# MASS SPECTRA OF THE SUBSTITUTED QUINUCLIDINES

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(Received 24 November 1969; accepted 2 January 1970)

Abstract—The mass spectra of the quinuclidine-2 (and -3)-ones and other functional derivatives of quinuclidine as well as 2-azaquinuclidine and benzoquinuclidine have been investigated. The fragmentation through the open form of the molecular ion and the applicability of Bredt's rule to amine fragmentation of the bridgehead nitrogen bicyclic systems are discussed.

IN THE previous paper<sup>1</sup> mass spectra of some quinuclidines have been considered from the point of view of the relaxation of the amine fragmentation according to Bredt's rule. Low intensities of  $\alpha$ -cleavage fragments have been observed in mass spectra of quinuclidine, 2- and 4-azaquinuclidines and 2-( $\alpha$ -hydroxyalkyl)-quinuclidines in contrast to the behaviour of the corresponding five- and six-membered monocyclic alkyleneimines.

This communication attepts to consider the open molecular ion fragmentation of the various functional derivatives of quinuclidine.

### Esters of the quinuclidinecarboxylic acids

 $\alpha$ -cleavage and elimination of the substituent in methyl quinuclidine-2-carboxylate (1) apparently correspond to open molecular ion fragmentation but not to the formation of the ion (a'), stabilization of which is prohibited by Bredt's rule (Fig. I):



This is confirmed by a sharp decrease in intensity of a and generally by decrease of molecular ion fragmentation in the low-voltage mass spectrum (Fig. 1). The excess of the energy of ionization over the ionization potential is already insufficient for the cleavage of two bonds: process A and  $\alpha$ -cleavage, peak [M]<sup>+</sup> remains the base peak



independent of the ionizing voltage. The last phenomenon is typical for an amine fragment, which is what the open form of the molecular ion is in this case.

The main course of fragmentation may be easily explained. Processes of type b lead to intensive fragments  $[M - 15]^+$  (c), with expulsion of a methyl radical:



b', m/e 140, with 1-6 and 4-5 bond cleavage and H-migration from the  $\alpha$ -position leads to the expulsion of an ethyl radical:



and b'', m/e 83, with expulsion of the neutral methylacrylate molecule:



The peaks of fragments of type a, m/e 168 and 110, b, m/e 140 and 82, b', m/e 198 and 154 and b'', m/e 83 are observed in spectra of dimethyl quinuclidine-2,3-dicarboxylate (II) and ethyl quinuclidine-4-carboxylate (III), respectively (Fig. 2).



Elimination of the 4-substituent in III facilitates the stabilization of the open form of molecular ion:



Similar processes have been observed in the mass spectrum of unsubstituted quinuclidine.<sup>1</sup>

# Esters of the 5-ketoquinuclidine-2-carboxylic acid

The mass spectra of methyl- (IV) and ethyl- (V) esters of the 5-ketoquinuclidine-2carboxylic acid are markedly different from each other (Fig. 3). The fragmentation of IV may be depicted by the scheme:



Degradation of V up to the first abundant fragment (m/e 125) takes place, however, without cleavage of the quinuclidine system:





This fact is confirmed by the similarity of the spectrum of V to that of quinuclidine-3one (VI) in the region of lower mass numbers (Fig. 4).

### Quinuclidine-3-one (VI) and quinuclidine-3-ole (VII)

The course of degradation of VI is similar in principle to that of IV and completely different from that of VII. In the mass spectrum of the latter the characteristic fragments  $[M - 15]^+$ ,  $[M - 17]^+$  and  $[M - 29]^+$  appear from the open form of  $[M]^{+}$  and determine the direction of the further fragmentation (Fig. 4):



#### Benzoquinuclidine (VIII)

The interesting one-step elimination of the vinyl-radical and subsequent dehydration up to the hydroquinolinium-ion is observed for benzoquinuclidine (VIII) together with the characteristic fragmentations (c' and d') from the open form of the molecular ion (Fig. 5):



# 6,6,8,8-Tetramethylquinuclidine-2-one (IX)

Amide resonance is hindered in quinuclidine-2-one according to Bredt's rule.<sup>2</sup> Thus, the high intensity of  $[M]^+$  in mass spectra of IX at 30 and 12 eV (Fig. 6) may be explained by the (amide type) fragment of the open form of  $[M]^+$ :







## 2-Acetyl-2-azaquinuclidine-3-one (X)

Ketene elimination is typical for the electron-impact degradation of diacylamines<sup>3</sup> and it may be depicted for X in the non-open form: (Fig. 7):



Thus, the low intensity of the amine fragment and its weakening in the low-voltage spectra are characteristic peculiarities of the mass-spectra of functional quinuclidine derivatives. Further, relatively high abundance of the molecular ion as a rule corresponds to the amine fragment of the open form of this ion.

#### EXPERIMENTAL

The mass spectra were measured with an MX-1303 mass spectrometer, using the heated steel inlet system at 20 to  $50^{\circ}$  and at electron voltages of 30 and 12 eV.

The starting materials were purified by vacuum distillation or sublimation. 1: b.p. 115° (12 mm);<sup>4</sup> II was prepared by esterification of quinuclidine-2,3-dicarboxylic acid<sup>5</sup> with a boiling 12% MeOH solution of HCl followed by isolation of the base with 50% K<sub>2</sub>CO<sub>3</sub> solution. The yield was 90%; b.p. 104 to 105° (0.5 mm). Found: C 58·21; H 7·58; N 5·98. C<sub>11</sub>H<sub>17</sub>NO<sub>7</sub> requires C 58·12; H 7·55; N 6·14. III was obtained by treating ethyl quinuclidine-2-carboxylate hydrochloride<sup>6</sup> with 50% K<sub>2</sub>CO<sub>3</sub> in H<sub>2</sub>O; b.p. 122 to 123° (14 mm). Found: C 65·85; H 9·38; N 7·66. C<sub>10</sub>H<sub>17</sub>NO<sub>2</sub> requires: C 65·54; H 9·35; N 7·64. IV: b.p. 113 to 114° (0.5 mm);<sup>7</sup> V: b.p. 107 to 108° (0.8 mm);<sup>8</sup> VI: m.p. 147 to 148°; subl. p. 100° (10 mm);<sup>9</sup> VII: m.p. 225 to 227°;<sup>10</sup> VIII: m.p. 68 to 69°;<sup>11</sup> IX was prepared by the following method: 15 g 2,2,6,6-tetramethylpiperidine-4-acetic acid hydrochloride<sup>\*</sup> and 150 ml SOCl<sub>2</sub> were boiled for 3 hrs. The residue after evaporation in vacuo was ground in 100 ml dry ethyl ether and then was boiled with 30 ml Et<sub>3</sub>N for 20 hrs. Solid products were separated, solvent was evacuated and IX was distilled in vacuo. The yield was 2·9 g (25%); b.p. 100 to 101° (5 mm);  $n_D^{20}$  1·4930;  $\nu_{c=0}$  1755 cm<sup>-1</sup>. Found: C 72·76; H 10·70; N 7·72; C<sub>11</sub>H<sub>19</sub>NO requires C 72·92; H 10·52; N 7·73. X: m.p. 124 to 126°.<sup>12</sup>

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  - The synthesis of this compound will be described separately.