HETEROCYCLIC ANALOGS OF PLEIADIENE

XXXVIII.* CHLORINATION OF 1,3-DIMETHYLPERIMIDONE, 1,3-DIMETHYL-2,3-DIHYDROPERIMIDINE, AND THE 1,3-DIMETHYLPERIMIDINIUM CATION

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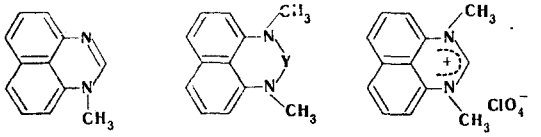
Chlorination of 1,3-dimethylperimidone, 1,3-dimethyl-2,3-dihydroperimidine, and the 1,3-dimethylperimidinium cation with 1-chlorobenzotriazole and sulfuryl chloride gave their dichloro, trichloro, and tetrachloro derivatives. It was established that the chlorination reactions of 1,3-dimethyl derivatives of perimidone and 2,3-dihydroperimidine are controlled by the magnitudes of the charges and, despite the unfavorable steric conditions, take place in the 4 and 9 positions, whereas chlorination of the 1,3-dimethylperimidinium cation takes place primarily in the 6 and 7 positions of the perimidine system.

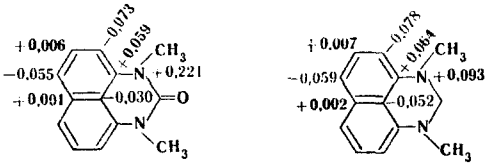
We have recently shown [2] that chlorination takes place primarily in the sterically more hindered 9 position in the reaction of 1-methylperimidine (I) with 1-chlorobenzotriazole (CBT). Despite the fact that the highest negative charge is located in the 9 position in the I molecule, this fact was extremely unexpected, since all of the other investigated electrophilic substitution reactions (nitration [3], acylation [4], and chlorination in acidic media [2]) took place mainly in the 6 and 7 positions and to a very small extent in the 4 position. It is evident that the N-methyl group, because of steric reasons, makes the 9 position inaccessible to these electrophiles. In addition, the indicated reactions are carried out in strongly acidic media and undoubtedly pass through the perimidinium cation; the 4 and 9 positions in the latter should be deactivated with respect to electrophiles to a greater degree than the 6 and 7 positions. On the other hand, the chlorination of I by means of CBT in an inert medium (chloroform or methylene chloride) most likely takes place in the neutral molecule. It is precisely this fact, in conjunction with the small size of the Cl^+ cation, that apparently makes reaction at the 9 position possible.



I II, III IV

II Y = C=O; III Y = CH_2

The present paper is devoted to a further study of this question in the case of 1,3-dimethylperimidone (II) and 1,3-dimethyl-2,3-dihydroperimidine (III). The electron density distributions in the molecules of these compounds are similar: in the π-surplus naphthalene rings the negative charge alternates between the 4(9) and 6(7) positions, and it is higher in the ortho positions with respect to the heteroatoms:



Proceeding from this, one might have expected that II and III would also undergo chlorination by CBT in the form of the neutral molecule in the 4 and 9 positions. The second

*See [1] for communication XXXVII.

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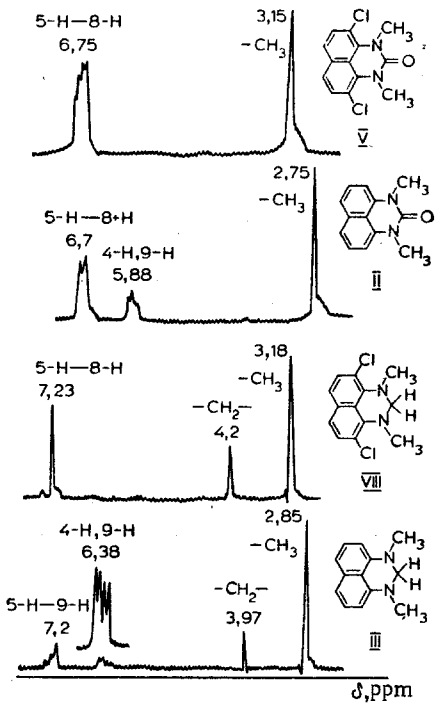
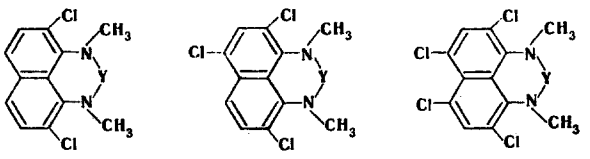


Fig. 1. PMR spectra: V) and II) in CF_3COOH; VIII) in CCl_4; III) in $CDCl_3$.

task in this research was to study this reaction also for an authentic perimidinium cation in the case of salt IV.



V, VIII VI, IX VII, X

V-VII Y=C=O; VIII-X Y=CH_2

The chlorination of II with an equimolar amount of CBT in chloroform leads, even in the case of pronounced dilution, to the formation of 1,3-dimethyl-4,9-dichloroperimidone (V) in 30% yield; more than half of the starting compound is regenerated in this case. This sort of reaction trend usually indicates that secondary substitution proceeds more rapidly than primary substitution. This situation is observed, for example, in those cases in which primary substitution takes place in the heteroaromatic cation, whereas secondary substitution occurs in the neutral molecule. However, II evidently [5] reacts with electrophiles in neutral form even in strongly acidic media. In view of this, the reason for the formation of a 4,9-dichloro derivative in the chloriantion of perimidone II with one equivalent of CBT remains unclear.

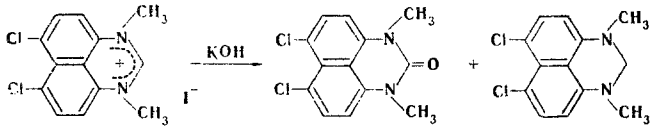
The chlorination of perimidone II with 2 and 3 moles of CBT under the same conditions leads to the formation of 4,9-dichloro and 4,6,9-trichloro derivatives V and VI, respectively, in almost quantitative yields. A mixture of trichloro and tetrachloro derivatives VI and VII in an overall yield of 92% with a product ratio of ~1:1 according to the PMR spectroscopic data is formed in the reaction with 4 moles of CBT.

An attempt to accomplish the chlorination of dihydroperimidine III by means of CBT was unsuccessful because of pronounced resinification of the reaction mixture; the chlorination of III was therefore carried out by means of sulfuryl chloride in acetic acid. A mixture of 4,9-dichloro and 4,6,9-trichloro derivatives VIII and IX in an overall yield of 48% with a product ratio of 5:1 is formed in the reaction of III with 1 mole of SO_2Cl_2. From the data on the basicities [6] and other electrophilic substitution reactions of dihydroperimidines [7] it may be assumed that under these conditions primary chlorination proceeds through

the protonated form of dihydropyrimidine III, whereas secondary chlorination proceeds through the neutral molecule of the 4-chloro derivative. A mixture of VIII and IX in overall yields of 76 and 90% and product ratios of 4:1 and 1:2, respectively, are also formed in the chlorination of III with 2 and 3 moles of SO_2Cl_2. When excess SO_2Cl_2 was used, the only product isolated was 1,3-dimethyl-4,6,7,9-tetrachloro-2,3-dihydroperimidine (X, in 42% yield).

The structures of the chloro derivatives obtained were proved mainly by means of PMR spectroscopy; this is illustrated below in the case of V and VIII (Fig. 1). In the PMR spectra of both substances the protons of the methyl groups appear in the form of a singlet and the characteristic quartet of the 4- and 9-H protons at 6.4 ppm vanishes. It is important to note that the chlorine atoms in the 4 and 9 positions due to magnetic deshielding cause a 0.3-0.4 ppm shift of the signals of the N-methyl groups to weak field as compared with the starting compounds or compounds that contain a chlorine atom in other positions (compare with the data on chloroperimidines [2]).

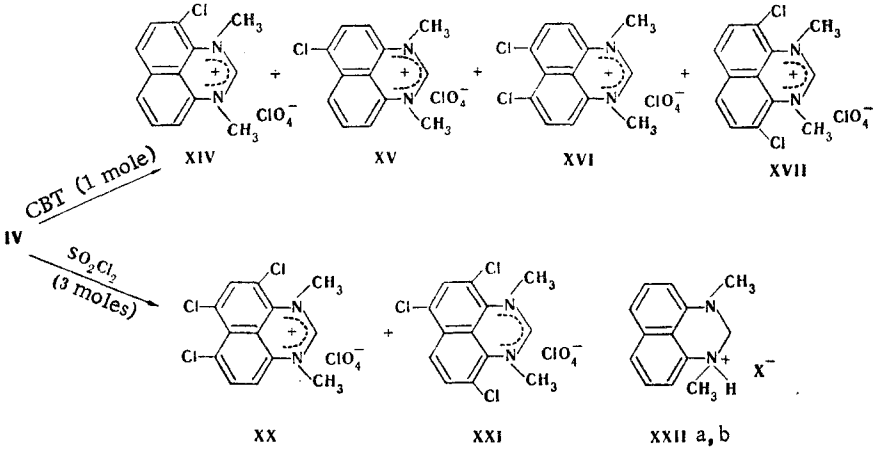
For the definitive elucidation of the structures of the dichloro-substituted V-VIII we obtained salts XI and their symmetrical isomers — 6,7-dichloro derivatives XII and XIII — by alternative synthesis by means of alkaline disproportionation [8]. As expected, isomers XII and XIII differed from the dichloro derivatives formed in the chlorination reactions.



XI XII XIII

The chlorination of 1,3-dimethylperimidinium perchlorate (IV) was carried out with both CBT in acetonitrile and with sulfuryl chloride in acetic acid. Similar results were obtained in both cases.

A complex mixture of 4-chloro- (XIV, 8%), 6-chloro- (XV, 30%), 6,7-dichloro- (XVI, 16%), and 4,9-dichloro-1,3-dimethylperimidinium perchlorate (XVII, 8%) is formed in the chlorination of salt IV with an equimolar amount of CBT in acetonitrile at 60°C (the choice of conditions was determined by the solubility of the starting salt). This was established by comparison of the chemical shifts of the protons of the N-methyl groups of authentic samples of XIV-XVI with the data for the PMR spectrum of the mixture.



XXII a R = H; b R = CH_3; $X^- = I^-$

According to the PMR spectral data, the chlorination of perchlorate IV with 2 moles of CBT leads to a mixture of 6,7-dichloro- and 4,9-dichloro-1,3-dimethylperimidinium perchlorate (XVIII and XIX) in a ratio of 94:6.

A mixture of 4,6,7- and 4,6,9-trichloro derivatives (XX and XXI) in a ratio of 67:33 is formed in the chlorination of salt IV with three or more moles of SO_2Cl_2.

The question as to why the 1,3-dimethylperimidinium cation is chlorinated primarily in the 6 and 7 positions whereas the 1,3-dimethyl-2,3-dihydroperimidinium cation (XXIIa) is chlorinated primarily in the 4 and 9 positions arises. The answer to this question evidently consists in the following. The positive charge in the cation of IV is distributed

uniformly between both nitrogen atoms, which should lead to rather pronounced deactivation of both ortho positions. On the other hand, in the cation of XXII delocalization of the positive charge to the second nitrogen atom through the π system is impossible, and the C atom adjacent to the uncharged nitrogen atom will be deactivated to a relatively lesser degree and undergoes attack by the electrophile more readily. In fact, the PMR spectroscopic data for salt XXIIb in CF_3COOH indicate a pronounced difference in the chemical shifts of the 4- and 9-H protons. Whereas the position of the signal of the 4-H proton (δ 6.6 ppm) differs by only 0.2 ppm from the position of the signal of this proton in the spectrum of the neutral III molecule, the signal of the 9-H proton adjacent to the ammonium nitrogen atom is shifted 1 ppm and is found at 7.6 ppm. Moreover, the signals of the 4- and 9-H protons in the spectrum of the cation of IV are found at 7.1 ppm, i.e., at weaker (by 0.66 ppm) field as compared with the neutral perimidine molecule.

Thus our study showed that the chlorination of 1,3-dimethyl derivatives of perimidone and 2,3-dihydroperimidine, like the chlorination of 1-methylperimidine, is controlled by the magnitudes of the charges and, despite the unfavorable steric conditions, takes place in the 4 and 9 positions. However, the chlorination of the 1,3-dimethylperimidinium cation proceeds primarily at the 6 and 7 positions; this is undoubtedly a consequence of a decrease in the electron density in the ortho positions under the influence of the positive charge of the heteroring. These results cast some doubt on the correctness of the calculation of the perimidinium cation by the Hückel MO method [3], according to which the electron density in the 4 and 9 positions is reduced insignificantly and to a lesser extent than in the 6 and 7 positions. Further study of the reason for the formation of dichloro-substituted compounds in the reaction of one equivalent of chlorinating agent with II and III is also required.

EXPERIMENTAL

The PMR spectra of the compounds were recorded with a Tesla BS-467 spectrometer (60 MHz) with hexamethyldisiloxane as the internal standard. The mass spectrum was obtained with an MKh-1305 mass spectrometer with an ionizing voltage of 60 eV. The course of the reactions was followed by means of thin-layer chromatography (TLC). The compounds were purified by chromatography on activity II (Brockmann classification) Al_2O_3. The charges in the II and III molecules were calculated by the simple Hückel MO method in accordance with [5]. The N-methyl groups were not taken into account in the calculations.

1,3-Dimethyl-6-chloroperimidinium Iodide. A 0.1-ml (1.5 mmole) sample of methyl iodide was added in a nitrogen atmosphere to a solution of 0.25 g (1.2 mmole) of 6(7)-chloroperimidine [2] and 0.1 g (1.5 mmole) of 85% KOH in 10 ml of alcohol, and the mixture was stirred at room temperature for 3 h. The alcohol was then removed by evaporation, and the residue was purified with a column filled with Al_2O_3 (elution with chloroform). The first reaction was collected and worked up to give 0.15 g (60%) of a mixture of 1-methyl-6-chloro- and 1-methyl-7-chloroperimidines. The mixture of isomers was refluxed with excess methyl iodide in alcohol for 3 h, after which the mixture was cooled, and the precipitate was removed by filtration and washed with alcohol to give 0.18 g (42%) of yellow prisms with mp 268°C (dec., from water). PMR spectrum (in CF_3COOH): 3.25 (6H, s, N–CH_3), 6.4 (1H, d, J_{ortho} = 7.5 Hz, 4-H), 6.6 (1H, d, J_{ortho} = 7.5 Hz, 9-H), 7.2 (2H, m, 7- and 8-H), 7.5 (1H, d, J_{ortho} = 7.5 Hz, 5-H), and 8.1 ppm (1H, s, 2-H). Found: C 43.8; H 3.3; Cl + I 45.2; N 7.9%. $C_{13}H_{12}ClIN_2$. Calculated: C 43.6; H 3.4; Cl + I 45.3; N 7.8%.

1,3-Dimethyl-4-chloroperimidinium Iodide. An alcohol solution of 1-methyl-4-chloroperimidine [2] was refluxed with excess methyl iodide for 8 h, after which the mixture was cooled, and the resulting crystals were removed by filtration and washed with alcohol to give yellow needles with mp 200°C (from water) in 18% yield. PMR spectrum (in CF_3COOH): 3.16 (3H, s, 1-CH_3), 3.65 (3H, s, 3-CH_3), 6.4 (1H, q, J_{ortho} = 6.2 Hz , J_{meta} = 2.0 Hz, 9-H), 7.0 (4H, m, 5-H–8-H), and 7.82 ppm (1H, s, 2-H). Found: C 44.0; H 3.7; Cl + I 45.5; N 7.5%. $C_{13}H_{12}ClIN_2$. Calculated: C 43.6; H 3.4; Cl + I 45.3; N 7.8%.

1,3-Dimethyl-6,7-dichloroperimidinium Iodide (XI). A solution of 0.25 g (1 mmole) of 1-methyl-6,7-dichloroperimidine [2] and 0.2 ml of methyl iodine in 10 ml of alcohol was refluxed for 3 h, after which it was cooled, and the precipitate was removed by filtration and washed with alcohol to give 0.4 g (100%) of yellow needles with mp 260°C (dec., from alcohol). PMR spectrum (in CF_3COOH): 3.2 (6H, s, N–CH_3), 6.48 (2H, d, J_{ortho} = 8.0 Hz, 4- and 9-H), and 7.24 (2H, d, J_{ortho} = 8.0 Hz, 5- and 8-H), and 7.9 ppm (1H, s, 2-H). Found: C

40.0; H 2.9; Cl + I 50.0; N 7.3%. $C_{13}H_{11}Cl_2IN_2$. Calculated: C 39.7; H 2.8; Cl + I 50.3; N 7.1%. Perchloric acid (30%) was added dropwise to a warm solution of salt XI in water, and the precipitated 1,3-dimethyl-6,7-dichloroperimidinium perchlorate was removed by filtration and washed with water to give yellow needles with mp 231°C (dec., from water).

1,3-Dimethyl-6,7-dichloro-2,3-dihydroperimidine (XIII). A 0.07-g (1.3 mmole) sample of KBH_4 was added in portions to a suspension of 0.2 g (5 mmole) of salt XI in 7 ml of water, during which the yellow solid became colorless. The precipitate was removed by filtration and washed with water to give 0.14 g (98%) of colorless prisms with mp 105-106°C (from alcohol). Found: C 58.3; H 4.2; Cl 26.7; N 10.5%. $C_{13}H_{12}Cl_2N_2$. Calculated: C 58.4; H 4.5; Cl 26.6; N 10.5%.

1,3-Dimethyl-6,7-dichloroperimidone (XII) and 1,3-Dimethyl-6,7-dichloro-2,3-dihydroperimidine (XIII). A suspension of 0.2 g (5 mmole) of salt XI in 10 ml of 10% NaOH solution was stirred at 90°C for 30 min, after which the colorless solid was removed by filtration and washed with water until the wash waters were neutral. It was then refluxed three times with 10% hydrochloric acid with removal of the undissolved perimidone XII by filtration each time. The yield of colorless needles of XII, with mp 195-196°C (from butanol), was 0.07 g (50%). Found: C 55.5; H 3.8; Cl 25.6; N 9.7%. $C_{13}H_{10}Cl_2N_2O$. Calculated: C 55.5; H 3.6; Cl 25.3; N 10.0%. The addition of 22% ammonium hydroxide to the HCl solution precipitated 0.06 g (46%) of colorless prisms of dihydroperimidine XIII with mp 105-106°C (from alcohol). With respect to its physical properties the product was identical to the product obtained above.

Chlorination of 1,3-Dimethylperimidone (II). A) A solution of 0.38 g (2.5 mmole) of 1-chlorobenzotriazole in 30 ml of chloroform was added dropwise with stirring at room temperature in the course of 1.5 h to a solution of 0.53 g (2.5 mmole) of perimidone II in 120 ml of chloroform, after which the chloroform was removed by evaporation, and the residue was dissolved in the minimum amount of benzene. The benzene solution was passed through a column filled with Al_2O_3 (elution with petroleum ether). Workup of the first fraction (R_f 0.3) gave 0.2 g (30%) of pink prisms of 1,3-dimethyl-4,9-dichloroperimidone (V) with mp 200-201°C (from butanol). Found: C 55.7; H 3.7; Cl 25.5; N 10.1%. $C_{13}H_{10}Cl_2N_2O$. Calculated: C 55.5; H 3.6; Cl 25.3; N 10.0%. Subsequent elution with benzene gave a fraction with R_f 0.2 containing 0.3 g (57%) of starting perimidone II.

B) A solution of 0.76 g (5 mmole) of CBT in 20 ml of chloroform was added dropwise with stirring in the course of 45 min to a solution of 0.53 g (2.5 mmole) of II in 70 ml of chloroform. The product was purified by chromatography on Al_2O_3 (benzene). Workup of the eluate gave 0.7 g (100%) of perimidone V as pink prisms with mp 200-201°C (from butanol). No melting-point depression was observed for a mixture of this product with a sample obtained by method A.

C) A solution of 2.24 g (15 mmole) of CBT in 30 ml of chloroform was added dropwise with stirring in the course of 1 h to a solution of 1.06 g (5 mmole) of perimidone II in 80 ml of chloroform, and the chloroform solution was concentrated and purified by chromatography on Al_2O_3 (elution with chloroform) to give 1.5 g (98%) of cream-colored prisms of 1,3-dimethyl-4,6,9-trichloroperimidone (VI) with mp 192-193°C (from butanol) and R_f 0.8. PMR spectrum (in CF_3COOH): 3.17 (6H, s, N—CH_3) and 6.87 ppm (3H, m, 5-, 7-, and 8-H). Found: C 50.2; H 3.0; Cl 33.4; N 9.3%. $C_{13}H_9Cl_3N_2O$. Calculated: C 50.0; H 2.9; Cl 33.1; N 9.0%.

D) The experiment was carried out by the above method with a fourfold molar excess of CBT. Thin-layer chromatography on Al_2O_3 (elution with petroleum ether) indicated the presence of two substances with R_f 0.4 and 0.6. Chromatography with a column filled with Al_2O_3 (elution with petroleum ether) yielded 0.4 g (46%) of colorless needles of 1,3-dimethyl-4,6,7,9-tetrachloroperimidone (VII) with mp 224-225°C (from butanol) and R_f 0.6. Found: C 44.4; H 2.1; Cl 40.8; N 7.9%. M 350 (by mass spectrometry). $C_{13}H_8Cl_4N_2O$. Calculated: C 44.6; H 2.3; Cl 40.6; N 8.0%. Also obtained was 0.36 g (46%) of cream-colored prisms of trichloro derivative VI with mp 192-193°C (from butanol) and R_f 0.4. No melting-point depression was observed for a mixture of this product with a genuine sample of VI.

Chlorination of 1,3-Dimethyl-2,3-dihydroperimidine (III). A) A solution of 0.4 ml (5 mmole) of sulfuryl chloride in 5 ml of acetic acid was added dropwise with stirring to a suspension of 1.0 g (5 mmole) of III in 10 ml of glacial acetic acid, during which the solid dissolved completely. The mixture was stirred at 60°C for 2 h, after which it was

cooled and poured into 50 ml of water. The aqueous mixture was neutralized with 22% ammonium hydroxide, and the liberated oil (1 g) was extracted with 20 ml of chloroform. Thin-layer chromatography on Al_2O_3 (elution with petroleum ether) indicated the presence of three substances with R_f 0.2, 0.35, and 0.5. They were separated with a column filled with Al_2O_3 (elution with petroleum ether). Workup of the first fraction gave 0.1 g (8%) of light-yellow prisms of 1,3-dimethyl-4,6,9-trichloro-2,3-dihydroperimidine (IX) with mp 106°C (from alcohol) and R_f 0.5. PMR spectrum (in CCl_4): 3.2 (6H, s, N–CH_3), 4.2 (2H, s, CH_2), 7.2 (1H, d, J_{ortho} = 3 Hz, 8-H), 7.4 (1H, d, J_{ortho} = 3 Hz, 7-H), and 7.6 ppm (1H, s, 5-H). Found: C 51.6; H 3.2; Cl 35.3; N 9.1%. $C_{13}H_{11}Cl_3N_2$. Calculated: C 51.6; H 3.6; Cl 35.4; N 9.3%. Workup of the second fraction gave 0.45 g (40%) of colorless prisms of 1,3-dimethyl-4,9-dichloro-2,3-dihydroperimidine (VIII) with mp 124°C (from alcohol) and R_f 0.35. Found: C 58.5; H 4.7; Cl 26.3; N 10.2%. $C_{13}H_{12}Cl_2N_2$. Calculated: C 58.4; H 4.5; Cl 26.6; N 10.5%. The column was extracted with benzene to give 0.2 g (20%) of starting III (R_f 0.2) as colorless prisms with mp 150-151°C (from alcohol). No melting-point depression was observed for a mixture of this product with a genuine sample of III.

B) A mixture of 1 g (5 mmole) of perimidine III and 0.8 ml (10 mmole) of sulfuryl chloride in 15 ml of acetic acid was stirred at 80°C for 2 h, after which the product was isolated as in the preceding experiment. The colorless oil was extracted with hot pentane to give 0.8 g (60%) of colorless prisms of 4,9-dichloro derivative VIII with mp 124°C (from alcohol). A total of 0.25 g (16%) of light-yellow prisms of 4,6,9-trichloro-2,3-dihydroperimidine (IX), with mp 106°C (from alcohol), precipitated from the pentane solution when it was allowed to stand in a refrigerator.

C) The experiment was carried out by the method indicated above. The mixture of products was separated with a column filled with Al_2O_3 (elution with petroleum ether) to give 0.4 g (30%) of dichloroperimidine VIII, with mp 124°C (from alcohol), and 0.9 g (60%) of trichloroperimidine IX with mp 106°C (from alcohol).

D) A solution of 2 ml (25 mmole) of sulfuryl chloride in 10 ml of acetic acid was added dropwise with stirring in the course of 30 min to a suspension of 1 g (5 mmole) of perimidine III in 20 ml of acetic acid, and the mixture was stirred at 90°C for 2 h. It was then cooled and poured into 50 ml of water, and the aqueous mixture was neutralized with 22% ammonium hydroxide. The resulting oil was extracted with 50 ml of benzene and purified by chromatography with a column filled with Al_2O_3 (elution with benzene). The yield of light-yellow prisms of 1,3-dimethyl-4,6,7,9-tetrachloro-2,3-dihydroperimidine (X), with mp 136-137°C (from alcohol) and R_f 0.9, was 0.7 g (42%). PMR spectrum (in CF_3COOH): 3.17 (6H, s, N–CH_3), 4.68 (2H, s, CH_2), and 7.32 ppm (2H, s, 5- and 8-H). Found: C 46.5; H 2.9; Cl 42.5; N 8.3%. $C_{13}H_{10}Cl_4N_2$. Calculated: C 46.4; H 3.0; Cl 42.3; N 8.3%.

Chlorination of 1,3-Dimethylperimidinium Perchlorate (IV). A) A solution of 0.3 g (2 mmole) of CBT in 5 ml of acetonitrile was added dropwise with stirring to a warm solution of 0.6 g (2 mmole) of salt IV in 15 ml of acetonitrile, and the mixture was stirred at 60-65°C for 1 h. The acetonitrile was removed by evaporation, the residue was treated with hot benzene to remove the benzotriazole, and the yellow solid was removed by filtration and washed with alcohol to give 0.6 g of yellow needles with mp 211-212°C (from alcohol). According to the data from the PMR spectrum, the solid was a mixture of chloro derivatives XIV-XVII; however, the results of elementary analysis corresponded to a monochloro derivative. Found: C 46.5; H 3.1; Cl 22.0; N 8.5%. $C_{13}H_{12}Cl_2N_2O_4$. Calculated: C 47.1; H 3.6; Cl 21.5; N 8.5%.

B) A suspension of 1.49 g (5 mmole) of salt IV and 0.4 ml (5 mmole) of sulfuryl chloride in 30 ml of glacial acetic acid was stirred at 100°C for 2 h, after which it was cooled, and the yellow precipitate was removed by filtration and washed with alcohol and ether. The yield of the mixture of chloro derivatives was 1.5 g. The yellow needles had mp 211-212°C (from water).

C) A solution of 0.61 g (4 mmole) of CBT in 5 ml of acetonitrile was added in portions to a warm solution of 0.6 g (2 mmole) of salt IV in 15 ml of acetonitrile, during which the initially formed dark-green flakes dissolved completely. The mixture was stirred at 60-70°C for 1 h, and the reaction product was isolated as in experiment A. The yield of the mixture of dichloro derivatives XVIII and XIX was 0.7 g. The yellow needles had mp 200-201°C (from water). Found: C 43.0; H 3.2; Cl 29.0; N 7.8%. $C_{13}H_{11}Cl_3N_2O_4$. Calculated: C 42.7; H 3.0; Cl 29.1; N 7.7%.

D) The experiment was carried out as in method B. The yield of the mixture of dichloro derivatives was 80%. The yellow needles had mp 200-201°C (from water).

E) A mixture of 0.75 g (2.5 mmole) of salt IV and 0.6 ml (7.5 mmole) of sulfuryl chloride in 10 ml of acetic acid was stirred at 100°C for 1 h, during which part of the solid initially dissolved, after which a copious yellow precipitate formed. The mixture was cooled, and the crystals were removed by filtration and washed with alcohol. The yield of the mixture of trichloro derivatives XX and XXI was 0.9 g (90%). The light-yellow needles had mp 249°C (dec., from water). Found: C 39.3; H 2.6; Cl 35.3; N 6.8%. $C_{13}H_{10}Cl_4N_2O_4$. Calculated: C 39.0; H 2.5; Cl 35.5; N 7.0%.

F) The experiment was carried out by the method indicated above with a fourfold molar excess of sulfuryl chloride. The yield was 80%. The yellow needles had mp 250°C (dec., from butanol). With respect to its physicochemical properties the product was identical to the compound obtained above.

1,1,3-Trimethyl-2,3-dihydroperimidinium Iodide (XXIIb). This compound was obtained by the method in [6]. PMR spectrum (in CF_3COOH): 2.98 (3H, s, 3-CH_3), 3.25 (6H, s, 1-CH_3), 4.5 (2H, s, CH_2), 6.62 (1H, q, J_{ortho} = 6.0 Hz, J_{meta} = 3.0 Hz, 4-H), 7.25 (4H, m, 5-H–8-H), and 7.60 ppm (1H, q, J_{ortho} = 6.8 Hz, J_{meta} = 1.8 Hz, 9-H). UV spectrum (in methanol), λ_{max} (log ε): 248 (4.36) and 333 nm (3.81). The UV spectrum of the cation thus was almost the same as the spectrum of the neutral molecule [6].

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