

## Iminopropadienones, RN=C=C=C=O: Syntheses and Reactions

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Phenyliminopropadienone, PhN=C=C=C=O, is prepared and characterized, and initial chemical reactions are described.

We have generated a new class of cumulenes, the iminopropadienones, RN=C=C=C=O **3** from three different precursors (**1**, **4** and **11**) by flash vacuum pyrolysis (FVP) as indicated in Schemes 1–3. Each reaction has been directly monitored by mass spectrometry and IR spectroscopy,<sup>†</sup> and the identity of **3a** in particular has been established by direct observation and by chemical trapping reactions.

The mass spectrometric monitoring of the FVP of **1a** is illustrated in Fig. 1. The starting material (*m/z* 213) starts

disappearing at 500 °C (preparative experiments showed that this process was complete at 700 °C). At the same time, signals at *m/z* 27 (HCN), 43 (HNCO) and 143 (**3a**) strongly increased in intensity. The compositions of these species were established by IR spectroscopy. The Ar matrix IR spectrum shows bands at 2247, 2141, 1633, 1619, 1490, 1284, 1210, 754, 685 and 565 cm<sup>-1</sup> associated with **3a** (the same bands are observed in **3a** derived from **4a** and **11a**), together with a band at 2259 cm<sup>-1</sup> due to HNCO. While monomeric HCN is difficult to detect in an Ar matrix,<sup>1a</sup> expansion of the volatile FVP

<sup>†</sup> Apparatus for FVP-MS and FVP-IR (UV) were as previously described.<sup>1a</sup>

All new compounds (including **3**) gave satisfactory high resolution mass measurements.

Compound **11a** was prepared from 5-[bis(methylthio)methylene]-2,2-dimethyl-1,3-dioxane by sequential treatment with aniline (1.1 equiv.) and dimethylamine (3 equiv.) according to the general procedure;<sup>1b</sup> yield 82%; m.p. 192–194 °C; <sup>13</sup>C NMR (CDCl<sub>3</sub>) δ 26.31 (q, C-CH<sub>3</sub>), 41.71 (q, N-CH<sub>3</sub>), 75.76 (s, C-5), 102.29 (s, C-2), 122.91 (d), 126.04 (d), 129.52 (d), 138.85 (s, Ph-C-1), 163.44 (s), 164.34 (s); <sup>1</sup>H NMR (CDCl<sub>3</sub>) δ 1.69 (s, 6H, Me<sub>2</sub>), 2.93 (s, 6H, NMe<sub>2</sub>), 7.0–7.4 (m, 5H, Ph), 9.34 (br s, 1H, NH). **11b** and **4** were prepared analogously.

Compound **16** (X = NMe<sub>2</sub>) was prepared by isolating (–196 °C) **3a** [observed at 2243 cm<sup>-1</sup> (neat)] together with HNMe<sub>2</sub> from the FVP of **11a**. Warming to –20 to –10 °C caused disappearance of **3a** and formation of **16** (X = NMe<sub>2</sub>), IR ν<sub>max</sub>/cm<sup>-1</sup> 2039; <sup>1</sup>H NMR (CDCl<sub>3</sub>) δ 3.02 (s, 6H, NMe<sub>2</sub>), 4.98 (s, 1H, C=C–H) 7.2–7.4 (m, 5H, Ph).

Compounds **17a–d** (Table 1) were separated and purified by column chromatography (SiO<sub>2</sub>, 70–230 mesh; Et<sub>2</sub>O). **17a**: yellow oil; R<sub>f</sub> (TLC; Et<sub>2</sub>O) 0.85; <sup>13</sup>C NMR (CDCl<sub>3</sub>) δ 35.94 (t, C-2), 52.33 (q, OMe), 53.78 (q, OMe), 120.99 (d), 123.43 (d), 129.08 (d), 147.95 (s), 156.81 (s), 168.23 (s); <sup>1</sup>H NMR (CDCl<sub>3</sub>) δ 3.16 [s, 2H, H(C-2)], 3.62 (s, 3H, OMe), 3.78 (s, 3H, OMe), 6.73 (m, 2H, Ph), 6.99 (m, 1H, Ph), 7.20 (m, 2H, Ph); **17b–d** were isolated and characterized analogously.

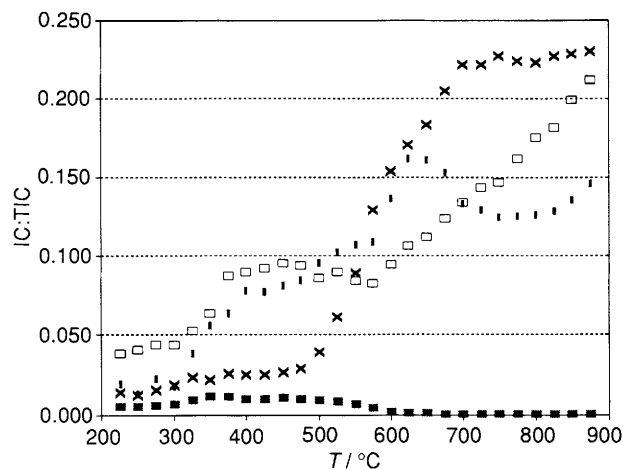
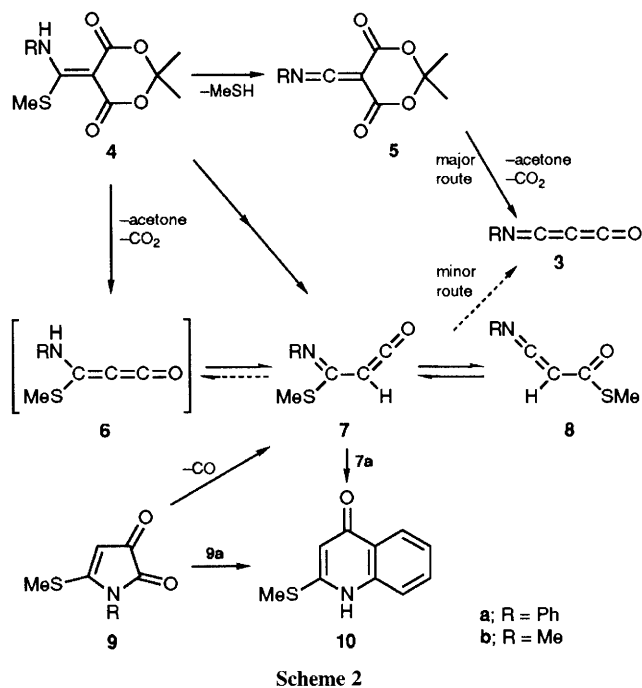
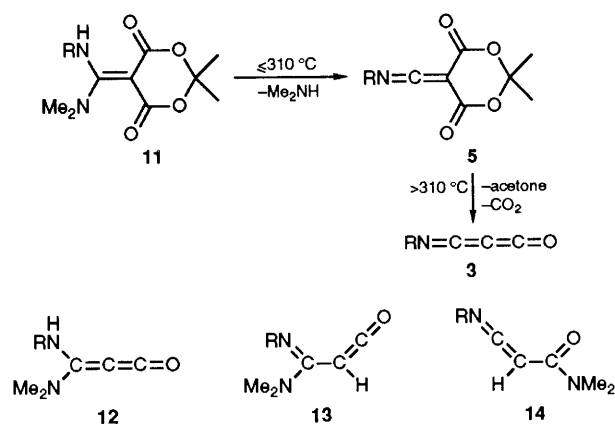
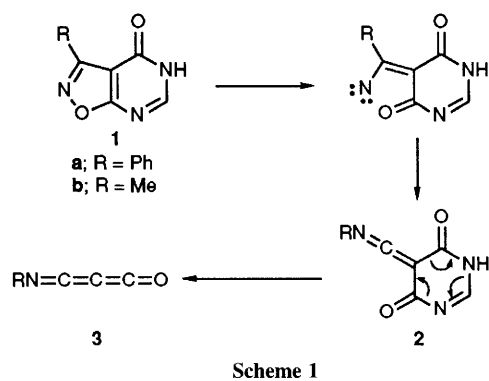


Fig. 1 Mass spectral monitoring of selected ions as a function of temperature in the FVP of **1a**. Ordinate: ion current (IC) vs. total ion current (TIC). ■: *m/z* 213 (**1**); X: *m/z* 143 (PhNC<sub>3</sub>O); □: *m/z* 43 (HNCO); ▨: *m/z* 27 (HCN).



products into an IR gas cell readily permitted the observation of HCN ( $3311\text{ cm}^{-1}$ ) and HNCO ( $3531, 2270\text{ cm}^{-1}$ ).<sup>2</sup>

The first band of **3a** at  $2247\text{ cm}^{-1}$  is extremely strong, and often split into a doublet due to different sites in the matrix, the second peak occurring at  $2243\text{ cm}^{-1}$ . The second fundamental of **3a** at  $2140\text{ cm}^{-1}$  is weak. Isotopic labelling experiments are in excellent agreement with *ab initio* molecular orbital calculations of the IR frequencies and intensities and confirm the assignment of these two bands to cumulenic stretching vibrations.<sup>3</sup> MeN=C=C=C=O **3b** was generated and observed analogously ( $2279, 1418\text{ cm}^{-1}$ ). The Ar matrix UV spectrum of **3a** (generated from **1a** and **11a**) showed  $\lambda_{\text{max}}$  238, 328, 332, 336, 340 and  $343\text{ nm}$ , and as such corresponds to a cumulog of phenyl isocyanate with extended conjugation.<sup>4</sup>

The mechanism of formation of **3** from **1** (Scheme 1) involves initial breaking of the relatively weak N–O bond and rearrangement to a transient ketenimine **2**, similar to the formation of *N*-phenylketenimine in the FVP of 3-phenylisoxazol-5(4*H*)-one.<sup>5</sup> The ketenimine **2** then fragments in much the same way as the Meldrum's acid precursors **4** and **11** described below.

We have previously reported the FVP of Meldrum's acid derivatives **4a** and **4b** to imidoalkenes **7** and oxoketenimines **8** (Scheme 2) taking place at  $400\text{--}500^\circ\text{C}$ .<sup>6</sup> We now find that, above  $600^\circ\text{C}$ , a competing elimination of methanethiol becomes important, leading to the cumulenes **3a** and **3b**, which had IR spectra in every respect identical with those obtained from **1**. In the case of **4a**, FVP at  $700^\circ\text{C}$  gave rise to strong signals for **3a**, together with bands due to the quinolone

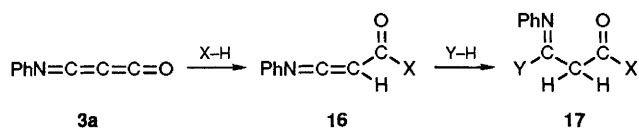
Table 1 Trapping of **3a** with nucleophiles<sup>a</sup>

Precursor	Cold trap temperature/ $^\circ\text{C}$	Added nucleophile	Products <b>17</b>			
			X	Y	Yield (%)	
<b>1</b>	$-80$	MeOH	<b>17a</b>	OMe	OMe	57
<b>11a</b>	$-190$	MeOH	<b>17b</b>	NMe <sub>2</sub>	OMe	73
<b>11a</b>	$-80$	MeOH	<b>17a</b>	OMe	OMe	43
			<b>17b</b>	NMe <sub>2</sub>	OMe	25
<b>1</b>	$-80$	HNEt <sub>2</sub>	<b>17c</b>	NEt <sub>2</sub>	NEt <sub>2</sub>	49
<b>11a</b>	$-190$	HNEt <sub>2</sub>	<b>17d</b>	NMe <sub>2</sub>	NEt <sub>2</sub>	61
<b>11a</b>	$-80$	HNEt <sub>2</sub>	<b>17c</b>	NEt <sub>2</sub>	NEt <sub>2</sub>	54
			<b>17d</b>	NMe <sub>2</sub>	NEt <sub>2</sub>	30

<sup>a</sup> Yields not optimized. **3a** generated by FVP of **1a** ( $700^\circ\text{C}$ ) or **11a** ( $600^\circ\text{C}$ ) was isolated on a cold finger at the temperature indicated. The cold finger had been previously coated with the added nucleophile at the same temperature. Reaction occurred on warming between  $-20^\circ\text{C}$  and room temp.<sup>†</sup>

**10**. In contrast, FVP of the pyrroledione **9a** at  $700\text{--}800^\circ\text{C}$  gave no trace of **3a** but only the quinolone **10**. Since **9** is a precursor of **7** and **8**,<sup>6</sup> we can assert that the interconverting **7** and **8** are not the precursors of **3**, or they are so to only a very minor extent. In the FVP of **9b**, weak bands ascribable to **3b** at  $2279\text{ cm}^{-1}$  were in fact observed, but the very high intensity of this band implies that only traces of **3b** were formed, from either **7b**, **8b**, or **6b**. Therefore, the overwhelming source of cumulenes **3a** and **3b** must be direct elimination of MeSH from **4**, giving the transient ketenimine **5**. Direct evidence in support of elimination *via* **5** was obtained in the FVP of **11** (Scheme 3).

Whereas in the case of **4** (and **9**) the imidoalkene-oxoketenimine rearrangement<sup>6</sup> ( $7 \rightleftharpoons 8$ ) is still the major reaction channel, this becomes a very minor pathway in the case of the dimethylamino-substituted Meldrum's acid derivative **11a**. At the very mildest pyrolysis conditions ( $310^\circ\text{C}$ ), very weak bands ascribable to ketenimines are observed at  $2040$  and  $2050\text{ cm}^{-1}$ , and another very weak band at  $2137\text{ cm}^{-1}$  may be due to the imidoalkene **13a**. However, already at  $360^\circ\text{C}$  and above, IR bands due to **3a** become strong, and all signals possibly due to **12a** and **14a** vanish. Moreover, no quinolone **15** was detectable in these reactions, thus excluding formation of imidoalkene **13a** to any significant extent. One or both of the weak bands at  $2040, 2050\text{ cm}^{-1}$  may therefore be ascribed to the transient ketenimine **5a**, which is the immediate precursor of **3a**. This was corroborated by on-line



FVP-MS, which at 350°C revealed the formation of a thermally produced transient of  $m/z$  245, **5a**.

In the FVP-MS of **11b** (200–700°C) there was a slight indication of transient formation at a low intensity of an intermediate corresponding to **12b**, **13b**, or **14b** ( $m/z$  126) at 350–400°C, but formation of  $\text{Me}_2\text{NH}$  ( $m/z$  45) and  $\text{MeNC}_3\text{O}$  (**3b**;  $m/z$  81) also became prominent from 350°C onwards (along with  $\text{CO}_2$  and acetone). Ar matrix IR spectroscopy confirmed the formation of **3b** together with  $\text{Me}_2\text{NH}$ ,  $\text{CO}_2$  and acetone (FVP at 450–700°C).

The iminopropadienones **3** are extremely stable thermodynamically. The IR spectra remain unchanged up to FVP temperatures of 1000°C, and the neat, isolated compounds **3** are still observable by IR spectroscopy at room temperature. Being formally monoimines of carbon suboxide ( $\text{C}_3\text{O}_2$ ), cumulenes **3** are, however, extremely reactive towards nucleophiles. Reaction takes place at the 'ketenic'  $\text{C}=\text{O}$  group first, giving ketenimines **16**. These react with a second nucleophile to afford malonic acid imides **17** in good yields† (cf. Table 1). When cumulene **3a** is generated by dimethylamine elimination from **11a** it reacts with the dimethylamine on warm-up, giving ketenimine **16** ( $\text{X} = \text{NMe}_2$ ),† *i.e.* the same product as would have resulted from the nonobserved pathway **11** → **12** → **13** → **14**. The dimethylamine can be partially removed by using a –80°C cold finger, thus allowing trapping of the ketene function by a second nucleophile (Table 1).

Aryliminopropadienones can now be prepared in good yields. Further investigations of their physical and chemical properties will be reported.<sup>3,7</sup> Additional evidence for the structures of  $\text{PhNCCCO}$ ,  $\text{MeNCCCO}$  and  $\text{HNCCCO}$  has been adduced by neutralization–reionization mass spectrometry.<sup>7</sup>

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