MASS-SPECTROMETRIC STUDY OF THE CYCLIZATION OF DIAZO KETONES.

2.* CYCLIZATION OF 1-DIAZO-4-SULFONYLAMINOBUTAN-2-ONES TO N-SULFONYLPYRROLIDIN-3-ONES

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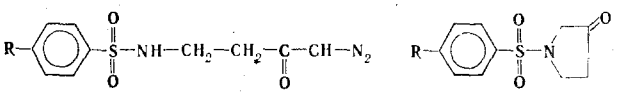
A comparison of the mass spectra of 1-diazo-4-sulfonylamino-butan-2-ones and N-sulfonylpyrrolidin-3-ones makes it possible to conclude that under the conditions of electron impact and chemical ionization the molecular ions of the investigated diazo ketones lose a molecule of nitrogen and undergo partial cyclization to the corresponding pyrrolidinones without undergoing the Wolff rearrangement.

We have previously shown [1] that in the ionization chamber of a mass spectrometer both under the influence of electron impact (EI) and under conditions of chemical ionization (CI) 1-diazo-3-sulfonylaminopropan-2-ones eliminate a molecule of nitrogen and, without undergoing the Wolff rearrangement, undergo partial cyclization to N-sulfonylazetidin-3-ones. In the present research we investigated the analogous cyclization of 1-diazo-4-sulfonylaminobutan-2-ones (I) to the corresponding N-sulfonylpyrrolidin-3-ones (II) in the ionization chamber of a mass spectrometer by comparison of the fragmentation of the molecular ions (M^+) of pyrrolidinones II and the $[M - N_2]^+$ ions of diazo ketones I (EI) and the fragment of the protonated molecular ions (MH^+) of pyrrolidinones II and the $[MH - N_2]^+$ ions of diazo ketones I (CI).†



I a-e,g,h IIa-h

a R=H; b R=CH_3; c R=OCH_3; d R=Cl; e R=Br; f R=$COCH_3$; g R=NO_2; h R=$NHCOCH_3$

Molecular-ion (M^+) peaks are not observed in the EI mass spectra of diazo ketones I, while the $[M - N_2]^+$ ion peaks are rather intense. The fraction of the current of $[M - N_2]^+$ ions in the total ion current remains virtually unchanged as a function of the electronic properties of the substituent in the benzene ring and is approximately 10 times lower than the average value only in the case of Ig (R = NO_2) (see Table 1). The M^+ peaks of II are also rather intense, but their relative intensity depends to a greater degree on substituent R and in the case of electron-donor substituents exceeds the intensity of the $[M - N_2]^+$ ion peaks in the mass spectra of the corresponding diazo ketones by a factor of three to four.

In the interaction of diazo ketones I (A) with ionizing electrons the molecule losses an electron from the position with the highest electron density, as a result of which unstable ion radical B is formed (see Scheme 1); ion-radical B cannot be recorded, since it immediately eliminates a molecule of nitrogen (heterolytic cleavage of the CH—N_2 bond) with the formation of ion radical C, in which the positive charge, an unpaired electron, and a "lagoon" free orbital are concentrated on the terminal carbon atom. (See top, following page.)

Electrophilic attack by this carbon atom at the nitrogen atom with subsequent migration of a hydrogen atom leads to stable ion radicals E, which are similar to the M^+ ions of pyrrol-

*See [1] for Communication 1.
†The formation of II from diazo ketones I under the influence of concentrated sulfuric acid was demonstrated in [2].

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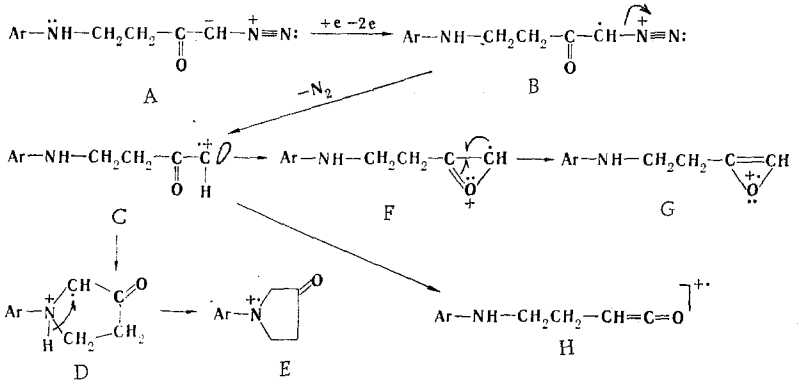
Scheme 1



idones II. However, rather stable ion radical G may develop in the case of attack at the oxygen atom of the carbonyl group. The Wolff rearrangement [3-6] may lead to structure H.* An analysis of the mass spectra obtained makes it possible to conclude that the bulk of the $[M - N_2]^+$ ions exist in the E form. The mass-spectrometric fragmentation of this ion with structures G and H should lead to the formation of $ArSO_2\overset{+}{N}H{=}CH_2$ ions, the peaks of which would have rather high intensities. However, peaks of this ion are observed only in the mass spectra of Ic,d,f, but their intensities are very low. The fact that F_6 ions eliminate a molecule of ketene (see Scheme 2) rather than a $CHCO^{\bullet}$ radical also constitutes evidence in favor of cyclic structure E. The loss of a $CHCO^{\bullet}$ radical is also characteristic for structures G and H; however, the fact that the intensities of the peaks of these ions are low in the mass spectra of all diazo ketones I, as well as the possibility of their formation directly from M^+ through elimination of a $CHCON_2$ particle by the latter, makes valid the assertion that if some of the $[M - N_2]^+$ ions also exist in the G or H form, the amount is very small. The fact that the analogous ions of 1-diazo-3-sulfonylaminopropan-2-ones III undergo cyclization in the ionization chamber of a mass spectrometer to azetidin-3-ones, i.e., they do not undergo rearrangement via the Wolff mechanism [1], may also serve as evidence that $[M - N_2]^+$ ions do not undergo the Wolff rearrangement but rather form a pyrrolidinone ring.

As we have previously demonstrated [1], the first act in the fragmentation of the M^+ ions of N-sulfonylazetidin-3-ones was splitting out of a molecule of CO, whereas the subsequent fragmentation of the $[M - CO]^+$ ions determined the entire pattern of the dissociative ionization. The M^+ ions of II in the first stage of fragmentation also eliminate a molecule of CO with the formation of F_1 ions, which subsequently undergo fragmentation with cleavage of the S-N bond, as a result of which F_2 and F_7 ions are formed, either with the successive ejection of a molecule of SO_2 and a hydrogen atom or ejection of an SO_2H radical in one step (see Scheme 2). In the case of splitting out of a molecule of SO_2 rearrangement with the formation of a new Ar—C bond [1] occurs, as evidenced by the presence in the mass spectra of all of the compounds of peaks of an F_5 ion, the elementary composition of which for Ib and IIb was confirmed by high-resolution mass spectrometry (HRMS).

The only difference in the mass spectrometric behavior of II and azetidin-3-ones is the fact that cleavage of the S—bond also occurs in M^+; F_2 and F_6 ions are formed by this cleavage. In accordance with Stevenson's rule, in the homolytic cleavage of a bond in an ion the charge is retained on the fragment with the lower ionization potential. The fact that in the mass spectra of the investigated compounds the peaks of both F_2 and F_6 ions are quite intense makes it possible to conclude that the arylsulfonyl and pyrrolidine fragments have close ionization potentials. Electron-donor substituents in the benzene ring lower the ionization potential of the arylsulfonyl fragment, as a consequence of which the fraction of the current of F_6 ions in the total ion current decreases. Electron-acceptor substituents have the opposite effect. This dependence is not observed for F_2 ions, which confirms their formation by several pathways (see Scheme 2).

*One also might have assumed attack of the electrophilic center at the oxygen atom of the sulfo group with the formation of a seven-membered heteroring; however, an analysis of the mass spectra completely repudiates cyclization of this sort.

TABLE 1. Intensities of the Peaks of the Characteristic Fragment Ions in the EI Mass Spectra of I and II in Percent of the Total Ion Current*

Compound	M, M−N_2	F_1	F_2	F_3	F''_3	F_4	F_5	F_6	F_7	F_8	F_9	F_{10}, F_{15}
Ia	0,2	1,0	3,4	0,7	0,1	0,6	0,2	1,0	1,6	10,0	9,3	3,5
IIa	0,7	1,9	4,5	0,4	1,3	1,0	0,2	1,7	2,2	16,4	10,1	—
Ib	0,3	0,9	3,1	0,2	0,5	0,6	0,4	0,9	1,5	7,4	8,4	3,8
IIb	0,8	1,5	3,7	0,3	0,9	0,9	0,6	1,5	2,4	13,3	9,0	—
Ic	0,2	0,4	3,2	0,2	0,5	0,3	1,1	0,5	1,0	4,0	2,7	5,8
IIc	0,9	1,2	6,2	0,6	0,2	0,5	2,5	1,1	2,2	8,4	3,4	—
Id	0,2	0,5	3,9	0,1	0,2	0,2	0,1	0,7	1,6	10,9	6,9	2,7
IId	0,7	1,5	5,5	—	0,4	0,3	0,1	1,8	2,2	24,3	7,0	—
Ie	0,2	0,5	2,5	0,1	0,2	0,3	—	1,0	1,6	12,9	3,4	3,1
IIe	0,2	1,0	3,4	0,1	0,2	0,2	—	1,5	2,2	28,3	3,7	—
IIf	0,4	1,5	3,1	0,2	0,5	0,3	0,1	2,0	2,2	22,4	5,5	—
Ig	0,1	0,1	1,3	0,1	0,1	0,1	0,1	0,4	1,0	4,4	2,4	2,9
IIg	0,2	1,2	4,8	—	0,2	0,2	—	2,3	3,1	47,0	6,0	—
Ih	0,2	0,2	1,1	0,2	0,1	0,1	0,4	0,5	0,6	2,4	0,9	1,5
IIh	0,4	1,1	6,7	1,4	0,3	0,7	2,4	1,6	3,5	22,4	4,1	—

*The total ion current was calculated with a computer over the range from the ion with m/z 40 to the ion with m/z 349; ~50% of the total ion current is due to the current of background ions.

TABLE 2. Intensities of the Peaks of the Characteristic Fragment Ions in the CI Mass Spectra of I and II in Percent of the Total Ion Current*

Compound	MH^+ $[MH-N_2]^+$	F_1	F_2	F'_2	F_6	F'_6	F_9	F'_9	F_{10}	F'_{10}	F_{11}	F'_{11}	F'_{13}	F_{15}
Ia	14,4	0,1	0,1	0,4	15,4	0,7	—	—	0,1	0,5	—	0,1	0,3	—
IIa	45,5	0,5	0,1	0,6	2,0	0,4	—	0,1	0,3	0,2	—	—	—	—
Ib	22,5	0,1	0,3	2,2	1,3	0,4	0,1	—	0,8	1,3	—	0,1	6,2	0,3
IIb	47,2	0,5	0,2	0,6	1,5	0,4	0,1	0,1	0,4	0,2	0,1	0,1	—	—
Ic	14,2	0,2	0,3	0,4	9,4	0,3	—	—	0,4	0,2	0,2	0,2	0,4	—
IIc	13,9	0,3	0,3	0,5	2,2	0,6	—	—	0,3	0,5	0,2	0,3	—	—
Id	5,1	—	—	0,1	6,0	0,6	0,1	0,1	0,1	0,1	—	0,1	0,3	0,1
IId	33,1	0,5	—	0,5	2,0	0,6	—	—	0,2	—	—	—	0,6	0,1
Ie	3,3	0,3	0,3	0,3	6,1	0,5	0,3	0,1	0,3	0,3	0,1	0,3	0,3	0,1
IIe	32,4	0,5	0,1	0,2	2,6	0,8	—	—	0,3	—	—	—	—	—
IIf	24,7	0,3	0,2	0,3	3,0	3,8	—	2,1	0,2	0,6	0,2	0,7	—	—
Ig	3,3	0,1	0,1	0,1	5,0	0,1	0,1	0,1	—	—	—	—	—	—
IIg	21,4	0,5	0,1	0,2	4,0	1,2	0,1	0,2	0,1	0,2	—	0,2	—	0,1
Ih	5,8	0,2	0,2	0,4	0,9	0,8	—	1,0	0,2	0,6	—	3,7	2,8	—
IIh	13,3	0,1	0,1	0,4	2,0	0,3	—	2,6	0,1	0,4	0,1	3,0	0,1	—

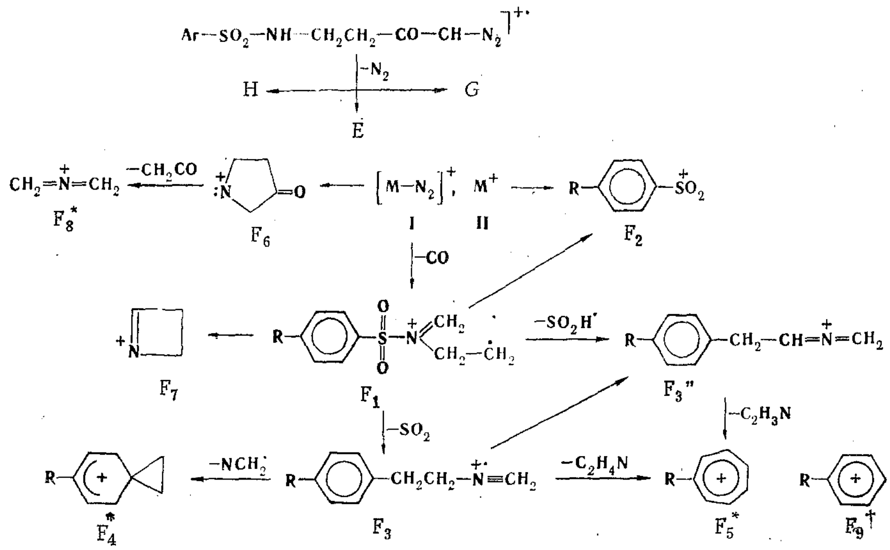
*The total ion current was calculated with a computer over the range of m/z values from 60 to 349. Approximately 50% of the total ion current in this case is due to the fraction of low-intensity peaks of background ions.

Ejection of a molecule of SO_2 by the F_2 ions and a molecule of $CH_2{=}CO$ by the F_6 ions leads to F_9 and F_8 ions, respectively. The fraction of current of the F_8 ions in the total ion current increases as the electron-acceptor properties of the substituent become more pronounced, reaching 47% in the case of the nitro-substituted compound. This dependence is displayed much more weakly in the mass spectra of diazo ketones I. The F_8 ions are formed, in all likelihood, precisely from the F_6 ions, since the relative intensities of the peaks of these ions change symbatically, which constitutes evidence for their genetic link.

The principal pathways in the mass-spectrometric fragmentation of the $[M - N_2]^+$ ions of I and the M^+ ions of II virtually coincide and can be described by Scheme 2.

However, some differences in the mass-spectrometric fragmentation of I and II under electron impact should be noted. Thus, the relative intensities of the peaks of F_1-F_9 ions in the mass spectra of pyrrolidinones II are always higher than the intensities of the peaks of the analogous ions in the mass spectra of diazo ketones I. This is due to the fact that the mass spectra of diazo ketones contain a number of low-intensity peaks of ions, the formation of which is associated with rearrangements of the sulfo group [1, 7] [Ar—SO^+ (F_{10}), Ar—S^+

Scheme 2



(F_{11}), and $Ar{-}O^+$ (F_{12})], as well as peaks of the specific ions $Ar{-}SO_2{-}\overset{+}{N}H_2$ (F_{13}), $Ar{-}SO_2{-}NH{-}CH_2{-}\overset{+}{C}H_2$ (F_{14}), and Ar–CH(CO–CH$_2$)(NH–CH$_2$) [ring] (F_{15}), which are evidently formed in the mass-spectrometric fragmentation of the M^+ ions of diazo ketones I or from the $[M - N_2]^+$ ion, which has the G or H structure (see Scheme 1). The contribution of the current of the F_{10}-F_{15} ions to the total ion current is 1.50-5.80% (Table 1).

Thus an analysis of the electron impact (EI) mass spectra of I and II showed a very great similarity in their fragmentation processes, which makes it possible to conclude that 1-diazo-4-sulfonyl-aminobutan-2-ones undergo cyclization in the ionization chamber of the mass spectrometer under the influence of electron impact to the corresponding N-sulfonylpyrrolidin-3-ones. The presence in the mass spectra of diazo ketones I of peaks of specific ions constitutes evidence that some of the M^+ ions undergo fragmentation without cyclization (possibly undergoing the Wolff rearrangement or closing to form an oxirane ring). The differences in the relative intensities of the common fragment ions also indicate that only some of the molecules of diazo ketones I undergo cyclization to pyrrolidinones II.

The fragmentation processes of I and II under conditions of chemical ionization (CI) (with isobutane as the gas reactant) remain the same as under EI conditions, although there are a number of differences. Thus the relative intensities of the peaks of protonated molecular ions (MH^+) of pyrrolidinones II and the $[MH - N_2]^+$ ions of diazo ketones I are very high (see Table 2) and reach, respectively, 47.2 and 22.5% of the total ion current in the case of methyl-substituted Ib and IIb. In the analysis of the MH^+ peaks of the pyrrolidinones one's attention is drawn to their low intensities for IIc and IIh (R = OCH_3 and $NHCOCH_3$). These substituents usually led to an increase in the relative intensities of the ion peaks owing to their ability to delocalize positive charge [1]. Peaks of cluster ions are present in all the CI mass spectra: $[M - N_2, + C_3H_5]^+$, $[M - N_2 + C_3H_7]^+$, $[M - N_2, + C_3H_3]^+$, and $[M - N_2, + C_4H_9]^+$ for I and $[M + C_3H_3]^+$, $[M + C_3H_5]^+$, $[M + C_3H_7]^+$, and $[M + C_4H_9]^+$ for II.

Protonation of I and II at the oxygen atom of the carbonyl group is the most likely process in the case of chemical ionization, although it is not the only possible process, as evidenced by the presence of peaks of ions of the F'_n series in the mass spectra (see below). The fact that one and the same ion (F_1) is formed in the first step of fragmentation by splitting out of a carbonyl group in the case of both electron impact and chemical ionization, i.e., a molecule of CO (EI) and an $HCO^{\bullet}$ radical (CI), respectively, are split out, constitute evidence in favor of protonation at the carbonyl group.

*The elementary composition of the ion was confirmed by mass spectrometry (HRMS).

†In principle, the formation of F_9 ions from M^+, F_{1-3}, F''_3, and F_4 ions is possible.

TABLE 3. Mass Spectra of Ia-h and IIa-h

Compound	m/z values (relative intensities of the ion peaks in percent of the maximum peak)
	1. Electron impact
IIa	197 (10,1), 141 (33,8), 125 (13,4), 109 (9,8), 78 (11,1), 77 (92,7), 56 (15,9), 51 (39,8), 50 (11,9), 42 (100)
IIb	211 (10,4), 155 (36,3), 139 (18,7), 123 (11,2), 91 (100), 84 (10,4), 65 (34,6), 56 (17,3), 42 (87,6), 41 (13,0)
IIc	171 (81,4), 139 (50,9), 123 (35,7), 121 (27,7), 107 (67,9), 92 (48,5), 77 (79,9), 64 (47,9), 63 (36,8), 42 (100)
IId	177 (13,5), 175 (38,2), 140 (13,9), 120 (19,9), 113 (15,6), 111 (48,9), 56 (13,5), 44 (12,8), 43 (12,9), 42 (100)
IIe	221 (10,0), 219 (9,7), 157 (13,0), 155 (13,0), 108 (14,0), 76 (15,0), 75 (16,7), 56 (12,1), 50 (16,6), 42 (100)
IIg	186 (30,4), 122 (54,0), 102 (47,7), 82 (31,6), 76 (44,8), 75 (52,1), 50 (56,0), 44 (34,4), 43 (38,4), 42 (100)
IIh	198 (16,0), 125 (32,5), 93 (26,3), 92 (18,5), 65 (27,2), 55 (14,7), 45 (20,1), 44 (34,4), 43 (100), 42 (35,6)
Ia	197 (11,5), 141 (27,5), 132 (7,7), 105 (6,2), 84 (10,2), 78 (6,8), 77 (61,9), 56 (13,2), 51 (24,4), 42 (100)
Ib	211 (11,3), 155 (27,7), 146 (6,9), 119 (7,0), 91 (67,6), 84 (10,9), 65 (23,6), 56 (17,8), 42 (100), 41 (9,8)
Ic	255 (10,5), 227 (14,1), 171 (73,4), 123 (19,2), 121 (29,9), 107 (40,6), 92 (23,4), 77 (39,0), 56 (25,8), 42 (100)
Id	231 (4,5), 177 (6,3), 175 (16,3), 113 (6,8), 111 (22,1), 84 (7,4), 75 (11,1), 56 (8,9), 50 (5,4), 42 (100)
Ie	221 (6,7), 219 (6,4), 157 (6,4), 155 (6,6), 84 (5,5), 76 (9,0), 75 (9,0), 56 (8,0), 50 (10,0), 42 (100)
If	239 (6,6), 183 (13,7), 119 (24,6), 91 (7,3), 84 (8,9), 76 (6,3), 56 (9,7), 50 (5,2), 43 (23,2), 42 (100)
Ig	186 (10,2), 122 (12,7), 76 (9,3), 75 (7,7), 56 (6,6), 55 (5,2), 50 (12,4), 43 (6,7), 42 (100), 41 (7,0)
Ih	198 (29,8), 148 (10,8), 134 (18,2), 108 (11,9), 92 (14,9), 65 (29,7), 56 (15,8), 43 (87,0), 42 (100), 41 (12,6)
	2. Chemical ionization
Ia	256 (3,5), 228 (6,6), 227 (10,8), 226 (76,5), 127 (2,8), 86 (4,4), 85 (8,0), 84 (100), 83 (2,5), 71 (2,1)
Ib	279 (14,2), 242 (8,5), 241 (16,1), 240 (100), 239 (6,8), 238 (8,7), 172 (34,5), 157 (12,5), 141 (7,2), 84 (7,3)
Ic	258 (7,4), 257 (15,2), 256 (100), 255 (4,9), 246 (4,0), 188 (3,4), 173 (3,5), 155 (3,0), 85 (6,1), 84 (81,1)
Id	262 (22,6), 261 (10,0), 260 (48,9), 226 (33,7), 86 (10,0), 85 (11,0), 84 (100), 71 (22,1), 69 (7,4), 61 (15,8)
Ie	306 (23,7), 304 (23,6), 226 (6,6), 86 (8,8), 85 (11,0), 84 (100), 71 (19,8), 70 (6,0), 69 (5,5), 61 (13,2)
Ig	273 (6,3), 272 (9,3), 271 (50,5), 270 (3,7), 241 (4,5), 86 (2,6), 85 (6,9), 84 (100), 83 (2,9), 71 (4,2)
Ih	285 (8,6), 284 (16,8), 283 (100), 215 (55,0), 169 (9,5), 168 (79,5), 136 (20,0), 86 (16,4), 84 (19,5), 71 (11,8)
IIa	228 (6,2), 227 (10,6), 226 (100), 225 (6,0), 197 (1,4), 143 (1,6), 125 (0,5), 86 (0,7), 85 (0,6), 84 (4,9)
IIb	242 (5,7), 241 (9,9), 240 (100), 239 (6,0), 211 (1,2), 157 (1,5), 139 (0,9), 86 (0,9), 85 (0,7), 84 (3,7)
IIc	258 (7,1), 257 (15,2), 256 (100), 255 (8,1), 240 (23,7), 172 (9,6), 84 (19,7), 71 (17,2), 69 (9,6), 61 (36,9)
IId	264 (3,2), 263 (5,7), 262 (42,6), 261 (17,9), 260 (100), 259 (5,9), 240 (4,7), 226 (21,0), 84 (10,5), 71 (5,5)
IIe	308 (5,9), 307 (13,4), 306 (100), 305 (18,3), 304 (97,4), 303 (5,3), 226 (8,5), 86 (5,5), 85 (2,2), 84 (17,6)
IIf	270 (7,0), 269 (17,5), 268 (100), 267 (5,6), 169 (3,0), 153 (3,4), 121 (10,7), 86 (19,7), 84 (13,5), 61 (19,9)
IIg	273 (7,2), 272 (17,4), 271 (100), 270 (8,2), 242 (2,5), 241 (4,7), 89 (5,8), 86 (6,7), 85 (2,4), 84 (22,0)
IIh	285 (7,0), 284 (19,7), 283 (100), 282 (4,7) ,200 (3,4), 184 (3,4), 168 (27,8), 136 (24,6), 85 (4,4), 84 (18,4)

The second most intense peak in the CI mass spectra under consideration is the peak of F_6 ions, which are formed as a result of cleavage of the S–N bond in the MH^+ ions of II and in the $[MH - N_2]^+$ ions of I. In the case of pyrrolidinones the F_6 ion has, in all likelihood, a cyclic structure (see Scheme 2). In the mass spectra of diazo ketones I the relative intensity of the peak of these ions generally proves to be considerably higher (by a factor of seven in the case of the unsubstituted compound). This makes it possible to assume that either the F_6 ion, which is formed in the fragmentation of diazo ketones I, may exist in some other more stable form in addition to the cyclic form or that the S–N bond in the diazo ketones is much weaker, and cyclization of the resulting fragment after its cleavage is facilitated [1].

Another difference in the CI and EI mass spectra is the absence of peaks of ions that are characteristic for a rearrangement process with splitting out of a molecule of SO_2; however, on the other hand, peaks of ions, the formation of which is due to rearrangements of the sulfo group (F_{10} and F_{11}), are present in the spectra of both I and II.

The fact that the peak of an ion that has an m/z value that is 2 amu greater (F'_2, F'_6, and F'_{9-11}) accompanies each of the peaks of F_2, F_6, and F_{9-11} ions is very important. The presence in the CI mass spectra of peaks of these ions indicates the occurrence in the ionization chamber of the mass spectrometer of ion-molecular reactions, which we noted and examined in detail in [1]. Ion-molecular reactions that occur in the case of chemical ionization of haloaromatic compounds when hydrogen and methane were used as the gas reactants were investigated in [8, 9]. In this case one of the principal peaks in the mass spectra proves to be the peak of the $[MH-Hal, +H]^+$ ion in the case of ionization by hydrogen and $[MH-Hal, +CH_3]^+$ in the case of ionization by methane. By varying the conditions used to obtain the mass spectra, including the pressure of the gas reactant in the ionization chamber, the authors were able to show that the indicated ions are formed as a result of ion-molecular reactions in both one step (in the reaction of MH^+ and the gas reactant with splitting out of a molecule of HHal) and in two steps (in the case of elimination by MH^+ of a halogen atom and subsequent reaction of the resulting ion radical with a molecule of the gas reactant). In the case of I and II the reaction of the gas reactant with MH^+ may proceed via many pathways, as a result of which all of the indicated ions of the F'_n series and some specific ions are formed. Thus reaction with substitunt R in the benzene ring is observed when unshared electron pairs are present on the atoms of the substituting group but proceeds most actively in the case of halosubstituted compounds. As a result of this reaction, intense peaks of $[MH-Hal, +H]^+$ ions are observed in the CI mass spectra of I and IId,e; this is in agreement with the data in [1, 8, 9]. These results constitute evidence that replacement of a halogen atom by a hydrogen atom rather than by a carbon radical (which is observed in the case of ionization by methane [8, 9] occurs in the case of chemical ionization by isobutane. This is possibly associated with the large volume of the isobutane molecule. Reaction of a molecule of the gas reactant with MH^+ at the nitrogen atom is most characteristic in the case of diazo ketones I. The intensities of such ions are, as a rule, low but in the case of Ib,h reach anomalously high values (6.2 and 2.8%, respectively, in the total ion current).

It should be especially emphasized that the intensities of the peaks of all of the F'_n ions are very unstable and change substantially from scanning to scanning; this constitutes evidence for the random character of the ion-molecular reactions and for their pronounced dependence on small changes in the parameters of the apparatus in obtaining the mass spectra (the ionizing-electron energy, the pressure of the gas reactant, and the presence of impurities in it), the avoidance of which is impossible.

Thus a comparison of the CI mass spectra of 1-diazo-4-sulfonyl-aminobutan-2-ones and N-sulfonylpyrrolidin-3-ones makes it possible to conclude that the MH^+ (II) and $[MH - N_2]^+$ (I) ions have very similar structures. The certain differences in the relative intensities of the peaks of the common ions and the F_{13}-F_{15} ions that are formed only in the fragmentation of I constitute evidence that not all of the MH^+ ions of diazo ketones I undergo intramolecular cyclization with the loss of a molecule of nitrogen: some of them undergo fragmentation with cyclization. However, these differences are still less substantial than in the case of the EI mass spectra or in the case of 1-diazo-3-sulfonylaminopropan-2-ones [1]. Consequently, the percentage of cyclization in the case of chemical ionization by isobutane of 1-diazo-4-sulfonylaminobutan-2-ones is higher than in the noted cases; this is also in agreement with the theoretical data (the five-membered ring is more stable than the four-membered ring) and with the data in [2].

EXPERIMENTAL

The mass spectra were obtained with a Varian MAT-44S spectrometer. The EI mass spectra were recorded at 100-220°C, an ionizing-electron energy of 75 eV, and an emission current of 0.6 mA. The CI mass spectra were obtained in an ionization chamber at 33.3 Pa, an ionizing-electron energy of 160 eV, an emission current of 0.7 mA, and temperatures of 100-240°C. The high-resolution mass spectra were obtained with a Varian MAT-311A spectrometer.

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INTRAMOLECULAR CYCLIZATION OF N-PHTHALYL-β-ARYL-β-ALANINE PHENYLHYDRAZIDE

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The reaction of N-phthalyl-β-aryl-β-alanine N'-methyl-N'-phenylhydrazides with phosphorus oxychloride (at ∿80°C) is accompanied by further transformations of the initially formed 2-aminoindole derivatives and leads to isoindolo[1',2':2,3]-pyrimido[5,6-b]indole derivatives. Intermediate 2-aminoindoles were isolated at lower reaction temperatures. The hydrolysis of the isoindolo[1',2':2,3]pyrimido[5,6-b]indole derivatives was studied. The structures of the compounds obtained were established on the basis of the PMR, IR, and UV spectra and the results of elementary analysis.

We have previously established [1] that the Kost reaction in the case of N-acyl-β-phenyl β-alanine phenylhydrazides is accompanied by further transformations of the intermediately formed 2-aminoindoles, which lead primarily to 2-imino-3-benzylidene derivatives of indole.

Another example of an unusual transformation for phenylhydrazides of phthalimide derivatives of β-phenyl-β-alanine (Ia,b) has been described in a brief communication [2]. It was found that the reaction of the indicated hydrazides with phosphorus oxychloride at 80-83°C does not lead to 2-aminoindole derivatives of the II type but rather exclusively to compounds with a cyclic structure — pyrimidoindoles IIIa,b. The structure of IIIa,b was confirmed by the results of physicochemical methods of investigation. Thus the IR spectrum of IIIa contains absorption bands at 1720 (C=O) and 1620 cm^{-1} (C=N) but does not contain the absorption bands at 3220 (NH), 1770 and 1705 (phthalimide C=O group), and 1670 cm^{-1} (hydrazide C=O) that are characteristic for starting hydrazide Ia. An unresolved multiplet of aromatic protons at 6.1-7.0 ppm is observed in the PMR spectrum of IIIa [in D_7-dimethylformamide (d_7-DMF)], and the spectrum contains a singlet with an intensity of one proton unit at 3.85 ppm and a singlet of three protons of a methyl group attached to a nitrogen atom at 2.05 ppm. The set of these data, as well as the results of elementary analysis and the data from the mass spectra, which contains a molecular-ion peak with m/z 363 (which corresponds to the value calculated for this compound), made it possible to assign the IIIa structure to the compound obtained. (Formula, top, following page.)

By varying the conditions for the rearrangement of hydrazide Ia, viz., by carrying out the reaction at lower temperature (~40°C), we isolated intermediate IIa, through a step involving the formation of which, as we assumed, the reaction proceeds; in addition to IIa, which was obtained in 70% yield, we also isolated IIIa in 6% yield. The structure of IIa was confirmed by spectral data. Broad absorption bands at 2500-3400 cm^{-1}, which correspond to the absorption of the salt form of an amino group, and absorption bands at 1775, 1720,

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