New Mass Spectra

Mass Spectra of Some Oxazolidines Formed by Reaction of Ephedrine and Pseudoephedrine with Aliphatic Ketones

In a recent contribution to this journal,[1] we described the mass spectra of ten oxazolidines synthesized by reaction of ephedrine and pseudoephedrine with various aromatic aldehydes. Since oxazolidines formed by the reaction of the ephedrines with aliphatic ketones are also widely reported in the literature,[2,3] we decided to record the mass spectra of ten of these compounds. With the exception of **1a** (ephedrine–acetone derivative),[4] none of these spectra have previously been reported. The compounds were synthesized by reflux of ephedrine or pseudoephedrine with slight excess of ketone in an organic solvent by methods previously described in the literature.[5] See Fig. 1.

Mass spectra were recorded on a Hewlett-Packard Model 5970B/5890A gas chromatograph–mass spectrometer system. Compounds were dissolved in methanol at a concentration of 0.008 mg cm^{-3}. Injections of 1 μl were made on to a 12.5 m, 0.22 mm inner diameter HP-1 high-performance capillary column, coated with a 0.3 μm film of cross-linked dimethyl silicone gum stationary phase, using a Hamilton syringe. A split-splitless injection system was used with a 30:1 split ratio. Compounds were run on a temperature program between 70 °C and 250 °C at a rate of 25 °C per minute. The total ion chromatograms for each of these compounds had retention times of between 4 and 11 minutes under these conditions.

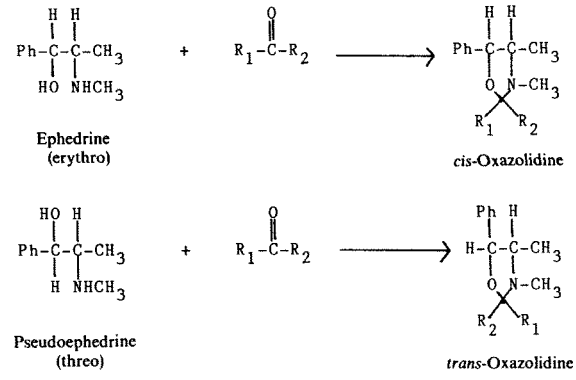
The mass spectrum and data for the ephedrine–cyclohexanone derivative (**3a**) are shown in Fig. 2 and Table 1.

Table 1. Mass spectral data for ephedrine–cyclohexanone derivative (3a)

m/z	M – ?	Relative abundance
245	0*	27.0
203*	42	11.8
202*	43	100
148*	97	54.3
118*	127	26.9
117	128	12.8
91*	154	10.1
56	189	10.0
55*	190	11.7

One can see from these data that major peaks occurred at *m/z* 245 (m^+), 203, 202 (base), 148, 118, 117, 91, 56 and 55. Those peaks which also occur in the spectra of the other compounds were noted. Their relative abundances are shown in Table 2.

These data indicate that for this class of compound the structure can be inferred from the mass spectra. Molecular ions were noted for all ten of the compounds, although they were quite small for the acetone derivatives (**1a**, **1b**). The base peaks for the acetone derivatives were *m/z* 148. This peak was also prominent in the other eight compounds and probably represents loss of ketone from position 2 of the oxazolidine ring. A prominent peak was observed at *m/z* 202 in the eight compounds which were synthesized from cyclic ketones (**2a**, **b**–**5a**, **b**). It was the base peak for all of these compounds



1a from ephedrine, $R_1=R_2=CH_3$
1b from pseudoephedrine, $R_1=R_2=CH_3$
2a from ephedrine, $R_1=R_2=$
2b from pseudoephedrine, $R_1=R_2=$
3a from ephedrine, $R_1=R_2=$
3b from pseudoephedrine, $R_1=R_2=$
4a from ephedrine, $R_1=R_2=$ –CH_3
4b from pseudoephedrine, $R_1=R_2=$ –CH_3
5a from ephedrine, $R_1=R_2=$ –tBu
5b from pseudoephedrine, $R_1=R_2=$ –tBu

Figure 1. Synthesis of oxazolidines.

Table 2. Abundances of major fragments of oxazolidines

Compound	Molecular ion	m/z 203	m/z 202	m/z 148	m/z 118	m/z 91	M – 106
1a	0.4	—	—	100	2.7	11.7	38.6
1b	0.4	—	—	100	2.8	13.1	45.1
2a	9.3	12.6	77.9	72.2	100	18.7	34.6
2b	12.3	13.1	100	52.4	72.8	11.0	13.5
3a	27.0	11.8	100	54.3	26.9	10.1	8.7
3b	14.1	16.7	100	74.4	42.0	14.0	8.7
4a	9.4	15.8	100	59.5	25.4	11.7	4.0
4b	6.1	15.1	100	51.5	25.1	12.1	2.7
5a	6.3	15.7	100	38.8	10.4	5.0	—
5b	6.0	14.1	100	34.9	10.6	6.7	1.6

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except the ephedrine-cyclopentanone derivative (**2a**). It was absent in the acetone derivatives, and possibly arises from fragmentation of the alicyclic ring.

The fragment at *m/z* 118 was the base peak for the ephedrine–cyclopentanone derivative **2a**. It was also observed in the other nine compounds. It possibly represents the fragment $[Ph{-}CH{=}CH{-}CH_3]^+$. Fragments at *m/z* 91, $[C_7H_7]^+$, were also seen in all of the compounds.

In our earlier paper, we stated that the base peaks for oxazolidines formed from the ephedrines and aromatic aldehydes normally were found at M − 106, probably resulting from loss of benzaldehyde from position 5 of the oxazolidine ring. From the data we can see that similar peaks were prominent in the acetone derivatives (**1a**, **1b**) and the cyclopentanone derivatives (**2a**, **2b**) but were small or absent in the other six compounds.

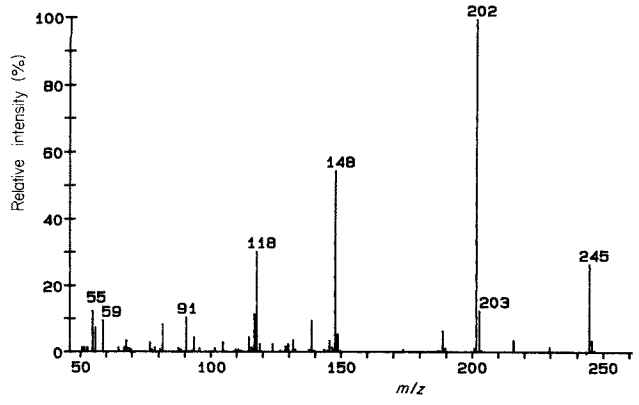

Figure 2. Mass spectrum of *cis*-2,2-cyclohexylidene-3,4-dimethyl-5-phenyl oxazolidine (**3a**).

In summary, these compounds appear to fragment by an identifiable pattern which gives rise to a molecular ion and peaks at *m/z* 148, 118 and 91. Those oxazolidines synthesized from the ephedrines and cyclic ketones also give a prominent peak at *m/z* 202 which is usually the base peak.

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