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# $^1H$ AND $^{13}C$ NMR STUDY OF AZIDO-TETRAZOLE TAUTOMERISM OF 2-AZIDO-4-METHYLPYRIMIDINE

**V. P. Krivopoalov, V. O. Mamatyuk, and V. P. Mamaev***

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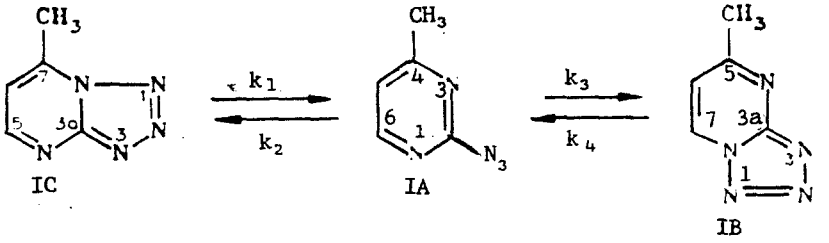
*Using $^1H$ and $^{13}C$ NMR and IR spectroscopic methods, it was found that 2-azido-4-methylpyrimidine exists in solutions in tautomeric equilibrium with two tetrazole forms, the ratio between which is determined by the polarity of the solvent, while in a crystalline state, according to the $^{13}C$ NMR CP MAS data it has the structure of the 7-methyltetrazolo[1,5-a]pyrimidine isomer.*

It was previously reported [1] that the condensation of 5-aminotetrazole with 4,4-dimethoxybutan-2-one or nitrosation of 2-hydrazino-4-methylpyrimidine produces one and the same product which, according to the authors, has the structure of 5-methyltetrazolo[1,5-*a*]pyrimidine (IB). However, it was found in [2] by $^1H$ and $^{13}C$ NMR methods that by the first method instead of compound IB, the isomeric 7-methyltetrazolo[1,5-*a*]pyrimidine (IC) is formed, existing in a $CDCl_3$ solution in equilibrium with 2-azido-4-methylpyrimidine (IA):

Scheme 1




In discussing the scheme of formation of compound I, the authors of [1] did not take into account the ability of the substituted 5-aminotetrazoles to undergo the thermally reversible Dimroth rearrangement, proceeding via the intermediate formation of substituted C-azidoformamidine ("guanylazide") [3, 4], and also the possibility of reversible recyclization of the IC ⇌ IB isomers, which possibly is the cause for the inconsistency with [2].

On analyzing the data for the tautomeric equilibrium of compound I [2] and 2-azido-4,6-dimethylpyrimidine (II) in a $CDCl_3$ solution [5], it was pointed out that the amounts of the azide forms are comparable in both cases, although a decrease in the relative stability of the azide tautomer, symbatical to the number of the electron-donor methyl group: 2-azi...pyrimidine (IIIA) > (IA) > (IIA), should have been expected.

In view of the above contradictory data, we undertook a detailed investigation of the tautomeric equilibrium IC ⇌ IA ⇌ IB in solvents of various polarities, and also determined the structure of compound I in the crystalline state.

*Deceased.

Novosibirsk Institute of Organic Chemistry, Siberian Branch, Academy of Sciences of the USSR, Novosibirsk 630090.
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TABLE 1. Tautomeric Composition of Compounds I-III, % in Solvents at 23-25°C

| Compound | Tautomer | Composition in | | | | |
|---|---|---|---|---|---|---|
| | | $CCl_4$ | $CDCl_3$ | acetone-$D_6$ | DMSO-$D_6$ | $CD_3OD$ |
| I | A | 70 | 45 | 8 | 2 | 11 |
| | B | 5 | 11 | 23 | 28 | 24 |
| | C | 25 | 44 | 69 | 70 | 65 |
| II | A | | 18 | 4 | <1 | 5 |
| | B | | 82 | 96 | 99 | 95 |
| III | A | | 79* | 18 | 4* | 25 |
| | B | | 21* | 82 | 96* | 75 |

*According to data in [16], at 22°C.

TABLE 2. PMR Spectra of 2-Azido-4-methylpyrimidine (IA)

| Solvent | Chemical shifts δ, ppm, with reference to TMS (J, Hz) | | |
|---|---|---|---|
| | 5-H ($J_{5,6}$; $J_{5,6\text{-}CH_3}$), d | 6-H ($J_{6,5}$), d | 4-$CH_3$ ($J_{4\text{-}CH_3,5}$) |
| $CCl_4$ | 6,92 (5,0) | 8,41 (5,0) | 2,51 s |
| $CDCl_3$ | 6,89 (5,0) | 8,41 (5,0) | 2,47 s |
| Acetone-$D_6$ | 7,15 d.q. (5,0; 0,4) | 8,53 (5,0) | 2,48 d (0,4) |
| DMSO-$D_6$ | 7,19 (5,0) | 8,55 (5,0) | 2,44 s |
| $CD_3OD$ | 7,15 (5,0) | 8,51 (5,0) | 2,52 s |
| $CF_3COOH$ | 7,55 (6,1) | 8,71 (6,1) | 2,88 s |

TABLE 3. PMR Spectra of Tetrazolo[1,5-*a*]pyrimidines IB, IC

| Compound | Solvent | Chemical shifts, δ, ppm, with reference to TMS (J, Hz) | | | | |
|---|---|---|---|---|---|---|
| | | 5-H ($J_{5,6}$) d | 6-H | 7-H ($J_{7,6}$), d | 5-$CH_3$, s | 7-$CH_3$ ($J_{CH_3,6}$), d |
| IB | $CCl_4$ | | 7,22 d ($J_{6,7}$=7,0) | 9,08 (7,0) | 2,82 | |
| | $CDCl_3$ | | 7,16 d ($J_{6,7}$=7,0) | 8,94 (7,0) | 2,80 | |
| | Acetone-$D_6$ | | 7,50 d ($J_{6,7}$=7,0) | 9,40 (7,0) | 2,80 | |
| | DMSO-$D_6$ | | 7,49 m | 9,58 (7,0) | 2,72 | |
| | $CD_3OD$ | | 7,43 d ($J_{6,7}$=7,0) | 9,36 (7,0) | 2,82 | |
| IC | $CCl_4$ | 8,86 (4,1) | 7,19 d·q ($J_{6,5}$=4,1; $J_{6,CH_3}$=1) | | | 3,06 |
| | $CDCl_3$ | 8,89 (4,2) | 7,12 d·q ($J_{6,5}$=4,2; $J_{6,CH_3}$=1) | | | 3,02 |
| | Acetone-$D_6$ | 9,02 (4,2) | 7,46 d·q ($J_{6,5}$=4,2; $J_{6,CH_3}$=1) | | | 3,05 |
| | DMSO-$D_6$ | 9,02 (4,2) | 7,49 m | | | 2,93 |
| | $CD_3OD$ | 9,00 (4,2) | 7,40 d·q ($J_{6,5}$=4,2) | | | 3,04 |

We synthesized compound I by methods described in [1, 2]. Its identity was confirmed by TLC on Silufol UV-254, using $CH_2Cl_2$–$CH_3COOC_2H_5$, 9:1 v/v mixture as eluent, and also by the coincidence of IR spectra in KBr. The absence of an absorption band of the azido group in the 2100-2200 $cm^{-1}$ region in the IR spectra taken in the crystalline state and in the DMSO solution, indicates that, under these conditions, the compound exists in the tetrazole forms IB and/or IC. In $CHCl_3$

solution a strong azide band is recorded in this region, which indicates the presence of the azide form IA, whereby the result agrees qualitatively with the data for the solution in $CHBr_3$ [2].

In the PMR spectrum of compound I directly after dissolution in $CDCl_3$, after cooling to –50°C, as well as at room temperature, at the initial instant signals of tautomer IC are recorded and then signals of the second tautomer IA and of the third minor one IB, which was not detected previously in [2]. The ratio of the tautomers under the equilibrium conditions is given in Table 1.

The spectral parameters of tautomers IC and IA (Tables 2 and 3) are close to the data in [2], except for the chemical shift of the 7-$CH_3$ group protons in compound IC.*

The characteristic value in the PMR spectrum of structure IB, making it possible to distinguish between the tetrazole forms IB and IC, is the increased value of SSCC $^3J_{6\text{-H},7\text{-H}}$ = 7.0 Hz, compared with $^3J_{5\text{-H},6\text{-H}}$ Hz = 4.2 for IC and its absence between the 6-H atom and the 5-$CH_3$ group protons, while in the structure of IC the SSCC $^4J_{6\text{-H},CH_3}$ = 1 Hz. The authors of [2] in fact expected these spectral parameters for tautomer IB, compared with structure IC, on the basis of the generalized PMR spectral parameters for azolo[1,5-*a*]pyrimidines [7]. This difference in the spectral parameters of compounds IB and IC is due to the increase in the double-bond character of the $C_{(6)}$–$C_{(7)}$ bond, as confirmed by the x-ray structural analysis data (XRSA) of 5-azidotetrazolo[1,5-*a*]pyrimidine [8] and also by the XRSA and quantum chemical calculations carried out for other azaindolizines [7, 9].

Converting from $CDCl_3$ to more polar solvents leads only to a change in the equilibrium ratio of these three tautomeric forms, whereby the amount of the azide tautomer decreases and that of the tetrazole forms increases (Table 1). This agrees well with the data in [6], according to which the stabilization of the tetrazole form is promoted by more polar solvents. As in the case of the solution in $CDCl_3$, in the PMR spectrum of compound I directly after the dissolution in DMSO-$D_6$, first signals of one tautomer IC are recorded, after a few hours the signals of tautomer IB appear in considerable amounts, and after a few hours the signals of the third minor tautomer – azide IA are recorded, the ratio between which under equilibrium conditions is given in Table 1. On rerecording of the spectrum of this ampul after 8 months, the character and ratio of the tautomeric forms did not change.

As expected, on transition from azide IIIa to IA and from IA to IIA, the amount of the azide form at equilibrium decreases, i.e., the stability of the tetrazole forms in these compounds is symbatic with the number of electron-donor methyl groups introduced into the 4- and 4,6-positions of 2-azidopyrimidine (Table 1). Assuming that in azide IA the electron density on the $N_{(3)}$ atom is increased compared with the $N_{(1)}$ atom due to the action of the +I-effect of the methyl group, a higher nucleophilicity and basicity could be expected of the $N_{(3)}$ atom and not of $N_{(1)}$, and hence the tetrazole form IC should be more stable than IB. The last fact is confirmed by the quantitative data we obtained on the ratio of the tetrazole tautomers IC and IB in solvents with various polarities (Table 1). For example, in the solutions of $CDCl_3$ and acetone-$D_6$, the ratio of tautomers IC:IB is equal to 4:1 and 3:1, respectively. The experimental data obtained agree well with the result of the quantum chemical examination of the azido-tetrazole tautomerism by means of the ab initio [11, 12] and MNDO [13] methods, according to which the cyclization is effected in several stages, and the motive force of this process is the reaction of an unshared electron pair of the aza atom with the terminal nitrogen atom of the azido group.

The above-described observations on the dynamics of change in the NMR spectra in solutions of compound I with time made it possible to carry out the kinetic measurements. The direct and reciprocal rate constants for the tautomerization of compound I (see Scheme 1) in a $CDCl_3$ solution at 20°C were determined by the PMR method: $k_1 = (1.77 \pm 0.01)\cdot10^{-4}$, $k_2 = (1.71 \pm 0.02)\cdot10^{-4}$, $k_3 = (0.97 \pm 0.07\cdot10^{-4}$, and $k_4 = (4.03 \pm 0.39)\cdot10^{-4}\cdot sec^{-1}$. The analysis of the rate constants of the intramolecular cyclization of the azido group $k_2$ and $k_3$ also indicates the increased nucleophilicity of the $N_{(3)}$ atom compared with the $N_{(1)}$ atom on compound IA. Comparison of $k_1$ and $k_4$ shows the $N_{(1)}$–$N_{(8)}$ bond is more readily cleaved in tetrazole IB than in IC. These differences are undoubtedly related to the proximity of the electron-donor methyl group to the reaction center. We should note that, according to the PMR spectral data, compound IV in the $CDCl_3$ solution has structure IVB [14], i.e., replacement of the methyl groups by the more electron-donor ethyl groups enhances the stabilization of the tetrazole form to a still greater extent (see scheme on page 1373).

We also made a detailed study of the structure of compound I in solutions and in the crystalline state by the $^{13}C$ NMR method, which made it possible to examine the change in the chemical shifts of the carbon atom and the $^{13}C$-$^1H$ SSCC on transition from the azide form to the tetrazole tautomers and to use the previously proposed spectral criteria for an unequivocal determination of the structure of the tautomers. It is known that during the isomerization of 2-azidopyrimidines into tetra-

*According to the data in [2], the chemical shift of the 7-$CH_3$ group protons in IC is equal to 3.50 ppm; there may have been a typographical error here, since in azolo[1,5-*a*]pyrimidines the signal of this group is present at ~3 ppm [5, 10].

TABLE 4. $^{13}C$ NMR Spectra of 2-Azidopyrimidines in $CF_3COOH$

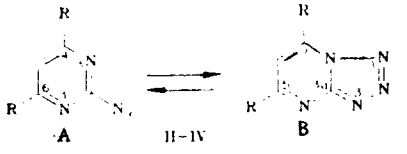
| Compound | Chemical shifts, δ, ppm with reference to TMS and $^nJ_{^{13}C-^1H}$, Hz | | | | |
|---|---|---|---|---|---|
| | $C_{(2)}$ | $C_{(4)}$ | $C_{(5)}$ | $C_{(6)}$ | $CH_3$ |
| IA | 158,2; $^3J_{C_{(2)},6\text{-}H}$ = =8,9 | 179,3 | 119,6; $^1J_{C_{(5)},5\text{-}H}$ = 179,4; $^2J_{C_{(5)},6\text{-}H}$ = 5,2; $^3J_{C_{(5)},CH_3}$ = 3,7 | 153,6; $^1J_{C_{(6)},6\text{-}H}$ = =193,8; $^2J_{C_{(6)},5\text{-}H}$ = 2,5 | 23,9; $^1J_{C_{(Me)},H}$ = 131,4; $^3J_{C_{(Me)},5\text{-}H}$ = 1,8 |
| IIA | 157,6 | 172,5 | 118,4; $^1J_{C_{(5)},5\text{-}H}$ = 176,6; $^3J_{C_{(5)},CH_3}$ = 3,8 | 172,5 | 21,8; $^1J_{C_{(Me)},H}$ = 131,3; $^3J_{C_{(Me)},5\text{-}H}$ = 2,3 |
| IIIA | 159,1 | 160,2; $^1J_{C_{(4)},4\text{-}H}$ = =195 | 118,8; $^1J_{C_{(5)},5\text{-}H}$ = 182,6 | 160,2; $^1J_{C_{(6)},6\text{-}H}$ = 195 | |

TABLE 5. $^{13}C$ NMR Spectra of Tetrazolo[1,5-*a*]pyrimidines in DMSO-$D_6$

| Compound | Chemical shifts, δ, ppm with reference to TMS and $^nJ_{^{13}C-^1H}$, Hz | | | | | |
|---|---|---|---|---|---|---|
| | $C_{(3a)}$ | $C_{(5)}$ | $C_{(6)}$ | $C_{(7)}$ | 5-$CH_2$ | 7-$CH_3$ |
| IB | 154,4; $^3J_{C_{(3a)},7\text{-}H}$= =3,1 | 170,2; $^2J_{C_{(5)},6\text{-}H}$ = =3,0 $^2J_{C_{(5)},CH_2}$ = =6,3 $^3J_{C_{(5)},7\text{-}H}$ = =6,3 | 114,3; $^1J_{C_{(6)},6\text{-}H}$ = =174,8 $^2J_{C_{(6)},7\text{-}H}$ = =3,5 $^3J_{C_{(6)},CH_2}$ = =3,5 | 133,7; $^1J_{C_{(7)},7\text{-}H}$ = =197,0 $^2J_{C_{(7)},6\text{-}H}$ = 4,4 | 25,1; $^1J_{C,H}$ = 128,5 | |
| IC | 154,6; $^3J_{C_{(3a)},5\text{-}H}$= =15,1 | 158,8; $^1J_{C_{(5)},5\text{-}H}$ = =187,2 $^2J_{C_{(5)},6\text{-}H}$ = =3,1 | 112,4; $^1J_{C_{(6)},6\text{-}H}$ = =174,5 $^2J_{C_{(6)},5\text{-}H}$ = =9,6 $^3J_{C_{(6)},CH}$ = =4,8 | 146,8; $^2J_{C_{(7)},CH_3}$ = 3,7 $^2J_{C_{(7)},6\text{-}H}$ = 6,0 $^3J_{C_{(7)},5\text{-}H}$ = 6,7 | | 16,6; $^1J_{C,H}$ = 131,6 $^3J_{C,6\text{-}H}$ = 3,4 |
| IC* | 153,4 | 159,1 | 112,7 | 146,9 | | 17,2 |

*In a crystalline state.

Scheme 2




II R=$CH_3$; III R=H; IV R=$C_2H_5$

zolo[1,5-*a*]pyrimidines, for example compounds II and III on transition from solvent $CF_3COOH$ to DMSO-$D_6$ or from $CDCl_3$ to DMSO-$D_6$ [16], in the $^{13}C$ NMR spectra the signal of the $C_{(7)}$ atom in annelated tetrazoles undergoes 21-30 ppm shift to the strong field, compared with the same signal in the azide form. This is due to a change in the hybridization of the neighboring nitrogen atom, i.e., transition from a "pyridine" type nitrogen atom to a "pyrrole" type nitrogen. The last factor also causes a significant decrease in the SSCC $^3J_{C_{(3a)}7\text{-}H}$ = 3.22 Hz, compared with $^3J_{C_{(3a)}5\text{-}H}$ = 14.97 Hz in the structure of IIIB [15]. These spectral parameters, i.e., the strong-field shift of the signal of the $C_{(7)}$ atom and the decrease in the $^{13}C$–$^1H$ SSCC in tetrazolo[1,5-*a*]pyrimidines provide a diagnostic indication in establishing the path cyclization of the azido group, and are particularly useful when two nonequivalent reaction centers are present in the molecule of 2-azido-pyrimidines, such as, for example, in compound IA.

In the $^{13}C$ NMR spectrum of compound I in a $CF_3COOH$ solution, only signals of azide IA are recorded. Under similar conditions, spectral parameters were also obtained for the azide forms of compounds II and III, which made it possible to assign unequivocally the signals of the carbon atoms in isomer 1A (Table 4). In the $^{13}C$ NMR spectrum of compound I directly after dissolution in DMSO-$D_6$, only one set of signals of the carbon atoms is recorded, which practically coincide with the data for tautomer IC [2]. However, after a repeated run of the spectrum approximately 24 h later, lower intensity signals were also recorded in it of the second tetrazole tautomer IB (Table 5). As expected, these structures are characterized by strong-field shifts of the signals of the $C_{(7)}$ atoms by 32 and 20 ppm, respectively, compared with the signals of the same atoms in azide IA in the $CF_3COOH$ solution. The structure of tautomers IB and IC is also confirmed by other spectral criteria, namely by the low value of SSCC $^3J_{C_{(3a)}7\text{-}H} = 3.1$ Hz for IB, compared with $^3J_{C_{(3a)}5\text{-}H} = 15.1$ Hz for IC (compare these values with the corresponding SSCC for IIIB, given above).

It follows from the analysis of the $^{13}C$ NMR spectra of compounds Ia and II in $CF_3COOH$ and DMSO-$D_6$ solutions (see Tables 4 and 5 and [15]) that on transition from the azide forms IA and IIA to the tetrazole structures, strong-field shifts are observed of both the $C_{(7)}$ atom signals in the latter, as well as signals of the carbon atoms of the 7-$CH_3$ groups bound to them, while the values of the chemical shifts of the carbon atoms of the 5-$CH_3$ groups in IB and IIB change inappreciably. Thus, the strong field signals of the carbon atom of the methyl group also serve as characteristic indications for the determination of the direction of the cyclization of the azido group in the case of asymmetric 2-azido-4-methylpyrimidines.

We determined the structure of compound I in the crystalline state by the high resolution $^{13}C$ NMR method for a solid body (CP MAS, see Table 5 and Experimental). Comparison of the obtained value of the chemical shifts of the carbon atoms in the CP MAS spectrum with the data for the spectra of this compound in DMSO-$D_6$, unequivocally indicates that in a solid-state compound I is present in the tetrazole form IC (compared, for example, with [17]). This agrees well with the above data, obtained from the analysis of the $^1H$ and $^{13}C$ NMR spectra of compound I directly after dissolution in $CDCl_3$ and DMSO-$D_6$.

Thus, by using the IR and NMR spectroscopy methods, it was found that 2-azido-4-methylpyrimidine in a crystalline state is present in the isomeric form of 7-methyltetrazolo[1,5-*a*]pyrimidine, while in solutions it exists in the form of a tautomeric equilibrium of the azide and two tetrazole structures (see Scheme 1), the relative content of which depends on the properties of the solvent. With increase in the polarity of the latter, the equilibrium shifts in the direction of the tetrazole forms, low-polarity solvents stabilize the azide form, while trifluoroacetic acid completely shifts the equilibrium in the direction of the azide form. Introduction of alkyl groups into the 4,6-positions favors the stabilization of the tetrazole forms.

## EXPERIMENTAL

The IR spectra of the compounds were run on a UR-20 spectrophotometer and the PMR spectra (200.13 MHz) and the $^{13}C$ NMR spectra (50.32 MHz) were recorded on Bruker WP-200 SY and AV-200 pulse spectrometers with stabilization with respect to the NMR deuterium signal of the solvent. The high-resolution $^{13}C$ NMR spectrum (75.46 MHz) of the crystalline I was obtained on a Bruker CXP-300 spectrometer, using cross polarization on protons and rotation under a magnetic angle (CP MAS), rate of rotation 3250 Hz, time of contact 5 μsec; the chemical shifts were measured relative to TMS as external standard. The solvents $CCl_4$, acetone-$D_6$, DMSO-$D_6$, were preliminarily dried on 4 Å molecular sieves. Commercial $CDCl_3$ and $CD_3OD$ were used and $CF_3COOH$ was purified by distillation. The kinetic measurements were carried out on a Bruker WP-200 ST apparatus at 20°C, for which compound I was rapidly dissolved immediately before measurement in an ampul with $CDCl_3$ and placed at once into the NMR spectrometer sensor. The rate of the tautomeric transformations was determined by the PMR method from the time-dependent change in the relative intensity of the methyl signals of tautomers IA, IB, and IC. The mathematical treatment of the results obtained and the calculation of the tautomerization rate constants was carried out according to a kinetic equation of a consecutive reversible first-order reaction of the type $A \underset{k_2}{\overset{k_1}{\rightleftharpoons}} B \underset{k_4}{\overset{k_3}{\rightleftharpoons}} C$ according to the method in [18] on a Hewlett–Packard-2000 computer.

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**sym-TRIAZINE DERIVATIVES.**

# 9.* REACTION OF sym-TRIAZINES CONTAINING TRICHLOROMETHYL AND ETHOXYCARBONYL GROUPS WITH PHENYLHYDRAZINE

**N. V. Alekseeva, K. F. Turchin, O. S. Anisimova, Yu. N. Sheinker, and L. N. Yakhontov**

UDC 547.491'556.8.04'877.07: 543.51'422

*Using the example of the reaction of 1,3,5-triazines simultaneously containing trichloromethyl and ethoxycarbonyl substituents with phenylhydrazine, it was shown that the presence of even one ester group leads to ring transformation. Depending on the number of the ester groups in the initial 1,3,5-triazine, the reaction products are either 1,2,4-triazole or 1,2,4-triazine derivatives.*

It was previously shown that in the reaction of 2,4,6-triethoxycarbonyl-1,3,5-triazine (I) with phenylhydrazine (II) the product is 5-amino-6-oxo-1-phenyl-3-ethoxycarbonyl-1,6-dihydro-1,2,4-triazine (III, Scheme 1 on page 1376) [1].

It was of interest to study the reaction of hydrazine II with 1,3,5-triazines also containing other substituents besides the ethoxycarbonyl groups. The most easily accessible were 2,4,6-tris(trichloromethyl)-, 2,4-bis(trichloromethyl)-6-ethoxycarbonyl- and 2-trichloromethyl-4,6-bis(ethoxycarbonyl)-1,3,5-triazines (IV, V, and VI) which were obtained by joint trimerization of trichloroacetonitrile and ethyl cyanoformate by a method described in [2].

*For Communication 8, see [1].

S. Ordzhonikidze Scientific-Research Chemical Pharmaceutical Institute, Moscow 119815. Translated from Khimiya Geterotsiklicheskikh Soedinenii, No. 12, pp. 1655-1664, December, 1990. Original article submitted April 20, 1989.