phenyl, but the proton affinity is higher in aniline than in aminofurazan. Hence, the reason why the nucleophilic activity of aminofurazan is appreciably lower than for aniline is that the +I-effect of furazanyl is lower than that of phenyl.

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THERMOLYSIS OF QUATERNARY SALTS OF 2,3,3-TRIMETHYLINDOLENINE AND INDOCARBOCYANINES

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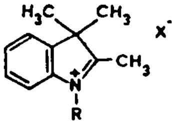
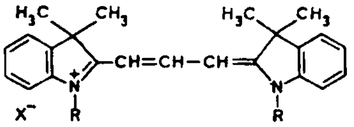
The rearrangement of alkyl- and aryl-substituted indoles, indolenines, and quaternary salts of the latter, which involves the migration of the hydrocarbon substituents between the 2 and 3 positions, has been the subject of many studies (e.g., [1,2]). The conversion of 2-ethyl- and 2-isopropyl-3,3-dimethylindolenine methiodides to 3-ethyl- and 3-isopropyl-2, 3-dimethylindolenine methiodides has been reported [1]. The authors assumed that any 2,3,3-trialkylindolenine alkiodide undergoes decomposition at a certain temperature to a 1,2,3-trialkylindole and an alkyl iodide as a result of elimination of the alkyl group from the 2 position and migration of the 3-alkyl group to the 2 position. The resulting alkyl iodide subsequently enters the 3 position of the indole. However, no evidence of this rearrangement pathway was presented.

In the present research we investigated the pathways of the thermal transformations of quaternary 2,3,3-trimethylindolenine salts (Ia-d) and indocarbocyanine salts (IIa-d) with the aid of pyrolytic gas chromatography.



Ia-d



IIa-d

I,II a-c R=CH_3; d R=C_2H_5; a,d X=I; b X=Br, c X=Cl

The investigated compounds were heated to 300°C in the vaporization chamber of a gas chromatograph with a flame-ionization detector. The pyrolysis products were identified from the chromatographic characteristics of the individual compounds, the presence of which was assumed in the pyrolyzate, and also from the UV spectra of the isolated fractions of the pyrolyzate. Data on the compositions and structures of the chromatographically identified compounds with an indication of the relative retention times (α_{rel}) and the relative percentages of each of them in the mixture are presented in Table 1.

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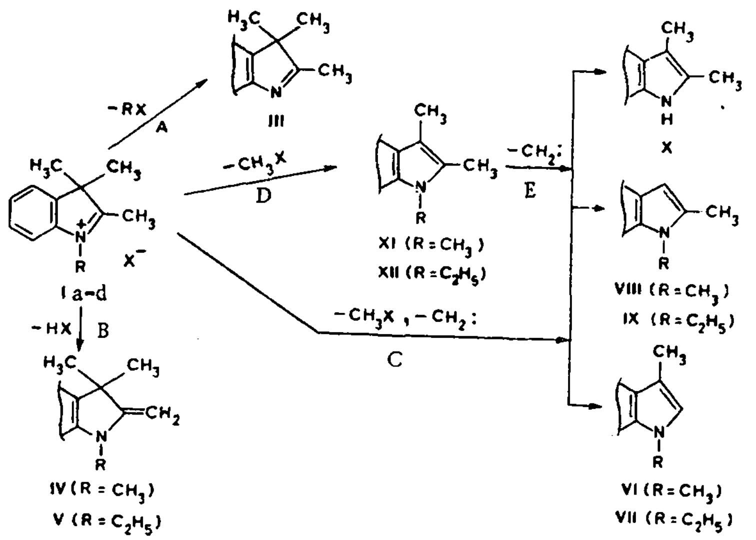
The results of the study show that the thermal destruction of the 2,3,3-trimethylindolenine quaternary salts (I) takes place via several principal pathways (Scheme 1). It was shown by chromatography that methane, ethylene, ethane, and cyclopropane are formed as volatile products in the pyrolysis of Ia. The presence of cyclopropane in the hydrocarbon mixture definitely attests to the possibility of the formation of carbene in the pyrolysis of Ia [7]. The formation of 2,3,3-trimethylindolenine (III) occurs as a result of elimination of the alkyl group attached to the nitrogen atom in the form of an alkyl halide (Pathway A), while the formation of 1-alkyl-3,3-dimethyl-2-methyleneindolines (IV, V) occurs as a result of splitting out of a hydrogen halide (Pathway B).

Scheme 1



It was noted that the latter are formed under relatively mild conditions (at 20-40°C below the melting points of the corresponding quaternary salts). The splitting out of a methyl group from the 3 position in the form of methyl iodide (Pathway D) leads to 1-methyl- or 1-ethyl-2,3-dimethylindoles (XI, XII). The isolation of a mixture of 1,3- (VI), 1,2- (VIII), and 2,3-dimethylindole (X) in the pyrolysis of Ia can be explained by competitive splitting out of methyl iodide and carbene directly from the quaternary salt (Pathway C) and through the intermediate formation of 1,2,3-trimethylindole (XI) (Pathway D).

A study of the competitive reactions involved in the pyrolysis of Ia and XI by a comparison of the areas of the peaks of the disubstituted indoles (VI, VIII, and X) showed that reactions via Pathways C and E are approximately equally probable.

A small amount of 1,3,3-trimethyl-2-methyleneindoline (IV) and an appreciable amount of 1,2,3-trimethylindole (XI) are detected among the volatile products of the pyrolysis of Id, along with III, V, and XII (Pathways A, B, and D). This constitutes evidence for the possibility of migration of the 3-methyl group to the 1 position (III → XI), elmination of carbene from the N-ethyl substituent (V → IV), or other more complex rearrangements.

The production of a mixture of dialkylindoles (VI-X) in the pyrolysis of Id can also be explained by reaction via Pathways C and E. It is also possible that these or other dialkylindoles are formed by more complex multistep rearrangements associated with reactions involving splitting out and migration of alkyl groups to the 1,2, and 3 positions of quaternary salt Id and of indolines IV and V or from the 3 position of indolenine III. However, it follows from the results of the study that, in addition to the reaction pathways proposed in [1] for the pyrolysis of quaternary 2,3,3-trimethylindolenine salts (I), other processes involving the elimination and migration of alkyl groups occur.

TABLE 1. Relative Retention Times and Relative Percentages (%) of the Volatile Products of the Pyrolysis of Quaternary Salts Ia-d and Indocarbocyanine Salts IIa-d

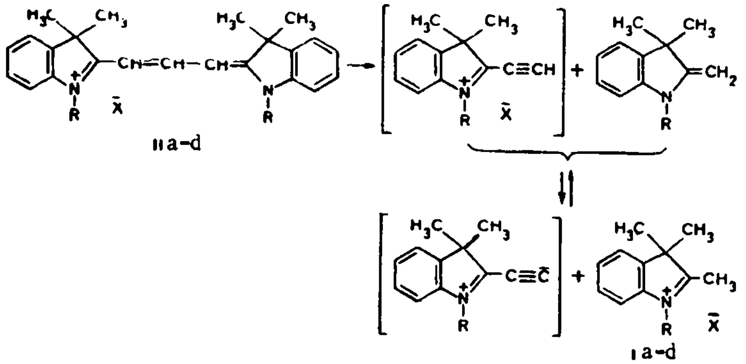
Compound	Volatile pyrolysis products (preparative method)	α_{rel}	Relative percentages							
			Ia	Ib	Ic	Id	IIa	IIb	IIc	IId
III	2,3,3-Trimethylindolenine (3)	1,00	8,3	16,7	31	6,3	9	12,8	17	4,8
IV	1,3,3-Trimethyl-2-methyleneindoline (3)	1,37	4	13,5	17	2,7	4	17,3	59	0,6
V	1-Ethyl-3,3-dimethyl-2-methyleneindoline (4)	1,78				5,4				4,6
VI	1,3-Dimethylindole (5)	1,89	1,8	2,9	10	0,6	9	4,1	4,0	
VII	1-Ethyl-3-methylindole (5)	2,44				1,0				9
VIII	1,2-Dimethylindole (5)	2,55	1,9	2,9	1,3	3,3	4	6,0	2,0	
IX	1-Ethyl-2-methylindole (6)	2,66				1,3				1,8
X*	2,3-Dimethylindole (6)	3,28	8	10	2,7	6,4	5	3,8	2,0	1,4
XI*	1,2,3-Trimethylindole (6)	4,44	76	54	38	10	69	56	16	14
XII	1-Ethyl-2,3-dimethylindole (6)	5,00				63				64

*These samples were provided by I. I. Grandberg and L. G. Yudin.

The data presented in Table 1 on the relative percentages of volatile products of the pyrolysis of I constitute evidence for the dependence of the thermal destruction on the character of the anion. Pathway D with the formation of XI is the preferred process in the pyrolysis of iodide Ia, while reactions via Pathways A and B with the formation of, respectively, III and IV are of considerably lesser significance. The amount of XI becomes considerably smaller in the pyrolysis of bromide Ib, although it still predominates (Pathway D), whereas the amounts of products of pyrolysis via Pathways A and B (III and IV) increase appreciably, and their overall percentages become comparable to the percentage of XI in the mixture. This ratio changes to an even greater extent in favor of III and IV in the pyrolysis of chloride Ic. This change in the ratio of the products in the pyrolyzates of Ia-c can be explained by the existence of crystalline quaternary salts I in the form of ion pairs [8] with different degrees of transfer of the negative charge of the anion to the cation in accordance with the nucleophilicity of the anion. Since the degree of charge transfer increases on passing from the chloride to the bromide and iodide, a proton of the methyl group in the 2 position and a methyl cation from the I position are more readily eliminated in the case of chloride Ic and with greater difficulty in the case of iodide Ia, since bromide Ib occupies an intermediate position in this series. The ratio of the 1,3- (VI), 1,2- (VIII), and 2,3-dimethylindole (X) also changes on passing from iodide Ia to bromide Ib and chloride Ic. Thus the VI:VIII:X ratio in the case of Ia is 2:2:8, as compared with 3:3:10 for Ib and 10:1:3 for Ic. These ratios show that the elimination of carbene from the methyl group in the 3 position of Ia-c to give VIII is negligible in all cases. The splitting out of carbene from the 2-methyl group of Ia and Ib is of minor significance; however, despite the decrease in the amount of intermediately formed 1,2,3-trimethylindole (XI), it is a significant process in the case of Ic. On the other hand, the elimination of carbene from the methyl group in the 1 position to give X is an appreciable process in the case of Ia and Ib but is negligible in the case of Ic; this is also associated with the decrease in the yield of XI.

It is apparent from Table 1 that the compositions and structures of the volatile products of the pyrolysis of indocarbocyanines IIa-d are similar to the compositions and structures of the pyrolyzates of the corresponding quaternary salts Ia-d; this evidently indicates the formation of the latter in the pyrolysis of the dyes. As in the case of the corresponding quaternary salts, the relative percentages in the pyrolyzates of 2,3,3-trimethylindoleninine (III) and particularly 1,3,3-trimethyl-2-methyleneindoline (IV) increase successively on passing from iodide IIa to bromide IIb and chloride IIc, whereas the relative percentage of 1,2,3-trimethylindole (XI) decreases. One may imagine the following scheme for the thermal conversions of the indocarbocyanines (Scheme 2).

Scheme 2



Ethynyl derivatives of indolenine were not detected among the volatile products of pyrolysis of the dyes; this may be explained by their instability.

EXPERIMENTAL

Compounds III-IX and XII were obtained by the methods in [3-6]. Chromatography was carried out with a Khrom 3-IKZ chromatograph with a pyrolytic adapter and a flame-ionization detector. The pyrolysis temperature was 300°C.

Analysis of the Hydrocarbon Fraction of the Pyrolyzate. The column was 3 m long and had a diameter of 3 mm, the stationary phase was Porapak Q (60-80 mesh), the thermostat temperature was 40°C, and the carrier-gas (nitrogen) flow rate was 20 ml/min.

Analysis of the High-Boiling Fraction of the Pyrolyzate. The column was 2 m long and had a diameter of 3 mm, the solid support was Cellite 545 (50-60 mesh), the stationary phase was Apiezon L (15% of the mass of the packing), the thermostat temperature was 130°C, and the carrier-gas (nitrogen) flow rate was 20 ml/min.

The individual compounds were accumulated with a Khrom 3-IKZ chromatograph with the aid of a preparative adapter.

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