

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-

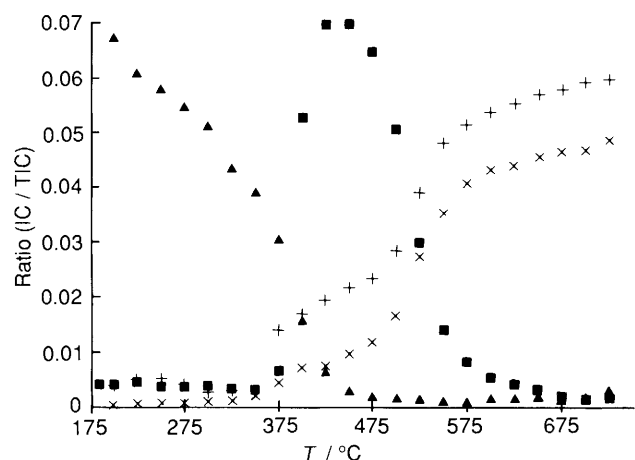


Fig. 1 FVP-MS monitoring of the decomposition of **1**. Ion current vs. total ion current (TIC) as a function of temperature ($^{\circ}\text{C}$). \blacktriangle : m/z 321 \times 5; \blacksquare : m/z 293; \times : m/z 177; $+$: m/z 116.

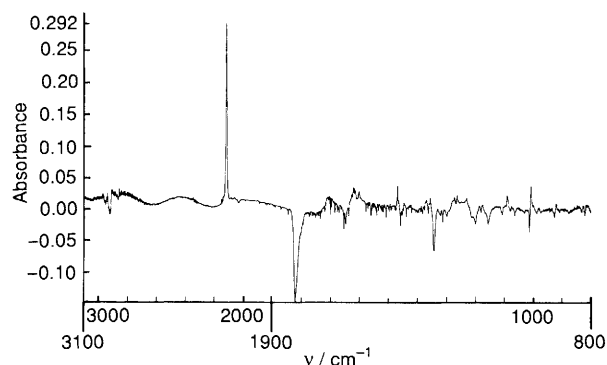


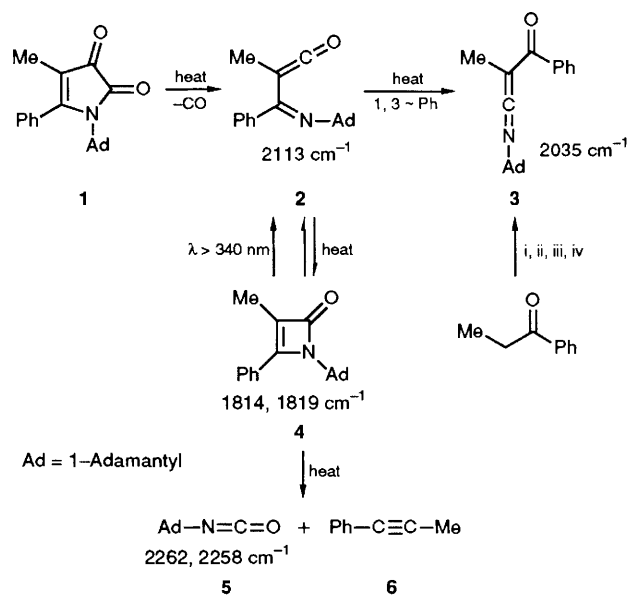
Fig. 2 Difference IR spectrum (Ar, 18 K), showing the formation of **2** (positive peaks) on photolysis of **4** (negative peaks) at $\lambda > 430$ nm for 15 min

phenyl-2,3-dihydropyrrole-2,3-dione **1** in the temperature range 400–750 $^{\circ}\text{C}$ (ca. 10^{-5} mbar) was monitored by direct on-line mass spectrometry⁴ 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 $^{\circ}\text{C}$ 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 $^{\circ}\text{C}$, 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 $^{\circ}\text{C}$ and above, **2** is removed from the equilibrium by an imidoylketene–oxo-ketenimine rearrangement⁴ 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%



Scheme 1 Reagents: i, HCO_2Et , NaOEt , EtOH ; ii, $\text{NH}_2\text{OH}\cdot\text{HCl}$, EtOH ; iii, $\text{Ad}\cdot\text{OH}$, HClO_4 , Et_2O ; iv, Et_3N , CH_2Cl_2

yield based on **1**, from FVP of **1** at 675 $^{\circ}\text{C}$).[‡] 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.[‡]

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 $^{\circ}\text{C}$ and isolated in Ar. Irradiation at $\lambda > 340$ nm (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 $\lambda > 280$ nm; at $\lambda > 405$ nm the reaction $4 \rightarrow 2$ 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 $^{\circ}\text{C}$.

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 $2 \rightarrow 3$ involves the most facile 1,3-shift of a phenyl

[‡] 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 $^{\circ}\text{C}$ (toluene); $^1\text{H NMR}$ (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 $^{\circ}\text{C}$; IR (KBr) 1627s, 1557m cm^{-1} ; HRMS calcd for $\text{C}_{21}\text{H}_{32}\text{N}_2\text{O}$ 328.25129; found: 328.2514.

Compound **3**: m.p. 89–90 $^{\circ}\text{C}$; IR (KBr) 2034, 1622 cm^{-1} ; $^1\text{H NMR}$ (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); $^{13}\text{C NMR}$ (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-Cl), 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.

[†] 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.

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

The research was supported by the Deutsche Forschungsgemeinschaft (C. W. and K. P. N.) and the Australian Research Council.

Received, 16th December 1991; Com. 1106303K

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