MASS-SPECTROMETRIC STUDY OF THE CYCLIZATION OF DIAZO KETONES.

4.* CYCLIZATION OF N'-PHENYL-3-UREIDO- AND N'-PHENYL-3-THIOUREIDO-1-DIAZOALKAN-2-ONES. 2-ANILINO-5,6-DIHYDRO-4H-1,3-THIAZIN-5-ONES

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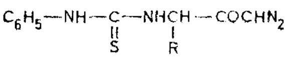
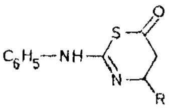
A comparison of the mass spectra of N'-phenyl-3-thioureido-1-diazo-alkan-2-ones (I) with the mass spectra of 2-anilino-5,6-dihydro-4H-1,3-thiazin-5-ones (II) and N'-phenyl-3-ureido-1-diazoalkan-2-ones (III) makes it possible to conclude that under the influence of electron impact the molecular ions of the diazo ketones, through the loss of a molecule of nitrogen, undergo only partial cyclization to the corresponding thiazinones (oxazinones in the case of III). In the case of diazo ketones III virtually all of the $[M - N_2]^+$ ions undergo fragmentation without cyclization. Under chemical-ionization conditions (with isobutane as the gas-reactant) the principal fragmentation of the protonated ions of I and III entails cleavage of the C–N bonds. Only a small part of these ions lose a molecule of nitrogen, but it is impossible to establish the structures of the resulting $[MH - N_2]^+$ ions from the mass-spectrometric data.

It has been recently shown [1-3] that some diazo ketones eliminate a molecule of nitrogen in the ionization chamber of the mass spectrometer and from heterocyclic products without undergoing the Wolff rearrangement. Continuing our research in this direction we studied the possibility of the cyclization of N'-phenyl-3-thioureido-1-diazoalkan-2-ones (I) to 2-anilino-5,6-dihydro-4H-1,3-thiazin-5-ones (II)† by comparison of their mass spectra obtained under the influence of electron impact (EI) and under chemical-ionization (CI) conditions. In addition, we studied the mass spectra of the oxygen analogs of diazo ketones I (IIIa,c,d) obtained under the same conditions:

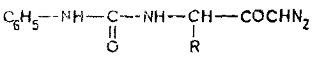


$C_6H_5{-}NH{-}\underset{S}{\underset{\|}{C}}{-}NH\underset{R}{\underset{|}{C}}H{-}COCHN_2$

I a-d



II a-d



$C_6H_5{-}NH{-}\underset{O}{\underset{\|}{C}}{-}NH{-}\underset{R}{\underset{|}{C}}H{-}COCHN_2$

III a,c,d

I–III a R=H; b R=CH_3; c R=C_2H_5; d R=CH_2Ph

The mass-spectrometric behavior of II under electron impact is similar in many respects to the behavior of the previously investigated 2-phenyl-5,6-dihydro-4H-1,3-oxazin-5-ones [5]; however, owing to the presence of an amino group and a sulfur atom, substantial differences are observed in this case. The molecular ions (M^+) of II undergo fragmentation via at least 10 pathways. The diversity of the fragmentation pathways is due to the existence of the M^+ ions in several tautomeric forms [6-8], not including the cyclic form that is produced by migration of the amino nitrogen atom to the sulfur atom with cleavage of the C–S bond [8].

The principal pathways of fragmentation of II can be represented by a general scheme (Scheme 1). The intensities of the M^+ and the peaks of the fragment ions in the

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*See [1], for communication 3.

†The possibility of this cyclization under the influence of acidic agents was demonstrated in [4].

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

Compound	M^+	$[M-H]^+$	F_1	F_2	F_3	F_4	F_5	F'_5	F_6	F'_6	F_7	F'_7	F_8	F'_8
Ia	5,1	1,8	0,9	0,3	0,6	2,1	3,6	1,5	0,2	0,2	0,6	1,2	2,7	3,0
IIa	5,4	3,0	0,3	0,3	0,3	2,4	6,9	1,5	0,3	0,8	0,6	0,3	4,2	3,0
Ib	2,7	0,3	0,3	0,3	0,6	2,4	0,3	0,3	—	0,3	0,3	0,6	1,8	5,4
IIb	4,2	0,3	0,3	0,6	0,2	3,5	4,7	0,7	0,3	1,3	0,3	0,5	3,3	5,5
Ia	1,0	0,3	0,3	0,2	—	0,9	0,2	0,3	—	—	0,3	—	1,2	9,0
IIc	5,4	0,3	—	0,2	0,3	8,0	7,0	0,9	0,3	1,5	0,4	0,9	3,2	5,4
Id	1,5	0,1	0,1	0,2	0,3	3,3	0,3	—	—	—	0,5	0,3	1,5	2,2
IId	3,3	0,3	—	—	0,3	3,7	2,0	0,3	0,2	0,3	0,4	0,5	2,0	4,2
IIIa	4,2	0,7	0,6	0,7	—	0,5	0,3	0,1	—	0,3	—	—	3,0	12,4
IIIc	1,3	—	0,5	0,3	—	0,3	0,4	0,3	—	0,5	0,3	—	1,0	14,4
IIId	1,5	0,3	0,4	—	—	0,6	0,4	—	—	0,3	0,5	1,8	5,1	16,3

TABLE 1 (continued)

Compound	F_9	F'_9	F_{10}	F'_{10}	F_{11}	F_{12}	F_{13}	F'_{13}	F_{14}	F_{15}	F_{16}	77	51
Ia	0,9	2,4	1,9	2,0	4,2	2,5	0,9	1,2	—†	—†	0,1	13,3	9,0
IIa	1,5	4,8	1,0	3,3	4,2	1,5	1,2	1,0	—	—	—	11,1	10,3
Ib	—	0,6	1,2	1,3	1,3	4,9	1,2	1,0	14,4	—†	—	11,7	7,0
IIb	1,0	4,0	0,9	2,5	7,3	4,0	0,9	0,7	—	—	—	12,0	9,0
Ic	—	0,4	0,6	0,5	0,6	6,0	0,8	0,5	8,5	13,3	0,1	14,5	9,0
IIc	0,9	4,0	0,9	2,7	6,5	5,0	1,2	1,0	—	—	—	10,0	6,4
Id	—	0,3	1,3	1,3	3,0	3,3	0,3	0,9	3,6	1,8	0,2	9,0	5,0
IId	0,3	1,3	1,0	2,5	12,0	2,0	0,4	0,6	—	—	—	11,4	7,5
IIIa	—	—	—	—	1,2	7,5	—	—	—†	—†	1,0	6,7	5,1
IIIc	—	—	0,5	0,5	0,3	7,2	—	—	17,1	7,0	2,1	3,0	4,0
IIId	—	—	1,0	2,1	2,1	7,5	—	—	16,3	9,0	3,0	8,0	9,0

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*The total ion current was computed over the m/z range from 40 to 350.

†The peaks of these ions have m/z values below 40.

total ion current are presented in Table 1.

The $[M-H]^+$ ions may be formed not only as a result of elimination of a hydrogen atom from the 4 or 6 position of the heteroring to form a conjugated system of π bonds but also as a result of elimination of a hydrogen atom from the ortho position of the benzene ring with simultaneous cyclization at the nitrogen or sulfur atom to give a five-membered heteroring [5, 7, 9]. The formation of this ion is confirmed by the presence in the mass spectra of peaks of $C_6H_5SH^+$ (F_{13}) and $C_6H_5S^+$ (F'_{13}) ions [9], the intensities of which constitute ∿1% of the total ion current. However, elimination of a hydrogen atom from the 6 position of the heteroring is most likely, since when a substituent is introduced in this position, the relative intensity of the peak of the $[M-H]^+$ ion decreases by a factor of six as compared with the unsubstituted compound.

As in the case of oxazinones [5], peaks of $[M-CO]^+$ and $[M-CHO]^+$ ions (F_1 and F_2, phenolic fragmentation) are observed in the mass spectra of thiazinones II, but their relative intensities are lower. The formation of $[M-SH]^+$ ions (F_3) confirms the possibility of the existence of M^+ in open form G [8], as also indicated by the formation of F'_9 ions, which are genetically related to the F_3 ions.

The principal pathway of the fragmentation of the M^+ ions of thiazinones II is splitting out of NHCHR and CH_2CO molecules in any sequence, as a result of which F_4, F_5, and F'_8 ions, the peaks of which have high intensities, are formed. The F_4 ions confirm the existence of the M^+ ions primarily in imino forms D-F [6, 7]. Retrodiene fragmentation (ejection of a molecule of ketene) leads to F_5 ions (open structure), which then can split out an N=CHR particle without migration of an amino hydrogen atom. These processes confirm the realization also of amino structures (A-C) for the M^+ ions. Splitting out of a molecule of a substituted ketene from the M^+ ions (to give F_6 ions) is less characteristic.

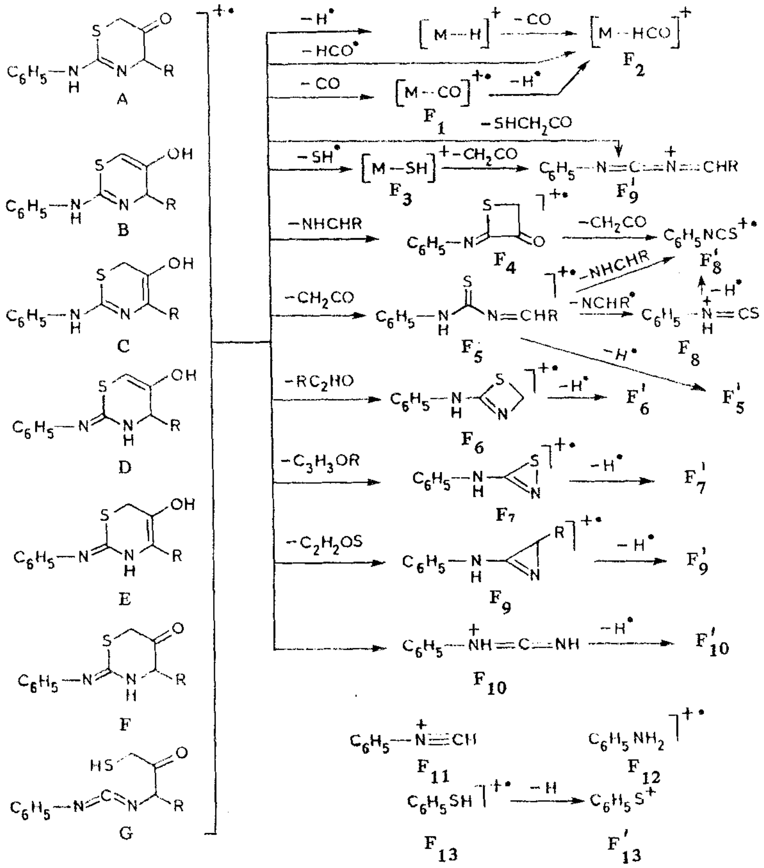
Cleavage of the heteroring at two bonds leads to the formation of low-intensity peaks of F_7 and F_9 ions [10, 11]. Cleavage of the $C_{(2)}-S$ and $N-C_{(6)}$ bonds leads to F_{10} and F'_{10}

ions; the development of F_{10} ions suggests migration of a hydrogen atom from the fragment undergoing elimination. The F_{11} ions can be produced from various fragments, as demonstrated in [7].

The relative intensity of the peak of the rearranged F_{12} ions increases with the introduction of substituent R, and one of the hydrogen atoms of the α-carbon atom of the substituent consequently participates in the rearrangement [12]. In the case of IId (R = CH_2Ph) the increase in the relative intensity of the peak of F_{12} ions is expressed more weakly as a consequence of the steric hindrance created by the benzene ring of the substituent.

The maximum peaks in the mass spectra are the peaks of the $C_6H_5^+$ ions and the genetically related $C_4H_3^+$ ions.

Scheme 1



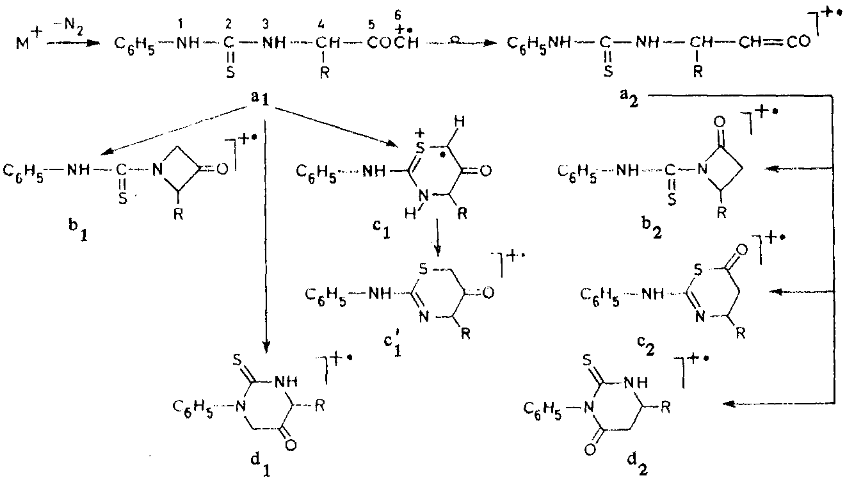
It is apparent from Scheme 1 that the $[F_n - H]^+ = F'_n$ ions correspond to many F_n ions. The fragmentation of $[M - H]^+$ ions should make a definite contribution to the formation of these ions. The elimination of a hydrogen atom from the corresponding F_n ion also cannot be excluded. However, fragmentation of the parent ion, which proceeds with or without migration of a hydrogen atom, is most likely; both possible F_n and F'_n ions are formed in this case. This migration may take place both at the instant of fragmentation and prior to it (tautomerism of the parent ion).

It should be noted that the peaks of the $[M - R]^+$ ions that are characteristic for the fragmentation of 1,3-thiazines [6] and 1,3-thiazin-6-ones [8] are completely absent in the mass spectra of IIb,c and have a very low intensity in the spectrum of IId.

As in previous studies [1-3], M^+ peaks were not recorded in the mass spectra of diazo ketones I and III, and the peaks of $[M - N_2]^+$ ions are somewhat less intense than the M^+ peak in the mass spectra of heterocycles II. In its general features the pattern of the fragmentation of the $[M - N_2]^+$ ions remains the same as for thiazines II; however, some peculiarities of their fragmentation make it possible to draw a conclusion regarding the structures of these ions.

One should have expected several possible structures of the $[M - N_2]^+$ ion considering the possibility of the Wolff rearrangement [13, 14] and the site of electrophilic attack with the formation of various heterocyclic compounds [1-3]:

Scheme 2



The structures of the $[M - N_2]^+$ ions (a_2, b_2, c_2, and d_2) are due to a Wolff rearrangement, which we did not observe during a study of other series of diazo ketones, in which there was a possibility for cyclization of the $[M - N_2]^+$ ions; however, one cannot exclude a priori the possibility of this rearrangement also in this case.

It is apparent from Table 1 that the relative intensities of the peaks of the F_5 ions in the mass spectra of diazo ketones I and III decrease significantly as compared with II, whereas the peak of the F_6 ions vanishes virtually completely. In addition, intense peaks of $\overset{+}{N}H_2{=}CHR$ (F_{14}) and $[F_{14} - NH_3]^+$ (F_{15}) ions appear. At the same time the relative intensity of the peak of F_4 ions remains virtually unchanged for diazo ketones I and decreases markedly for diazo ketones III. Since the formation of this ion can be conceived of as occurring only from a cyclic structure, part of the $[M - N_2]^+$ ions apparently undergo cyclization to one of the six-membered heterocycles. The formation of the F_4 ion is impossible in the case of azetidinone rings b_1 or b_2, which makes it possible to reject this sort of structure for the $[M - N_2]^+$ ion. The complete absence in the mass spectra of a peak of $[M - N_2, -SCO]^+$ ions refutes cyclization of rearranged ion a_2 to thiazine ring c_2. The intense F_{12} ion peak observed in the mass spectra of all of the investigated diazo ketones constitutes evidence against the realization of structures d_1 and d_2. Thus the thiazine (oxazione for III) structure of the c_1' ring proves to be most probable. The changes in the relative intensities of the peaks of the common fragment ions of I and II are due to the fact that structure c_1' also may not be realized in final form, and the $[M - N_2]^+$ ions with the c_1 structure already begin to undergo fragmentation, i.e., prior to migration of a hydrogen atom. It is apparent that the formation of F_4 ions from the c_1 structure is not restricted by anything, while the elimination of a molecule of ketene cannot be realized, and this leads to a decrease in the intensities of the peaks of F_5 ions. A certain (although small) part of the c_1 ions have time prior to fragmentation to undergo rearrangement to c_1' ions, since the peak of F_5 ions does not vanish completely. In the mass spectra of diazo ketones III the peak of the F_4 ion also has very low intensity, i.e., the number of a_1 ions that undergo cyclization is still smaller in this case. The increase in the intensity of the peaks of the F_9 ions and the appearance in the mass spectra of the diazo ketones of peaks of the F_{14} and F_{15} ions constitute evidence that the bulk of the $[M - N_2]^+$ ions undergo fragmentation without cyclization. We have previously noted [2, 3] that some of the M^+ ions of the diazo ketones immediately eliminated a $CHCON_2$ particle. This ion could also have been formed from an $[M - N_2]^+$ ion with a linear structure. In the mass spectra of

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

Compound	MH^+	$[MH-N_2]^+$	F_1	F'_2	F_2	F_3	F_4	F_5	F_6	F_7	F_8	F_9	F_{10}	F_{11}
Ia	0,8	26,0	0,6	1,8	0,4	0,2	8,8	22,0	6,4	—†	1,2	0,4	0,4	—
IIa	67,4	—	0,6	—	—	0,8	—	—	—	—	—	—	—	—
Ib	—	30,0	0,8	5,2	1,2	1,4	11,0	16,0	11,0	1,2	5,8	0,8	2,0	—
IIb	67,4	—	0,8	0,2	0,2	0,4	—	—	—	—	—	—	—	—
Ic	0,2	27,8	0,2	7,0	1,6	1,6	16,4	18,8	6,4	3,0	9,0	0,8	1,8	—
IIc	71,2	—	1,8	—	—	—	—	—	—	—	—	—	—	—
Id	0,2	12,8	0,4	5,4	0,4	1,6	10,0	2,8	2,4	1,6	2,8	0,4	2,0	—
IId	70,0	—	0,4	0,4	0,3	0,3	1,5	—	—	—	—	—	—	—
IIIa	0,5	30,0	0,6	0,4	1,0	0,5	7,0	1,4	2,0	—	—	—	0,4	0,8
IIIc	—	32,8	2,8	0,5	0,8	0,5	1,2	1,2	5,2	0,4	0,4	5,6	5,6	2,0
IIId	—	35,5	0,2	3,3	5,6	3,3	6,5	0,8	2,0	1,0	1,2	15,6	0,6	11,8

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*The total ion current was computed over the m/z range from 60 to 440.

†The m/z values were below 60.

diazo ketones III the peak of the $[M - N_2, -CHCO]^+$ (F_{16}) ion is quite intense, which confirms the conclusion that the $[M - N_2]^+$ ions exist primarily in the linear form. The intensity of the peak of F_{16} ions in the mass spectra of diazo ketones I is very low; however, this is not associated with the fact that this process does not take place but rather with the fact that in this case the F_{16} ion is very unstable and undergoes fragmentation virtually at the instant of formation. It is not possible to state whether or not the Wolff rearrangement occurs in this case. The $[M - N_2]^+$ ions exist primarily in one of the linear structures a_1 or a_2, but one cannot determine which of them is preferable from the mass-spectrometric data.

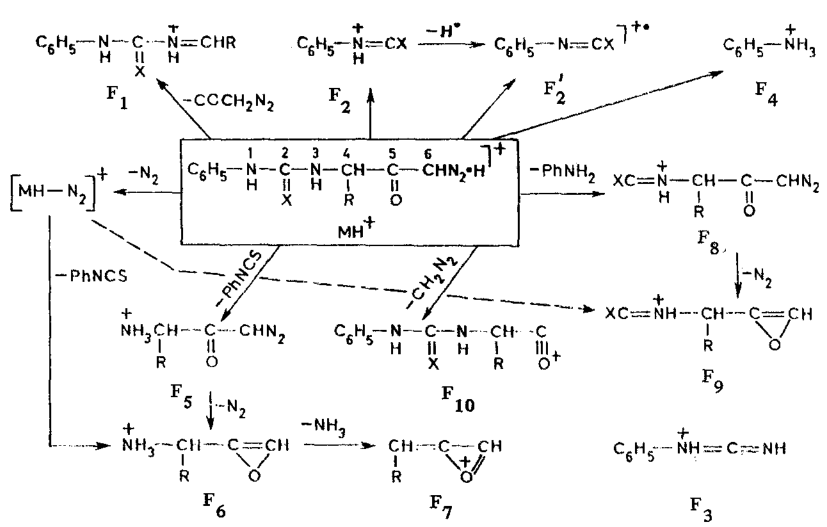
The fragmentation of the F_{16} ion proceeds with cleavage of one of the C—N bonds with simultaneous migration of a hydrogen atom from the nitrogen atom of the particle being eliminated to the nitrogen atom of the fragment ion [16]. Intense peaks of F_{12} and F_{14} ions develop in this fragmentation. The high intensities of the peaks of these ions once again confirm that the bulk of the $[M - N_2]^+$ ions undergo fragmentation from a linear structure. It should be noted that in the case of migration of a hydrogen atom from the $N_{(1)}$ atom to the $N_{(3)}$ atom and cleavage of the $N_{(1)}—C_{(2)}$ bond charge may also be retained on the other fragment, which leads to an increase in the intensity of the peak of F'_8 ions, particularly in the case of diazo ketones III. The F_{13} ion, by eliminating a molecule of ammonia, is converted to the F_{15} ion.

Thus a comparison of the electron impact (EI) mass spectra of I-III makes it possible to conclude that only a small part of the $[M - N_2]^+$ ions of diazo ketones I undergo cyclization to thiazinones II without undergoing the Wolff arrangement, while the bulk of them undergo fragmentation without cyclization; in this case it is not possible to state whether or not the Wolff rearrangement occurred. Diazo ketones III form virtually no cyclic $[M - N_2]^+$ ions, and the entire pattern of the dissociative ionization of these compounds entails the linear form of this ion.

The chemical ionization (CI) mass spectra of the investigated compounds differ considerably from the electron impact (EI) mass spectra. A substantially smaller number of peaks of fragments ions are observed in the CI mass spectra of II; peaks of ions formed in the profound stages of fragmentation are virtually absent in them, whereas signals of ions formed as a result of fragmentation processes that are not characteristic for the fragmentation of these compounds under electron impact are observed in the mass spectra of diazo ketones I and III in addition to common fragment ions. The differences in the CI mass spectra of I and II are so substantial that one may immediately assert that if cyclization of the $[MH - N_2]^+$ ions does occur, it takes place to a very small extent.

The principal and virtually only peak in the mass spectra of thiazinones II is the peak of the protonated molecular ion (MH^+), and the intensities of the peaks of the other ions do not exceed 3% of the total ion current (see Table 2). The principal fragmentation pathways under chemical ionization conditions of diazo compounds I and III are presented in Scheme 3.

Scheme 3



In contrast to the previously studied diazo ketones [2, 3], peaks of fragments that contain a diazo group (F_5 and F_8) are observed in the fragmentation of I and III; consequently, in the diazo ketones under consideration the bond between the carbon atom and the diazo group is stronger. The elimination of a molecule of diazomethane by the MH^+ ions also constitutes evidence for this.

The site of cleavage of the bonds in the $\overset{+}{MH}$ ions is determined by the site of protonation of the molecule. Thus a molecule of diazomethane is eliminated (F_{10} ions are formed) in the case of protonation at the $C_{(6)}$ atom bonded to the diazo group (which, as a consequence, has excess electron density); in the case of protonation at the $N_{(1)}$ atom the $N_{(1)}$—C bond is cleaved, and F_8 ions are formed, whereas a molecule of aniline is split out in the form of a neutral fragment. The F_4 ion is formed in the case of cleavage of this bond with simultaneous migration of a hydrogen atom from the $N_{(3)}$ atom to the $N_{(1)}$ atom. Protonation at the $N_{(3)}$ atom leads to cleavage of the $C_{(2)}$—$N_{(3)}$ bond to give the F_2 ion, and F_2 and F_5 ions are formed if a hydrogen atom migrates from the $N_{(1)}$ atom to the $N_{(3)}$ atom [17]. Cleavage of the $N_{(3)}$—$C_{(4)}$ bond, as a result of which F_{11} ions are formed after migration of a hydrogen atom from the fragment being eliminated to the $N_{(3)}$ atom, is also observed in the case of diazo ketones III. The peak of the F_{11} ion is more intense when substituent R is present, and one may consequently conclude that migration of a hydrogen atom from the substituent is preferable.

It is apparent from the scheme presented above that all of the fragment ions can be formed directly from the MH^+ ions, and the mass-spectrometric data therefore do not make it possible to draw more or less rigorous conclusions regarding the structure of the $[MH - N_2]^+$ ions. Nevertheless, starting from the fact that the principal ion current in the mass spectra of diazo ketones I and III is due to fragmentation of the MH^+ rather than the $[MH - N_2]^+$ ions, as previously observed in [2, 3], it may be assumed that the $[MH - N_2]^+$ ions have stable structures, possibly precisely thiazinone structure II (or an oxazinone structure for III), which, as demonstrated above, undergo virtually no fragmentation under chemical ionization conditions. It is impossible from the CI mass spectra to draw a conclusion as to whether or not the Wolff rearrangement occurs [13, 14], although it should be pointed out that previous studies [2, 3] cast doubt on the possibility of this rearrangement for diazo ketones with similar structures.

The CI mass spectra of all of the analyzed compounds contain peaks of cluster ions: $[M - N_2, + C_3H_3]^+$, $[M - N_2, + C_3H_5]^+$, $[M - N_2, + C_3H_7]^+$, and $[M - N_2, + C_4H_9]^+$ for diazo ketones I and II; $[M + C_3H_3]^+$, $[M + C_3H_5]^+$, $[M + C_3H_7]^+$, and $[M + C_4H_9]^+$ for thiazinones II.

TABLE 3. Mass Spectra of I-III

Compound	m/z values (relative intensities of the ion peaks in percent relative to the maximum peak)*
	Electron impact
Ia	206 (35,1); 164 (29,3); 104 (34,9); 78 (61,0); 77 (100); 55 (44,1); 51 (68,5); 50 (30,9); 43 (45,7); 41 (33,8)
Ib	220 (14,6); 177 (15,6); 135 (34,4); 93 (30,7); 77 (78,4); 51 (46,3); 44 (100); 43 (25,1); 42 (22,5); 41 (40,5)
Ic	135 (60,7); 100 (20,4); 93 (41,5); 77 (100); 66 (20,3); 58 (61,1); 51 (65,2); 50 (26,6); 42 (21,1); 41 (97,8)
Id	205 (22,9); 177 (40,1); 135 (23,1); 120 (37,4); 104 (33,1); 93 (36,2); 91 (66,5); 77 (100); 65 (63,0); 51 (57,4)
IIa	206 (45,6); 164 (63,7); 136 (38,4); 131 (42,1); 118 (29,1); 104 (63,2); 77 (100); 51 (92,3); 49 (56,4); 45 (32,9)
IIb	220 (31,2); 178 (38,6); 145 (32,5); 136 (30,5); 135 (42,9); 104 (59,9); 93 (30,0); 77 (100); 51 (76,2); 42 (54,7)
IIc	234 (46,4); 192 (61,7); 177 (70,3); 136 (36,8); 135 (77,5); 104 (62,6); 93 (50,2); 77 (100); 51 (62,2); 41 (81,9)
IId	296 (15,0); 205 (32,3); 135 (22,8); 119 (24,8); 104 (100); 103 (18,8); 91 (40,4); 77 (65,6); 65 (23,4); 51 (44,0)
IIIa	119 (29,6); 93 (18,3); 91 (17,0); 77 (16,3); 65 (11,1); 64 (14,0); 51 (12,8); 44 (24,2); 43 (100); 42 (17,0)
IIIc	119 (86,4); 93 (40,6); 91 (54,3); 71 (29,8); 64 (46,9); 58 (100); 56 (36,9); 51 (22,7); 42 (25,9); 41 (42,7)
IIId	120 (100); 119 (32,4); 103 (60,2); 93 (46,3); 91 (85,9); 77 (49,8); 70 (53,0); 65 (39,0); 51 (57,0); 42 (30,4)
	Chemical ionization
Ia	221 (6,0); 209 (8,3); 208 (13,1); 207 (100); 142 (5,6); 136 (7,5); 101 (5,5); 100 (98,6); 94 (38,1); 72 (26,9)
Ib	223 (8,5); 222 (16,2); 221 (100); 220 (7,2); 207 (9,0); 156 (22,5); 136 (18,1); 114 (62,9); 94 (43,3); 86 (42,2)
Ic	237 (7,9); 236 (17,0); 235 (100); 170 (40,0); 136 (27,1); 128 (80,6); 100 (26,9); 94 (70,7); 93 (8,2); 83 (13,3)
Id	298 (24,4); 297 (100); 283 (22,4); 235 (92,8); 232 (25,2); 221 (42,0); 190 (21,6); 162 (21,2); 136 (50,4); 94 (96,0)
IIa	209 (6,3); 208 (13,5); 207 (100); 206 (4,7); 119 (2,6); 71 (11,5); 70 (3,1); 69 (6,8); 67 (3,6); 61 (10,4)
IIb	277 (1,7); 263 (2,3); 259 (2,0); 223 (5,8); 222 (17,1); 221 (100); 220 (3,4); 219 (2,0); 179 (1,5); 178 (1,8)
IIc	291 (2,2); 277 (1,8); 273 (2,8); 237 (7,4); 236 (17,8); 235 (100); 234 (5,1); 193 (2,5); 192 (1,4); 61 (2,7)
IId	353 (1,9); 339 (3,0); 335 (2,5); 300 (1,4); 299 (8,5); 298 (25,0); 297 (100); 296 (5,0); 238 (1,4); 64 (2,9)
IIIa	192 (14,6); 191 (100); 190 (5,4); 137 (2,9); 120 (3,1); 119 (2,5); 100 (4,8); 94 (25,3); 93 (3,0); 72 (7,6)
IIIc	220 (17,1); 219 (100); 218 (4,1); 205 (20,0); 191 (8,6); 177 (8,7); 137 (5,8); 126 (18,4); 100 (17,1); 94 (4,5)
IIId	282 (24,2); 281 (100); 280 (7,0); 189 (7,6); 188 (47,0); 162 (6,0); 137 (39,3); 120 (23,4); 119 (18,3); 94 (22,4)

*The 10 maximum peaks in the spectra are presented in this table.

Thus an analysis of the CI mass spectra of I-III showed that under the conditions of chemical ionization by isobutane the MH^+ ions of diazo ketones I and III undergo fragmentation via several pathways, depending on the site of protonation. The fragmentation processes are accompanied by rearrangements of the hydrogen atom and ion-molecular reactions. Although MH^+ peaks are not observed in the mass spectra of the diazo ketones (or have very low intensities), precisely these ions determine the fragmentation of the investigated compounds. The $[MH - N_2]^+$ ions possibly have the cyclic structure of thiazinones; however, one cannot draw an unambiguous conclusion regarding this only from the mass-spectrometric data.

The electron-impact and chemical-ionization mass spectra of all of the investigated compounds are presented in Table 3.

EXPERIMENTAL

The mass spectra were obtained with a Varian MAT-44S spectrometer at 80-220°C. The electron-impact spectra were recorded at an ionizing-electron energy of 75 eV and a cathode emission current of 0.5 μA. The chemical-ionization spectra (with isobutane as the gas-reactant at a pressure of 30 Pa in the ionization chamber) were recorded at an energy of 160 eV and an emission current of 0.1 μA.

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