SYNTHESIS AND PROPERTIES OF PHENYL(METHYL)-SUBSTITUTED 2- AND 4-NITROSOPYRIMIDINES*

G. G. Moskalenko, V. F. Sedova,
and V. P. Mamaev†

UDC 547.853:542.943

Phenyl(methyl)-substituted 2- and 4-nitroso- and azoxypyrimidines were synthesized for the first time by the oxidation of phenyl(methyl)-substituted 2- and 4-hydroxyaminopyrimidines by activated MnO_2, Ag_2CO_3 on zeolite, or $BaMnO_4$. Certain chemical properties of the synthesized nitrosopyrimidines were studied, such as reduction, nucleophilic substitution of the nitroso group, the condensation reaction with aniline and hydroxyaminopyrimidines.

Unlike aromatic nitroso comounds, nitrosoazines have not yet been adequately investigated. This is largely due to the difficulties in the synthesis of nitroso derivatives of π-deficient heterocyclic compounds, in particular compounds with the nitroso group in the α-position with respect to the nitrogen atom in the azine ring [2, 3].

Mainly 5-nitroso derivatives have been synthesized in the pyrimidine series. The nitroso group can be introduced by direct nitrosation into an even position of the pyrimidine ring only in the case of two compounds in the presence of several strong electron-donor substituents [4, 5]. Unsubstituted 2-nitrosopyrimidine was obtained by oxidation of S,S-dimethyl-N-(pyrimidin-2-yl)sulfylimine [6]. Attempts to obtain derivatives of 4-nitrosopyrimidine by the last method were unsuccessful [7].

We have previously proposed a method for the synthesis of phenyl(methyl)-substituted 2- and 4-hydroxyaminopyrimidines from the corresponding chloro derivatives [8] and described the behavior of these compounds in the presence of oxidizing agents [1, 9, 10]. No further data are available in the literature on the oxidation of hydroxyaminopyrimidines.

The present work deals with the oxidation of phenyl(methyl)-substituted 2- and 4-hydroxyaminopyrimidines to nitroso derivatives and the study of the chemical properties of

TABLE 1. Oxidation of 4-Hydroxyamino-2,6-diphenylpyrimidine (Ia) by Activated MnO_2

Solvent	Method of preparation MnO_2	Time of preliminary mixing of MnO_2, min	Yield, %	
			IIa	IIIa
$CHCl_3$	A	0	51	42
$CHCl_3$	A	10	91	—
$CHCl_3$*	B	10	40	52
$CHCl_3$*	B **	0	40	50
$CHCl_3—C_2H_5OH$ (4 : 1)	B	0	98	—

*The solvent was passed through Al_2O_3 to remove the alcohol.

†A 1-g portion of MnO_2 was preliminarily washed with alcohol (20 ml) and $CHCl_3$* (50 ml).

---

*For preliminary communication, see [1].

†Deceased.

Novosibirsk Institute of Organic Chemistry, Siberian Branch, Academy of Sciences of the USSR, Novosibirsk 630090. Translated from Khimiya Geterotsiklicheskikh Soedinenii, No. 7, pp. 962-968, July, 1989. Original article submitted January 5, 1988; revision submitted July 21, 1988.

TABLE 2. Characteristics of Compounds Ic,g, IIa-d,f-j, IIIa,d,e,i,j, IVa -g, Va

Compound	Empirical formula	T_{mp}, °C*	Yield, % (method)
Ic	$C_{10}H_9N_3O$	139...142 (dec.)	46
Ig	$C_{10}H_9N_3O$	184...185 (dec.)	91
IIa	$C_{16}H_{11}N_3O$	167...170 (dec.)	91 (C), 96 (G)
IIb	$C_{10}H_7N_3O$	120...122 (dec.)	86 (E)
IIc	$C_{10}H_7N_3O$	150...153 (dec.)	94 (C)
IId	$C_{11}H_9N_3O$	147...152 (dec.)	93 (C), 90 (F)
IIf	$C_{16}H_{11}N_3O$	181...183 (dec.)	98 (C)
IIg	$C_{10}H_7N_3O$	158...160 (dec.)	90 (C)
IIh	$C_{10}H_7N_3O$	136...138 (dec.)	95 (C)
IIi	$C_6H_7N_3O$	111...112 (dec.)	97 (E), 95 (F), 93 (G)
IIj	$C_4H_3N_3O$	127...129 (dec.)	98 (C)
IIIa	$C_{32}H_{22}N_6O$	191...194 (dec.)	98
IIId	$C_{22}H_{18}N_6O$	161...162 (dec.)	75
IIIe	$C_{22}H_{18}N_6O$	141...142 (dec.)	79 (F)
IIIi	$C_{12}H_{14}N_6O$	138...141 (dec.)	98 (C)
IIIj	$C_8H_6N_6O$**	124...126 (dec.)	16 (C)***
IVa	$C_{22}H_{16}N_4$	159...161	91
IVb	$C_{16}H_{12}N_4$	75...77	77
IVc	$C_{16}H_{12}N_4$	72...73	88
IVd	$C_{17}H_{14}N_4$	116...118	91
IVe	$C_{17}H_{14}N_4$	103...105	52
IVf	$C_{22}H_{16}N_4$	142...146	60
IVg	$C_{16}H_{12}N_4$	146...148	67
Va	$C_{17}H_{14}N_2O$	118...119	39

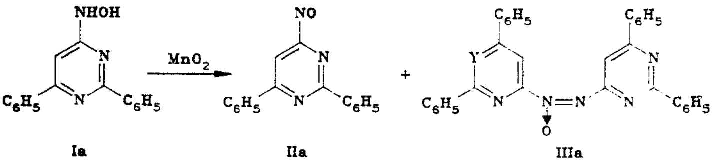
*Compound Ic was crystallized from benzene, Ig — from acetonitrile, IIa, d — from ethylacetate, IVa,f — from a hexane—benzene mixture, IVb-e, g — from hexane, Va from petroleum ether 70...100°C. Compounds IIb,c,f-j, IIIa,d,e,i,j were reprecipitated by ether from $CHCl_3$ solution.

**High resolution mas spectrum: found 202.0611; calculated 202.0603.

***Obtained by using a low-activity MnO_2.

the latter. As the oxidizing agents, we selected the activated MnO_2 and silver carbonate on a zeolite, with which the hydroxyamino group can be oxidized to the nitroso group in aromatic and heteroaromatic compounds under mild conditions [3, 11, 12], as well as barium manganate.

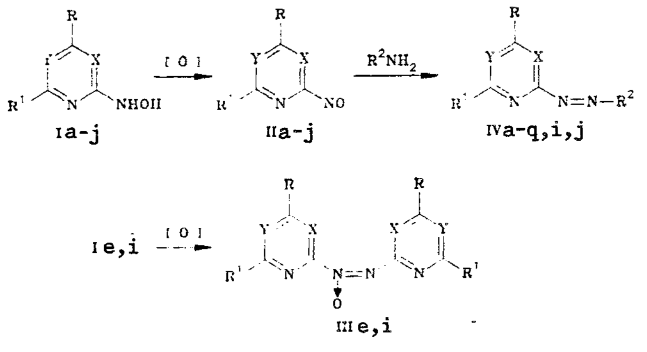
The action of activated MnO_2 on 4-hydroxyamino-2,6-diphenyl—pyrimidine (Ia) in chloroform at room temperature gives a mixture of 4-nitroso-2,6-diphenylpyrimidine (IIa) and 2,2',6,6'-tetraphenyl-4,4'-azoxypyrimidine (IIIa) (Table 1), the latter being the condensation product of the nitrosopyrimidine IIa formed with the initial hydroxyaminopyrimidine Ia. An important factor determining the ratio of the nitroso- and azoxy derivatives is the activity of the MnO_2 used. We have mainly used MnO_2 obtained from manganese sulfate according to [13] and in its activity corresponding to conditions described in the experimental part. To obtain higher yields of nitrosopyrimidines, it was necessary to find conditions, which suppress the condensation reaction. However even on carrying out the reaction in acetonitrile, methylene chloride and ether, with decrease in the reaction temperature to −30°C, and using various methods of mixing the reagents and varying the ratios of hydroxyaminopyridine Ia and the activated MnO_2 from 1:5 to 1:10 (by weight), also resulted in a mixture of compounds IIa and IIIa (according to TLC data).



Ia IIa IIIa

Nitrosopyrimidine IIa could be obtained free of the azoxy compound IIIa by using MnO_2 which before oxidation was preliminarily suspended in chloroform, and the mixture was stirred for 10 min. Under these conditions, from compounds Ic,d,f-h,j, the corresponding nitrosopyrimidines IIc,d,f-h,j were synthesized in high yields (Table 2), including the unsubstituted

2-nitrosopyrimidine (IIj), which the authors of [6] did not succeed in isolating. In the case of 2-hydroxyamino-4,6-dimethylpyrimidine (Ii), oxidation at room temperature led to the formation of 4,4',6,6'-tetramethyl-2,2'-azoxypyrimidine (IIIi) in quantitative yield. The corresponding nitrosopyrimidine was obtained only by oxidation at −10°C. The same temperature was required for the preparation of pure nitroso compound IIb. The nitroso derivative IIe was found to be unstable, and therefore it could not be isolated in pure state and characterized.



I-IV a-e X = CH, f-j X = N; a-e Y = N, f, h-i Y = CH, g Y = C–C_6H_5; a, b, e, f, h R = C_6H_5, c, g, j R = H, d, i R = CH_3; a, c, d, f R^1 = C_6H_5, b, g, h, j R^1 = H, e, h R^1 = CH_3; IVA-i R^2 = C_6H_5, j R^2 = C_6H_4–OCH_3-p.

In most cases, compounds II and III have similar R_f values, which impedes the separation of their mixture by the TLC method. Therefore, the purity of compounds II was confirmed by the combination of TLC, PMR and mass spectra data. Thus, in some experiments, during the oxidation of pyrimidine Ij, the content of nitrosopyrimidine IIj varied, according to the PMR spectral data, from 80 to 98%, while azoxypyrimidine IIIj was the by-product.

The composition of the reaction mixture during the oxidation is greatly influenced by the presence of an alcohol. Thus, during the oxidation of pyrimidine Ia, the use of chloroform not containing an alcohol led to increase in the amount of the azoxy compound IIIa, while the use of a chloroform–alcohol mixture (4:1) gave pure nitrosopyrimidine IIa (Table 1). It was independently shown that alcohol suppresses the condensation reaction between compounds Ia and IIa: the reaction in chloroform is concluded in the course of 30 min, while in a chloroform–alcohol (4:1) mixture it takes 30 h. At the same time, the alcohol does not appreciably change the activity of MnO_2 during a short-time treatment (Table 1). A similar condensation reaction was carried out in chloroform between compounds Id and IId.

$$\text{Ia,d} + \text{IIa,d} \rightarrow \text{IIIa,d}$$

In addition to analytical and structural data, the structure of the nitrosopyrimidines obtained by their conversion during the condensation with aniline into the corresponding 2- and 4-phenylazopyrimidines IVa-g,i. From the unsubstituted 2-nitrosopyrimidine (IIj) and p-anisidine, the azo derivative IVj previously described in [6], was synthesized. Pure azo derivative IVh could not be obtained.

The action of freshly prepared silver carbonate on zeolite on the hydroxypyrimidines Id,i also led to 2- and 4-nitroso derivatives IId,i, while, in contrast to the oxidation with activated MnO_2, the nitroso derivative IIi was obtained at room temperature. At the same time, during the oxidation of pyrimidine Ie, instead of the expected nitroso derivative, azoxypyrimidine IIIe was isolated. The results obtained (yield of the product, conditions and time of carrying out the reaction) show that silver carbonate on zeolite has no particular advantages over the activated MnO_2 in the synthesis of nitrosopyrimidines, while its instability on storage makes its use less convenient.

The first data on the use of barium manganate for the oxidation of organic compounds were published in 1978 [14], and its high activity, comparable with that of MnO_2, was noted. However, $BaMnO_4$ was not used for the oxidation of hydroxylamine. We showed that hydroxyaminopyrimidines are also oxidized to nitroso derivatives by barium manganate. In particular, 2- and 4-nitrosopyrimidines IIa,i were obtained in yields of more than 90% by the action of this oxidant.

All the isolated nitrosopyrimidines IIa-d,f-i are in the form of colorless or yellow crystals, which are stable in the solid state at room temperature and in dilute solutions in

TABLE 3. PMR and Mass Spectra of Compounds Ig, IIa-d, f-j, IIIa,d,e,i,j, IVa-g

Compound	PMR spectrum, δ ,ppm (in $CDCl_3$)*				Mass spectrum, M^+, $M^+/(M+2)^+$**
	CH_3	4-H	5-H (2-H)	CH_{arom}	
Ig	—	8,50 (2H)	—	7,13 (5H)	—
IIa	—	—	8,18	7,03...7,39 (3H); 7,49...7,66 (3H); 7,91...8,03 (2H); 8,21...8,37 (2H)	261, 100/833
IIb	—	—	*** (8,76)	7,39...7,66 (3H); 8,08...8,32 ($2H+H^5$)	185, 100/30
IIc	—	9,10, d, J=5 Hz	***	7,17...7,47 ($3H+H^5$); 7,60...8,03 (2H)	185, 100/50
IId	2,60	—	7,57	7,00...7,43 (3H); 7,70...8,07 (2H)	199, 100/50
IIf	—	—	***	7,27...7,63 (6H); 7,87...8,37 ($4H+H^5$)	—, 0/100
IIg	—	8,87 (2H)	—	7,46...7,62 (5H)	185, 100/4
IIh	—	8,70, d, J=5 Hz	***	7,10...7,57 (3H); 7,57...8,00 ($2H+H^5$)	185, 100/63
IIi	7,37 (6H)	—	7,20	—	137, 100/14
IIj	—	8,68 (2H), d, J=5 Hz	7,40, t J= =5 Hz	—	109, 100/7
IIIa	—	—	8,30 & 8,50	7,40...7,62 (12H); 8,20...8,39 (4H); 8,56...8,74 (4H)	
IIId	2,62 & 2,67	—	7,63 & 7,83	7,30...7,63 (6H); 8,33...8,80 (4H)	382, —
IIIe	2,77 & 2,87	—	8,20 & 8,40	7,30...7,70 (6H); 7,83...8,33 (4H)	382, —
IIIi	2,37 (6H) & 2,47 (6H)	—	6,90 & 7,30	—	
IIIj	—	8,88 (2H), d, J=5 Hz & 9,00 (2H), d, J=5 Hz	7,28, t, J= =5 Hz & 7,68, t, J= =5 Hz	—	202, —
IVa	—	—	7,80	7,30...7,67 (11H); 7,93...8,33 (2H); 8,53...8,83 (2H)	—
IVb	—	—	7,93 (9,27)	7,30...7,67 (6H); 7,86...8,23 (4H)	—
IVc	—	8,77, d, J=5 Hz	***	7,17...7,51 ($6H+H^5$); 7,80...8,10 (2H); 8,27...8,61 (2H)	—
IVd	2,60	—	7,23	7,37...7,70 (6H); 7,97...8,23 (2H); 8,43...8,80 (2H)	—
IVe	2,83	—	7,73	7,37...7,60 (6H); 7,90...8,30 (4H)	—
IVf	—	—	8,10	7,33...7,73 (9H); 8,00...8,43 (6H)	—
IVg	—	9,03 (2H)	—	7,23...7,73 (8H); 7,90...8,27 (2H)	—

---

*Solvent for compound Ig — CF_3COOH.

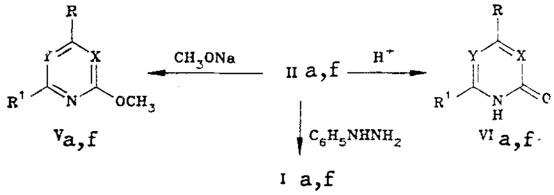
**The values of $M^+/(M + 2)^+$ are normalized with respect to M^+. Compounds IIIa,i do not give ion M^+, but only an ion with m/z $(M - 28)^+$, present also in the spectra of compounds IIId,e,j.

***The proton signal occurs in the region of aromatic protons.

chloroform produce a green color, characteristic of nitroso compounds. The nitroso derivative IIb is less stable in solution than in the solid state, and in some cases its spontaneous decomposition was observed. Compounds IIa-d, f-i are sparingly soluble in most organic solvents, with the exception of chloroform and methylene chloride.

Except for compound IIf, the synthesized nitrosopyrimidines have in the mass spectrum a peak of molecular ion (Table 3) and one of the most intense peaks in the spectrum $(M - 30)^+$, i.e., $(M - NO)^+$. The characteristic feature of these compounds is the presence in the mass spectrum of a fairly intense peak of an ion with m/z $(M + 2)^+$. The intensity of this peak relative to the peak of M^+ depends on the type of the substitution and substituent (see Table 3). The absence in compounds II obtained of an admixture of the initial hydroxyamino derivatives I was confirmed by a negative reaction with $FeCl_3$, TLC data, and the difference between mass spectra of I and II. To establish the reason for the appearance of the intense peak of $(M + 2)^+$ requires additional investigation.

Taking 2- and 4-nitrosopyrimidines IIa,f as an example, it was shown that by the action of phenylhydrazine on the nitrosopyrimidines, the nitroso group is reduced to a hydroxyamino group, while the action of sodium methylate in a mixture of chloroform with methanol on these compounds at room temperature gives methoxypyrimidines Va,f. The last reaction is completed after 10 min, which indicates a high nucleophilic mobility of the nitroso group. For comparison: The conversion of 4-chloro-2,6-diphenylpyrimidine into compound Va requires boiling in methanol in the presence of sodium methylate for 30 min [15].



V, VI a X=CH, Y=N, R=C_6H_5, R¹=C_6H_5; f X=N, Y=CH, R=C_6H_5, R¹=C_6H_5

It is known that in an acidified aqueous medium, 2- and 4-nitrosopyridines convert into N-pyridylpyridones [16]. In contrast, 2- and 4-nitrosopyrimidines IIa,f remain unchanged under these conditions. With increase in the amount of the acid, nitroso pyrimidines IIa,f are hydrolyzed with the formation of oxopyrimidines VIa,f.

EXPERIMENTAL

The IR spectra were recorded on a UR-20 spectrophotometer in KBr tablets (c = 0.25%) or in chloroform. The PMR spectra were run on Varian A 56/60 and Bruker WP-200 SY spectrometers, using HMDS as internal standard. The mass spectra were taken on MS-902 at 70 eV and Finnigan MAT-8200 spectrometers. The compounds were identified according to TLC on Silufol UV-254 plates with chloroform as eluent, according to melting points and IR spectra. The activated MnO_2 was obtained from $MnSO_4$ (method A) and $MnCl_2$ (method B) according to [13], silver carbonte on zeolite according to [17], $BaMnO_4$ – according to [14].

The characteristics of the synthesized compounds are listed in Tables 2, 3. The data of the elemental analysis of the synthesized compounds for C, H, N correspond to calculated values.

Standardization of Activated MnO_2. A 0.4-ml portion of benzyl alcohol was added at 20°C to a suspension of 2.5 g MnO_2 in 25 ml of dry ether. The mixture was stirred for 15 min, the precipitate was filtered, and washed with 10 ml of ether. A 0.4-ml portion of phenylhydrazine was added to the filtrate, and the mixture was stirred for 1 h. The solution was evaporated, and the residue was washed with pentane (10 ml), hot water (25 ml), and dried. Benzaldehyde phenylhydrazone was obtained. The activated MnO_2 was used in further operations if not less than 0.30 g of the above hydrazone was obtained.

Hydroxyaminopyrimidines Ic,g were obtained similarly as in [6] from the corresponding chloropyrimidines.

Oxidation of Hydroxyaminopyrimidines I. A. A 6-g portion of MnO_2 was added to a solution of 0.79 g (3 mmoles) of compound Ia in 100 ml of $CHCl_3$, and the mixture was stirred for 10 min at 20°C. The precipitate was filtered and washed with chloroform (100 ml). The chloroform was evaporated, and the residue was chromatographed on a plate with silica gel (0...140 μm), using chloroform as eluent. Yield, 0.40 g (51%) of nitrosopyrimidine IIa and 0.32 g (42%) of azoxypyrimidine IIIa.

B. The reaction was performed in a similar way as by method A in a chloroform—alcohol mixture (4:1). The solution was evaporated, the residue was washed with a small amount of ether and nitrosopyrimidine IIa was obtained in 98% yield (Table 1).

C. A suspension of 6 g of MnO_2 in 100 ml of $CHCl_3$ was stirred for 10 min at 20°C, 0.79 g (3 mmoles) of hydroxyaminopyrimidine Ia was added, and the mixture was stirred for another 10 min. The precipitate was filtered, washed with chloroform (100 ml) and the filtrate was evaporated. The residue was washed with ether (5 ml). Yield 0.71 g (91%) of nitrosopyrimidine IIa.

In a similar way, nitrosopyrimidines, IIc,d,f-h,j were obtained from hydroxyaminopyrimidines Ic,d,f-h,j, and could be used in further operations without additional purification.

During the oxidation of hydroxyaminopyrimidine Ii under the above conditions, azoxypyrimidine IIIi was obtained.

D. A suspension of 1 g of MnO_2 was stirred for 10 min in 20 ml $CHCl_3$, and passed over a layer of Al_2O_3. A 0.10-g portion (0.4 mmole) of compound Ia was added and the mixture was stirred for another 10 min. The precipitate was filtered and washed with chloroform (20 ml). Further isolation of compounds IIa and IIIa was carried out according to method A (Table 1).

E. A suspension of 3 g of MnO_2 in 100 ml of $CHCl_3$ was stirred for 10 min at 20°C, and then cooled to −10°C. A 0.21-g portion (0.5 mmole) of hydroxyaminopyrimidine Ii was added and the mixture was stirred for 10 min at −10°C and for 30 min at 20°C. Isolation of the product was carried out according to method C. Yield, 0.18 g of nitrosopyrimidine IIi.

Nitrosopyrimidine IIb was obtained from compound Ib in a similar way.

F. A 0.30-g portion (1.5 mmole) of hydroxyaminopyrimidine Id was added to a suspension of 3 g of silver carbonate on zeolite in 100 ml of $CHCl_3$, and the mixture was stirred for 10 min in darkness at 20°C. The isolation of the product was carried out according to method C. Yield, 0.27 g of compound IId.

Nitrosopyrimidine IIi was synthesized from compound Ii in a similar way.

In the oxidation under the above conditions of compound Ie, azoxypyrimidine IIIe was obtained.

G. A 5.12-g portion (20 mmole) of $BaMnO_4$ was added to a solution of 0.53 g (2 mmole) of compound Ia in 100 ml of $CHCl_3$ and the mixture was stirred for 10 min. The product was isolated according to method A. Yield, 0.50 g of nitrosopyrimidine IIa.

Nitrosopyrimidine IIi was synthesized from compound Ii in a similar way.

Azoxypyrimidines (IIIa,d). A 0.26-g portion (1 mmole) of hydroxyaminopyrimidine Ia was added to a solution of 0.26 g (1 mmole) of nitrosopyrimidine (IIa) in 40 ml of $CHCl_3$, and the mixture was stirred for 30 min at 20°C. The solution was evaporated and the residue was washed with ether (5 ml). Yield, 0.50 g (98%) of azoxypyrimidine IIIa.

In a similar way, azoxypyrimidine IIId was obtained by a reaction of equimolar amounts of compounds Id and IId.

Azopyrimidines (IVa-g,i,j. A. A suspension of 5 g of MnO_2 in 100 ml of $CHCl_3$ was stirred for 10 min at 20°C, then cooled to −10°C, and 0.50 g (2.5 mmole) of hydroxyaminopyrimidine Ie was added, and stirring was continued for 10 min more. The precipitate was filtered and washed with chloroform (100 ml). A 0.23-g portion (2.5 mmole) of aniline and 1 ml of acetic acid were added to the filtrate, and the mixture was stirred for 30 min at 20°C. The solution was evaporated and the residue was passed through a layer of Al_2O_3, using chloroform as eluent. Yield, 0.36 g of phenylazopyrimidine IVe.

B. A 0.28-g portion (3 mmole) of aniline and 1 ml of acetic acid were added to a solution of 0.60 g (3 mmole) of nitrosopyrimidine Id in 40 ml of $CHCl_3$, and the mixture was stirred for 30 min at 20°C. The isolation of the product was carried out by method A. Yield, 0.80 g of phenylpyrimidine IVd.

Compounds IVa-c,f,g,i,j were obtained in a similar way. Compound IVi: yield, 35%, mp 72...73°C. According to the data in [18], mp 72-74°C. Compound IVj: yield, 70%, mp 107... 108°C. According to the data in [6], mp 108...109°C.

Methoxypyrimidines (Va,f). A solution of 0.50 g (7 mmole) of sodium methylate in 10 ml of MeOH was added to a solution of 0.26 g (1 mmole) of nitrosopyrimidine IIf in 40 ml of $CHCl_3$, and the mixture was stirred for 10 min. The solution was evaporated and the residue was washed with water (10 ml). Yield, 0.15 g (58%) of 2-methoxy-4,6-diphenylpyrimidine (Vf), mp 80...82°C (from petroleum ether 40...70°C). According to the data in [15], mp 81...82°C.

4-Methoxy-2,6-diphenylpyrimidine (Va) was obtained in a similar way in a 39% yield from nitrosopyrimidine IIa; mp 118...119°C.

Hydrolysis of nitrosopyrimidines IIa,f. A. One drop of concentrated H_2SO_4 was added to a suspension of 0.30 g (1.2 mmole) of nitrosopyrimidine IIf in 25 ml of water. The mixture was boiled for 2.5 h, and the precipitate was filtered. Yield, 0.25 g of the initial compound IIf.

B. A 5 ml portion of conc. HCl was added to a suspension of 0.30 g (1.2 mmole) of nitrosopyrimidine IIf in 10 ml of alcohol. The precipitate was filtered, washed with 10 ml of water, and dried. Yield, 0.10 g (35%) of oxopyrimidine VIf, mp 235...237°C. According to data in [18], mp 237-239°C.

In a similar way, on boiling nitrosopyrimidine IIa for 15 min and dilution of the solution obtained with water (100 ml), oxopyrimidine VIa was obtained in a 72% yield; mp > 260°C. According to data in [18], mp 291°C.

Reduction of Nitrosopyrimidines IIa,f. A 1-ml portion of phenylhydrazine was added to a suspension of 0.30 g (1.2 mmole) of nitrosopyrimidine IIa in 10 ml of alcohol, and the mixture was boiled for 20 min. The solution was evaporated, the residue was washed with hot water (20 ml) and recrystallized from a benzene-petroleum ether (70...100°C) mixture. Yield, 0.15 g (50%) of hydroxyaminopyrimidine Ia, mp 150...152°C (dec.).

Hydroxyaminopyrimidine If was obtained in 67% yield from nitrosopyrimidine IIf in a similar way.

LITERATURE CITED

1. G. G. Moskalenko, V. F. Sedova, and V. P. Mamaev, Izv. Akad. Nauk SSSR, Ser. Khim., No. 3, 702 (1987).
2. G. Feuer, (ed.), Chemistry of Nitro and Nitroso Groups [Russian translation], Vol. 1, Mir, Moscow (1972).
3. M. Demeneunynck, N. Tohme, M.-F. Lhomme, and J. Lhomme, J. Heterocycl. Chem., 21, 501 (1984).
4. J. H. Chesterfield, D. T. Hurst, J. F. W. McOmie, and M. S. Tute, J. Chem. Soc., No. 3, 1001 (1964).
5. D. J. Brown, The Pyrimidines, Interscience, N.Y., London (1962), p. 151.
6. E. C. Taylor, C.-P. Tseng, and J. B. Rampal, J. Org. Chem., 47, 552 (1982).
7. D. T. Hurst, Aust. J. Chem., 36, 2119 (1983).
8. G. G. Moskalenko, V. F. Sedova, and V. P. Mamaev, Khim. Geterotsikl. Soedin., No. 11, 1523 (1986).
9. V. P. Mamaev, V. F. Sedova, G. G. Moskalenko, V. N. Odinokov, V. R. Akhmetova, and G. A. Tolstikov, Izv. Akad. Nauk SSSR, Ser. Khim., No. 4, 954 (1986).
10. G. G. Moskalenko, V. F. Sedova, and V. P. Mamaev, Izv. Akad. Nauk SSSR, Ser. Khim., No. 3, 701 (1987).
11. E. P. Popadopoulos and C. H. Issidorides, J. Org. Chem., 31, 615 (1966).
12. R. A. Abramovitch and E. M. Smith, J. Heterocycl. Chem., 12, 969 (1975).
13. A. J. Fatiadi, Synthesis, No. 2, 65 (1976).
14. H. Firouzabadi and E. Ghaderi, Tetrahedron Lett., No. 9, 839 (1978).
15. F. Roeterdink and H. C. van der Plas, J. Chem. Soc., Perkin 1, No. 11, 1202 (1976).
16. E. C. Taylor, K. A. Harrison, and J. B. Rampal, J. Org. Chem. 51, 101 (1986).
17. L. Fieser and M. Fieser, Reagents for Organic Synthesis [Russian translation], Vol. 5, Mir, Moscow (1971), p. 389.
18. V. P. Mamaev, (ed.), Pyrimidines, Tables of Compounds of Pyrimidine Series 1966-1972 [in Russian], Novosibirsk (1976).