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# ELECTRON-IMPACT STUDIES

# XCV<sup>†</sup>—SKELETAL REARRANGEMENT FRAGMENTS IN THE MASS SPECTRA OF 3,5-DIPHENYLISOXAZOLE AND 3,5-DIPHENYLPYRAZOLE

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Abstract—The ion  $[C_{13}H_{\theta}]^+$  (*m/e* 165) is produced from the molecular ion of 3,5-diphenylisoxazole by the processes  $[M - CO - H_2CN^{\cdot}]$  and  $[M - CO - HCN - H^{\cdot}]$  and from that of 3,5-diphenylpyrazole by the eliminations  $[M - N_2H^{\cdot} - C_2H_2]$ . These processes have been studied by <sup>2</sup>H and <sup>13</sup>C labelling. A correlation between photochemical, thermal and electron-impact decompositions is noted for 3,5-diphenylisoxazole.

### INTRODUCTION

THE EXTENSIVE rearrangement processes which produce  $[C_{13}H_9]^+$  in the mass spectra of diphenyl-imidazoles,<sup>1</sup> pyrazoles,<sup>2,3</sup> oxazoles<sup>1,3-5</sup> and isoxazoles<sup>3</sup> have been studied by <sup>2</sup>H labelling.<sup>1,3</sup> The formation of  $[C_{13}H_9]^+$  by rearrangement processes also occurs from other heterocyclic systems including diphenyl-2-pyrones,<sup>6</sup> 1,2,4-oxadiazoles,<sup>7</sup> thiazoles<sup>1</sup> and 1,2,3-thiadiazole.<sup>8</sup>



3,5-Diphenylisoxazole (I) is known<sup>9</sup> to undergo photochemical transformation to 2,5-diphenyloxazole (III) through the intermediacy of the benzoylazirine (II), and it has been suggested<sup>3,5,10</sup> that the electron-impact fragmentations of isoxazoles may be rationalised in terms of decomposition of radical cations corresponding to II. The behaviour of 3,5-diphenylisoxazole has also been determined under flash pyrolytic conditions at 900 °C, and the sequences  $I \rightarrow III$ ,  $I \rightarrow V \rightarrow VI + VII$  and  $I \rightarrow V \rightarrow VIII \rightarrow VI + VII$  operate.<sup>11</sup> Fluorene (VI) is always produced in higher yield than phenalene (VII). It is probable that the benzoyl azirine (II) is an intermediate in the various thermal processes.<sup>ef.12</sup>

In earlier reports<sup>3,13</sup> we suggested on the basis of metastable characteristics, that the  $[M - CO]^+$  ion formed from the 3,5-diphenylisoxazole molecular ion did not

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correspond to a 2,3-diphenylazirine ion radical, i.e. the molecular ion of V, and that the decomposing form of the  $[C_{13}H_9]^+$  ion had the properties of a phenalenyl rather than a fluorenyl cation. Subsequent studies on other systems<sup>14</sup> have shown that these interpretations may be in error, as the differences observed<sup>3,13</sup> between metastable ratios for the different ions are not large enough to determine unequivocally whether the decomposing ions have different structures, or whether they have the same structure but different energy characteristics. Because of this difficulty, and as the thermal results (above) appear to conflict with our previous rationale<sup>3,13</sup> for the electronimpact decompositions,\* we decided to reinvestigate 3,5-diphenylisoxazole by studying the metastable decompositions<sup>†</sup> of <sup>2</sup>H and <sup>13</sup>C labelled derivatives. This paper describes studies of 3,5-diphenylisoxazole and of the corresponding 3,5-diphenylpyrazole.

## **RESULTS AND DISCUSSION**

3,5-Diphenylisoxazole (I)

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The spectrum of 3,5-diphenylisoxazole (I) is shown in Fig. 1, while that of its <sup>2</sup>H derivative (IX) is reproduced in Ref. 3.<sup>‡</sup> The measurement of metastable ions in the first field free region of the mass spectrometer show that m/e 165  $[C_{13}H_9]^+$  is formed from the  $[M - CO]^+$  ion by the eliminations  $[(M - CO) - H_2CN']$  and [(M - CO) - HCN - H'], with the abundance ratio of the metastable ions for the two processes  $[(M - CO) - H_2CN']$  and [(M - CO) - HCN] being in the ratio 91:9. The  $[M - CO]^+$  ion from IX loses HCN,  $(DCN + H_2CN)$  and HDCN in the ratio 0.1:9.9:90. This shows that the overall loss of  $H_2CN'$  from the  $[M - CO]^+$  ion of I involves loss of the isoxazole ring hydrogen (with a minimum of scrambling with the phenyl hydrogens) together with a hydrogen from the phenyl rings.



The molecular ion of X undergoes specific elimination of <sup>13</sup>CO, and the  $[M - {}^{13}CO]^{+}$  ion loses H<sub>2</sub>CN and H<sub>2</sub><sup>13</sup>CN in the ratio 1:1§ in the first field free region of the

\* There may, of course, be no correlation between the structures of the product species from the thermal and electron-impact degradation of 3,5-diphenylisoxazole. Nevertheless, the *apparent* correlation requires investigation.

† Facilities for metastable defocusing<sup>15</sup> were not available for the initial study.<sup>3</sup>

‡ All processes shown by schematic arrows in Fig. 1 have been substantiated by metastable defocusing.

§ This ratio could be in error (c.  $\pm 5\%$ ) because of the small contribution due to loss of H<sup>13</sup>CN from the [M - <sup>13</sup>CO] ion.



mass spectrometer. This means that after loss of CO each of the two remaining isoxazole ring carbons is lost to the same extent during elimination of H<sub>2</sub>CN'. No carbon scrambling occurs between the heterocyclic and the phenyl rings. A previous <sup>13</sup>C labelling study has shown that the decomposing form of the 2,3-diphenylazirine molecular ion loses each azirine ring carbon equally during elimination of H<sub>2</sub>CN'.<sup>16</sup> We now propose that there is a direct analogy between the thermal, photochemical and electron-impact behaviour of 3,5-diphenylisoxazole with all reactions proceeding through the benzoylazirine intermediate (II or *a*). Elimination of CO from *a* produces the 2,3-diphenylazirine ion radical which decomposes through a symmetrical form (perhaps *b* or a further rearranged species) to yield  $[C_{13}H_9]^+$ . No further information is available concerning the structure of  $[C_{13}H_9]^+$ . Other fragmentations reported<sup>3</sup> for 3,5-diphenylisoxazole are in accord with the <sup>13</sup>C labelling data.

### 3,5-Diphenylpyrazole (II)

The  $[C_{13}H_9]^+$  ion is formed from the molecular ions of 4,5-diphenylpyrazole<sup>3</sup> and diphenylimidazoles<sup>1</sup> by the processes [M - HCN - HCN - H'] and  $[M - C_2H_3N_2']$ . An unusual feature of these spectra is the reversible hydrogen rearrangements which occur between N—H and the *ortho* hydrogens of the phenyl rings.<sup>1,3</sup> 3,5-Diphenylpyrazole behaves differently from other diphenylpyrazoles, -imidazoles and -isoxazoles, for in this case  $[C_{13}H_9]^+$  is produced by the eliminations  $[M - N_2H' - C_2H_2]$ .



The spectrum of XI is shown in Fig. 2. The molecular ion decomposes by losses of  $N_2D'$  and  $N_2H'$  in the ratio 1:2 in the source, and 1:4 and 1:5, respectively, in the



first and second field free regions. This result parallels the reversible hydrogen rearrangements observed for 4,5-diphenylpyrazole.<sup>3</sup> The reversible transfer of a phenyl hydrogen to nitrogen followed by back transfer of either H or D occurs prior to or during the initial eliminations (N<sub>2</sub>D and N<sub>2</sub>H from XI), and as the lifetime of the decomposing molecular ion increases, H/D scrambling in the phenyl rings competes with the reversible transfer reaction. Proof of the D transfer to the phenyl substituents is substantiated by the observation of the two processes  $[M]^{+} \rightarrow [C_6H_5]^+$  and  $[M]^{+} \rightarrow$  $[C_6H_4D]^+$  (2.5:1) in the first field free region of the mass spectrometer. The spectra of XI and XII establish that there is no exchange between the 1- and 4-H/D atoms, or between the 4-H (or D) and the phenyl hydrogens. The metastable decompositions of XI, XII and XIII in the first field free region demonstrate that the  $[M - N_2H]^+$  ion from 3,5-diphenylpyrazole eliminates  $C_2H_2$  after *complete* carbon and hydrogen scrambling. Other fragmentations shown in Fig. 2 are unexceptional, and occur without prior equilibration of the N—H and phenyl hydrogens.

### EXPERIMENTAL

Mass spectra were measured at 70 eV, using a source pressure of  $1 \times 10^{-6}$  Torr, with an Hitachi Perkin-Elmer RMU-7D mass spectrometer modified to allow the sensitive measurement of metastable ions as previously described.<sup>17</sup> Samples were introduced at 150 °C through the all glass inlet system.

Compound IX was available from a previous study.<sup>3</sup> The spectra of the deuteriated pyrazoles XI ( $d_0 = 3$ ,  $d_1 = 95$ ,  $d_2 = 2\%$ ) and XII ( $d_1 = 18$ ,  $d_2 = 82\%$ ) were determined by introducing 3,5-diphenylpyrazole directly into the mass spectrometer with D<sub>2</sub>O,<sup>18</sup> and then measuring the spectrum after 5 min (for XI) and 3h (for XII).

The <sup>13</sup>C labelled compounds X and XIII. The reaction<sup>19</sup> between benzoic acid  $\alpha$ -<sup>13</sup>C (<sup>13</sup>C = 61%) and methyllithium yielded acetophenone- $\alpha$ -<sup>13</sup>C (80% yield), which on treatment<sup>20</sup> with ethyl benzoate and sodium ethoxide gave 1,3-diphenylpropan-1,3-dione-1<sup>13</sup>C (<sup>13</sup>C = 61%, 75% yield). The dione was converted to X and XIII by treatment with hydroxylamine<sup>21</sup> and hydrazine hydrochloride,<sup>22</sup> respectively. Each compound shows <sup>13</sup>C = 61%, but both the 3- and 5-positions are labelled (<sup>13</sup>C = 30.5% at each position).

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