remove the sum of the bases. The extract was dried with anhydrous potassium carbonate and evaporated.

A 108-mg sample of adduct IVa was isolated in the preparative separation of 318 mg of the mixture of bases obtained in the reaction of vinylpyridine Ia with nitrile II. IR spectrum: 2250 cm^{-1}. PMR spectrum, δ: 1.9-2.4 (broad m, 4H, 6,7-CH_2), 2.9 (broad t, 2H, 8-CH_2), 3.95 (broad t, 1H, 5-CH), 7.1 (q, 1H, 3-H), 7.7 (broad d, 1H, 4-H), and 8.5 (broad d, 1H, 2-H). The picrate had mp 144-146°C (from methanol). Found: C 49.9; H 3.7; N 17.6%. $C_{16}H_{13}N_5O_7$. Calculated: C 50.1; H 3.4; N 17.9%. The mass spectrum coincided with the mass spectrum of IVa (Table 3). In addition, 23 mg of VI, with mp 43-45°C [1], was isolated.

The mass spectra of IVa-d, Va, and Vc are presented in Table 3. We were unable to isolate these compounds in individual form (except for IVa).

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MASS SPECTRA OF STEREOISOMERIC cis- AND trans-2-ALKYL-3-ARYL(HETARYL)-4-(METHOXYCARBONYL)-3,4-DIHYDRO-1H-ISOQUINOL-1-ONES AND 1,2,3,4-TETRAHYDROISOQUINOLINES

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UDC 543.51:547.833.3.7.8.9:541.634

The molecular ions of the trans isomers of the investigated compounds are more stable than those of the cis isomers. Their principal fragmentation pathways involve retrodiene fragmentation of the molecular ions, which proceeds with greater probability in the case of the cis isomers, or loss of substituents from the 4 or 3 position. The latter process is characteristic only for tetrahydroisoquinoline derivatives, is not observed for 3,4-dihydro-1H-isoquinol-1-one derivatives, and proceeds more readily in the case of the trans isomers.

We recently described the synthesis and stereochemistry of 3,4-disubstituted derivatives of 1,2,3,4-tetrahydroisoquinoline and 3,4-dihydro-1H-isoquinol-1-one [1-5].

Since difficulties were encountered in the establishment of the stereochemistry of these compounds by NMR methods in a number of cases, to establish the dependence of the mass-spectral fragmentation on the stereochemistry of compounds of this type we studied the behavior of a series of cis and trans isomers of Ia-g and IIa-e, as well as the isomeric trans-III and E-IV, under the influence of electron impact.

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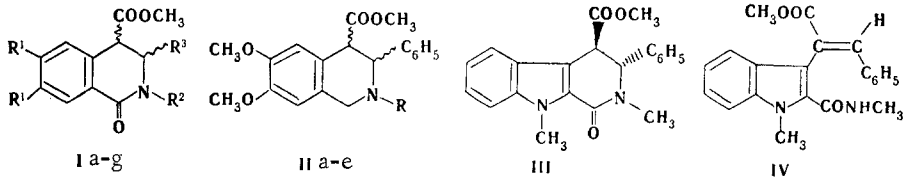
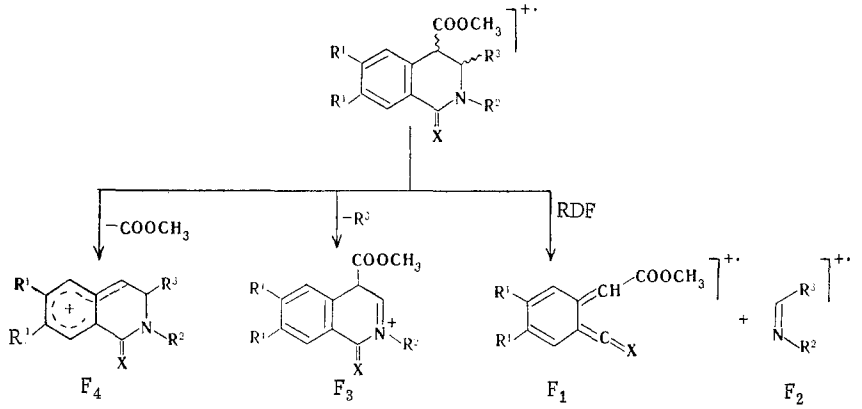


I a-g II a-e III IV

I a $R^1=CH_3O$; $R^2=CH_3$; $R^3=C_6H_2$; b $R^1=CH_3O$; $R^2=CH_3$; $R^3=3,4\text{-}CH_2O_2C_6H_3$; c $R^1=H$; $R^2=CH_3$; $R^3=3,4\text{-}(CH_3O)_2C_6H_3$; d-g $R^1=H$; $R^3=$ 1-methyl-3-indolyl; d $R^2=CH_3$; e $R^2=C_6H_5$; f $R^2=C_3H_7$; g $R^2=CH_2C_6H_5$; II a $R=H$; b $R=CH_3$; c $R=C_2H_5$; d $R=C_3H_7$; e $R=C_6H_5CH_2$

The mass spectra were recorded with Varian MAT-311 and AEI MS-30 spectrometers at an ionization energy of 70 eV. The reproducibility of the mass spectra of the same compounds recorded with different spectrometers was no less than 5-8%.



F_4 F_3 F_1 F_2

X = O, H_2

An analysis of the mass spectra obtained makes it possible to note that a rather intense molecular-ion peak is observed for all of the compounds and that the stability of the molecular ions (W_M) of the trans isomers is always higher than that of the cis isomers. The principal fragmentation of the molecular ions of I and II proceeds via three pathways. The first and principal of these pathways entails retrodiene fragmentation (RDF) of the isoquinoline ring with elimination of nitrogen and C_3 atoms with the corresponding substituents. The analogous fragmentation of tetrahydroisoquinolines has been previously noted [6, 7]. As expected, the retrodiene fragmentation of the molecular ions of the cis isomers proceeds more readily (Table 1). The intensities of the peaks of the resulting F_1 and F_2 ions are associated with the presence or absence of electron-donor substituents in each of them. Thus the peaks of F_2 fragments are more intense in the mass spectra of Ic-g, which contain an indole residue or a dimethoxyphenyl grouping as substituent R^3, while the peaks of F_1 ions, which also include dimethoxyphenyl groups, are more intense in the mass spectra of Ia, b and IIa-e.

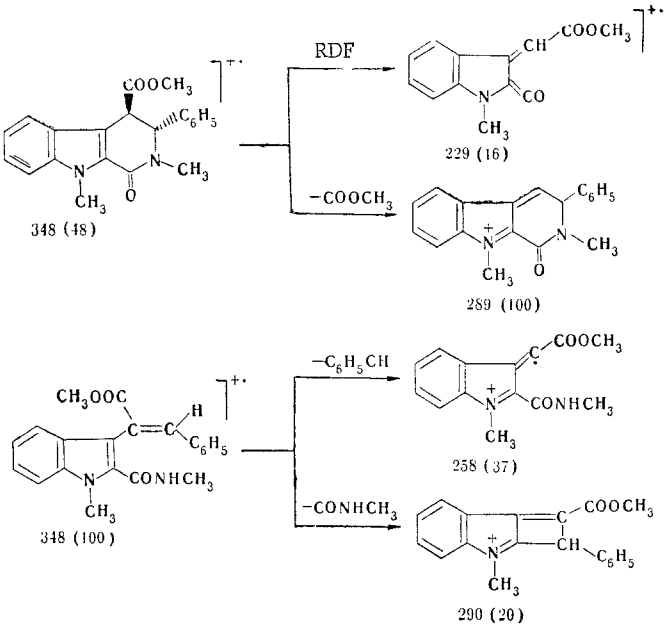
The second most significant fragmentation pathway for the molecular ions of the investigated compounds is the loss of a methoxycarbonyl group (the F_4 ion), which proceeds more efficiently in the case of the cis isomers ($I_{F_4}/I_{cis\text{-}M} > I_{F_4}/I_{trans\text{-}M}$). Finally, the third characteristic fragmentation pathway for tetrahydroisoquinolines entails elimination of of substituent R^3; it also proceeds more efficiently (the F_3 ion) for the cis isomers. However, it should be emphasized that this fragmentation pathway is characteristic only for IIa-e, since the amide nitrogen atom in Ia-g is apparently incapable of stabilizing the resulting positive charge. All of the indicated fragmentation pathways were confirmed by determination of the precise molecular masses and the empirical formulas of the fragments obtained by means of the high-resolution mass spectra.

Thus when one is dealing with a pair of isomeric compounds, it is possible to rigorously assign their configuration on the basis of the mass spectra. However, these difficulties are not great enough to make the assignment with respect to the mass spectrum of one of the isomers. As regards the differences between cyclic III and open form IV, the differences here are more noticeable. Thus the loss of a CH_3NHCO fragment (the ion with m/e 290) by the

TABLE 1. Intensities of the Peaks of the Characteristic Ions of I and II (Σ_{39}%)

Compound	Configuration	W_M	F_1		F_2		F_4		F_3	
			I	I/I_M	I	I/I_M	I	I/I_M	I	I/I_M
Ia	trans	6,2	11,6	1,8	4,2	0,70	5,5	0,89	—	—
Ib	cis	5,2	26,8	5,2	0,35	0,07	2,5	0,55	—	—
		6,4	25,6	4,0	0,40	0,06	3,1	0,50	—	—
Ic	trans	7,3	5,4	0,95	12,3	2,16	8,3	1,40	—	—
	cis	10,5	7,1	0,83	15,7	1,84	7,9	0,93	—	—
Id	trans	10,0	0,6	0,07	17,0	2,2	2,4	0,26	—	—
	cis	15,4	0,8	0,05	18,6	1,5	3,9	0,25	—	—
Ie	trans	17,5	—	—	13,0	0,94	19,4	1,08	—	—
	cis	25,0	—	—	14,9	0,74	24,4	0,91	—	—
If	trans	4,4	0,4	0,09	2,7	0,6	1,4	0,32	—	—
	cis	5,6	0,2	0,05	1,8	0,4	1,0	0,18	—	—
Ig	trans	4,5	0,4	0,1	2,2	0,6	0,3	0,07	—	—
	cis	5,4	0,3	0,06	1,0	0,2	0,2	0,04	—	—
IIa	trans	5,5	15,6	3,2	0,8	0,2	2,9	0,61	0,9	0,25
	cis	8,1	13,4	1,7	0,7	0,09	4,4	0,52	1,6	0,18
IIb	trans	3,2	12,9	4,2	0,94	0,29	2,5	0,78	1,05	0,35
	cis	8,1	9,6	1,4	0,8	0,1	3,4	0,42	2,5	0,30
IIc	trans	3,5	10,5	4,0	0,6	0,2	2,7	0,89	1,4	0,50
	cis	5,4	8,1	1,9	0,3	0,1	4,1	0,76	2,0	0,41
IId	trans	1,6	10,6	8,8	0,5	0,4	3,3	2,0	0,8	0,58
	cis	2,7	8,3	3,3	0,5	0,3	3,8	1,4	1,1	0,43
IIe	trans	0,9	11,5	15,7	0,5	0,5	0,8	1,1	0,9	1,1
	cis	2,0	5,2	2,3	0,3	0,2	0,8	0,5	1,0	0,55

molecular ion is characteristic for the mass-spectral fragmentation of IV, while the molecular ion of III eliminates a methoxycarbonyl group (the ion with m/e 289). In addition, an



intense peak of an ion with m/e 258 [(M—C_6H_5CH)] which is absent in the mass spectrum of cyclic form III, is present in the mass spectrum of IV.

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HETEROCYCLIC ANALOGS OF PLEIADIENE.

51.* N-ACYLPERIMIDINES: RING OPENING INSTEAD OF DEACYLATION UNDER THE INFLUENCE OF NUCLEOPHILES

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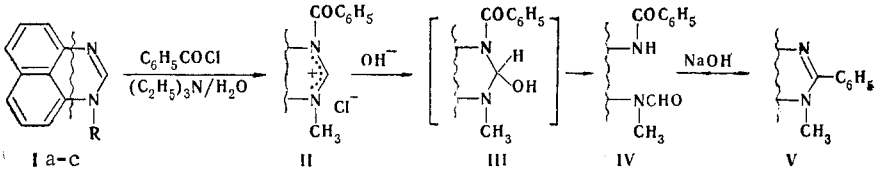
N-Acetyl- and N-benzoylperimidines, as well as quaternary salts based on them, were synthesized. It is shown that the heteroring is opened to give N-acyl derivatives of 1,8-naphthalenediamine by the action of nucleophiles on N-acylperimidines and N-benzoylperimidine salts.

We have previously observed recyclization in series of 1-substituted perimidines (Ia, for example), which consists in opening of their heteroring by the action of aromatic acid chlorides (the scheme for benzoyl chloride is presented below) in the presence of triethylamine to give 1,8-naphthalenediamine derivative (IV) [2-4]. The latter is readily converted to a 1,2-disubstituted perimidine (V) when it is heated with alkali, during which the radical of the acyl chloride used is incorporated in the 2 position. It was assumed that the first step in the process yields an N-acylperimidinium salt (II), which adds a hydroxide ion extremely readily to give pseudobase III, the open form of which is a compound of the IV type.



I a-c II III IV V

I a R = CH_3; b R = CH_3CO; c R = C_6H_5CO

A distinctive feature of the reaction is that it does not take place in a number of other diazole systems, particularly benzimidazoles and naphthimidazoles, the 1-substituted derivatives of which remain unchanged under the same conditions. It might have been assumed that the possibility of recyclization for Ia is due to two circumstances: the high positive charge in the 2 position of perimidines [5, 6] and the increased strength of the N–acyl bond in salts II. The combination of these factors should result in attack by the bases on the μ-carbon atom to give pseudobase III rather than attack on the carbonyl carbon atom of salts II (in this case the starting compound is regenerated, i.e., the reaction does not occur). In this connection, the aim of the present research was to obtain N-acylperimidines and their quaternary salts and to study their properties, particularly their behavior with respect to nucleophiles. It should be noted that the simplest N-acylperimidines have heretofore been unknown. The so-called perinones [7] should perhaps be regarded as a close model of them.

*See [1] for Communication 50.

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