The IR spectra of KBr pellets of the compounds were obtained with a UR-10 spectrometer. The UV spectra of solutions of the compounds in CH_3OH were obtained with an SF-8 spectrophotometer. The PMR spectra of solutions of the compounds in CF_3COOH [with hexamethyldisiloxane (HMDS) as the internal standard] and d_6-DMSO (with HMDS as the external standard) were recorded with a Tesla BS-467 spectrometer (60 MHz).

5H-1,7-Dimethyl-2-phenylthiazolo[3,4-b][1,2,4]triazole-5-thione (IVa). A mixture of 0.32 g (2 mmole) of 5-methyl-3-aminothiazolidine-2-thion-4-one and 0.30 g (2 mmole) of N-methylbenzimidoyl chloride was fused at 80°C in the course of an hour. The crystallized melt was triturated with CH_3CN, and the reaction product was removed by filtration and crystallized (Table 1).

5H-1,2,7-Triphenylthiazolo[3,4-b][1,2,4]triazole-5-thione (IVd). A mixture of 0.22 g (1 mmole) of 5-phenyl-3-aminothiazolidine-2-thion-4-one and 0.21 g (1 mmole) of N-phenylbenzimidoyl chloride was fused at 120°C in the course of an hour, after which the melt was triturated with acetone, and the reaction product was removed by filtration and crystallized.

Compounds IVb-f were similarly obtained from the corresponding aminorhodanines and benzimidoyl chlorides.

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MASS-SPECTROMETRIC STUDY OF THE CYCLIZATION

OF DIAZO KETONES.

## 1. CYCLIZATION OF 1-DIAZO-3-SULFONYLAMINOPROPAN-2-ONES

TO N-SULFONYLAZETIDIN-3-ONES

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

It was recently shown [1] that 1-diazo-3-sulfonylaminopropan-2-ones (I) are converted to N-sulfonylaze-tidin-3-ones (II) by the action of concentrated sulfuric acid. In order to investigate the possibility of the occurrence of similar processes in the gas phase we studied the mass spectra of two series of compounds (Ia-k and IIIa-j) under the conditions of electron impact and chemical ionization.

Ia-k   IIa-j
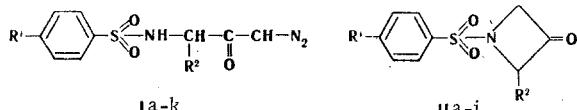
I, II a $R^1=R^2=H$; b $R^1=CH_3$, $R^2=H$; c $R^1=OCH_3$, $R^2=H$; d $R^1=Cl$, $R^2=H$; e $R^1=NO_2$, $R^2=H$; f $R^1=NHCOCH_3$, $R^2=H$; g $R^1=R^2=CH_3$; h $R^1=CH_3$, $R^2=C_2H_5$; i $R^1=CH_3$, $R^2=CH_2Ph$; j $R^1=NHCOCH_3$, $R^2=CH_3$; I k $R^1=NHCOCH_3$, $R^2=C_2H_5$

The literature contains a great deal of data that characterize the mass-spectral fragmentation of azetidin-2-ones under conditions of electron impact.
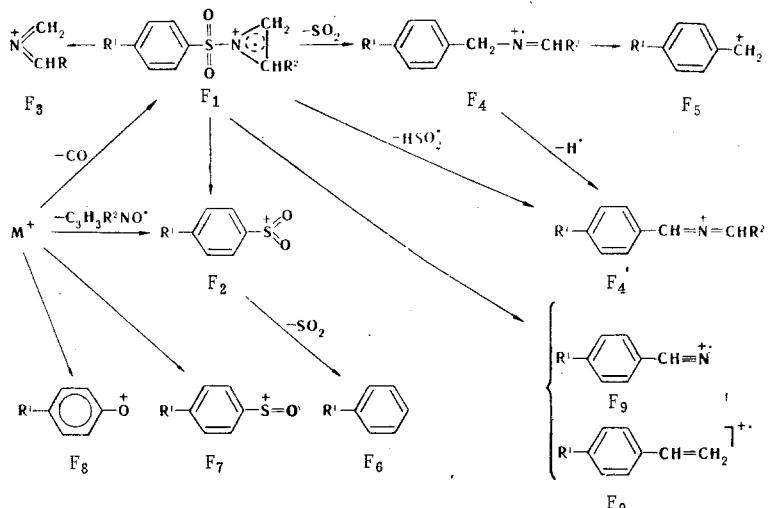
It has been shown [2, 3] that the principal fragmentation pathway is destruction of the heteroring with ejection of a molecule of ketene; the charge may be retained on either of the resulting fragments. The ejection of a molecule of ketene also might have been expected in the case of azetidin-3-ones; however, it was noted in [4] that N-substituted azetidin-3-ones undergo fragmentation by the successive elimination of a molecule of CO and the remaining heteroring fragment. Similar processes are observed in the mass-spectrometric fragmentation of a series of II.

The principal pathways in the mass-spectral fragmentation of azetidin-3-ones under electron impact can be represented by the general scheme presented above.

The fragments indicated below are recorded in addition to the indicated ions in the spectra of Ia-k.
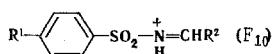
We were able to record molecular ions peaks (M^+) in the electron-impact mass spectra of the cyclic compounds only for IIc, f, j, which contain strong electron-donor substituents in the benzene ring. The fractions of the M^+ current in the total ion current were 0.16, 0.25, and 0.03%, respectively (see Table 1). Molecular ion peaks were not recorded in the mass spectra of the diazo ketones. In the case of Ib-d, f, j we observed $[M-N_2]^+$ ion peaks, the m/z values of which coincided with the m/z values of the M^+ peaks of the azetidinones.

In the first stage of the fragmentation the investigated azetidinones eliminate a molecule of CO with cleavage of the four-membered ring to give F_1 ions. The relative intensity of the peak of F_1 ions increases regularly as the electron-donor properties of substituent R^1 increase, whereas the introduction of substituent R^2 leads to an appreciable decrease in the intensity of the peak of this ion. A similar process involving the loss of a molecule of CO by the $[M-N_2]^+$ ion under the influence of electron impact is also observed in the mass spectra of all of the diazo ketones; however, the intensity of the F_1 fragments in their spectra is somewhat lower than in the case of the azetidinones. A molecule of CO can be eliminated only from the cyclic structure, and the $[M-N_2]^+$ ions of the diazo ketones consequently at least partially form an azetidin-3-one ring. This means that the Wolff rearrangement [5, 6] does not occur during splitting out of a molecule of nitrogen from the M^+ ion of the diazo ketones; this would lead to the subsequent formation of azetidin-2-ones, which, as indicated above, eliminate a molecule of ketone rather than a molecule of CO. The rearrangement evidently does not take place because of the large size of the fragment that must migrate. In addition, in this case the carbonyl group is not bonded directly to the benzene ring as it is in the compounds investigated in the indicated papers.

TABLE 1. Intensities of the Peaks of the Characteristic Fragment Ions in the Electron-Impact 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_4†	F_5	F_6	F_7	F_8	F_9	F_{10}
IIa	—	0,3	0,2	46,7	0,1	0,6	3,3	0,1	0,1	0,1	—
Ia	0,1	—	2,2	20,4	—	—	9,9	0,3	1,1	0,1	0,8
IIb	—	0,3	0,2	49,8	0,1	0,5	2,4	0,1	0,1	0,1	—
Ib	0,1	0,1	1,7	38,5	0,1	0,2	4,9	0,7	0,7	0,1	1,4
IIc	0,2	0,4	0,6	47,0	0,2	0,5	1,2	0,2	0,4	—	—
Ic	0,1	0,1	0,6	25,4	0,2	0,3	1,2	0,2	0,4	—	0,1
IId	—	0,4	0,3	54,7	—	0,2	2,5	0,1	0,1	0,1	—
Id	—	0,1	5,4	43,4	0,1	0,1	16,6	0,9	0,9	0,1	2,4
IIe	—	0,2	0,3	33,7	0,1	0,1	1,1	0,1	0,1	—	—
Ie	—	0,1	1,6	32,5	0,1	0,1	2,8	0,2	1,3	—	0,6
IIf	0,3	0,5	0,9	58,7	0,9	1,0	1,5	0,1	0,2	—	—
If‡											
IIg	—	0,1	0,2	35,7	—	0,2	1,7	0,1	0,1	0,1	—
Ig	—	—	2,6	5,6	—	0,1	6,0	0,2	0,1	—	2,2
IIh	—	0,1	0,4	27,2	—	0,2	2,1	0,1	0,1	0,1	—
Ih	—	—	1,9	2,8	—	0,1	5,2	0,2	0,†	—	1,6
IIi	—	0,1	1,3	10,5	—	2,8	5,6	0,1	0,1	0,1	—
Ii	—	0,1	1,6	10,0	0,1	2,7	5,7	0,4	0,2	0,2	—
IIj	0,1	0,1	0,2	35,6	—	0,1	0,3	0,1	0,1	0,1	—
Ij	0,1	0,1	0,6	38,3	—	0,1	0,9	0,1	0,1	0,1	0,1
Ik	—	0,1	0,9	10,9	—	0,1	0,6	0,1	0,1	0,1	0,1

*The calculation of the total ion current was made with a computer from m/z 60 to m/z 349; 50% of the total ion current was the fraction of the current of the background ions.

†Ion F_4 consists of the sum of the two ions indicated in the scheme of the fragmentation of F_4 and F'_4. The first term prevails when there are electron-donor substituents in the benzene ring, while the second term prevails in the case of acceptor substituents.

‡ The principal fragmentation pathways of If are associated with fragmentation of the substituent.

The F_1 ions undergo subsequent fragmentation with cleavage of the C — S and S — N bonds. Cleavage of the S — N bond results in the formation of F_2 and F_3 ions, i.e., the charge can be retained on either of the resulting fragments; however, from the fact that the intensities of the peaks of the F_3 ions exceed the intensity of the peaks of the F_2 ions by more than an order of magnitude, it may be concluded that the charge in the M^+ and F_1 ions is localized primarily on the nitrogen atom. The elementary composition of the F_3 ion in the case of Ib and IIb was confirmed by high-resolution mass spectrometry (the experimental m/z value for the F_3 ion for IIb is 42.0339, which is in agreement with the calculated value). It should be noted that the presence of an electron-donor substituent in the benzene ring leads to a certain increase in the intensity of the peak of the F_3 ion, whereas the introduction of an R^2 substituent in the heteroring leads to a decrease in the intensity of this peak. Chloro derivative IId [7], in the mass spectrum of which the peak of the F_3 ion is very intense, constitutes an exception in this case. The intensity of the peak of F_3 ions is somewhat lower in the mass spectra of the diazo ketones in the case of Ia-f, i, j and considerably lower in the case of Ig, h. Consequently, the introduction of an R^2 substituent in the diazo ketone molecule has a substantial effect on its fragmentation under the conditions of electron impact, possibly preventing the cyclization of $[M-N_2]^+$ ions.

In addition, the F_1 ions may lose a molecule of SO_2. As a result of a rearrangement that takes place simultaneously with elimination, F_4 ions are formed. A similar rearrangement was observed in [8, 9]; however, in the case of splitting out of a molecule of SO_2 a new Ar — N bond was formed during fragmentation of the investigated sulfamines. In our research we observed peaks of F_5 ions, which are rather intense in some cases, in all of the mass spectra of both the azetidines and the diazo ketones. The elementary compositions of these ions in the mass spectra of Ib and IIb were established by high-resolution mass spectrometry. Consequently, an Ar — C rather than an Ar — N bond is formed when a molecule of SO_2 is split out. Simultaneous ejection of a molecule of SO_2 evidently occurs at the moment of attack by the radical center of the F_1 ion on the benzene ring:
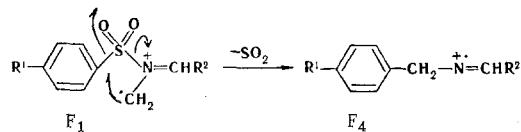
It should be noted that a low intensity peak of the alternative ion

$$R^1-\langle\!\!\langle\ \rangle\!\!\rangle-\overset{+}{C}HR^2 \quad (F_5)$$
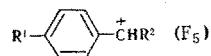
is observed in the mass spectra of Ig and IIg in addition to the peak of an F_5 ion. From the point of view of thermodynamics the radical center of the F_1 ion should be located at the secondary carbon atom, and the peak of the F'_5 ions should consequently be more intense than the peak of the F_5 ion for all of the compounds with an R^2 substituent. Since this is not observed, one may conclude that steric hindrance created by substituent R^2 during radical attack exists. As a result of this, whereas one still observes a low-intensity peak of an F'_5 ion when the volume of the substituent is relatively small ($R^2 = CH_3$), when its volume is increased, this process is suppressed completely.

The F_4 ion may split out a hydrogen atom to give an F'_4 ion. The ratio of the intensities of the peaks of these ions ($I_{F'_4}/I_{F_4}$) depends substantially on the electronic properties of substituent R^1 and increases as the electron-acceptor character of this substituent increases. The F'_4 ion is possibly also formed directly from F_1 ions by elimination of an HSO_2· radical.

Low-intensity F_9 ion peaks are observed in the electron-impact mass spectra of Ia-f and IIa-f. High-resolution mass spectrometry made it possible to establish that the peak with m/z 118* observed in the mass spectra of Ib and IIb is due to two ions with the compositions C_9H_{10} and C_8H_8N in a ratio of 1:3 (see the scheme presented above). They are probably genetically associated with the F_1 ion, which confirms its cyclic structure.

Cleavage of the C−S bond in the M^+, F_1, and F_2 ions leads to the formation of F_6 ions, the relative intensity of the peaks of which in the mass spectra of the diazo ketones is greater than in the spectra of the corresponding azetidinones. This may constitute evidence that the Ar−S bond in the diazo ketones is weaker than in the azetidinones, i.e., some of the F_6 ions in the case of the diazo ketones are formed without prior cyclization of the $[M-N_2]^+$ ions.

Processes associated with rearrangement of the sulfo group are traced in the electron-impact mass spectra of all of the investigated compounds [8]. As a result of these processes, $R^1-Ar-SO^+$ (F_7) and R^1-Ar-O^+ (F_8) ions are formed. The peaks of these ions are much more intense in the mass spectra of the diazo ketones, and the linear structure of the diazo ketones consequently favors rearrangement of the sulfo group; thus some of the diazo ketone molecules undergo fragmentation without cyclization.

The spectra of azetidinones IIa,e,f,h,i contain low-intensity peaks of $R^1-Ar-SO_2-\overset{+}{N}H=CH_2$ (F'_{10}) ions, which are formed as a result of splitting out of a molecule of ketene from M^+. The introduction of alkyl radical R^2 in the heteroring does not change the m/z value of the peak of this ion, i.e., an R^2CHCO molecule is split out in this case. Alternative splitting out of a molecule of unsubstituted ketene is not observed for any of the investigated compounds. However, this ion is recorded in the mass spectra of the diazo ketones only in the fragmentation of Ih,i, whereas the peak of the $R^1-Ar-SO_2-\overset{+}{N}H=CH-R^2$ (F_{10}) ion is very intense and consequently is characteristic exclusively for the fragmentation of linear diazo ketone molecules. The peak of the F'_{10} ion in the mass spectra of the diazo ketones constitutes evidence that some of the molecules undergo cyclization after the elimination of a molecule of nitrogen, since the formation of this fragment from a linear structure is impossible.

We recorded the mass spectra of all of the investigated compounds at a low ionizing electron energy (23 eV); the fragmentation pathways of both series of compounds remained the same, but the relative intensities of the F_2 and F_6 ion peaks increased by a factor of approximately two.

An analysis of the electron-impact mass spectra showed that the fragmentation of the azetidinones and the corresponding diazo ketones is described by a common scheme. This identical character makes it possible to conclude that the 1-diazo-3-sulfonylaminopropan-2-ones undergo cyclization to N-sulfonylazetidin-3-ones in the ionization chamber of the mass spectrometer under the influence of electron impact, i.e., either the M^+ ions of the azetidinones and the $[M-N_2]^+$ ions of the diazo ketones have a common cyclic structure or they have the same excited transition state. The presence in the mass spectra of all of the diazo ketones of intense F_{10} ion peaks constitutes evidence that some of the diazo ketone molecules undergo fragmentation without cyclization. This is also indicated by the difference in the relative intensities of the common ions of I and II.

The conditions of chemical ionization (with isobutane as the gas-reactant) differ significantly from the conditions of electron impact, and there are therefore significant differences in the mass spectra of the investi-

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*Here and subsequently in the text the numbers that characterize the ions are the mass-to-charge ratios (m/z).

gated compounds. During chemical ionization these differences are expressed primarily in the greater relative intensity of the peaks of the protonated molecular ions (MH^+) of the azetidinones (up to 38.7% of the total ion current in the case of chloro derivative IId) and the peaks of the $[MH - N_2]^+$ ion of the diazo ketones (up to 42.8% of the total ion current in the case of methoxy derivative Ic). In addition, MH^+ peaks are recorded in the mass spectra of Ia, c-h in the case of chemical ionization.

The peaks of the ions previously examined under the conditions of electron impact, viz., F_2, F_3, F_6, and F_7, remain the most intense peaks of the characteristic ions in the spectra in the case of chemical ionization; however, new intense signals also appear. For example, the peak of ions with m/z 70 (F_{11}) for the unsubstituted azetidinone ring, which is shifted by the corresponding number of atomic mass units when substituent R^2 is introduced, has a rather high intensity. This peak is due to the ion formed in the cleavage of the $S - N$ bond in the MH^+ ions of the azetidinones or in the $[MH - N_2]^+$ ion of the diazo ketones. In all likelihood, the F_{11} ion in the case of the azetidinones has cyclic structure
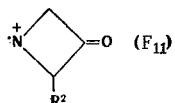

The relative intensity of the peak of this ion in the case of the diazo ketones is greater by a factor of three to seven, and this constitutes evidence for its existence in another form (oxiran $\overset{+}{N}H - CH_2 - C = CH$, for example)

or that the $S - N$ bond in the diazo ketone molecule is weaker than in the azetidinone molecules, in agreement with the conclusions drawn from an analysis of the electron-impact mass spectra.

It should be noted that the F_1, F_2, F_6, and F_7 ions are accompanied by fragments that are 2 amu (the mass of the hydrogen molecule) heavier and that their intensities are often higher than the intensities of the F_n ions. In addition, the mass spectra of all of the diazo ketones and some of the azetidinones contain a rather intense peak of an $R^1 - Ar - SO_2 - \overset{+}{N}H_3$ (F_{12}) ion, which is probably also formed as a result of the addition of a hydrogen molecule to the nitrogen atom, as well as peaks of $[F_{11} + H_2]$ (F'_{11}) and $[F_{13} + H_2]$ (F'_{13}) ions.
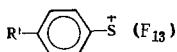
This fact indicates that the MH^+ ions of the azetidinones and the $[MH - N_2]^+$ ions of the diazo ketones, as well as the fragment ions during their lifetime, can undergo a secondary reaction with the gas-reactant, since under the conditions of chemical ionization the pressure in the ionization chamber is $\sim 10^5 - 10^6$ times greater than under the conditions of electron impact; the increase in the pressure is due exclusively to the gas-reactant. In all likelihood, one of the following reactions takes place:

$$MH^+ + C_4H_{10} \rightarrow [MH - A + H]^+ + C_4H_9^{\cdot} + A^{\cdot},$$

$$MH^+ + C_4H_{10} \rightarrow [MH - B + H]^{+\cdot} + C_4H_9^{\cdot} + B,$$
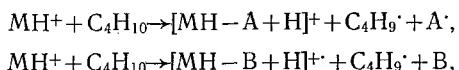
where A and B are the eliminated fragments. Since the lifetimes of the ions are very brief, the reaction is subject to kinetic rather than thermodynamic control, i.e, the labile hydrogen atom of the isobutane molecule attacks the MH^+ ion at either of the centers that are capable of accepting it. From the observed fragmentation of the compounds, the most favorable sites for attack can be assumed to be
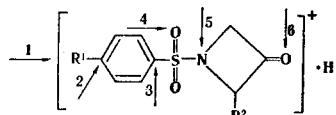
Simultaneously with this attack certain bonds undergo cleavage to give F'_n ions. Thus F'_1, F'_2, F'_6, F'_7, F'_{11}, and F_{12} are formed. The F'_{13} ion is probably formed by an ion-molecular reaction with the participation of these fragments in which there is greater accessibility to the electrons of the sulfur atom. In the case of chloro derivative IId the mass spectrum contains an intense (0.35% of the total ion current) peak of an $[MH - Cl + H]^+$ ion. It is probably formed by attack on the benzene ring at the side of addition of a chlorine atom, i.e., via pathway 2; the $Ar - Cl$ bond is cleaved, and an Ar-H bond is formed [10-14].

It is apparent from Table 2 that the relative intensities of the peaks of the F_1 and F'_1 ions are small for all of the compounds. The formation of these ions is the first step in the fragmentation, and the fact that a protonated F_1 ion is not formed constitutes evidence in favor of MH^+, which is protonated at the carbonyl group, although other variants are not excluded. The low intensities of the peaks of these ions can be explained by

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

Com-pound	MH^+	MH^+, $MH-N_2$	F_1	F'_1	F_2	F'_2	F_3†	F_6	F'_6	F_7	F'_7	F_{10}	F_{11}	F'_{11}	F_{12}	F_{13}	F'_{13}
Ia	1,4	27,5	—	—	—	0,3		—	—	—	—	0,1	0,1	0,2	1,8	—	—
IIa	—	37,2	0,1	—	0,2	0,3		—	0,1	0,1	—	—	0,2	0,3	—	—	—
Ib	—	30,0	0,1	—	0,4	0,5		0,1	—	0,2	0,3	0,1	3,4	0,7	0,4	—	0,2
IIb	—	32,6	0,1	0,1	0,2	0,2		0,1	—	0,2	—	—	0,2	0,1	—	—	0,2
Ic	0,1	42,8	0,2	0,1	1,0	0,3		—	0,1	0,3	0,3	0,2	1,9	0,9	0,7	0,1	0,1
IIc	—	32,1	0,2	—	1,1	0,3		—	—	0,1	—	—	0,2	0,5	—	0,1	—
Id	7,6	20,1	0,2	—	0,1	0,4		0,1	—	0,3	0,3	0,9	2,9	1,0	0,6	0,2	—
IId	—	38,7	—	—	0,1	0,2		—	—	—	—	—	0,2	0,4	—	—	—
Ie	1,3	1,0	0,6	0,7	—	—		0,2	0,3	—	0,2	2,1	1,5	1,5	0,1	0,3	—
IIe‡																	
If	—	1,0	0,2	0,1	0,3	0,1		0,2	1,4	0,6	0,2	0,3	0,6	1,4	1,0	0,2	0,8
IIf	—	27,3	—	0,7	0,6	—		—	0,1	—	—	—	0,3	0,1	0,5	0,1	—
Ig	1,7	33,5	—	—	0,5	0,6		—	—	0,3	0,2	1,5	1,3	0,1	0,8	—	—
IIg	—	34,9	—	—	0,2	0,2		0,1	—	0,2	0,1	—	0,3	0,2	0,2	—	—
Ih	0,9	28,9	—	—	0,3	0,2	2,7	0,2	—	0,3	0,2	1,1	1,7	0,1	0,6	—	—
IIh	—	29,3	0,1	—	0,1	0,2	1,8	0,1	0,1	0,1	0,1	—	0,3	0,3	0,1	0,1	—
Ii	—	20,8	—	—	0,1	0,1	1,4	0,3	—	0,2	0,5	0,1	1,8	0,3	2,7	—	—
IIi	—	26,5	—	—	0,1	0,3	1,6	0,1	—	—	—	—	0,4	0,5	0,2	—	0,1
Ij	—	16,5	—	0,2	0,2	0,1		—	0,2	0,1	0,2	0,2	0,2	0,4	2,5	—	—
IIj	—	29,5	0,2	—	0,3	0,1		—	0,3	0,2	0,2	—	0,3	0,3	0,2	—	—
Ik	—	12,1	—	1,0	0,1	—	1,5	—	0,1	—	—	0,5	0,5	0,2	4,9	—	—

*The total ion current was calculated with a computer from m/z 60 to m/z 399; ~50% of the total ion current was the fraction of the current of the background ions.

†The F_3 ion is present in all spectra but is found in the region of unrecordable masses.

‡ We were unable to obtain the mass spectra even when the substance was heated above 240°C.

TABLE 3. Mass Spectra of Ia–k and IIa–j

Com-pound	m/z values (relative intensities of the ion peaks in percent of the maximum peak)*
1	2
	Electron impact
Ia	170 (4,2), 141 (11,0), 93 (5,5), 78 (5,4), 77 (49,8), 51 (25,5), 50 (9,5), 44 (4,2), 43 (27,6), 42 (100)
Ib	184 (3,8), 155 (4,6), 139 (1,8), 107 (1,8), 92 (2,3), 91 (12,8), 55 (6,3), 43 (18,4), 42 (100), 41 (5,5)
Ic	107 (3,0), 92 (3,2), 77 (5,0), 64 (3,7), 63 (2,8), 51 (1,5), 50 (1,9), 43 (3,5), 42 (100), 41 (5,4)
Id	175 (8,8), 113 (9,1), 111 (28,7), 75 (25,2), 69 (8,1), 51 (9,8), 50 (18,2), 43 (9,3), 42 (100), 41 (17,8)
Ie	202 (6,8), 186 (5,6), 139 (4,3), 122 (9,9), 92 (4,2), 75 (8,1), 64 (5,0), 43 (8,1), 42 (100)
If	214 (34,2), 173 (10,7), 172 (98,9), 156 (53,7), 124 (27,2), 108 (29,9), 92 (32,4), 65 (19,0), 60 (31,5), 42 (100)
Ig	198 (36,4), 155 (42,7), 92 (9,1), 91 (100), 69 (76,0), 65 (30,0), 63 (5,9), 57 (5,7), 56 (94,0), 55 (8,8)
Ih	212 (33,7), 155 (40,5), 92 (11,7), 91 (100), 70 (59,0), 69 (9,6), 65 (36,1), 63 (7,4), 55 (6,4), 43 (18,5)
Ii	155 (15,5), 133 (12,5), 132 (100), 117 (6,4), 105 (26,2), 104 (6,4), 92 (7,9), 91 (56,2), 77 (8,4), 65 (18,8)
Ij	198 (1,6), 172 (2,1), 134 (1,8), 108 (2,4), 92 (3,2), 65 (5,5), 60 (2,3), 57 (4,9), 56 (100), 55 (5,2)
Ik	198 (8,3), 172 (12,8), 156 (8,8), 125 (8,0), 108 (9,4), 93 (12,0), 92 (11,0), 70 (100), 69 (8,5), 65 (16,5)
IIa	183 (0,6), 91 (1,3), 78 (0,9), 77 (7,0), 65 (0,5), 52 (0,6), 51 (8,4), 44 (3,2), 43 (12,1), 42 (100)
IIb	197 (0,7), 155 (0,4), 105 (1,4), 92 (0,5), 91 (4,8), 89 (0,3), 65 (3,2), 44 (18,5), 43 (35,5), 42 (100)
IIc	213 (0,9), 171 (1,2), 121 (1,0), 107 (2,8), 92 (2,8), 77 (4,9), 64 (3,7), 63 (2,4), 43 (14,2), 42 (100)
IId	217 (0,5), 113 (1,1), 111 (3,4), 85 (0,6), 76 (0,9), 75 (5,5), 74 (1,2), 51 (1,5), 43 (8,4), 42 (100)
IIe	122 (0,7), 76 (3,3), 75 (2,6), 74 (1,3), 64 (1,0), 63 (1,0), 51 (1,1), 50 (5,9), 43 (27,4), 42 (100)
IIf	134 (2,5), 108 (2,3), 106 (2,8), 93 (2,7), 92 (3,2), 65 (5,4), 64 (2,0), 63 (1,9), 43 (15,8), 42 (100)
IIg	155 (0,5), 105 (0,5), 91 (5,0), 89 (0,8), 65 (4,9), 64 (0,7), 63 (1,4), 56 (100), 44 (4,2), 43 (4,2)
IIh	155 (1,1), 105 (0,7), 92 (0,8), 91 (7,5), 89 (0,9), 71 (15,8), 70 (100), 43 (5,4), 42 (30,4), 41 (23,0)
IIi	155 (13,0), 133 (13,4), 132 (100), 105 (29,5), 104 (7,4), 91 (53,5), 77 (10,6), 65 (22,6), 51 (7,6), 41 (18,7)

(continued)

TABLE 3 (continued)

1	2
IIj	134 (0,9), 93 (1,3), 92 (1,7), 65 (4,8), 64 (1,3), 63 (1,0), 67 (7,2), 56 (100), 43 (9,6), 42 (2,4)

<p align="center">Chemical ionization</p>

1	2
Ia	240 (5,2), 214 (6,2), 213 (15,5), 212 (100), 211 (2,9), 170 (0,4), 158 (6,5), 143 (1,0), 72 (0,8), 70 (0,7)
Ib	228 (7,1), 227 (15,2), 226 (100), 225 (3,0), 172 (1,4), 157 (2,1), 155 (1,4), 72 (1,8), 71 (3,0), 70 (14,1)
Ic	244 (6,7), 243 (16,5), 242 (100), 241 (4,6), 188 (1,9), 171 (2,8), 72 (1,2), 71 (2,6), 70 (5,2), 69 (1,3)
Id	274 (9,4), 272 (28,2), 249 (5,3), 248 (35,5), 247 (16,2), 246 (100), 245 (5,3), 204 (0,8), 202 (2,4), 70 (14,8)
Ie	285 (12,6), 215 (22,2), 136 (22,9), 91 (18,2), 73 (16,0), 72 (12,5), 71 (17,7), 70 (16,5), 61 (100), 60 (25,2)
If	270 (71,4), 215 (39,0), 136 (54,6), 110 (57,8), 109 (100), 102 (85,8), 97 (39,0), 74 (39,3), 73 (58,7), 72 (43,6)
Ig	268 (5,5), 242 (6,7), 241 (13,1), 240 (100), 239 (3,2), 198 (5,5), 172 (2,8), 157 (2,3), 155 (1,9), 84 (5,8)
Ih	282 (3,8), 256 (8,9), 255 (18,0), 254 (100), 253 (2,9), 212 (4,8), 184 (4,0), 172 (2,6), 98 (6,5), 70 (11,2)
Ii	318 (9,4), 317 (29,4), 316 (100), 254 (13,4), 240 (3,8), 172 (16,7), 160 (10,7), 157 (4,2), 132 (7,9), 71 (3,6)
Ij	285 (7,4), 284 (17,0), 283 (100), 216 (2,0), 215 (16,5), 168 (4,8), 167 (1,9), 86 (2,4), 69 (2,8), 61 (2,4)
Ik	299 (7,7), 298 (17,5), 297 (100), 271 (8,1), 215 (45,1), 168 (77,8), 98 (5,3), 71 (10,2), 70 (15,9), 69 (5,7)
IIa	214 (6,4), 213 (15,5), 212 (100), 211 (2,9), 183 (0,2), 141 (0,4), 140 (0,9), 125 (0,2), 70 (0,5), 69 (1,0)
IIb	228 (6,2), 227 (15,8), 226 (100), 225 (2,9), 197 (0,3), 157 (0,8), 155 (0,8), 139 (0,5), 125 (0,5), 70 (0,6)
IIc	244 (7,3), 243 (13,4), 242 (100), 241 (2,7), 213 (0,6), 173 (1,1), 172 (0,7), 171 (4,1), 72 (0,9), 70 (0,6)
IId	288 (0,5), 250 (1,9), 249 (5,3), 248 (35,6), 247 (16,3), 246 (100), 245 (3,2), 212 (1,3), 72 (0,9), 70 (0,5)
IIf	271 (6,2), 270 (15,0), 269 (100), 268 (1,0), 215 (1,9), 198 (2,4), 177 (0,3), 71 (1,7), 70 (1,2), 69 (1,5)
IIg	242 (5,9), 241 (16,2), 240 (100), 239 (2,9), 172 (0,6), 157 (0,6), 155 (0,6), 139 (0,6), 86 (0,6), 84 (1,0)
IIh	256 (6,7), 255 (16,9), 254 (100), 253 (3,1), 184 (1,4), 157 (0,8), 98 (1,3), 71 (3,1), 70 (7,4), 69 (1,3)
IIi	318 (8,2), 317 (25,0), 316 (100), 315 (2,6), 184 (1,4), 172 (1,2), 162 (2,6), 160 (2,0), 157 (1,7), 132 (7,1)
IIj	285 (7,5), 284 (17,2), 283 (100), 282 (2,8), 254 (0,9), 198 (1,0), 168 (1,0), 136 (1,0), 86 (0,9), 84 (0,9)

*The 10 most intense ion peaks in the mass spectra are presented.

the fact that the S–N bond is cleaved more readily under the conditions of chemical ionization than the bond in the azetidinone ring. This is also indicated by the presence in the spectra of intense peaks of F'_{11} and F_{11} ions. The peaks of F_3 ions, which are the maximum peaks in the electron–impact mass spectra, also have relatively low intensities. The relative intensities of the peaks of these ions are presented in Table 2 for Ia-g, j and IIa-g, j, since their mass is 60 amu lower, whereas we commenced scanning of the mass spectra from this value in connection with the superimposed fragmentation of isobutane in the low-mass region. However, we were able to indirectly establish that their relative intensities do not exceed 5% in the total ion current, i.e., lower by a factor of ~10 than in the case of electron impact.

In contrast to the corresponding electron–impact mass spectra, a rearrangement process with splitting out of a molecule of SO_2 is not observed in the case of chemical ionization. In addition, a peak of the F_8 ion is also absent in all of the mass spectra.

In comparing the chemical-ionization mass spectra of the diazo ketones and the corresponding azetidinones it may be stated that on the whole the compounds of both series undergo identical fragmentation, although there is a certain difference in the relative intensities of the common ions. This is probably associated with partial cyclization of the diazo ketones to azetidinones after the elimination of a molecule of nitrogen. The $[MH-70]^+$ (F_{10}) ion peak, which is present in the mass spectra of all of the investigated compounds of the I series and is formed by splitting out of an $HCOCHN_2$ particle from the MH^+ ions of the diazo ketones, indicates that not all of the molecules undergo cyclization. The F_{10} ion is formed precisely from a linear ion, since when an alkyl R^2 substituent is present in the molecule, the peak of this ion is shifted by the corresponding number of atomic mass units. In addition, in the mass spectra of the azetidinones themselves the $[MH-CH_2COH]^+$ ion peak is completely absent, and only an $[MH-R^2CHCOH]^+$ fragment ($R^2=C_2H_5$ and CH_2Ph) is observed. A peak of this ion is also recorded in the mass spectra of Ih, i with the indicated substituents. The splitting out of unsubstituted ketene from Ig-k evidently takes place from a linear ion, whereas the splitting out of alkyl-substituted ketones takes place from a cyclic ion. The introduction of an R^2 substituent does not have such a significant effect on the

change in intensity of the peaks of the characteristic ions as that observed in the electron-impact mass spectra. In addition, the intensities of the peaks of the F_{11} and F'_{11} ions increase somewhat, which indicates their greater stabilities. In the case of chemical ionization that R^2 substituent evidently does not hinder cyclization of the diazo ketones to azetidinones but possibly even favors it; this is in agreement with the data in [1]. This different effect of the R^2 substituent in the case of electron impact and chemical ionization can be explained if one takes into account that the conditions of chemical ionization are extremely similar to the conditions of direct protonation of diazo ketones with concentrated sulfuric acid, which was carried out by Sipyagin and Kartsev [1].

Thus 1-diazo-3-sulfonylaminopropan-2-ones undergo cyclization to the corresponding N-sulfonylazetidin-3-ones with prior splitting out of a molecule of nitrogen under the influence of electron impact and under conditions of chemical ionization in the ionization chamber of the mass spectrometer. However, some diazo ketone molecules undergo fragmentation without cyclization. The introduction of an allyl R^2 substituent retards cyclization under the conditions of electron impact, whereas under the conditions of chemical ionization it does not hinder it.

EXPERIMENTAL

The mass spectra were obtained with a Varian MAT-44S spectrometer. The electron-impact mass spectra were recorded at 100-220°C and ionizing-electron energies of 75 eV (cathode emission current 0.4-0.6 mA) and 23 V (emission current 0.1 mA). The chemical-ionization mass spectra were recorded at a pressure of 33.3 Pa in the ionization chamber, an ionizing-electron energy of 160 eV (emission current 0.7 mA), and temperatures of 100-240°C. The high-resolution mass spectra were obtained with a Varian MAT-311A spectrometer. A system for direct introduction of the substances into the ion source was used in all cases.

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