

## Short Communication

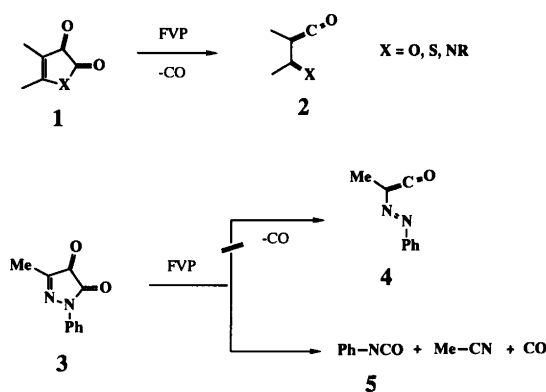
# On the Thermal Fragmentation of 3-Methyl-1-phenylpyrazole-4,5-dione

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Over the last years we have demonstrated that heterocyclic five-membered diones of type **1** are very useful precursors for the preparation of acylketenes **2**.<sup>1</sup> Under flash vacuum pyrolysis (FVP) conditions these diones readily extrude CO to form highly reactive ketenes **2** (Scheme 1), which are usually not isolable under normal reaction conditions, but can be conveniently detected by low-temperature IR spectroscopy or by real-time monitoring of the pyrolysis reactions by mass spectrometry.<sup>1</sup> These conjugated ketenes **2** are interesting cumulenenic species and a number of fascinating rearrangements have been observed.<sup>1</sup>



Scheme 1.

From the above one would expect that the pyrazole-4,5-dione system **3** might react in a similar way and thus provide an entry into the hitherto unreported class of azoketenes **4**. However, as we report herein, the thermal

fragmentation pattern of dione **3** is distinctly different from the previously reported fragmentation of diones **1**.

FVP of **3** at 750°C (ca.  $10^{-5}$  mbar) with isolation of the products in an Ar matrix at 18 K permitted the observation of several strong bands in the  $2260\text{ cm}^{-1}$  region of the IR spectrum, i.e., in the region typical of isocyanates, but not of ketenes (Fig. 1). On the basis of the matrix IR spectrum of genuine phenyl isocyanate (**5**) [Fig. 2(c)] we assign these bands [Fig. 2(a)] essentially to **5** and conclude that fragmentation of dione **3** into Ph–NCO, Me–CN and CO must have occurred (see below). Although the detection of **5** in the pyrolysis mixture by IR spectroscopy was straightforward, it was not easy to confirm the presence of acetonitrile in the pyrolysate. As can be seen from Fig. (2b), the bands due to acetonitrile in the  $2300\text{--}2240\text{ cm}^{-1}$  region are not prominent and furthermore, they are in the same region as absorptions of matrix-isolated **5**. We therefore investigated the  $1700\text{--}800\text{ cm}^{-1}$  region of the IR spectra more closely [Fig. 2(a)–(c)]. The five characteristic bands of MeCN [Fig. 2(b)] could easily be located in the spectrum of the pyrolysate [Fig. 2(a)], together with bands due to **5**. The band for CO can be seen in the typical region at  $2148\text{ cm}^{-1}$ . Note that CO is a far weaker absorber than phenyl isocyanate (**5**).

While the IR spectroscopic investigations described above provide compelling evidence that the three fragmentation products Ph–NCO (**5**), Me–CN and CO of **3** have been identified, they fall short of being absolute proof. Additional strong evidence was adduced by real-time monitoring of the FVP reaction of **3** by mass spectrometry, using a reactor situated immediately in front of the ion source of the spectrometer (Fig. 3). The starting material **3** ( $m/z$  188) started to disappear at temperatures above 300°C and reached a minimum at 650°C, whereas, at the same time, masses corresponding to Ph–NCO ( $m/z$  119) and MeCN ( $m/z$  41) increased significantly.

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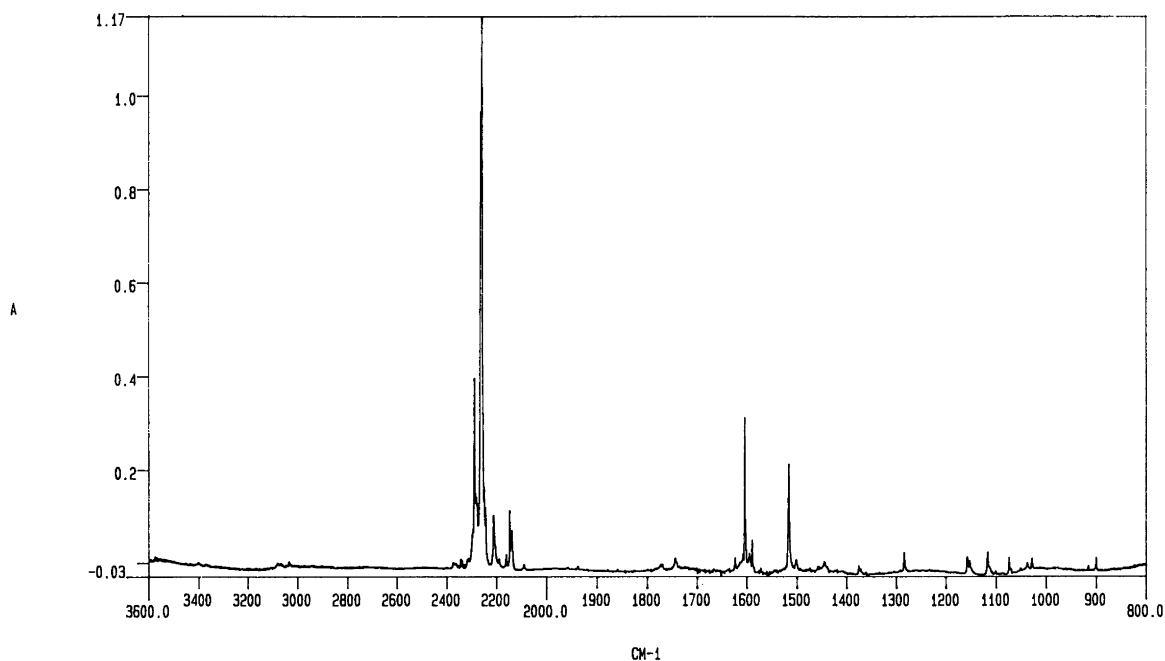
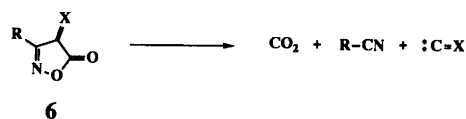


Fig. 1. FT-IR spectrum (Ar, 18 K) of the product of FVP of **3** at 750°C ( $10^{-5}$  mbar).

At first sight the unusual fragmentation of pyrazole-dione **3** might seem surprising, but one can understand that, here, the cleavage of the weak N–N bond in the pyrazole ring eventually leading to Ph–NCO, Me–CN and CO is preferred over the cheletropic [4 + 2] cyclo-reversion found in diones of type **1**. In fact, the fragmentation of pyrazolediones is analogous to that of isoxazol-5(4*H*)-ones of type **6**, which have been studied in great detail.<sup>2,3</sup> Indeed, on attempted preparation of 4,5-dihydroisoxazole-4,5-dione (**6**, X = O), spontaneous decomposition to CO<sub>2</sub>, RCN and CO occurs<sup>4</sup> (Scheme 2).



Scheme 2.

### Experimental

Flash vacuum pyrolysis (FVP) was carried out in unpacked quartz tubes (10 cm length; 0.8 cm i.d.) using

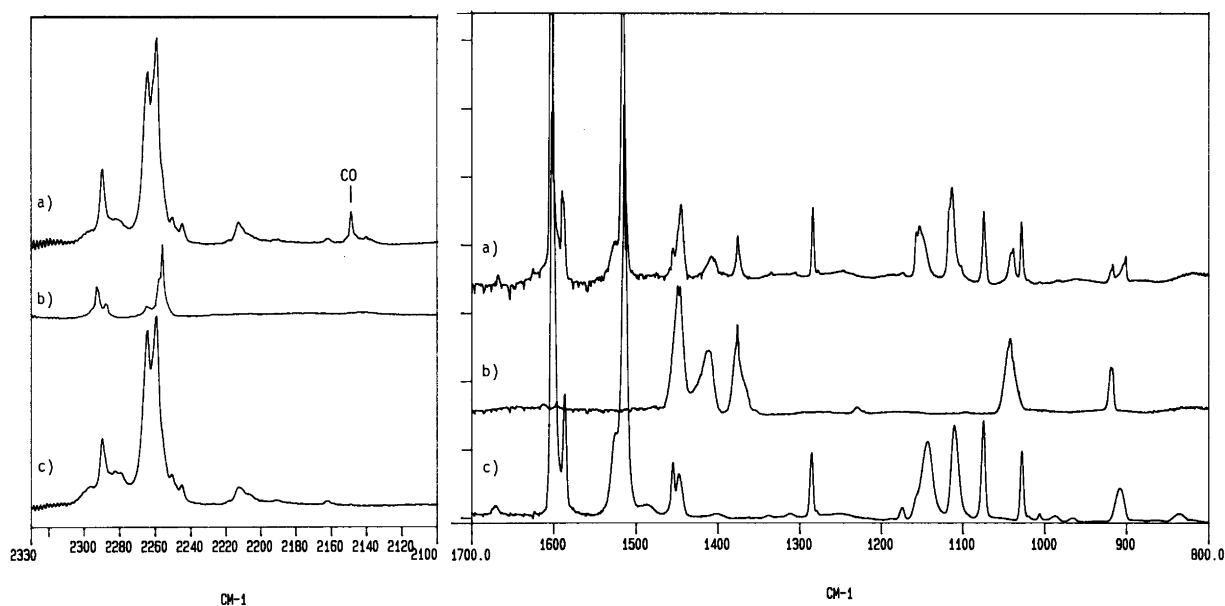


Fig. 2. Comparison of FT-IR spectra of the pyrolysate of **3** (a) with acetonitrile (b) and phenyl isocyanate **5** (c) in the regions 2330–2100  $\text{cm}^{-1}$  and 1700–800  $\text{cm}^{-1}$  (for exact values of bands see the Experimental).

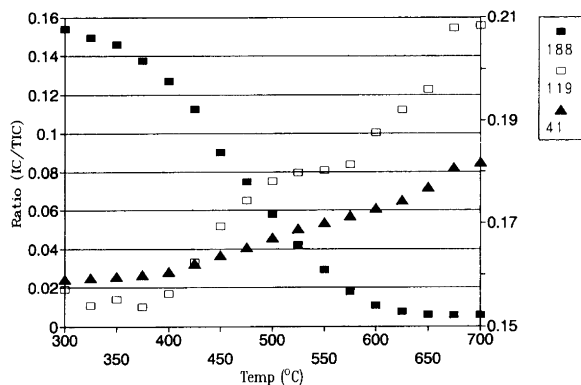


Fig. 3. FVP-MS monitoring of the decomposition of **3**. Ion current vs. total ion current (TIC) as a function of temperature ( $^{\circ}\text{C}$ ) for  $m/z$  188,  $m/z$  119 and  $m/z$  41.

the apparatus previously described.<sup>3</sup> Pyrolysis products were condensed in an Ar matrix at ca. 18 K.

FVP-MS was carried out in an apparatus similar to that used for matrix isolation as previously described.<sup>1c</sup> FT-IR spectra were recorded on a Perkin-Elmer 1720X spectrometer at a resolution of  $1\text{ cm}^{-1}$ .

3-Methyl-1-phenylpyrazole-4,5-dione (**3**) was prepared according to the literature.<sup>5</sup>

*FVP of dione 3.* **3** was pyrolyzed at  $750^{\circ}\text{C}$  ( $10^{-5}$  mbar) and the products isolated in Ar matrix at 18 K (if lower pyrolysis temperatures were used signals due to starting material remained in the spectrum). The IR spectrum (Fig. 1) showed bands which were all assignable to Ph-NCO, Me-CN or to CO on the basis of comparison with authentic spectra obtained from Ph-NCO and Me-CN in Ar matrix.

Ph-NCO (**5**) [Fig. 2(c)]: 3065 (w), 3028 (w), 3010 (w), 2290 (s), 2264 (vs), 2259 (vs), 2250 (w), 2245 (w), 2213 (w), 1598 (m), 1583 (w), 1513 (m), 1453 (w), 1446 (w), 1283 (w), 1142 (w), 1109 (w), 1075 (w), 1028 (w), 908 (w), 837 (w)  $\text{cm}^{-1}$ .

Me-CN [Fig. 2(b)]: 3001 (w), 2942 (w), 2293 (w), 2288 (w), 2266 (w), 2257 (m), 1449 (m), 1446 (w), 1411 (w), 1376 (w), 1042 (w), 919 (w)  $\text{cm}^{-1}$ .

The band at  $2148\text{ cm}^{-1}$  is due to CO.

*FVP-mass spectrometry of 3* (Fig. 3). The molecular ions of **3**, Ph-NCO (**5**) and Me-CN were monitored by mass spectrometry as a function of temperature. The intensities of the molecular ion of **3** decreased to zero on going from 300 to  $700^{\circ}\text{C}$ , and those of Ph-NCO and Me-CN increased at the same time. Note that FVP temperatures used for mass spectrometry and for IR spectroscopy should not be directly compared. Owing to different apparatus design, temperatures are usually lower in the MS investigations.

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## References

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