20. The Thermal Benzoxazinone-Benzoxazole Conversion, a Reexecution of a Mass Spectrometric Decay by Thermolysis

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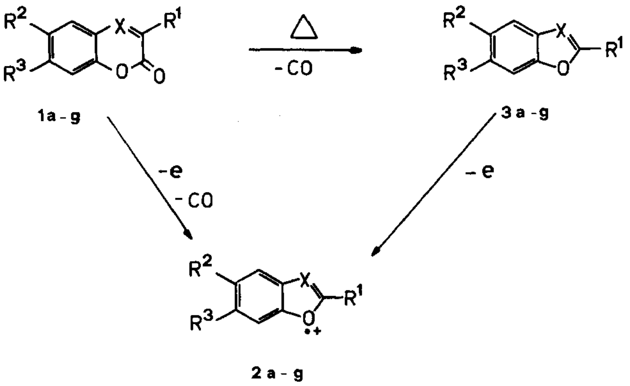
Summary

The base peak in the mass spectrum of several 1,4,2-benzoxazinone derivatives **1a–f** (*cf. Scheme 1* and the Table) suggests a clean carbon monoxide elimination leading to benzoxazole radical cations **2a–f**. This benzoxazinone-benzoxazole conversion can be reproduced quantitatively by flash vacuum thermolysis.

The isomeric 2,4,1-benzoxazinone **4** (*cf. Scheme 2*) eliminates carbon dioxide – the resulting biradical species **5** does not recombine to benzazete **10** but fragments into nitrile and benzyne (**7**).

Mass spectra of alkyl- and aryl substituted 1,4,2-benzoxazinones **1a–f** (*cf. Scheme 1* and the Table) all show that the most important decomposition step from the parent ion is the extrusion of carbon monoxide. The resulting radical cation gives rise to the base peak at M^{+}-28 mass units. The further fragmentation pattern is closely related to that of the corresponding 1,3-benzoxazoles **3a–f**. (Fig. 1). This observation can be interpreted easily by assuming the presence of a 1,3-benzoxazole radical cation **2a–f** as common intermediate.

Scheme 1



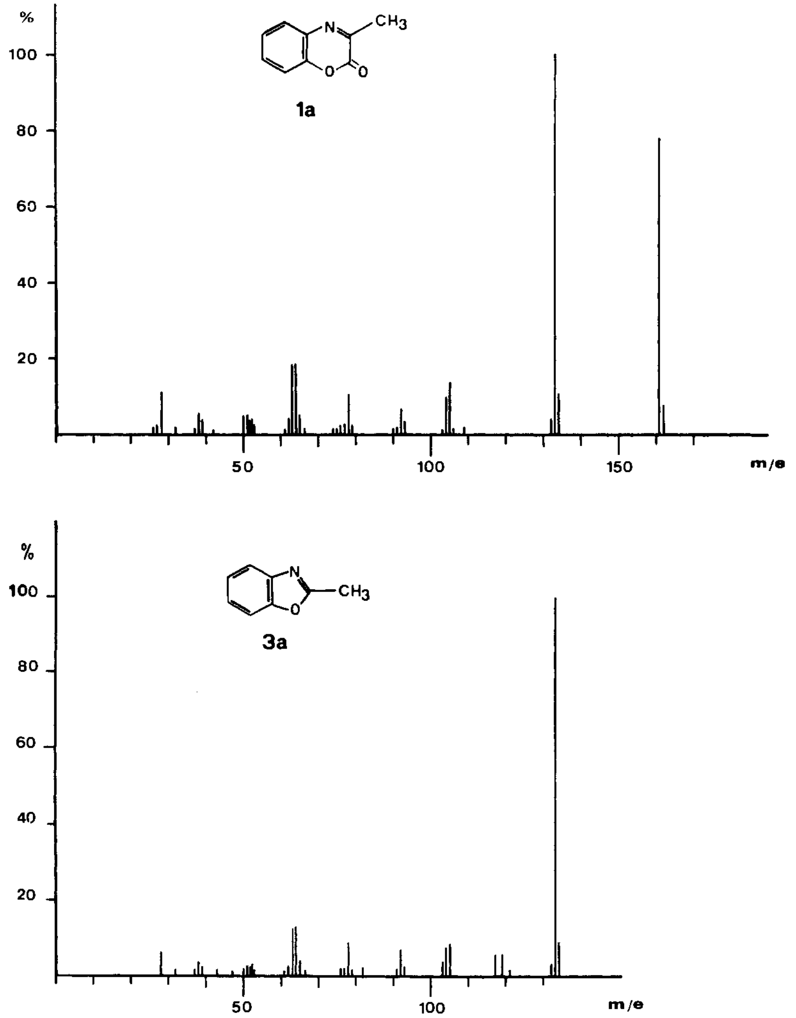


Fig. 1. *Mass spectra of 3-methyl-1,2,4-benzoxazinone* (**1a**) *and 2-methyl-1,3-benzoxazole* (**3a**) (70) eV

The same characteristic fragmentation patterns have been reported for cumarine (**1g**) [1] where the benzofuran radical cation (**2g**) occurs as intermediate. Other types of cumarines [1] [2], chromanones [3], all pyrone isomers [1] [4–6] and several other aromatic cycles which contain a carbonyl group [7] [8] behave similarly. In all these cases the only concurring fragmentation consists in a previous splitting off of a substituent.

The question arises now whether such an elimination of a part of a heterocyclic system only proceeds from a radical cationic intermediate or it is just a process caused by thermal excitation of the parent molecule (an assumption which is reasonable since this reaction affords very low ionisation tension (~ 5 eV)). The latter hypothesis

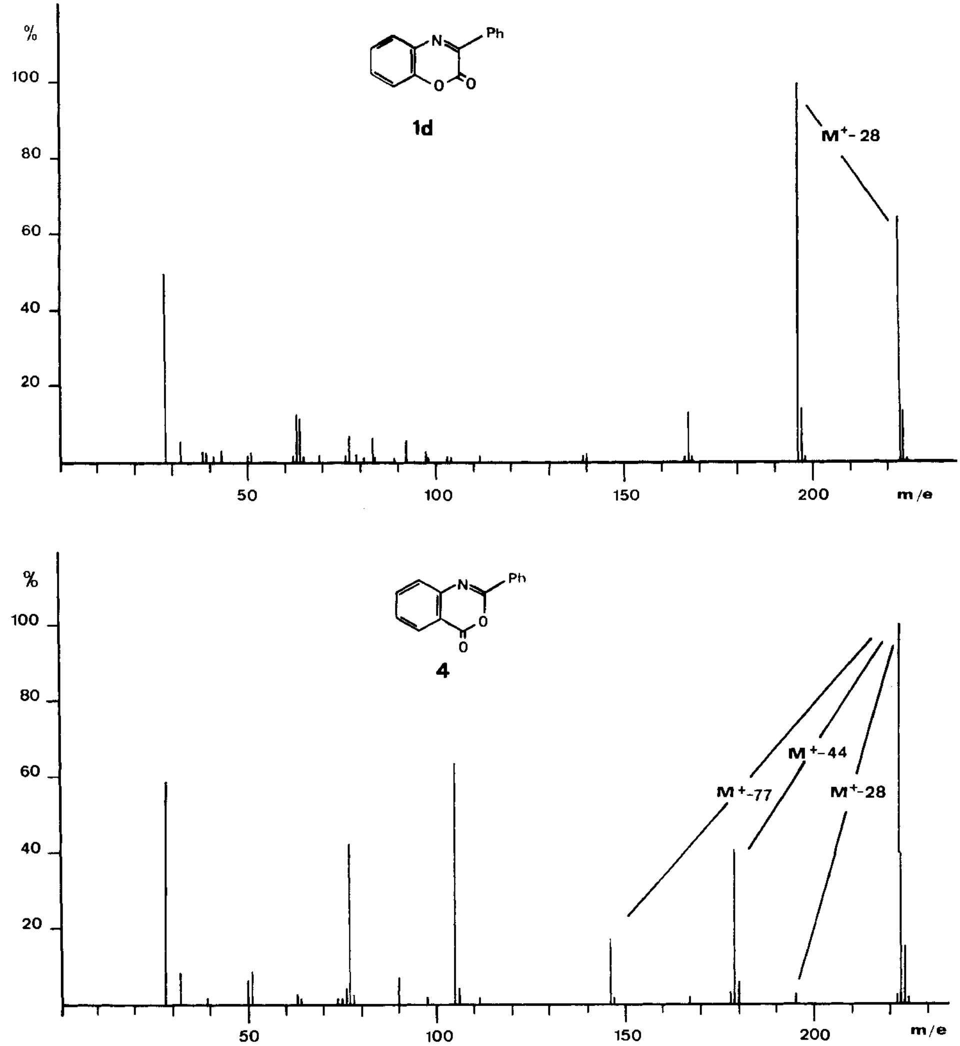


Fig. 2. *Mass spectra of 3-phenyl-1,4,2-benzoxazinone* (**1d**) *and 3-phenyl-2,4,1-benzoxazinone* (**4**) (70 eV)

could be tested by effecting thermal elimination of carbon monoxide from the benzoxazinones **1a–f**: flash vacuum thermolysis of **1a–g** at temperatures between 550–650°/0,01 Torr resulted in a clean and nearly quantitative conversion to the corresponding benzoxazoles **3a–g**. Only traces of further decomposed products were detected.

The isomeric 3-phenyl-2,4,1-benzoxazinone **4** shows quite a different behaviour: in the MS., only a small peak at M^{+}-28 mass units, corresponding to a loss of carbon monoxide can be detected (Fig. 2). A rather large peak at M^{+}-44 suggests the elimination of carbon dioxide. Though, other processes are competitive, in this case the

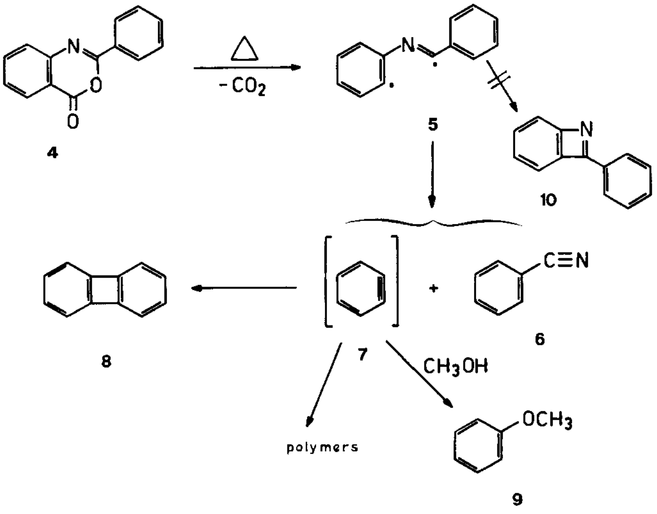
Table. *Benzoxazoles obtained by masspectrometric decay and by flash vacuum thermolysis of benzoxazinones*

3[a]	a	b	c	d	e	f	g[1]
X	N	N	N	N	N	N	CH
R^1	CH_3	CH_3	CH_3	C_6H_5	C_6H_5	C_6H_5	H
R^2	H	CH_3	H	H	CH_3	H	H
R^3	H	H	CH_3	H	H	CH_3	H
Yield (%)[b]	92	95	>95	>95	>95	>95	93
m.p.	–	–	–	103°	103°	92°	–
b.p.	201°	215°	203°	–	–	–	174°
Lit.	[9]	[10]	[11]	[9]	[12]	[13]	[14]

[a] Products have been identified by IR., NMR., MS. and elemental analysis.
[b] Yields of analytically pure products.

phenyl substituent splits off leading to a peak at M^+-77. Benzoyl radical cation, *m/e* 105, which is the base peak, is probably not formed in a direct fragmentation of **4**, a metastable peak at *m/e* 56,53 (corresponding to a decay 195−90=105 *m/e*) points out that the carbon monoxide elimination proceeds. For thermolysis a temperature of 900° was required. In the cold trap only traces of carbon monoxide were detected; the major component of the gaseous fraction was carbon dioxide (shown by IR. spectroscopy). In the condensed phase a 50% yield of benzonitrile (**6**), a small amount

Scheme 2



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[1] Cumarone **3g** has already been obtained from cumarine **1g** by passing it through a tin-covered iron tube at 860° [15] or a nickel-catalyst at 350° [16].

of dibenzocyclobutane (**8**) along with unidentified polymeric products were found. When the thermolysis was carried out in presence of methanol-vapour a considerable amount of anisole could be isolated.

This result can be explained easily by first assuming the formation of a biradical **5**. Even though a recombination of **5** to form 2-phenyl-benzazete (**10**) might be expected, no products derived from this species have been found. This behaviour of **5** is in perfect agreement with the results obtained by *Rees et al.* [17] [18]: pyrolysis of 3-phenyl-1,2,4-benzotriazine does not lead to formation of 2-phenyl-benzazete (**10**).

We will further attempt to find a general correlation between mass spectroscopy and thermolysis since this method offers the possibility to predict the formation of reactive intermediates and/or new synthetic pathways.

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