

# MASS SPECTRUM OF 4-OXOQUINOLIZIDINE

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A mass spectral study of 4-oxoquinolizidine is discussed in this communication. The spectrum (Table 1) has features significantly dissimilar to the spectra of 1-, 2-, and 3-oxoquinolizidine<sup>1</sup> which indicates quite different fragmentation pathways. The major fragmentation patterns which the molecule undergoes upon electron impact are shown in Scheme 1; the presence of metastable peaks is depicted by an asterisk.

TABLE 1  
MASS SPECTRUM OF 4-OXOQUINOLIZIDINE

<i>m/e</i>	154	153	152	139	138	126	125
<i>I</i> (%)	11.37	100.0	53.33	5.68	62.74	2.35	24.39 <sup>a</sup>
<i>m/e</i>	124	112	111	110	99	98	97
<i>I</i> (%)	6.66	9.80	4.11	3.92	1.96	10.58	67.84 <sup>b</sup>
<i>m/e</i>	96	85	84	83	82	70	69
<i>I</i> (%)	9.01	2.54	38.43	47.84	8.62	4.70	23.13
<i>m/e</i>	68	67	57	56	55	54	53
<i>I</i> (%)	6.27	5.09	4.70	10.98	27.84	7.45	3.92

<sup>a</sup> C<sub>7</sub>H<sub>11</sub>NO.

<sup>b</sup> C<sub>6</sub>H<sub>11</sub>N.

The base peak occurs at *m/e* 153, due to the molecular ion *a*, which gives rise to *b* (*m/e* 152) by loss of a hydrogen radical, most probably from C10.

The peak at *m/e* 138 (*c*, *I* 55%) is likely due to the loss of a methyl radical from *a*; the initial step is fission of the C10-C1 bond and transfer of an unspecified hydrogen atom.

The peak at *m/e* 125 (*d*) was shown by high-resolution measurements to have the composition C<sub>7</sub>H<sub>11</sub>NO; its production must have involved elimination of ethylene from the molecular ion. Such behaviour is a consequence of the lactam structure of *a* (cf. piperid-2-one<sup>2</sup>); a peak of *m/e* 125 in the mass spectra of 1- and 3-oxoquinolizidine was due to the loss of carbon monoxide.<sup>1</sup>

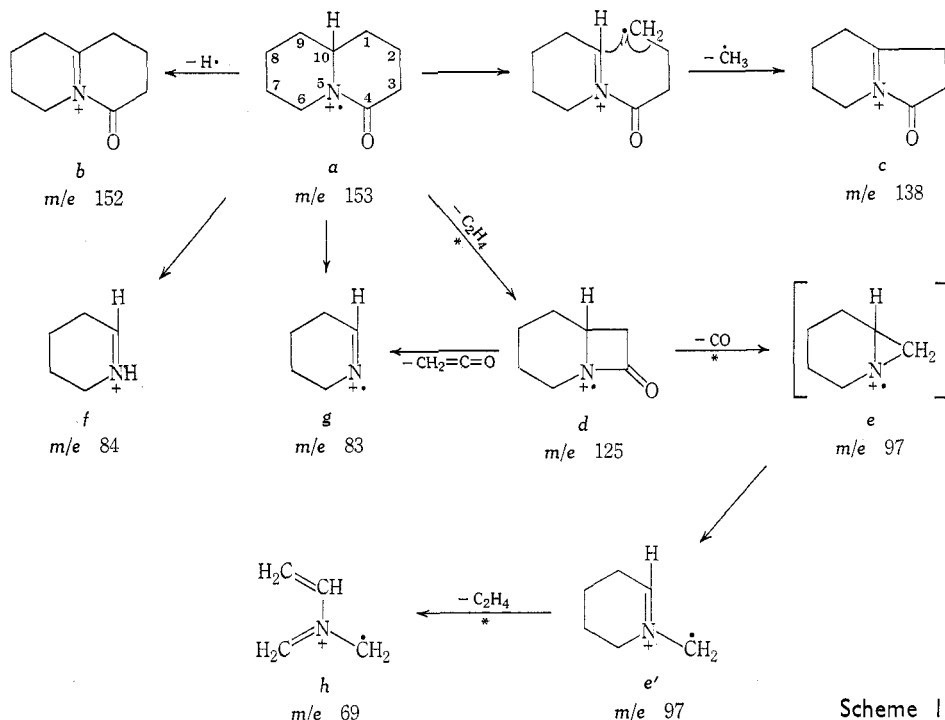
Further decomposition of *d* by loss of carbon monoxide (cf. piperid-2-one<sup>2</sup>) formed *e* (*m/e* 97) shown by high resolution measurements to have the composition C<sub>6</sub>H<sub>11</sub>N. The metastable peak arising from this fragmentation occurred at *m/e* 75.0 (calc. *m/e* 75.25). There followed rearrangement of *e* to *e'*, then loss of ethylene to form *h* (*m/e* 69).

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<sup>1</sup> Hussain, M., Robertson, J. S., and Watson, T. R., *Aust. J. Chem.*, 1970, **23**, 773.

<sup>2</sup> Duffield, A. M., Budzikiewicz, H., and Djerassi, C., *J. Am. chem. Soc.*, 1964, **86**, 5536.

The ion *f* (*m/e* 84) may arise from *a* by fission of the C10-C1 bond, transfer of hydrogen to nitrogen, most probably from C3 of the leaving fragment, then rupture of the C4-C5 bond (cf. pyrrolid-2-one<sup>2</sup>). The radical *g* (*m/e* 83) probably arises from molecular ion *a* as well as from *d* (*m/e* 125).



### Experimental

The method of Bohlmann *et al.*<sup>3</sup> was modified for the synthesis of 4-oxoquinolizidine. 1,1-Diethoxycarbonyl-3-(2-pyridyl)propane<sup>4</sup> (35 g), Raney nickel W-7 (8.0 g), and dioxan (160 ml) were heated at 210–215° under a hydrogen pressure of 135 atm for 2 hr. The catalyst was removed by filtration, the solvent distilled off under reduced pressure, and the product distilled at 2 mm; b.p. 104–106°,  $n_D^{25}$  1.5062 (lit. b.p. 84–86°/0.2 mm). The infrared spectrum confirmed the lactam structure of the compound. The sample was found to be analytically pure by g.l.c. under the conditions described previously.<sup>1</sup>

The mass spectrum was recorded using an AEI MS902 double-focusing mass spectrometer operating at an ionizing potential of 70 eV and a source pressure of the order of  $10^{-7}$  mm. Samples were introduced into the ionizing chamber by the direct insertion technique.

### Acknowledgment

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<sup>3</sup> Bohlmann, F., Ottawa, N., and Keller, R., *Liebigs Ann.*, 1954, **587**, 162.

<sup>4</sup> Boekelheide, V., and Rothchild, S., *J. Am. chem. Soc.*, 1949, **71**, 879.