air to 1,3-diadamantylurea (isolated in 20% yield based on **1**, from FVP of **1** at 675 °C).‡ Compound **6** was identified by GC–MS comparison with authentic material. Compound **3** was stable up to room temperature and was identified by synthesis from propiophenone in four steps as indicated in Scheme 1.[6]‡



1

2

3

4

5

6

Scheme 1 *Reagents*: i, HCO_2Et, NaOEt, EtOH; ii, $NH_2OH.HCl$, EtOH; iii, Ad-OH, $HClO_4$, Et_2O; iv, Et_3N, CH_2Cl_2

Further evidence for the assignment of the 1814, 1819 cm^{-1} species to the azetinone **4** was adduced by matrix photolysis. A mixture of **2** and **4** was generated by FVP of **1** at 500 °C and isolated in Ar. Irradiation at λ > 340 nm for 15 min (1000 W high pressure Hanovia Xe-Hg lamp with cutoff filters) completely converted the azetinone **4** into the ketene **2** as seen from the difference IR spectrum (Fig. 2). These spectra permit an assignment of several bands belonging to **2** and **4**, respectively.‡ A similar result was obtained on 10 min irradiation at λ > 280 nm; at λ > 405 nm the reaction **4** → **2** was very slow. When **4** was isolated as a neat solid at 77 K (together with **2**), it remained detectable by IR spectroscopy until 0 °C.

The results reported herein clearly demonstrate the relationship between **2**, **3** and **4**. It is the first time that a monocyclic azetinone has been identified, and the first time it has been seen in reactions of this type.[3,4,6] Furthermore, the reaction **2** → **3** involves the most facile 1,3-shift of a phenyl

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† FVP temperatures used for mass spectrometry and for IR spectroscopy should not be directly compared. Due to different apparatus design, temperatures are lower in the MS investigations.

‡ Compound **1** was prepared from propiophenone *N*-adamantylimine and oxalyl chloride (1 : 1) in the presence of triethylamine (2 equiv.); dark red crystals, m.p. 240–243 °C (toluene); ^1H NMR ($CDCl_3$) δ 1.42 (s, 3 H; CH_3), 1.99 (s, 15 H; adamantyl), 7.20 (m, 5 H; phenyl); correct elemental (C, H and N) analysis.

Compound **2** (from IR difference spectrum): IR (Ar matrix, 18 K) 2113 vs, 1615, 1601, 1468, 1369, 1261, 1688, 1007 cm^{-1}.

Compound **4** (from IR difference spectrum): IR (Ar matrix, 18 K) 1820 s, 1647, 1459, 1342, 1200, 1156, 1014 cm^{-1}.

1,3-Diadamantylurea: m.p. *ca.* 300 °C; IR (KBr) 1627s, 1557m cm^{-1}; HRMS calcd for $C_{21}H_{32}N_2O$ 328.25129; found: 328.2514.

Compound **3**: m.p. 89–90 °C; IR (KBr) 2034, 1622 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.53, 1.56 and 1.61 (br s, 6 H; adamantyl), 1.66 (br s, 6 H; Ad.), 1.90 (s, 3 H; CH_3), 2.04 (br s, 3 H; Ad.), 7.34–7.38 (m, 2 H; *m*-phenyl), 7.41–7.45 (m, 1 H; *p*-phenyl), 7.63–7.66 (m, 2 H; *o*-phenyl); ^{13}C NMR ($CDCl_3$), δ 10.34 (q, ^1J 130.6 Hz; CH_3), 29.38 (d, ^1J 131.3 Hz; Ad-C3), 35.50 (t, ^1J 125.1 Hz; Ad-C4), 43.23 (t, ^1J 131.3 Hz, Ad-C2), 61.80 (m; Ad-C1), 69.25 (q, ^2J 5.9 Hz, C-3), 127.32 (dt, ^1J 160 Hz, ^2J 6.2 Hz; phenyl-C3), 127.73 (dd, ^1J 159.9 Hz, ^2J 8.5 Hz; phenyl-C2), 130.48 (dt, ^1J 161 Hz, ^2J 8 Hz; phenyl-C4), 140.15 (t, ^2J 7 Hz; phenyl-C1), 174.64 (m, *J* 4.5 Hz; CO), 194.97 (m, *J* 3.5 Hz; C=N); satisfactory elemental C, H and N analysis.

group yet discovered in the series of ketene–ketene rearrangement.[4] The even greater migratory aptitude of an SMe group was described in the preceding communication.[4]

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