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MASS-SPECTROMETRIC STUDY OF THE CYCLIZATION OF DIAZO KETONES.

6.* CYCLIZATION OF 1-DIAZO-3-AROYLAMINOPROPAN-2-ONES AND 2-PHENYL-5,6-DIHYDRO-4H-1,3-OXAZIN-5-ONES

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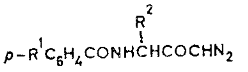
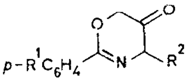
An analysis of the electron-impact mass spectra of 1-diazo-3-aroylaminopropan-2-ones made it possible to conclude that some $[M - N_2]^+$ ions have the 1,3-oxazin-5-one structure, some exist in the form of a cyclic intermediate that is produced in the first step of the cyclization process, and some decompose without rearrangements, i.e., they exist in a linear form. The Wolff rearrangement does not occur. Alkyl substituents in the 4 position of the resulting heterocycle hinder cyclization. Under chemical-ionization conditions the $[MH - N_2]^+$ ions exist in similar forms. The analysis of the mass spectra in this case is complicated by ion-molecular reactions.

Continuing our investigation of the cyclization of diazo ketones in the gas phase we studied the electron-impact (EI) and chemical-ionization (CI) mass spectra of a series of 1-diazo-3-aroylaminopropan-2-ones (I) and 2-aryl-5,6-dihydro-4H-1,3-oxazin-5-ones (II). Compounds II were obtained from the corresponding diazo ketones I by the action of concentrated sulfuric acid, and their structure was established by a number of spectral methods [2].



$p\text{-}R^1C_6H_4CONH\underset{}{\overset{R^2}{\overset{|}{C}}}HCOCHN_2$

I a-i



II a-i

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 $R^1=Br$, $R^2=H$; f $R^1=NO_2$, $R^2=H$; g $R^1=H$, $R^2=CH_3$; h $R^1=H$, $R^2=C_2H_5$; i $R^1=H$, $R^2=Bz$

The mass-spectrometric fragmentation of oxazinones II under the influence of electron impact was discussed in detail in [3].

In the present research we again subjected heterocycles II to mass-spectrometric analysis under conditions identical to those under which diazo ketones I were analyzed. In addition, all of the mass spectra were calculated by hand, which made it possible to introduce certain corrections in the fragmentation scheme and in the table of intensities of the peaks of the characteristic fragment ions that are presented in [3].

Molecular-ion peaks (M^+) were not recorded in the electron-impact spectra of diazo ketones I, and the $[M - N_2]^+$ ions, which may have different structures, considering the possibility of cyclization at the heteroatoms and the Wolff rearrangement [4-6], had the maximum m/z values:

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*See [1] for communication 5.

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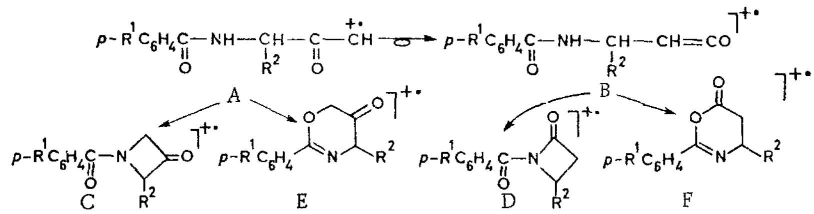
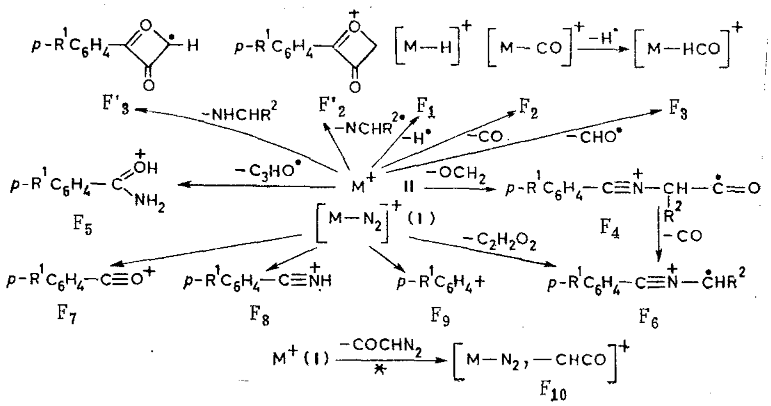


The principal pathways of the mass-spectrometric fragmentation of the M^+ (III) and $[M - N_2]^+$ (I) ions under electron impact can be represented by the general scheme*



In addition to the indicated ion peaks, peaks of $[M - N_2, - CHCO]^+$ (F_{10}) ions, which are formed from $[M - N_2]^+$ ions with linear structure A, are recorded in the mass spectra of diazo ketones I. The complexity of the spectra of diazo ketones I and heterocycles II makes it possible to conclude that certain amounts of diazo ketones I undergo cyclization to oxazines II.

The formation of the $[M - H]^+$ ion in the fragmentation of II was discussed in detail in [3]. The intensity of the peak of this ion is somewhat lower in the mass spectra of diazo ketones I, and this makes it possible to conclude that not all of the $[M - N_2]^+$ ions have the M^+ structure of heterocycles II.

The $[M - 28]^+$ and $[M - 29]^+$ ions ($[M - N_2, - 28]^+$ and $[M - N_2, 29]^+$ ions, respectively, for the diazo ketones) are composite ions: $[M - CO]^+$ (F_2) and $[M - NCHR^2]^+$ (F'_2) and $[M - CHO]^+$ (F_3) and $[M - NHCHR^2]^+$ (F'_3) ions. The relative contributions of these isobaric ions for Ia-f and IIa-f to the total ion current cannot be established even by means of high-resolution mass spectrometry, since the intensities of their peaks are very low. The introduction of substituent R^2 leads to separation of the ions and makes it possible to establish that the F'_2 and F'_3 ions, i.e., those that do not contain a nitrogen atom, are the predominant species. It should be emphasized that the formation of F'_2 and F'_3 ions from azetidinone structures C and D is impossible. In addition, intense peaks of $[M - CO]^+$ ions should be observed in the fragmentation of azetidin-3-ones (structure C) [7], whereas intense peaks of $[M - CH_2CO]^+$ ions should be observed in the fragmentation of azetidin-2-ones (structure D) [8], but this is not observed in the spectra of diazo ketones I. It follows from the information set forth above that the $[M - N_2]^+$ ions of diazo ketones I do not exist in the C or D forms. The complete absence in the spectra of diazo ketones I of $[M - N_2, - CO_2]^+$ and $[M - N_2, - CH_2CO]^+$ ion peaks constitutes convincing evidence that the F structure of the $[M - N_2]^+$ ions also is not realized [9]. One cannot draw a direct conclusion that confirms or refutes the existence of the $[M - N_2]^+$ ions in keto form B from the electron impact mass spectra; however, the complete absence of cyclic derivatives of this structure (D and F) makes it possible to assert [10] that the ketene form of the $[M - N_2]^+$ ions also does not exist, and, consequently, the Wolff rearrangement [4-6] also does not occur in this case.

In the successive elimination of CH_2O and CO molecules from the M^+ ions of heterocycles II (correspondingly, from the $[M - N_2]^+$ ions of diazo ketones I) F_4 and F_6 ions are formed. The latter may also be formed in one step in the case of splitting out of a $C_2H_2O_2$ particle.

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*The compositions of the F_5 and F_8 ions were confirmed by high-resolution mass spectrometry.

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[a]

Compound	M^+ $[M-N_2]$	F_1	F_2	F'_2	F_3	F'_3	F_4	F_5	F_6	F_7	F_8	F_9	F_{10}[b]
Ia	4,5	0,5	1,3[c]		0,8[в]		0,3	0,1	0,9	34,7	8,0	22,4	2,1
IIa	5,8	2,2	1,9		1,7		4,2	0,7	20,6	24,0	1,0	14,8	—
Ib	3,8	0,3	0,8		0,5		—	—	0,5	24,9	5,9	12,4	0,8
IIb	3,0	1,2	0,9		0,6		1,2	0,3	16,9	19,0	0,6	13,6	—
Ic	2,6	0,3	2,0		0,6		—	—	0,7	24,0	6,3	4,3	0,6
IIc	4,0	1,2	0,7		1,0		1,2	0,3	18,4	21,0	1,1	12,8	—
Id	3,3	1,6	2,7		1,3		—	—	0,9	14,4	5,4	7,2	0,7
IId	3,3	1,6	1,1		1,3		2,7	2,5	14,1	23,3	0,4	13,3	—
Ie	5,0	1,5	1,5		1,5		0,5	—	0,5	30,0	10,0	11,5	2,0
IIe	3,1	1,8	1,1		1,1		2,7	1,3	14,2	19,7	2,2	8,4	—
If	3,4	0,7	1,7		1,1		0,4	0,1	1,0	15,2	4,5	0,5	1,4
IIf	1,3	0,6	0,8		0,6		2,5	4,7	8,1	8,8	1,8	1,8	—
Ig	1,9	—	0,2	0,4	—	1,1	—	—	0,2	43,6	6,0	19,2	7,5
IIg	0,9	0,7	0,5	1,1	0,5	2,2	—	0,1	5,7	21,1	11,9	12,4	—
Ih	0,7	0,1	0,3	1,0	0,4	1,0	—	0,1	0,1	31,3	3,2	11,2	4,1
IIh	0,3	0,7	0,1	0,2	0,2	2,6	—	—	0,9	25,9	13,0	13,7	—
Ii	0,6	0,1	—	0,2	—	1,1	—	—	—	31,1	2,2	12,0	2,4
IIi	0,5	0,2	—	0,1	—	3,2	—	—	—	19,4	10,6	10,6	—

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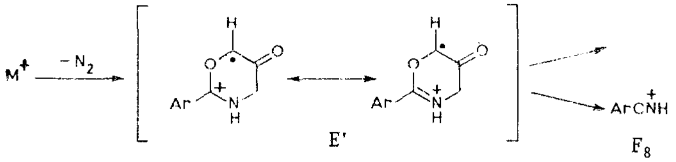
[a] The total ion current was calculated over the range from the ion with m/z 50 to the ion with m/z 300. [b] The genetic relationship between the F_{10} ions and the M^+ and $[M - N_2]^+$ ions was confirmed by the peaks of the corresponding metastable ions (obtained with an MKh-1303 spectrometer). [c] Isobaric ions.

One's attention is directed to the fact that the intensities of the F_6 ion peaks in the spectra of heterocyclic compounds II are significantly higher (by a factor of 10-20) than in the spectra of the corresponding diazo ketones I. Its formation from the $[M - N_2]^+$ ion with linear form A is impossible, and, consequently, some of the $[M - N_2]^+$ ions have the 1,3-oxazin-5-one structure (E). However, proceeding from the intensities of the F_6 ion peaks (see Table 1) and taking into account the fact that the relative intensities of the M^+ (II) and $[M - N_2]^+$ (I) ion peaks are approximately equal, one may conclude that the fraction of the $[M - N_2]^+$ ions in the 1,3-oxazin-5-one form does not exceed 10% of the overall amount of these ions. The virtually total absence of F_4 and F_5 ion peaks in the spectra of diazo ketones I, the low intensity of the F_1 ion peaks, and the increase in the contribution to the total ion current of F_7 ions, which are formed by simple cleavage of the amide bond in the case of diazo ketones, also constitute evidence for the small number of cyclic $[M - N_2]^+$ ions (E). It follows from the information set forth above that the $[M - N_2]^+$ ions exist only in the A and E forms; the percent of the latter is low. Nevertheless, one cannot ascribe all of the remaining $[M - N_2]^+$ ions to the fraction with linear form A, since in this case the intensities of the F_{10} ion peaks would be considerably higher, and the intensities of the F_2 and F_3 ion peaks would be significantly lower.

For the answer to this problem, one's attention should be directed to the high intensity of the peak of F_8 ions in the mass spectra of diazo ketones Ia-f as compared with the corresponding oxazines IIa-f. The formation of these ions in the case of diazo ketones can be represented by the scheme

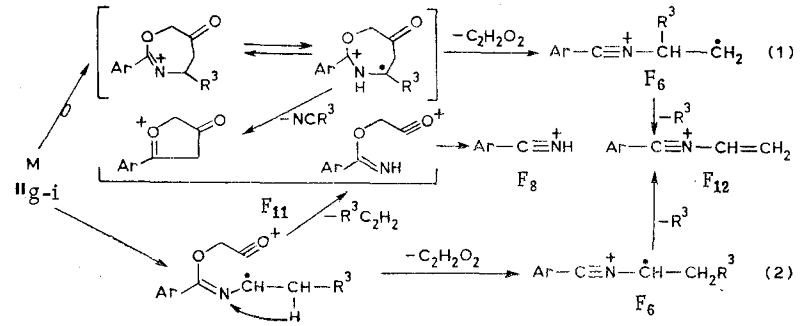


Intermediate E', which is formed in the cyclization process, is unstable and may undergo fragmentation to give the F_8 ion prior to rearrangement to 1,3-oxazin-5-one E, which also leads to a sharp increase in the intensities of the peaks of F_8 ions in the spectra of the diazo ketones. The F_2 and F_3 ions may be formed directly from intermediate E', whereas the F_6 ions can be formed only from oxazinone E. The data in Table 1 graphically demonstrate that the difference in the relative intensities of the peaks of the F_2 and F_3 ions in the spectra of I and II is small, whereas the difference is extremely substantial in the case of

F_6 ions; this also constitutes evidence for the formation of intermediate E' in the fragmentation process. The information presented above makes it possible to assume that the bulk of the $[M - N_2]^+$ ions exist precisely in the form of intermediate E'.

Under the conditions of the mass-spectrometric experiments the formation of intermediate E' is possible both in the case of electrophilic attack and in the case of radical attack at the oxygen atom. Localization of the charge primarily on the aryl fragment of the molecule (the formation of F_{5-9} ions) constitutes evidence that precisely electrophilic attack takes place in this case (just as in solutions), i.e., the mechanisms of cyclization of the diazo ketones in solutions and in the gas phase under electron impact are identical.

It is apparent from Table 1 that when an alkyl substituent (R^2) is present in the molecule, the relative intensity of the peak of F_8 ions in the spectra of heterocycles IIg-i increases significantly, whereas this is not observed in the spectra of the corresponding diazo ketones I. This is explained by the development of a new fragmentation pathway that is associated with rearrangement of the M^+ ions of the oxazinones. One might have proposed two mechanisms of the formation of the F_8 ion, where R^3 = H, CH_3, and C_6H_5 for IIg, h, i, respectively:



To select the correct mechanism from the two alternative mechanisms the elementary composition of the F_{11} ions was determined by means of high-resolution mass spectrometry, which showed that the F_{11} ion contains a nitrogen atom (calculated value 162.0555, found 162.0531), i.e., fragmentation proceeds via the second mechanism. The R^2 substituent also determines the formation of F_{12} ions.

The relative intensities of the F_{11} and F_{12} ion peaks in the total ion current are presented below:

	Ig	IIg	Ih	IIh	Ii	IIi
F_{11}	0.1	3.2	0.1	4.3	0.2	3.2
F_{12}	0.2	3.8	0.6	6.3	0.5	0.9

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[a]

Compound	MH^+ $[MH-N_2]^+$	F'_3	F_5	F'_5[b]	F_6	F_7	F_8	F_{10}
Ia	81,1	0,2	0,5	—	0,9	2,4	0,3	4,0
IIa	72,0	0,4	1,4	6,8	1,2	1,6	0,2	0,4
Ib	84,8	0,2	—	—	1,6	2,3	—	0,2
IIb	70,3	0,2	1,4	13,7	1,4	1,9	0,2	0,2
Ic	85,8	0,1	0,1	—	0,4	2,0	0,2	0,3
IIc	86,0	0,1	0,1	0,3	0,3	1,0	0,1	0,1
Id	84,1	0,4	0,6	—	1,4	0,9	0,3	0,4
IId	49,2	0,3	5,4	21,2	1,3	2,5	1,3	1,3
Ie	80,5	0,4	0,2	0,1	1,0	1,4	0,3	0,2
IIe	79,6	0,3	1,0	2,8	1,0	1,5	—	0,1
If	85,0	0,2	0,8	0,1	0,3	1,3	0,1	0,7
IIf	This substance did not give a mass spectrum							

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[a] The total ion current was calculated over the range from the ion with m/z 60 to the ion with m/z 350. [b] The F'_5 ion is the protonated F_5 ion ($[F_5 + H]^+$).

TABLE 3. Mass Spectra of I and II

Compound	m/z values (intensities of the ion peaks in % of the maximum ion peak)[a]
	Electron impact
Ia	175 (26,3), 105 (100), 104 (26,2), 78 (15,5), 77 (97,0), 76 (9,2), 69 (24,8), 57 (14,9), 55 (19,1), 51 (46,2)
Ib	189 (13,1), 120 (12,1), 119 (100), 118 (21,1), 91 (50,8), 78 (10,2), 72 (11,6), 70 (7,7), 65 (23,6), 56 (14,8)
Ic	136 (10,2), 135 (100), 134 (25,3), 107 (18,3), 92 (18,3), 78 (14,3), 77 (35,9), 76 (9,4), 64 (12,1), 63 (10,0)
Id	141 (36,1), 139 (100), 138 (30,1), 111 (49,9), 75 (40,2), 72 (51,4), 70 (38,9), 57 (69,4), 56 (78,1), 55 (31,2)
Ie	255 (15,1), 253 (15,5), 185 (100), 184 (44,4), 183 (99,9), 182 (30,8), 157 (37,4), 155 (40,7), 76 (51,6), 75 (60,6)
If	220 (20,4), 150 (100), 149 (31,0), 120 (25,0), 104 (57,5), 103 (18,0), 92 (26,8), 76 (46,9), 75 (26,5), 69 (17,8)
Ig	189 (4,7), 148 (18,4), 146 (2,8), 106 (8,2), 105 (100), 104 (13,7), 78 (5,0), 77 (45,1), 76 (8,3), 51 (15,7)
Ih	175 (3,4), 162 (12,5), 105 (100), 104 (10,0), 77 (35,4), 72 (7,8), 57 (15,0), 56 (10,8), 55 (8,5), 51 (9,6)
Ii	224 (7,5), 106 (8,9), 105 (100), 104 (7,7), 91 (10,6), 86 (13,2), 78 (19,0), 77 (40,6), 57 (6,1), 51 (10,0)
IIa	175 (25,8), 174 (10,0), 147 (9,1), 145 (19,0), 117 (87,5), 105 (100), 90 (20,5), 89 (12,5), 77 (70,0), 51 (32,5)
IIb	189 (13,1), 132 (11,7), 131 (85,5), 119 (100), 91 (69,5), 89 (15,5), 77 (14,9), 65 (47,0), 63 (20,7), 51 (17,8)
IIc	205 (19,6), 148 (9,3), 147 (87,8), 136 (9,8), 135 (100), 134 (18,2), 107 (60,0), 92 (9,1), 77 (18,6), 64 (9,4)
IId	153 (21,8), 152 (19,5), 151 (60,0), 141 (33,9), 140 (27,3), 139 (100), 113 (20,0), 111 (58,4), 89 (21,0), 75 (38,8)
IIe	197 (74,4), 195 (71,5), 185 (100), 183 (99,3), 157 (44,4), 155 (44,0), 116 (34,7), 89 (45,3), 76 (48,8), 75 (40,6)
IIf	190 (28,3), 167 (53,3), 162 (90,0), 151 (21,0), 150 (100), 149 (22,2), 121 (21,6), 120 (15,0), 116 (41,0), 104 (20,0)
IIg	162 (13,5), 131 (26,0), 130 (18,8), 105 (100), 104 (59,2), 103 (37,9), 77 (56,3), 76 (14,5), 51 (37,1), 50 (19,1)
IIh	162 (17,2), 146 (10,0), 130 (23,4), 105 (100), 104 (52,2), 103 (17,2), 77 (54,2), 57 (11,2), 51 (22,6), 50 (10,8)
IIi	174 (19,1), 162 (16,2), 146 (19,1), 118 (14,8), 105 (100), 104 (55,6), 103 (21,9), 91 (49,9), 77 (57,1), 51 (33,8)
	Chemical ionization
Ia	216 (0,9), 214 (1,8), 178 (2,6), 177 (13,1), 176 (100), 175 (4,3), 134 (5,0), 122 (0,9), 117 (1,2), 105 (3,5)
Ib	232 (1,7), 230 (1,4), 228 (2,6), 192 (1,8), 191 (15,4), 190 (100), 189 (4,3), 176 (1,5), 131 (2,0), 119 (3,0)
Ic	248 (1,4), 246 (1,1), 244 (2,3), 208 (2,1), 207 (15,3), 206 (100), 205 (5,7), 164 (0,3), 147 (0,4), 135 (1,8)
Id	252 (1,6), 250 (1,8), 248 (3,4), 246 (3,4), 213 (3,9), 212 (32,0), 211 (12,5), 210 (100), 209 (5,0), 151 (1,4)
Ie	294 (2,9), 292 (4,5), 258 (3,6), 257 (12,3), 256 (100), 255 (17,5), 254 (95,7), 253 (5,7), 176 (3,3), 71 (2,8)
If	223 (2,1), 222 (14,5), 221 (100), 220 (3,8), 191 (1,7), 179 (0,9), 167 (1,0), 150 (1,6), 71 (1,1), 61 (1,7)
IIa	214 (1,8), 178 (1,8), 177 (12,9), 176 (100), 175 (4,3), 123 (10,2), 122 (1,9), 117 (1,6), 105 (2,3), 71 (2,1)
IIb	228 (2,4), 192 (2,1), 191 (15,5), 190 (100), 189 (4,4), 138 (1,9), 137 (21,2), 136 (2,2), 119 (2,7), 71 (1,7)
IIc	248 (1,2), 244 (2,1), 208 (2,3), 207 (15,0), 206 (100), 205 (6,3), 135 (1,6), 71 (1,8), 69 (1,1), 61 (1,1)
IId	212 (32,6), 211 (12,9), 210 (100), 209 (5,5), 159 (15,0), 158 (7,9), 157 (41,9), 156 (12,4), 89 (27,4), 75 (13,6)
IIe	294 (2,4), 257 (11,8), 256 (100), 255 (19,4), 254 (94,2), 253 (7,1), 203 (3,5), 201 (3,6), 176 (2,4), 71 (1,7)
IIf	This substance did not give a mass spectrum.

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[a] The 10 most intense peaks in the spectrum are presented.

The existence of a difference in the relative intensities of the F_{11} and F_{12} ion peaks in the spectra of diazo ketones I and the corresponding heterocycles II serves as yet another piece of evidence that only a small number (even smaller than in the case of unsubstituted diazo ketones Ia-f) on the $[M - N_2]^+$ ions have oxazine structure II. Evidence for this is also provided by the increase in the intensities of the peaks of F_{10} ions that are characteristic for fragmentation of $[M - N_2]^+$ ions with linear structure A.

The chemical-ionization mass spectra of I and II prove to be less informative, since ∿80% of the total ion current is due to the fraction of MH^+ (II) and $[MH - N_2]^+$ (I) ions. The MH^+ peaks of diazo ketones I are recorded only in the case of unsubstituted Ia. The intensities of the peaks of the fragment ions do not exceed 1-2% in the total ion current. Fragmentation with the formation of F'_5 ions, the intensities of the peaks of which are anomalously high in some cases (see Table 2), constitutes an exception.

The $[MH - N_2, - NHCHR^2]^+$ ion peaks indicate that a certain number of $[MH - N_2]^+$ ions have a cyclic structure. In addition, peaks of $[MH - 42]^+$ ions ($[MH - N_2, - 42]^+$ ions for the diazo ketones) are observed in the spectra of heterocycles II and diazo ketones I; this corresponds to elimination of a molecule of ketene in the case of fragmentation via a retrodiene mechanism. This process was not observed in the fragmentation of the investigated compounds under electron impact. The existence of this fragmentation masks elimination of a CHCOH particle (protonation at the oxygen atom) by the $[MH - N_2]^+$ ions with linear form A to give F_{10} ions; this makes the determination (even approximate) of some of the $[MH - N_2]^+$ ions that undergo fragmentation without cyclization impossible. Peaks of $[MH - N_2, - Hal, + H]^+$ (I) and $[MH - Hal, + H]^+$ (II) ions, which are formed as a result of ion-molecular reactions [7, 11-14], were recorded in the chemical-ionization mass spectra of the halogen-containing compounds.

Thus an analysis of the electron-impact mass spectra of 1-diazo-3-aroylaminopropan-2-ones showed that the $[M - N_2]^+$ ions formed in the first step of the fragmentation can undergo further fragmentation directly from the linear form, but the bulk of these ions undergo ring closing to give a six-membered heterocyclic ion; the degree of formation of 2-aryl-5,6-dihydro-4H-1,3-oxazin-5-ones is no more than 10%, and the principal fragmentation processes are due to a cyclic intermediate that is formed in the first step of the cyclization process. The mechanisms of cyclization under electron impact in the gas phase and in solution under the influence of concentrated sulfuric acid are similar and lead to identical results. Substituents (R^1) in the benzene ring have virtually no effect on the cyclization, whereas substituents R^2, in all likelihood, hinder it somewhat.

The chemical-ionization mass spectra confirm the existence of some of the $[MH - N_2]^+$ ions of the diazo ketones in the form of six-membered heterocycles but do not give additional information.

EXPERIMENTAL

The mass spectra were obtained with a Varian MAT-44S mass spectrometer. The electron-impact mass spectra were recorded at 40-220°C and an ionizing-electron energy of 75 eV (and an emission current of 0.5 mA). The chemical-ionization spectra were recorded at a pressure of 33.3 Pa in the ionization chamber and at an electron energy of 160 eV with isobutane as the reactant gas. The high-resolution spectra were obtained with a Varian MAT-311A spectrometer at 40-100°C and an electron energy of 70 eV.

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REDUCTIVE DEUTERATION OF 4-BENZAMIDO-3-OXO-2-(4-METHOXYCARBONYLBUTYLIDENE)TETRAHYDROTHIOPHENE TO GIVE THE 3-DEUTEROXY DERIVATIVE AND ITS PROTOTROPIC ISOMERIZATION

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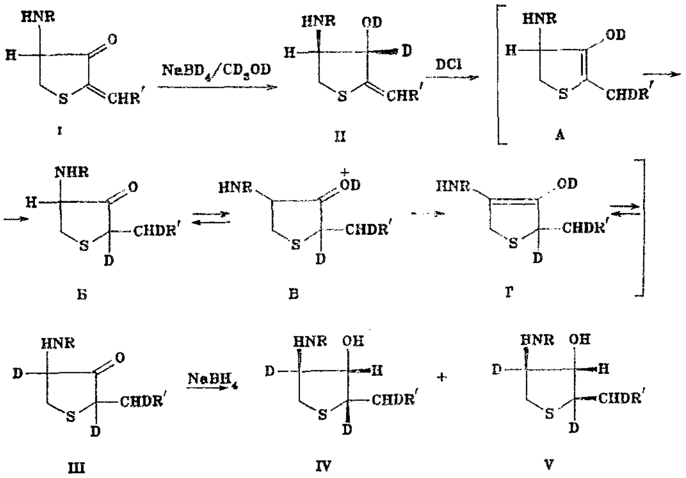
The prototropic rearrangement of a deuterated 3-hydroxytetrahydrothiophene with a β,γ-exocyclic double bond is accompanied by deuterium migration along the double bond. Thus 4-r-benzamido-3-t-deuteroxy-3-c-deutero-2-(4-methoxycarbonylbutylidene)tetrahydrothiophene gives cis- and trans-4-r-benzamido-3-oxo-2-(4-methoxycarbonylbutyl)tetrahydro-2,4,4'-d_3-thiophene, which, as a result of reduction with sodium borohydride, gives two isomers, viz., 4-r-benzamido-3-t-hydroxy-2-t- and -2-c-(4-methoxycarbonylbutyl)tetrahydrothiophenes that are deuterated in the 2, 4, and 4' positions.

We have previously observed the ability of a 3-hydroxytetrahydrothiophene with a β,γ-exocyclic double bond in the 2 position to undergo prototropic isomerization [1]. It was of interest to follow the character of this reaction under deuteration conditions.



$R = COC_6H_5$, $R' = (CH_2)_3COOCH_3$

We obtained 4-r-benzamido-3-t-deuteroxy-3-c-deutero-2-(4-methoxycarbonylbutylidene)-tetrahydrothiophene (II) from 4-benzamido-3-oxo-2-(4-methoxycarbonylbutylidene)tetrahydrothiophene (I) [2] by reduction with sodium borodeuteride in deuterated methanol at 0°C. The fact that two deuterium atoms enter the 3 position in the reductive deuteration follows from an examination of the ^1H NMR spectrum of II and a comparison of this spectrum with the spectrum of nondeuterated analog III. In the ^1H NMR spectrum of II the 3-H signal (δ 4.60-4.95 ppm) is almost absent, whereas the multiplicity of the 4-H signal (4.82 ppm), correspondingly, is lower than in the spectrum of its nondeuterated analog, which constitutes evidence for deuteration in the 3 position of the tetrahydrothiophene

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