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Electron ionization-induced fragmentation of *N*- and *O*-alkoxymethylated carbostyril and phenanthridinone†

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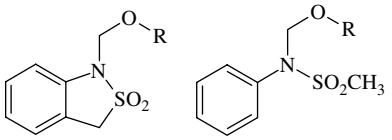
Unimolecular fragmentation patterns of *N*-alkoxymethylated carbostyril and phenanthridinone and their *O*-alkoxymethyl isomers were studied. The main fragmentation reaction observed for the studied compounds is the elimination of an aldehyde molecule. The main products of this reaction are the appropriate *N*-methyl derivatives, but ions with other structures are also formed. This reaction is supposed to proceed via 1,3-H shift in the alkoxymethyl group in the case of the *N*-alkoxymethyl derivatives and by a multi-step mechanism for *O*-alkoxymethylated compounds. Another important fragmentation common for all studied compounds is the loss of an alkyl radical from *N*- and *O*-alkoxymethyl groups, yielding the appropriate stable isomeric cations, which, according to the results of the further fragmentation, undergo fast equilibration reaction via an ion–neutral complex. This process is accompanied by the unusually high kinetic energy release value. Copyright © 2004 John Wiley & Sons, Ltd.

KEYWORDS: fragmentation mechanisms; ion–neutral complex; kinetic energy release; *N*-alkoxymethyl derivatives; carbostyril; phenanthridinone

INTRODUCTION

In a previous paper we have described fragmentation patterns of *N*-alkoxymethyl derivatives of benzosultams and methanesulfonanilides (**1** and **2**).[1]

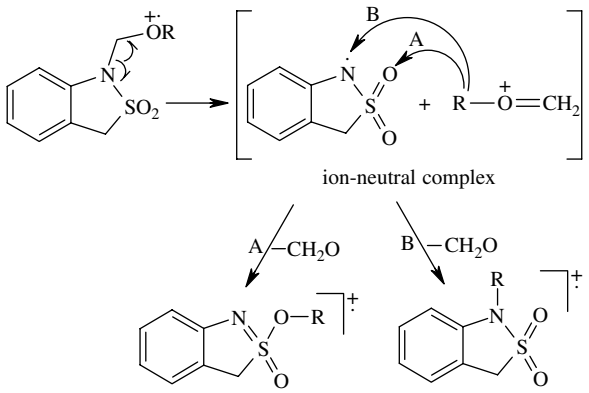


1 **2**

R = CH_3, C_2H_5

It was demonstrated that the molecular ions of these compounds undergo a unique rearrangement reaction resulting in the loss of a formaldehyde molecule independently on the substituent R. This fragmentation has been rationalized by the mechanism involving an ion–neutral complex (INC) (Scheme 1).

The crucial step in this process consists in an alkyl group transfer from oxonium cation to one of the nucleophilic centers of the radical within INC. The ability of oxonium ions to alkylate the appropriate nucleophilic reagents in a gas phase is well known;[2,3] however, only in a paper by Tu and Holmes[4] was a reaction mechanism similar to that proposed by us described. Such fragmentation reactions proceeding via INC are still weakly recognized although several examples of them were reviewed in the early 1990s.[5–8] Since that time, many articles dealing with INC have been published but no more recent review is available. Constant interest in INC prompted us to search for other compounds with *N*-alkoxymethyl groups which should undergo fragmentation according to this mechanism. It should be noted also that many compounds with *N*-alkoxymethyl groups in their molecules are biologically active products, mainly herbicides, and are manufactured on a large scale. Better understanding of the fragmentation patterns of these compounds



Scheme 1. Elimination of CH_2O molecule from the molecular ions of *N*-(alkoxymethyl)benzosultams involving an ion–neutral complex.

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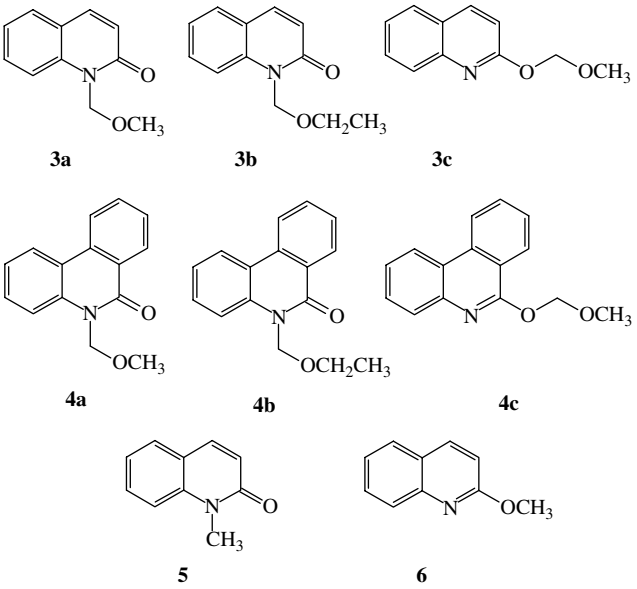
will help to develop methods for their detection and quantitation in environmental samples. Moreover, alkoxymethyl groups are readily applied as *O*- and *N*-protective groups in organic synthesis,[9] so information about their fragmentation patterns is still of interest.

In a previous paper,[10] we presented our results of the study of electron ionization (EI)-induced fragmentation of *N*-alkoxymethyl derivatives of anilides which are analogues of **2**. It turned out that in the case when the sulfonyl group has been replaced by the carbonyl moiety, practically no elimination of formaldehyde took place. Instead, the elimination of an alkyl radical was the dominant process. In this paper, we describe our results concerning another class of compounds bearing an *N*-alkoxymethyl substituent: *N*-alkoxymethyl derivatives of carbostyril (1*H*-quinolin-2-one) and phenanthridinone (5*H*-phenanthridin-6-one). The latter are compounds of considerable interest in organic chemistry owing to their biological activity.[11,12]

Preliminary examination of the EI mass spectra of *N*-(methoxymethyl)carbostyril (**3a**) and *N*-(methoxymethyl) phenanthridinone (**4a**) (see Fig. 1) revealed that the elimination of a CH_2O molecule is an important fragmentation channel. This observation prompted us to study the mechanism of this process in detail, particularly in terms of the possible participation of the ion–neutral complexes. Additionally, molecular ions of **3a** and **4a** undergo another competitive reaction: elimination of an alkyl radical. This seemingly trivial process appeared also to be interesting, because (i) it was not observed for compounds **1** and **2** (R═CH_3), (ii) it was accompanied by an unusually high kinetic energy release compared with typical heterolytic bond cleavage reactions, as proved by the mass analyzed ion kinetic energy (MIKE) spectrum, and (iii) it proceeds in the same manner also for *O*-methoxymethylated derivatives **3c** and **4c**.

In order to explain this and other features of the fragmentation mechanisms of **3a** and **4a**, we decided to study also their analogues with a different alkoxymethyl group, i.e. *N*-(ethoxymethyl)carbostyril (**3b**) and *N*-(ethoxymethyl)phenanthridinone (**4b**), and their *O*-methoxymethylated isomers, i.e. *O*-(methoxymethyl)carbostyril (**3c**) and *O*-(methoxymethyl)phenanthridinone (**4c**) (Scheme 2). During the course of this work, it was found necessary also to synthesize *N*-methylcarbostyril (**5**) and 2-methoxyquinoline (**6**) as model compounds. Fragmentation of compounds **5** and **6** upon EI conditions has been already described by Clugston and MacLean,[13] but we decided to study these two compounds again using more modern methods.



Scheme 2. Compounds used in the study.

EXPERIMENTAL

Compounds

Compounds **3a**, **3c**, **4a** and **4c** were obtained by the alkylation of carbostyril and phenanthridinone with chloromethyl methyl ether in NaH–THF and separation of the products using column chromatography. *N*-Ethoxymethylated derivatives **3b** and **4b** were prepared in the same way, using $CH_3CH_2OCH_2Cl$ as an alkylating agent. Surprisingly, in this reaction no *O*-ethoxymethylated isomers were formed. The purity of all compounds under study was tested by gas chromatography/mass spectrometry (GC/MS) and their structures were confirmed by the ^{1}H NMR and ^{13}C NMR spectra. Compounds **5** and **6** were prepared according to known methods.

*N-(Methoxymethyl)carbostyril (**3a**)*

^{1}H NMR (500 MHz, $CDCl_3$), δ: 3.41 (s, 3H, OCH_3); 5.71 (s, 2H, NCH_2O); 6.63 (d, 1H, ^3J = 9.5 Hz, —CH═); 7.15–7.60 (m, 4H, ArH); 7.64 (d, 1H, ^3J = 9.5 Hz, —CH═). ^{13}C NMR (125 MHz, $CDCl_3$), δ: 56.2 (OCH_3); 72.8 (NCH_2O); 114.9 (Ar); 120.4 (Ar); 121.1 (—CH═); 122.4 (Ar); 128.3 (Ar); 130.4 (Ar); 138.8 (Ar); 139.9 (—CH═); 162.4 (CO). MS, *m/z* (%): 189 ($M^{+\bullet}$, 58); 174 (63); 159 (36); 158 (28); 147 (10); 146 (100); 131 (7); 130 (22); 129 (34); 128 (86); 117 (6); 116 (8); 103 (11); 102 (11); 90 (7); 89 (15); 77 (22); 76 (6); 75 (8); 63 (11); 51 (16); 50 (7); 45 (63); 39 (7). HRMS: calculated for $C_{11}H_{11}NO_2$, 189.0767; found, 189.0789. M.p. 60–61 °C (white crystals from hexane–ethyl acetate).

*N-(ethoxymethyl)carbostyril (**3b**)*

^{1}H NMR (400 MHz, $CDCl_3$), δ: 1.19 (t, 3H, ^3J = 6.8 Hz, OCH_2CH_3); 3.67 (q, 2H, ^3J = 6.8 Hz, OCH_2CH_3); 5.78 (s, 2H, NCH_2O); 6.65 (d, 1H, ^3J = 9.6 Hz, —CH═); 7.23–7.55 (m, 4H, ArH); 7.68 (d, 1H, ^3J = 9.2 Hz, —CH═). ^{13}C NMR (100 MHz, $CDCl_3$), δ: 15.1 (OCH_2CH_3); 64.4 (OCH_2CH_3); 71.7 (NCH_2O); 115.4 (Ar); 120.6 (Ar); 121.4 (—CH═); 122.6 (Ar); 128.5 (Ar); 130.6 (Ar); 139.1 (Ar); 140.1 (—CH═); 162.7 (CO). MS, *m/z* (%): 203 ($M^{+\bullet}$, 25); 174 (32); 159 (100); 158 (33); 146 (92); 145 (34); 129 (28); 128 (61); 117 (24); 103 (8); 91 (2); 90 (10); 79 (13); 77 (16); 63 (5); 59 (12); 51 (10). Elemental analysis: calculated for $C_{12}H_{13}NO_2$, C 70.93, H 6.40, N 6.89; found, C 71.11, H 6.50, N 6.81%. M.p. 34–35 °C (white crystals from hexane–ethyl acetate).

*O-(Methoxymethyl)carbostyril (**3c**)*

^{1}H NMR (500 MHz, $CDCl_3$), δ: 3.58 (s, 3H, OCH_3); 5.70 (s, 2H, OCH_2O); 6.94 (d, ^3J = 8.8 Hz, —CH═); 7.32–7.88 (m, 4H,

ArH); 8.00 (d, 1H, ^3J = 8.8 Hz, —CH═). ^{13}C NMR (125 MHz, $CDCl_3$), δ: 57.4 (OCH_3); 92.0 (OCH_2O); 112.9 (—CH═); 124.3 (Ar); 125.3 (Ar); 127.3 (Ar); 127.5 (Ar); 129.5 (—CH═); 139.1 (Ar); 146.3 (Ar); 160.9 (—N═C═). IR (KBr), ν: 3052, 2954, 2828, 1619, 1609, 1574, 1508, 1429, 1384, 1315, 1238, 1157, 1088, 981, 945, 823, 757 cm^{-1}. MS, m/z (%): 189 ($M^{+\bullet}$, 13); 174 (40); 159 (39); 158 (22); 147 (8); 146 (83); 145 (6); 131 (5); 130 (13); 129 (30); 128 (62); 117 (7); 116 (9); 102 (8); 101 (12); 89 (18); 77 (12); 76 (5); 63 (13); 62 (6); 51 (10); 50 (9); 45 (100); 39 (13). M.p. 62–63 °C (white crystals from hexane–ethyl acetate) (lit.[14] 66–67 °C).

*N-(Methoxymethyl)phenanthridinone (**4a**)*

^{1}H NMR (500 MHz, $CDCl_3$), δ: 3.44 (s, 3H, OCH_3); 5.76 (s, 2H, NCH_2O); 7.20–8.54 (m, 8H, ArH). ^{13}C NMR (125 MHz, $CDCl_3$), δ: 56.3 (OCH_3); 73.5 (NCH_2O); 115.9 (Ar); 118.9 (Ar); 121.4 (Ar); 122.7 (Ar); 122.8 (Ar); 124.9 (Ar); 127.7 (Ar); 128.9 (Ar); 129.3 (Ar); 132.6 (Ar); 133.8 (Ar); 136.7 (Ar); 162.1 (CO). MS, m/z (%): 239 ($M^{+\bullet}$, 85); 224 (85); 209 (26); 208 (22); 197 (13); 196 (100); 180 (13); 179 (31); 178 (66); 166 (17); 152 (16); 151 (9); 140 (8); 139 (9); 76 (6); 45 (37). M.p. 87–88 °C (white crystals from hexane–ethyl acetate) (lit.[15] 93–94 °C).

*N-(Ethoxymethyl)phenanthridinone (**4b**)*

^{1}H NMR (500 MHz, $CDCl_3$), δ: 1.87(t, 3H, ^3J = 6.8 Hz, OCH_2CH_3); 3.69 (q, 2H, ^3J = 6.8 Hz, OCH_2CH_3); 5.79 (s, 2H, NCH_2O); 7.20–8.49 (m, 8H, ArH). ^{13}C NMR (125 MHz, $CDCl_3$), δ: 14.9 (OCH_2CH_3); 64.2 (OCH_2CH_3); 72.1 (s, 2H, NCH_2O); 116.1 (Ar); 118.9 (Ar); 121.4 (Ar); 122.6 (Ar); 122.7 (Ar); 124.9 (Ar); 127.6 (Ar); 128.8 (Ar); 129.3 (Ar); 132.6 (Ar); 133.8 (Ar); 136.7 (Ar); 161.9 (CO). MS, m/z (%): 253 ($M^{+\bullet}$, 25); 224 (46); 209 (85); 197 (16); 196 (100); 195 (57); 180 (9); 179 (31); 178 (88); 167 (46); 166 (37); 152 (28); 151 (23); 140 (16); 139 (17); 89 (11); 76 (14); 59 (13). Elemental analysis: calculated for $C_{16}H_{15}NO_2$, C 75.88, H 5.92, N 5.53; found, C 75.66, H 5.98, N 5.59%. M.p. 88–89 °C (white crystals from hexane–ethyl acetate).

*O-(Methoxymethyl)phenanthridinone (**4c**)*

^{1}H NMR (500 MHz, $CDCl_3$), δ: 3.65 (s, 3H, OCH_3); 5.89 (s, 2H, OCH_2O); 7.44–8.55 (m, 8H, ArH). ^{13}C NMR (125 MHz, $CDCl_3$), δ: 57.6 (OCH_3); 92.3 (OCH_2O); 119.8 (Ar); 121.8 (Ar); 122.0 (Ar); 122.6 (Ar); 124.6 (Ar); 124.9 (Ar); 127.2 (Ar); 128.1 (Ar); 128.7 (Ar); 130.9 (Ar); 135.0 (Ar); 142.9 (Ar); 157.6 (—N═C═). MS, m/z (%): 239 ($M^{+\bullet}$, 45); 224 (61); 209 (32); 208 (20); 197 (13); 196 (100); 195 (10); 181 (5); 180 (20); 179 (36); 177 (10); 167 (9); 166 (21); 152 (12); 151 (14); 140 (14); 139 (10); 75 (5); 45 (46). HRMS: calculated for $C_{15}H_{13}NO_2$, 239.0914; found, 239.0946. M.p. 52–53 °C (white crystals from hexane–ethyl acetate).

Mass spectra

All mass spectra were recorded on an AMD-604 double-focusing mass spectrometer with BE geometry (AMD Intectra, Germany). Standard EI spectra were obtained under the following conditions: electron energy 70 eV, cathode emission current 0.5 mA, acceleration voltage 8 kV, ion source temperature 200 °C. Samples were introduced using a direct insertion probe heated, when required, from 30 to 100 °C. Liquid matrix secondary ion mass spectrometry (LSIMS) was performed using a 10 keV Cs^+ gun as a primary ion beam source and *m*-nitrobenzyl alcohol (NBA) as a matrix.

Accurate mass measurements for all significant peaks were performed by the narrow-range high-voltage scanning technique at a 10 000 resolving power (10% valley definition) using perfluorokerosene (PFK) as the reference compound. The accuracy of mass measurements was better than 10 ppm with the exception of a few poorly resolved peaks resulting from ions with the same nominal mass.

Fragmentation pathways were confirmed by MIKE and B/E = constant linked scan fragment ion spectra recorded for metastable decomposition and, when required, also for the collision-induced dissociation (CID) products. Both MIKE and B/E linked scan spectra were recorded using a 30 s scan time. Eight consecutive spectra were averaged to improve the signal-to-noise ratio. In the CID experiments helium was used as the collision gas. The pressure in the collision chamber was set to reduce the parent ion abundance by 50%.

Calculations

Kinetic energy release, KER($T_{0.5}$), values were calculated for a peak width at 50% of its height and were corrected for the width of the parent ion peak in accordance to the equation given elsewhere.[16,17] Series of three consecutive measurements for two selected ions show that the reproducibility of KER($T_{0.5}$) values is better than 4%.

Density functional theory (DFT) calculations were performed using the Gaussian 98 program package.[18] The DFT B3LYP/6–31G(d) method was used for geometry optimization and frequency calculations. ZPE corrections were scaled by the usual factor of 0.9804. Final energy was calculated at the B3LYP/6–311 + G(d,p) level.

RESULTS AND DISCUSSION

EI mass spectra of **3a**, **3c**, **4a** and **4c** are presented in Fig. 1. All fragmentation reactions described in this paper were confirmed by the fragment ion spectra, both MIKE and B/E linked scan (metastable and, if necessary, also CID), and by the results of accurate mass measurements of the relevant product ions.

The fragmentation pattern of *N*-(methoxymethyl)carbostyril (**3a**) is representative for all compounds under study. The main fragmentation pathways of the molecular ion of **3a** are presented in Scheme 3.

The molecular ion of **3a** decomposes along three main pathways giving rise to abundant ions in the spectrum. We shall concentrate on two of them because the formation of $CH_3OCH_2^+$ cation is a fairly trivial process and does not require any comments.

Elimination of formaldehyde and acetaldehyde

The elimination of formaldehyde (from methoxymethyl derivatives) and acetaldehyde (from ethoxymethyl derivatives) molecules opens up one of the main fragmentation channels of the compounds under study. Interestingly, it takes place both for *N*-(methoxymethyl)carbostyril (**3a**)

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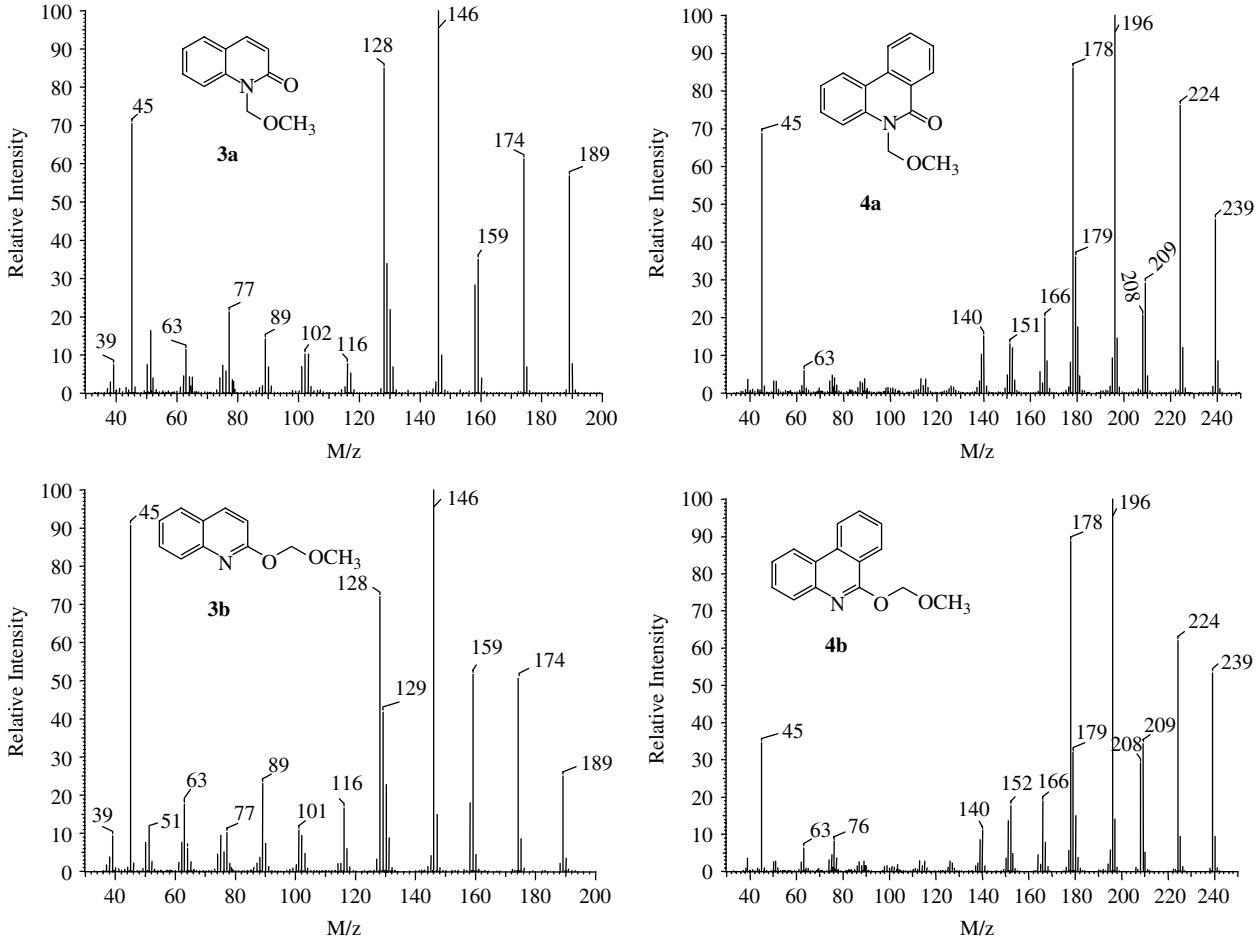
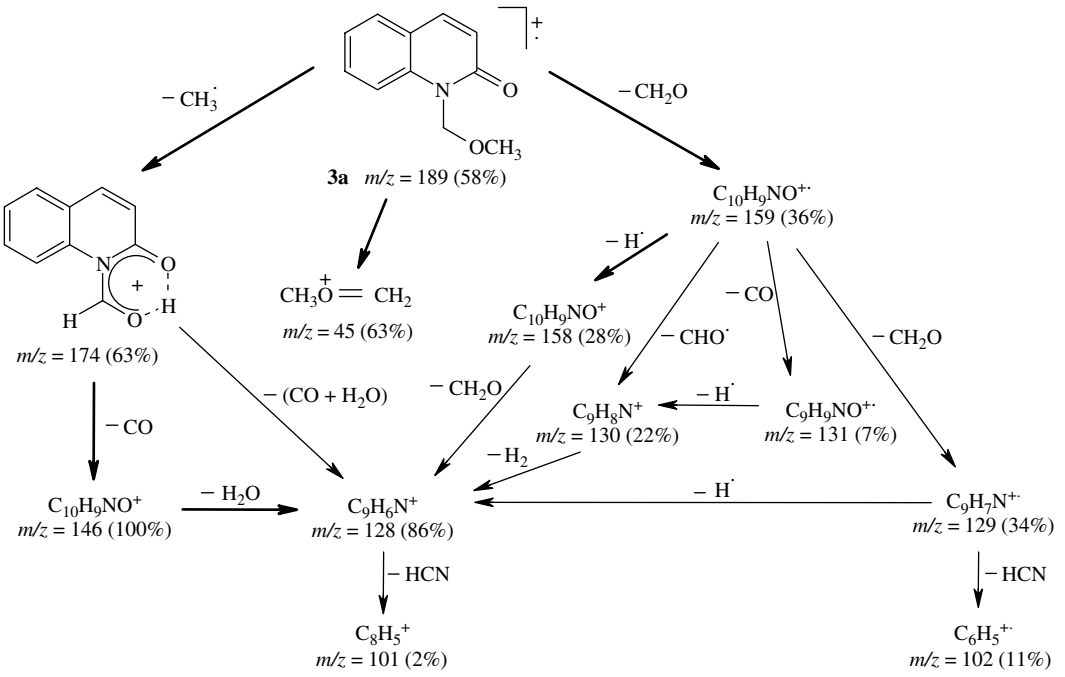


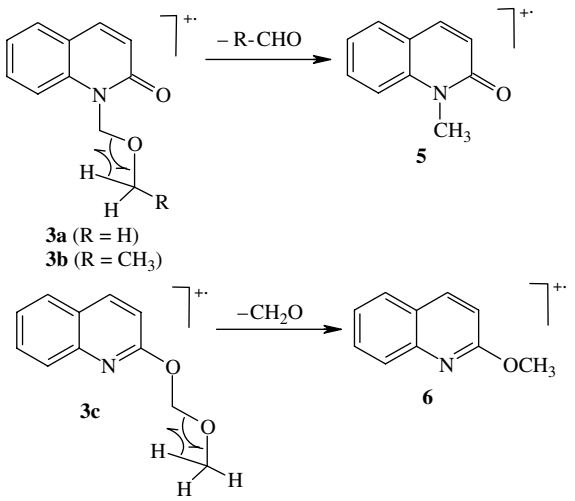
Figure 1. 70 eV EI spectra of the molecular ions of *N*-(methoxymethyl)carbostyril (**3a**), *N*-(methoxymethyl)phenanthridinone (**4a**) and their *O*-methoxymethylated isomers **3c** and **4c**.



Scheme 3. Fragmentation pathways of the molecular ion of *N*-(methoxymethyl)carbostyril (**3a**). Main pathways are marked with bold arrows.

and its *O*-isomer (**3c**). Additional hints at the mechanism of this process is provided by the mass spectrum of *N*-(ethoxymethyl)carbostyril (**3b**). In this case, an elimination of a formaldehyde molecule was not observed. The main fragment ion, giving the most intense signal in the EI spectrum of **3b**, corresponds to the loss of acetaldehyde instead. The same results were obtained also for the phenanthridinone derivatives **4a**–**c**. These results clearly show that, in contrast to *N*-(alkoxymethyl)benzosultams and *N*-(alkoxymethyl)methanesulfonanilides, *N*-(alkoxymethyl) carbostyril and *N*-(alkoxymethyl)phenanthridinone do not undergo fragmentation involving ion–neutral complexes because, in the case of the former, source of the formaldehyde fragment was the N—CH_2—O moiety in the *N*-alkoxymethyl group.[1]

The most likely product of the aldehyde molecule loss from the molecular ions of **3a** and **3b** is *N*-methylcarbostyril radical cation formed by a 1,3-H shift in the *N*-alkoxymethyl group as presented in Scheme 4. A similar reaction was described by Hettler *et al*. for the *N*-propoxymethyl derivative of saccharin[19] and by us for *N*-(alkoxymethyl)acetanilides.[10] In an analogous way, *O*-(methoxymethyl)carbostyril (**3c**) should give 2-methoxyquinoline (**6**) radical cation.



Scheme 4. Mechanism of the formation of the radical cation of *N*-methylcarbostyril (**5**) from the molecular ions of *N*-(alkoxymethyl)carbostyrils **3a** and **3b** and formation of the radical cation of 2-methoxyquinoline (**6**) from the molecular ion of *O*-(methoxymethyl)carbostyril (**3c**).

Further fragmentation of the *m/z* 159 ions derived from **3a**–**c** and molecular ions of *N*-methylcarbostyril (**5**) and 2-methoxyquinoline (**6**) shows that the situation is not so simple. The CID *B/E* spectra of these ions (Fig. 2) are similar to each other, but with some important differences. In all cases the *m/z* 158 ion was the main fragment but much more diagnostic are four ions between *m/z* 128 and 131 (see insets in Fig. 2). According to the accurate mass measurement results, these ions have the following formulae: $[M - CH_2O - CH_3O]^+$ at *m/z* 128, $[M - CH_2O - CH_2O]^+$ at *m/z* 129, $[M - CH_2O - CHO]^+$ at *m/z* 130 and $[M - CH_2O - CO]^{+\bullet}$ at *m/z* 131. Comparing the relative intensities of the peaks with *m/z* 128 to 131 in the CID *B/E* spectra, it can be seen that they are very close for **3b** and **3c** and fairly similar for **3a**, except for the intensity of the *m/z* 129 peak. This result looks rather surprising because, if the mechanism presented in Scheme 4 is correct, *m/z* 159 ions derived from the molecular ions of **3a** and **3b** should have the same structure. Nevertheless, this moderate difference can be attributed to different energies of the ions formed from the different precursors.

Comparison of the spectra shown in Fig. 2 leads to some important conclusions. CID *B/E* spectra of the molecular ions of *N*-methylcarbostyril (**5**) and 2-methoxyquinoline (**6**) are different with respect to the relative intensities of the *m/z* 128–131 peaks. This result indicates that under CID conditions *N*- and *O*-methyl derivatives of carbostyril do not isomerize to each other or to the third, common product before fragmentation. Consequently, it is not true that the elimination of formaldehyde from the molecular ions of **3a** and **3c** leads only to the molecular ions of **5** and **6**, respectively. On the other hand, CID *B/E* spectra of *m/z* 159 ions derived from the molecular ions of **3a**–**c** are all much more similar to the spectrum of *N*-methylcarbostyril (**5**) than the spectrum of 2-methoxyquinoline (**6**). One of the possible rationalizations is that, indeed, loss of an aldehyde molecule from the molecular ions of *N*-(alkoxymethyl)carbostyrils **3a** and **3b** results in the formation of *N*-methylcarbostyril (**5**), at least as the main product, according to the mechanism shown in Scheme 4. Other isomeric ions with *m/z* 159 can also be formed and are responsible for increased abundance of the *m/z* 129 fragment compared with the spectrum of **5**.

Because the CID *B/E* spectrum of the *m/z* 159 ion derived from the molecular ion of *O*-(methoxymethyl)carbostyril (**3c**) is also very similar to the spectrum of *N*-methylcarbostyril (**5**), this compound, among others, can also be a product of the CH_2O elimination from **3c**. Several mechanisms of this reaction, each requiring at least two hydrogen shift processes, can be proposed but on the present stage of the study they are purely speculative. We have started a series of calculations which should help to identify possible intermediates but the results are far from completion.

Concluding, both *N*- and *O*-alkoxymethyl derivatives of carbostyril undergo elimination of an aldehyde molecule from the terminal OR group resulting in the formation of *N*-methylcarbostyril as the main product. CID *B/E* spectra show that other isomeric product ions are also formed because the relatively intense *m/z* 129 peak which is present in these spectra is not produced in such yield by the fragmentation of *N*-methylcarbostyril. The same results were obtained for the analogous phenanthridinone derivatives.

Elimination of an alkyl radical

For all compounds under study, elimination of an alkyl radical is the dominant process, under both high-energy and metastable conditions (Figs 1 and 3).

This process appeared to be interesting mainly because it is accompanied by an unusually high KER($T_{0.5}$) value as for simple heterolytic bond cleavage (Table 1).

For instance, the measured value of KER($T_{0.5}$) for *N*-(methoxymethyl)carbostyril (**3a**) was 424 meV and for

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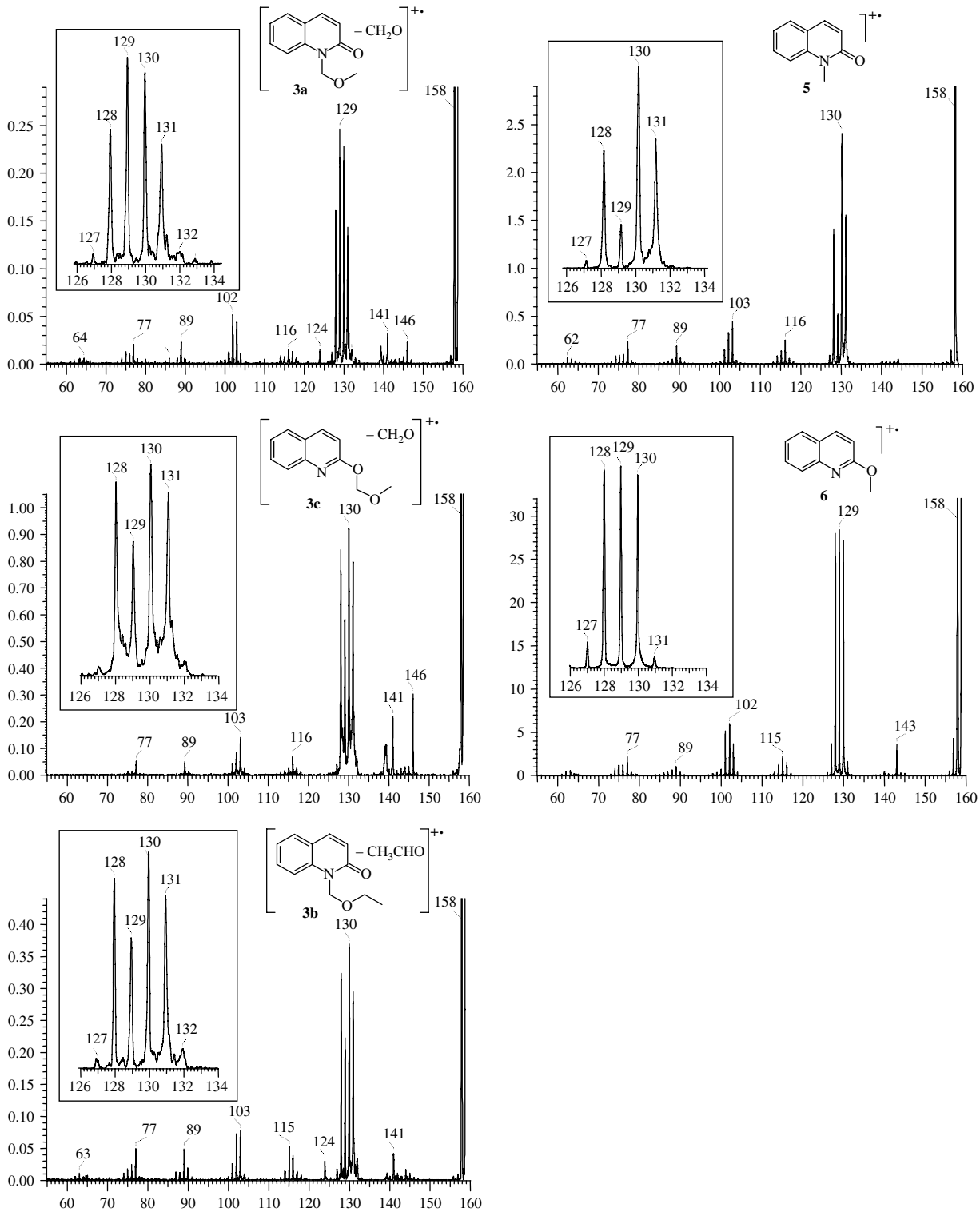

Figure 2. CID *B/E* spectra of the *m/z* 159 ions derived from different sources.

O-(methoxymethyl)carbostyril (**3c**) 445 meV, whereas for elimination of the same radical from the molecular ion of acetophenone under the same conditions it is just 16 meV. These findings indicate that the rearrangement of the molecular ions of the presented compounds will to occur just before the C—O bond cleavage. Moreover, comparison of the CID-MIKE spectra of $[M - CH_3]^+$ ions at *m/z* 174, formed from **3a** and **3c**, showed that they are identical within the experimental error. In particular, the half-widths of the *m/z* 146 peaks resulting from the CO elimination are almost identical, indicating the same KER values for this process. This means that both $[M - CH_3]^+$ ions are likely to have the same structure. In order to rationalize the observed results, we propose the fragmentation mechanism in Scheme 5, which is analogous in part to one described in a previous paper.[10]

After the 1,4-H shift, the heterolytic cleavage of the O—CH_3 bond has takes place for both molecular ions

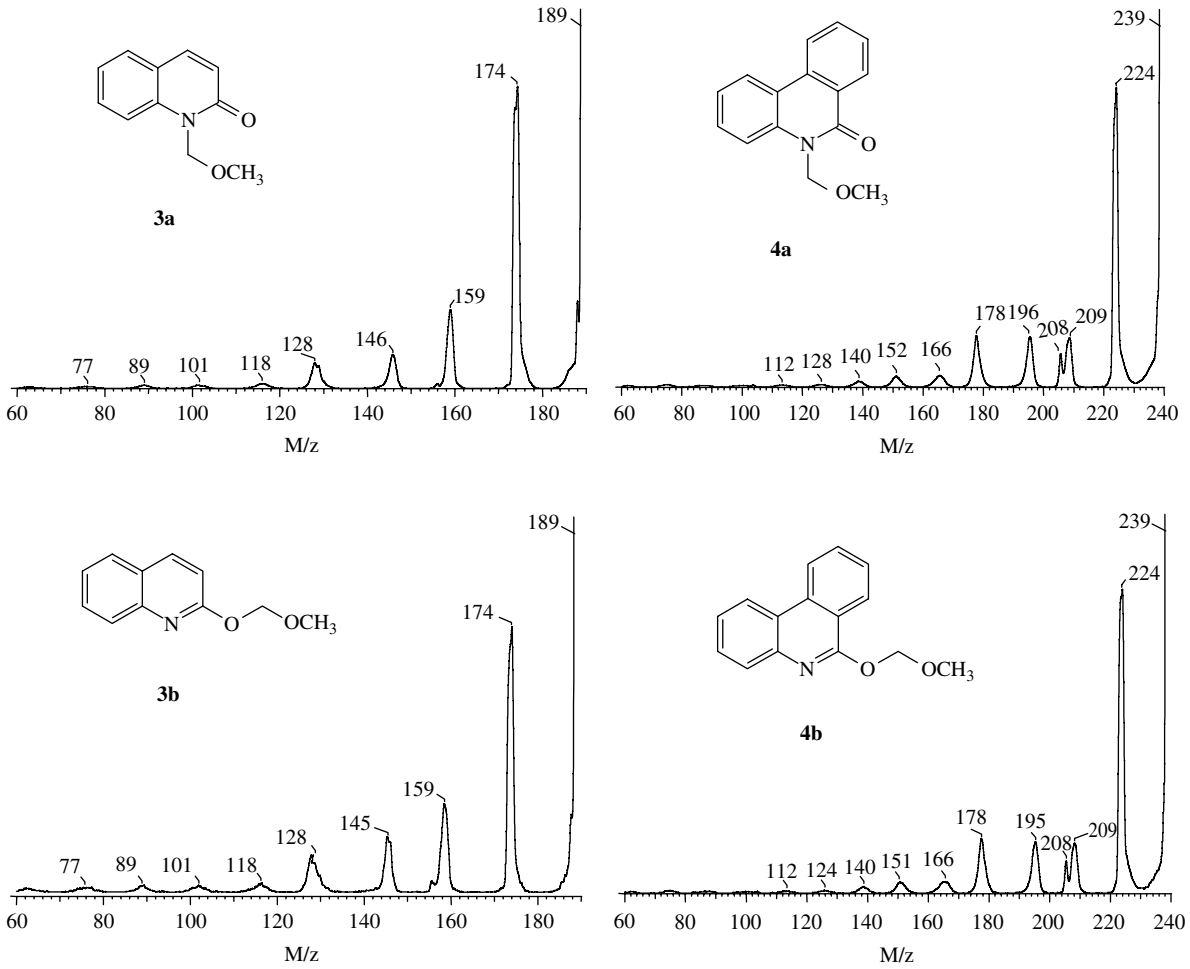

Figure 3. MIKE spectra of the molecular ions of *N*-(methoxymethyl)carbostyril (**3a**), *N*-(methoxymethyl)phenanthridinone (**4a**) and their *O*-methoxymethylated isomers **3c** and **4c**.

Table 1. KER($T_{0.5}$) values for the alkyl radical elimination under metastable fragmentation conditions from the molecular ions of all compounds under study, with the KER($T_{0.5}$) value for the methyl radical elimination from the molecular ion of acetophenone recorded under the same conditions added for comparison (see text)

$M^{+\bullet} - R^{\bullet} \rightarrow$ (R = CH_3, C_2H_5)	KER ($T_{0.5}$) (meV)
3a *N*-(methoxymethyl)carbostyril	424
3b *N*-(ethoxymethyl)carbostyril	411
3c *O*-(methoxymethyl)carbostyril	445
4a *N*-(methoxymethyl)phenanthridinone	450
4b *N*-(ethoxymethyl)phenanthridinone	427
4c *O*-(methoxymethyl)phenanthridinone	386
Acetophenone	16

of **3a** and **3c** to give highly stabilized cations **7** and **8** at *m/z* 174, respectively. According to what was written above, these two ions must rearrange to one common structure before further fragmentation. There are three most likely possibilities: (i) structure **7**, (ii) structure **8** or (iii) another structure to which both ions, **7** and **8** ions can rearrange. Transformation of **7** into **8**, and also the reverse process, require [1,3] shifts of the formyl group and a proton. Possible routes for these reactions are presented in Scheme 6.

The first step involves the presence of an ion–neutral complex of 2-hydroxyquinoline and $[H—C{=}O]^+$ cation, which is formed as the result of heterolytic cleavage of the initial ion **3a**. Within this complex on formylation process can occur, yielding the appropriate cation of the protonated 2-quinolyl formate. In the subsequent step, a 1,3-H shift occurs, leading directly to the cation **8**. The reverse sequence of reactions can lead from ion **8** to **7**. The same rationalization can be applied to explain the elimination of the methyl radical from molecular ions of *N*- and *O*-(methoxymethyl)phenanthridinones **4a** and **4c**.

We tried to select the most probable reaction path by modeling ions **7** and **8** and possible transition states, including ion–neutral complexes shown in Scheme 6. Using the B3LYP/6–311+G(d,p)//B3LYP/6–31G(d) DFT method, we found that ion **8** is about 9 kcal mol^{-1} (1 kcal = 4.184 kJ) more stable than its *N*-formyl isomer **7**. Unfortunately, our attempts to model the transition states between the structures **7** and **8** have been unsuccessful so far, so we are not able at present to estimate the activation energy required for interconversion of these ions. Preliminary calculations showed that it should be possible to model the respective

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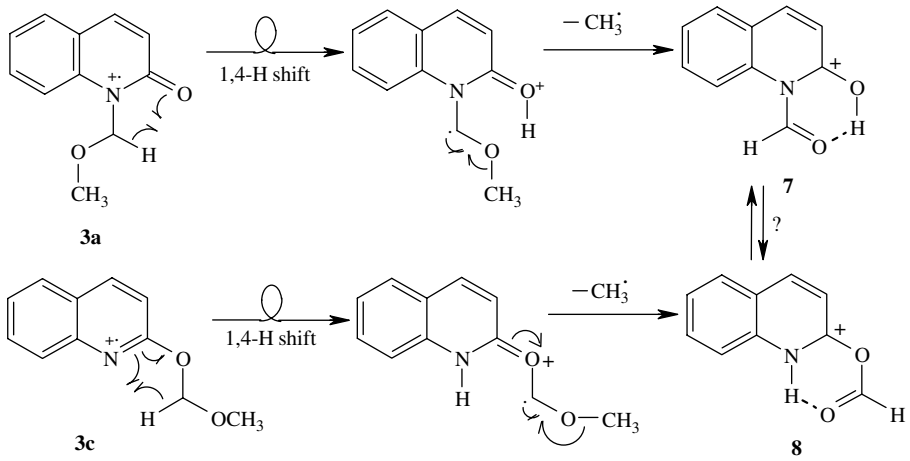
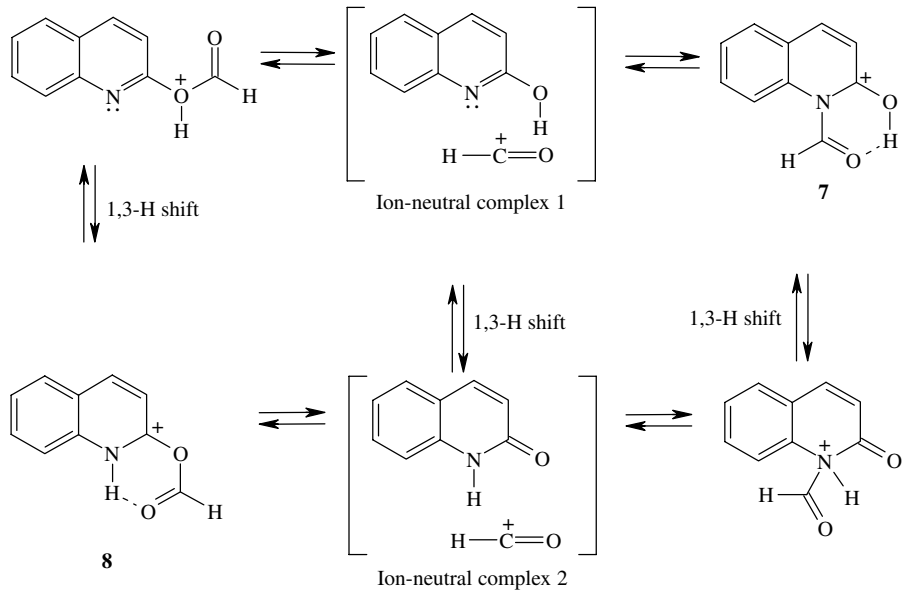
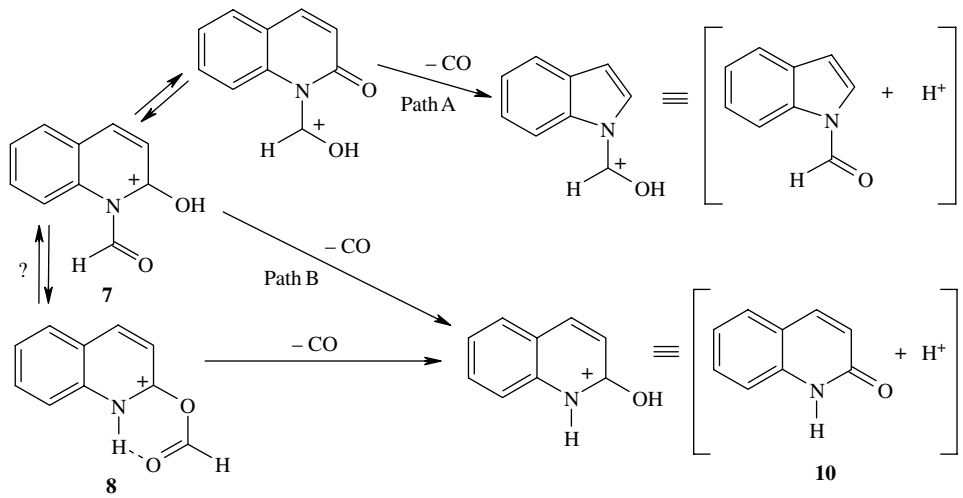


Scheme 5. Postulated mechanism of the formation of the isomeric cations **7** and **8** by elimination of the methyl radical from *N*- and *O*-methoxymethyl groups of the molecular ions of **3a** and **3c**.



Scheme 6. Possible mechanisms of the mutual transformation of the isomeric cations **7** and **8** by subsequent [1,3] shifts of the formyl cation and a proton. Formyl cation shift is supposed to proceed through an ion–neutral complex.



Scheme 7. Possible competitive pathways of the extrusion of CO molecule from the $[M - CH_3]^+$ ions of the general structure **7** and **8** derived from the molecular ions of isomeric *N*- and *O*-(methoxymethyl)carbostyrils (**3a** and **3b**). The experiments with model compounds **9** and **10** show that path A is not operative (see text).

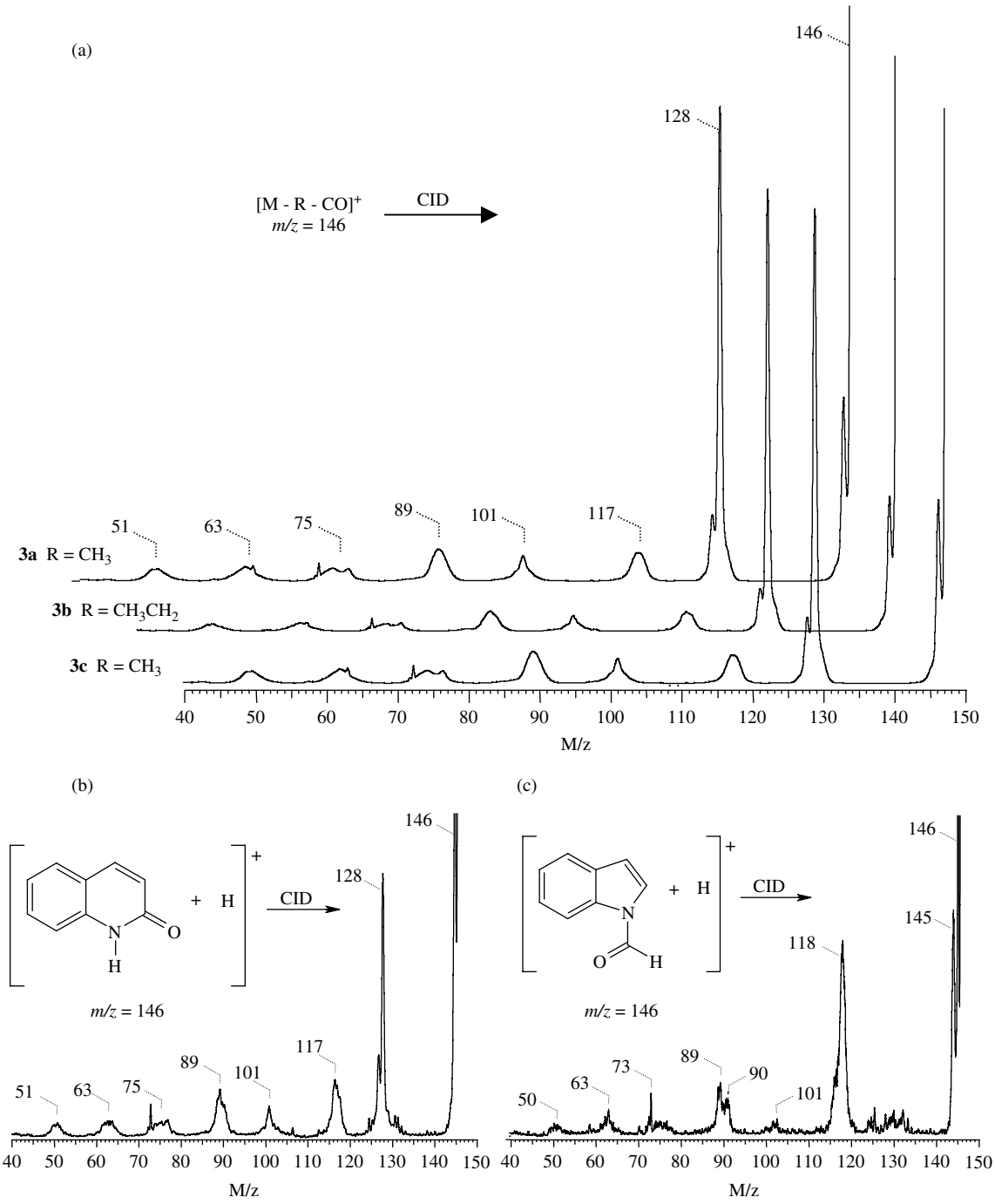


Figure 4. (a) CID-MIKE spectra of $[M - CH_3 - CO]^+$ ions at *m/z* 146, resulting from the molecular ions of *N*-(methoxymethyl) carbostyril (**3a**), *N*-(ethoxymethyl)carbostyril (**3b**) and *O*-(methoxymethyl)carbostyril (**3c**). For comparison there are given CID-MIKE-LSIMS(+) spectra of (b) the protonated carbostyril **10** and (c) protonated *N*-formylindole **9**.

transition states but the number of possible conformations to be analyzed is very high. The results of this theoretical study will be published upon completion.

Further decomposition of the $[M - CH_3]^+$ ion consists of the extrusion the CO molecule (Scheme 3). At this point, the question concerning the structure of $[M - CH_3 - CH_3 - CO]^+$ arises. It is well documented,[4] that both unsubstituted molecules of carbostyril and phenanthridinone and their *N*-alkylated derivatives readily expel a CO molecule to yield indole and carbazole, respectively. If the same process takes place for *N*-(methoxymethyl)carbostyril (and phenanthridinone), then $[M - CH_3 - CO]^+$ cation should have the structure of the protonated *N*-formylindole **9** (and carbazole) (path A in Scheme 7).

On the other hand, if the same reaction takes place on a carbonyl group attached to the nitrogen (ion **7**) or oxygen (ion **8**) atom in the form of the formyl substituent (path B in Scheme 7), then the protonated carbostyril cation **10** is expected. In order to confirm which hypothesis is correct, we recorded CID-MIKE LSIMS(+) spectra of the protonated carbostyril (**10**) and *N*-formylindole (**9**) (Fig. 4).

Comparison of these spectra with the shapes of the respective CID-MIKE spectra recorded for $[M - CH_3 - CO]^+$ ions of **3a–c** unambiguously shows that the latter are likely to have the structure of the protonated carbostyril. This result, however, does not give an answer to the question concerning the structure(s) of the ion(s) resulting from an alkyl group elimination from the molecular ions of compounds **3a–c**. Protonated carbostyril (**10**) can be formed from both ions **7** (along path B in Scheme 7) and **8**, so the question of their mutual interconversion is still open.

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