Positional selectivity in reactions of pyrrole and its N-substituted derivatives with electrophiles

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Dedicated to Professor Boris A. Trofimov on his 65th birthday
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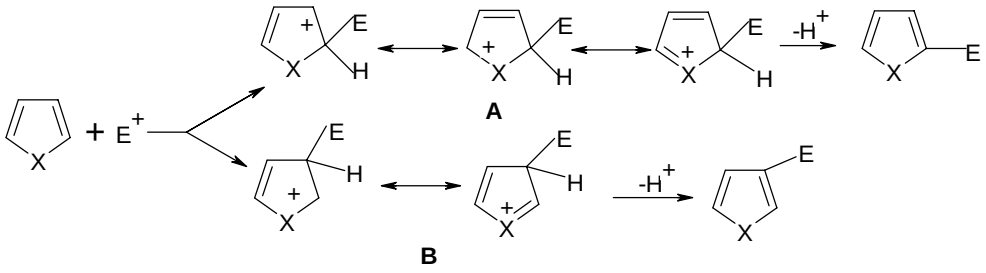
Abstract
Experimental data on the positional selectivity (α:β-ratios) in reactions of N-substituted pyrroles with electrophiles have been considered. Based on the results of quantum chemical calculations of model N-R-pyrroles (R=H, Me, Et, *i*-Pr, *t*-Bu, CH=CH_2, C≡CH, Ph, $PhSO_2$, 4-$O_2NC_6H_4$) and their α- or β-protonated σ-complexes, carried out using *ab initio* methods (RHF/6-31G(d), MP2/6-31G(d)//RHF/6-31G(d)), and within the framework of density functional theory (B3LYP/6-31G(d)), it has been shown that the predominant α- or β-orientation is determined by steric factors and charges on the atoms β-C, α-C, N, and on the substituents at the N atom. We conclude that it is not determined by differences in the relative stabilities of the onium state N^+ depending on the nature of a substituent at the N atom, or reflecting the role of the heteroatom in the stabilization of σ-complexes formed by β-substitution.

Keywords: Pyrroles, electrophilic substitution, substrate selectivity, positional selectivity, cationic σ-complexes, quantum chemical calculations, *ab initio* RHF/6-31G(d) and MP2/6-31G(d) methods, DFT B3LYP/6-31G(d) method

Introduction

It is well known that the effect of the heteroatom in 5-membered heterocyclic rings is displayed in an increased reactivity of the α-position, which is usually interpreted as the result of the higher stability of the corresponding σ-complex (**A**) having better conditions for delocalization of the charge compared with its isomer (**B**) formed on attack at the β-position (Scheme 1).



Scheme 1

The reactivity and positional selectivity of electrophilic substitution reactions of pyrrole, furan, and thiophene was studied quantitatively 30 years ago.[1,2] It should be noted that the difference in reactivity, which falls by approximately 10 orders of magnitude in the series pyrrole >> furan > thiophene, does not correlate with the sequence of positional selectivity (the ratio of products of α- and β-substitution), which is furan > thiophene > pyrrole.[1,2]

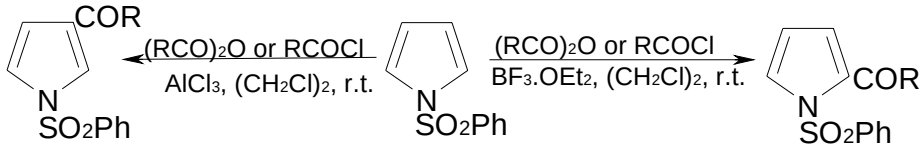
About 20 years ago one of us put forward a hypothesis explaining the reason for the non-correspondence of the series of substrate and positional selectivities of electrophilic substitution reactions of five-membered heterocycles with one heteroatom.[3,4] The gist of it was that the formation of β-substituted compounds proceeding through a σ-complex of type **B,** in which only the heteroatom and one of the α-carbon atoms participate in charge delocalization, must depend more on the ability of element X to exist in the onium state, than for the formation of α-substituted compounds. In the latter case, all the ring atoms except the geminal C atom participate in charge delocalization of cation **A**. In reality, a reduction in the stability of onium states in the series $N^+ > S^+ > O^+$ correlates well with experimental data on the ability of pyrrole, thiophene, and furan to form β-substituted products.

Recently we succeeded in confirming this interpretation by quantum chemical calculations carried out by *ab initio* RHF/6-31G(d) and MP2/6-31G(d)//RHF/6-31G(d) methods, as well as within the framework of density functional theory (B3LYP/6-31G(d)) for the first members of the series, including selenophene, as well as for benz-annelated five-membered heterocycles with one heteroatom.[5] It was shown that, in contrast to the known sequence of relative reactivity (substrate selectivity) in electrophilic substitution reactions (pyrrole >> furan > selenophene > thiophene[1,2]), which may be explained by the different conditions for delocalization of electron density on ring atoms with the participation of heteroatoms belonging to a different group and period of the Periodic System, the positional selectivity reduces in the sequence: furan>> selenophene ≥ thiophene > pyrrole, corresponding to that for the relative stability of the onium state of the elements ($O^+ < Se^+ \leq S^+ < N^+$), in agreement with the hypothesis already suggested[3,4] (but for the series that did not include selenophene and its derivatives).

Results and Discussion

The low positional selectivity of pyrrole as compared to thiophene, selenophene, and, especially, furan allows one to overcome the α-orienting effect of the heteroatom by the introduction of even relatively weak type II directors, and to direct an electrophile practically exclusively into the position 4.[5] The present communication is devoted to the orientation of electrophilic substitution reactions of N-substituted pyrroles, for which a considerable effect of a substituent at the nitrogen atom on the α:β-ratio should be expected, taking into account the foregoing. It is important to mention that, according to numerous data of quantum chemical calculations carried out by semi-empirical methods[6] (see also the references cited in the review[7] devoted to N-vinylpyrrolium ions), σ-complexes modeling the substitution at the α-position of N-unsubstituted pyrroles are thermodynamically preferable than their β-isomers, while kinetic factors (higher negative charge) favor β-substitution.

As follows from the literature data, the α:β-ratio is influenced by such factors as the character and steric requirement of a substituent at the nitrogen atom as well as the electrophile nature that, in its turn, may be dependent on the solvent used. The effect of the N-phenylsulfonyl substituent was studied in detail. This substituent was simultaneously offered by two groups of researchers[8–11] as an original protecting group that owing to its electron-withdrawing effect deactivates preferably the α-position and allows one to obtain β-substituted derivatives, the $PhSO_2$ group being readily removed on alkaline hydrolysis.[10] The effect of the $PhSO_2$ group was studied in most detail for Friedel–Crafts acylation.[8–15] The role of the nature of the reagent reveals itself most distinctly in the fact that in the presence of aluminum chloride the 3-acyl-substituted derivatives are obtained, while reaction in the presence of boron trifluoride etherate gives the 2-isomers[10] (Scheme 2).

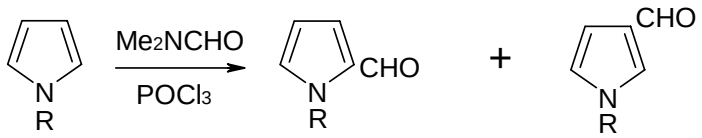


Scheme 2

It is important to note that 1-(phenylsulfonyl)pyrrole gives only 2-substituted derivatives on both Rieche formylation with alkyl dichloromethyl ethers[8,9] and Vilsmeier formylation in the $DMF–POCl_3$ system,[8] as well as on cyanation with cyanogen bromide in the presence of $AlCl_3$ or with chlorosulfonyl isocyanate.[8,11] In contrast, nitration ($HNO_3–Ac_2O$) proceeds almost exclusively in the 3-position.[10] As was established recently, the same orientation applies to the sulfonation of unsubstituted pyrrole and N-methylpyrrole with pyridine sulfotrioxide.[16] The differences in orientation given above are usually interpreted within the framework of the HSAB principle: the orientation for a "hard" electrophile is determined mainly by negative charge in position 3, while the substitution in position 2 in the case of "softer" electrophiles is the result of orbital control.[9]

The high efficiency of the N-triisopropylsilyl substituent used as another "protective" group for the preparation of β-substituted pyrroles is based, as proposed in Ref. 17, on steric shielding of α-positions. Among electrophiles directed by a 1-(*i*-Pr)$_3$Si group into position 3 are Br^+, I^+,

NO_2^+, and RCO^+ cations. It is interesting to note that Vilsmeier formylation of 1-(tri-isopropylsilyl)pyrrole is also directed into position 3. The protecting group is removed from the nitrogen atom quantitatively under the action of fluoride anion.[17] The fact that the percentage of β-aldehydes from Vilsmeier formylation of N-alkylpyrroles increases from N-methyl- to N-(*t*-butyl)pyrrole can be explained by the increasing steric shielding of the α-positions by an N-alkyl group in the same sequence[18] (Scheme 3).



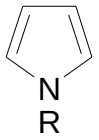
R	α:β-ratio	
Me	α- isomer only	-
Et	11.5	1
i-Pr	1.9	1
t-Bu	1	14

Scheme 3

We have proposed that such a variation of orientation can also be caused by stabilization of the onium state of the heteroatom by electron-release and destabilization of the latter by electron-withdrawing substituents.[5,19,20]

The orientation of electrophilic substitution in the pyrrole series depends also on the nature of the electrophile. Electrophilic hydrogen–deuterium exchange was investigated[21] for substituted pyrroles carrying on the N atom a deactivating group X (X = Ac, PhCO, $MeSO_2$, CF_3SO_2, $PhSO_2$, Me_3N^+, Me_2NH^+). In all cases, the rate of exchange in α-positions exceeds that in β-positions by more than one order of magnitude. Allylation of N-methylpyrrole is directed preferably to the α-position (the α:β-ratio is 4:1)[22] while silylation proceeds exclusively in the β-position.[23] These examples can undoubtedly be explained by the effect of the electrophile's nature. However, there are facts that show the substantial role of steric factors. Thus, the positional selectivity on alkylation of N-(phenylsulfonyl)pyrrole in the presence of $AlCl_3$ changes from preferential α-substitution (with EtBr), through the formation of 1:1 mixture of α- and β-substituted derivatives (with *i*-PrCl), to preferential (80%) formation of the β-substituted derivative in the case of *t*-BuCl.[11]

In the present work, we have carried out a quantum chemical investigation of model N-R-pyrroles **1a–j** and their α- and β-protonated σ-complexes **2a–j**, **3a–j**, respectively. Calculations were carried out using the *ab initio* methods RHF/6-31G(d) and MP2/6-31G(d)//RHF/6-31G(d) (using electron correlation according to second order perturbation theory, with the geometry calculated preliminarily by RHF/6-31G(d) method) as well as by the DFT B3LYP/6-31G(d) method (hybrid density functional with complete optimization of geometry). The Gaussian 94 set of programs [24] was used.



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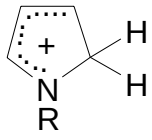

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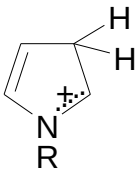

3

1–3: R = H (**a**), Me (**b**), Et (**c**), *i*-Pr (**d**), *t*-Bu (**e**), CH=CH_2 (**f**), C≡CH (**g**), Ph (**h**), $PhSO_2$ (**i**), 4-$O_2NC_6H_4$ (**j**)

The values of the differences in the energies of α-protonated (**2a–j**) and β-protonated (**3a–j**) cations ($\Delta E_{\alpha-\beta}$) that can characterize the positional selectivity of electrophilic substitution are presented in Table 1. The $\Delta E_{\alpha-\beta}$ values obtained by all three methods do not indicate on preferential β-substitution in any of the molecules **1a–j** studied. At the same time, a comparison of $\Delta E_{\alpha-\beta}$ values shows that the presence of an alkyl substituent at the N atom of the cycle in molecules **1b–e** makes β-substitution relatively more probable than in the case of pyrrole (**1a**), while other substituents should promote the formation of α-substituted derivatives to approximately the same or greater extent as in the case of pyrrole.

Thus, the calculated values of total energies of the cationic σ-complexes obtained by α- and β-protonation of model molecules of N-phenylsulfonylpyrrole (**1i**) and N-(4-nitrophenyl)pyrrole (**1j**) are consistent with experimental data concerning preferable reactivity of their α-positions, while the role of steric factors and charges on atoms should be considered for interpretation of the increase in percentage of β-substituted derivatives on formylation of N-alkylpyrroles in the sequence: Me < Et < *i*-Pr < *t*-Bu. **See Table 1 on page 232.**

Table 2. Lengths of the bonds C–C and C–N, Ă (RHF/6-31G) in cycles of pyrrole, N-substituted pyrroles, and of 2*H*- and 3*H*-pyrrolium ions formed by them

Molecule (cation)	$N_{(1)}$-$C_{(2)}$	$N_{(1)}$-$C_{(5)}$	$C_{(2)}$-$C_{(3)}$	$C_{(3)}$-$C_{(4)}$	$C_{(4)}$-$C_{(5)}$
Pyrrole (**1a**)	1.36	1.36	1.36	1.43	1.36
2*H*-Pyrrolium (**2a**)	1.46	1.29	1.49	1.34	1.44
3*H*-Pyrrolium (**3a**)	1.27	1.44	1.49	1.50	1.32
1-Methylpyrrole (**1b**)	1.36	1.36	1.36	1.42	1.36
1-Methyl-2*H*-pyrrolium (**2b**)	1.46	1.28	1.49	1.33	1.44
1-Methyl-3*H*-pyrrolium (**3b**)	1.27	1.44	1.49	1.50	1.32
1-Ethylpyrrole (**1c**)	1.36	1.36	1.36	1.42	1.36
1-Ethyl-2*H*-pyrrolium (**2c**)	1.46	1.28	1.49	1.33	1.45
1-Ethyl-3*H*-pyrrolium (**3c**)	1.27	1.44	1.49	1.50	1.32
1-Isopropylpyrrole (**1d**)	1.36	1.37	1.36	1.42	1.36
1-Isopropyl-2*H*-pyrrolium (**2d**)	1.46	1.28	1.49	1.33	1.45
1-Isopropyl-3*H*-pyrrolium (**3d**)	1.27	1.44	1.49	1.50	1.32
1-(*t*-Butyl)pyrrole (**1e**)	1.37	1.37	1.36	1.42	1.36
1-(*t*-Butyl)-2*H*-pyrrolium (**2e**)	1.47	1.28	1.49	1.33	1.45
1-(*t*-Butyl)-3*H*-pyrrolium (**3e**)	1.27	1.44	1.49	1.50	1.32
1-Vinylpyrrole (**1f**)	1.37	1.37	1.35	1.43	1.35
1-Vinyl-2*H*-pyrrolium (**2f**)	1.46	1.29	1.49	1.33	1.44
1-Vinyl-3*H*-pyrrolium (**3f**)	1.28	1.44	1.49	1.50	1.32
1-Ethinylpyrrole (**1g**)	1.38	1.38	1.35	1.43	1.35
1-Ethinyl-2*H*-pyrrolium (**2g**)	1.47	1.30	1.49	1.34	1.44
1-Ethinyl-3*H*-pyrrolium (**3g**)	1.28	1.45	1.48	1.50	1.32
1-Phenylpyrrole (**1h**)	1.37	1.37	1.36	1.43	1.36
1-Phenyl-2*H*-pyrrolium (**2h**)	1.46	1.28	1.49	1.33	1.45
1-Phenyl-3*H*-pyrrolium (**3h**)	1.28	1.44	1.49	1.50	1.32
1-(Phenylsulfonyl)pyrrole (**1i**)	1.39	1.39	1.35	1.44	1.35
1-(Phenylsulfonyl)-2*H*-pyrrolium (**2i**)	1.47	1.29	1.49	1.34	1.44
1-(Phenylsulfonyl)-3*H*-pyrrolium (**3i**)	1.28	1.44	1.49	1.50	1.32
1-(4-Nitrophenyl)pyrrole (**1j**)	1.38	1.38	1.35	1.43	1.35
1-(4-Nitrophenyl)-2*H*-pyrrolium (**2j**)	1.47	1.29	1.49	1.34	1.44
1-(4-Nitrophenyl)-3*H*-pyrrolium (**3j**)	1.28	1.44	1.49	1.50	1.32

Table 3. Bond angles, deg. (RHF/6-31G) in cycles of pyrrole, *N*-substituted pyrroles, and of 2*H*- and 3*H*-pyrrolium ions formed by them

Molecule (cation)	$C_{(2)}N_{(1)}C_{(5)}$	$N_{(1)}C_{(2)}C_{(3)}$	$C_{(2)}C_{(3)}C_{(4)}$	$C_{(3)}C_{(4)}C_{(5)}$	$C_{(4)}C_{(5)}N_{(1)}$
Pyrrole (**1a**)	109.5	108.2	107.1	107.1	108.2
2*H*-Pyrrolium (**2a**)	111.1	101.2	110.3	106.5	110.8
3*H*-Pyrrolium (**3a**)	111.8	109.3	101.7	109.1	108.0
1-Methylpyrrole (**1b**)	108.5	108.8	106.9	106.9	108.8
1-Methyl-2*H*-pyrrolium (**2b**)	109.9	102.2	109.7	106.6	111.6
1-Methyl-3*H*-pyrrolium (**3b**)	110.4	110.4	101.4	108.8	109.0
1-Ethylpyrrole (**1c**)	108.5	108.9	106.9	106.9	108.9
1-Ethyl-2*H*-pyrrolium (**2c**)	109.7	102.3	109.7	106.5	111.8
1-Ethyl-3*H*-pyrrolium (**3c**)	110.3	110.5	101.4	108.7	109.1
1-Isopropylpyrrole (**1d**)	108.3	109.1	106.8	107.0	108.9
1-Isopropyl-2*H*-pyrrolium (**2d**)	109.7	102.5	109.6	106.5	111.7
1-Isopropyl-3*H*-pyrrolium (**3d**)	110.0	110.8	101.2	108.8	109.2
1-(*t*-Butyl)pyrrole (**1e**)	107.7	109.4	106.8	106.9	109.2
1-(*t*-Butyl)-2*H*-pyrrolium (**2e**)	109.0	102.8	109.6	106.5	112.2
1-(*t*-Butyl)-3*H*-pyrrolium (**3e**)	109.4	111.1	101.3	108.6	109.6
1-Vinylpyrrole (**1f**)	108.2	109.0	106.9	107.3	108.7
1-Vinyl-2*H*-pyrrolium (**2f**)	110.0	102.1	109.8	106.7	111.5
1-Vinyl-3*H*-pyrrolium (**3f**)	110.0	110.7	101.3	109.1	109.0
1-Ethinylpyrrole (**1g**)	108.7	108.2	107.5	107.4	108.2
1-Ethinyl-2H-pyrrolium (**2g**)	110.4	101.4	110.3	106.9	111.0
1-Ethinyl-3H-pyrrolium (**3g**)	110.9	109.7	101.9	109.3	108.2
1-Phenylpyrrole (**1h**)	108.3	108.8	107.1	107.1	108.8
1-Phenyl-2H-pyrrolium (**2h**)	109.9	102.1	109.8	106.6	111.5
1-Phenyl-3H-pyrrolium (**3h**)	110.3	110.4	1015	108.8	109.0
1-(Phenylsulfonyl)pyrrole (**1i**)	108.8	107.9	107.7	107.7	107.9
1-(Phenylsulfonyl)-2H-pyrrolium (**2i**)	110.5	101.5	110.3	106.7	111.1
1-(Phenylsulfonyl)-3H-pyrrolium (**3i**)	110.9	109.8	101.7	109.1	108.5
1-(4-Nitrophenyl)pyrrole (**1j**)	108.1	108.7	107.2	107.2	108.7
1-(4-Nitrophenyl)-2H-pyrrolium (**2j**)	109.9	111.5	106.6	109.9	102.0
1-(4-Nitrophenyl)-3H-pyrrolium (**3j**)	110.4	108.8	108.9	101.6	110.3

See Table 4 on page 233.

The main geometric characteristics of the systems studied, as calculated by the RHF/6-31G(d) method, are given in Tables 2 and 3. On going from the neutral molecule to the cation in the case of 2*H*-pyrrolium ions, the bonds $N_{(1)}–C_{(2)}$, $C_{(2)}–C_{(3)}$, $C_{(4)}–C_{(5)}$ are lengthened; on the other hand, the bonds $N_{(1)}–C_{(5)}$, $C_{(3)}–C_{(4)}$ are shortened. In the case of the 3*H*-pyrrolium ions, the

bonds $N_{(1)}$–$C_{(2)}$ and $C_{(4)}$–$C_{(5)}$ are shortened but the bonds $N_{(1)}$–$C_{(5)}$, $C_{(2)}$–$C_{(3)}$, and $C_{(3)}$–$C_{(4)}$ are lengthened. This clearly reflects the changes in their multiplicity on going from a neutral molecule to a σ-complex. The geometries of the neutral molecules of N-isopropylpyrrole (**1d**) and N-(*t*-butyl)pyrrole (**1e**) are evidence of steric strain. The bonds $N_{(1)}$–$C_{(2)}$ and $N_{(1)}$–$C_{(5)}$ in **1d** differ markedly from one another in length, while in **1e** the distances between the centers of the hydrogen atom in position 2 and the nearest H atoms of two methyl groups (2.39 Å) are lower or equal to the sum of Van der Waals radii. Also, the distance from the center of H atom in the 5 position to the center of the nearest H atom of the methyl group (2.33 Å) is lower than the sum of Van der Waals atoms that is equal to 2.4 Å.[25] Twisting of the molecules **1d,e** is evident also from bond angles that are not equal for angles $N_{(1)}C_{(2)}C_{(3)}$ and $C_{(4)}C_{(5)}N_{(1)}$ (the differences are 0.2 deg.) and $C_{(2)}C_{(3)}C_{(4)}$ and $C_{(3)}C_{(4)}C_{(5)}$ (the differences are 0.2 and 0.1 deg., respectively).

The charges on the atoms, calculated according to Mulliken and natural orbital analysis methods using the set given in ref. 24 are presented in Table 4. Unsymmetrical distribution of charges on the atoms in molecules **1d** and **1e** can be also regarded as a result of perturbation of their geometrical symmetry. A similar distribution in the case of N-vinylpyrrole (**1f**) is caused by the arrangement of the vinyl group that is nearly coplanar with the ring, which provides for conjugation of both fragments. As a whole, the data of Table 4 show that the C atoms in the β-positions carry marked negative charges while the charges on the C atoms in the α-positions are nearly zero. The charge values can be used to explain the β-substitution products, but these values have no predictive ability.

Conclusions

It is evident that there is a need in further quantum chemical investigation of electrophilic substitution in the pyrrole series. It should be mentioned that a previous study[26] performed by the semi-empirical CNDO/2 method revealed a dependence of orientation of electrophilic substitution in the series of five-membered heterocycles upon the electrophile's characteristics such as electronegativity, ionic and covalent radii, a probability of preferential β-substitution being predicted for reactions of pyrrole with electrophiles having characteristics near to that of silicon atom. It is possible that modern quantum chemical calculations for real but not model electrophiles, and accounting for the solvent effects, will allow a prediction of orientation of electrophilic substitution in N-substituted pyrrole derivatives.

References

1. Marino, G. *Adv. Heterocycl. Chem*. **1971**, *13*, 235.
2. Marino, G. *Chem. Heterocycl. Comp.* **1973,** *9*, 537.
3. Belen'kii, L.I. *III International Symposium on Furan Chemistry, Collection of Papers,* p 4, Smolenice, Czechoslovakia, 1979.

4. Belen'kii, L.I. *Chem. Heterocycl. Comp.* **1980**, *16*, 1195.
5. Belen'kii, L.I.; Suslov, I. A.; Chuvylkin, N. D. *Khim. Geterotsikl. Soed.* **2003**, *38* [*Chem. Heterocycl. Comp.* **2003**, *39*, No. 1, in press].
6. Abronin, I.A.; Belen'kii, L. I.; Gol'dfarb, Ya. L. *New Trends in Heterocyclic Chemistry,* Mitra, R.B.; Ayyangar, N.R.; Gogte, V.N.; Acheson, R.M.; Cromwell, N., Eds. Elsevier: Amsterdam, 1979, p 154.
7. Sigalov, M.V.; Trofimov, B. A. *Zh. Org. Khim.* **1995,** *31*, 801.
8. Xu, R.X.; Anderson, H.J.; Gogan, N.J.; Loader, C.A.; McDonald, R. *Tetrahedron Lett*. **1981**, *22*, 4899.
9. Rokach, J.; Hamel, P.; Kakushima, M.; Smith, G. M. *Tetrahedron Lett*. **1981**, *22*, 4901.
10. Kakushima, M.; Hamel, P.; Frenette, R.; Rokach, J. *J. Org. Chem.***1983***, 48*, 3214.
11. Anderson, H. J.; Loader, C.A.; Xu, R.X.; Le, N.; Gogan, N.J.; McDonald, R.; Edwards, L.G. *Can. J. Chem.* **1985**, *63*, 896.
12. De Micheli, C.; De Amici, M.; Locati, S. *Farmaco, Ed. Sci.* **1984**, *39*, 277.
13. Ezaki, N.; Sakai, Sh. *Yakugaku Zasshi* **1984**, *104*, 238; *Chem. Abstr*. **1984**, *101*, 130471.
14. Lainton, J.A.H.; Huffman, J.W.; Martin, B.R.; Compton, D.R. *Tetrahedron Lett*. **1995**, *36*, 1401.
15. Nicolaou, J.; Demopoulos, V. J. *J. Heterocycl. Chem*. **1998**, *35*, 1345.
16. Mizuno, A.; Kan, Y.; Fukami, H.; Kamei, T.; Miyazaki, K.; Matsuki, S.; Oyama, Y. *Tetrahedron Lett*. **2000,** *41*, 6605.
17. Bray, B.L.; Mathies, P.H.; Naef, R.; Solas, D.R.; Tidwell, Th.T.; Artis, D.R.; Muchowski, J. M. *J. Org. Chem.* **1990**, *55*, 6317.
18. Candy, C. F.; Jones, R.A; Wright, P.H. *J. Chem. Soc. (C)* **1970**, 2563.
19. Belen'kii, L.I. *Heterocycles* **1994**, *37*, 2029.
20. Belen'kii, L.I. *16th Intern. Congr. Heterocycl. Chem. Abstracts,* OP-V-20. August 10–15, 1997, Montana State University – Bozeman, USA.
21. Gilow, H.M.; Hong, Y.H.; Millins, P. L.; Snyder, R.C.; Casteel, Jr., W.J. *J. Heterocycl. Chem*. **1986**, *23*, 1475.
22. Renard, M.; Hevesi, L. *Chem. Commun*. **1986**, 688.
23. Majchrzak, M.W.; Simchen, G. *Tetrahedron* **1986**, *42*, 1299.
24. Frisch, M.J.; Trucks, G.W.; Schlegel, H.B.; Gill, P.M.W.; Johnson, B.; Robb, M.A.;. Cheeseman J.R; Keith, T.; Petersson, G.A.; Montgomery, J.A.; Raghavachari, K.; Al-Laham, M.A.; Zakrzewski, V.G.; Ortiz, J.V.; Foresman, J.B.; Cioslowski, J.; Stefanov, B.B.; Nanayakkara, A.; Challacombe, M.; Peng, C.Y.; Ayala, P.Y.; Chen, W.; Wong, M.W.J.; Andres, L.; Replogle, E.S.; Gomperts, R.; Martin, R.L.; Fox, D.J; Binkley, J.C.; Defrees, D.J.; Baker, J.; Stewart, J.P.; Head-Gordon, M.; Gonzalez, C.; Pople, J.A. *Gaussian 94, Revision E.1*, Gaussian, Inc., Pittsburgh PA, 1995.
25. Vol'kenshtein, M.V. *Stroenie I Fizicheskie Svoistva Molekul*, USSR Acad. Sci. Press: Moscow, 1955, p 129 *[Structure and Physical Properties of Molecules (in Russian)]*.
26. Abronin, I.A.; Belen'kii, L.I.; Zhidomirov, G.M.; Gol'dfarb, Ya.L. *Zh. Org. Khim.* **1981**, *17*, 1134.