# APPLICATION OF MASS SPECTROMETRY IN STRUCTURAL AND STEREOCHEMICAL INVESTIGATIONS

## II.† MASS SPECTRA OF 3-ACYLOXYQUINUCLIDINES AND BENZO(b)QUINUCLIDINES

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The mass spectra of 3-acetoxy- and 3-benzoxy-substituted quinuclidines and benzo(b)quinuclidines were investigated. The fragmentation of the investigated compounds is realized from the open form of the molecular ion that is produced after cleavage of the bridge bond containing the substituents. Subsequent elimination of an acyl group leads to the formation of characteristic fragments, the peaks of which are the maximum-intensity peaks in the spectra.

The fragmentation of various substituted $\beta$-quinuclidones and $\beta$-benzo(b)quinuclidones from the open form of the molecular ion [3-5] was investigated in [1, 2]. In the present communication we examine the mass spectra of 3-acetoxy- and 3-benzoxy-substituted quinuclidines and benzo(b)quinuclidines. It is shown that for these compounds fragmentation is also realized from the open form of the molecular ion that develops as a result of cleavage of the bridge bond containing the substituents.

The mass spectra of 3-acetoxy- (I) and 3-benzoxyquinuclidine (II) are presented in Fig. 1. At 30 eV the maximum peaks in the spectra are those of fragments with m/e 126, which are formed from $M^{+\cdot}$ (m* = 93.5, m* = 69) as a result of the loss of acetyl and benzoyl groups. The stability of these fragments can be

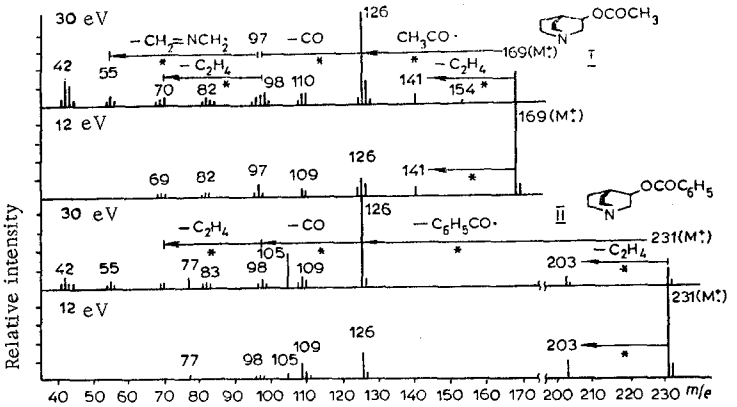


Fig. 1. Mass spectra of 3-acetoxy- (I) and 3-benzoxyquinuclidine (II).

† See [2] for communication I.

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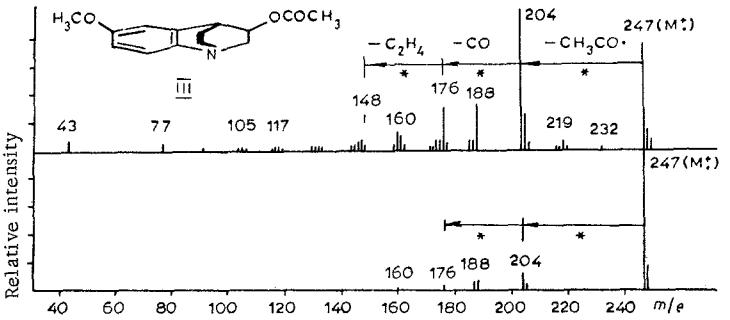
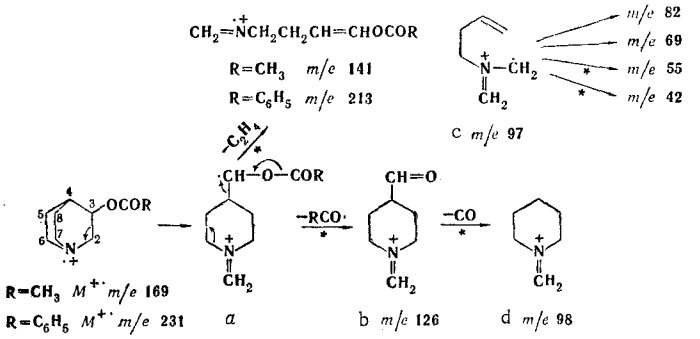


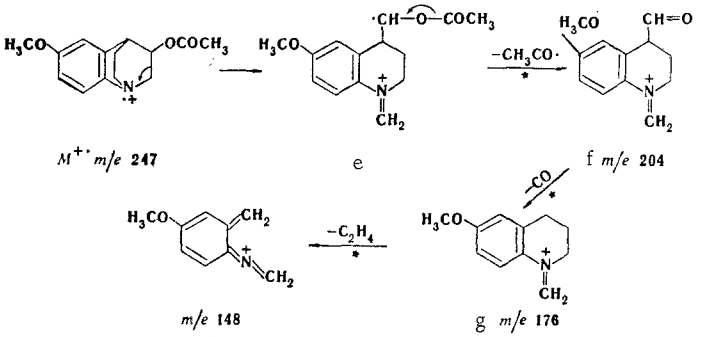

Fig. 2. Mass spectra of syn-3-acetoxy-6-methoxybenzo(b)-quinuclidine (III).

explained only by their formation from the open form of the molecular ion (*a*), which is formed on cleavage of the $C_2-C_3$ bridge bond. This is in agreement with the rather high intensity of the molecular-ion peaks for I and II at both 30 eV and 12 eV; this is typical for the amine fragment, which is also the open molecular form.




Detachment of carbon monoxide from ion b with migration of a hydrogen atom to $C_4$ (in both cases the process is confirmed by metastable peak m* = 76) leads to fragment d with m/e 98. At the same time, a considerable difference in the spectra is the presence of a fragment with m/e 97 during the disintegration of I. This difference is displayed particularly distinctly at a low ionizing voltage. This fragment can apparently form only from the molecular ion. Since the mass spectrum of I is identical to the mass spectrum of 3-quinuclidone [1] up to m/e 97, it seems possible to assign structure c to the ion with m/e 97. It is interesting to note that a fragment of corresponding structure (c) is formed in the presence of $M^+$ in the disintegration of 3-quinuclidone during the elimination of carbon monoxide, while its peak is the maximum-intensity peak in the spectra at 30 and 12 eV. The absence of an analogous fragment in the disintegration of II can be explained by the occurrence in $M^{+\cdot}$ of a competitive reaction to form a benzoylium ion with m/e 105, the peak of which is also observed at 12 eV.

As in the disintegration of the similar quinuclidine analog (I), the elimination of an acetyl group from open ion e, which leads to fragment f with m/e 204, is clearly expressed in the fragmentation of syn-3-acetoxy-6-methoxybenzo(b)quinuclidine (III) (Fig. 2, and the scheme below). The splitting out of carbon monoxide from f and of ethylene from g with m/e 176 is confirmed by the metastable ions (m* = 152, m* = 122.8).



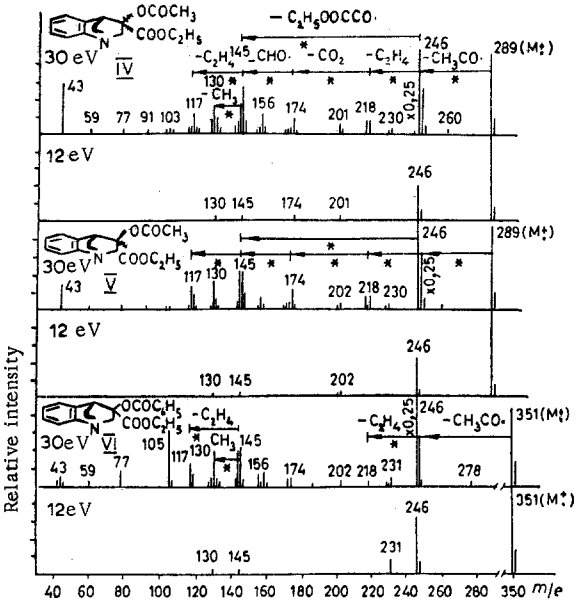



Fig. 3

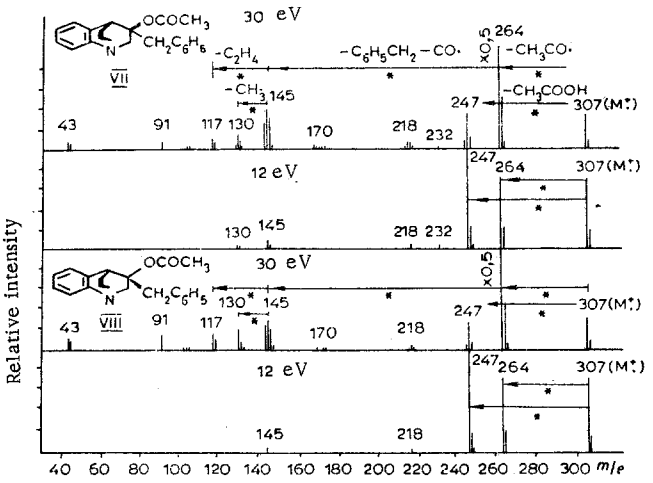
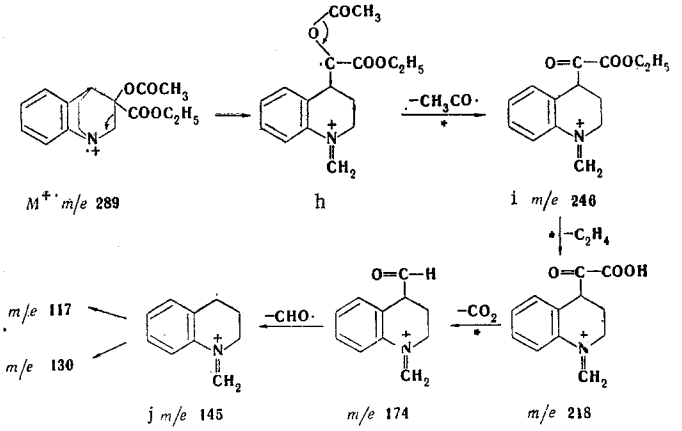



Fig. 4

Fig. 3. Mass spectra of syn- and anti-3-acetoxy-3-carbethoxybenzo(b)quinuclidines (IV and V) and syn-3-carbethoxy-3-benzoxybenzo(b)quinuclidine (VI).

Fig. 4. Mass spectra of syn- and anti-3-acetoxy-3-benzylbenzo(b)quinuclidines (VII and VIII).

The practically completely identical character of the mass spectra of the epimeric (with respect to $C_3$) syn- and anti-3-acetoxy-3-carbethoxybenzo(b)quinuclidines (IV and V)† (Fig. 3) can also be explained by fragmentation from open molecular ion h (see the scheme below), in which the stereochemical differences vanish. In the case of IV and V, as also for monoacetoxy-substituted quinuclidines and benzo(b)quinuclidine (I and III), the predominant process in the disintegration of the open molecular ion is elimination of an acetyl group (m* = 210) with the formation of fragment i with m/e 246, the peak of which is a maximum in the spectra. The disintegration of ion i with the formation of fragment j with m/e 145 occurs either as a multistep process with the elimination of ethylene (m* = 193), carbon dioxide (m* = 139), and a formyl radical (m* = 121.5) or in one step (m* = 85). We described the subsequent disintegration of ion j in detail during an investigation of the fragmentation of benzo(b)-3-quinuclidone [1].




A similar fragmentation scheme is observed for syn-3-carbethoxy-3-benzoxybenzo(b)quinuclidine (VI) (Fig. 3). Because of fragmentation from the open molecular ion k, the mass spectra of the epimeric (with respect to $C_3$) syn-and anti-3-acetoxy-3-benzylbenzo(b)quinuclidines (VII and VIII) (Fig. 4 and the scheme below) are also identical. A peculiarity of the spectra of VII and VIII as compared with the mass spectra of III, IV, and V is the presence of a peak of fragment *l* with m/e 247, which corresponds to the splitting

†With syn or anti orientation of the $COOC_2H_5$ group relative to the benzene ring.

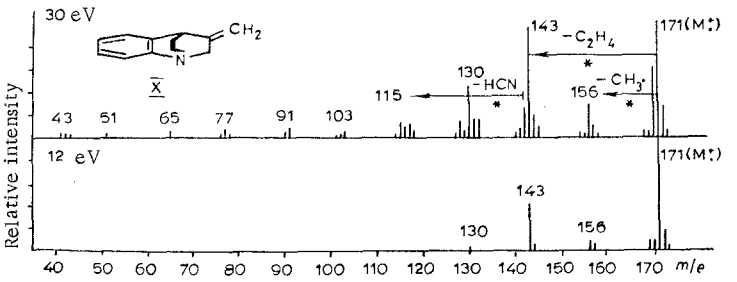
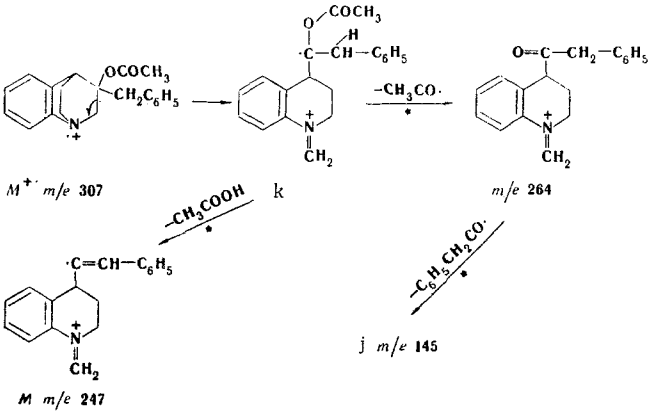
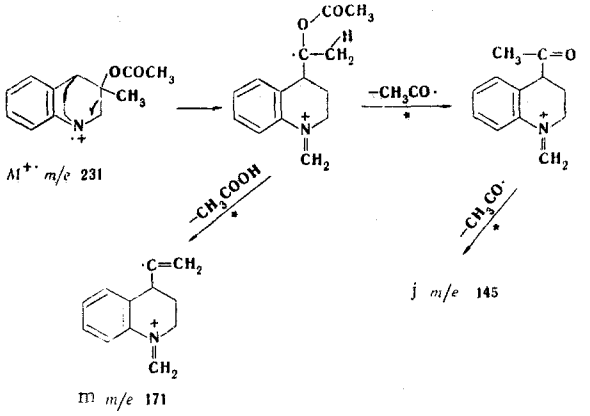



Fig. 5. Mass spectrum of 3-methylenebenzo(b)quinuclidine.

out of a molecule of acetic acid from $M^{+\cdot}$. The peak of fragment *l* is maximum in intensity in the spectrum at 12 eV. The elimination of $CH_3COOH$ (m* = 199) occurs as a result of one-step ejection of the hydrogen atom of the benzyl group and an acetoxy radical. The predominance of this process at 12 eV is probably explained by the increasing role of the frequency factor at a low ionizing voltage for rearrangements that occur through multimembered transition states [6].




The disintegration of anti-3-acetoxy-3-methylbenzo(b)quinuclidine (IX) is basically similar to the fragmentation of VII and VIII.

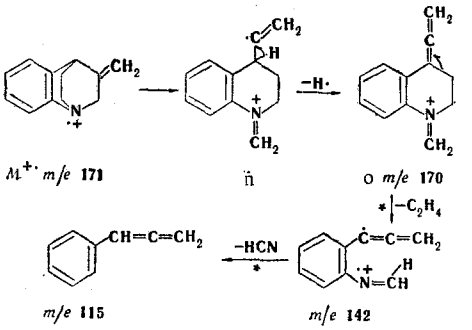



The splitting out of a molecule of $CH_3COOH$ (m* = 126.5) leads to the open molecular ion of 3-methylenebenzoquinuclidine (m) with m/e 171. The possibility of the occurrence of this process is confirmed by the mass spectrum of 3-methylenebenzo(b)quinuclidine (X) (Fig. 5).

It is interesting to note that the disintegration of X is yet another confirmation of the fragmentation of the bicyclic quinuclidine system from the open molecular ion. In fact, the presence of an intense peak of the M−1 ion at 30 eV in the mass spectrum of X can be explained only by the existence of $M^{+\cdot}$ in the n form. The subsequent ejection of $H^{\cdot}$ from n leads to stable structure o with m/e 170, the subsequent disintegration of which is confirmed by the metastable ion. (See scheme on next page.)

Thus an examination of the data obtained makes it possible to assume that the fragmentation of the investigated compounds is realized from the open form of the molecular ion, which is formed on cleavage

of the bridge bond containing the substituents, with ejection of an acetyl or benzoyl group. This process leads to characteristic fragments, the peaks of which are maximum in intensity in the spectra. In addition,




the spectra contain fragment peaks that are also characteristic for other similar functionally substituted quinuclidines and benzo(b)quinuclidines.

## EXPERIMENTAL

The mass spectra of the compounds were recorded with an MKh-1303 mass spectrometer with "direct" introduction of the sample into the ion source at ionizing voltages of 50, 30, and 12 eV. The inlet temperature was 20°, the temperature of the ionization chamber was 125°, and the emission current was 75 mA. The substances were purified prior to the recording of the spectra by distillation or sublimation in vacuo.

3-Acetoxyquinuclidine (I). This compound had bp 73-74° (0.4 mm) [7].

3-Benzoxyquinuclidine (II). This compound had bp 148-150° (0.3 mm) [7].

syn-3-Acetoxy-6-methoxybenzo(b)quinuclidine (III). This compound was synthesized from ethyl quininate through syn-3-hydroxy-6-methoxybenzo(b)quinuclidine and had bp 142-144° (0.4 mm).

syn- and anti-3-Acetoxy-3-carbethoxybenzo(b)quinuclidines (IV and V). These compounds were synthesized from benzo(b)-3-quinuclidone. Compound IV had mp 78-80°, while V had bp 134-136° (0.6 mm).

syn-3-Carbethoxy-3-benzoxybenzo(b)quinuclidine (VI). This compound had mp 106-107°.

syn- and anti-3-Acetoxy-3-benzylbenzo(b)quinuclidines (VII and VIII). These compounds were synthesized by the reaction of benzo(b)-3-quinuclidone with benzylmagnesium chloride and subsequent acylation of the 3-benzyl-3-hydroxybenzo(b)quinuclidine. Compound VII had mp 92-94°, while VIII had mp 132-133°.

anti-3-Acetoxy-3-methylbenzo(b)quinuclidine (IX). This compound was prepared by the method used to obtain VII and VIII and had mp 62-63°.

3-Methylenebenzo(b)quinuclidine (X). This compound was obtained as follows. A 6.8-g (0.036 mole) sample of a mixture of syn- and anti-3-methyl-3-hydroxybenzo(b)quinuclidines and 70 ml of thionyl chloride were refluxed for 7 h, after which the mixture was evaporated. The residue was treated with 25% potassium carbonate solution to isolate a mixture of 3-methyl-3-chlorobenzo(b)quinuclidine and X. A 3.5-g sample of the mixture was heated for 20 h with a solution of 1.2 g (0.21 mole) of potassium hydroxide in 50 ml of ethanol in an ampul at 150-160° to give 1.8 g of X with bp 152-154° (30 mm). Found: N 8.00%. $C_{12}H_{13}N$. Calculated: N 8.19%.

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