1.4405; d_4^{20} 0.8784. IR spectrum (thin layer): 1620 (C=C), 1660 (C=N), 3100 cm^{-1} (=C-H). PMR spectrum (in CCl_4): 7.53 (1H, q, N=CH), 6.32 (1H, q, OCH=C), 4.08 (1H, q, trans-C=CH), 3.87 (1H, q, cis-C=CH), 3.75 (2H, m, OCH_2), 3.54 (2H, m, NCH_2), 1.87 ppm (3H, d, CH_3). Found: C 63.3; H 9.6; N 12.2%. Mr_D 34.02. $C_6H_{11}NO$. Calculated: C 63.7; H 9.8; N 12.4%. Mr_D 34.37.

On conducting the reaction in a similar manner in 200 ml monoethanolamine, 41.6 g (48%) oxazolidine IIb was obtained.

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MASS SPECTROMETRIC STUDY OF 1,2,4- AND 1,3,4-OXADIAZOLES CONTAINING INDOLE SUBSTITUENTS

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1,2,4- and 1,3,4-Oxadiazoles containing indole substituents decompose upon electron impact due to breakage of bonds in the oxadiazole ring. Skeletal rearrangements may occur in the molecular ions of 2,5-diaryl-1,3,4-oxadiazoles due to migration of the aryl groups.

There has recently been increasing interest in indole derivatives containing 1,2,4- and 1,3,4-oxadiazole fragments since compounds have been found among these bisheterocyclic systems possessing a broad range of biological activity.

Extensive information is not available on the dissociative ionization of aryloxadiazoles [1-6] upon electron impact and the possibility of the mass spectrometric differentiation of substituted 1,2,4- and 1,3,4-oxadiazoles and of positional isomers has not been adequately evaluated. In this regard, we studied the electron impact mass spectra of 1,2,4- (I-IV) and 1,3,4-oxadiazoles (V-X) containing a 3-indolyl or (3'-indolyl)methyl group as one of the substituents. We studied both common and specific pathways for the decomposition of these compounds and elucidated diagnostic fragmentation patterns suitable for the differentiation of isomers. The mass spectral data for 1,2,4-oxadiazoles I-IV at 70 eV ionizing electron energy are given in Table 1, while the corresponding data for V-X are given in Table 2.

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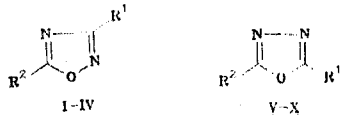
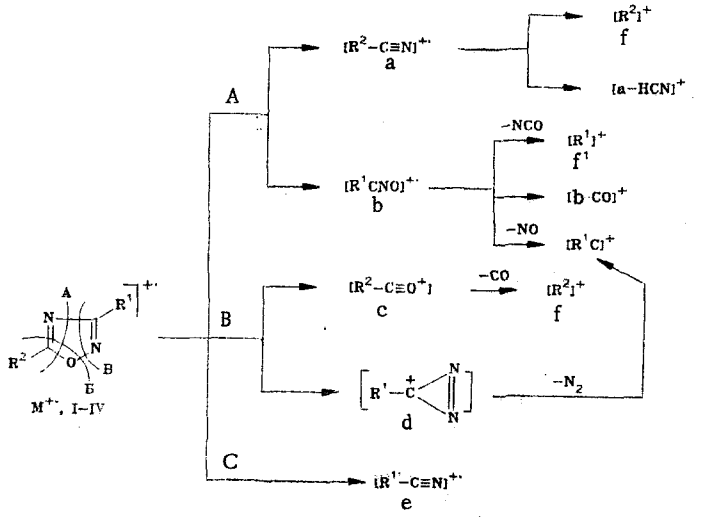


I-IV V-X (indolyl-3')methyl

I, VII R^1 = indolyl-3, II, IV, VIII, X R^1 = C_6H_5, III, IX R^1 = *n*-$NO_2C_6H_4$, V R^1 = H, VI R^1 = CH_2Cl; I R^2 = C_6H_5, II, III, V–IX R^2 = indolyl-3, IV, X R^2 = (индолил-3′)метил

The mass spectra of oxadiazoles I-X display rather strong molecular ion peaks (M^+) which are sometimes accompanied by $[M - H]^+$ ion peaks. The major processes for the decomposition of M^+ of these compounds are related to the loss of the aryl substituent or breakage of the oxadiazole ring. The processes involving break age of the oxadiazole ring hold the greatest interest relative to structural analysis since they are characteristic for the entire series of compounds studied.

For 3,5-diaryl-1,2,4-oxadiazoles I-IV, among the most advantageous dissociative ionization processes, we should note three major directions due to the process which is the reverse of 1,3-dipolar addition: breakage of the O–$C_{(5)}$ and $C_{(3)}$–$N_{(4)}$ (pathway A) and breakage of O–N and N–$C_{(5)}$ bonds (B) or of the O–N and $C_{(3)}$–$N_{(4)}$ bonds (C). As a result of the oxadiazole ring by the first two pathways, the charge may be localized on both parts of the molecule. In this case, the peaks for the ions formed have strong intensity in the spectra of I-IV.



The primary ions (a-e) undergo further decomposition through pathways typical for cyanides and diazo compounds [7].

We should note that, despite the common nature of the dissociative ionization of 1,2,4-oxadiazoles I-IV, the differences in the structural elements contribute to the form of the mass spectrum. Thus, the presence of the (3'-indolyl)methyl substituent in IV suppresses the decomposition due to breakage of the oxadiazole ring. This is a result of the favorable "benzyl" cleavage leading to the maximum peak for the ion with m/z 130.* This ion most likely has quinolinium structure [7]. The maximum peaks in the mass spectra of I and II correspond to the $[b - NO]^+$ (or $[d - N_2]^+$) ions, while the major peak in the spectrum of II is due to type-a ions. On the other hand, the peak for the type-b ion ($[C_6H_5CNO]^+$) has greatest intensity in the mass spectrum of 3,5-diphenyl-1,2,4-oxadiazole [4].

The M^+ ion for 1,3,4-oxadiazoles V-X, in contrast to the corresponding ions of the 1,2,4 analogs, decompose mainly along pathways A and B and also with the formation of aroyl ions. In this case, the peaks with m/z 144 (type-g ions) are the maximum peaks in the spectra of V-IX. The peaks with m/z 116 are apparently the result of the further decomposition of the type-g ion through elimination of a CO molecule. The minor fragmentation for M^+ of V-X are accompanied by the formation of arylnitrile radical-ions as a result of breakage of the O–$C_{(5)}$

*The numbers given for the ions in the schemes are the corresponding m/z values.

TABLE 1. Characteristic Ions in the Mass Spectra of 3,5-Diaryl-1,2,4-Oxadiazoles I-IV

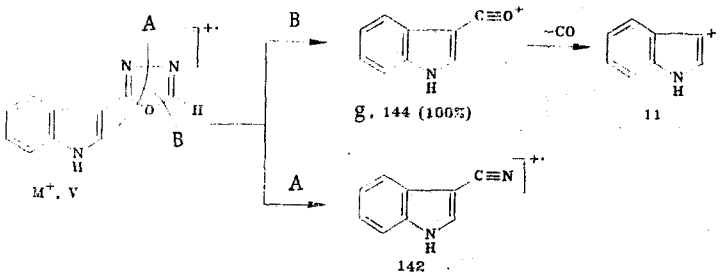
Compound	m/z Values (intensity as % of the maximum peak)											
	M^+	$[M-H]^+$	a	$[b-HCN]^+$	b	$[b-CO]^+$	$[R'C]^+$	c	d	c	f	f'
I	261 (12)	260 (3)	103 (38)	76 (3)	158 (58)	130 (14)	128 (100)	105 (20)	156 (74)	142 (7)	77 (8)	116 (2)
II	261 (53)	260 (6)	142 (100)	115 (7)	119 (28)	91 (3)	89 (6)	144 (73)	117 (36)	103 (3)	116 (62)	77 (3)
III	306 (72)	—	142 (75)	115 (34)	164 (14)	136 (4)	134 (100)	144 (68)	162 (28)	--	116 (49)	- -
IV	275 (17)	274 (3)	156 (22)	129 (72)	119 (46)	91 (25)	89 (13)	158 (55)	117 (3)	103 (7)	130 (100)	77 (15)

TABLE 2. Mass Spectra Of Compounds

Compound*	m/z Value (%)†
V	101 (27), 102 (28), 103 (29), 114 (8), 115 (23), 116 (33), 127 (5), 128 (37), 129 (52), 142 (13), 143 (10), 144 (100), 185 (M^+, 64)
VI	101 (10), 102 (7), 103 (7), 115 (13), 116 (24), 128 (14), 142 (17), 143 (9), 144 (100), 198 (24), 233/235 (M^+, 33/11)
VII	101 (11), 102 (11), 103 (12), 114 (5), 115 (10), 116 (33), 128 (15), 129 (54), 142 (12), 143 (5), 144 (100), 243 (34), 244 (13), 300 (M^+, 50)
VIII	105 (50), 115 (30), 116 (75), 117 (34), 118 (7), 142 (14), 143 (9), 144 (100), 204 (15), 205 (9), 261 (M^+, 23)
IX	101 (9), 102 (7), 103 (7), 104 (17), 105 (7), 115 (12), 116 (23), 120 (12), 128 (9), 129 (5), 142 (18), 143 (8), 144 (100), 150 (13), 204 (8), 276 (7), 305 (17), 306 (M^+, 41)
X	103 (26), 104 (9), 105 (27), 115 (6), 116 (12), 117 (10), 118 (5), 119 (6), 130 (100), 144 (32), 145 (13), 217 (6), 275 (M^+, 42).

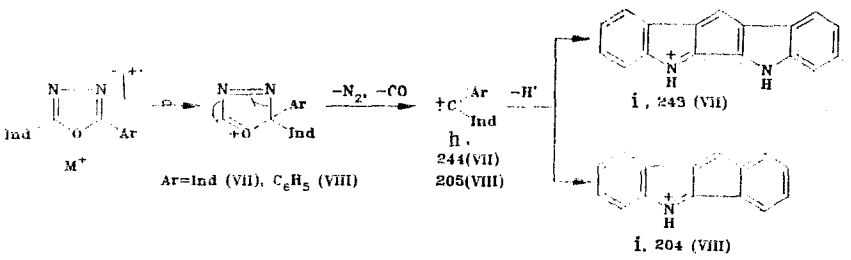
*2-(3'-indolyl)- (V), 2-chloromethyl-5-(3'-indolyl)- (VI), 2,5-bis(3'-indolyl)- (VII), 2-phenyl-5-(3'-indolyl)- (VIII), 2-(para-nitrophenyl)-5-(3'-indolyl)- (IX), 2-phenyl-5-[(3'-indolyl)methyl]-1,3,4-oxadiazole (X).
†Peaks are given in the range from 100 to M^+ with intensity ≥5%.

and N–N or O–$C_{(2)}$ and N–N bonds. When R^1 is not an aromatic substituent (V and VI), there are no peaks in the spectra for $[R^1CO]^+$ and $[R^1CN]^+$.



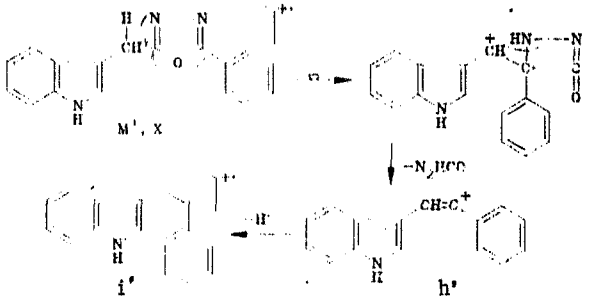
Benzyl cleavage with the formation of the maximum peak for the (3'-indolyl)methyl cation is the major fragmentation process for X upon electron impact. On the other hand, the decomposition pathways noted for the other 1,3,4-oxadiazoles (V-IX) are less pronounced.

The most diagnostic pathway for the decomposition of M^+ of 1,3,4-oxadiazoles VII and VIII which permits the reliable distinction of these compounds from other isomeric oxadiazoles is related to a rearrangement process. This process may be a consequence of the initial migration of an aryl group to the carbon atom bearing the other aryl group and subsequent cleavage of the oxadiazole ring:



The formation of type-h and type-i ions was noted for 2,5-diphenyl-1,3,4-oxadiazole [2]. A similar pathway for dissociative ionization was also found in the case of p-nitrophenyl derivative IX. However, this pathway is obtained not in M^+ but rather in the $[M - NO]^+$ and $[M - NO_2]^+$

ions, resulting in the formation of ions with m/z 220, 219, 204 and 203, respectively. In going to X which contains a methylene unit between the oxadiazole ring and the indole system, the N_2CHO species is eliminated with the formation of h' ions after migration of the phenyl group, while subsequent elimination of a hydrogen atom leads to a type-i' ion:



We should note that the peaks for ions b-d, g, h, h', i,i', $[R^1]^+$ and $[R^2]^+$ are the most important for the determination of the position of the aryl substituents and the nature of the oxadiazole ring. This is well illustrated in the case of isomeric phenyl(indolyl)oxadiazoles I, II and VIII. Thus, the finding of strong peaks of the $[IndCNO]^+$(1958)and $[IndCN_2]^+$ (156) ions, on one hand, and $[C_6H_5CO]^+$ (105) ions, on the other, in the spectrum of 1,2,4-oxadiazole I unequivocally proves the location of the indolyl group at $C_{(3)}$ and of the phenyl group at $C_{(5)}$. On the other hand, the spectrum of 3-phenyl-5-indolyl-1,2,4-oxadiazole II shows peaks for the $[C_6H_5CNO]^+$ (119), $[IndCO]^+$ (144) and $[C_6H_5CN_2]^+$ (117) ions indicating the opposite arrangement of these substituents in the 1,2,4-oxadiazole ring relative to isomer I. The mass spectrum of the third structural isomer VIII shows medium-intensity peaks for j (205) and i ions (204), which permits the assignment of this compound to the 1,3,4-oxadiazole series.

EXPERIMENTAL

The 1,2,4-oxadiazole (I-IV) and 1,3,4-oxadiazole derivatives (V-X) were prepared in our previous work [8]. The samples studied were crystalline substances with mp 159-161°C (I), 172-174°C (II), 242-244°C (III), 154-155°C (IV), 193-195°C (V), 202-204°C (VI), 172-173°C (VII), 263-264°C (VIII), 302-304°C (IX), and 110-114°C (X).

The mass spectra were taken on an LKB-2091 mass spectrometer with direct sample inlet into the ion source (70 eV ionizing electron voltage, 25 μA emission current and 200°C ion source temperature) with 90-150°C evaporation temperature for the samples.

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