Chemistry of Heterocyclic Compounds, Vol. 42, No. 7, 2006

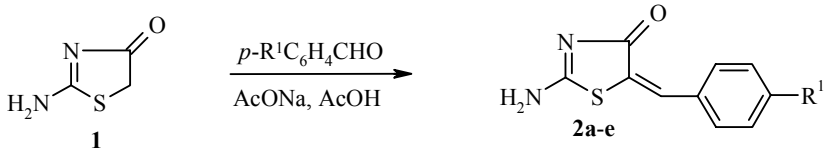
HETEROPHASE N-AMINOMETHYLATION OF 5-ARYLIDENEPSEUDOTHIOHYDANTOINS BY ARYLAMINES AND AQUEOUS FORMALDEHYDE IN AROMATIC SOLVENTS: EFFECT OF SUBSTITUENTS IN THE HETEROCYCLIC SUBSTRATE AND THE ARYL AMINE ON THE EFFICIENCY OF THE PROCESS

S. M. Ramsh, N. L. Medvedskiy, and S. O. Uryupov

We have obtained a series of 3-aryl-7-arylidene-3,4-dihydro-2H-[1,3]thiazolo[3,2-a][1,3,5]triazin-6(7H)-ones by means of heterophase aminomethylation of 2-amino-5-arylidene-1,3-thiazol-4(5H)-ones with aqueous formaldehyde and aromatic amines in benzene or toluene. We explain the effect of substituents in the heterocyclic substrate and the aryl amine on the efficiency of the process within a detailed scheme for one of the possible aminomethylation reaction routes.

Keywords: 2-amino-5-arylidene-1,3-thiazol-4(5H)-ones (5-arylidenepseudothiohydantoins), 3-aryl-7-arylidene-3,4-dihydro-2H-[1,3]thiazolo[3,2-*a*][1,3,5]triazin-6(7H)-ones, aminomethylation, synthesis.

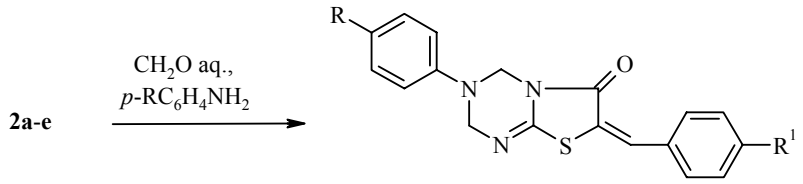
We previously developed a method for obtaining derivatives of 3,4-dihydro-2H-[1,3]thiazolo[3,2-*a*]-[1,3,5]triazin-6(7H)-one by N-aminomethylation of either 2-amino-1,3-thiazol-4(5H)-one (pseudothiohydantoin, **1**) or its 5-arylidene derivative with aqueous formaldehyde and aliphatic or aromatic amines in ethanol [1, 2]. Subsequently high biological activity was observed in derivatives of 3,4-dihydro-2H-[1,3]thiazolo[3,2-*a*][1,3,5]triazin-6(7H)-one [3]. Among other compounds, in [1] 7-benzylidene-3-phenyl-3,4-dihydro-2H-[1,3]thiazolo[3,2-*a*][1,3,5]triazin-6(7H)-one (**3a**) was synthesized starting from 2-amino-5-benzylidene-1,3-thiazol-4(5H)-one (5-benzylidenepseudothiohydantoin, **2a**) and aniline. The aim of this work was to synthesize analogs of compound **3a** with substituents on both phenyl rings: 7-R^1-benzylidene-3-R-phenyl-3,4-dihydro-2H-[1,3]thiazolo[3,2-*a*][1,3,5]triazin-6(7H)-ones **3**. In order to achieve this goal, the previously proposed [1, 2] method for obtaining compounds **3** was modified. In this work, we also analyzed and explained the effect of the R^1 substituents in 2-amino-5-R^1-benzylidene-1,3-thiazol-4(5H)-one (5-R^1-benzylidenepseudothiohydantoin, **2**) and R in the arylamine on the efficiency of the aminomethylation process.



1 **2a-e**

2 a R^1 = H, **b** R^1 = NEt_2, **c** R^1 = NMe_2, **d** R^1 = OMe, **e** R^1 = NO_2

St. Petersburg State Technical University, St. Petersburg 198013, Russia; e-mail: gsramsh@mail.wplus.net. Translated from Khimiya Geterotsiklicheskikh Soedinenii, No. 7, pp. 1095-1104, July, 2006. Original article submitted June 20, 2005.



3a-n

The starting arylidenepseudothiohydantoins **2a-e** were obtained by the conventional method: boiling pseudothiohydantoin **1** with aromatic aldehydes in glacial acetic acid in the presence of sodium acetate [4]. This method is based on the Grenacher reaction, which in turn is a special case of the Knoevenagel reaction [5], a typical case of nucleophilic addition to a carbonyl group occurring via a base catalysis mechanism [6].

We attempted to synthesize thiazolotriazines **3** according to the well-known method in [1]: aminomethylation of compounds **2** with aqueous formaldehyde and aromatic amines in ethanol. The "unsubstituted" thiazolotriazine **3a** was obtained rather easily by such a method, although in order to achieve a 30% yield the reaction time was increased 20-fold compared with that indicated in [1]. However, as we established, this method cannot be used as a universal method for obtaining analogs of compound **3a** with substituents on both phenyl rings. Attempts to synthesize compounds **3l** (R = H, $R^1 = NO_2$) and **3n** ($R = R^1 = NO_2$) with the most unfavorable substituent combinations (see below) were unsuccessful due to the high recovery (~85%) of the starting compound **2e** and the meager yield, on the order of 1-2%. Obviously under the given conditions, these compounds are formed too slowly, and prolonged heating in aqueous ethanol probably does not promote an increase in yield due to its significant solvolysis.

We also could not obtain thiazolotriazine **3l** by aminomethylation of substrate **2e** with aniline and paraform in benzene; the starting compound **2e** did not dissolve, and remained unchanged even in boiling solvent. The failure of this experiment may be explained as follows. We know [7] that the aminomethylation reaction is accelerated in hydroxyl-containing media; furthermore, hydroxymethylation, which is also possible both as one of the steps in the aminomethylation reaction and as one of the steps in formation of the target material, also is favored by hydroxyl-containing solvents. Finally, the anhydroformaldehyde aniline formed from paraform and aniline [1] in itself probably does not have aminomethylating properties, and the equilibrium content of the aminomethylating species formed as a result of its hydration (methylolphenylamine (anilinomethanol)) is too low in such a reaction medium.

Based on the above, we decided to carry out the aminomethylation reaction in an aromatic solvent immiscible with water: benzene or toluene, using formaldehyde in the form of an aqueous solution as the methylene component. Boiling the reaction mixture, besides accelerating the process, should ensure at least a minimum concentration of substrate **2** in the liquid phase, while vigorous stirring should ensure its dispersion and fine emulsification of the water in the organic solvent, with an increase in the contact surface area between the solid and the two liquid phases. Such a synthesis procedure proved to be successful, and allowed us to obtain a series of novel arylidene thiazolotriazines **3b-n**.

We assume that owing to the presence of water in the reaction mixture, a concentration of the aminomethylating species (methylol phenylamine) sufficient for the reaction to occur is maintained, and aminomethylation occurs either in the aqueous phase or in the wet benzene, and the reaction product **3** generally is deposited in the benzene phase, which to some degree prevents its solvolysis. Visual evidence for the extent of aminomethylation was the gradual complete or partial disappearance of the precipitate of heterocyclic substrate **2**.

The ratio of the reagents in each case was selected by trial and error, aiming for an acceptable "reaction time–yield" combination.

Compound **3l** was obtained in the highest yield with six times as much aminomethylating agents as substrate **2e**, and after boiling for 3.5 h, the recovery of starting compound **2e** was 55% while the yield of

reaction product **3l** after recrystallization was only 9%. When using stoichiometric amounts of reagents, compound **3l** was obtained in even lower yield.

In synthesis of other thiazolotriazines **3** (Tables 1 and 2), we noted that although excess aminomethylating agents also promote an increase in the extent of conversion of the heterocyclic substrate **2**, increasing the rate and shifting the equilibrium for aminomethylation toward the reaction product **3**, the product of reaction between the arylamine and formaldehyde formed with an excess (anhydroformaldehyde aniline in the case of aniline) interferes with separation of compound **3**. So the rest of the thiazolotriazines **3** were obtained using a 1.5-fold or slightly greater excess of formaldehyde (3-3.5 moles per mole substrate) and a stoichiometric or slightly greater amount of arylamine (1-1.2 moles per mole substrate). We should point out that the yield only very approximately reflects how readily reaction occurs and the extent of conversion of the starting compounds **2** to form target compound **3**, while the reaction time is a more objective characteristic.

In order to obtain compounds **3a,b,d,e,i,j**, brief boiling of the reaction mixture was required to completely dissolve the starting compound (10-15 min). The boiling time was much longer for obtaining compounds **3h,g,m** (several hours), and the starting compound was completely dissolved only in the case of compound **3h**. The low yield of compound **3i** (R = H, R^1 = OMe) (only 14%) is obviously connected with the complications involved in isolating and purifying it.

Compounds **3c,f,k,n**, the products of aminomethylation of 5-arylidenepseudothiohydantoins **2a,b,d,e** by *p*-nitroaniline, are much more difficult to obtain than compound **3**, which does not contain a nitro group. The reaction time for obtaining these compounds is approximately an order of magnitude longer than when obtaining compounds **3** (with no nitro group), and is of the same order of magnitude as the reaction time for obtaining compounds **3l,m**, which also contain a nitro group. The solubility of compounds **3** containing a nitro group is extremely low in benzene, toluene, acetonitrile, acetone, chloroform, dioxane, DMF, DMSO, acetic acid, ethanol, and ethyl acetate, which makes it very difficult to recrystallize them and to record their ^{1}H NMR spectra.

In the IR spectra of compounds **3a-n** (Table 2), there are no absorption bands for stretching vibrations of the NH groups, which are present in the spectra of the starting compounds **2a-e**, while the frequencies of the stretching vibrations for the C=O and C=N groups lie within the ranges 1690-1710 and 1625-1665 cm^{-1} respectively, which is typical of their analogs [1, 2].

The ^{1}H NMR spectra of thiazolotriazines **3a-n** in heated DMSO-d_6 are similar to the spectra of previously synthesized substituted thiazolotriazines [1, 2]. The signals from the protons of the methylene groups 2H-2 and 2H-4 appear at 5.22-5.54 ppm and 4.91-5.22 ppm respectively, while the signals from aromatic protons of the 3-aryl and 7-arylidene groups and also the CH protons of the arylidene groups appear in the range 6.73-8.32 ppm. When a substituent is present, the aromatic protons appear as pairs of doublets. Overlap of individual signals generally gives a complex multiplet pattern in the aromatic absorption region.

Thus from the synthesis results we trace out the following qualitative patterns, although not entirely clearly (not surprisingly for a synthesis experiment rather than a specially devised physicochemical experiment). The compounds formed most readily and/or in highest yield are **3e,h,j**, i.e., the compounds where electron-donor substituents are present both in the arylamine moiety and in the arylidene group. The "unsubstituted" compound **3a**, and also compounds **3b,d,g,i** with one electron-donor group in the molecule, are intermediate with respect to how readily the reaction occurs and the achievable yield. Compounds **3c,f,k**, which have a nitro group in the arylamine moiety, are more difficult to obtain; and compounds **3l-n** with a nitro group in the arylidene group are the most difficult to obtain and have the lowest yields. Among the latter, compound **3n** (with nitro groups on both phenyl rings) has the poorest parameters.

Our earlier experiments on aminomethylation of pseudothiohydantoin [1] with aqueous formaldehyde and aniline provided indirect evidence that of all the possible routes [8] for the aminomethylation reaction, the route with intermediate formation of methylol arylamine is realized. The reaction of aniline with formaldehyde occurs rather rapidly, and first we see precipitation from the reaction mixture of anhydroformaldehyde aniline, a

TABLE 1 Synthesis Reaction Conditions and Characteristics of Compounds **3a-n**

Compound	R	R^1	Reaction time, h	Solvent for recrystallization	mp, °C	Empirical formula	Found, % / Calculated, %				Yield, %
							C	H	N	S	
3a*	H	H	2.0	Toluene	179-180 (180 [1])	$C_{18}H_{15}N_3OS$	67.01 / 67.27	4.47 / 4.70	13.02 / 13.07	10.20 / 9.98	54
3b	OMe	H	1.5	Benzene–hexane, 2:1*[2]	146-148	$C_{19}H_{17}N_3O_2S$	65.59 / 64.94	5.24 / 4.88	11.92 / 11.96	9.49 / 9.12	51
3c	NO_2	H	1.0	Acetonitrile	189-192	$C_{18}H_{14}N_4O_3S$	59.58 / 59.01	3.92 / 3.85	15.23 / 15.29	8.43 / 8.75	18
3d	H	NEt_2	0.17	Benzene*[2]	187	$C_{22}H_{24}N_4OS$	67.06 / 67.32	6.10 / 6.16	14.31 / 14.27	7.93 / 8.17	36
3e	OMe	NEt_2	0.25	Benzene*[2]	171-173	$C_{23}H_{26}N_4O_2S$	65.19 / 65.38	6.12 / 6.20	13.57 / 13.26	7.31 / 7.59	50
3f	NO_2	NEt_2	1.0	Benzene	233	$C_{22}H_{23}N_5O_3S$	59.83 / 60.40	5.09 / 5.30	15.49 / 16.01	7.15 / 7.33	37
3g	H	NMe_2	3.5	Benzene	193	$C_{20}H_{20}N_4OS$	66.40 / 65.91	5.94 / 5.53	15.77 / 15.37	8.77 / 8.80	26
3h	OMe	NMe_2	3.5	Benzene*[2]	138-141	$C_{21}H_{22}N_4O_2S$	63.58 / 63.94	5.84 / 5.62	13.73 / 14.20	8.21 / 8.13	39
3i	H	OMe	0.17	Benzene–hexane, 2:1*[2]	147-148	$C_{19}H_{17}N_3O_2S$	64.58 / 64.94	4.99 / 4.88	11.98 / 11.96	9.03 / 9.12	14
3j	OMe	OMe	0.25	Benzene*[2]	143-144	$C_{20}H_{19}N_3O_3S$	62.84 / 62.98	5.58 / 5.02	11.38 / 11.02	8.45 / 8.41	20
3k	NO_2	OMe	2.0	Benzene	219	$C_{19}H_{16}N_4O_4S$	57.51 / 57.57	4.20 / 4.07	14.10 / 14.13	7.54 / 8.09	44
3l	H	NO_2	3.5	Benzene–hexane, 3:1	203	$C_{18}H_{14}N_4O_3S$	58.98 / 59.01	4.14 / 3.85	15.10 / 15.29	8.25 / 8.75	9
3m	OMe	NO_2	4.0	Acetonitrile	202	$C_{19}H_{16}N_4O_4S$	57.59 / 57.57	4.47 / 4.07	14.10 / 14.13	8.15 / 8.09	9
3n	NO_2	NO_2	5.0	Acetonitrile	245	$C_{18}H_{13}N_5O_5S$	52.12 / 52.55	3.18 / 3.19	17.26 / 17.02	7.31 / 7.79	6

* Reaction conducted in toluene; in all remaining cases, in benzene.

*[2] Recrystallization adding Al_2O_3.

TABLE 2 Spectral Characteristics of Compounds **3a-n**

Compound	IR spectrum (thin film), ν, cm^{-1}		^1H NMR spectrum, δ, ppm				
	C=O	C=N	2H-2, s	2H-4, s	CH, Ar, m	R, s	R^1, s
3a	1700	1625	5.35	5.01	6.92-7.66	—	—
3b	1710	1635	5.30	4.98	6.86-7.69	3.70	—
3c	1710	1665	5.51	5.19	7.24-8.16	—	—
3d	1695	1635	5.34	5.02	6.76-7.55	—	3.42 ($C\underline{H}_2CH_3$), 1.14 ($CH_2C\underline{H}_3$)*
3e	1695	1630	5.26	4.93	6.76-7.53	3.70	3.40 ($C\underline{H}_2CH_3$), 1.14 ($CH_2C\underline{H}_3$)*
3f	1695	1635	5.49	5.19	6.75-8.18	—	3.41 ($C\underline{H}_2CH_3$), 1.12 ($CH_2C\underline{H}_3$)*
3g	1700	1625	5.35	5.03	6.79-7.59	—	3.00
3h	1690	1630	5.22	4.91	6.73-7.53	3.56	2.83
3i	1690	1625	5.38	5.05	6.95-7.65	—	3.81
3j	1700	1635	5.29	4.95	6.82-7.66	3.67	3.80
3k	1690	1625	5.50	5.18	6.99-8.16	—	3.95
3l	1700	1635	5.38	5.05	6.94-8.32	—	—
3m	1700	1635	5.31	4.99	6.86-8.31	3.70	—
3n	1705	1640	5.54	5.22	7.26-8.32	—	—

* Quartet from methylene protons, triplet from methyl protons of the ethyl group, J = 7.5 Hz.

precursor of which is methylol arylamine*, which then is consumed in the reaction with the heterocyclic substrate. This means, first of all, that the first step of aminomethylation (formation of methylol arylamine) is not the rate-determining step, and the equilibrium for it is established rather rapidly; secondly, the equilibrium for the second step (formation of the N-aminomethyl derivative), while it is generally achieved, is established appreciably more slowly, and the rate of the process as a whole or the final equilibrium should be influenced by electronic effects of substituents both on the arylamine and the heterocyclic component of the reaction.

The recently obtained experimental data also fit entirely into the likely scheme for the formation of the end product of reaction **3** and the detailed scheme for the N-aminomethylation reaction with preliminary equilibrium in the step of formation of the aminomethylating species methylol arylamine, rapidly established before the rate-determining step of the reaction between this species and the heterocyclic substrate **2**, which also may be an equilibrium step. Our theoretical analysis in accordance with these schemes for the cross effect of substituents R^1 in heterocyclic substrate **2** and R in the arylamine on the rates and equilibria of the reactions of aminomethylation and subsequent cyclization*[2] predicts that donor substituents R facilitate the reaction and conversely acceptor substituents R slow down the reaction in the aryl amine, in addition to the more noticeable facilitating effect of donor substituents R^1 and the retarding effect of acceptor substituents R^1 on the heterocyclic substrate **2**, which on the whole is consistent with the presented results of the synthesis experiments.

We should point out that the precipitate of reaction product **3** formed from the reaction mixture during the process may promote successful occurrence of the process and mask substituent effects.

EXPERIMENTAL

The ^{1}H NMR spectra were recorded on a Bruker AM-200 (200 MHz) and a Bruker AM-300 (300 MHz) in DMSO-d_6, internal standard HMDS (δ 0.05 ppm). The IR spectra were obtained on an IKS-29 spectrometer in nujol. TLC was run on Silufol UV-254 plates, eluent 1:2 acetone–hexane. The starting compounds **2a-e** are not chromatographically mobile in this solvent system. For low-solubility compounds **3c,f,k-n**, we also used the system 1:9 ethanol–chloroform.

Starting 5-Arylidenepseudothiohydantoins 2a-e were obtained according to a modified method from [4]. Pseudothiohydantoin **1** (0.2 mol) was boiled with equimolar amounts of the aromatic aldehyde and anhydrous sodium acetate in 100 mL glacial acetic acid with vigorous stirring. Then the reaction mixture was cooled down. The precipitate formed was filtered out, washed with water, and recrystallized from acetic acid. The precipitates of compounds **2a,b** were washed before filtration from a 300 ml flask of water. The boiling time was 80 min, 20 min, 20 min, 20 min, and 150 min respectively.

7-Benzylidene-3-phenyl-3,4-dihydro-2H-[1,3]thiazolo[3,2-*a*][1,3,5]triazin-6(7H)-one (3a). Compound **2a** (0.80 g, 3.9 mmol), aniline (0.47 g, 0.46 ml, 5.0 mmol), and formalin (1.10 ml, 13.6 mmol) in toluene (9 ml) was boiled with stirring for 2 h. The precipitate formed was filtered out and recrystallized from toluene.

7-Benzylidene-3-(4-nitrophenyl)-3,4-dihydro-2H-[1,3]thiazolo[3,2-*a*][1,3,5]triazin-6(7H)-one (3c). Compound **2a** (4.08 g, 20 mmol), *p*-nitroaniline (2.76 g, 20 mmol), and formalin (4.8 ml, 60 mmol) in benzene (50 ml) were boiled with stirring for 1 h. The gummy precipitate falling out of the reaction mixture after cooling was ground with hexane to a crystalline consistency, and the precipitate obtained was recrystallized from acetonitrile.

7-[(4-Diethylamino)benzylidene]-3-phenyl-3,4-dihydro-2H-[1,3]thiazolo[3,2-*a*][1,3,5]triazin-6(7H)-one (3d). Compound **2b** (5.51 g, 20 mmol), aniline (2.05 g, 2.01 ml, 22 mmol), and formalin (4.8 ml, 60 mmol) in benzene (100 ml) were boiled with stirring for 10 min until the starting compound was completely dissolved.

---

* Anhydroformaldehyde aniline plays the role of the depo form of its own precursor: methylol arylamine.

*[2] Additional data can be obtained from the authors.

The precipitate falling out from the hot organic layer as it cooled was recrystallized twice from benzene over Al_2O_3.

Compounds 3g (50/15), **3b** (20/50), **3j** (20/50), **3h** (11/50), and **3e** (15/30) were obtained similarly. In parentheses are given the amount of substrate (mmol)/amount of solvent (ml) used for the synthesis.

7-(4-Methoxybenzylidene)-3-phenyl-3,4-dihydro-2H-[1,3]thiazolo[3,2-*a*][1,3,5]-triazin-6(7H)-one (3i). Compound **2d** (11.7 g, 50 mmol), aniline (5.40 g, 5.28 ml, 58 mmol), and formalin (12.0 ml, 150 mmol) in benzene (100 ml) were boiled with stirring for 10 min until the starting compound was completely dissolved. The organic layer was separated, the benzene was driven off at 25°C under vacuum almost to dryness, and the residue was treated with benzene (75 ml). Hexane (100 ml) was added to the benzene extract. The mixture obtained was brought to boiling over Al_2O_3 and filtered. The precipitate falling out as the filtrate cooled was recrystallized from a 2:1 benzene–hexane mixture over Al_2O_3.

7-(4-Methoxybenzylidene-3-(4-nitrophenyl)-3,4-dihydro-2H-[1,3]thiazolo[3,2-*a*][1,3,5]triazin-6(7)-one (3k). Compound **2d** (1.87 g, 8 mmol), *p*-nitroaniline (1.10 g, 8 mmol), and formalin (1.9 ml, 24 mmol) in benzene (50 ml) were boiled for 2 h with stirring, and then cooled down to room temperature. The precipitate was filtered out and recrystallized from benzene.

Compound 3f was obtained similarly from compound **2b** (3.58 g, 13 mmol), *p*-nitroaniline (1.80 g, 13 mmol), and formalin (3.6 ml, 45 mmol).

7-(4-Nitrobenzylidene)-3-phenyl-3,4-dihydro-2H-[1,3]thiazolo[3,2-*a*][1,3,5]triazin-6(7H)-one (3l). Compound **2e** (3.75 g, 15 mmol), aniline (8.38 g, 8.20 ml, 90 mmol), and formalin (7.2 ml, 90 mmol) in benzene (200 ml) were boiled for 3.5 h with stirring. The hot reaction mixture was filtered to remove unreacted starting compound (2.10 g). The precipitate falling out from the filtrate after cooling was recrystallized from a 3:1 benzene–hexane mixture.

Compound 3n was obtained similarly from compound **2e** (5.00 g, 20 mmol), *p*-nitroaniline (2.76 g, 20 mmol), and formalin (4.8 ml, 60 mmol).

3-(4-Methoxyphenyl)-7-(4-nitrobenzylidene)-3,4-dihydro-2H-[1,3]thiazolo[3,2-*a*][1,3,5]triazin-6(7H)-one (3m). Compound **2e** (5.00 g, 20 mmol), *p*-anisidine (2.50 g, 20 mmol), and formalin (4.8 ml, 60 mmol) in benzene (50 ml) were boiled for 4 h with stirring. The reaction mixture was filtered to remove undissolved starting compound. The filtrate was dried for 24 hours by calcium chloride, the benzene was driven off under vacuum, and the residue was recrystallized from acetonitrile.

REFERENCES

1. S. Yu. Solov'eva-Yavits, S. M. Ramsh, and A. I. Ginak, *Khim. Geterotsikl. Soedin.*, **477** (1981) [*Chem. Heterocycl. Comp.*, **17**, 340 (1981)].
2. S. Yu. Solov'eva-Yavits, S. M. Ramsh, and A. I. Ginak, *Khim. Geterotsikl. Soedin.*, 1204 (1983). [*Chem. Heterocycl. Comp.*, **19**, 961 (1983)].
3. S. M. Ramsh, T. S. Basieva, O. Yu. Uryupov, S. Yu. Solov'eva, V. M. Vinogradov, A. I. Ginak, B. I. Krivoruchko, I. A. Shelkovnikov, and Yu. N. Shanin, USSR Inventor's Certificate 1095612; *B. I.*, No. 20, 197 (1984).
4. D. Liberman, J. Himbert, and L. Hengl, *Bull. Soc. Chim. Fr.,* 1120 (1948); *Chem. Abstr.*, **43**, 3819 (1949).
5. K. V. Vatsuro and G. L. Mishchenko, *Name Reactions in Organic Chemistry* [in Russian], Khimiya, Moscow (1976), p. 152, p. 215.
6. J. March, *Organic Chemistry* [Russian translation], Mir, Moscow (1987), Vol. 3, p. 379, p. 387.
7. V. Tychlopoulos and J. H. P. Tyman, *Synth. Commun.*, **16**, 1401 (1986).
8. M. Tramontini, *Synthesis*, 703 (1973).