HETEROCYCLIC ANALOGS OF PLEIADIENE.

54.* SYNTHESIS, BASICITIES, AND BEHAVIOR WITH RESPECT TO ELECTROPHILIC AGENTS OF 2-FLUOROMETHYL- AND 2-DIFLUOROMETHYLPERIMIDINES. SYNTHESIS OF PERIMIDINE-6(7)-CARBOXYLIC ACIDS

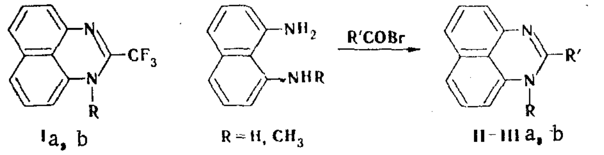
G. G. Yurchuk and A. F. Pozharskii

UDC 547.856.7'221.07

2-Fluoromethyl derivatives of perimidine and 1-methylperimidine were obtained by the reaction of naphthalene-1,8-diamines with bromides of fluoroacetic acids. It is demonstrated in the case of acidic deuterium exchange and trifluoroacetylation that the decrease in the basicity in the 2-methyl-, 2-fluoromethyl-, 2-difluoromethyl-, and 2-trifluoromethylperimidine series promotes electrophilic substitution in the naphthalene ring. The previously unknown 6(7)-carboxylic acids of the perimidine series were obtained by alkaline hydrolysis of the trifluoroacetyl group.

We have previously shown [2, 3] that the introduction of perfluoroalkyl groups in the 2 position of the perimidine molecule substantially modifies its physicochemical properties. Thus, for example, in contrast to simple perimidines, 2-trifluoromethylperimidines (I) are readily acylated in the naphthalene ring by trifluoroacetic anhydride. It has been assumed that the reason for this is the low basicity of 2-perfluoroalkylperimidines, as a consequence of which they react with electrophiles in the base form rather than in the form of the unreactive cations. In order to make a further study of this problem in the present research we synthesized 2-difluoromethyl- and 2-fluoromethylperimidines (II, III) and studied their behavior with respect to two electrophilic agents, viz., trifluoroacetic anhydride and deuterated acetic acid (CD_3COOD). It was assumed that the stepwise increase in the basicities in the order III > II > I would be accompanied by an increase in the concentration of the cation of the substrate in the reaction mixture and by a gradual decrease in the reactivity.

Perimidines II and III were obtained in ~70% yields by the action of fluoro- and difluoroacetyl bromides on naphthalene-1,8-diamine and its N-methyl derivatives.



I–III a R=H; I–III b R=CH_3; II a,b R'=CHF_2; III a,b R'=CH_2F

Data on the basicities of the investigated compounds and their behavior in trifluoroacetylation and acidic deuterium exchange are presented in Table 1. It is apparent from Table 1 that the introduction of one fluorine atom in the methyl group of 2-methylperimidine gives rise to a 2.7-2.9 pK_a unit decrease in the basicity, while the overall effect of three fluorine atoms in Ia is 8.4 orders of magnitude.

As in the case of I [3], the trifluoroacetylation of II and III was carried out at 100°C in a sealed ampul with excess trifluoroacetic anhydride. The process does not take place at an appreciable rate at lower temperatures. In contrast to 2-methylperimidine and

---

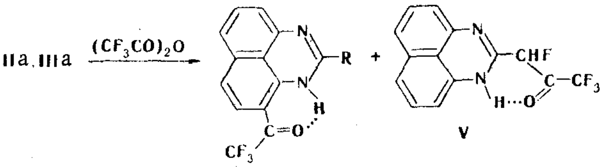
*See [1] for Communication 53.

Rostov State University, Rostov-on-Don 344006. Translated from Khimiya Geterotsiklicheskikh Soedinenii, No. 8, pp. 1106-1113, August, 1981. Original article submitted November 19, 1980.

TABLE 1. Basicity Constants, pK_a Values, and Behavior with Respect to Electrophilic Agents of I-III

Compound	pK_a (in CH_3CN)	Overall yield of trifluoroacetylation products, %	No. of protons exchanged with CD_3COOD
Ia	6,30	86 [3]	1,3
Ib	6,64	58 [3]	0,6
IIa	8,99	67	1,0
IIb	9,36	49	0,4
IIIa	11,87	32	2,0 (CH_2F)
IIIb	12,30	40	2,0 (CH_2F)
2-Methylperimidine	14,70 [4]	0	0

perimidine (pK_a 13.7 [4]), 2-fluoromethylperimidines (III) do undergo trifluoroacetylation, although the products are obtained in relatively low yields. A decrease in the basicity by two to three orders of magnitude evidently creates a small but sufficient (for the reaction) concentration of the free base in the mixture. When a second and a third fluorine atom are introduced successively in the 2-methyl group, the ease of trifluoroacetylation increases even more, as evidenced by the increase in the overall yields of the reaction products (Table 1). It should be noted that, as in the case of 2-trifluoromethylperimidines I [3], the pathway of trifluoroacetylation of II and III depends markedly on whether or not the pyrrole N—H group is free. The N—H-unsubstituted Ia [3], IIa, and IIIa give exclusively an ortho-acylation product (IV), in which there is a strong intramolecular hydrogen bond (IHB). The signal of the chelated proton of the N—H group shows up in the PMR spectra of IV at δ 12.3 ppm. The $\nu_{C=O}$ band in the IR spectra is shifted to 1625 cm^{-1} as a consequence of strong conjugation, while the ν_{N-H} band does not show up even in the spectra of dilute solutions in chloroform. Yet another compound containing an IHB was isolated in the acylation of 2-fluoromethylperimidine (IIIa). The structure of a product involving trifluoroacetylation in the CH_2F group (V) was assigned to it on the basis of PMR spectroscopic data (the doublet from the protons of the CH_2F group had an integral intensity of one proton unit).

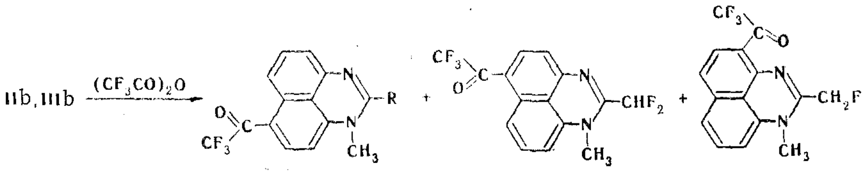


IVa, b IV a R=CHF_2; IV b R=CH_2F

In contrast to IIa and IIIa, their N-methyl derivatives are acylated primarily in the para positions. Thus a mixture of 6- and 7-trifluoroacetyl derivatives in a ratio of 1:1 was isolated in an overall yield of 49% in the case of 1-methyl-2-difluoromethylperimidine (IIb). We were able to separate the mixture by chromatography, and a 7-substituted structure (VIa) was assigned to the more deeply colored isomer (in analogy with the 6- and 5-nitro derivatives of 1-methylperimidine [5]). The difference in the λ_{max} values for the long-wave absorption bands of the two isomers is 18 nm. Compounds VIa and VII are orange and yellow, respectively. The PMR spectra of the two substances are very similar, and a characteristic peculiarity of them, which is also peculiar to other 6(7)-acylperimidines [3, 6], is the presence at weak field (8.5 ppm) of a doublet of second peri proton that is deshielded by a carbonyl group. We also isolated two isomeric monotrifluoroacetyl-substituted compounds in the trifluoroacetylation of 1-methyl-2-fluoromethylperimidine (IIIb). A 7-substituted structure (VIb) was assigned to the compound formed in greater amounts (29%) on the basis of the presence in the PMR spectrum of a doublet of a peri proton at 8.5 ppm. The spectrum of the second substance, which was formed in 11% yield, did not contain a doublet at weak field and thus was not a p-acyl-substituted compound. Since the N-methyl group interferes with trifluoroacetylation in the 9 position [3, 6], one must assume that this compound is 1-methyl-2-fluoromethyl-4-trifluoroacetylperimidine (VIII).

Thus, the results of these experiments confirmed the assumption that the ease of trifluoroacetylation in the perimidine series increases as the basicity of the molecule decreases. However, this conclusion is not extended to those weakly basic compounds whose naphthalene ring already contains substituents that inhibit electrophilic-substitution re-

]



VIa, b VII VIII

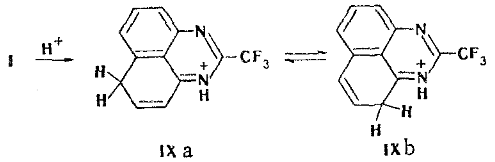
VI a R=CHF₂; VI b R=CH₂F

actions (for example, NO_2, acetyl, etc.). Thus, 6(7)-nitroperimidine (pK_a 10.3 [5]) and 4(9)-acetylperimidine do not undergo trifluoroacetylation.

Further confirmation of these principles was obtained by a study of acidic deuterium exchange in the perimidine series. The process was carried out under the following standard conditions: The sample was heated in a certain amount of d_4-acetic acid at 80°C for 20 min, after which the solution was maintained at room temperature for another 5 h. The course of the reaction was followed from the change in the integral intensities of the signals of the protons in the PMR spectrum of the mixture. We found that perimidine and 1-methyl- and 2-methylperimidines under these and more severe conditions (refluxing in CF_3COOD for 3 h) do not undergo H–D exchange either in the naphthalene ring or in the methyl groups.* 2-Fluoromethylperimidines IIIa, b also did not undergo exchange of the protons of the naphthalene ring in CD_3COOD, but the protons of the CH_2F group were completely exchanged. The possibility of the latter reaction is evidently determined by the tendency of the methylene protons to undergo tautomerization under the influence of the fluorine atoms. Exchange of the H–D protons of the naphthalene ring, which takes place relatively slowly in CD_3COOD but considerably more rapidly in CF_3COOD, also becomes possible with difluoromethylperimidines. Thus when Ib is heated in CF_3COOD at 100°C for 1 h, 2.5 protons are exchanged, whereas only 0.6 of a proton is exchanged in CD_3COOD under standard conditions. Unfortunately, the complex form of the PMR spectra made it impossible to establish the sequence of exchange of the protons, although, in analogy with the behavior of 2-methylperimidine in D_2SO_4 [8], it may be assumed that the reaction involves only the o- and p-hydrogen atoms of the naphthalene ring.

We were unable to accomplish deuterium exchange in 6(7)-nitro-2-methylperimidine by means of CD_3COOD or CF_3COOD, although the basicity of this compound (pK_a 10.9) made it possible to hope that a certain amount of the free base is present in the mixture. As in the attempts to trifluoroacetylate similar compounds, the reaction evidently does not take place in this case because of deactivation of the naphthalene ring by the nitro group.

One of the interesting peculiarities of 2-perfluoroalkylperimidines, particularly I, which we previously noted in [2], is the development of a bright-red coloration when they are dissolved in strong acids (concentrated HCl, CF_3COOH, etc.). Since the N protonation of perimidines usually does not affect their color and electronic absorption spectra [9], it was assumed that I undergoes C protonation to give cations of the IX type:



IX a IX b

In fact, the electronic absorption spectrum of 2-trifluoromethylperimidine in trifluoroacetic acid changes markedly as compared with the spectrum in methanol or acetic acid: A long-wave maximum appears in it at 440-450 nm (Table 2 and Fig. 1a). In this connection, it seemed of interest to examine the behavior of perimidines II and III in strongly acidic media. We found that the spectra of II in CF_3COOH also change and that II in CF_3COOH give a red coloration (Table 2 and Fig. 1b) that is associated with the presence of an absorption maximum at 435 nm. 2-Fluoromethylperimidines III retain their yellow coloration under these conditions, and their electronic spectra in the long-wave region do not change on passing

---

*However, we assumed that when perimidine is heated in an $NaOH–C_2H_5OD$ system, the protons in the 4 and 9 positions undergo gradual exchange, which amounts to ∿50% after 5 h. Thus in this case, as in reactions with allyl and benzyl halides [7], the amibent character of the perimidine N anion is manifested.

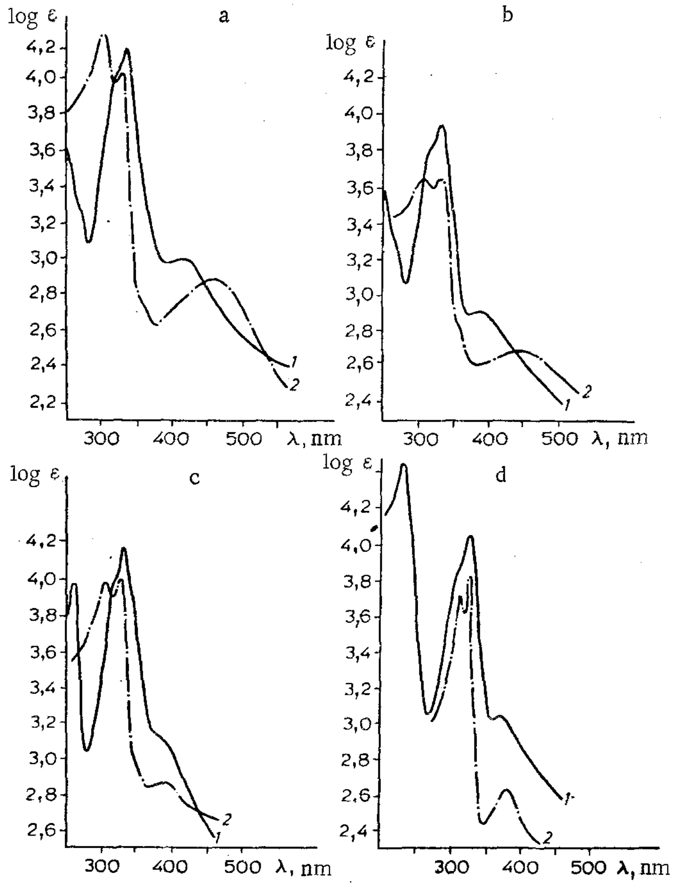


Fig. 1. Electronic absorption spectra of 2-R-perimidines: 1) in methanol; 2) in trifluoroacetic acid; a) Ia; b) IIa; c) IIIa; d) 2-methylperimidine.

TABLE 2. Electronic Absorption Spectra of Perimidines I–III

Compound	λ_{max} (log ε)		
	CH_3OH	CF_3COOH	CH_3COOH
Ia	334 (4,13) 410 (2,98)	299 (4,21) 324 (4,08) 450 (2,88)	334 (4,06) 376 (2,71)*
Ib	334 (4,16) 410 (3,17)	305 (3,69) 324 (3,68) 443 (2,91)	334 (4,13) 410 (3,14)
IIa	333 (4,44) 380 (3,14)	311 (3,84) 327 (3,86) 435 (2,92)	
IIIa	260 (3,96) 332 (4,13) 370 (3,14)*	309 (3,94) 323 (3,93) 380 (2,88)	

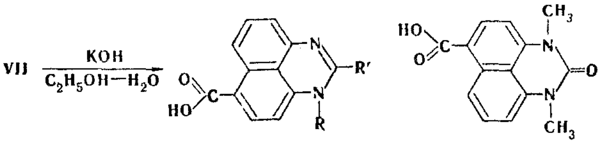
*Shoulder.

from methanol to trifluoroacetic acid. The change in the spectrum of IIIa in the 310-330 nm region is typical for N protonation, as evidenced by a comparison with the spectrum of 2-methylperimidine (Fig. 1d).

These data are evidently in agreement with the hypothesis of C protonation of perimidines I and II, which is due to their decreased basicity. However, all attempts to record protonated particles of the IX type by means of the PMR spectra of solutions in CF_3COOH and $CF_3COOH-(CH_3)_2CO$ at 20 to −40°C were unsuccessful: A signal corresponding to the protons of the CH_2 group was not observed in the spectrum, although it is clearly observed at 3.63

ppm in the case of C protonation of the 1,3-dimethyl-2,3-dihydroperimidinium cation in concentrated H_2SO_4 [8]. Unfortunately, it is impossible to record the PMR spectra of I-III in H_2SO_4 because of their rapid sulfuration [8]. It is obvious that the problem of the existence of cations of the IX type requires further study.

Since 4(9)- and 6(7)-trifluoroacetyl derivatives of I-III became accessible as a result of our research, we made an attempt to synthesize the previously unknown perimidinecarboxylic acids from them by alkaline hydrolysis of the trifluoroacetyl group. We found that 4(9)-trifluoroacetyl derivatives IV (including those with R = CF_3) undergo resinification when they are heated with aqueous alcoholic alkali (the conditions for the hydrolysis of 3-trifluoroacetylindoles [10]); this is evidently a consequence of the instability of the initially formed N anion [2]. On the other hand, the hydrolysis of VII, which contain a substituent attached to the nitrogen atom, proceeds very smoothly and makes it possible to obtain acids X in good yields. We similarly obtained acid XI from the previously described 6-trifluoroacetyl-1,3-dimethylperimidone [3]:



X a-c XI

X a R=C_6H_5, R'=CF_3; b R=CH_3, R'=CHF_2; c R=CH_3, R'=CH_2F

EXPERIMENTAL

The IR spectra of the compounds were recorded with a UR-20 spectrometer. The PMR spectra were recorded with a Tesla BS-467 spectrometer (60 MHz) with hexamethyldisiloxane as the internal standard. The UV spectra were obtained with a Specord UV-vis spectrophotometer. Chromatography was carried out on Al_2O_3 (activity IV). The basicity constants were measured by the method in [11].

2-Difluoromethylperimidine (IIa). A solution of 1.6 g (0.01 mole) of difluoroacetyl bromide in 10 ml of dry benzene was added at 20°C with stirring in the course of 5 min to a solution of 1.6 g (0.01 mole) of naphthalene-1,8-diamine in 30 ml of dry benzene, during which a copious white precipitate that rapidly changed to green formed instantaneously. The mixture was refluxed with stirring for 1 h, after which it was cooled, and the resutling precipitate was removed by filtration and treated with 100 ml of water to give 0.6 g (11%) of colorless water-insoluble N,N'-bis(difluoroacetyl)naphthalene-1,8-diamine (see [2]), which could not be purified because of its low solubility.

The aqueous mother liquor was neutralized with 5-7% ammonium hydroxide to pH 5-6, and 1.6 g (73%) of light-green crystals of perimidine IIa with mp 144-146°C (from octane) was removed by filtration. IR spectrum ($CHCl_3$): 3428 cm^{-1} (N—H). PMR spectrum (in $CDCl_3$): 6.04 (t, CHF_2, J_{H-F} = 54.75 Hz), 6.5 (m, 4-H, 9-H), and 7.1 ppm (m, 4H). Found: C 66.3; H 3.5; N 12.6%. $C_{12}H_8F_2N_2$. Calculated: C 66.1; H 3.7; N 12.8%.

2-Fluoromethylperimidine (IIIa). This compound, with mp 179-179.5°C (from octane), was similarly obtained in 74% yield. The yellow-green crystals darkened rapidly in light. IR spectrum (in $CHCl_3$): 3430 cm^{-1} (N—H). PMR spectrum (in $CDCl_3$): 4.9 (d, CH_2F, J_{H-F} = 47 Hz), 6.4 (m, 4-H, 9-H), and 7.1 ppm (m, 4H). Found: C 71.7; H 4.6; N 13.6%. $C_{12}H_9FN_2$. Calculated: C 72.0; H 4.5; N 14.0%.

1-Methyl-2-difluoromethylperimidine (IIb). A solution of 1.6 g (0.01 mole) of difluoroacetyl bromide in 10 ml of dry benzene was added with stirring in the course of 5 min to a solution of 1.7 g (0.01 mole) of N-methylnaphthalene-1,8-diamine in 30 ml of dry benzene, and the mixture was refluxed with stirring for 1 h. It was then cooled, and the resulting precipitate was removed by filtration. Compound IIb was isolated, and this precipitate was treated with 300 ml of water with subsequent washing on the filter with another 100 ml of cold water. The yield of yellow crystals with mp 134.5°C (from octane) was 1.7 g (72%). Found: C 67.6; H 4.3; N 11.9%. $C_{13}H_{10}F_2N_2$. Calculated: C 67.2; H 4.2; N 12.1%.

1-Methyl-2-fluoromethylperimidine (IIIb). A solution of 1.4 g (0.01 mole) of fluoroacetyl bromide in 10 ml of dry benzene was added with stirring in the course of 5 min to a solution of 1.7 g (0.01 mole) of N-methylnaphthalene-1,8-diamine in 30 ml of dry benzene, and the mixture was refluxed with stirring for 1 h. It was then cooled, and the precipitate was removed by filtration. Perimidine IIIb was extracted from the precipitate by dissolving it in 250 ml of hot water with subsequent neutralization to pH 5-6 with 5-7% ammonium hydroxide. Workup gave 1.5 g (69%) of yellow crystals with mp 95-96.5°C (from octane). Found: C 73.0; H 5.5; N 13.1%. $C_{13}H_{11}FN_2$. Calculated: C 72.9; H 5.1; N 13.1%.

2-Difluoromethyl-9-trifluoroacetylperimidine (IVa). A mixture of 0.1 g (0.5 mmole) of IIa with 0.5 g (2.5 mmole) of trifluoroacetic anhydride was heated in a sealed ampul at 100°C for 1.5 h, after which it was cooled and treated with water (15-20 ml). The yellow-orange precipitate was removed by filtration and chromatographed on aluminum oxide in benzene to give 0.097 g (67%) of yellow needles with mp 172.5°C (from alcohol). IR spectrum (in $CHCl_3$): 1625 cm^{-1} (C=O). PMR spectrum (in $CDCl_3$): 6.25 (t, 1H, J_{H-F} = 54 Hz), 7.26 (m, 5H), and 12.28 ppm (s, N–H). Found: C 53.7; H 2.1; N 8.9%. $C_{14}H_7F_5N_2O$. Calculated: C 53.5; H 2.2; N 8.9%.

Trifluoroacetylation of Perimidine IIIa. A mixture of 0.4 g (2.0 mmole) of IIIa with 2.1 g (0.01 mole) of trifluoroacetic anhydride was heated at 100°C in a sealed ampul for 1.5 h, after which it was cooled and poured over 20 g of crushed ice. The aqueous mixture was stirred and neutralized with 5-7% ammonium hydroxide, and the precipitate was removed by filtration, washed with water, and dried. The reaction products were separated by chromatography on Silochrom in benzene.

The first fraction was worked up to give 0.07 g (12%) of orange crystals of 2-(1,3,3,3-tetrafluoroacetonyl)perimidine (V) with mp 230-231°C (dec., from dibutyl ether). IR spectrum (in $CHCl_3$): 1660 cm^{-1} (C=O). PMR spectrum (in CF_3COOH): 5.5 (d, 1H, J_{H-F} = 44.25 Hz) and 7.2 ppm (m, 6H). Found: C 57.0; H 2.6; N 9.3%. $C_{14}H_8F_4N_2O$. Calculated: C 56.8; H 2.7; N 9.5%.

The second fraction was worked up to give 0.11 g (20%) of orange-yellow crystals of 2-fluoromethyl-9-trifluoroacetylperimidine (IVb) with mp 191-192°C (from alcohol). IR spectrum (in $CHCl_3$): 1623 cm^{-1} (C=O). PMR spectrum (in CF_3COOH): 5.4 (d, 2H, J_{H-F} = 45.75 Hz) and 7.3 ppm (m, 5H). Found: C 56.7; H 2.7; N 9.5%. $C_{14}H_8F_4N_2O$. Calculated: C 56.8; H 2.7; N 9.5%.

The third fraction (0.21 g) was identified as starting perimidine IIIa.

1-Methyl-2-difluoromethyl-7-trifluoroacetylperimidine (VIa) and 1-Methyl-2-difluoromethyl-6-trifluoroacetylperimidine (VII). A mixture of 0.5 g (2.2 mmole) of perimidine IIIa and 2.3 g (0.01 mole) of trifluoroacetic anhydride was heated in a sealed ampul at 100°C for 3 h, after which it was cooled and poured over 20 g of crushed ice. The aqueous mixture was neutralized with 5-7% ammonium hydroxide, and the orange precipitate was removed by filtration, washed with water, and dried. The reaction products were separated by chromatography on Al_2O_3 (elution with benzene).

Workup of the first fraction gave 0.18 g (25%) orange crystals of perimidine VIa with mp 184°C (from alcohol). IR spectrum (in $CHCl_3$): 1683 cm^{-1} (C=O). UV spectrum (in CH_3OH), λ_{max} (log ε): 237 (4.45), 263 (4.58), 333 (3.74), and 450 nm (3.53). PMR spectrum (in CF_3COOH): 3.35 (s, 3H), 6.73 (t, 1H), 6.78 (d, 9-H, J_{98} = 9 Hz), 7.08 (d, 4-H, J_{45} = 7.5 Hz), 7.41 (t, 5-H), 8.0 (d, 8-H, J_{89} = 9 Hz), and 8.5 ppm (d, 6-H, J_{65} = 9 Hz). Found: C 54.8; H 2.7; N 8.6%. $C_{15}H_9F_5N_2O$. Calculated: C 54.9; H 2.7; N 8.5%.

Workup of the second fraction gave 0.17 g (24%) of yellow crystals of VII with mp 160-161°C (from alcohol). IR spectrum (in $CDCl_3$): 1685 cm^{-1} (C=O). UV spectrum (in CH_3OH), λ_{max} (log ε): 239 (4.46), 260 (4.34), 330 (3.87), and 432 nm (3.76). PMR spectrum (in CF_3COOH): 3.35 (s, 3H), 6.70 (t, 1H), 6.90 (m, 2H), 7.43 (t, 8-H), 7.91 (d, 5-H, J_{54} = 7.5 Hz), and 8.5 ppm (d, 7-H, J_{78} = 9 Hz). Found: C 54.6; H 3.0; N 8.1%. $C_{15}H_9F_5N_2O$. Calculated: C 54.9; H 2.7; N 8.5%.

1-Methyl-2-fluoromethyl-7-trifluoroacetylperimidine (VIb) and 1-Methyl-2-fluoromethyl-4-trifluoroacetylperimidine (VIII). A mixture of 0.5 g (2.3 mmole) of IIIb and 2.3 g (0.01 mole) of trifluoroacetic anhydride in 4 ml of dry dichloroethane was heated in a sealed ampul at 100°C for 3 h, after which it was cooled and poured over 20 g of crushed ice. The aqueous mixture was stirred thoroughly and neutralized with 5-7% ammonium hydroxide, and the reaction products were extracted with benzene. The mixture was separated by chromatography on Al_2O_3 (elution with benzene).

The first fraction was worked up to give 0.08 g (11%) of orange-yellow crystals of perimidine VIII with mp 146-147°C (from alcohol). IR spectrum (in $CHCl_3$): 1682 cm^{-1} (C=O). PMR spectrum (in CF_3COOH): 2.83 (s, 3H), 5.33 (d, 2H, J_{H-F} = 44.25 Hz), and 7.2 ppm (m, 5H). UV spectrum (in CH_3OH), λ_{max} (log ε): 245 (4.08), 283 (4.29), 337 (3.77), and 455 nm (3.86). Found: C 57.9; H 3.1; N 9.3%. $C_{15}H_{10}F_4N_2O$. Calculated: C 58.1; H 3.2; N 9.0%.

The second fraction was worked up to give 0.21 g (29%) of bright-yellow crystals of trifluoroacetyl derivative VIb with mp 167-168°C (from aqueous alcohol). IR spectrum (in $CHCl_3$): 1680 cm^{-1} (C=O). PMR spectrum (in CF_3COOH): 3.1 (s, 3H), 5.4 (d, 2H, J_{H-F} = 44.25 Hz), 6.7 (d, 9-H, J_{98} = 8 Hz), 7.0 (d, 4-H, J_{45} = 7.5 Hz), 7.38 (t, 5-H), 8.0 (d, 8-H, J_{89} = 8 Hz), and 8.5 ppm (d, 6-H, J_{65} = 8 Hz). UV spectrum (in CH_3OH), λ_{max} (log ε): 238 (4.35), 330 (3.92), and 447 nm (3.90). Found: C 58.0; H 3.1; N 9.4%. $C_{15}H_{10}F_4N_2O$. Calculated: C 58.1; H 3.2; N 9.4%.

The third fraction, which was found at the start, was a difficult-to-separate mixture of substances.

Hyrolysis of 6(7)-Trifluoroacetyl Derivatives of Perimidine and 1,3-Dimethylperimidone. A 0.3-mmole sample of the 6(7)-trifluoroacetyl derivative and 4.5 mmole of potassium hydroxide were dissolved in 3 ml of a mixture of alcohol with water (5:2 by volume), and the solution was refluxed with stirring for 5-10 min. It was then cooled, diluted to twice its original volume with water, and acidified to pH 2-3. The precipitated acid was removed by filtration, washed with water, and dried.

1-Phenyl-2-trifluoromethylperimidine-6(7)-carboxylic Acid (Xa). This compound was obtained in 96% yield as green crystals with mp >350°C (from alcohol). Found: C 63.8; H 3.4; N 7.5%. $C_{19}H_{11}F_3N_2O_2$. Calculated: C 64.0; H 3.1; N 7.9%.

1-Methyl-2-difluoromethylperimidine-6(7)-carboxylic Acid (Xb). This compound was obtained in 95% yield as light-green crystals with mp 289-290°C (from alcohol). Found: C 60.6; H 4.0; N 10.3%. $C_{14}H_{10}F_2N_2O_2$. Calculated: C 60.9; H 3.6; N 10.1%.

1-Methyl-2-fluoromethylperimidine-6(7)-carboxylic Acid (Xc). This compound was obtained in 95% yieldas light-green crystals with mp 235-236°C (from alcohol). IR spectrum (mineral oil): 3400 (O—H) and 1665 cm^{-1} (C=O). Found: C 65.0; H 4.4; N 11.2%. $C_{14}H_{11}FN_2O_2$. Calculated: C 65.0; H 4.3; N 10.9%.

1,3-Dimethylperimidone-6-carboxylic Acid (XI). This compound was obtained in 94% yield as pale-green crystals with mp 309°C. IR spectrum (mineral oil): 3400 (O—H) and 1665 cm^{-1} (C=O). Found: C 65.5; H 5.0; N 10.8%. $C_{14}H_{12}N_2O_3$. Calculated: C 65.6; H 4.7; N 10.9%.

LITERATURE CITED

1. A. F. Pozharskii, V. V. Dal'nikovskaya, and T. A. Maksimova, Khim. Geterotsikl. Soedin., No. 7, 980 (1981).
2. A. F. Pozharskii, G. G. Yurchuk, and L. L. Gervits, Khim. Geterotsikl. Soedin., No. 3, 413 (1979).
3. A. F. Pozharskii and G. G. Yurchuk, Khim. Geterotsikl. Soedin., No. 3, 418 (1979).
4. V. I. Minkin, V. A. Bren', A. D. Garnovskii, and R. I. Nikitina, Khim. Geterotsikl. Soedin., No. 4, 552 (1972).
5. A. F. Pozharskii, V. N. Koroleva, O. M. Bagrova, B. A. Semavich, and V. A. Bren', Khim. Geterotsikl. Soedin., No. 1, 84 (1980).
6. A. F. Pozharskii, I. V. Borovlev, and I. S. Kashparov, Khim. Geterotsikl. Soedin., No. 4, 543 (1975).
7. A. F. Pozharskii and A. A. Konstantinchenko, Khim. Geterotsikl. Soedin., No. 7, 964 (1979).
8. A. F. Pozharskii, V. V. Kuz'menko, V. N. Koroleva, and G. G. Yurchuk, Khim. Geterotsikl. Soedin., No. 5, 691 (1980).
9. A. F. Pozharskii, I. S. Kashparov, P. J. Halls, and V. G. Zaletov, Khim. Geterotsikl. Soedin., No. 4, 543 (1971).
10. J. Bourdais and A. Lorre, J. Heterocycl. Chem., 12, 1111 (1975).
11. V. I. Minkin and V. A. Bren', Reakts. Sposob. Org. Soedin., Tartu, 4, No. 1, 113 (1967).