

Structure and Nucleophilic Reactivity of Aliphatic Amines. A New Opinion

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Abstract—Nucleophilic reactivity of alkylamines is determined by steric effect of the alkyl radicals. On the one hand, this effect hampers interaction of the reactant molecules and, on the other, changes bond angles at the nitrogen atom, thus favoring rehybridization of the unshared electron pair which is responsible for the ability of amines to act as nucleophiles.

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It is commonly accepted that the reactivity of alkylamines is related primarily to electron-donating and steric effects of the alkyl groups. However, attempts to estimate quantitatively the effect of amine structure on the nucleophilic reactivity using the Taft equation were unsuccessful [1, 2]. A number of special equations were proposed [3], but they turned out not to be universal, i.e., their application was not free from some limitations. Some authors [4–6] believed that structure–basicity and structure–nucleophilic reaction rate correlations for alkylamines can be drawn with the use of only steric constants (E_S [5] or E_R [6]) of alkyl groups, but such correlations were not clearly substantiated.

The present article describes a new approach which makes it possible to derive quantitative relations between the structure of alkylamines and their nucleophilic reactivity. Analysis of relations between the structure of alkylamines and *N*-alkyl- and *N,N*-dialkylanilines and their basicity [7–9] showed that electron-donating inductive effect of alkyl groups on the nitrogen atom is not reflected in the basicity constants. It was found that the main factor determining basic properties of amines is steric effect of alkyl groups, which induces change of bond angles at the nitrogen atom ($sp^3 \rightarrow sp^2$ rehybridization) and hence changes hybridization of the lone electron pair (increases its *p* character). It was also shown [10] that the state of LEP on the nitrogen atom in alkylamines depends only on the nature and number of hydrocarbon radicals, i.e. it is determined only by the molecular geometry.

Therefore, while studying structure–reactivity relations in the series of alkylamines, the *p* character of the nitrogen LEP should be used as quantitative structure parameter.

The ability of alkylamines to react with electrophiles is also related to the presence of LEP on the nitrogen atom; therefore, hybridization of LEP should affect nucleophilic reactivity of amines. Variation in the hybrid state of the nitrogen atom upon replacement of hydrogen atoms in ammonia by alkyl groups has been extensively studied. We showed in [8] that the bond angles at the nitrogen atom in primary alkylamines do not depend on the alkyl nature, i.e. hybridization of orbitals on the nitrogen atom, including its LEP, remains unchanged upon introduction of various hydrocarbon radicals. It may be presumed that the rate constants of nucleophilic reactions of primary amines are determined only by steric effect of alkyl groups which hamper approach of reactant molecules. In fact, this is confirmed by the data in Table 1 where parameters of correlations between the steric constants F^H of alkyl groups [2] and the rate constants of reactions of primary alkylamines with different electrophiles, measured in various solvents, are collected.

Unlike primary amines, the nature of alkyl groups in secondary and tertiary amines affects orbital hybridization of the nitrogen atom. In this case the reaction rate constants are determined by steric effect of the alkyl groups which, on the one hand, changes bond angles at the nitrogen atom (i.e., its hybrid state and correspondingly *p* character of the LEP) and, on the

Table 1. Parameters of correlations $\log k = \log k^0 + \rho F^H$ for reactions of primary alkylamines with different electrophiles

Equation no.	Reagent, solvent, temperature, °C	$\log k^0$	ρ	s_0	r
1	Allyl bromide, benzene, 100 [11, 12]	$-(1.99 \pm 0.02)$	$-(0.38 \pm 0.009)$	0.03	0.999
2	Methyl iodide, benzene, 30 [13]	$-(3.10 \pm 0.003)$	$-(0.13 \pm 0.003)$	0.003	0.999
3	Phenyl vinyl ketone, water, 25 [14]	0.91 ± 0.08	$-(0.39 \pm 0.03)$	0.09	0.993
4	<i>p</i> -Nitrophenyl acetate, water, 25 [15]	3.66 ± 0.12	$-(0.78 \pm 0.05)$	0.11	0.996
5	<i>o</i> -Chlorophenyl ethyl ether, 95% ethanol, 70 [16]	$-(5.25 \pm 0.04)$	$-(0.26 \pm 0.02)$	0.04	0.989
6	<i>o</i> -Bromophenyl ethyl ether, 95% ethanol, 70 [16]	$-(3.72 \pm 0.04)$	$-(0.27 \pm 0.03)$	0.05	0.986
7	<i>p</i> -Methoxyphenyl vinyl ketone, 10% ethanol, 25 [17]	0.67 ± 0.19	$-(0.45 \pm 0.08)$	0.22	0.983
8	Phenacyl bromide, benzene, 25 [18]	$-(2.31 \pm 0.03)$	$-(0.34 \pm 0.02)$	0.04	0.997
9	Phenacyl bromide, benzene, 25 [18] ^a	$-(0.63 \pm 0.21)$	$-(0.95 \pm 0.08)$	0.22	0.994
10	Phenacyl bromide, benzene, 25 [18] ^b	$-(0.76 \pm 0.16)$	$-(0.95 \pm 0.06)$	0.12	0.998

^a Secondary methylamines.

^b Tertiary methylamines.

other, hampers reactant approach. In the series of secondary and tertiary amines, both these factors act in parallel, and correlation like $\log k = f(\Sigma F^H)$ seems to be reasonable. This is confirmed by Eqs. (9) and (10) (Table 1), as well by the correlations given in [5, 6].

A quite different pattern is observed in the series including ammonia, methylamine, dimethylamine, and trimethylamine. Successive replacement of hydrogen atoms in the ammonia molecule by methyl groups is accompanied by variation of the bond angles at the nitrogen atom and *p* order (*p*) of the nitrogen LEP [7]. However, the characters of these variations are different, as follows from the bond angles and *p* values [7] for ammonia ($\angle HNH$ 107.3°, *p* = 0.690), methylamine ($\angle HNH$ 106°, $\angle CNH$ 112°, *p* = 0.770), dimethylamine ($\angle CNC$ 112.5°, $\angle CNH$ 109.9°, *p* = 0.780), and trimethylamine ($\angle CNC$ 108.7°, *p* = 0.728). It is seen that the *p* order appreciably increases in going from ammonia to methylamine, changes insignificantly in going from methylamine to dimethylamine, and sharply decreases in going to trimethylamine. Obviously, these data are to be taken into account. Fairly good correlations $\log k = f(p, \Sigma F^H)$ for reactions of ammonia, methylamine, dimethylamine, and trimethylamine with different electrophiles support the above stated (Table 2). Comparison of the rate constants (some of which are given in Tables 3 and 4) shows that secondary amines react at the highest rate, which is consistent with the maximal *p* character of the nitrogen LEP therein.

The data in Table 3 show that the rate constants can also change in a different order, depending on the alkyl radical nature or reaction temperature. Parameters of

the correlation $\log k = f(p, \Sigma F^H)$ (Table 2), calculated on the standard scale, indicates that the rate constant increases in parallel with *p* if the coefficient ϕ (δ/ρ ratio) ranges from 0.5 to 1.5 (the *p* character prevails). If the coefficient ϕ is equal or larger than 2 (steric effect prevails), the maximal reaction rate is observed for trialkylamines.

Litvinenko et al. [21] studied reactions of methylamines with phenacyl bromide and its *p*-methyl-, *p*-chloro-, and *p*-nitro-substituted analogs and found that the main factor determining the reaction rate is the electronic nature of electrophile. This conclusion is confirmed by analysis of the correlations $\log k = f(p, F^H)$ [Eqs. (15a), (16a), (19a), and (20a); Table 2]; the parameters ρ and δ in all these equations are almost similar.

In the reactions of propyl and allyl bromides with a series of methylamines (Table 3) the electronic nature of the electrophile determines the character of variation of the rate constants in the series of primary, secondary, and tertiary alkylamines. The highest rates are observed in the reactions of primary methylamine with propyl bromide [$\phi = -1.88$, Eq. (4a), Table 2] and tertiary trimethylamine with allyl bromide [$\phi > 2$, Eq. (5a), Table 2].

It is interesting to elucidate how the relations found for methylamines will change in going to other alkylamines. For this purpose, parameters of the correlations $\log k = f(p, \Sigma F^H)$ for the reactions of ethylamines with methyl iodide [13], nitroethane [20], and phenacyl bromide [18] were compared with those found for analogous reactions of methylamines. There are no

Table 2. Parameters of correlations $\log k = \log k^0 + \rho p + \delta \Sigma F^H$ and $\log k = \log k^0 + \rho p K_{BH^+} + \delta \Sigma F^H$ for reactions of methyl- and ethylamines with different electrophiles

Equation no.	Reagent, solvent, temperature, °C	$\log k^0$	ρ	δ	s_0	φ	r
1	Methyl bromide, benzene,	$-(7.30 \pm 0.40)$	6.42 ± 0.55	1.57 ± 0.07	0.04		0.999
1a	51.2 [19]	0	0.39 ± 0.03	0.78 ± 0.03	0.06	2.0	0.999
2	Methyl bromide, benzene,	$-(6.76 \pm 0.12)$	6.52 ± 0.16	0.88 ± 0.02	0.01		0.999
2a	100 [19]	0	0.57 ± 0.01	0.63 ± 0.01	0.03	1.11	0.999
3	Ethyl bromide, benzene,	$-(7.92 \pm 1.51)$	5.78 ± 2.08	0.99 ± 0.25	0.14		0.986
3a	100 [19]	0	0.49 ± 0.14	0.69 ± 0.14	0.32	1.41	0.986
4	Propyl bromide, benzene,	$-(13.55 \pm 1.64)$	13.27 ± 2.25	$-(3.05 \pm 0.28)$	0.15		0.996
4a	100 [19]	0	0.57 ± 0.09	$-(1.07 \pm 0.09)$	0.18	-1.88	0.996
5	Allyl bromide, benzene,	$-(6.72 \pm 0.90)$	5.57 ± 1.24	1.56 ± 0.15	0.08		0.997
5a	100 [19]	0	0.35 ± 0.08	0.80 ± 0.08	0.15	2.29	0.997
6	Methyl iodide, benzene,	$-(10.75 \pm 0.08)$	8.94 ± 0.11	2.81 ± 0.01	0.007		0.999
6a	30 [13]	0	0.32 ± 0.004	0.83 ± 0.04	0.007	2.59	0.999
7	Methyl iodide, benzene,	$-(9.31 \pm 0.03)$	0.51 ± 0.003	2.86 ± 0.007	0.004		0.999
7a	30 [13] ^a	0	0.32 ± 0.002	0.84 ± 0.002	0.004	2.63	0.999
8	Methyl iodide, benzene,	$-(12.63 \pm 0.95)$	0.87 ± 0.09	0.20 ± 0.05	0.08		0.999
8a	30 [13] ^b	0	0.75 ± 0.03	0.30 ± 0.08	0.10	0.40	0.999
9	Methyl iodide, benzene,	$-(10.51 \pm 1.04)$	0.64 ± 0.10	0.26 ± 0.05	0.13		0.995
9a	30 [13] ^c	0	0.67 ± 0.10	0.52 ± 0.10	0.19	0.78	0.995
10	Nitroethane, water, 0 [20]	$-(7.91 \pm 0.05)$	9.67 ± 0.07	1.52 ± 0.009	0.005		0.999
10a		0	0.53 ± 0.004	0.67 ± 0.004	0.007	1.26	0.999
11	Nitroethane, water, 0 [20] ^a	$-(6.36 \pm 0.07)$	0.55 ± 0.07	1.57 ± 0.02	0.01		0.999
11a		0	0.51 ± 0.07	0.69 ± 0.07	0.01	1.35	0.999
12	Nitroethane, water, 0 [20] ^b	$-(7.30 \pm 0.09)$	0.65 ± 0.02	0.24 ± 0.01	0.02		0.999
12a		0	0.63 ± 0.02	0.42 ± 0.01	0.02	0.67	0.999
13	<i>o</i> -Chlorophenyl ethyl ether,	$-(12.88 \pm 0.23)$	9.54 ± 0.33	1.06 ± 0.04	0.02		0.999
13a	ethanol, 70 [16]	0	0.63 ± 0.02	0.57 ± 0.02	0.04	0.90	0.999
14	<i>o</i> -Bromophenyl ethyl ether,	$-(13.66 \pm 1.33)$	12.53 ± 1.83	1.36 ± 0.23	0.12		0.996
14a	ethanol, 70 [16]	0	0.64 ± 0.09	0.56 ± 0.09	0.17	0.88	0.996
15	<i>p</i> -Methylphenacyl bromide,	$-(18.25 \pm 0.07)$	19.62 ± 0.09	3.10 ± 0.01	0.006		0.999
15a	benzene, 25 [21]	0	0.52 ± 0.002	0.67 ± 0.002	0.005	1.29	0.999
16	Phenacyl bromide, benzene,	$-(17.73 \pm 0.79)$	18.83 ± 1.09	3.25 ± 0.13	0.07		0.999
16a	25 [21]	0	0.50 ± 0.03	0.70 ± 0.03	0.05	1.40	0.999
17	Phenacyl bromide, benzene,	$-(14.28 \pm 0.58)$	1.04 ± 0.06	3.42 ± 0.13	0.07		0.999
17a	25 [21] ^a	0	0.48 ± 0.03	0.73 ± 0.03	0.05	1.52	0.999
18	Phenacyl bromide, benzene,	$-(22.02 \pm 1.04)$	1.87 ± 0.10	$-(0.55 \pm 0.05)$	0.09		0.997
18a	25 [21] ^b	0	1.47 ± 0.08	$-(0.76 \pm 0.08)$	0.10	-0.52	0.999
19	<i>p</i> -Chlorophenacyl bromide,	$-(18.16 \pm 0.15)$	19.55 ± 0.22	3.24 ± 0.03	0.01		0.999
19a	benzene, 25 [21]	0	0.51 ± 0.01	0.69 ± 0.01	0.01	1.35	0.999
20	<i>p</i> -Nitrophenacyl bromide,	$-(18.22 \pm 0.44)$	20.02 ± 0.60	3.09 ± 0.08	0.04		0.999
20a	benzene, 25 [21]	0	0.53 ± 0.02	0.67 ± 0.02	0.03	1.26	0.999

^a Methylamines.^b Ethylamines.^c Butylamines.

Table 3. Rate constants $k \times 10^6$, $l \text{ mol}^{-1} \text{ min}^{-1}$, for reactions of methylamines with alkyl bromides in benzene at 100°C [19]

Alk in AlkBr	NH ₃	MeNH ₂	Me ₂ NH	Me ₃ N
Methyl ^a	1381	10674	35574	39326
Methyl	5471	31910	59954	47437
Ethyl	124	490	1534	1053
Propyl	44	60	21	0.5
Allyl	1380	8302	30833	34263

^a At 51.2°C.**Table 4.** Rate constants ($l \text{ mol}^{-1} \text{ s}^{-1}$) for reactions of alkylamines with methyl iodide in benzene at 30°C [13]

R	RNH ₂	R ₂ NH	R ₃ N
H	–	–	2.61×10^{-5}
CH ₃	7.28×10^{-4}	4.87×10^{-3}	8.89×10^{-3}
C ₂ H ₅	5.62×10^{-4}	2.78×10^{-3}	1.85×10^{-3}
C ₄ H ₉	5.53×10^{-4}	1.49×10^{-3}	6.87×10^{-4}

exhaustive experimental data on the bond angles at the nitrogen atom in all ethylamines, which are necessary to calculate p orders of the LEP on the nitrogen atom. Therefore, correlations $\log k = f(pK_{\text{BH}^+}, \Sigma F^{\text{H}})$ were used. The replacement of p by pK_{BH^+} seems to be quite reasonable, for a functional dependence exists between these parameters [7].

On the one hand, good quality of the correlations $\log k = f(pK_{\text{BH}^+}, F^{\text{H}})$ [Eqs. (7)–(9), (11), (12), (17), and (18), Table 2] confirms the above assumption; on the other hand, it rationalizes sometimes unsuccessful attempts of some authors [14–18] (see also relevant references given in [2]) to derive quantitative relations between the rate constants of reactions of alkylamines and their basicity constants. The latter parameter reflects only the effect of the state of the LEP, i.e., only one factor responsible for the rates of reactions of secondary and tertiary alkylamines. As far as the rate constants of nucleophilic reactions of primary alkylamines depend only on the steric effect of alkyl radicals that shield the reaction center, while their basicity constants are almost similar (i.e., they do not depend on the alkyl group nature), correlations like $\log k = f(pK_{\text{BH}^+})$ seems to be unreasonable.

As follows from the correlations $\log k = f(pK_{\text{BH}^+}, \Sigma F^{\text{H}})$ for the methyl- and ethylamine series [Eqs. (7a) and (8a), (11a) and (12a), (17a) and (18a)] the coefficient ϕ strongly changes in going from methyl- to ethylamines. In the series of ethylamines,

the contribution of the p order of the LEP prevails, and the rate constants increase in parallel with p . The observed differences in the effects of methyl and ethyl radicals suggest that a structure–reactivity correlation like $\log k = f(p, \Sigma F^{\text{H}})$ or $\log k = f(pK_{\text{BH}^+}, \Sigma F^{\text{H}})$, general for all alkylamines, is quite difficult to derive. The more so, it is very difficult to obtain a correlation involving not only alkylamines but also arylamines and nitrogen-containing heterocyclic compounds (see [22] and references therein), for the orbital hybridization of the nitrogen atom in these compounds changes in considerably different ways.

Rehybridization of nitrogen orbitals in arylamines is governed only by electronic properties of substituents in the benzene ring. Structure–basicity studies in the aniline series [23] showed that electron-donating substituents favor $sp^2 \rightarrow sp^3$ rehybridization which leads to reduced p order of the nitrogen LEP; as a result, conjugation between the LEP and benzene ring becomes weaker, and transmission of the substituent effect decreases. By contrast, electron-withdrawing substituents favor $sp^3 \rightarrow sp^2$ rehybridization of the nitrogen atom, the p character of its LEP increases, conjugation with the aromatic ring becomes stronger, and the substituent effect is transmitted better (the above stated applies only to *para*- and *meta*-substituted anilines). Therefore, the reaction constant in the correlation $\log k = f(pK_{\text{BH}^+})$ for anilines having electron-withdrawing substituents should be larger than in analogous correlation for anilines having electron-donating groups. Comparison of the reaction constants in the correlations $\log k = f(pK_{\text{BH}^+})$ [22] for the reactions of diphenyl chlorophosphate with anilines containing electron-donating [$\log k = -(12.32 \pm 0.62) + (0.87 \pm 0.06)pK_{\text{BH}^+}$, $r = 0.996$, $s_0 = 0.06$] and electron-withdrawing substituents [$\log k = -(19.47 \pm 0.04) + (1.66 \pm 0.005)pK_{\text{BH}^+}$, $r = 0.999$, $s_0 = 0.002$] supports the above assumption: transmission of the electronic effect of electron-withdrawing substituents is more effective by a factor of ~ 2 .

Apart from substituents in the benzene ring, the state of the nitrogen atom in *N*-alkyl- and *N,N*-dialkyl-anilines depends on the steric effect of the *N*-alkyl group. Insofar as hybridization of the nitrogen atom changes due to electronic effect of substituents in the ring and steric effect of the *N*-alkyl groups in different ways [23], it becomes even more difficult to draw a general correlation for such compounds.

Hybridization of the nitrogen atom in aza heterocycles (such as pyridine and imidazole derivatives) does not change upon introduction of various substit-

uents. Therefore, the rate constants of their reactions are determined only by electronic effects of substituents in the heteroring, and correlation like $\log k = f(pK_{BH^+})$ should be fulfilled, which is the case [22, 24].

Thus, the rate constants of nucleophilic reactions of alkylamines, as well as the character of their variation in the series ammonia–alkylamines–dialkylamines–trialkylamines, are determined mainly by steric effect of the alkyl groups. On the one hand, alkyl groups on the nitrogen atom shield the reaction center and hamper approach of the reactants to each other. On the other hand, replacement of hydrogen in ammonia molecule by alkyl groups changes bond angles at the nitrogen atom, favoring its $sp^3 \rightarrow sp^2$ rehybridization and increase in the p character of the nitrogen LEP which is responsible for nucleophilic reactivity of amines.

EXPERIMENTAL

Steric effects of alkyl groups were characterized by steric constants F^H taken from [2]. This choice was based on the following. In keeping with the experimental data [9], steric effect of alkyl radicals, favoring $sp^3 \rightarrow sp^2$ rehybridization of the nitrogen atom and increased p order of the nitrogen LEP, appreciably increases in going from methyl to ethyl group and almost does not change upon further extension of the carbon chain. The same order is typical of variation of the rate constants for reactions of primary aliphatic amines. For example, the reactions of methylamine and ethylamine with allyl bromide are characterized by rate constants k of 8302×10^{-6} and $3807 \times 10^{-6} \text{ l mol}^{-1} \times \text{min}^{-1}$, respectively [11, 12], whereas the corresponding values for propylamine and methylamine are 3783×10^{-6} and $3790 \times 10^{-6} \text{ l mol}^{-1} \text{ min}^{-1}$, respectively. Comparison of different steric constants of alkyl groups, given in [2], showed the same order of variation of F^H values, i.e., considerable increase in going from methyl group ($F^H = 0.26$) to ethyl ($F^H = 1.08$) and insignificant change in going from ethyl to propyl ($F^H = 1.05$), butyl ($F^H = 1.16$), and pentyl groups ($F^H = 1.16$).

The series ammonia, methylamine, dimethylamine, trimethylamine was selected taking into account available published data on the rate constants of their reactions with various electrophiles and experimentally measured bond angles at the nitrogen atom, which were used to calculate [7] p orders of the nitrogen LEP. The rate constants for nucleophilic reactions of alkylamines were taken from [11–22].

The correlations given in Table 2 were derived using the minimum possible number of points for two-

parameter equations (ammonia, mono-, di-, and trialkylamine). The reason is that the character of variation of the bond angles at the nitrogen atom (and hence of the p order of its LEP) strongly depends on the nature of the alkyl group. Nevertheless, fairly good quality of the obtained correlations, as well as the fact that their physical sense does not contradict previously formulated concepts on the role of LEP in the reactivity of amines, makes it possible to believe that these correlations are valid.

REFERENCES

- Hall, H., *J. Org. Chem.*, 1964, vol. 29, p. 3539; Hansson, J., *Svensk Kem. Tidskr.*, 1954, vol. 66, p. 351; Litvinenko, L.M. and Popov, A.F., *Zh. Obshch. Khim.*, 1968, vol. 38, p. 1969.
- Pal'm, V.A., *Osnovy kolichestvennoi teorii organicheskikh reaktsii* (Principles of the Quantitative Theory of Organic Reactions), Leningrad: Khimiya, 1977, p. 319.
- Swain, C. and Scott, C., *J. Am. Chem. Soc.*, 1953, vol. 75, p. 141; Edwards, J.O., *J. Am. Chem. Soc.*, 1954, vol. 76, p. 1540; Hansson, J., *Acta Chem. Scand.*, 1954, vol. 8, p. 36; Edwards, J.O., *J. Am. Chem. Soc.*, 1956, vol. 78, p. 1819; Suhr, H. and Grube, H., *Chem. Ber.*, 1966, vol. 70, p. 544; Bogatkov, S.B., Popov, A.F., and Litvinenko, L.M., *Reakts. Sposobn. Org. Soedin.*, 1975, vol. 11, p. 985.
- Ritchie, C.D., *J. Phys. Chem.*, 1961, vol. 65, p. 2091; Charton, M., *J. Am. Chem. Soc.*, 1977, vol. 99, p. 5686; De Tar, F., *J. Org. Chem.*, 1980, vol. 45, p. 5174.
- Akshentsev, V.V., Dragalov, V.V., and Chimishkyan, A.L., *Zh. Org. Khim.*, 1987, vol. 23, p. 305.
- Galkin, V.I., Sayakhov, R.D., and Cherkasov, R.A., *Zh. Org. Khim.*, 1994, vol. 30, p. 3.
- Korzhenetskaya, N.G., Mestechkin, M.M., and Matveev, A.A., *Zh. Obshch. Khim.*, 1992, vol. 62, p. 626.
- Korzhenetskaya, N.G., Mestechkin, M.M., and Lyashchuk, S.N., *Russ. J. Org. Chem.*, 1996, vol. 32, p. 474; Korzhenevskaya, N.G., Rybachenko, V.I., and Kovalenko, V.V., *Izv. Ross. Akad. Nauk, Ser. Khim.*, 2003, no. 4, p. 848.
- Korzhenetskaya, N.G., Titov, E.V., Chotii, K.Yu., and Chekhuta, V.G., *Zh. Org. Khim.*, 1987, vol. 23, p. 1228; Korzhenevskaya, N.G., *Reakts. Sposobn. Org. Soedin.*, 1988, vol. 25, p. 159; Korzhenevskaya, N.G., Mestechkin, M.M., Chotii, K.Yu., Abdusalamov, A.V., Ulanenko, K.B., and Rybachenko, V.I., *Zh. Obshch. Khim.*, 1992, vol. 62, p. 1148.
- Korzhenev'ska, N.G., *Dokl. Akad. Nauk Ukrainy*, 1993, vol. 9, p. 123.
- Menshutkin, N., *Zh. Russ. Khim. Ob-va.*, 1897, vol. 29, p. 444.

12. Menshutkin, N., *Zh. Russ. Khim. Ob-va.*, 1898, vol. 30, p. 232.
13. Okamoto, K., Fukui, S., Nitta, J., and Shingu, H., *Bull. Chem. Soc. Jpn.*, 1967, vol. 40, p. 1920.
14. Šestáková, J., Horák, V., and Zuman, P., *Collect. Czech. Chem. Commun.*, 1966, vol. 39, p. 3889.
15. Klopman, G. and Evans, R.C., *Tetrahedron*, 1978, vol. 34, p. 269.
16. Daukshas, V.K. and Paplaitis, V.L., *Zh. Vses. Khim. Ob-va.*, 1972, vol. 17, p. 357.
17. Denis, G.I., Kunškaite, L.Yu., Vaitkevichyus, A.K., and Klimavichyus, A.V., *Reakts. Sposobn. Org. Soedin.*, 1975, vol. 12, p. 275.
18. Litvinenko, L.M., Popov, A.F., and Gel'bina, Zh.P., *Dokl. Akad. Nauk SSSR*, 1972, vol. 203, p. 343; *Zh. Obshch. Khim.*, 1970, vol. 40, p. 356.
19. Menshutkin, N., *Zh. Russ. Khim. Ob-va.*, 1895, vol. 27, p. 137.
20. Pearson, R.G. and Williams, F.V., *J. Am. Chem. Soc.*, 1954, vol. 76, p. 258.
21. Litvinenko, L.M., Popov, A.F., Gel'bina, Zh.P., and Kirillov, E.V., *Reakts. Sposobn. Org. Soedin.*, 1973, vol. 10, p. 175.
22. Solomoichenko, T.N., Sadovskii, Yu.S., Savelova, V.A., Piskunova, Zh.P., and Popov, A.F., *Russ. J. Org. Chem.*, 1997, vol. 33, p. 1434.
23. Korzhenevskaya, N.G. and Kal'nitskii, N.R., *Zh. Obshch. Khim.*, 1987, vol. 57, p. 1810; Korzhenevskaya, N.G. and Titov, E.V., *Ukr. Khim. Zh.*, 1988, vol. 54, p. 184.
24. Callo, R., Roussel, Ch., and Berg, U., *Adv. Heterocycl. Chem.*, 1988, vol. 43, p. 173.