MASS-SPECTRAL STUDY OF HETEROCYCLIC ANALOGS OF 4-DIMETHYLAMINO- AND 4-AZIDOCHALCONES

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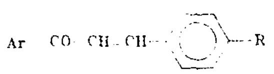
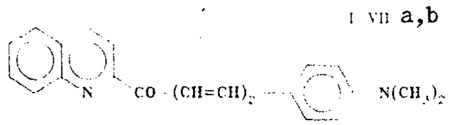
The predominant pathway in the mass-spectral fragmentation of 4-dimethylamino- and 4-azidochalcones under the influence of electron impact is cleavage of the aryl—CO and CO—CH bonds and localization of the charge on the fragment with the lower ionization energy. The characteristic "chalcone" rearrangement with the ejection of a molecule of CO from the molecular ion and subsequent cyclization and aromatization of the stilbene derivative is also observed; in the case of azides this process takes place only after the loss of a molecule of nitrogen by the molecular ion. The differences in the pathways of fragmentation of the hetero analogs make it possible to identify compounds with α, β, and γ orientations of the substituent relative to the heteroring nitrogen atom.

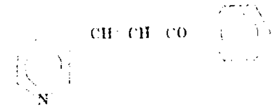
In this research we studied the behavior under the influence of electron impact (EI) of 4-dimethylaminochalcone (Ia) and 4-azidochalcone (Ib) as compared with the corresponding heterocyclic analogs IIa, b-VIIa, b, and IX and vinylog VIII.



I-VII a,b



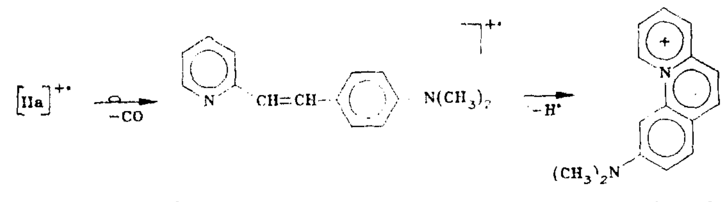
VIII



IX

I-VII: a) R = $N(CH_3)_2$; b) R = N_3; I) Ar = phenyl; II) Ar = 2-pyridyl; III) Ar = 3-pyridyl; IV) Ar = 4-pyridyl; V) Ar = 2-quinolyl; VI) Ar = 4-quinolyl; VII) Ar = 1-isoquinolyl

The molecular-ion peaks (M^+) in the mass spectra of all amines Ia-VIIa and VIII have the maximum intensity (see Table 1). A property common to all of the amines is also the presence in the spectra of peaks of $[M - 28]^+$ and $[M - 29]^+$ rearrangement ions, which may be associated either with fragmentation of the dimethylamino group [1] or with the successive ejection of a molecule of CO and an H atom [2]. The measured precise masses of these ions for Va (274.1456 and 273.1396) correspond to the compositions $C_{19}H_{18}N_2$ (calculated value 274.1466) and $C_{19}H_{17}N_2$ (calculated value 273.1388), i.e., $[M^+ - CO]$ and $[M^+ - CO, - H]$ processes are observed. It is known that in I ejection of a molecule of H_2 and cyclization to dimethylaminophenanthrene (the $[M - 30]^+$ ion) occur under the influence of EI after the ejection of a molecule of CO from M^+ and ring contraction to a dimethylaminostilbene structure [2]. For heterocyclic analogs of aminochalcone I the loss of only one H atom is observed after the $[M^+ - CO]$ process; this may be associated with aromatization as a result of cyclization at the N atom, as, for example, for the α-pyridine derivative:



For compounds with a substituent that is not in the α position relative to the nitrogen atom, in the case of aromatization one should have observed the loss of two H atoms to give $[M - 30]^+$ ions, as in the case of I; however, the mass spectra of these compounds contain peaks only $[M - 29]^+$ ions, i.e., the loss of only one H atom occurs. It might be assumed that this is associated either with a skeletal rearrangement through Dewar structures and subsequent

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TABLE 1. Mass Spectra of 4-Dimethylaminochalcone and Its Heterocyclic Analogs (20 eV)

Amine	m/z (I, % of I_{max})								
	M^+	$[M-1]^+$	$[M-15]^+$	$[M-28]^+$	$[M-29]^+$	ArH^+	F_1	F_2	F_4
Ia*	251 (100)	250 (33)	236 (2)	223 (8)	222 (14)	78 (3)	77 (24)	174 (36)	146 (16)
IIa	252 (100)	251 (4)	—	224 (7)	223 (20)	79 (4)	78 (1)	174 (66)	146 (27)
IIIa	252 (100)	251 (24)	237 (11)	224 (1)	223 (10)	—	78 (2)	174 (26)	146 (12)
IVa	252 (100)	251 (22)	237 (14)	224 (1)	223 (7)	—	—	174 (43)	146 (16)
Va	302 (100)	301 (3)	—	274 (28)	273 (44)	129 (14)	128 (1)	174 (54)	146 (25)
VIa	302 (100)	301 (17)	287 (24)	274 (4)	273 (17)	129 (5)	128 (1)	174 (42)	146 (17)
VIIa	302 (100)	301 (8)	287 (3)	274 (8)	273 (23)	129 (13)	128 (10)	174 (17)	146 (11)
VIII	328 (100)	327 (16)	331 (4)	300 (7)	299 (25)	129 (79)	128 (25)	174**	146 (27)

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*An additional peak of $[M-30]^+$ ions with m/z 221 (I 33%).

**Additional peaks of $[M-26]^+$ ions with m/z 302 (I 8%) and vinylogs of F_2 ions with m/z 174 + 26 = 200 (I 20%) and F_4 ions with m/z 146 + 26 = 172 (I 66%).

TABLE 2. Mass Spectra of 4-Azidochalcone and Its Heterocyclic Analogs (70 eV)

Azide	m/z (I, % of I_{max})*												
	M^+	$[M-26]^+$	M_1^+	$[M_1-1]^+$	$[M_1-26]^+$	$[M_1-27]^+$	$[M_1-28]^+$	$[M_1-29]^+$	F_3	ArH^+	F_1	F_2	F_4
Ib	249 (18)	223 (4)	221 (70)	220 (20)	195 (45)	194 (11)	193 (28)	192 (20)	105 (87)	78 (9)	77 (100)	144 (6)	116 (10)
IIb	250 (14)	224 (1)	222 (42)	221 (38)	196 (23)	195 (11)	194 (2)	193 (8)	106 (21)	79 (41)	78 (100)	144 (3)	116 (9)
IIIb	250 (18)	224 (6)	222 (74)	221 (32)	196 (45)	195 (8)	194 (9)	193 (24)	106 (65)	79 (51)	78 (100)	144 (7)	116 (17)
IVb**	250 (5)	224 (2)	222 (24)	221 (8)	196 (18)	195 (16)	194 (16)	193 (14)	106 (57)	79 (25)	78 (66)	144 (9)	116 (17)
Vb	300 (31)	274 (14)	272 (55)	271 (34)	246 (20)	245 (27)	244 (8)	243 (20)	—	129 (67)	128 (100)	144 (2)	116 (8)
VIb	300 (43)	274 (17)	272 (95)	271 (50)	246 (41)	245 (13)	244 (24)	243 (55)	156 (44)	129 (31)	128 (100)	144 (16)	116 (25)
VIIb	300 (26)	274 (18)	272 (67)	271 (49)	246 (36)	245 (25)	244 (8)	243 (23)	—	129 (51)	128 (100)	144 (1)	116 (10)
IX**	250 (6)	224 (2)	222 (33)	221 (4)	196 (3)	195 (14)	194 (39)	193 (44)	—***	79 (7)	78 (32)	144 (13)	116 (2)

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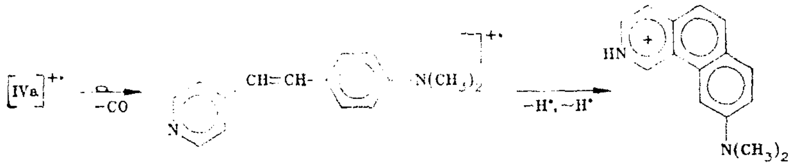
*$M_1^+ = [M-28]^+$, $F_3 = ArCO^+$, $F_1 = Ar^+$, $F_5' = [Ar\text{—}CH{=}CH\text{—}CO^+]$, Ar = 3-Py.

**The peaks with m/z 51 have I = 100%.

***F_5' 132 (I 45%).

cyclization of the type observed for the α derivative or with migration of one H atom to the heteroring nitrogen atom during aromatization of the cyclization products, as, for example, for the γ-pyridine derivative:

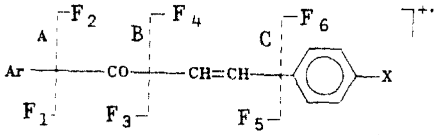


Peaks of $[M-28]^+$ ions are also observed in the mass spectra of azides Ib-VIIb and IX (see Table 2); in the low-energy (12 eV) spectra they have the maximum intensities. For these compounds one should have expected competition between processes involving the ejection of CO and N_2 molecules. The measured precise mass of the $[M-28]^+$ ion of Vb (272.0950) corresponds to the composition $C_{18}H_{22}N_2O$ (calculated value 272.0947), i.e., only the $[M^+ - N_2]$ process is primarily observed. In analogy with the fragmentation of phenyl azide [3], the $[M-28]^+$ ion then loses C_2H_2 and HCN molecules; in addition, the characteristic "chalcone" fragmentation — ejection of a molecule of CO — is observed for $[M-28]^+$ ions.

One's attention is directed to the presence in the mass spectra of the azides of peaks of $[M-26]^+$ ions that reach significant intensities, particularly in the low-energy region, as, for example, in the spectrum of VIIb [46% (12 eV)]. The formation of these ions can be explained by two processes: either by the ejection of a molecule of acetylene from the chalcone ligament — a process that is not observed for chalcone itself [2] — or by reduction of the nitrene in the ionization chamber, which was previously observed for phenyl azide [3]. The precise mass of the $[M-26]^+$ ion for azide Va (274.1070) corresponds to the composition $C_{18}H_{14}N_2O$ (calculated value 274.1103), which constitutes evidence in favor of the second process, i.e., $[M-26]^+ = [M - N_2, + 2H]^+$ (or $[M + 2H, - N_2]^+$).

The fragmentation of M^+ with the loss of acetylene is observed only for VIII, which contains two vinyl groups (the ion with m/z 302).

To evaluate other pathways for the fragmentation of analogs of Ia, b under the influence of electron impact (EI) it is convenient to regard the $[M-28]^+$ ion for azides as a pseudomolecular M_1^+ ion and to compare it with the molecular ion M^+ of the amines; the structures of these ions and the fragmentation processes can then be represented (disregarding the possible dehydroazepine structure of the nitrenephenyl fragment) in the form

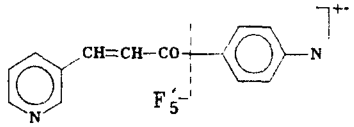


For amine M^+ X = $N(CH)_3$; for azide M_1^+ X = N

Fragmentation at the A bond is most characteristic for all of the investigated compounds; in the case of the amines the charge is localized primarily on the F_2 fragment — the peaks of these ions are second in intensity after the molecular ions in the spectra of the analogs of aminochalcone Ia (see Table 1). For the analogs of azidochalcone Ib, as a result of a similar fragmentation pathway, the charge is localized primarily on the F_1 fragment as compared with the F_2 fragment with m/z 144 (see Table 2). The peaks of both ions have relatively low intensities in the low-energy region of the spectrum (12 eV); however, their intensities increase substantially at an ionization energy of 70 eV; the peaks of the F_1 ions become the maximum peaks in the spectra.

A similar charge distribution is also observed in the case of fragmentation at the **B** bond: for the azides the charge is localized on the F_3 fragment, while for the amines it is localized on the F_4 fragment, which contains a dimethylamino group, with m/z 146. This sort of charge redistribution in the cleavage of the **B** bond from the F_3 fragment to the F_4 fragment on passing from the azides to the amines corresponds to the relationship of the ionization energies: nitrene-containing fragment > heterocyclic residue > dimethylanil fragment. In fact, the ionization energy of aniline is 7.14 eV [4], the ionization energy of the acylaryl fragment ranges from 8 to 9 eV [4], and the appearance energy of the peak of the phenylnitrenium ion in the mass spectrum of phenyl azide is 9.1 eV [5].

Fragmentation at the C bond is not characteristic for the investigated compounds — peaks of F_5 and F_6 ions are absent in the spectra. Compound Ia, in the spectrum of which a low-intensity F_6 peak with m/z 120 (5%) is observed, and isomer IX, in which ejection of nitrenephenyl radical F_6 (X = N) from M^+ leads to the appearance of an F_5' ion with m/z 132, constitute exceptions (see Table 2).



A comparison of the mass spectra of the azides and amines reveals certain peculiarities in the mass-spectral behavior of the isomeric compounds. Among the analogs of azidochalcone Ib the greatest difference is manifested in the case of fragmentation at the **B** bond: in the spectrum of 4-pyridyl derivative IVb the peaks of the F_3 (m/z 106) and F_4 (m/z 116) ions have increased intensities as compared with the peaks of 2- and 3-pyridyl derivatives IIb and IIIb, i.e., the presence of a nitrogen atom in the para position relative to the substituent weakens the **B** bond as compared with the presence of a nitrogen atom in the ortho and meta positions.

Similarly, in the spectra of 4-quinolyl azide VIb the peak of F_3 ions (m/z 156) has significant intensity, while peaks of these ions are not observed at all (neither at 12 eV nor at 70 eV) in the spectra of 2-quinolyl and 1-isoquinolyl azides Vb and VIIb.

The compounds with 2-pyridyl (IIa) and 2-quinolyl (Va) radicals stand out among the analogs of aminochalcone Ia — peaks of $[M - 15]^+$ ions, which are associated with the loss of a methyl group from the dimethylamino fragment [1] are absent in their mass spectra, and, on the other hand, the peaks of $[M - 28]^+$ and $[M - 29]^+$ ions, which are associated with the ejection of a molecule of CO and subsequent cyclization and aromatization, have increased intensities as compared with the spectra of the isomers. One's attention is directed to the increased intensities of the peaks of $[ArH]^+$ ions in the spectra of IIa, Va, VIIa, and VIII, which contain a substituent in the ortho position relative to the nitrogen atom of the heterocyclic ring. This is probably associated with the formation of $[ArH]^+$ ions due to migration of an H atom from the F_2 fragment to the heteroring nitrogen atom (in the F_1 fragment) in the case of cleavage of the **A** bond, and the ortho orientation of the F_2 fragment facilitates this migration.

Thus an examination of the mass spectra of heterocyclic analogs of 4-dimethylamino- and 4-azidochalcones makes it possible to ascertain common regularities and some peculiarities in the behavior of these compounds under the influence of electron impact. The predominant fragmentation pathway is cleavage of the aryl—CO and CO—CH bonds in the "chalcone" ligament with localization of the charge on the fragment with a lower ionization energy; in the case of the γ isomers the peaks of ions formed by cleavage of the CO—CH bond have higher relative intensities than in the case of the α and β isomers. The characteristic "chalcone" rearrangement with the ejection of a molecule of CO from M^+ and subsequent cyclization and aromatization of the stilbene derivative is observed; for azides this process occurs only after the loss of a molecule of nitrogen from M^+. In this case, on the other hand, in the spectra of the α isomers the peaks of ions formed as a result of rearrangement and cyclization have increased intensities. The observed differences in the fragmentation of the hetero analogs make it possible to identify compounds with α, β, and γ orientations of the substituent with respect to the heteroring nitrogen atom.

EXPERIMENTAL

The high-resolution mass spectra were recorded with a Hitachi M80B spectrometer with a system for processing Moscow Oblast Department of Public Health data; the ionizing-electron energies were 12 and 70 eV (for the azides) and 20 eV (for the amines), the emission current was 100 μA, and the temperature of the ionization chamber was 200°C.

All of the investigated compounds were synthesized by the method in [6] by condensation of the corresponding aldehyde with the acetylarene.

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