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CHROMATOGRAPHIC MASS-SPECTROMETRIC CHARACTERISTICS OF SUBSTITUTED 4-ACYL-1,3,4-OXADIAZOLINES

I. G. Zenkevich and V. N. Yandovskii

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4-Acyl-1,3,4-oxadiazolines were characterized by their mass spectra and retention indexes. It was shown that the spectra of ionic series of compounds of a given class in conjunction with homologous increments of the retention indexes make it possible to carry out their group identification, in particular, to distinguish acyloxadiazolines from the isomeric diacyl- and isobaric monoacylhydrazones, which have similar regularities in electron-impact fragmentation, and that the complete analysis of their mass spectra makes it possible to unambiguously establish the position and character of the hydrocarbon radicals in the molecules.

The reaction of ketone acylhydrazones with carboxylic acid anhydrides in pyridine is a general method for the synthesis of 2-substituted 4-acyl-1,3,4-oxadiazolines. A series of compounds of this class have been synthesized and characterized by this method [1].

Proof of the structures of these compounds by spectral methods is complicated by difficulties in establishing the positions of alkyl radicals R^4 and R^5. In the PMR spectra the signals of the former are shifted only slightly to weak field as compared with the signals of the protons of the latter. In order to develop independent proof for the structures of acyloxadiazolines and methods for their chromatographic mass-spectrometric identification based on the use of statistically treated spectra of ionic series [2] and homologous increments of the retention indexes [3], in the present research we studied the mass spectra of 26 compounds of this class in the case of ionization by electron impact. The following three series of acyloxadiazolines were investigated: 1) compounds with alkyl radicals R^1-R^4 (I-XVI); 2) 5,5-pentamethylene-substituted compounds (XVII-XX); 3) phenyl-substituted acyloxadiazolines with phenyl radicals in the acyl residue (XXI, XXII) and in the 2 position of the ring (XXIII-XXVI).

The regularities in the fragmentation of acyloxadiazolines under electron impact have not been previously investigated. The mass spectra of precursors of oxadiazolines, viz., acylhydrazones containing chiefly aryl groups (see the literature cited in [4]), have been studied in relatively great detail. Of the aliphatic acylhydrazones, the methylformylhydrazones of various carbonyl compounds have been characterized in greatest detail [5].

A. A. Zhdanov Leningrad State University. Translated from Khimiya Geterotsiklicheskikh Soedinenii No. 5, pp. 623-631, May, 1984. Original article submitted June 23, 1983.

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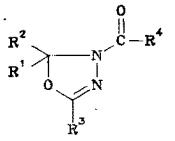
TABLE 1. Intensities of the Principal Peaks in the Mass Spectra of 4-Acyl-1,3,4-oxadiazolines at 70/12 eV (% Σ_{27}), Indexes, and Increments of the Retention Indexes



Compound	R¹	R²	R³	R⁴	M	M⁺	A1	A2=B2	B1	C1	C2	D	Retention index I	i_I
Homologous series 2														
I	Me	Me	Me	Me	156	9/56	1/3	40/5	9/36	12/0	—*	11/0	1050	−50
II	Me	Et	H	Me	156	6/51	6/37	41/4	2/8	15/0	—	—†	1050	−50
III	Me	Me	Me	Et	170	8/67	1/2	33/2	8/20	9/0	6/0	11/0	1140	−60
IV	Me	Me	Et	Me	170	8/67	1/3	31/2	4/12	7/0	—	11/0	1140	−60
V	Me	Et	Me	Me	170	6/56	5/30	45/10	1/4	12/0	—	3/0	1110	−90
VI	Me	Et	H	Et	170	5/44	6/37	35/7	3/12	15/0	9/0	—†	1130	−70
VII	Me	Me	Et	Et	184	6/64	1/2	37/3	8/31	12/0	9/0	11/0	1240	−60
VIII	Me	Et	Me	Et	184	5/54	4/26	38/8	2/8	8/0	5/0	3/0	1200	−100
IX	Me	Et	Et	Me	184	5/56	4/28	40/10	1/2	7/0	—	3/0	1200	−100
X	Et	Et	Me	Me	184	5/46	5/33	60/19	1/2	8/0	—	1/0	1190	−110
XI	Et	Et	H	Et	184	4/42	6/43	47/10	2/5	12/0	8/0	—†	1230	−70
XII	Me	Et	Et	Et	198	5/49	4/27	51/15	2/9	8/0	8/0	1/0	1280	−120
XIII	Et	Et	Me	Et	198	5/48	4/32	50/14	1/3	6/0	5/0	1/0	1270	−130
XIV	Et	Et	Et	Et	212	4/49	4/30	62/18	1/3	7/0	7/0	1/0	1360	−140
XV	Me	Et	*i*-Pr	*i*-Pr	226	4/54	2/20	44/16	3/10	6/0	15/0	2/0	1340	−260
XVI	Et	Et	*i*-Pr	*i*-Pr	240	3/35	2/23	54/37	2/5	5/0	14/0	1/0	1410	−290
													$\overline{i_I} \pm S = -110 \pm 70$	

					M	M⁺	A1	B2	B1	C1	C2		
Homologous series 0													
XVII	$(CH_2)_5$		H	Me	182	6/53	1/0	28/1	20/44	9/0	—	1390	90
XVIII	$(CH_2)_5$		Me	Me	196	7/60	1/0	34/1	20/38	8/0	—	1470	70
XIX	$(CH_2)_5$		H	Et	196	6/49	0	22/0	22/51	8/0	6/0	1460	60
XX	$(CH_2)_5$		Me	Et	210	4/52	0	23/1	13/36	6/0	5/0	1510	10
												$\overline{i_I} \pm S = 60 \pm 30$	

					$M(y_M)$	M⁺	A1	C1	C2	E1	E2		
XXI	Me	Me	H	Ph	204 (8)	10/88	2/1	26/1	14/0	1/7	22/3	1540	140
XXII	$(CH_2)_5$		H	Ph	244 (6)	11/84	0	24/0	12/0	5/13	27/3	1980	280

					$M(y_M)$	M⁺	A1	B1	B2	F1	F2		
XXIII	Me	Me	Ph	Me	218 (8)	7/56	1/2	10/35	27/6	30/2	10/0	1560	60
XXIV	Me	Me	Ph	Et	232 (8)	6/56	1/1	13/39	30/4	29/1	9/0	1630	30
XXV	$(CH_2)_5$		Ph	Me	258 (6)	7/67	1/0	18/32	23/0	21/1	7/0	2010	210
XXVI	$(CH_2)_5$		Ph	Et	272 (6)	6/58	1/0	24/41	23/0	20/1	6/0	2060	160

*No peak was recorded (m/z <25).

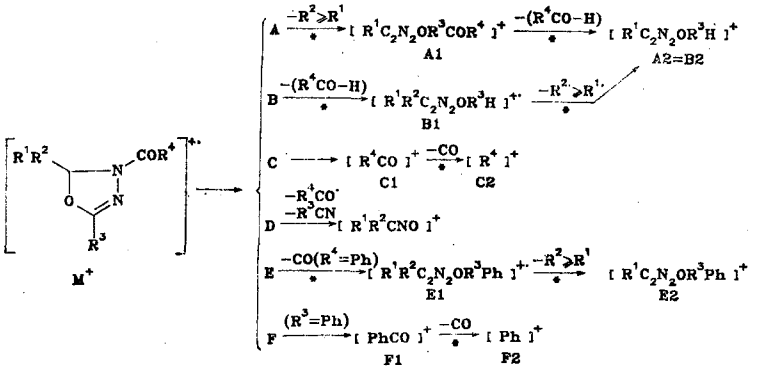
†Overlapped with the isotope peak of an intense peak of an ion with an m/z value smaller by one unit.

A study of the regularities in the dissociative ionization of 4-acyl-1,3,4-oxadiazolines is of particular interest in connection with the similarity in the mechanisms of the fragmentation under electron impact of some heterocyclic compounds and their acyclic isomers (diacylhydrazones in this case). This sort of similarity was observed, for example, for alkyl-substituted perhydro-1,3,4-thiadiazines and the corresponding thiohydrazones [6], as well as for their oxygen analogs, viz., perhydro-1,3,4-oxadiazines and hydroxyhydrazones.

The R^1-R^4 radicals for all of the investigated 4-acyl-1,3,4-oxadiazolines are indicated in Table 1, and their molecular masses, intensities of the peaks of the molecular and principal fragment ions in percent of the total ion current at 70 and 12 eV, their retention indexes on a slightly polar SE-30 stationary phase measured during chromatographic mass-spectrometric analysis simultaneously with recording of the mass spectra, and the homologous increments of the retention indexes are presented. The letter designations of the fragment ions in Table 1 correspond to their designations in the overall fragmentation scheme (see below). The complete mass spectra of acyloxadiazolines I-XXVI at 70 eV calculated by averaging (three to four measurements) the spectra of each compound are presented in Table 2; the relative errors in the determination of the intensities of the major peaks (greater than 10% of the maximum peak) do not exceed ±15% on the average ($\Delta I/\bar{I}$ ratios, where ΔI are the confidence intervals, with reliability $\alpha = 0.95$, corresponding to average intensities $\bar{I}$).

All oxadiazolines I-XXVI contain a ring with a p-π-p system of O—C=N—N conjugation and, as a consequence of this, are characterized by extremely high resistance to electron impact; the intensities of the peaks of the molecular ions in the overall ion current (the W_M values) amount to 3-11% Σ_{27} at 70 eV and 35-84% at 12 eV. If one examines the $W_M(12\text{ eV})/W_M(70\text{ eV})$ ratio ($W_{M_{70}}{}^{12}$), it proves to be high (10 ± 2 and much greater for the investigated acyloxadiazolines than the values for other hydrazine derivatives and is not overlapped with them within the error limits: 4.5 ± 1.5 for alkylhydrazines [7], 5 ± 1.5 for acylhydrazones, 6.5 ± 1.5 for 2-pyrazolines, 4.5 ± 1.5 for nitrosamines, etc. Thus the indicated ratio proves to be extremely characteristic for acyloxadiazolines I and is useful in their group identification.

The principal pathways of the fragmentation of the molecular ions of 4-acyl-1,3,4-oxadiazolines A-F can be represented by the following scheme:



The asterisks in this scheme mean that the given process in the mass spectra is confirmed by peaks of metastable ions. Depending on the character of R^1-R^4, the ratio of the intensities of the peaks formed as a result of processes A-F changes significantly. For alkyl-substituted I-XVI, where R^1-R^4 = H and C_nH_{2n+1}, the principal fragmentation processes in the case of electron impact turn out to be processes involving splitting out of the larger of R^1 or R^2 (β cleavage with respect to the ring N and O atoms) to give ions of the A1 type (1-6% Σ_{27} at 70 eV and 2-37% at 12 eV) and competitive processes involving the elimination of ketene (R^4CO—H) from the acyl group attached to the N_4 atom, which lead to ions of the B1 type, amounting to 1-9% Σ_{27} at 70 eV and 2-36% at 12 eV. The latter process is characteristic for compounds of the most diverse classes containing an acyl group attached to the nitrogen atom [8]. In the next step of the fragmentation the A1 and B1 ions form identical secondary fragment ions A2 = B2 (see the scheme), which hinders establishment of the true ratio of processes A and B. The secondary character of these ions is confirmed by the significant decrease in the intensities of their peaks when the ionizing-electron energy is decreased (31-62% Σ_{27} at 70 eV and 2-37% at 12 eV) and by the corresponding peaks of metastable ions. The peaks of the A2 = B2 = $[M - R^2 - (R^4CO - H)]^+$ ions are maximal in the spectra of all of the aliphatic acycloxadiazolines (I-XX), and this makes it possible to readily establish the character of R^2 and R^4 in the stage of structural analysis from the mass spectra. The same compounds (I-XX) at 70 eV are characterized by appreciable peaks of acyl ions $[R^4CO]^+$ (6-19% Σ_{27}) and, if $R^4 \geqslant C_2H_5$, the corresponding hydrocarbon ions $[R^4]^+$ (5-9%). The peaks of these ions are also useful in the interpretation of the mass spectra of these compounds (they determine the acyl group), but they can evidently be formed via different mechanisms, including mechanisms other than one-step processes. In addition, their identification is complicated by the presence of less intense peaks of $[R^3CO]^+$ ions.

TABLE 2. Mass Spectra of 4-Acyl-1,3,4-oxadiazolines I-XXVI at 70 eV; m/z Values (%)*

Compound	m/z values (%)
I	156 (21), 114 (22), 100 (6), 99 (100), 72 (28), 71 (3), 57 (12), 56 (3), 55 (6), 43 (32), 42 (6), 41 (4)
II	156 (12), 127 (14), 114 (6), 99 (16), 86 (5), 85 (100), 73 (4), 57 (4), 43 (37), 42 (8), 41 (5), 29 (7), 28 (4), 27 (5)
III	171 (3), 170 (22), 128 (7), 115 (3), 114 (22), 113 (23), 100 (6), 99 (100), 83 (4), 73 (3), 72 (31), 71 (3), 57 (26), 56 (4), 55 (5), 43 (16), 42 (5), 41 (4), 29 (16), 28 (3), 27 (6)
IV	171 (3), 170 (24), 128 (12), 114 (22), 113 (100), 100 (3), 99 (43), 73 (3), 72 (38), 71 (6), 57 (26), 56 (4), 55 (5), 43 (23), 42 (6), 41 (5), 39 (3), 29 (13), 28 (3), 27 (4)
V	170 (12), 141 (11), 128 (3), 113 (16), 100 (5), 99 (100), 86 (6), 69 (4), 57 (12), 43 (28), 42 (6), 41 (4), 29 (4), 27 (4)
VI	170 (14), 141 (16), 115 (3), 114 (9), 113 (4), 99 (14), 86 (5), 85 (100), 73 (7), 69 (3), 58 (3), 57 (44), 55 (4), 43 (8), 42 (6), 41 (5), 29 (27), 28 (4), 27 (8)
VII	184 (15), 129 (3), 128 (21), 114 (7), 113 (100), 99 (13), 97 (3), 72 (29), 71 (3), 57 (33), 56 (4), 55 (4), 43 (4), 42 (4), 41 (4), 29 (26), 27 (6)
VIII	184 (13), 155 (11), 128 (5), 127 (3), 114 (3), 113 (38), 100 (6), 99 (100), 86 (8), 83 (3), 69 (4), 57 (21), 56 (3), 43 (14), 42 (5), 41 (3), 29 (14), 28 (3), 27 (5)
IX	184 (12), 155 (9), 127 (14), 114 (7), 113 (100), 99 (19), 86 (8), 71 (6), 69 (4), 57 (16), 43 (18), 42 (5), 41 (4), 29 (13), 28 (4), 27 (4)
X	184 (8), 155 (8), 114 (7), 113 (100), 71 (4), 57 (6), 43 (14), 42 (3), 29 (3)
XI	184 (8), 155 (12), 128 (4), 127 (3), 100 (6), 99 (100), 73 (5), 57 (25), 56 (4), 55 (3), 43 (4), 41 (3), 29 (18), 28 (3), 27 (5)
XII	198 (9), 169 (7), 142 (3), 127 (13), 114 (7), 113 (100), 86 (7), 71 (3), 69 (3), 57 (17), 43 (3), 42 (3), 29 (15), 27 (4)
XIII	198 (8), 169 (8), 127 (20), 114 (7), 113 (100), 83 (3), 71 (3), 57 (12), 56 (3), 43 (8), 42 (3), 29 (11), 27 (3)
XIV	212 (6), 183 (6), 128 (8), 127 (100), 71 (4), 57 (11), 29 (12)
XV	226 (8), 197 (5), 157 (3), 156 (5), 141 (12), 128 (8), 127 (100), 113 (8), 86 (4), 71 (12), 70 (3), 43 (33), 42 (4), 41 (7), 27 (4)
XVI	240 (5), 211 (4), 142 (9), 141 (100), 127 (5), 71 (10), 56 (3), 55 (3), 43 (30), 41 (6), 29 (4), 27 (4)
XVII	183 (3), 182 (23), 141 (7), 140 (71), 139 (6), 112 (6), 111 (22), 98 (10), 97 (100), 96 (4), 95 (9), 94 (3), 84 (17), 81 (5), 72 (3), 69 (3), 67 (7), 59 (5), 55 (9), 54 (5), 53 (3), 46 (6), 43 (28), 42 (5), 41 (11), 39 (5), 29 (4), 27 (5)
XVIII	197 (3), 196 (21), 155 (6), 154 (61), 153 (4), 125 (12), 112 (17), 111 (100), 99 (4), 98 (14), 96 (4), 95 (3), 84 (3), 67 (4), 60 (6), 57 (3), 56 (4), 55 (7), 54 (4), 43 (26), 42 (5), 41 (7), 39 (3), 27 (3)
XIX	197 (4), 196 (24), 141 (12), 140 (98), 139 (7), 125 (6), 112 (8), 111 (21), 99 (4), 98 (9), 97 (100), 96 (6), 95 (11), 94 (3), 84 (12), 81 (7), 72 (4), 69 (4), 67 (8), 59 (5), 55 (11), 54 (6), 53 (3), 46 (8), 43 (4), 42 (4), 41 (13), 39 (6), 29 (32), 28 (6), 27 (10)
XX	211 (3), 210 (9), 168 (21), 155 (7), 154 (61), 153 (4), 139 (12), 126 (6), 125 (38), 113 (5), 112 (22), 111 (100), 98 (13), 96 (6), 95 (4), 86 (3), 85 (4), 84 (4), 83 (6), 81 (4), 71 (6), 69 (4), 67 (6), 60 (8), 57 (28), 56 (6), 55 (12), 54 (7), 53 (3), 44 (4), 43 (29), 42 (8), 41 (15), 39 (6), 29 (30), 28 (6), 27 (10)
XXI	205 (5), 204 (37), 189 (9), 176 (6), 162 (10), 161 (83), 147 (10), 119 (11), 118 (9), 106 (9), 105 (100), 104 (4), 103 (5), 91 (3), 90 (3), 78 (4), 77 (52), 76 (4), 63 (3), 51 (13), 50 (5), 43 (8), 42 (8), 41 (4), 39 (6)
XXII	245 (6), 244 (41), 216 (19), 187 (7), 174 (16), 173 (100), 160 (14), 147 (14), 118 (5), 106 (8), 105 (98), 104 (8), 103 (8), 91 (4), 77 (48), 67 (4), 55 (8), 51 (10), 41 (12), 39 (6)
XXIII	219 (3), 218 (22), 177 (4), 176 (34), 162 (10), 161 (89), 119 (5), 118 (4), 106 (8), 105 (100), 77 (32), 51 (7), 43 (15), 42 (4)
XXIV	233 (3), 232 (19), 177 (6), 176 (44), 162 (11), 161 (100), 119 (4), 106 (8), 105 (99), 77 (32), 57 (12), 51 (6), 43 (3), 42 (3), 29 (3)
XXV	259 (5), 258 (28), 217 (12), 216 (79), 215 (5), 187 (10), 174 (16), 173 (100), 161 (4), 160 (12), 122 (4), 118 (4), 106 (8), 105 (97), 104 (5), 103 (4), 96 (4), 78 (3), 77 (32), 67 (3), 55 (3), 54 (3), 51 (5), 43 (14), 42 (3), 41 (6), 39 (3), 28 (3)
XXVI	273 (5), 272 (24), 217 (16), 216 (100), 215 (4), 187 (10), 174 (16), 173 (96), 160 (9), 122 (4), 106 (8), 105 (91), 104 (5), 103 (3), 96 (4), 77 (28), 67 (3), 57 (11), 55 (3), 51 (4), 41 (5), 29 (13), 27 (3)

*Peaks with intensities less than 3% or with m/z less than 27 are not presented.

Intense peaks of ions with m/z 72 (11% Σ_{27} at 70 eV) are observed in the mass spectra of compounds with $R^1 = R^2 = CH_3$ (I, III, IV, and VII). Replacement of the indicated radicals by a C_2H_3 group leads to the appearance of peaks with m/z 86 = 72 + 14 of lower intensity (3% Σ_{27} at 70 eV), whereas if $R^1 = R^2 = C_2H_3$, the intensity of the peaks with m/z 100 decreases to ~1% of the total ion current. The determination of the empirical formula of the ion with m/z 72 in the spectrum of I with an MKh-1320 high-resolution spectrometer indicates that its composition is C_3H_6NO (measured value 72.045, calculated value 72.045). Thus it may be assumed that ions of this type (D) are formed as a result of splitting out of

$R^4CO^\cdot$ and R^3CN fragments from M^+ and have the general formula $[R^1R^2CNO]^+$; the intensity of their peaks decreases sharply in the presence of competitive processes involving fragmentation of the molecular ions.

5,5-Pentamethylene-4-acyl-1,3,4-oxadiazolines XVI-XX are characterized by overwhelming preponderance of fragmentation pathway B as compared with pathway A; the intensities of the peaks of B1 ions amount to 13-22% Σ_{27} at 70 and 36-51% Σ_{27} at 12 eV. Process A is hindered in this case, since it involves the cleavage of two C—C bonds in the ring and leads to the development of $[M - C_3H_7]^+$ ions. In the next step of the fragmentation the ions of the B1 type also split out $C_3H_7^\cdot$ radicals, which gives secondary fragment ions with the general formula $[CH_2CHC_2N_2OR^3H]^+$. If it is assumed that the fragmentation of the pentamethylene group with the elimination of a $C_3H_7^\cdot$ fragment leads to the formation of a vinyl group in the 5 position, its conjugation with the ring in the resulting ion explains the high intensity of the corresponding B2 ions (22-34% Σ_{27} at 70 eV, the maximum peaks in the spectra).

Peaks of ions formed via mechanism C, viz., $[PhCO]^+$ and $[Ph]^+$, predominate in the mass spectra of 4-benzoyl-1,3,4-oxadiazolines XXI and XXII. In addition, the appreciable [M — 28] ion peaks can be explained by a skeletal rearrangement with the elimination of a CO particle (pathway E). The subsequent transformations of $[M - CO]^{+\cdot}$ ions involve splitting out of R^1 and R^2 or $C_3H_7^\cdot$ when $R^1R^2 = (CH_2)_5$.

2-Phenyl-substituted acyloxadiazolines XXII-XXVI are also characterized by intense peaks of $[PhCO]^+$ and $[Ph]^+$ ions (pathway F).

The mass-spectrometric characteristics of 16 compounds of one homologous series, viz., alkyl-substituted 4-acyl-1,3,4-oxadiazolines, which belong to the homologous series $y_M = 2$, enable one to calculate the average spectrum of the ionic series for them and use it for the group identification of other compounds of this class [2]. The statistically treated spectrum of the ionic series of compounds of this homologous series has the following form (the intensities of the ionic series in the order of the increase in their numbers from 0 to 13 are listed; standard deviations S are indicated by the subscripts):

$$4_1, 70_7, 16_8, 2_1, 0, 0, 0, 0, 0, 0, 0, 1_1, 1_1, 6_1 \quad (\Sigma S = 20).$$

On the basis of this spectrum one can indicate homologous series of peaks of the major fragment ions in the mass spectra of any compounds of this class, i.e., primarily those peaks that, within the limits of the standard deviations, may exceed 10% of the total ion current. This includes peaks of series 1 and 2, whereas the peaks of the remaining series are not characteristic precisely because of their low intensities.

Additional information necessary for the mass-spectrometric characterization of a given homologous series in concise form includes the general empirical formula, viz., $C_nH_{2n-2}N_2O_2$ (formal unsaturation 3), the relationship between the number (n) of carbon atoms in the molecule and parameter x (the higher orders of the 14th representation of the molecular mass number), viz., $n = x - 4$, the molecular mass of the simplest homolog (unsubstituted 4-formyl-1,3,4-oxadiazoline, $M_1 = 100$), and the level of intensities of the molecular-ion peaks in the designations adopted in [9] at 70 eV, viz., II (1-10% of the total ion current). 5,5-Pentamethylene-4-acyl-1,3,4-oxadiazolines ($y_M = 0$) can be similarly characterized: $C_nH_{2n-4}N_2O_2$, $n = x - 4$, II, $M_1 = 168$ (major peaks of series 0, 1, and 13):

$$34_2, 17_4, 1_1, 1_1, 2_1, 0, 0, 0, 0, 0, 0, 5_2, 2_1, 38_3.$$

Aryl-substituted acyloxadiazolines (aryl radicals in the 2 position of the ring or in the acyl group attached to the N_4 atom), $y_M = 8$: $C_nH_{2n-10}N_2O_2$, $n = x - 3$, II, $M_1 = 176$ (major peaks of series 7 and 8):

$$1_1, 4_2, 0, 0, 0, 1_1, 3_2, 64_3, 21_3, 4_1, 0, 1_1, 0, 1_1,$$

and 5,5-pentamethylene-2-aryl-4-acyl-1,3,4-oxadiazolines, $y_M = 6$: $C_nH_{2n-12}N_2O_2$, $n = x - 3$, II, $M_1 = 244$ (major peaks of series 5, 6, and 7):

$$1_1, 3_2, 0, 0, 0, 25_2, 29_5, 33_5, 2_1, 1_1, 1_1, 1_1, 1_1, 3_2.$$

The reliability of the mass-spectrometric characterization of the last three groups of homologs by means of the spectra of the ionic series is poorer than in the case of alkyl-substituted acyloxadiazolines, since the numbers of investigated members of the series are, respectively, four, three, and three (the standard deviations can be refined in the case of a more detailed characterization [2]).

The mass spectrum of the ionic series of alkyl-substituted 4-acyl-1,3,4-oxadiazolines differs significantly from the spectra of ionic series of most of the 25 most important classes of organic compounds of series 2 published in [2], and this constitutes the basis of their reliable group identification. If the sum of the absolute values of the differences in the intensities of the corresponding ionic series D is used as a measure of the coincidence of such spectra of two classes of substances (a and b) [2], the following condition may serve as a criterion of the possibility of distinguishing compounds of each of them from one another:

$$D=\sum_{y=0}^{13}|\bar{I}_y^a-\bar{I}_y^a|>\sum_{y=0}^{13}S_y^a+\sum_{y=0}^{13}S_y^b,$$

where $\Sigma S_y a$ and $\Sigma S_y b$ are the sums of the standard deviations of all of the ionic series of classes a and b.

When this inequality is not satisfied, the group identification from the spectra of the ionic series is ambiguous. In conformity with this criterion, aliphatic ketones (D = 33 < 23 + 20), diketones (D = 15 < 22 + 20), monoacylhydrazones (D = 30 < 29 + 20), and alkyl iodides (D = 34 < 23 + 20) have spectra of the ionic series that are closest to those of acyloxadiazolines. All of the alternative classes except the third are excluded from consideration when even the minimal additional mass-spectrometric (intensities of the molecular-ion peaks, isotope ratios, etc.) or chemical (the presence of nitrogen in the compound) information is available. In the case of acylhydrazones, however, coincidence of the spectra of the ionic series reflects similar regularities in the fragmentation of compounds of these classes in the case of electron impact. The refined spectrum of the ionic series of monoacylhydrazones calculated with allowance for the data obtained in this research has the form

$$11_5, 51_8, 17_7, 5_5, 0, 0, 0, 0, 0, 0, 0, 2_1, 4_3, 10_4 \quad (\Sigma S=33)$$

$$C_nH_{2n}N_2O,\ n=x-3,\ II,\ M_1=72.$$

The determination of the structures of alkyl-substituted acyloxadiazolines on the basis of the established fragmentation principles includes, first, the determination of the total number of carbon atoms in R^1-R^4 from the expression $N = (M - M_1)/14$, where M is the molecular mass of the compound, and M_1 is the mass of the simplest homolog (M_1 = 100). The differences in the mass numbers of the molecular ion and the peaks of the fragment ions closest to it (M_f) of series 1 indicate the masses of R^1 and R^2 (the more intense peak corresponds to splitting out of a larger radical), whereas the corresponding differences for the peaks of series 2 indicate the mass of acyl residue R^4CO. The number of carbon atoms in radical R^4 is $n^4 = (M - M_f - 28)/14$. The differences in the mass numbers of the M^+ peak and the maximum peak M_{max} make it possible to refine the total number of carbon atoms in $R^2 \geqslant R^1$ and R^4 from the expression $n^2 + n^4 = (M - M_{max} - 29)/14$. Radical R^3 is not directly involved in the principal processes of fragmentation of the molecular ions, and the number of carbon atoms in it is not determined by analysis of the characteristic differences but is established from the expression $n^3 = N - n^1 - n^2 - n^4$ (n^i is the number of carbon atoms in the i-th radical). In practice, it is convenient to use the absolute value of M_{max} for this. Thus, if $R^1 = CH_3$, whereas $R^2 = CH_3$ or C_2H_5, M_{max} = 85 corresponds unambiguously to R^3 = H, M_{max} = 99 corresponds to $R^3 = CH_3$, etc. However, if $R^1 = R^2 = C_2H_5$, M_{max} = 99 corresponds to R^3 = H, M_{max} = 113 corresponds to $R^3 = CH_3$, etc.

Example: proof of the structures of two isomeric compounds, viz., 2,5,5-trimethyl-4-propionyl-1,3,4-oxadiazoline (III) and 5,5-dimethyl-2-ethyl-4-acetyl-1,3,4-oxadiazoline (IV).

Both compounds have a molecular mass of 170, and R^1-R^4 are consequently contained in the sum [(170-100)/14 = 5] of the carbon atoms. Peaks of [M − 15] ions are present in the spectra of each of them (with intensities ∿1% Σ_{27} at 70 eV and less than 3% of the maximum peak; they are therefore not presented in Table 2). On the basis of this it may be assumed that $R^1 = R^2 = CH_3$ for both commpounds. The maximum peak in the spectrum of III with m/z 99 makes it possible to calculate $n^2 + n^4 = (170 - 99 - 29)/14 = 3$, but then $R^4 = C_2H_5$, and $n^3 = 5 - 1 - 1 - 2 = 1$. In the spectrum of IV, M_{max} = 113, and, consequently, $n^2 + n^4 = 2$, $R^4 = CH_3$, and $R^3 = C_2H_5$. Thus the structures of the acyloxadiazolines under consideration correspond unambiguously to their mass spectra.

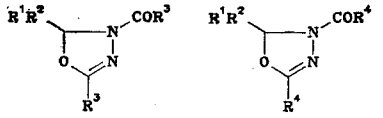
The chromatographic characterization of the compounds of the investigated types of 4-acyl-1,3,4-oxadiazolines is based on the use of homologous increments of the retention indexes [3]:

$$i_I = I - 100x,$$

where I is the gas-chromatographic retention index of the investigated compound, and x is the number of higher orders of the 14th representation of its molecular mass number. The set of homologs in turn can be characterized by the interval of the homologous increments of the retention indexes, which gives valuable additional information for the chromatographic mass-spectrometric identification of compounds of the investigated classes (see Table 1). High accuracy in the measurement of the indexes is not required for purposes of classification of the substances, and the arithmetic indexes [10] rounded off to 10 units, which makes it possible to disregard their temperature dependence, are therefore indicated in Table 1.

Alkyl-substituted 4-acyl-1,3,4-oxadiazolines in a column with a slightly polar stationary phase (SE-30 silicone elastomer) have significant negative homologous increments of the retention indexes (—110 ± 70), i.e., their indexes are, on the average, 100 units smaller than in the case of normal alkanes with the same molecular masses. The introduction of a ring made up of carbon atoms into the molecule sharply increases the i_I value to 60 ± 30. The presence of aromatic substituents also has a similar effect (i_I = 80 ± 60), whereas the simultaneous presence of pentamethylene and aryl groups brings the homologous increments of the retention indexes up to 220 ± 60.

The set of examined mass-spectrometric and chromatographic parameters of 4-acyl-1,3,4-oxadiazolines makes it possible to reliably identify compounds of this class and distinguish them from compounds of other series. Such data are extremely useful, for example, in establishing the character of impurities in preparations of these compounds. Thus, if R^3 differs from R^4 by n methylene groups, acyloxadiazoline impurities with masses that differ from the mass of the principal component by ±n14 are detected in certain similar samples:



They may be formed by transacylation of the starting acylhydrazone with the subsequent formation of an oxadiazoline ring and also by transacylation of the oxadiazoline [11]. Information regarding the molecular masses and calculation of the corresponding homologous increment of the index are sufficient for their group identification.

Admixtures of isomeric (with respect to acyloxadiazolines) diacylhydrazones, which have similar qualitative regularities in fragmentation under electron impact, were detected in XI and XVII-XX. Their identification was possible only by recourse to quantitative characteristics of the mass spectra and the retention parameters. The intensities of the peaks of the molecular ions of acyclic diacylhydrazones are several times lower than in the case of acyloxadiazolines (0.1-1% of the ion current), and the homologous increments of the indexes are greater by 20-50 units.

Acyloxadiazolines II, VI, XI, XVII, XXI, and XXII, which contain a hydrogen atom in the 2 position of the ring (R^3 = H), are thermally unstable and require special precautions under the conditions of gas-chromatographic analysis (the temperature of the chromatograph vaporizer should not exceed 150°C). The products of thermal decomposition of these compounds are monoacylhydrazones of the corresponding carbonyl compounds $R^1R^2C{=}N{-}NHCOR^4$, which are formed as a consequence of splitting out of a molecule of CO. Such monoacylhydrazones are identified from the very high values of the homologous increments of the retention indexes, which amount to 490 ± 70 if R^1 and R^2 = C_nH_{2n+1} and 620 ± 70 if R^1R^2 = $(CH_2)_5$, and, additionally, from the $W_{M_{70}}$ [12] parameter.

EXPERIMENTAL

4-Acyl-1,3,4-oxadiazolines I-XXVI were obtained by the method in [1] from ketone monoacylhydrazones and carboxylic acid anhydrides in pyridine. The mass spectra and chromatographs with respect to the total ion current were recorded with an LKB-2091 chromatographic mass spectrometer. The mass spectra were recorded under the following conditions: The ionization energies were 70 and 12 eV, the emission current was 25 μA, the accelerating voltage was 3.5 kV, and the separator and ion-source temperature was 200°C. Chromatographic analysis was carried out under the following conditions: temperature programming from 70°C at 5°C/min for I-XVI, from 100°C (5°C/min) for XVII-XX, and from 150°C (5°C/min) for XXI-XXVI

with helium as the carrier gas at a flow rate of 20 ml/min. The analyses were carried out on 10% solutions in ether with the addition of ~50% (based on the amount of acyloxadiazoline) of a mixture of four n-alkanes C_nH_{2n+2} (n = 11, 13, 15, and 17) as reference components for calculation of the retention indexes. Acylhydrazones $R^1R^2CNNHCOR^4$ necessary for the comparative chromatographic mass-spectrometric characterization [R^1, R^2, R^4: CH_3, CH_3, H; CH_3, C_2H_5, H; CH_3, CH_3, CH_3; CH_3, C_2H_5, CH_3; C_2H_5, C_2H_5, H; C_2H_5, C_2H_5, CH_3; C_2H_5, C_2H_5, C_2H_5; $(CH_2)_5$, H; $(CH_2)_5$, CH_3; CH_3, CH_3, C_6H_5; $(CH_2)_5$, C_6H_5] were synthesized by the methods used in [1]. Statistical treatment of the mass spectra of the individual compounds, calculation of the spectra of the ionic series, and averaging of these spectra were carried out by means of an NR 2114 V computer.

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DIAZO CARBONYL DERIVATIVES OF HETEROCYCLES.

4.* DIAZOACETYL DERIVATIVES OF MERCAPTOBENZAZOLES AND MERCAPTOQUINOLINES

V. G. Kartsev, T. S. Pokidova, and A. V. Dovgilevich

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In a number of cases the classical method of acylation of diazomethane by the halides of the corresponding acids is not suitable for the synthesis of functionally substituted diazo ketones, since the reaction is accompanied by side processes. Different methods for the introduction of a diazo carbonyl function into molecules are used in these cases [2]. It seems expedient to use haloalkyl diazomethyl ketones with an active halogen atom in the α position for this purpose. The literature does not contain information on nucleophilic substitution reactions of the halogen atom in such diazo ketones.

We have previously demonstrated the possibility of the synthesis of 1-diazo-3-(2-benzimidazolylmercapto)propanone on the basis of bromomethyl diazomethyl ketone [3].

In the present research we extended the possibility of this method in order to prepare difficult-to-obtain diazo carbonyl derivatives of mercaptobenzazoles and mercaptoquinolines. We used 2-mercaptobenzimidazole, 2-mercaptobenzoxazole, 2-mercaptobenzothiazole, 2-mercaptoquinoline, and 8-mercaptoquinoline as mercaptoheterocyclic models. We selected 1-diazo-3-bromopropanones IIa-c as the alkylating diazo ketones to study steric effects on the course of the reaction. The reaction was carried out at room temperature in methanol in presence of an equivalent amount of sodium methoxide:

*See [1] for communication 3.

Branch of the Institute of Chemical Physics, Academy of Sciences of the USSR, Chernogolovka 142432.

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