100°C for 20 h, after which the mixture was cooled, and the solvent was removed by vacuum evaporation. The residue was chromatographed in a chloroform–methanol system (4:1).

The constants, spectral characteristics, and yields of III-IX are presented in Tables 2 and 3.

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HETEROCYCLIC ANALOGS OF PLEIADIENE

XXXV.* INVESTIGATION OF CHLORINATION OF PERIMIDINE AND ITS 1- AND 2-METHYL DERIVATIVES

V. V. Kuz'menko and A. F. Pozharskii

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The mono-, di-, tri-, and tetrachloro derivatives of perimidine and 1- and 2-methylperimidines were obtained by chlorination with sulfuryl chloride and 1-chlorobenzotriazole. Primarily the 6 and 7 positions are initially attacked by the electrophile in acidic media (SO_2Cl_2–CH_3COOH), whereas the 9 and 4 positions of the perimidine system become more active under neutral conditions (1-chlorobenzotriazole in $CHCl_3$).

The naphthalene ring of the perimidine molecule (Ia) has a high degree of π-surplus character and readily undergoes attack by electrophilic reagents. The 6 and 7 (para) positions are more active in the nitration [2] and acylation [3] of perimidine; the 4 and 9 (ortho) positions are the next most active positions. Electrophilic substitution in the 5 and 8 (meta) positions could not be accomplished. These reactions proceeded most rapidly in strongly acidic media through a perimidinium cation. In the present research we studied the chlorination of some perimidines (Ia-d) with sulfuryl chloride and 1-chlorobenzotriazole (CBT) [4] for the first time. It was assumed that the use of the latter reagent in aprotic solvents would make it possible for the first time to observe electrophilic substitution in the neutral perimidine molecule.

The chlorination of perimidine Ia with an equimolar amount of sulfuryl chloride in acetic acid leads to the formation of a mixture of 6(7)-chloro- and 4(9)-chloroperimidines (IIa and IIIa) in a ratio of 8:1, which are separable by chromatography. The structures of the monochloroperimidines cannot be established by means of the PMR, IR, and UV spectra, since they differ very little for the isomers. It is interesting that ν_{NH} bands appear at 3420-3450 cm^{-1} in the IR spectra of both compounds in dilute solutions in chloroform; this indicates the absence of the intramolecular hydrogen bond that is very characteristic for 4(9)-nitro- and 4(9)-acetylperimidines, which are easily distinguished from the 6(7) isomers on this basis. They were therefore identified by alternative synthesis (by reduction and cyclization with formic acid of 4-chloro- and 2-chloro-1,8-dinitronaphthalenes).

* See [1] for communication XXXIV.

Rostov State University. Scientific-Research Institute of Physical and Organic Chemistry, Rostov-on-Don 344006.

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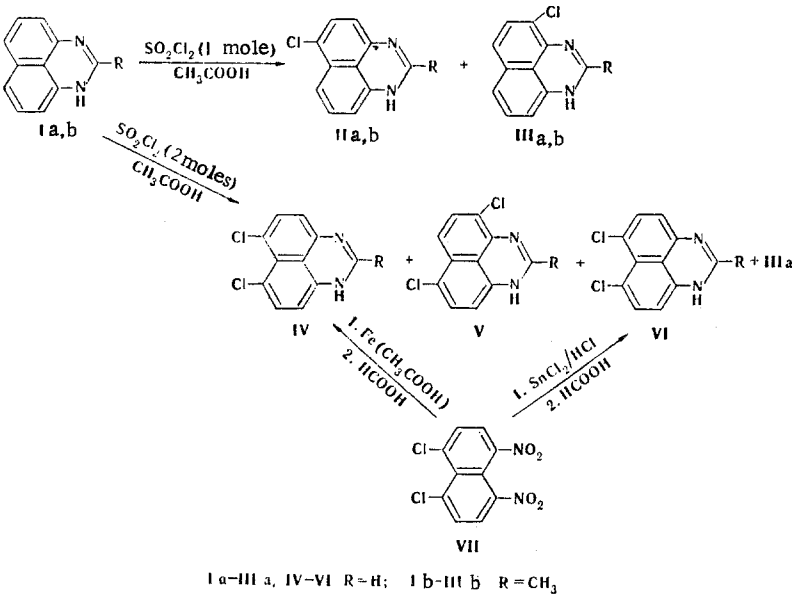
TABLE 1. Chloroperimidines

Compound	mp, °C*	ν_{NH}, cm^{-1}	Found, %				Empirical formula	Calc., %				Yield, %
			C	H	Cl	N		C	H	Cl	N	
IIa	194—195†	3420	65,2	3,6	17,5	13,5	$C_{11}H_7ClN_2$	65,0	3.5	17.7	13.8	80
IIb	175—176†	3420	66,7	4,5	16,2	12,8	$C_{12}H_9ClN_2$	66.5	4,2	16.4	12,9	74
IIIa	172—173†	3450	64,8	3,4	17.5	14,0	$C_{11}H_7ClN_2$	65,0	3,5	17,7	13,8	10
IV	179—180†	3410	55,9	2,7	29,8	11,5	$C_{11}H_6Cl_2N_2$	55,7	2,5	30,0	11,8	33
V	185—186†	3420	56,0	2,5	30,1	11,9	$C_{11}H_6Cl_2N_2$	55,7	2.5	30,0	11,8	30
VI	181†	3400	48.8	2,0	38.9	10,5	$C_{11}H_5Cl_3N_2$	48,6	1,8	39,3	10,3	81
VIII	247—248†	3390	45,2	2,1	44,3	8,6	$C_{12}H_6Cl_4N_2$	45,0	1,9	44,4	8,8	98
X	185—186	—	66,6	4,0	17,0	13,1	$C_{12}H_9ClN_2$	66,4	4,1	16,6	12,9	84
XI	188—189	—	57,5	3,1	28,1	11,1	$C_{12}H_8Cl_2N_2$	57,4	3,2	28,3	11,2	90
XII	197—198	—	57.3	3,0	28,5	11,2	$C_{12}H_8Cl_2N_2$	57,4	3,2	28,3	11,2	40
XIII	200—201	—	50,5	2,5	37,5	9,5	$C_{12}H_7Cl_3N_2$	50,4	2,4	37,3	9,6	85
XIV	228—229	—	44,9	2,0	44,1	8,8	$C_{12}H_6Cl_4N_2$	45,0	1,9	44,4	8,8	75
XVI	197—198	—	50,6	2,6	37.6	9,9	$C_{12}H_7Cl_3N_2$	50,4	2,4	37,3	9,6	70
XVII	172—173	—	53,5	3,3	33,8	8.8	$C_{14}H_{11}Cl_3N_2$	53,6	3.5	33,9	8.9	51
XVIII	117—118	—	58,9	3.5	27,0	10.8	$C_{13}H_{10}Cl_2N_2$	59,0	3,7	26,8	10,6	45
XIX	159—160	—	52,3	2,9	35,8	9,0	$C_{13}H_9Cl_3N_2$	52,0	3,0	35,7	9,3	75
XX	210—211	—	46,5	2,2	42,7	8,5	$C_{13}H_8Cl_4N_2$	46,7	2,4	42,5	8,4	60

* The compounds were recrystallized: IIa, V, and VI from aqueous alcohol, IIb, IIIa, and IV from ethyl acetate, VIII, XI, ethyl acetate, VIII, XI, XIII, XIV, XVI, XVII, and XX from butanol, X from benzene with octane, and XII, XVIII, and XIX from alcohol.
† These compounds decomposed on melting.



Ia–IIIa, IV–VI R = H; Ib–IIIb R = CH_3

The only reaction product was 2-methyl-6(7)-chloroperimidine (IIb) (74%) in the chlorination of 2-methylperimidine (Ib) under the same conditions.*

The chlorination of perimidine Ia with 2 moles of sulfuryl chloride leads to a mixture of 4(9)-chloroperimidine (IIIa) (14%), 4(9),6,7-trichloroperimidine (VI) (18%), 6,7-dichloroperimidine (IV) (10%), and dichloroperimidine V (30%), the precise structure of which was not established. It is presumably 4,7-dichloroperimidine (V). The structures of IV and VI were confirmed by alternative synthesis from 1,8-dichloronaphthalene (VII). It is interesting that VI is formed by reduction of naphthalene VII with $SnCl_2$ in HCl with subsequent heating in formic acid. The incorporation of a third chlorine atom in this case evidently occurs in the step involving the formation of the diamine rather than after cyclization, in analogy with the reduction of 1-nitronaphthalene to 4-chloronaphthylamine [6].

4(9),6,7-Trichloroperimidine (VI) is formed in 81% yield in the chlorination of perimidine Ia with 3 or more moles of sulfuryl chloride at 110-115°C. We were unable to obtain a tetrachloroperimidine by direct

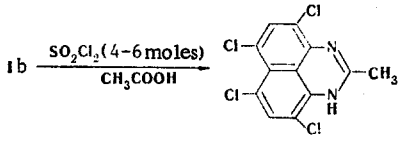
* According to the data in [5], IIb obtained from 4-chloro-1,8-dinitronaphthalene has mp 127°C. Our sample, which we obtained both by chlorination of Ib and from 4-chloro-1,8-dinitronaphthalene, has mp 175-176°C.

TABLE 2. PMR Spectra of Chloroperimidines

Compound*	δ, ppm				J, Hz	
	C—CH_3	N—CH_3	H_2	H_4—H_9	$J_{4,9}$	$J_{5,8}$
IIa	—	—	7,48 s	$2H_{4,9}$ 6,55 m; $3H_{5,7,8}$ 7,31 m	—	—
IIb	2,25 s	—	—	$5H_{4-9}$ 6,85 m	—	—
IIIa	—	—	7,48 s	$4H_{5-8}$ 7,20 m; H_9 6,46 q	J_{ortho}=6,0 J_{meta}=2,5	
IV	—	—	7,45 s	$2H_{4,9}$ 6,35 d; $2H_{5,8}$ 7,28 d	8,30	8,30
V	—	—	7,55 s	$3H_{5,6,8}$ 7,25 m; H_9 6,50 m	—	—
VI	—	—	7,54 s	H_5 7,42 s; H_8 7,24 d; H_9 6,44 d	$J_{8,9}$=8,0	
VIII	2,40 s	—	—	$2H_{5,8}$ 7,17 s	—	—
X	—	3,22 s	7,83 d	$4H_{5-8}$ 7,10 m H_9 6,53 q	J_{ortho}=6,80 J_{meta}=3,0	
XI	—	3,80 s	7,85 d	$4H_{5-8}$ 7,15 m	—	—
XII	—	3,27 s	7,82 s	H_4 6,45 d; $2H_{5,8}$ 7,05 d; H_9 6,35 d	9,0	9,0
XIII	—	3,80 s	7,92 d	H_5 7,45 d; H_6 7,12 d; H_8 7,15 s	$J_{5,6}$=9,0	
XIV	—	3,78 s	7,90 s	$2H_{5,8}$ 7,17 s	—	—
XVI	—	3,27 s	7,95 s	H_5 7,15 s; H_8 7,20 d; H_9 6,55 d	$J_{8,9}$=9,0	
XVII	—†	—	7,92 d	$3H_{5,8,9}$ 7,28 m	—	—
XVIII	2,45 s	3,60 s	—	$4H_{5-8}$ 7,10 s	—	—
XIX	2,45 s	3,60 s	—	H_5 7,52 d; H_6 7,15 d; H_8 7,20 s	$J_{5,6}$=9,0	
XX	2,45 s	3,55 s	—	$2H_{5,8}$ 7,15 s	—	—

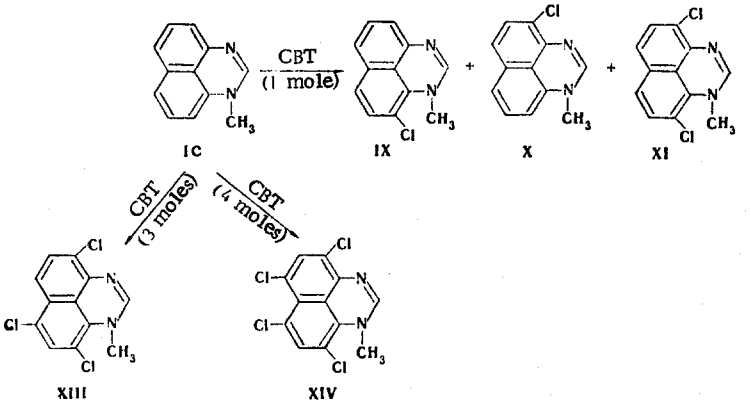
* Compounds IIa, IIIa, and IV-VI in DMSO, and X-XX in CF_3COOH.
† The $NCH(CH_3)_2$ group gives signals at 1.25 (d, 6H) and 5.2 ppm (m, 1H) with J = 6.7 Hz.

chlorination of Ia with sulfuryl chloride. On the other hand, 2-methylperimidine is chlorinated with excess sulfuryl chloride to the tetrachloro derivative (VIII); i.e., the methyl group increases the activity of the naphthalene ring appreciably with respect to electrophiles.



VIII

An attempt to accomplish the chlorination of Ia,b by the action of CBT in acetonitrile as recommended recently in [7] was unsuccessful because of pronounced resinification. It is known that perimidines with a free NH group are easily oxidized, whereas 1-chlorobenzotriazole is not only a chlorinating agent but also a strong oxidizing agent [4, 8]. In fact, the chlorination of 1-methylperimidine (Ic) with CBT proceeds without resinification an under mild conditions. Thus a mixture of 9-chloro- (IX) (53%), 4-chloro- (X) (10%), and 4,9-dichloro-1-methylperimidine (XI) (27%) is formed in the reaction of 1 mole of CBT in chloroform at 0°C. This was established by comparison of the chemical shifts of the singlets of the protons of the 1-methyl groups of genuine samples with data from the spectrum of the mixture (see below).



We were able to isolate only 1-methyl-4,9-dichloroperimidine (15%) from the mixture. 1-Methyl-4-chloroperimidine (X) was obtained by alternative synthesis by methylation of 4-chloroperimidine.

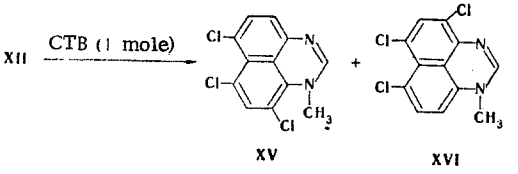
The chlorination of Ic with 2 moles of CBT proceeds very selectively to give only 4,9-dichloro derivative XI in 90% yield. The location of one of the chlorine atoms in the 4 position in XI can be judged from the fact that it cannot be quaternized even on prolonged refluxing with methyl iodide in alcohol; this is characteristic

for other 1,4-disubstituted perimidines [9]. The isomeric 1-methyl-6,7-dichloroperimidine (XII), obtained by methylation of IV with methyl iodide, readily undergoes this reaction. The location of the second chlorine atom in the 9 position follows from the PMR spectroscopic data. We found that the signal of the 1-methyl group in the 4-, 6-, and 7-chloro-substituted derivatives (mono-, di-, and trisubstituted) of 1-methylperimidine is found at 3.2 ppm, while in a number of other cases it is observed at 3.75 ppm. We also associate these instances with the deshielding effect of the chlorine atom in the 9 position. In the case of XI the signal of the CH_3 group appears at 3.80 ppm.

Trichloro derivative XIII is formed in 85% yield in the chlorination of Ic with 3 moles of CBT. The product does not undergo quaternization with CH_3I, i.e., one of the chlorine atoms is in the 4 position. The signal of the 1-CH_3 group is found at 3.75 ppm in the PMR spectrum of XIII, and the other chlorine atom consequently is found in the 9 position. It is not possible to establish the location (6 or 7 position) of the third chlorine atom by means of the spectrum or by chemical means. However, if one takes into account the fact that the trend of the chlorination of 1-methylperimidine Ic is determined by the effective negative charges in the neutral molecule [10] (see below), it may be assumed that the compound formed in the reaction is 4,7,9-trichloro-1-methylperimidine (XIII).

The chlorination of 1-methylperimidine with 4 or more moles of CBT leads to 1-methyl-4,6-7,9-tetrachloroperimidine (XIV) in 75% yield. Compound XIV is also formed in the chlorination of XIII with 1-chlorobenzotriazole.

We also carried out the chlorination of 1-methyl-6,7-dichloroperimidine (XII) with 1 mole of CBT, in which an inseparable mixture of two trichloro derivatives (XV and XVI) is formed. According to the PMR spectral data, this mixture consists of 1-methyl-6,7,9-trichloroperimidine (XV) (83%) and 1-methyl-4,6,7-trichloroperimidine (XVI) (17%). The latter was obtained by methylation of VI.



XV XVI

Thus chlorination with 1-chlorobenzotriazole primarily takes place in the 9 position only if the volume of the group attached to 1-N does not hinder attack on this position by the electrophile. Thus only 1-isopropyl-4,6,7-trichloroperimidine (XVII) is formed in the reaction of 4 moles of CBT with 1-isopropylperimidine.

Similar regularities are observed in the chlorination of 1,2-dimethylperimidine (Id) with 1-chlorobenzotriazole. We also obtained 4,9-dichloro- (XVIII), 4,79-trichloro- (XIX), and 4,6,7,9-tetrachloro-1,2-dimethylperimidine (XX) in the individual state.

The investigation showed that perimidines undergo electrophilic substitution in different directions in acidic and neutral media. Primarily the 6 and 7 (para) positions undergo attack by the electrophile in acidic media, whereas the 9 and 4 (ortho) positions become more active under neutral conditions when appreciable steric hindrance is absent. These differences indicate indirectly that nitration [2], chlorination in CH_3COOH, and acylation in polyphosphoric acid (PPA) [3] proceed through the perimidinium cation, whereas the neutral molecule undergoes chlorination by 1-chlorobenzotriazole in aprotic media. Let us note that the direction of chlorination with CBT is in agreement with the effective negative charges of the neutral molecule ($C_9 > C_4 > C_7 > C_6$), whereas para orientation in the cation correlates with the electrophilic localization energy.

EXPERIMENTAL

The IR spectra of solutions of the compounds in chloroform were measured with a UR-20 spectrometer. The UV spectra of methanol solutions of the compounds were recorded with an SF-4A spectrophotometer. The PMR spectra were recorded with a Tesla BS-467 spectrometer with hexamethyldisiloxane as the internal standard. The course of the reactions was followed by means of TLC. The compounds were purified by chromatography with columns filled with Al_2O_3 (Brockmann activity IV).

4(9)-Chloroperimidine (IIIa). A 5.0-g (0.02 mole) sample of 1,8-dinitro-2-chloronaphthalene [11] was added in portions with stirring at 90°C to a suspension of 8.0 g of powdered iron in 100 ml of xylene, 20 ml of water, and 1 ml of acetic acid, after which the mixture was stirred for 3 h on a boiling-water bath. It was then treated with 2.5 ml of 40% NaOH, and the water was removed by distillation with xylene (three 50-ml portions). The filtrates were combined and treated with 20 ml of concentrated HCl, and the gray precipitate of

1,8-diamino-2-chloronaphthalene dihydrochloride was removed by filtration and washed with petroleum ether to give 1.0 g of product. Without further purification, the diamine was refluxed with 5 ml of formic acid for 1 h, after which the mixture was diluted to twice its volume with water, and the product was purified with activated charcoal. The yield of yellow-green crystals was 0.25 g (6%). UV spectrum, λ_{max} (log ε): 237 (4.62) and 340 nm (4.13).

6(7)-Chloroperimidine (IIa). This compound was obtained by the method described above from 1,8-dinitro-4-chloronaphthalene [5]. Workup gave yellow-green crystals, with mp 198°C (dec.) (mp 200°C [5]), in 54% yield. UV spectrum, λ_{max} (log ε): 330 nm (4.18).

2-Methyl-6(7)-chloroperimidine (IIb). This compound was obtained from 1,8-dinitro-4-chloronaphthalene by reduction with iron and subsequent cyclization with acetic anhydride. Workup gave greenish crystals with mp 175-176°C (dec.) (mp 127°C [5]).

1,8-Dichloro-4-nitronaphthalene. A mixture of 9.8 g (0.05 mole) of 1,8-dichloronaphthalene and 20 ml of HNO_3 (sp.gr. 1.40) was heated to 50°C, during which the temperature rose spontaneously to 80°C; cooling was necessary to prevent ejection of the reaction mixture. After spontaneous heating ceased, the temperature was raised to 90°C, and the mixture was stirred for 1 h. It was then cooled and poured over 40 g of crushed ice. The yellow precipitate was removed by filtration and washed with water until the wash waters were neutral. The yield of yellow needles, with mp 134-135°C (from butanol), was quantitative (10.6 g). Found: C 49.7; H 2.0; Cl 29.5; N 5.5%. $C_{10}H_7Cl_2NO_2$. Calculated: C 50.0; H 2.1; Cl 29.3; N 5.8%.

1,8-Dichloro-4,5-dinitronaphthalene (VII). A 2-ml sample of HNO_3 (sp.gr. 1.50) was added dropwise with vigorous stirring to 1.2 g (5 mmole) of 1,8-dichloro-4-nitronaphthalene, during which the nitric acid began to boil spontaneously. The mixture was refluxed for 10 min, after which it was cooled and poured over 50 g of ice. The resulting yellow precipitate was removed by filtration and washed with water until the wash waters were neutral. The yield was 1.2 g. The mixture was treated with boiling alcohol, and the precipitate was removed by filtration to give 0.5 g (35%) of pale-yellow needles with mp 198-199°C (from butanol). PMR spectrum (DMSO): 8.06 (d, 2- and 7-H) and 8.44 ppm (d, 3- and 6-H, J = 12 Hz). Found: C 42.0; H 1.3; Cl 25.0; N 9.5%. $C_{10}H_4Cl_2N_2O_4$. Calculated: C 41.8; H 1.4; Cl 24.7; N 9.8%. The compound can also be obtained from 1,8-dichloronaphthalene by refluxing in HNO_3 (sp.gr. 1.50), but the yield in this case did not exceed 20%.

6,7-Dichloroperimidine (IV). The method used to prepare IIIa was employed to obtain this compound from VII by reduction with iron in a weakly acidic medium and subsequent cyclization of the resulting 1,8-dichloro-4,5-diaminonaphthalene with formic acid. Workup gave light-yellow prisms in 33% yield.

4,6,7-Trichloroperimidine (VI). A suspension of 1.43 g (5 mmole) of dichloronaphthalene VII in 10 ml of alcohol was added to a solution of 7.9 g (35 mmole) of $SnCl_2 \cdot 2H_2O$ in 30 ml of concentrated HCl, and the mixture was heated on a boiling-water bath for 2 h. It was then cooled, and the precipitated tin complex was removed by filtration and washed with concentrated HCl. A suspension of the complex in 50 ml of water was made alkaline to pH 10 with excess 40% NaOH and extracted with $CHCl_3$. The solvent was removed, and the residue was refluxed with 15 ml of formic acid for 30 min. The mixture was then purified and worked up by the method described for IIIa to give 0.6 (40%) of yellow-green crystals.

1-Methyl-4-chloroperimidine (X). 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 4(9)-chloroperimidine and 0.1 g (1.5 mmole) of 85% KOH in 10 ml of alcohol, and the mixture was stirred at 50°C for 2 h. It was then evaporated to dryness, and the residue was dissolved in 3 ml of benzene. The solution was then subjected to chromatography with a column filled with Al_2O_3 (elution with benzene) to give 0.22 g (84%) of yellow prisms.

1-Methyl-6,7-dichloroperimidine (XII). A solution of 0.66 ml (10 mmole) of methyl iodide in 5 ml of alcohol was added dropwise in a nitrogen atmosphere to a solution of 1.9 g (8 mmole) of IV and 0.66 g (10 mmole) of 85% KOH in 20 ml of alcohol, and the mixture was stirred at room temperature for 3 h. It was then evaporated to dryness, and the residue was chromatographed on Al_2O_3 (elution with chloroform) to give 0.8 g (40%) of gray-green crystals.

1-Methyl-4,6,7-trichloroperimidine (XVI). A solution of 0.2 ml (3 mmole) of methyl iodide in 5 ml of alcohol was added dropwise in a nitrogen atmosphere to a solution of 0.7 g (2.7 mmole) of VI and 0.2 g (3 mmole) of 85% KOH in 15 ml of alcohol, and the mixture was stirred at room temperature for 2.5 h and at 60°C for 30 min. Purification by chromatography with a column filled with Al_2O_3 (elution with chloroform) gave 0.55 g (70%) of yellow-green prisms.

1-Isopropylperimidine. A 6-ml (64 mmole) sample of isopropyl bromide was added dropwise in a nitrogen atmosphere to a solution of 8.4 g (50 mmole) and Ia and 3.3 g (50 mmole) of 85% KOH in 100 ml of alcohol, and the mixture was stirred on a boiling-water bath for 5 h. It was then cooled, and the precipitated KBr was removed by filtration. The solvent was removed by evaporation to dryness, and the residue was chromatographed twice on Al_2O_3 (elution with benzene) to give 2.1 g (20%) of light-brown prisms with mp 127°C (from octane) (mp 67-68°C [12]). PMR spectrum ($CDCl_3$): 1.35 [d, $(CH_3)_2$, J = 7.5 Hz], 3.95 (m, N–CH<), 6.15 (t, 9-H), 6.75 (q, 4-H, J_{meta} = 6 Hz, J_{ortho} = 2 Hz), 7.1 (m, 5–8-H), and 7.35 ppm (s, 2-H). Found: C 79.9; H 6.5; N 13.0%. $C_{14}H_{14}N_2$. Calculated: C 80.0; H 6.7; N 13.3%.

Chlorination of Perimidine (Ia). A) With 1 Mole of Sulfuryl Chloride. A solution of 0.6 ml (7.5 mmole) of sulfuryl chloride in 5 ml of acetic acid was added dropwise to a solution of 1.2 g (7.5 mmole) of Ia in 20 ml of acetic acid, the temperature was gradually raised to 80°C, and the mixture was stirred at this temperature for 1 h. It was then cooled and diluted with 25 ml of water, and the aqueous mixture was neutralized with 22% NH_4OH. The resulting gray-green precipitate was removed by filtration and washed with water. The yield was 1.5 g. The precipitate was chromatographed with a column filled with Al_2O_3 (elution with ethyl acetate) to give 0.15 g (10%) of yellow-green crystals of 4(9)-chloroperimidine (IIIa). No melting-point depression was observed for a mixture of a sample of this product with a genuine sample of IIIa. 6(7)-Chloroperimidine (IIa) was extracted from the aluminum oxide with hot alcohol. Workup gave 1.2 g (80%) of greenish prisms. No melting-point depression was observed for a mixture of a sample of this product with a sample of IIa obtained by alternative synthesis.

B) With 2 Moles of Sulfuryl Chloride. A solution of 1.6 ml (20 mmole) of sulfuryl chloride in 5 ml of acetic acid was added dropwise to a solution of 1.68 g (10 mmole) of Ia in 25 ml of acetic acid, and the mixture was stirred at 80°C for 2 h. It was then cooled, and the precipitated gray crystals were removed by filtration and washed with acetic acid and ether. Chromatography with a column filled with aluminum oxide [elution with chloroform–ethyl acetate (1 : 1)] gave successively 4,7-dichloroperimidine (V) [0.25 g (10%)], trichloroperimidine VI [0.5 g (18%)], and dichloroperimidine IV [0.1 g (4%)]. The filtrate was diluted with 30 ml of water and treated with 22% ammonium hydroxide to precipitate gray-green crystals, which were removed by filtration. The mixture was separated with a column filled with aluminum oxide [elution with chloroform–ethyl acetate (1 : 1)] to give monochloroperimidine IIIa [0.3 g (14%)], dichloroperimidine V [0.5 g (21%)], and 6,7-dichloroperimidine (IV) [0.23 g (10%)]. With respect to their physicochemical properties, IIIa, IV, and VI were identical to the compounds obtained by alternative synthesis.

C) With 3 Moles of Sulfuryl Chloride. A 1.2-ml (15 mmole) sample of sulfuryl chloride was added to a solution of 0.84 g (5 mmole) of Ia in 15 ml of acetic acid, during which the mixture heated up spontaneously. It was then heated to 115°C and stirred at this temperature for 3 h. It was cooled, and the gray precipitate was removed by filtration and washed with ether. It was suspended in concentrated ammonium hydroxide, and the solid material was removed by filtration and washed with water. The yield of 4,6,7-trichloroperimidine (VI) was 1.2 g. No melting-point depression was observed for a mixture of a sample of this product with a genuine sample.

Chlorination of 2-Methylperimidine (Ib). A) With 1 Mole of Sulfuryl Chloride. The reaction was carried out as in the chlorination of perimidine with 1 mole of sulfuryl chloride, and the product was purified by chromatography with a column filled with aluminum oxide (elution with chloroform). The yield of 2-methyl-6(7)-chloroperimidine was 0.8 g (74%). The product was identical to the compound obtained by alternative synthesis.

B) With Excess Sulfuryl Chloride. A 2.4-ml (30 mmole) sample of sulfuryl chloride was added to a solution of 0.91 g (5 mmole) of Ib in 15 ml of acetic acid, and the mixture was heated at 80°C for 3 h. It was then cooled, and the dark-green crystals of tetrachloro-2-methylperimidine VIII were removed by filtration.

Chlorination of 1-Methylperimidine (Ic). With 1 Mole of 1-Chlorobenzotriazole. A solution of 0.38 g (2.5 mmole) of 1-chlorobenzotriazole in 20 ml of chloroform was added dropwise at 0°C in the course of 1 h to a solution of 0.45 g (2.5 mmole) of Ic in 50 ml of chloroform, after which the chloroform solution was concentrated and passed through a column filled with aluminum oxide (elution with chloroform). The 1-methyl-4,9-dichloroperimidine (XI) fraction with R_f 0.6 was collected. The yield of gray-green prisms of IC was 0.09 g (15%).

B) With 2 Moles of 1-Chlorobenzotriazole. The reaction was carried out under conditions similar to those described above. Purification by chromatography with a column filled with Al_2O_3 (elution with chloroform) gave dichloroperimidine XI in 90% yield.

C) With 3 Moles of N-Chlorobenzotriazole. The reaction of 0.45 g (2.5 mmole) of IX and 1.14 g (7.5 mmole) of CBT in 70 ml of chloroform at room temperature gave 0.6 g of 1-methyl-4,7,9-trichloroperimidine (XIII).

D) With Excess N-Chlorobenzotriazole. Treatment of 1-methylperimidine with excess CBT under the conditions in experiment C gave yellow green crystals of tetrachloro derivative XIV in 75% yield.

Reaction of 1-Methyl-6,7-dichloroperimidine with N-Chlorobenzotriazole. Equimolar amounts of XII and CBT were stirred in chloroform for 1 h. The product was purified by chromatography. The yield of trichloroperimidines XV and XVI, obtained as green prisms with mp 203-204°C (alcohol), was 90%. PMR spectrum (CF_3COOH): 3.25 (s, $-CH_3$, 17%), 3.67 (s, $-CH_3$, 83%), 6.63 (d, 4-H, J = 8 Hz), 7.17 (d, 5-H, J = 8 Hz), 7.17 (s, 8-H), and 7.73 ppm (s, 2-H).

1-Isopropyl-4,6,7-trichloroperimidine (XVII). A solution of 1.53 g (10 mmole) of CBT in 30 ml of chloroform was added dropwise in the course of 1 h to a solution of 0.5 g (2.5 mmole) of 1-isopropylperimidine in 70 ml of chloroform, and the product was purified by the usual general method. The yield of yellow needles of trichloro derivative XVII was 0.45 g.

Chlorination of 1,2-Dimethylperimidine with 1-Chlorobenzotriazole. A) With 2 Moles of CBT. Stoichiometric amounts of 1,2-dimethylperimidine and CBT were stirred in chloroform for 1 h, after which the mixture was concentrated and purified by chromatography on aluminum oxide (elution with benzene). The yield of bright-yellow prisms of dichloro derivative XVIII was 45%.

B) With 3 Moles of CBT. The experiment was carried out by the usual method, and the product was purified by chromatography on aluminum oxide (elution with chloroform). The yield of yellow-green prisms of 1,2-dimethyl-4,7,9-trichloroperimidine was 75%.

C) With 4 Moles of CBT. The reaction was carried out under conditions similar to those described above. Purification with a column filled with Al_2O_3 (elution with chloroform) gave yellow-green prisms of 1,2-dimethyl-4,6,7,9-tetrachloroperimidine (XX) in 60% yield.

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