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REACTION OF SUBSTITUTED 5-AMINOPYRIMIDINES WITH OXALYL CHLORIDE

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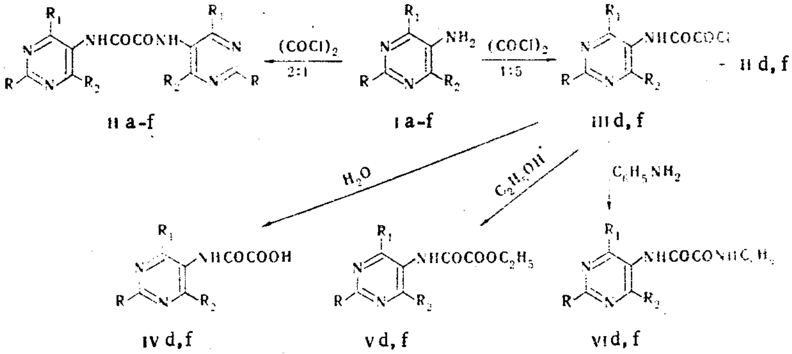
Depending on the reaction conditions and the substituents, N-(2,4,6-substituted 5-pyrimidinyl)oxamyl chlorides and N,N'-di(2,4,6-substituted 5-pyrimidinyl)oxamides are formed in the reaction of 5-aminopyrimidines with oxalyl chloride.

Pyrimidinyl isocyanates have been obtained as a result of the reaction of oxalyl chloride with 2- and 4-aminopyrimidines [1, 2]. It is known that the reactions of amino groups with oxalyl chloride proceed in different ways as a function of the basicities of the amino groups. In the present research we have studied the reaction of oxalyl chloride with 5-aminopyrimidines (I). Inasmuch as the amino groups attached to C-5 have higher basicities than the amino groups in the 2 and 4 positions, one might have expected the production of stable 5-pyrimidinyloxamyl chlorides (III).



a $R=R_1=R_2=H$; b $R=CH_3$, $R_1=R_2=H$; c $R=C_6H_5$, $R_1=R_2=H$; d $R=H$, $R_1=R_2=Cl$; e $R=CH_3$, $R_1=R_2=Cl$; f $R=C_6H_5$, $R=R_2=Cl$

N,N'-Di(5-pyrimidinyl)oxamides (II) or N-(5-pyrimidinyl)oxamyl chlorides (III) mixed with II were obtained under conditions close to those described in [1, 2] with 1 equivalent or with excess oxalyl chloride, respectively. Compounds Id, f with two chlorine atoms adjacent to the amino group form primarily acid chlorides IIId, f (70%) and oxamides IId, f in 25% yields, in contrast to amine Ic, which gives primarily oxamide IIc (80%). The structure of IIId, f was proved by hydrolysis, alcoholysis, and aminolysis to give, respectively, N-(5-pyrimidinyl)oxamic acids (IVd, f), oxamic acid esters (Vd, f), and N,N'-substituted oxamides (VId, f). In addition, N,N'-di(5-pyrimidinyl)oxamide IId, identical to the compound obtained by reaction of Id with one equivalent of oxalyl chloride, was obtained from acid chloride IIId and starting amine Id.

Two absorption bands at 3200-3500 cm^{-1} (NH$_2$ group) are observed in the IR spectra of starting aminopyrimidines Ia-f, whereas the spectra of the reaction products contain only one such absorption band (NH group) and an absorption band at 1720-1780 cm^{-1} (C=O group).

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TABLE 1. Compounds II and IV-VI

Compound	mp, °C*	Crystallization solvent	Empirical formula	Found, %				Calculated, %				Yield, %
				C	H	Cl	N	C	H	Cl	N	
IIa	>360†	DMFA	$C_{10}H_8N_6O_2$	49,2	3,4	—	33,9	49,2	3,3	—	34,4	84
IIb	>330	The same	$C_{12}H_{12}N_6O_2$	52,9	4,3	—	30,7	52,9	4,4	—	30,9	67
IIc	>350	The same	$C_{22}H_{16}N_6O_2$	66,7	4,5	—	21,2	66,7	4,1	—	21,2	78
IId	259—260	Ethanol	$C_{10}H_4Cl_4N_6O_2$	31,5	1,0	37,1	22,5	31,4	1,0	37,1	22,0	90
IIe	270—272	The same	$C_{12}H_8Cl_4N_6O_2$	35,2	2,0	34,5	20,5	35,2	2,0	34,6	20,5	83
IIf	>300	Dioxane	$C_{22}H_{12}Cl_4N_6O_2$	49,4	2,4	26,3	15,7	49,5	2,3	26,5	15,7	70
IVd	223—224	Benzene	$C_6H_3Cl_2N_3O_3$	31,0	1,2	29,7	17,3	30,5	1,3	30,0	17,8	72
IVf	170—172	The same	$C_{12}H_7Cl_2N_3O_3$	46,2	2,1	22,7	13,5	46,2	2,3	22,7	13,5	99
Vd	149—151	Carbon tetrachloride	$C_8H_7Cl_2N_3O_3$	36,5	2,7	26,9	16,2	36,4	2,8	26,8	15,9	82
Vf	213—215	Ethanol	$C_{14}H_{11}Cl_2N_3O_3$	49,8	3,1	20,7	12,6	49,4	3,3	20,8	12,4	96
VId	209—211	Benzene, ethanol	$C_{12}H_8Cl_2N_4O_2$	46,0	2,6	22,8	18,2	46,3	2,6	22,8	18,0	80
VIf	248—249,5	Ethanol	$C_{18}H_{12}Cl_2N_4O_2$	55,8	3,1	18,3	14,4	55,8	3,1	18,3	14,5	89

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*Compounds II and IV melt with decomposition.

†Chars without melting.

EXPERIMENTAL METHOD

The individuality of the compounds was monitored by means of thin-layer chromatography (TLC) on a loose layer of activity II Al_2O_3. The solvent was ethanol, the eluent was chloroform–methanol (3 : 1), and the chromatograms were developed in UV light. The IR spectra of KBr pellets and mineral oil suspensions of the compounds were recorded with a UR-20 spectrometer.

Starting 5-aminopyrimidines Ia-f were obtained by the methods in [3, 8].

N,N'-Di(2,4,6-substituted 5-pyrimidinyl)oxamides (IIa-f). A mixture of 10 mmole of Ia-f and 5 mmole of oxalyl chloride in 50 ml of solvent (chloroform for IIa-d and carbon tetrachloride for IIe,f) was refluxed for 2.5 h, after which it was cooled, and the solid was removed by filtration and washed with solvent. It was then treated with water, after which the water was removed by filtration, and the solid was washed with water until the washings were neutral. Oxamides II were obtained as white crystalline powders that were only slightly soluble in organic solvents and decomposed at high temperatures (Table 1).

N-(4,6-Dichloro-5-pyrimidinyl)oxamyl Chloride (IIId). A solution of 12.7 g (0.1 mole) of oxalyl chloride in 20 ml of chloroform was added dropwise with stirring to 3.3 g (0.02 mole) of Id in 60 ml of chloroform, after which the mixture was refluxed for 2.5 h. It was then cooled, and the precipitate was removed by filtration, without access to moisture, to give 0.9 g (24%) of oxamide IId. The chloroform mother liquor was evaporated, after which the syrupy residual IIId began to crystallize to give 3.7 g (73%) of IIId with mp 75-80° (dec., petroleum ether). Found: C 28.8; H 0.9; N 16.7%. $C_6H_2Cl_3N_3O_2$. Calculated: C 28.3; H 0.8; N 16.5%.

N-(4,6-Dichloro-2-phenyl-5-pyrimidinyl)oxamyl Chloride (IIIf). This compound was similarly obtained from 2.4 g (0.01 mole) of If and 6.35 g (0.05 mole) of oxalyl chloride in 40 ml of chloroform. The yield of oxamide IIf was 0.78 g (29%). The yield of acid chloride IIIf, with mp 143-146° (dec.), was 2.2 g (67%). Found: C 43.7; H 1.9; Cl 32.4; N 12.8%. $C_{12}H_6Cl_3N_3O_2$. Calculated: C 43.6; H 1.8; Cl 32.2; N 12.7%.

According to the analytical results, oxamides IId, f were identical to those presented in Table 1.

Reaction of Oxalyl Chloride with 2-Phenyl-5-aminopyrimidine (Ic). A solution of 6.4 g (0.05 mole) of oxalyl chloride in 10 ml of chloroform was added dropwise in the course of 5 min to 1.74 g (0.01 mold) of Ic in 50 ml of chloroform, during which a white precipitate formed. The mixture was refluxed with stirring for 2.5 h, after which it was cooled. The precipitated oxamide IIc was removed by filtration and washed to give 1.61 g (81%) of a product identical to the IIc presented in Table 1.

N-(4,6-Dichloro-2-substituted 5-pyrimidinyl)oxamic Acids (IVd, e, Table 1). Water (2 ml) was added to 15 mmole of IIId, f in 40 ml of acetone. After 10 min, the solution was vacuum evaporated, and the residue was washed with ice water and dried in a vacuum desiccator over P_2O_5 and KOH (for 24 h) to give hydrated IVd with mp 117-118° (dec.). The hydrate lost a water molecule on recrystallization from absolute benzene. In air, IVd again added a water molecule. Compound IVf charred without melting on slow heating to 315°; it melted with decomposition when the melting point tube was inserted into a block heated to 150°.

Ethyl N-(4,6-Dichloro-2-substituted 5-pyrimidinyl)oxamates (Vd, f, Table 1). Absolute ethanol (2 ml) was added to 0.01 mole of IIId, f in 30 ml of absolute benzene. After 15 min, the solvent was removed by distillation, and the residue was treated with ice water (40 ml). The resulting precipitate was removed by filtration and dried in a vacuum desiccator over P_2O_5 and KOH to give colorless plates (Vd) or needles (Vf).

N-Phenyl-N'-(4,6-dichloro-2-substituted 5-pyrimidinyl)oxamide (VId, f, Table 1). A mixture of 7 mmole of IIId, f and 14 mmole of freshly distilled aniline in 50 ml of absolute benzene was allowed to stand overnight. The resulting precipitate was removed by filtration and washed with benzene. The aniline hydrochloride was removed from the solid material with water. Workup gave VId (colorless prisms) or VIf (needles).

Reaction of Acid Chloride IIId with Aminopyrimidine Id. N,N'-Di-(4,6-dichloro-5-pyrimidinyl)oxamide (IId). A mixture of 1.27 g (5 mmole) of IIId and 0.82 g (5 mmole) of Id in 50 ml of chloroform was refluxed for 20-30 min, during which a precipitate formed. The mixture was cooled, and the precipitate was removed by filtration and washed with chloroform and water to give 1.73 g (91%) of IId with mp 260-261° (dec.). The product was identical to the IId obtained from Id and oxalyl chloride.

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HETEROCYCLIC ANALOGS OF PLEIADIENE

XXII.* SYNTHESIS AND SOME PHYSICAL PROPERTIES OF THE ACEPERIMIDYLENE HETEROAROMATIC SYSTEM

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Derivatives of a new heteroaromatic system – aceperimidylene – were obtained by dehydrogenation of aceperimidine and its substituted derivatives. The physical properties of the aceperimidylenes provide evidence that they have greater aromatic character than perimidines.

It has been established that the π-electron density of the perimidine (I) and aceperimidine (IIa) molecules is distributed nonuniformly, and this brings about a decrease in the aromatic character and an increase in the reactivities of these compounds with respect to both nucleophilic and electrophilic reagents [2]. One of the possible reasons for this is the presence in perimidines of only 13 peripheral π electrons, which, according to Platt, is of decisive significance in the manifestation of aromatic properties by polynuclear systems [3].

The aim of the present research was the synthesis and study of the electronic properties of a new heteroaromatic system – acenaphtho-[5,6-d,e]pyrimidine (III) – which we have called aceperimidylene. System III has 14 peripheral π electrons, and it should therefore, in conformity with Hückel's rule, differ substantially from molecules I and II with respect to its physical and chemical properties.

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*See [1] for communication XXI.

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