

A MASS SPECTRAL STUDY OF O-AROYL BENZO HYDROXIMOYL CHLORIDES

Evangelia A. VARELLA^a, Nicholas E. ALEXANDROU^a and Otto EXNER^b

^a *Laboratory of Organic Chemistry, University of Thessaloniki, Thessaloniki, Greece and*

^b *Institute of Organic Chemistry and Biochemistry, Czechoslovak Academy of Sciences, 166 10 Prague 6*

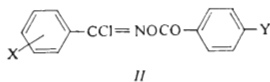
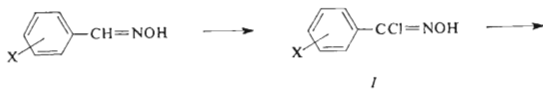
Received January 12th, 1983

Fifteen O-arylbenzohydroximoyl chlorides *IIa–IIo* have been synthesized and their fragmentation pattern upon electron impact studied. Evidence has been obtained of a Lossen–Tiemann type rearrangement with aryl migration to nitrogen.

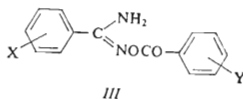
Aromatic hydroximoyl chlorides *I* are useful precursors for the preparation of nitrile oxides or amidoximes and several methods for their synthesis have been developed^{1–3}. Their O-acyl derivatives *II* served as models in determining configuration and conformation of the parent compounds by means of dipole moments⁴. Otherwise they have received little attention⁵. In particular, there is no systematic study of the mass spectra of these compounds, except a short report⁵ on the mass spectrum of O-benzoylbenzohydroximoyl chloride (*IIa*). The present note is an extension of our previous study of O-arylbenzamidoximes⁶. Our main intention was a search for fragmentation processes which would be analogous to well-known solution reactions of the hydroxylamine derivatives, in particular to the Lossen or Tiemann rearrangements.

The O-arylbenzohydroximoyl chlorides *II* were prepared by direct aroylation⁵ of the benzohydroximoyl chlorides *I* which in turn were obtained by chlorination^{1,3} of the corresponding benzaldoximes. The yield in *II* is relatively low but increases remarkably when X = OCH₃ and Y = NO₂. The IR spectra of compounds *II* display a high carbonyl stretching frequency⁵ between 1760 and 1790 cm⁻¹, i.e. some 40 cm⁻¹ higher than in the corresponding O-arylamidoximes⁶ *III*.

In Table I are given the main peaks of the mass spectra of the compounds *II*, i.e. either the most intensive ones or those deserving special attention. Example of a spectrum is given in Fig. 1. All the spectra display the molecular ion in a relative intensity of 2–12%. Further fragmentation is rather similar to that of O-arylbenzamidoximes⁶ *III*, the main differences being the impossibility of a cyclization reaction in *II* and much easier loss of the chlorine atom in *II* than of the NH₂ group in *III*. The splitting off the chlorine atom is analogous to that observed in the mass spectra



- | | |
|----------------------------------|---|
| a, X = Y = H | i, X = 4-NO ₂ , Y = H |
| b, X = H, Y = Cl | j, X = 2-NO ₂ , Y = H |
| c, X = H, Y = NO ₂ | k, X = 4-CH ₃ , Y = H |
| d, X = 4-Cl, Y = H | l, X = 4-OCH ₃ , Y = H |
| e, X = 4-Cl, Y = NO ₂ | m, X = 4-OCH ₃ , Y = NO ₂ |
| f, X = 3-Cl, Y = H | n, X = 2-OCH ₃ , Y = H |
| g, X = 2-Cl, Y = H | o, X = 2-OCH ₃ , Y = NO ₂ |
| h, X = 2-Cl, Y = NO ₂ | |



of imidoyl halides⁷. In general, there is no significant difference between the spectra of isomeric *ortho*-, *meta*-, and *para*-substituted derivatives, except the relative intensities of some ions. Similarly as with O-aroylbenzamidoximes⁶, no correlation⁸ of relative intensities with substituent constants could be obtained. Some details of the

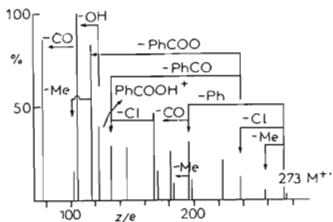


FIG. 1

Mass spectrum of O-benzoyl-4-methylbenzohydroximoyl chloride (IIk)

TABLE I
Principal fragment ions in the mass spectra of the compounds II

Compound	m/z (% relative intensities)
<i>Ila</i>	261/259 (8, $M^{+\cdot}$), 224 (11), 206 (9), 156/154 (42), 140/138 (20), 122 (36), 119 (43), 105 (75), 103 (100), 91 (27), 77 (86), 51 (57)
<i>Ilb</i>	297/295/293 (2, $M^{+\cdot}$), 260/258 (6), 223 (2), 205 (2), 158/156 (3), 141/139 (100), 119 (5), 113/111 (13), 104 (10), 103 (14), 91 (2), 77 (8), 51 (16)
<i>Ilc</i>	306/304 (6, $M^{+\cdot}$), 269 (17), 223 (32), 205 (6), 184/182 (3), 167 (14), 150 (19), 122 (26), 119 (28), 104 (58), 103 (100), 91 (14), 77 (73), 50 (85)
<i>Ild</i>	297/295/293 (2, $M^{+\cdot}$), 260/258 (2), 223 (1), 216 (1), 155/153 (4), 139/137 (18), 127/125 (5), 125/123 (3), 122 (6), 113/111 (10), 105 (100), 77 (29), 51 (14)
<i>Ile</i>	342/340/338 (2, $M^{+\cdot}$), 305/303 (1), 296/294/292 (1), 223 (2), 167 (22), 155/153 (17), 150 (44), 139/137 (100), 127/125 (9), 125/123 (4), 122 (19), 113/111 (8), 104 (18), 102 (22), 76 (27), 65 (36), 50 (39)
<i>Ilf</i>	297/295/293 (4, $M^{+\cdot}$), 260/258 (5), 223 (3), 188 (2), 155/153 (11), 139/137 (61), 127/125 (10), 125/123 (13), 122 (12), 113/111 (17), 105 (85), 77 (100), 51 (48)
<i>Ilg</i>	297/295/293 (3, $M^{+\cdot}$), 260/258 (2), 223 (2), 155/153 (10), 139/137 (59), 127/125 (9), 125/123 (14), 122 (87), 113/111 (10), 105 (100), 75 (97), 50 (22)
<i>Ilh</i>	342/340/338 (4, $M^{+\cdot}$), 305/303 (2), 296/294/292 (1), 223 (2), 167 (22), 155/153 (6), 150 (12), 139/137 (100), 127/125 (3), 125/123 (2), 122 (26), 113/111 (5), 104 (80), 102 (85), 75 (35), 65 (32), 50 (33)
<i>Ili</i>	306/304 (10, $M^{+\cdot}$), 269 (30), 227 (36), 223 (4), 205 (4), 199 (42), 164 (5), 148 (55), 136 (2), 122 (80), 105 (100), 77 (83), 50 (54)
<i>Ilj</i>	306/304 (12, $M^{+\cdot}$), 269 (9), 227 (29), 223 (2), 205 (2), 199 (71), 164 (15), 148 (39), 136 (12), 122 (11), 105 (100), 77 (77), 51 (32)
<i>Ilk</i>	275/273 (6, $M^{+\cdot}$), 260/258 (3), 238 (12), 223 (22), 198/196 (31), 183/181 (26), 170/168 (44), 146 (28), 133 (30), 122 (40), 118 (5), 117 (84), 105 (100), 102 (16), 77 (88), 51 (76)
<i>III</i>	291/289 (3, $M^{+\cdot}$), 276/274 (3), 254 (5), 223 (15), 186/184 (10), 149 (94), 135 (44), 133 (37), 122 (18), 121 (5), 119 (23), 105 (100), 77 (57), 51 (20)
<i>IIm</i>	336/334 (3, $M^{+\cdot}$), 299 (12), 253 (6), 222 (8), 214/212 (4), 205 (2), 186/184 (6), 167 (18), 150 (2), 149 (15), 133 (14), 122 (8), 121 (7), 104 (100), 77 (46), 50 (32)
<i>IIn</i>	291/289 (3, $M^{+\cdot}$), 274 (4), 254 (8), 223 (9), 186/184 (14), 149 (86), 135 (59), 133 (19), 122 (23), 121 (4), 119 (20), 105 (100), 77 (36), 51 (23)
<i>IIo</i>	336/334 (3, $M^{+\cdot}$), 299 (2), 253 (1), 222 (4), 214/212 (4), 205 (2), 186/184 (6), 167 (12), 150 (11), 149 (32), 133 (8), 122 (29), 121 (8), 104 (100), 77 (48), 51 (31)

reassignment is based on the determination of exact molecular weight (Table II) and on the transition $[\text{C}_6\text{H}_5\text{COOH}]^{+\cdot} \rightarrow [\text{C}_6\text{H}_5\text{CO}]^+$ evidenced in the spectrum of *Ila* by a metastable ion peak at m/z 90.4 (calculated 90.36). The actual ion $[\text{C}_6\text{H}_4\text{NO}_2]^+$ was detected in a small amount in the spectrum of the nitro derivative *Ile* (Table II) in addition to the ion of the substituted benzoic acid $[\text{4-NO}_2\text{C}_6\text{H}_4\text{COOH}]^{+\cdot}$. For the present, we have no explanation how these benzoic acid ions can come into existence, *i.e.* where is the origin of the OH hydrogen atom.

We have observed⁶ the ions of the elemental composition corresponding to ArCNO and ArCN already in the mass spectra of O-benzoylbenzamidoximes *III*. Without dealing with their actual structure, we wrote them as $[\text{Ar-CNO}]^{+\cdot}$ and $[\text{Ar-CN}]^{+\cdot}$, corresponding to the structures of nitrile oxides and nitriles, respectively. The same ions arise in the fragmentation of *II* from the precursor $[\text{M-Cl}]^+$ and give rather intensive signals; the ion $[\text{ArCN}]^{+\cdot}$ competes in intensity with the aroyl ion $[\text{ACO}]^+$ which is usually the base peak of the spectrum. Finally, these ions are transformed into $[\text{ArN}]^{+\cdot}$. The transitions have been documented by metastable peaks and the elemental composition of the ions has been determined (Table II). It follows conclusively that aryl migration from C to N, similar to the popular Lossen or Tiemann rearrangements⁹, must occur anywhere on the pathway from $[\text{M-Cl}]^+$ to $[\text{ArN}]^{+\cdot}$. We consider as most probable that the rearrangement proceeds just in the early stage so that the structure of intermediates would be $[\text{Ar-NCO}]^{+\cdot}$ and $[\text{Ar-NC}]^{+\cdot}$, corresponding to isocyanates and isonitriles, respectively. The same reasoning should

TABLE II

Exact molecular weights and elemental composition of some important ions

Compound	m/z (found)	Elemental composition	Assumed structure
<i>Ila</i>	122.0361	$\text{C}_7\text{H}_6\text{O}_2$	$\text{C}_6\text{H}_5\text{COOH}^{+\cdot}$
	119.0369	$\text{C}_7\text{H}_5\text{NO}$	$\text{C}_6\text{H}_5\text{NCO}^{+\cdot}$
	103.0413	$\text{C}_7\text{H}_5\text{N}$	$\text{C}_6\text{H}_5\text{NC}^{+\cdot}$
<i>Ild</i>	124.9995	$\text{C}_6\text{H}_4^{35}\text{ClN}$	$4\text{-ClC}_6\text{H}_4\text{N}^{+\cdot}$
	122.0352	$\text{C}_7\text{H}_6\text{O}_2$	$\text{C}_6\text{H}_5\text{COOH}^{+\cdot}$
<i>Ile</i>	167.0221	$\text{C}_7\text{H}_6\text{NO}_4$	$4\text{-NO}_2\text{C}_6\text{H}_4\text{COOH}^{+\cdot}$
	152.9976	$\text{C}_7\text{H}_4^{35}\text{ClNO}$	$4\text{-ClC}_6\text{H}_4\text{NCO}^{+\cdot}$
	137.0037	$\text{C}_7\text{H}_4^{35}\text{ClN}$	$4\text{-ClC}_6\text{H}_4\text{NC}^{+\cdot}$
	124.9967	$\text{C}_6\text{H}_4^{35}\text{ClN}$	$4\text{-ClC}_6\text{H}_4\text{N}^{+\cdot}$
	122.0239	$\text{C}_6\text{H}_4\text{NO}_2$	$4\text{-NO}_2\text{C}_6\text{H}_4^+$

TABLE III
Analytical data of the compounds II

Compound	M.p., ^a °C (yield, %)	IR (cm ⁻¹) (nujol) ν(C=O)	Formula (mol. weight)	Calculated/Found		
				% C	% H	% N
<i>Ila</i>	106–107 ^{b,c} (86)	1 765	C ₁₄ H ₁₀ ClNO ₂ (259·7)	—	—	—
<i>Ilb</i>	113–114 ^d (44)	1 760	C ₁₄ H ₉ Cl ₂ NO ₂ (294·1)	—	—	—
<i>Ilc</i>	140–142 (80)	1 775	C ₁₄ H ₉ ClN ₂ O ₄ (304·7)	55·26 54·95	2·96 2·84	9·21 8·95
<i>Ild</i>	82–83 ^e (40)	1 780	C ₁₄ H ₉ Cl ₂ NO ₂ (294·1)	—	—	—
<i>Ile</i>	166–167 ^b (74)	1 765	C ₁₄ H ₈ Cl ₂ N ₂ O ₄ (339·1)	49·70 50·06	2·37 2·35	8·28 8·60
<i>Ilf</i>	111–112 (30)	1 770	C ₁₄ H ₉ Cl ₂ NO ₂ (294·1)	57·34 57·42	3·07 3·29	4·78 4·62
<i>Ilg</i>	91–93 (40)	1 785	C ₁₄ H ₉ Cl ₂ NO ₂ (294·1)	57·34 57·14	3·07 3·02	4·78 4·68
<i>Ilh</i>	157–158 (65)	1 775	C ₁₄ H ₈ Cl ₂ N ₂ O ₄ (339·1)	49·70 50·03	2·37 2·63	8·28 8·14
<i>Ili</i>	183–185 ^b (20)	1 790	C ₁₄ H ₉ ClN ₂ O ₄ (304·7)	55·26 55·76	2·96 2·97	9·21 9·18
<i>Ilj</i>	192–194 ^b (16)	1 790	C ₁₄ H ₉ ClN ₂ O ₄ (304·7)	55·26 54·81	2·96 3·16	9·21 9·54
<i>Ilk</i>	105–107 (56)	1 785	C ₁₅ H ₁₂ ClNO ₂ (273·7)	65·93 66·01	4·39 4·44	5·13 5·24
<i>III</i>	83–84 (70)	1 775	C ₁₅ H ₁₂ ClNO ₃ (289·7)	62·28 62·63	4·15 3·90	4·84 4·48
<i>IIm</i>	113–114 (88)	1 785	C ₁₅ H ₁₁ ClN ₂ O ₅ (334·7)	53·89 53·72	3·29 3·05	8·38 8·18
<i>IIn</i>	87–88 (76)	1 780	C ₁₅ H ₁₂ ClNO ₃ (289·7)	62·28 61·94	4·15 4·34	4·84 4·96
<i>IIo</i>	107–109 (84)	1 770	C ₁₅ H ₁₁ ClN ₂ O ₅ (334·7)	53·89 54·06	3·29 3·42	8·38 8·15

^a Recrystallization solvent ethanol, unless otherwise indicated; ^b recrystallization solvent acetone; ^c literature⁵ gives 108°C; ^d literature⁴ gives 115°C; ^e literature⁴ gives 84°C.

apply also to the fragmentation of O-arylbzamidoximes and to the structure of the intermediates. When we reexamined the measured spectra⁶, we found peaks of $[\text{ArN}]^{+}$ in all the compounds *III*, even when they were not published in the previous paper⁶ due to their low relative intensity (2–10%). The ion $[\text{C}_6\text{H}_5\text{N}]^{+}$ in the spectrum of 4-chlorobenzoylbzamidoxime has now been evidenced by means of its elemental composition ($M = 91.0430$). We conclude that rearrangement reactions take place in the fragmentation of various hydroxylamine derivatives.

EXPERIMENTAL

All melting points are uncorrected and were obtained with a Kofler hot stage apparatus. The mass spectra were run at 70 eV on a RMU-6L Hitachi-Perkin-Elmer single focusing mass spectrometer using the direct insertion probe of the samples, the high-resolution measurements on a double focusing AEI 902 spectrometer at a resolving power of 10 000. Infrared spectra were measured in Nujol with a Perkin-Elmer 297 spectrophotometer. The analyses were performed with a Perkin-Elmer Analyzer, Model 240.

O-Arylbzohydroximoyl chlorides II. According to a general procedure⁵ these compounds were prepared by the reaction of the benzohydroximoyl chloride^{1,3} *I* with an equivalent amount of the appropriate aroyl chloride in anhydrous ether and in the presence of pyridine at 0°C. After stirring for 3 h, water was added to the reaction mixture and the O-arylbzohydroximoyl chloride was obtained from the ether solution and recrystallized. The analytical data of the compounds *II* are given in Table III.

Thanks are due to Dr L. Dolejš, Institute of Organic Chemistry and Biochemistry, Prague, for some comparative measurements, particularly for molecular weight determination.

REFERENCES

1. Chiang Y. H.: *J. Org. Chem.* **36**, 2146 (1971).
2. Liu K. C., Shelton B. R., Howe R. K.: *J. Org. Chem.* **45**, 3916 (1980).
3. Battaglia A., Dondoni A., Exner O.: *J. Chem. Soc., Perkin Trans. 2*, 1972, 1911.
4. Exner O., Jehlička V., Barbaro G., Dondoni A.: *This Journal* **42**, 833 (1977).
5. Chiang Y. H.: *J. Org. Chem.* **36**, 2155 (1971).
6. Varella E. A., Micromastoras E. D., Alexandrou N. E., Exner O.: *This Journal* **48**, 596 (1983).
7. Gal J., Phillips B. A., Smith R.: *Can. J. Chem.* **51**, 132 (1973).
8. Bursley M. M. in the book: *Advances in Linear Free Energy Relationships* (N. B. Chapman, J. Shorter, Eds), p. 443. Plenum Press, London 1972.
9. Smith P. A. S.: *The Chemistry of Open-Chain Nitrogen Compounds*, Vol. 2, p. 81, 93. Benjamin, New York 1966.