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4,6-DIMETHYLPYRIDINE-2,3-DICARBONITRILE AND ITS REACTION WITH *N*-ACYLHYDRAZINES

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An efficient method has been developed for the synthesis of 4,6-dimethylpyridine-2,3-dicarbonitrile. A study was carried out on the reaction of this compound with N-acylhydrazines to give two structural isomers, namely, N′-(7-amino-2,4-dimethyl-5H-pyrrolo[3,4-b]pyridin-5-ylidene)carbohydrazides and N′-(5-amino-2,4-dimethyl-7H-pyrrolo[3,4-b]pyridin-7-ylidene)carbohydrazides as well as disubstituted N′,N″-(2,4-dimethyl-5H-pyrrolo[3,4-b]pyridine-5,7-diylidene)dicarbohydrazides.

Keywords: *N′*-(7-amino-2,4-dimethyl-5*H*-pyrrolo[3,4-*b*]pyridin-5-ylidene)carbohydrazides, *N′*-(5-amino-2,4-dimethyl-7*H*-pyrrolo[3,4-*b*]pyridin-7-ylidene)carbohydrazides, *N*-acylhydrazones, 4,6-dimethylpyridine-2,3-dicarbonitrile, *N′,N″*-(2,4-dimethyl-5*H*-pyrrolo[3,4-*b*]pyridine-5,7-diylidene)dicarbohydrazides, nucleophilic substitution of hydrogen, cyanation.

Heterocyclic 1,2-dicarbonitriles such as 2,3-dicyanoazines hold considerable interest as precursors of azaphthalocyanine dyes used in the preparation of highly stable dyes, new functional materials for nonlinear optics, photoconductors, liquid crystals, electrochromic devices, solar energy devices, color monitors, laser systems for information storage [1-3], and in photodynamic therapy [4].

Heterocyclic 1,2-dicarbonitriles also serve as convenient starting blocks in the synthesis of condensed heterocycles. Analysis of the literature data showed that the reactions of 2,3-dicyanopyridines with *N*-nucleophiles, in particular, with amines, have hardly been studied [5-7]. In a study of the heterocyclization reactions of *N*-acylhydrazines with phthalodinitrile [8], pyridine-2,3-dicarbonitriles have attracted special attention, specifically 4,6-dimethylpyridine-2,3-dicarbonitrile. On one hand, the result of the cyclization reaction cannot be unequivocally predicted due to the asymmetry of this compound due to the presence of the nitrogen atom in the ring. Furthermore, the presence of a methyl group at C-4 in this dicarbonitrile may affect the regioselectivity of the reaction. Several products whose structures were not established have been formed in the reaction of pyridine-2,3-dicarbonitrile with ammonia or acid hydrazides [9].

The method for the synthesis of 2,3-dicyanopyridine involving conversion of derivatives of pyridine-2,3-dicarboxylic acid [10] cannot be used for the preparation of alkyl-substituted pyridine-2,3-dicarbonitriles. 2-Halopyridines already containing a nitrile group at C-3 of the pyridine ring have been used in an approach to the synthesis of alkyl-substituted pyridine-2,3-dicarbonitriles. The introduction of a second cyano group by nucleophilic substitution of halogen atoms by a cyanide ion should lead to alkyl-substituted pyridine-

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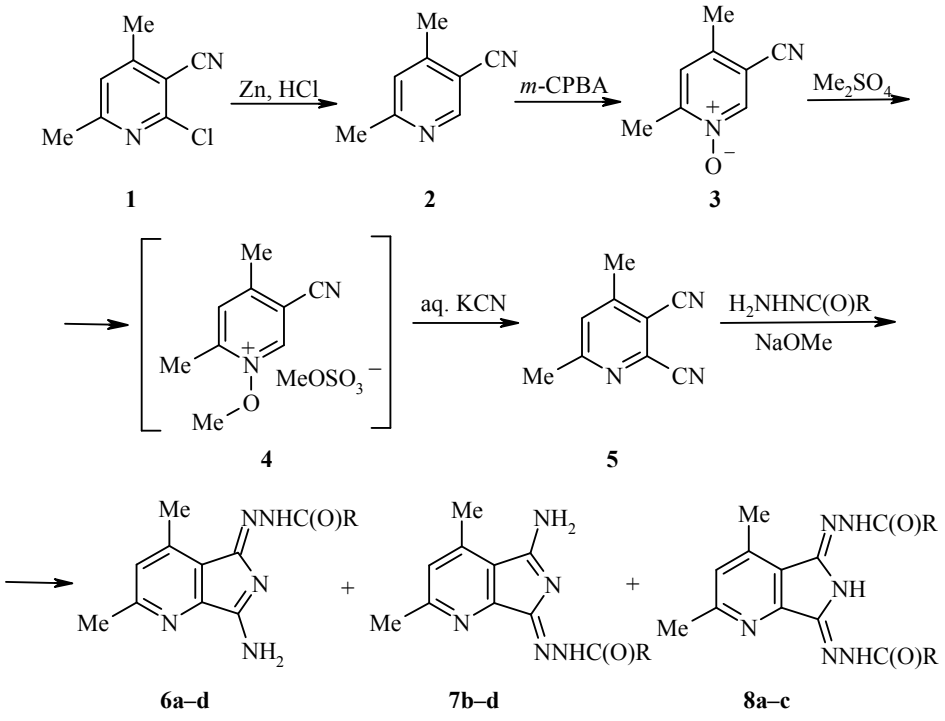
2,3-dicarbonitriles. Metal cyanides such as KCN and CuCN have often been used for this purpose and gives nitriles in good yield [11, 12]. An alternative approach to the synthesis of dicarbonitriles involves the use of pyridine *N*-oxides, which are very active in the nucleophilic substitution of α- and γ-hydrogen atoms by a cyano group using, for example, trimethylsilyl cyanide [13, 14]. Substitution of the α-hydrogen atom may also be accomplished by methylation of the *N*-oxides using dimethyl sulfate or methyl iodide and treatment of the resultant salt by alkali metal cyanides [15, 16].

We first tried the direct cyanation of 2-chloro-4,6-dimethylpyridine-3-carbonitrile (**1**) obtained from 4,6-dimethyl-2-oxo-1,2-dihydropyridine-3-carbonitrile [17] for the synthesis of 4,6-dimethylpyridine-2,3-dicarbonitrile (**5**). Cyanation using CuCN in *N*-methylpyrrolidone [11] or in DMSO under phase-transfer catalysis conditions [18] proved inefficient. Also, the bromine atom in 2-bromo-4,6-dimethylpyridine-3-carbonitrile [19] could not be directly replaced by a nitrile group in the reaction with KCN in DMF [12] or with CuCN [20].

Thus, we used a method for the synthesis of dinitrile **5** involving replacement of the hydrogen atom in an activated *N*-oxide. For this purpose, 2-chloropyridine-3-carbonitrile **1** was reduced to give pyridine-3-carbonitrile **2** [21] and then oxidized by *meta*-chloroperbenzoic acid (*m*-CPBA) [22] to give *N*-oxide **3**.



1 **2** **3** **4** **5** **6a–d** **7b–d** **8a–c**

R = **a** *cyclo*-C_3H_5, **b** 4-FC_6H_4, , **c** 4-Py, **d** 4-MeC_6H_4

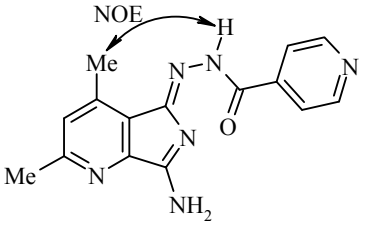
Two methods were tested for the next step in the cyanation. Initially, *N*-oxide **3** was treated with MeI in accord with the method described by Hibino and Sugino [23]. However, after work-up of the reaction mixture, the colorless precipitate isolated was identified using ^{1}H NMR spectroscopy as 4,6-dimethylpyridine-3-carboxamide, which probably formed due to hydrolysis of the starting compound. Dimethyl sulphate proved to be more effective alkylating agent [16]. The desired product, 4,6-dimethylpyridine-2,3-dicarbonitrile (**5**), was isolated in the reaction of *N*-oxide **3** with dimethyl sulfate and subsequent treatment with aqueous KCN.

The reaction of dinitrile **5** with an equivalent amount of hydrazides was carried out by the method described by Hordiyenko et al. [8]. Analysis of the mixture of crude products by LC/MS showed that all the hydrazides taken, except cyclopropanecarboxylic acid hydrazide, react with dinitrile **5** to give a mixture of structural isomers, *N′*-(7-amino-2,4-dimethyl-5*H*-pyrrolo[3,4-*b*]pyridin-5-ylidene)carbohydrazides **6b-d** and *N′*-(5-amino-2,4-dimethyl-7*H*-pyrrolo[3,4-*b*]pyridin-7-ylidene)carbohydrazides **7b-d.** In all cases except for the

reaction with the hydrazide of *p*-toluic acid, we obtained disubstituted products **8a-c**, whose content in the reaction mixture was 9, 11, and 46%, respectively. Unfortunately, these products could not be isolated as pure compounds. Products **8a-c** may be formed from the monosubstituted adducts as the result of replacement of an amino group by an *N*-acylhydrazine residue. We may assume that these compounds are similar in structure to previously studied *N′*,*N″*-1*H*-isoindole-1,3-diylidenedicarbohydrazides and exist in a symmetrical tautomeric form. We should note that the disubstitution products also could not be obtained in a similar reaction from phthalodinitrile [8]. However, they can be synthesized either from 1,3-substituted 1*H*-isoindoles – from highly reactive 1,1,3-trichloro-1*H*-isoindole [24] or from 1-imino-1*H*-isoindole-3-amine [25].

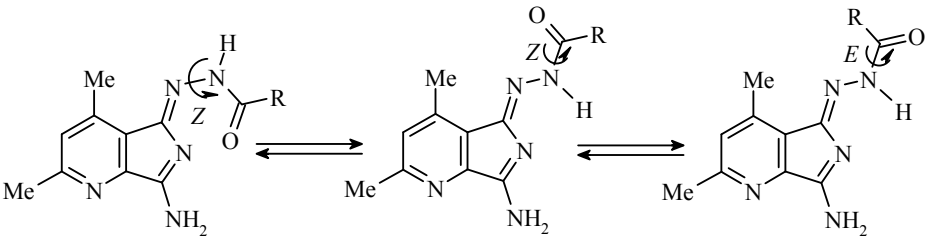
Specific criteria for the predominant formation of particular regioisomers in the reaction of dinitrile **5** with hydrazides could not be determined since the composition of the reaction products varies under the same reaction conditions. An attempt to obtain disubstituted product **8c** by heating dinitrile **5** with a 2.5-fold excess of isonicotinic acid hydrazide at reflux gives a mixture of three compounds **6c,7c,** and **8c** and the formation of mono- and disubstituted products was observed only after heating at reflux for 4 h.

The pyridinic nitrogen atom in dinitrile **5** should affect the direction of nucleophilic addition at the nitrile group. The most likely pathway presumably involves initial attack at the cyano group at C-2 position. A methyl substituent at C-4 in the pyridine ring, which creates additional steric hindrance to attack at the 3-cyano group, should also facilitate this direction of the reaction. However, the NOESY data for the isolated pure isomer **6c** showed that there is NMR coupling of the amino group proton of the hydrazone fragment with the protons of the methyl group at C-4 of the pyridine ring. This finding indicates that the isolated isomer is *N′*-(7-amino-2,4-dimethyl-5*H*-pyrrolo[3,4-*b*]pyridin-5-ylidene)pyridine-4-carbohydrazide (**6c**). This conclusion can probably also be drawn for the other major isolated pure compounds and should be assigned to the series *N′*-(7-amino-2,4-dimethyl-5*H*-pyrrolo[3,4-*b*]pyridin-5-ylidene)carbohydrazides **6a** and **6b**.



6c

Hydrazones **6a-c** have structural elements, which can account for both geometrical (the exocyclic C=N bond) and conformational isomers (amide NH−CO bond). Since previously studied *N′*-(3-amino-1*H*-isoindol-1-ylidene)carbohydrazides exist exclusively as (*Z*)-isomers relative to the C=N bond [8] and the presence of a methyl group at C-4 in compounds **6a-c** creates steric hindrance, we may assume that these compounds are also (*Z*)-isomers. The presence of the conformationally labile =N−NH−CO− fragment can also account for amide isomerism as seen previously for derivatives of *N′*-(3-amino-1*H*-isoindol-1-ylidene)carbohydrazides [8]. These findings suggest that the following forms are most likely in a solution of the equilibrium mixture of conformers formed due to rotation both relative to the N−N and N−C(O) bonds ((*Z*)-**6a-c**):



The forms given for the amide conformers were selected from a number of possible previously studied isoindole analogs [8]. The existence of the first form must be assumed since a nuclear Overhauser effect (NOE) is observed between the signals for the protons of the 4-CH_3 group and the hydrazinic NH proton. Two other forms obtained from the previous form as a result of rotation about the N−N bond are most probable since, as we have previously shown, isoindole analogs exist both in the solid state and in solution predominantly as the (*Z*)-amide conformer.

Indeed, the ^{1}H NMR spectrum of a solution of cyclopropyl derivative **6a** shows two sets of all the proton signals, in particular, the NH protons of the hydrazone fragment, which appear as rather narrow singlets in almost equal ratios. Previous data indicate that the strongest signal for the hydrazone NH proton, which has *syn* arrangement relative to the carbonyl oxygen atom ((*E*)-isomer), is shifted upfield relative to the corresponding signal of the (*Z*)-isomer [8, 26].

Since the (*Z*)-form is favored for aromatic isoindole carbohydrazides, the (*Z*)-conformer also presumably predominates for carbohydrazide **6c** with 10% (*E*)-form as the minor component. This conclusion is also by a single set of signals in the ^{1}H NMR spectrum of this compound with a slight additional set of aromatic proton signals. On the other hand, in contrast to the case of the isoindole analog, the ^{1}H NMR spectrum of 4-fluorophenyl derivative **6b** shows the presence of about 25% of the minor (*E*)-conformer as indicated by the appearance of a second set of additional methyl and aromatic protons. In this case, there is only one very broadened hydrazide proton signal, while the signal of the other amide isomer is not observed, probably due to exchange processes. The ^{19}F NMR spectrum of **6b** also shows only one signal.

Thus, 4,6-dimethylpyridine-2,3-dicarbonitrile may be readily obtained in an overall 35% yield from 4,6-dimethyl-2-oxo-1,2-dihydropyridine-3-carbonitrile. The key step in this conversion is the nucleophilic substitution of a hydrogen atom by a cyano group. The reaction of 4,6-dimethylpyridine-2,3-dicarbonitrile with *N*-acylhydrazines yields *N*′-(7-amino-2,4-dimethyl-5*H*-pyrrolo[3,4-*b*]pyridin-5-ylidene)carbohydrazides.

EXPERIMENTAL

The IR spectra were taken on a Perkin-Elmer Spectrum BX FTIR spectrometer for KBr pellets. The ^{1}H NMR spectra of **3, 5,** and **6a-c** and the ^{13}C NMR spectrum of compounds **3** and **5** were obtained on a Bruker Avance 500 spectrometer at 500 and 125 MHz, respectively, in $CDCl_3$ solution at 20°C with TMS as internal standard. The ^{19}F NMR spectrum of **6b** was taken on a Varian Mercury 400 spectrometer at 376 MHz in DMSO-d_6 solution at 20°C with C_6F_6 as the internal standard (δ -164.9 ppm). The GC/MS analysis was carried out on a Hewlett-Packard HP GC/MS 5890/5972 system (EI, 70 eV), while the LC/MS analysis was carried out on an Agilent 1100 system with a photodiode array detector and mass-selective Agilent LC/MSD SL detector. Analysis parameters: 4.6×15-mm Zorbax SB-C18 column, 1.8 μm; solvents: A) acetonitrile-water, 0.1% trifluoroacetic acid and B) water, 0.1% trifluoroacetic acid. Gradient elution was carried out. Atmospheric pressure chemical ionization (APCI) was used. The melting points were carried out on a Boetius microscopic hot stage. The thin-layer chromatographic analysis was carried out on Merck F_{254} TLC plastic sheets.

The commercially available reagents and solvents were used without further purification.

2-Chloro-4,6-dimethylpyridine-3-carbonitrile (**1**) was obtained according to Sculley and Hamilton [17]. 4,6-Dimethylpyridine-3-carbonitrile (**2**) was obtained in 68% yield by reduction using zinc in concentrated hydrochloric acid, mp 54°C (mp 56-57°C [21]).

4,6-Dimethylpyridine-3-carbonitrile *N*-oxide (3) was obtained according to Nagano et al. [22]. *m*-Chloroperbenzoic acid (3.88 g, 22 mmol) was added to a solution of 4,6-dimethylpyridine-3-carbonitrile (**2**) (2.7 g, 20 mmol) in dry ethyl acetate. After stirring for 1 h, the solvent was evaporated at reduced pressure and the solid residue was dissolved in 30 ml aqueous solution K_2CO_3 (4.15 g, 30 mmol) and then extracted with CH_2Cl_2 (3×50 ml) . The organic layer was dried over Na_2SO_4 and evaporated to give 2.7 g (90%) *N*-oxide **3** as a colorless powder; mp 128°C (mp 127-128°C [27]). IR spectrum, ν, cm^{-1}: 3030, 2235 (C≡N), 1622. ^{1}H NMR

spectrum, δ, ppm: 2.38 (3H, s, CH_3); 2.41 (3H, s, CH_3); 7.60 (1H, s, CH); 8.82 (1H, s, CH). ^{13}C NMR spectrum, δ, ppm: 17.8, 19.0, 110.4, 114.8, 128.5, 138.4, 141.2, 153.0. Mass spectrum, *m/z*: 149 $[M+H]^+$. Found, %: C 64.68; H 5.42; N 18.82. $C_8H_8N_2O$. Calculated, %: C 64.85; H 5.44; N 18.91.

4,6-Dimethylpyridine-2,3-dicarbonitrile (5). Freshly distilled dimethyl sulfate (2.5 g, 20 mmol) was added in an argon atmosphere to 4,6-dimethylpyridine-3-carbonitrile *N*-oxide (**3**) (2.7 g, 18 mmol) at 0°C. The reaction mixture was stirred for 2 h with heating on an oil bath at 90°C. Cooling the solution gave a precipitate of *N*-methoxypyridinium methyl sulfate **4**, which was dissolved in 20 ml water. An aqueous solution of KCN (3.9 g, 60 mmol) was then added dropwise to the solution obtained in an argon atmosphere. A brown precipitate of dicarbonitrile **5** formed immediately. The precipitate was filtered off, washed with water, dried, and crystallized to give 2.0 g (70%) **5** as pale-yellow crystals; mp 75°C (heptane). Carrying out the reaction in the air leads to a diminished product yield. Product **5** was identified using LC/MS as its monoamide (*m/z*: 176 $[M+H]^+$, purity >98.85%), which apparently formed as the result of hydrolysis of one of the nitrile groups on the stationary phase of the chromatographic system.

IR spectrum, ν, cm^{-1}: 2229 (C≡N), 1591 (C=N). ^{1}H NMR spectrum, δ, ppm: 2.59 (3H, s, CH_3); 2.64 (3H, s, CH_3); 7.39 (1H, s, H-3). ^{13}C NMR spectrum, δ, ppm: 20.3; 24.6; 112.5; 113.3; 114.6; 127.6; 136.1; 152.2; 163.8. Mass spectrum, *m/z*: 157. Found, %: C 68.47; H 4.51; N 27.15. $C_9H_7N_3$. Calculated, %: C 68.78; H 4.49; N 26.84.

Preparation of *N*'-(7-Amino-2,4-dimethyl-5*H*-pyrrolo[3,4-*b*]pyridin-5-ylidene)carbohydrazides 6a-c (General Method). 4,6-Dimethylpyridine-2,3-dicarbonitrile (**5**) (0.39 g, 2.5 mmol), corresponding carboxylic acid hydrazide (2.5 mmol), and metallic sodium (0.023 g, 1 mmol) were dissolved separately in dry methanol. The solutions were combined and heated at reflux for 4 h. The precipitate formed was filtered off, washed with methanol, and subjected either to chromatography or crystallization.

***N*'-(7-Amino-2,4-dimethyl-5*H*-pyrrolo[3,4-*b*]pyridin-5-ylidene)cyclopropanecarbohydrazide (6a)** was isolated from the crude mixture of products (LC/MS: 69% **6a**, retention time RT = 0.620, and 11% **7a**, RT =0.939) using preparative column chromatography (Kieselgel 60, acetonitrile–methanol gradient elution) to give 0.47 g (72%) **6a** as pale-yellow crystals; mp 250°C. IR spectrum, ν, cm^{-1}: 3337, 3206 (NH_2), 1663 (C=O), 1607 (C=N), 1504. ^{1}H NMR spectrum, δ, ppm: 0.76-0.93 (4H, m, $2CH_2$); 1.96 and 2.69 (1H, two m, CH); 2.58 (6H, two s, $2CH_3$); 7.11 and 7.12 (1H, two s, H-3); 7.55 and 8.59 (2H, two br. s, NH_2); 9.52 (0.56H, s) and 10.55 (0.44H, s, (*E*)- and (*Z*)-N=NH–CO). Mass spectrum, *m/z*: 258 $[M+H]^+$. Found, %: C 60.98; H 5.82; N 27.60. $C_{13}H_{15}N_5O$. Calculated, %: C 60.69; H 5.88; N 27.22.

***N*'-(7-amino-2,4-dimethyl-5*H*-pyrrolo[3,4-*b*]pyridin-5-ylidene)-4-fluorobenzohydrazide (6b)** was isolated from the crude mixture of products (LC/MS: 90% **6b**, RT = 0.864 and 5% **7b**, RT = 0.942) and recrystallized from DMF to give 0.4 g (52%) **6b** as pale-yellow crystals; mp 287°C. IR spectrum, ν, cm^{-1}: 3357, 3188 (NH_2), 1663 (C=O), 1607 (C=N), 1520, 1490. ^{1}H NMR spectrum, δ, ppm (*J*, Hz): 2.56, 2.60, 2.63, 2.66 (6H, all s, $2CH_3$); 7.14 and 7.34 (1H, two s, H-3); 7.37 and 7.42 (2H, two m, H-3'); 7.96 and 8.04 (2H, two m, H-2'); 10.42 (1H, br. s, N=NH–CO). ^{19}F NMR spectrum, δ, ppm: -107.82 (s). Mass spectrum, *m/z*: 312 $[M+H]^+$. Found, %: C 62.08; H, 4.62; N, 22.80. $C_{16}H_{14}FN_5O$. Calculated, %: C 61.73; H 4.53; N 22.50.

***N*'-(7-amino-2,4-dimethyl-5*H*-pyrrolo[3,4-*b*]pyridin-5-ylidene)pyridine-4-carbohydrazide (6c)** was isolated from the crude product mixture (LC/MS: 53% **6c**, RT = 1.438 and 46% **8c**, RT = 1.632) by preparative thin-layer chromatography with methanol as the eluent. The yield was 0.5 g (68%) **6c** as pale-yellow crystals; mp 189°C. IR spectrum, ν, cm^{-1}: 3541 (NH), 3336, 3210 (NH_2), 1672, 1655 (C=O), 1615 (C=N), 1544, 1514, 1483. ^{1}H NMR spectrum, δ, ppm (*J*, Hz): 2.58 and 2.65 (6H, two s, $2CH_3$); 7.19 and 7.28 (1H, two s, H-3); 7.76 and 7.85 (2H, two d, ^3J = 4.5, H-2'); 8.54 (2H, br. s, NH_2); 8.73, 8.77 (2H, two d, ^3J = 4.5, H-3'); 10.87 (1H, br. s, N=NH−CO). Mass spectrum, *m/z*: 295 $[M+H]^+$.

REFERENCES

1. C. C. Leznoff and A. B. P. Lever, *Phthalocyanines: Properties and Applications*, VCH, New York, (1989, 1993, 1996).
2. N. B. McKeown, *Phthalocyanine Materials: Synthesis, Structures, and Function*, Cambridge University Press, Cambridge, UK (1998).
3. R. Hirohashi, E. Sakamoto, and E. Ohno-Okumura, *Phthalocyanines as Functional Dyes*, ICP, Tokyo, Japan (2004).
4. A. E. O'Connor, W. M. Gallagher, and A. T. Byrne, *Photochem. Photobiol.*, **85**, 1053 (2009).
5. M. A. Kulikov, Yu. G. Vorob'ev, G. R. Berezina, and B. A. Stepanenko, *Zh. Obshch. Khim.*, **74**, 1031 (2004).
6. M. Yu. Kornilov and V. P. Makovetskii, *Ukr. Khim. Zh.*, **40**, 879 (1974).
7. V. Skala, J. Kuthan, J. Dedina, and J. Schraml, *Collect. Czech. Chem. Commun.*, **39**, 834 (1974).
8. O. V. Hordiyenko, A. V. Biitseva, M. Yu. Kornilov, N. Brosse, A. Hocquet, B. Jamart-Grégoire, O. V. Shishkin, and R. I. Zubatyuk, *Eur. J. Org. Chem.*, **12**, 2833 (2006).
9. W. Wolf and H. Vollmann, Ger. Pat. Appl. 1956941845; *Chem. Abstr.*, **53**, 34855 (1959).
10. L. I. M. Spiessens and M. J. O. Anteunis, *Bull. Soc. Chim. Belg.*, **89**, 205 (1980).
11. N. L. Colbry, E. F. Elslager, and L. M. Werbel, *J. Heterocycl. Chem.*, **21**, 1521 (1984).
12. A. M. Shestopalov, V. K. Promonenkov, Yu. A. Sharanin, L. A. Rodinovskaya, and S. Yu. Sharanin, *Zh. Obshch. Khim.*, **22**, 1517 (1984).
13. H. Vorbrüggen and K. Krolikiewicz, *Synthesis*, **4**, 316 (1983).
14. W. K. Fife, *Heterocycles*, **22**, 93 (1984).
15. W. E. Feely, G. Evanega, and E. M. Beavers, *Org. Synth.*, Coll. Vol. 5, 269 (1973).
16. G. Chelucci, M. A. Cabras, and A. Saba, *J. Heterocycl. Chem.*, **31**, 1289 (1994).
17. J. D. Sculley and C. S. Hamilton, *J. Am. Chem. Soc.*, **75**, 3400 (1953).
18. H. Heckmann and H. J. Metz, Pat. Appl. WO2004108836; *Chem. Abstr.*, **142**, 58224 (2005).
19. J. B. Paine III, *J. Heterocycl. Chem.*, **24**, 351 (1987).
20. L. I. Solov'eva, S. A. Mikhalenko, E. V. Chernykh, and E. A. Luk'yanets, *Zh. Obshch. Khim.*, **52**, 90 (1982).
21. M. Proštenik and I. Butula, *Chem. Ber.*, **110**, 2106 (1977).
22. H. Nagano, Y. Nawata, and M. Namana, *Chem. Pharm. Bull.*, **35**, 4068 (1987).
23. S. Hibino and E. Sugino, *J. Heterocycl. Chem.*, **27**, 1751 (1990).
24. O. V. Hordiyenko, I. V. Rudenko, A. V. Biitseva, A. V. Turov, A. Arrault, N. Brosse, O. Fabre, B. Jamart-Grégoire, R. I. Zubatyuk, and O. V. Shishkin, *Tetrahedron*, **65**, 6218 (2009).
25. P. Dydio, T. Zielin'ski, and J. Jurczak, *J. Org. Chem.*, **74**, 1525 (2009).
26. P. Bouchet, J. Elguero, R. Jacquier, and J.-M. Pereillo, *Bull. Soc. Chim. Fr.*, 2264 (1972).
27. X.-F. Duan, Z.-Q. Ma, F. Zhang, and Z.-B. Zhang, *J. Org. Chem.*, **74**, 939 (2009).