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MASS SPECTRA OF TRISUBSTITUTED 1,2,3,4-TETRAHYDRO-1,5-BENZODIAZOCIN-2-ONES

P. A. Sharbatyan, P.B. Terent'ev, S. A. Andronati, A. V. Bogat-skii, O. P. Rudenko and V. V. Danilin

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The mass spectra of 1,5-benzodiazocin-2-ones are characterized by multiline character due to the large number of pathways of fragmentation of the molecular ions. In a number of cases the same signal in the high m/e region corresponds to ions with different compositions. The principal fragmentation pathways were determined by high-resolution mass spectrometry. The possible structures of the fragment ions and the mechanisms of their formation are discussed. The mass spectra of model compounds were also investigated for this purpose.

In order to compare the mass spectrometric behavior of benzodiazepinones [1, 2] with their eight-membered analogs we studied the mass spectra of a series of trisubstituted 1,2,3,4-tetrahydro-1,5-benzodiazocin-2-ones (Table 1). The compounds were synthesized under conditions close to those described in [3]. Their structures were proved by IR and UV spectroscopy and polarography. Thus absorption bands of C = O (1670 cm^{-1}) and C = N (1615 cm^{-1}) bonds are observed in the IR spectrum of II (solution in CCl_4). The UV spectrum of this compound in ethanol is characterized by absorption at 249 nm. Like the corresponding 1h-2,3-dihydro-1,4-benzodiazepin-2-ones [4], these compounds are reduced on a dropping mercury electrode and give one polarographic wave at 950-1020 mV, which evidently corresponds to reduction of the $N_5 = C_6$ bond.

The mass spectra of the investigated compounds and the calculated stabilities with respect to electron impact (W_M) are given in Table 2, and the ratios of the intensities of some of the characteristic ions are given in Table 3.

The W_M values demonstrate that the stabilities of the benzodiazocine molecules with respect to electron impact are lower by a factor of 2-2.5 than the stabilities of benzodiazepinones [2]; this is apparently due to the increase in the number of possible fragmentation pathways. It is interesting to note that the stabilities of N-alkyl-1,5-benzodiazocine molecules with respect to electron impact approach the stabilities of 3-alkyl-substituted benzodiazepinones [2].

The $[M - H]^+$ ion peaks have higher intensities, and in all cases their intensities exceed the intensities of the molecular ion peaks (with a correction for the monoisotope effect). The J_{M-1}/M ratios for I-XI range from 1.02 to 1.87, whereas J_{M-1}/J_M is 3.56 for I (R^1 = H). The J_{M-28}/J_M value for this compound also differs substantially. Whereas it is 0.79-1.57 for the entire series of compounds, it is 3.05 for I.

The mass spectra of I obtained with an MKh-1303 spectrometer are presented in Fig. 1, and the high-

M. V. Lomonosov Moscow State University, Moscow 117526. Mechnikov Odessa State University.

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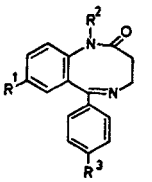
TABLE 1 

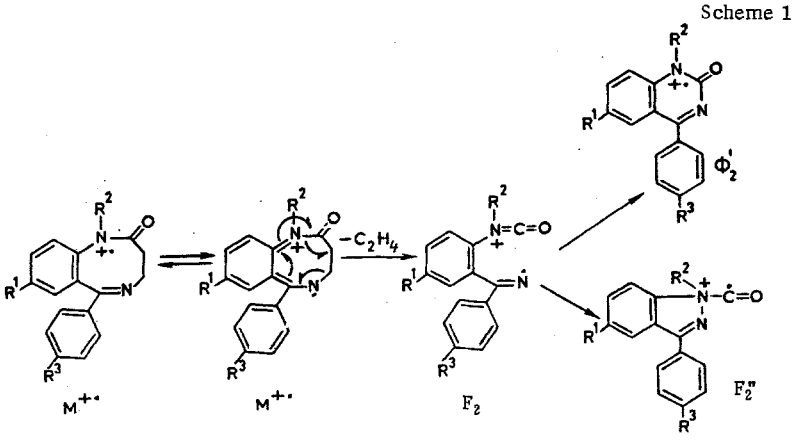
Compound	R¹	R²	R³	mp, °C	Found, %			Emperical formula	Calc., %			Yield, %
					C	H	N		C	H	N	
I	H	CH_3	H	149—150	77,5	6,3	10,7	$C_{17}H_{16}N_2O$	77,3	6,1	10,6	27
II	CH_3	CH_3	H	131—132	77,3	6,7	10,1	$C_{18}H_{18}N_2O$	77,7	6,5	10,0	32
III	CH_3	CH_3	Cl	153—154	69,3	5,7	9,2	$C_{18}H_{17}ClN_2O$	69,1	5,4	9,0	24
IV	CH_3	C_2H_5	H	113—114	78,2	6,9	9,7	$C_{19}H_{20}N_2O$	78,1	6,8	9,6	26
V	Cl	CH_3	H	169—170	68,0	5,4	9,6	$C_{17}H_{15}ClN_2O$	68,3	5,0	9,4	32
VI	Cl	C_3H_7	H	97—98	69,7	5,9	8,7	$C_{19}H_{19}ClN_2O$	69,8	5,8	8,6	21
VII	Cl	C_3H_5	H	128—129	70,3	5,1	8,8	$C_{19}H_{17}ClN_2O$	70,3	5,2	8,6	18
VIII	Br	CH_3	H	153—154	59,5	4,6	8,4	$C_{17}H_{15}BrN_2O$	59,2	4,3	8,2	30
IX	Br	C_2H_5	H	140—141	60,2	5,0	8,0	$C_{18}H_{17}BrN_2O$	60,5	4,8	7,8	27
X	Br	C_4H_9	H	115—116	60,0	5,7	7,4	$C_{20}H_{21}BrN_2O$	60,3	5,5	7,3	23
XI	Br	CH_3	Cl	181—182	54,3	3,9	7,5	$C_{17}H_{14}BrClN_2O$	54,0	3,7	7,4	19

resolution mass spectral data, from which it follows that the $[M-28]^+$ ion is formed only as a result of a single process – elimination of a C_2H_4 molecule – are presented in Table 4. Consequently, both splitting out of an H radical and splitting out of ethylene from the molecular ion of the 8-unsubstituted compound proceed at higher rates than in the case of the remaining compounds, in which the 8 position is substituted with a methyl group or a halogen atom. As previously noted in [2, 5], halogen displays an electron-donor effect during the fragmentation of the molecular ions of 1,4- or 1,5-benzodiazepinones. In all likelihood, this effect is retained in the case of benzodiazocines, and the observed experimental fact can then be explained by the fact that the molecular ions of benzodiazocines are stabilized through conjugation of the positive charge with the donor substituent in the 8 position.

The mechanism of the formation of $[M-H]^+$ ions (F_1) was not studied by means of deuterium labeling, but on the basis of the subsequent fragmentation of these ions it can be confidently asserted that they are different structures. In addition to elimination of a hydrogen atom from the ortho position of the 6-phenyl substituent, elimination of one of the methylene hydrogen atoms from the 3 or 4 position evidently makes a substantial contribution to the formation of F_1 ions.

The probable mechanism of the formation of $[M-C_2H_4]^+$ ions (F_2) can be represented by Scheme 1:

Scheme 1



To verify this scheme we made a thorough analysis of the mass spectrum of 1-N-methylquinazolinone (XII). The peak of the $[M-H]^+$ ions in the mass spectrum of XII has the maximum intensity and exceeds the intensity of the molecular ion peak by a factor of 1.61, whereas the J_{M-29}/J_{M-28} ratio in the mass spectra of I-XI ranges from 0.65 to 1.17 (Table 3). If one also takes into account the fact that the $[M-29]^+$ ions have three different compositions in a ratio of 1:1:1 (Table 4), the J_{F-H}/J_F value will be lower by a factor of three (0.25-0.40), i.e., lower by a factor of almost five than the analogous value for XII.

TABLE 2. Mass spectra of II-XIII

Compound	m/e values (relative intensities in percent of the maximium peak) of the fragment ion peaks
1	2
II	279 (5,6), 278 (69,1), 277 (100), 251 (9,5), 250 (92,5), 249 (76,5), 236 (9,6), 235 (75,9), 223 (45,5), 222 (58,6), 221 (15,5), 220 (8,3), 209 (6,7), 208 (75,5), 207 (9,7), 206 (5,0), 194 (6,3), 165 (6,0), 118 (15,5), 117 (16,2), 110 (14,3), 104 (8,4), 103 (7,6), 91 (19,0), 77 (22,7), 57 (9,8), 51 (5,1)
III	304 (17,5), 303 (36,4), 302 (75,5), 301 (88,7), 286 (24,5), 285 (37,6), 284 (100), 283 (67,0), 277 (5,9), 271 (18,2), 270 (11,5), 269 (76,2), 259 (11,9), 258 (27,2), 257 (63,2), 256 (79,0), 255 (19,0), 254 (7,4), 249 (7,8), 244 (19,7), 243 (10,4), 242 (84,7), 207 (5,4), 189 (12,5), 175 (5,2), 165 (9,5), 147 (6,0), 132 (8,5), 120 (8,2), 118 (7,9), 117 (25,0), 116 (7,4), 110 (5,1), 105 (5,1), 103 (5,9), 102 (5,4), 91 (23,5), 89 (9,8), 65 (10,1), 55 (21,8), 51 (6,4)
IV	293 (5,1), 292 (55,7), 291 (52,5), 265 (6,1), 264 (68,2), 263 (38,9), 250 (12,7), 249 (100), 237 (36,0), 236 (40,2), 235 (15,0), 223 (13,3), 222 (73,2), 221 (66,7), 220 (23,7), 209 (5,0), 208 (7,4), 165 (8,8), 118 (5,8), 117 (10,2), 104 (12,6), 103 (10,6), 91 (27,6), 89 (6,7), 78 (13,7), 77 (38,8), 76 (6,3), 75 (6,8), 55 (37,7), 51 (9,7)
V	300 (17,3), 299 (36,3), 298 (81,1), 297 (100), 272 (23,4), 271 (38,6), 270 (96,6), 269 (82,6), 257 (21,7), 256 (12,8), 255 (92,0), 245 (12,2), 244 (28,4), 243 (66,1), 242 (62,5), 241 (17,8), 240 (5,9), 235 (5,0), 230 (15,6), 229 (9,4), 228 (72,0), 227 (9,6), 205 (5,6), 193 (13,5), 177 (6,9), 165 (16,6), 163 (6,2), 152 (8,3), 151 (5,7), 127 (7,6), 125 (6,3), 117 (9,1), 111 (5,9), 110 (35,2), 104 (9,6), 103 (9,2), 91 (9,0), 89 (7,4), 77 (38,8), 76 (6,3), 75 (6,8), 55 (37,7), 51 (9,7)
VI	328 (9,5), 327 (16,3), 326 (40,5), 325 (42,9), 299 (8,7), 298 (15,9), 297 (100), 296 (33,3), 285 (5,0), 284 (12,7), 283 (20,6), 282 (44,4), 273 (8,3), 272 (10,3), 271 (56,8), 270 (21,4), 269 (55,6), 258 (21,4), 257 (23,4), 256 (100), 255 (48,8), 245 (6,7), 244 (6,7), 243 (49,6), 242 (16,2), 241 (60,7), 240 (11,5), 194 (12,3), 165 (17,2), 152 (5,2), 151 (16,4), 136 (24,9), 135 (13,2), 118 (9,5), 91 (24,4), 89 (6,7), 77 (23,4), 55 (22,6), 51 (6,1)
VII	326 (19,8), 325 (32,7), 324 (76,0), 323 (63,4), 298 (13,9), 297 (25,2), 296 (54,4), 295 (56,3), 285 (9,6), 284 (11,8), 283 (67,3), 282 (11,4), 281 (44,3), 271 (19,0), 270 (27,2), 269 (100), 268 (14,5), 267 (19,0), 257 (7,3), 256 (26,4), 255 (43,3), 254 (81,2), 253 (11,3), 252 (13,4), 243 (5,7), 242 (30,7), 241 (75,2), 240 (26,8), 229 (6,2), 228 (16,5), 227 (19,7), 219 (18,1), 218 (18,5), 217 (15,6), 206 (7,0), 205 (19,7), 204 (5,0), 193 (13,8), 192 (9,4), 191 (8,7), 179 (5,3), 178 (12,8), 177 (10,9), 166 (12,8), 165 (30,7), 164 (18,5), 163 (19,6), 152 (12,6), 151 (18,1), 150 (5,4), 138 (5,7), 136 (13,4), 117 (10,5), 116 (6,0), 115 (7,4), 104 (18,9), 103 (17,6), 102 (7,2), 92 (17,7), 91 (46,8), 89 (10,2), 82 (5,4), 81 (8,7), 77 (43,7), 75 (9,3), 69 (15,5), 65 (5,2), 55 (38,5), 51 (13,4)
VIII	344 (51,0), 343 (100), 342 (61,6), 341 (89,5), 316 (69,2), 315 (79,8), 314 (72,2), 313 (62,6), 301 (59,0), 300 (13,6), 299 (73,2), 298 (9,9), 297 (8,3), 289 (36,4), 288 (44,5), 287 (58,1), 286 (49,3), 285 (13,1), 274 (35,9), 273 (10,1), 272 (46,7), 271 (8,1), 270 (7,3), 269 (6,1), 236 (6,0), 235 (17,7), 208 (9,3), 207 (19,6), 206 (7,7), 205 (15,1), 193 (40,7), 189 (16,5), 178 (8,8), 177 (8,1), 165 (25,5), 163 (8,1), 152 (8,3), 151 (8,3), 118 (6,3), 117 (27,8), 110 (98,0), 105 (8,6), 104 (20,2), 103 (27,6), 102 (5,9), 91 (38,7), 90 (15,7), 89 (13,8), 78 (8,2), 77 (74,4), 76 (20,2), 75 (13,3), 65 (6,5), 63 (12,2), 55 (94,4), 51 (24,9)
IX	359 (10,0), 358 (83,3), 357 (94,7), 356 (94,4), 355 (76,1), 381 (6,7), 380 (76,4), 379 (59,2), 378 (77,6), 377 (45,7), 316 (10,4), 315 (98,5), 314 (18,2), 313 (100), 303 (33,2), 302 (37,3), 301 (55,2), 300 (33,3), 299 (12,7), 298 (6,0), 288 (39,3), 287 (60,1), 286 (61,6), 285 (51,8), 284 (15,4), 207 (18,2), 206 (9,4), 205 (11,6), 204 (6,8), 165 (14,9), 134 (12,7), 118 (5,2), 117 (15,1), 105 (5,3), 104 (20,2), 103 (27,6), 102 (5,9), 91 (38,7), 90 (15,7), 89 (13,8), 78 (8,2), 77 (74,7), 76 (24,6), 75 (12,4), 63 (15,2), 55 (28,8), 51 (19,8)
X	385 (7,3) 384 (50,6), 383 (60,6), 382 (51,6), 381 (56,4), 358 (38,7), 357 (32,0), 356 (40,0), 355 (2,53), 343 (32,6), 342 (10,0), 341 (33,3), 330 (41,3), 329 (92,0), 328 (44,1), 327 (44,0), 316 (52,0), 315 (88,1), 314 (63,3), 313 (80,1), 312 (6,7), 302 (42,0), 301 (43,3), 300 (47,3), 299 (40,2), 298 (26,7), 288 (33,2), 287 (100), 286 (92,0), 285 (16,7), 274 (5,5), 273 (10,0), 272 (7,2), 271 (6,7), 255 (10,0), 207 (13,3), 206 (26,0), 205 (26,6), 204 (5,9), 195 (7,3), 194 (35,3), 193 (10,7), 192 (7,3), 191 (5,3), 179 (9,3), 178 (10,0), 177 (6,6), 166 (7,3), 165 (40,6), 164 (11,2), 163 (8,0), 152 (8,4), 151 (21,1), 150 (6,6), 136 (21,0), 135 (10,1), 131 (6,3), 130 (10,6), 129 (6,6), 118 (11,3), 117 (25,3), 116 (8,0), 115 (7,3), 110 (12,1), 105 (10,1), 104 (22,6), 103 (25,3), 102 (6,6), 92 (7,3), 91 (54,7), 90 (14,7), 89 (10,7), 81 (12,1), 77 (44,1), 76 (10,7), 75 (7,3), 65 (5,1), 57 (41,3), 55 (76,0), 51 (9,3)

TABLE 2 Continued

1	2
XI	380 (16,2), 379 (30,7), 378 (87,9), 377 (95,9), 376 (72,5), 375 (59,8), 352 (20,1), 351 (30,0), 350 (100), 349 (75,8), 348 (71,7), 347 (44,0), 343 (14,2), 341 (14,5), 337 (9,8), 336 (9,7), 335 (63,8), 334 (10,2), 333 (42,6), 325 (10,2), 324 (20,2), 323 (60,1), 322 (72,2), 321 (60,3), 320 (52,1), 315 (5,2), 313 (5,3), 310 (12,2), 309 (8,8), 308 (63,7), 307 (16,1), 306 (48,3), 305 (7,1), 271 (5,0), 269 (13,2), 242 (5,0), 241 (7,3), 240 (5,4), 229 (6,1), 227 (22,3), 191 (5,5), 179 (5,0), 178 (12,3), 165 (15,8), 164 (10,3), 163 (9,1), 151 (13,2), 150 (16,7), 149 (13,2), 127 (7,1), 126 (22,3), 125 (9,7), 118 (15,3), 111 (14,7), 110 (19,8), 109 (17,6), 103 (7,8), 102 (16,7), 90 (8,2), 89 (13,4), 86 (14,7), 79 (11,3), 78 (41,4), 77 (11,9), 63 (12,3), 57 (11,8), 55 (9,7), 51 (6,8)
XII	272 (19,7), 271 (40,5), 270 (76,7), 269 (100), 254 (4,6), 230 (6,2), 228 (29,8), 77 (8,5)
XIII	214 (100), 186 (4,0), 185 (3,7), 173 (4,3), 172 (89,6), 171 (27,3),

TABLE 3. Stabilities with Respect to Electron Impact and Intensity Ratios of the Ion Peaks in the Mass Spectra of I-XI

Compound	W_M	$\frac{J_{M-1}}{J_M}$	$\frac{J_{M-28}}{J_M}$	$\frac{J_{M-29}}{J_{M-28}}$
I	4,16	3,56	3,05	0,82
II	6,92	1,69	1,34	0,86
III	6,79	1,43	1,57	0,82
IV	5,89	1,04	1,27	0,65
V	7,56	1,51	1,27	1,02
VI	3,75	1,24	0,98	0,98
VII	4,71	1,03	0,70	1,17
VIII	4,75	1,87	1,31	1,00
IX	9,21	1,02	0,88	0,70
X	3,92	1,17	0,79	0,74
XI	4,95	1,12	1,17	0,78

TABLE 4. High-Resolution Mass Spectrum of I

Masses observed	Masses calc.	Ionic composition	Group eliminated	Fraction of the ion, %
236,0941	,0949	$C_{15}H_{12}N_2O$	C_2H_4	100
235,1247	,1235	$C_{16}H_{15}N_2$	CHO	34
235,0945	,0997	$C_{16}H_{13}NO$	CH_3N	32
235,0896	,0875	$C_{15}H_{11}N_2O$	C_2H_5	34
221,1083	,1078	$C_{15}H_{13}N_2$	C_2H_3O	66
221,0716	,0714	$C_{14}H_9N_2O$	C_3H_7	34
209,1098	,1078	$C_{14}H_{13}N_2$	C_3H_3O	100
208,1035	,1001	$C_{14}H_{12}N_2$	C_3H_4O	100
207,0940	,0922	$C_{14}H_{11}N_2$	C_3H_5O	100
206,0974	,0969	$C_{15}H_{12}N$	C_2H_4NO	100
205,0776	,0765	$C_{14}H_9N_2$	C_3H_7O	100
194,0966	,0969	$C_{14}H_{12}N$	C_3H_4NO	100
193,0897	,0891	$C_{14}H_{11}N$	C_3H_5NO	100
165,0699	,0704	$C_{13}H_9$	$C_4H_7N_2O$	100

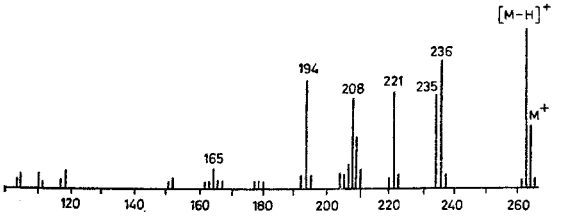
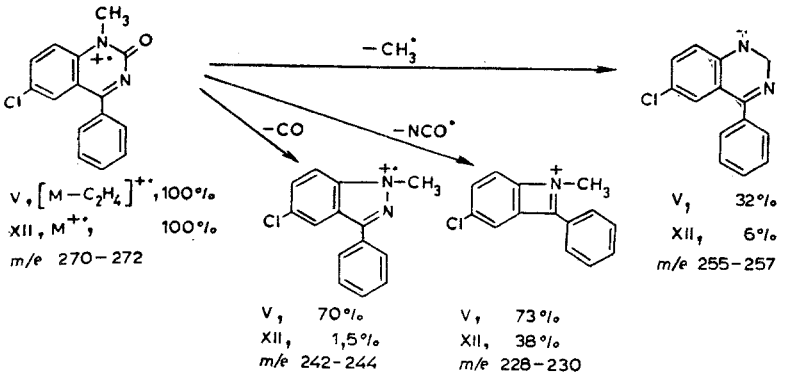


Fig. 1. Mass spectra of I.

In a comparison of the fragmentation of the $[M - C_2H_4]^+$ ions for V with the fragmentation of the molecular ions of XII it was also established that their fragmentation pathways are identical, but the $[M - C_2H_4]^+$ ions undergo considerably greater fragmentation than the molecular ions of N-methylquinazolinone (Scheme 2). Consequently, the $[M - C_2H_4]^+$ ions have a structure than differs from the structure of the molecular ions of XII. It is possible that after elimination of an ethylene molecule by the molecular ions of benzodiazocin-2-ones the heteroring remains partially open and undergoes partial closing to give not only C–N but also N–N bonds; however, one cannot exclude the possibility that the noted idfferences in the intensities of the peaks of the fragment ions are due to energy factors.

Scheme 2*

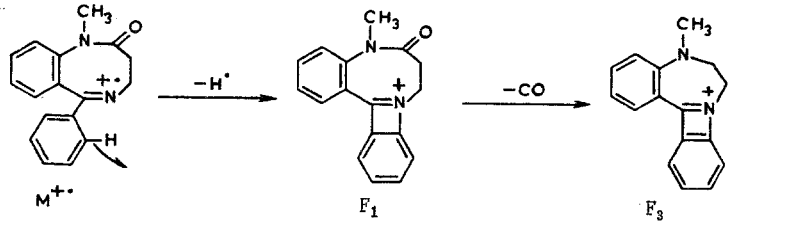


Fragmentation of the $[M - C_2H_4]^+$ ions with elimination of H·, Co, and NCO· is a general feature of all of the investigated series of compounds. Fragmentation via a fourth pathway proceeds in different ways depending on the R^2 substituent. When $R^2 = CH_3$ (I-III, V, VIII, and XI), a methyl radical is eliminated. When $R^2 = C_2H_5$ (IV and IX), C_3H_7 (VI), or C_4H_9 (X), the exocyclic β-C−C bond is cleaved with the elimination of, respectively, methyl, ethyl, or propyl radicals. When $R^2 = CH_2CHCH_2$, a C_2H_3· radical is eliminated as a result of β cleavage. All of these processes lead to the formation of rather intense (sometimes maximum) ion peaks in the mass spectra of benzodiazocin-2-ones.

As seen from Table 4, in the case of I the ions with m/e 235 have different compositions: $C_{16}H_{15}N_2$, $C_{16}H_{13}NO$, and $C_{15}H_{11}N_2O$; according to the intensity of the darkening of the photographic plate in the high-resolution mass spectrum, their ratios of their concentrations are approximately equal.

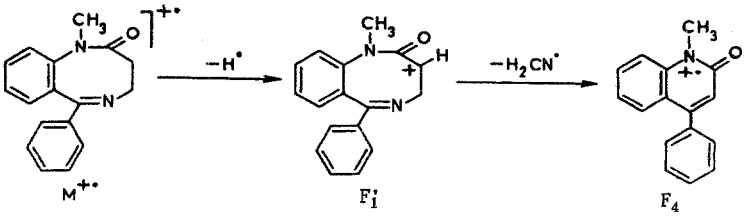
Ions of the composition $C_{16}H_{15}N_2$ are formed as a result of elimination of the group of CHO atoms, and this process can be represented by Scheme 3, although elimination of a CHO radical in one step is not excluded.

Scheme 3



Ions of the composition $C_{16}H_{13}NO$ are formed as a result of the loss of a group of CH_3N atoms, and here one can assume two-step elimination of H· and H_2CN· radicals with the formation of ions of the N-methylquinolone type. It is possible that in this case one of the methylene hydrogen atoms is eliminated in the first step of the fragmentation, since the formation of F_4 ions from F_1 ions would necessitate simultaneous cleavage of four chemical bonds, and this is less favorable energically speaking.

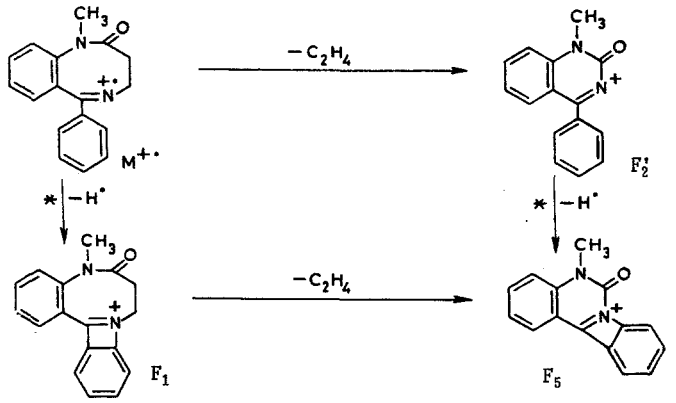
Scheme 4



Ions of the composition $C_{15}H_{11}N_2O$ are formed as a result of splitting out of a group of C_2H_5 atoms, and this process can be represented by elimination of a hydrogen atom and an ethylene molecule in a different sequence:

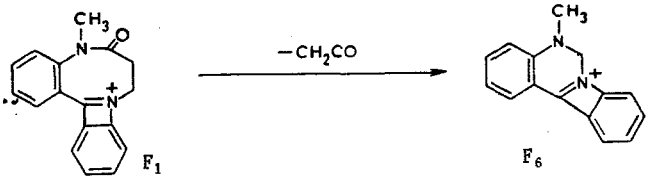
* The intensities of the peaks of the ions with m/e 270-272 were assumed to be 100%. The intensities of the peaks of ions of the indicated compositions are given in percent relative to them.

Scheme 5



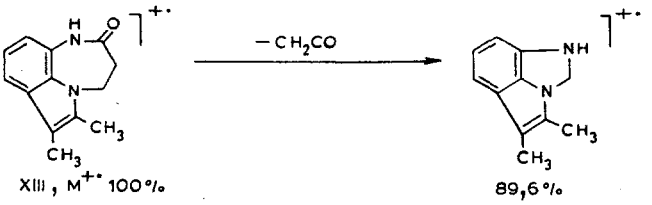
Ions with m/e 221, the peak of which amounts to 62% of the maximum peak, are formed as a result of fragmentation of the F_2 ions with elimination of a CH_3 group in the case of I, but, according to the data from the high-resolution mass spectrum (Table 4), only 30% of the intensity of this peak is due to ions of this composition. Processes that result in the loss of a group of C_2H_3O atoms make a major contribution to the formation of ions with m/e 221. Consequently, one can conceive of only a single pathway for their formation – splitting out of ketene from the F_1 ions:

Scheme 6



Elimination of a ketene molecule is the principal pathway in the fragmentation of 1,5-benzodiazepin-2-ones [5]. In addition, splitting out of CH_2CO and the corresponding peak of the metastable ion are observed in the mass spectrum of indoleazepinone XIII:

Scheme 7



These experimental facts adequately confirm the structure assigned to the F_1 ions, i.e., these ions are at least partially formed as a result of elimination of a hydrogen atom from the ortho position of the 6-phenyl substituent with simultaneous cyclization to the adjacent nitrogen atom.

The discussed pathways of fragmentation of benzodiazocin-2-ones I-XI are common to the entire series and, what is most important, ions with peaks of high intensity (40-100%) are formed as a result of these processes. These fragment ions can be used along with the molecular ions for mass fragmentographic analysis. In addition to them, rather intense (up to 35%) peaks of hydrocarbon fragment ions with m/e 77, 91, and 165 (C_6H_5, C_7H_7, and $C_{13}H_9$, respectively, according to data from the high-resolution mass spectra), which are characteristic for the mass spectrometric fragmentation of condensed aromatic systems [6], are observed in the mass spectra of the investigated compounds. It is interesting to note that $[C_6H_4Cl]^+$ ions are not observed in the mass spectra of III and XI, in which the 6-phenyl ring contains a chlorine atom. Consequently, the $[C_6H_5]^+$ ions are not simple fragment ions but rather are formed in complex fragmentation steps.

EXPERIMENTAL

The mass spectra of the investigated compounds were obtained with an MKh-1303 spectrometer with a system for direct introduction of the samples at an ionizing energy of 50 V and an emission current of 1.5 μA at temperatures 20-40° below the melting points of the substances. The high-resolution mass spectrum of I was obtained with a JEOL JMS-01-SG-2 mass spectrometer. The IR spectra of the compounds were recorded with an IKS-22 spectrometer. The UV spectra were recorded with the Specord UV-vis spectrophotometer. Polarographic reduction was carried out under the conditions described in [4].

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CYCLIZATION OF N^1-ARYL-N^3-ACETYL-p-NITROBENZAMIDRAZONES TO SUBSTITUTED 1,2,4-TRIAZOLES

M. O. Lozinskii, T. N. Kudrya, S. V. Bonadyk, and P. S. Pel'kis

UDC 547.792.5.7

The reaction of α-acetamido-p-nitroacetophenone with benzenediazonium salts gave N^1-aryl-N^3-acetyl-p-nitrobenzamidrazones, which are cyclized to 5-methyl-1-aryl-3-(p-nitrobenzoyl)-1,2,4-triazoles. The latter are quaternized at the nitrogen atom in the 4 position.

α-Acetamido-p-nitroacetophenone (I) is used as an intermediate in the synthesis of levomycetin [1]. Little study has been devoted to its chemical properties; in particular, its reactions at the active methylene group have not been investigated.

In the present research we studied the reaction of I with arenediazonium salts and showed that the products are N^1-aryl-N^3-acetyl-p-benzamidrazones (II). In the case of electron-donor substituents in the benzenediazonium salts the yields of II are close to quantitative, whereas in the case of electron-acceptor substituents (chloro and nitro groups) one observes the formation of a complex mixture of products, from which we were able to isolate, in addition to the amidrazone, a side product – 1,5-bis(p-chlorophenyl)-3-acetamidoformazan (VIII) – in the case of p-chlorobenzenediazonium chloride.

Compound II (Table 1) has the properties of polymorphism and phototropy. The UV spectra of IIa-h contain absorption maxima at 230-270 and 380-400 nm. Characteristic bands at 1580-1620 (C = N), 1670 and 1630 (C = O), and 3280-3340 cm^{-1} (NH) are observed in the IR spectra, and this confirms their hydrazone structure [2].

Institute of Organic Chemistry, Academy of Sciences of the Ukrainian SSR, Kiev 252660.

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