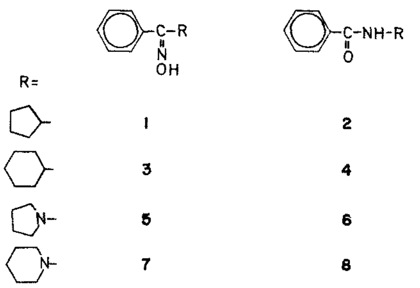
Concerning the Beckmann Rearrangement of Aryl Heteryl Ketoxime Ions

Hans-Fr. Grützmacher† and Christian Römer
Fakultät für Chemie, Universität Bielefeld, Universitätsstr. 25, 4800 Bielefeld 1, West Germany

The possible Beckmann rearrangement of aryl heteryl ketoxime ions has been investigated by studies on the 70 eV mass spectra, metastable ion spectra and collision induced dissociation spectra of pairs of isomeric ketoximes and corresponding amides. Aryl cycloalkyl ketoximes were also studied, and the molecular ions of these and the corresponding amides showed no evidence of interconversion. The introduction of the heterocyclic moieties made little change to this situation although some novel rearrangements were observed.

INTRODUCTION

The Beckmann rearrangement of ketoximes under acidic conditions is a well known reaction in organic chemistry. Recently, Maquestiau *et al.*[1] showed that a Beckmann type of rearrangement accompanies the loss of H_2O from protonated ketoxime ions under methane and isobutane chemical ionization conditions in a mass spectrometer by proving a nitrilium cation-structure for the resulting fragment ions. This is in accord with the accepted mechanism of the Beckmann rearrangement. Interestingly, however, a Beckmann rearrangement has also been reported by Kallury *et al.* for the odd-electron molecular ions of certain aryl heteryl ketoximes generated by electron impact.[2] We investigated the fragmentations of some aryl ketoximes and the isomeric amides by mass analysed ion kinetic energy (MIKE) and collisional activation (CA) MIKE spectrometry. If interconversion occurs between the molecular ions of the ketoximes and the corresponding amides, common features are expected to appear in the MIKE and CA MIKE spectra of the isomeric molecular ions. The compounds investigated are cyclopentyl phenyl ketoxime (**1**) and the isomeric *N*-cyclopentylbenzamide (**2**), cyclohexyl phenyl ketoxime (**3**) and *N*-cyclohexylbenzamide (**4**), α-(1-pyrrolidinyl)benzaldoxime (**5**) and the isomeric 1-benzamidopyrrolidine (**6**) and 2-(1-piperidyl)benzaldoxime (**7**) and 1-benzamidopiperidine (**8**). The aryl heteryl ketoximes **5** and **7** have been investigated by Kallury *et al.*[2] and particularly for **5** a Beckmann rearrangement of the molecular ions to **6** has been proposed, while **7** rearranges to a much lesser extent. The 'normal' aryl cycloalkyl ketoximes **1** and **3** are included for a comparison.



EXPERIMENTAL

The 70 eV mass spectra were recorded on a MAT 311A mass spectrometer, ion source temperature 150 °C, with direct sample insertion. The MIKE and CA MIKE spectra were recorded on a VG ZAB 2F mass spectrometer at 70 eV, ion source temperature ~180 °C, with direct insertion. The field free region collision gas was He.

RESULTS AND DISCUSSION

The 70 eV mass spectra of **1–8** are presented in Table 1, and the MIKE and CA MIKE spectra of the

Table 1. Characteristic ions in the 70 eV mass spectra of 1–8[a]

	1	2	3	4	5	6	7	8
$[M]^{+\cdot}$	50.8	34.5	71.6	32.6	15.7	3.3	13.2	3.0
$[M-H]^+$	40.9	3.7	29.2	1.9	—	—	—	—
$[M-OH]^+$	65.8	—	100	—	0.8	—	2.2	0.2
m/z 148	100	—	74.2	—	—	—	—	—
m/z 130	12.0	—	10.0	—	1.0	—	1.4	—
m/z 129	13.6	—	13.0	—	1.6	—	0.7	—
m/z 122	0.8	67.6	2.7	79.0	—	2.0	—	27.3
m/z 115	15.9	—	11.1	—	—	—	—	—
m/z 105	3.3	100	4.5	100	0.5	28.8	0.3	31.0
m/z 104	72.2	1.4	74.7	1.5	20.2	1.0	19.7	0.9
m/z 103	17.7	—	15.5	—	7.3	1.0	5.1	2.9
m/z 99	—	—	—	—	—	—	—	100
m/z 91	21.3	—	28.3	—	1.1	—	1.3	—
m/z 85	—	—	—	—	—	88.4	3.7	—
m/z 84	—	—	—	—	—	1.0	100	28.2
m/z 83	—	—	—	—	—	—	—	80.6
m/z 70	0.5	—	0.5	—	100	100	0.5	3.3

[a] Corrected for ^{13}C.

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† Author to whom correspondence should be addressed.

CCC-0030–493X/82/0017–0318$01.50

Table 2. MIKE spectra of the molecular ions of 1–8

	1	2	3	4	5	6	7	8
$[M-H]^+$	42	85	26	53	—	24	—	13
$[M-CH_3]^+$	3	1	5	2	5	2	6	2
$[M-OH]^+$	55	—	68	—	47	10	88	31
$[M-CH_2NO]^+$	—	—	—	—	—	36	—	17
m/z 122	—	14	—	44	—	3	—	5
m/z 100					—	—	1	18
m/z 86					2	1	—	—
m/z 84					—	—	5	3
m/z 70					43	23	—	—

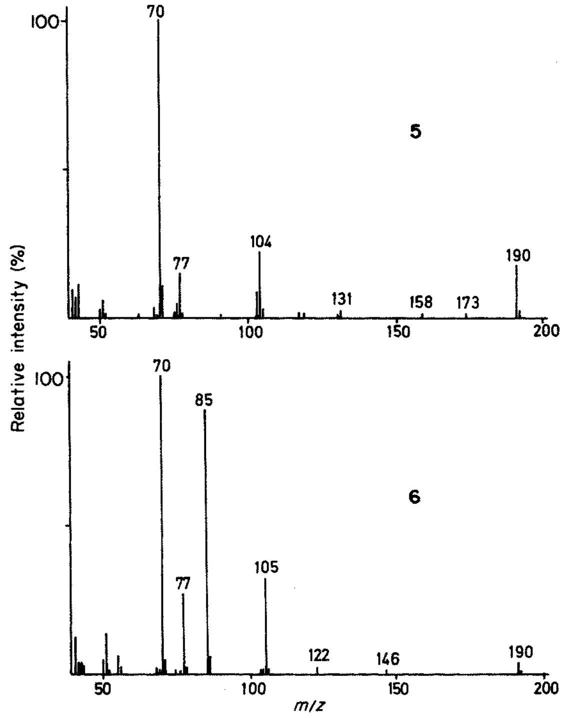


Figure 1. The 70 eV mass spectra of **5** and **6**.

molecular ions are presented in Tables 2 and 3 respectively. The molecular ions of **1–4** fragment as expected without any indication of an interconversion between ketoxime ions and amide ions. The loss of H˙ and HO˙, respectively, and the formation of $C_6H_6C{\equiv}\overset{+}{N}H$ ions *m/z* 104 and ions *m/z* 148 from phenyl ketoxime ions is known.[3] The two former reactions are also observed for the fragmentation of metastable molecular ions. In contrast, the isomeric benzamide ions fragment mainly by the reaction sequence $[M]^{+\cdot} \rightarrow m/z$ 122 $\rightarrow m/z$ 105 $\rightarrow m/z$ 77. The formation of protonated benzamide ions *m/z* 122 is also observed from metastable $[\mathbf{2}]^{+\cdot}$ and $[\mathbf{4}]^{+\cdot}$ ions, in addition to loss of a H-atom (Table 2), and corresponds obviously to an energetically favoured fragmentation path of these substituted benzamide ions. Since ions *m/z* 122 are observed neither in the 70 eV mass spectra nor in the MIKE spectra and CA MIKE spectra of the ketoximes, interconversion of the ions $[\mathbf{1}]^{+\cdot} \rightleftarrows [\mathbf{2}]^{+\cdot}$ and $[\mathbf{3}]^{+\cdot} \rightleftarrows [\mathbf{4}]^{+\cdot}$, respectively, in a mass spectrometer can be excluded.

The 70 eV mass spectrum of **5** (Fig. 1) obtained with both our instruments is very different from that reported in the literature.[2] The intensities of ions *m/z* 105 ($^{12}C_7H_5O$ and $^{13}C^{12}C_6H_6N \approx 1:5$) and *m/z* 77 are much less, and those of the molecular ions *m/z* 190 and fragment ions *m/z* 104 (C_7H_6N) and 70 (C_4H_8N) are much enhanced. Indeed, the main fragmentations of **5** resemble those of **7** and in both cases can be explained by the ketoxime structure of the reacting ions; i.e. loss of ˙OH, formation of $C_6H_5{\equiv}\overset{+}{N}H$ ions, *m/z* 104, and formation of $[C_4H_8N]^+$ and $[C_5H_{10}N]^+$ ions, respectively, from the pyrrolidine and piperidine moiety of **5** and **7**. The only indication of a possible Beckmann rearrangement of $[\mathbf{5}]^{+\cdot}$ ions is the small amount of benzoyl ions *m/z* 105 in the 70 eV mass spectrum of **5**, but in view of the bad reproducibility of this spectrum between different laboratories it appears that **5** is especially sensitive to thermal (catalytic ?) degradation in the inlet system and the ion source of a mass spectrometer.

Table 3. CA MIKE spectra of the molecular ions of 1–8[a]

1: 188 (436), 174 (118), 172 (415, ~157 (12), ~153 (16), 148 (14), ~137 (9), ~125 (8), ~115 (7), 104 (9), 92 (6), ~84 (5), ~70 (5), ~61 (4).

2: 188 (133), 164 (2), 160 (2), 148 (2), 131 (37), 122 (39), 116 (35), 113 (2), 105 (2), 98 (2), 92 (7), 85 (3), ~71 (2).

3: 202 (148), 188 (79), 186 (222), 175 (5), ~171 (12), ~162 (5), ~155 (9), ~151 (6), 148 (7), ~144 (6), ~139 (6), ~127 (5), 121 (3), 117 (7), ~106 (8), 98 (3), ~94 (4).

4: 202 (62), 188 (2), 166 (3), 160 (2), 133 (30), 122 (38), 118 (40), 105 (2), 98 (4), 94 (8), 86 (3), 75 (3), 72 (3), 63 (2).

5: 189 (12), 175 (2), 173 (10), 162 (3), 129 (2), 116 (16), 104 (2), 92 (7), 86 (52), 74 (5), 70 (29), 62 (2).

6: 189 (59), 173 (6), 152 (4), 146 (39), 131 (2), 122 (2), 116 (23), 105 (3), 99 (21), 92 (7), 86 (35), 74 (2), 70 (47), 62 (3).

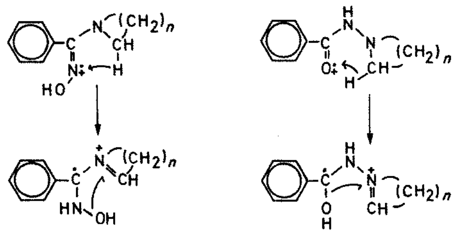
7: 203 (17), 189 (8), 187 (114), 177 (2), 130 (2), 117 (13), 100 (54), 94 (6), 84 (25), 75 (4), 64 (2).

8: 203 (43), 189 (4), 187 (47), 166 (4), 160 (32), 133 (18), 122 (19), 118 (27), 105 (2), 100 (74), 94 (7), 84 (12), 83 (23), 75 (6), 64 (3).

[a] Rel. int. (% total ion current) given in parentheses. Underlined signals were not used for normalization. A ~ signal indicates a broad signal over several mass numbers.

Furthermore, the 70 eV mass spectra of the amides **6** and **8** are very different from those of the isomeric ketoximes. In addition to peaks of the expected fragment ions *m/z* 122, 105, 77 and 70 (**6**) or 84 (**8**), large peaks for ions *m/z* 85 (**6**, $C_4H_9N_2$) and 99 (**8**, $C_5H_{11}N_2$) are observed exclusively in the spectra of the amides.

The differences between the fragmentations of the isomers **5** and **6** or **7** and **8** are maintained for the reactions of metastable ions (Tables 2 and 3). The loss of a CH_2NO fragment (probably OH + HCN) is typical for the fragmentation of metastable amide ions $[\mathbf{6}]^{+\cdot}$ and $[\mathbf{8}]^{+\cdot}$. This is observed neither in the MIKE spectra nor in the CA MIKE spectra of the isomers $[\mathbf{5}]^{+\cdot}$ and $[\mathbf{7}]^{+\cdot}$. Therefore, it is very unlikely that a Beckmann rearrangement is of any importance for the reactions of unstable, metastable and stable molecular ions of the aryl heteryl ketoximes **5** and **7**. However, fragmentations by rearrangement reactions of the molecular ions of the heteryl benzamides **6** and **8** *and* of the heteryl ketoximes **5** and **7** do occur. This is clearly seen from the loss of OH and CH_2NO from metastable $[\mathbf{6}]^{+\cdot}$ and $[\mathbf{8}]^{+\cdot}$ ions and the formation of ions $[C_4H_8NO]^+$, m/z 86 and $[C_5H_{10}NO]^+$, m/z 100, respectively. The latter ions, which require a transfer of the oxygen atom to the heterocyclic moiety, also give large signals in the CA MIKE spectra of the molecular ions of **5**–**8**. The mechanisms of these novel rearrangements are not yet known and will be investigated further. Probably the formation of a stable aminium ion by hydrogen migration from the heterocyclic ring to the carbonyl group (**6**, **8**) or the oxime group (**5**, **7**) occurs[3a] and leads to a reactive form of the molecular ions.



$n = 3$ **5** **6**
4 **7** **8**

Scheme 1

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Received 5 February 1982; accepted 5 February 1982.