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VICARIOUS NUCLEOPHILIC SUBSTITUTION OF HYDROGEN IN NITRO-SUBSTITUTED PYRROLES, AZOLES, AND BENZANNELATED SYSTEMS BASED ON THEM*. (REVIEW)

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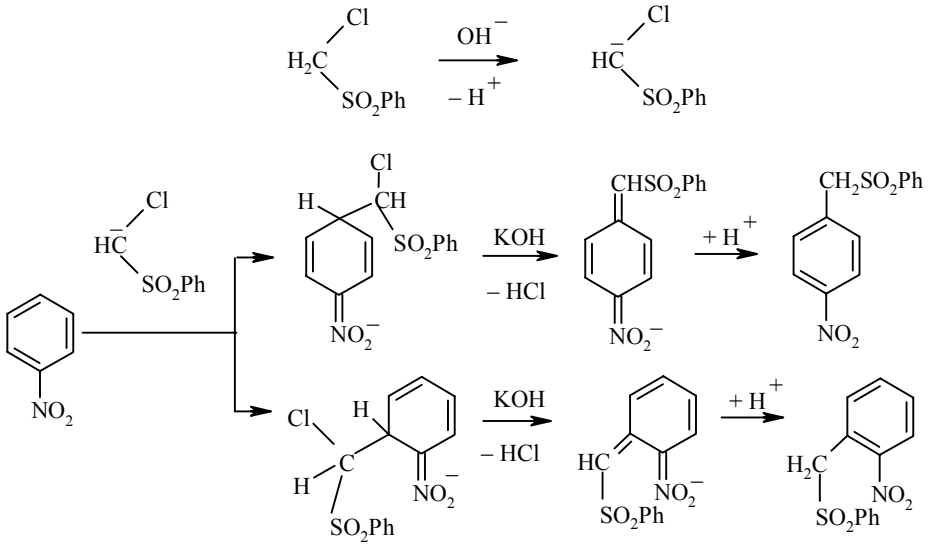
Published data on the participation of nitro-substituted pyrroles, azoles, and their benzannelated derivatives in vicarious nucleophilic substitution are reviewed.

Keywords: azoles, benzazoles, indoles, nitro-substituted pyrrole, vicarious nucleophilic substitution.

Nucleophilic substitution reactions in the aromatic series are among the fundamental processes of theoretical organic chemistry that continue to attract the serious attention of researchers. At the end of the seventies, largely on account of the work of Makosza and his co-workers [1], the concept of vicarious nucleophilic substitution was added to the arsenal of synthetic organic chemistry. A typical example of such a process is the reaction of nitrobenzene with chloromethyl phenyl sulfone, resulting in the formation of a mixture of *ortho*- and *para*-nitrobenzyl phenyl sulfones.



* Dedicated to the 80th birthday of Academician M. G. Voronkov.

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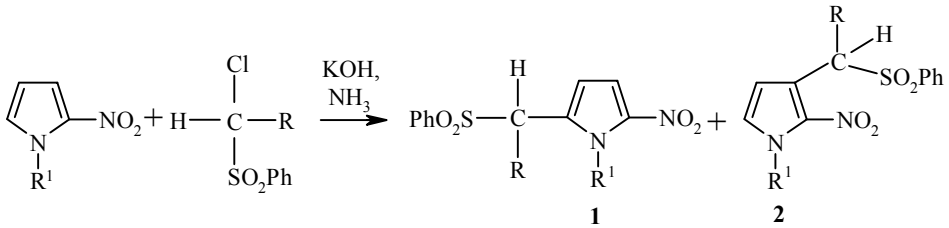
In reactions of this type a carbanion residue adds at the *ortho* or *para* position to the nitro group, and this is accompanied by the elimination of a halide and not a hydride anion from the intermediate σ^n-adduct. Thus, the halogen fulfills the role of leaving group instead of the hydrogen of the ring, which is not capable of being eliminated in the form of an anion. On the suggestion of Makosza this process was called "vicarious nucleophilic substitution of hydrogen" (VNS) [2, 3]. Interest in these reactions increased substantially after the synthesis of difficultly obtainable compounds such as 1,3,5-triamino-2,4,6-trinitrobenzene, 1,3-diamino-2,4,6-trinitrobenzene [4], 2,4-dinitro-1,3-phenylenediamine [5], and 4-amino-3,5-dinitropyrazole [6, 7] was realized by VNS. Vicarious nucleophilic substitution in six-membered aromatic and heteroaromatic systems has been reported in a fair amount of detail [2, 3, 8-12].

The only review specially devoted to VNS in heterocyclic compounds, among which there were few five-membered heterocycles, was published in 1991 [13]. In the mean time intensive investigations in this field have continued. For example, in the recently published review on the synthesis of indole and quinoline derivatives the great value of VNS in the construction of such systems was noted [14]. We therefore considered it expedient to examine data published over the last 10 years on VNS in nitro-substituted pyrroles, azoles, and their benzannelated derivatives.

Pyrroles

Several examples of VNS in N-substituted 2-nitropyrroles have been described in the literature [15-17], and these are summarized in Table 1.

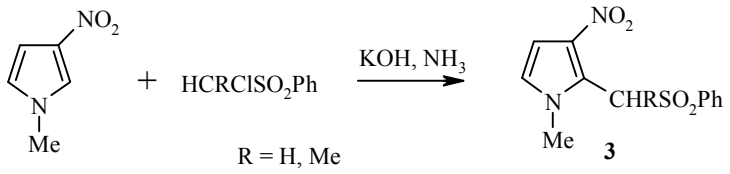


As seen from the data in Table 1, the nature of the substituent at the nitrogen atom has a determining effect on the position of the leaving group. Electron-donating alkyl substituents direct the reaction exclusively to position 5. The SO_2 group – a strong acceptor of electrons – directs the reaction to position 3, and in the case of 1-methoxymethyl-2-nitropyrrole a mixture of products with a preponderance of the 5-substituted isomer **1** is formed.

TABLE 1. The Structure and Yields of the Products from VNS (**1** and **2**) of Nitropyrroles with Chloromethyl Sulfones

R^1	R	Position of $CHRSO_2Ph$	Yield, %	
			1	**2**
Me	H	5	90	—
Me	Me	5	82	—
n-Pr	H	5	93	—
i-Pr	H	5	68	—
p-Ts	H	3	—	83
CH_2OMe	H	3, 5	74	14

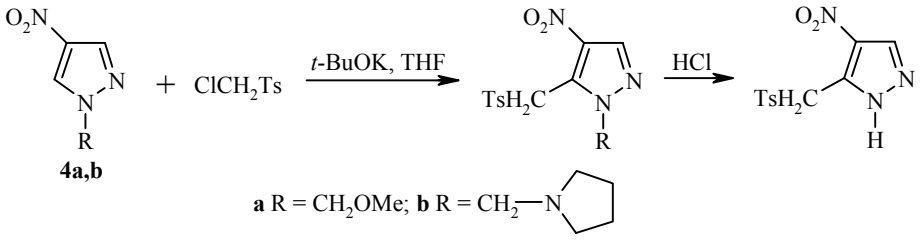
It is not yet possible to draw specific conclusions about the effect of the nature of the substituent at the nitrogen atom on the occurrence of VNS in 3-nitropyrroles. Only one paper is known on VNS involving 1-methyl-3-nitropyrrole and chlorophenyl sulfone (potassium hydroxide, ammonia), where 2-substituted 1-methyl-3-nitropyrrole **3** was isolated as the only product [17]. In an earlier communication [15] the authors erroneously determined the structure of the final product as 5-substituted 1-methyl-3-nitropyrrole, but as a result of further investigations they arrived at structure **3** [13].



Pyrazoles

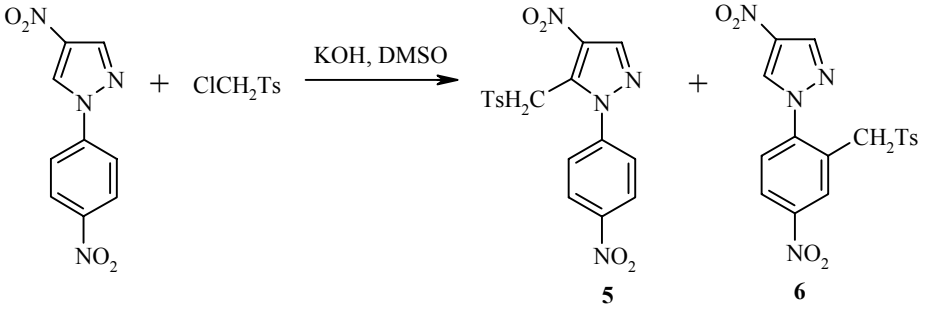
1-H-Nitropyrazoles and nitropyrazoles not substituted at the "pyrrole" nitrogen atom, like other nitroazoles, have clearly defined acidic characteristics. Therefore, during VNS (in systems like potassium hydroxide in DMSO, DMF, or THF) deprotonation of the substrate should be observed, and this in turn hinders the reaction of the nucleophile with the anions that form. This introduces certain restrictions into the VNS process.

It was possible to expand the region of application of VNS considerably by introducing protecting groups at the "pyrrole" atom of the substrate. Pyrrolidinomethyl and methoxymethyl groups were used successfully as protecting groups [18]. Thus, 4-nitropyrazole was alkylated by chloromethyl methyl ether, and the product **4** was brought into VNS, after which the protecting group was removed [18].

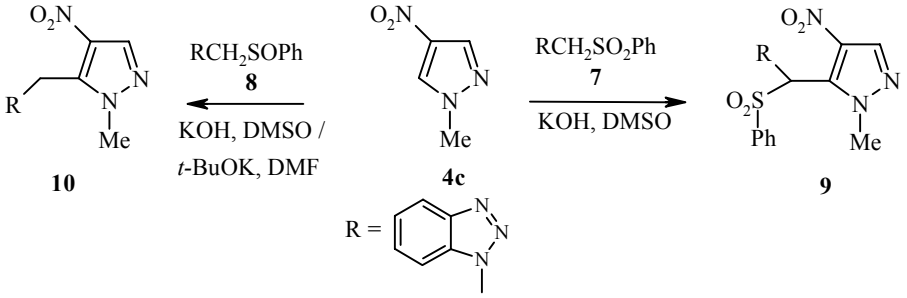


Surprising in this connection are reports on the successful use of VNS with 2,4-dinitro-, 2,5-dinitro-, and 2,4,5-trinitropyrroles and 3,5-dinitropyrazole not substituted at the nitrogen atom as substrates [4-7, 19]. The strong electron-withdrawing character of several nitro groups probably has an effect in these cases.

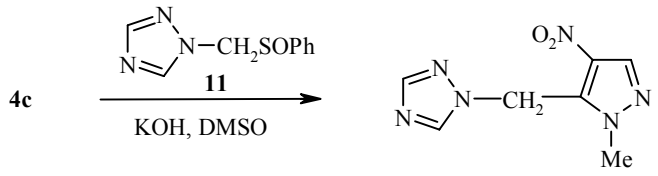
With *para*-tolyl chloromethyl sulfone 1-substituted 4-nitropyrazoles form the products from VNS at position 5 of the heterocycle. In the presence of a second nitro group (e.g., in 1-methyl-3,4-dinitropyrazole) the yield of the reaction product is significantly reduced. If position 5 is occupied (as, for example, in 1-methyl-5-nitro- or 1,5-dimethyl-4-nitropyrazoles) the reaction does not occur [20]. In 1-methyl-3,5-dinitropyrazole the same substituent occupies the only free position 4 of the pyrazole ring [20]. In 4-nitropyrazoles containing an *ortho*-nitrophenyl substituent at position 1 VNS only takes place at position 5 of the azole ring, and in the case of the *para*-nitrophenyl substituent it takes place in both the azole and the aryl fragments with the formation of the products **5** and **6** [20].



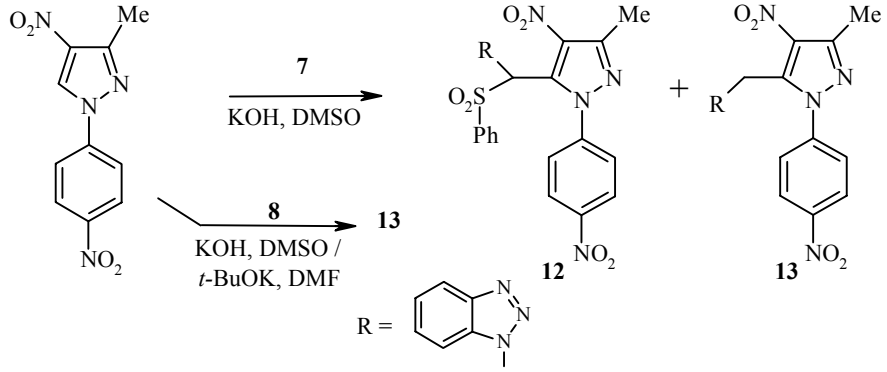
Recently a report appeared on the use of 1-(phenylsulfonylmethyl)- and 1-(phenylsulfinylmethyl)-benzotriazoles (**7**) and (**8**) as reagents in nucleophilic substitution with 1-methyl-4-nitropyrazole [21]. With the first reagent and potassium hydroxide in DMSO a small amount (3%) of the product from oxidative nucleophilic substitution (ONS) **9** is formed.



In the second case under the same conditions VNS occurs, and the yield of the product **10** amounts to 68%, but with potassium *tert*-butoxide in DMF it amounts to only 20%. 1-Methyl-4-nitropyrazole reacts similarly with 1-(phenylsulfinylmethyl)-1,3,4-triazole (**11**).



3-Methyl-4-nitro-1-(4-nitrophenyl)pyrazole in reaction with reagents **7** and **8** can undergo both VNS and ONS, and both the heterocycle and the benzene ring can participate in these processes. However, it was shown [21] that substitution takes place exclusively at position 5 of the pyrazole ring.



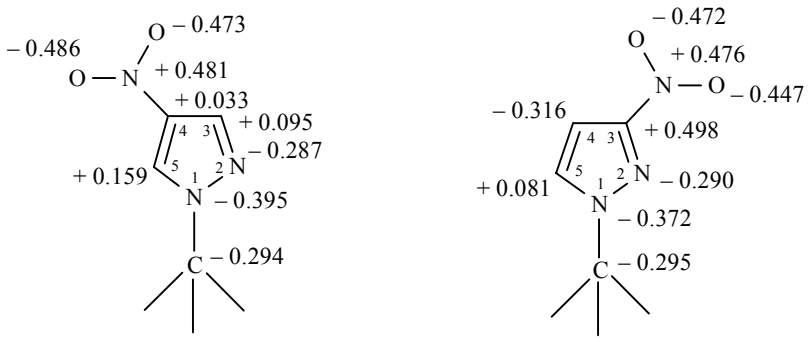


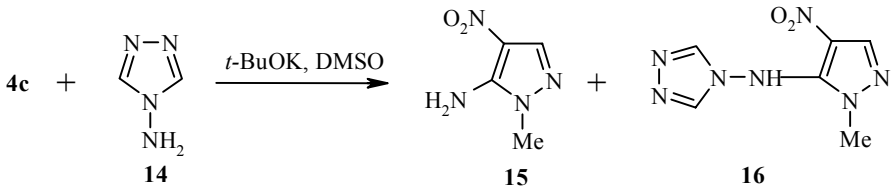
Fig. 1. The charges at the atoms in the molecules of 1-methyl-4-nitropyrazole and 1-methyl-3-nitropyrazole according to *ab initio* RHF 6-31G* calculations.

In the case of the sulfone **7** (potassium hydroxide, dimethyl sulfoxide) the product from ONS **12** is formed (41-45%), and traces of the product from VNS are formed. The reaction with the sulfoxide **8** takes place exclusively with VNS, and compound **13** is obtained with yields of 82% (potassium hydroxide, DMSO) and 32% (potassium *tert*-butoxide, DMF).

The reaction of 1-methyl-3-nitro- and 1-methyl-4-nitropyrazoles with 1,1,1-trimethylhydrazinium halides [22] and 4-amino-1,2,4-triazole [23] was investigated. Earlier these reagents had been used successively for the amination of certain nitro derivatives of aromatic hydrocarbons [24, 25]. When treated with 1,1,1-trimethylhydrazinium halides 1-methyl-4-nitropyrazole is aminated at the $C_{(5)}$ atom of the azole ring, but its isomer 1-methyl-3-nitropyrazole does not enter into this reaction. In order to explain such a significant difference in the behavior of these isomers in amination processes we carried out *ab initio* calculations (RFH 6-32G* [26]) on 1-methyl-3-nitro- and 1-methyl-4-nitropyrazoles. The calculations (Fig. 1) showed substantial differences in the density of charges at the atoms of these compounds, which agrees well the observed differences in their reactivity.

As seen from Fig. 1, the highest positive charge in 1-methyl-4-nitropyrazole is concentrated at the $C_{(5)}$ atom and is substantially higher than the charge at the $C_{(3)}$ atom. This agrees well with our observed amination of 1-methyl-4-nitropyrazole (**4c**) at position 5. At the same time, according to the calculated data, in 1-methyl-3-nitropyrazole nucleophilic attack can only take place at the $C_{(5)}$ atom, although the nucleophilicity of this substrate is significantly lower than that of the 1-methyl-4-nitro isomer. This probably also explains our unsuccessful attempts at the amination of 1-methyl-3-nitropyrazole [22]. Nevertheless, in spite of the simplicity of such an explanation analysis of the charge distribution does not make the mechanism of VNS entirely clear, since in some cases the reactions take place contrary to this factor.

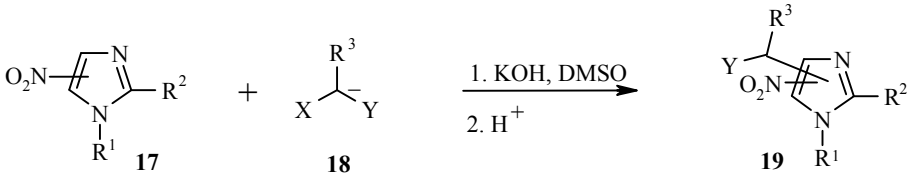
In a continuation of a study of the amination of 1-methyl-4-nitropyrazole (**4c**) 4-amino-1,2,4-triazole (**14**) [23], which had previously been used successfully for the amination of nitrobenzene and some of its derivatives [25], was used as aminating agent. Here, in addition to the expected amination product 5-amino-4-nitropyrazole (**15**), the yield of which amounted to 20%, 4-(1-methyl-4-nitro-5-pyrazolylamino)-1,2,4-triazole (**16**) was isolated with a 13% yield.



Initially it was suggested that the product **16** was formed at the first stage of the reaction and that it was subsequently transformed into the final pyrazole **15** as a result of heterolysis at the N–N bond. However, experiments on the supposed transformation **16** → **15** under the conditions of VNS showed that this was not so – in all cases the initial compound **16** was isolated from the reaction mixture, and no traces of the nitropyrazole were found.

Imidazoles

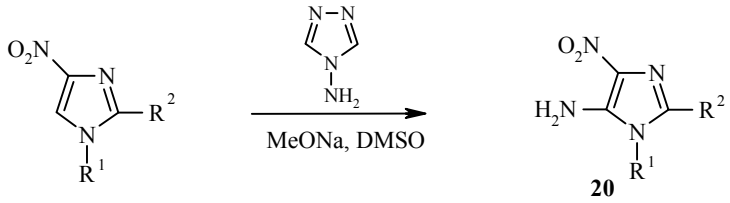
Alkyl-substituted nitro derivatives of imidazole react with carbanions containing leaving groups at the carbanionic centers, forming the products from VNS of hydrogen at the positions activated by the nitro groups [27]. Thus, in 1-alkyl-4-nitroimidazoles substitution takes place exclusively at position 5 [28]; a nitro group at this position directs the entering substituent to the $C_{(2)}$ and $C_{(4)}$ atoms (Table 2) [27].



17 **18** **19**

In 1,2-dimethyl-5-nitroimidazole VNS takes place only at the free position of the imidazole ring, i.e., the $C_{(4)}$ atom [27].

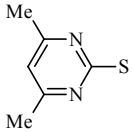
1-Aryl-4-nitroimidazoles and 1-aryl-2-methyl-4-nitroimidazoles enter into VNS under the influence of 4-amino-1,2,4-triazole in DMSO with the formation of 5-amino-1-aryl-4-nitroimidazoles (**20**) [29-31].



20

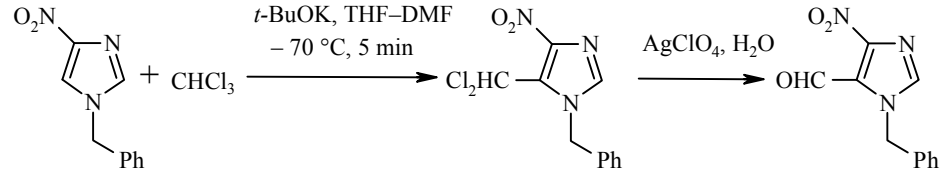
20 (yield, %) R^1 = Ph, R^2 = Me (45); R^1 = C_6H_4OMe-4, R^2 = Me (72); R^1 = C_6H_4Cl-3, R^2 = Me (0); R^1 = Ph, R^2 = H (30)

TABLE 2. The Yields of the Products from VNS in Nitroimidazoles with Various Carbanions

17			**18**				Yield of **19**, %
R^1	R^2	Position of NO_2	X	Y	R^3	Position of YR^3CH–	
Me	H	4	Cl	SO_2Ph	H	5	83
Me	H	5	Cl	CN	H	4	10
Me	H	5		CN	H	4	58
Me	H	5	Cl	SO_2Ph	H	4	63
						2	13
Me	H	5	Cl	CN	Me	4	21
						2	23
Me	Me	5	Cl	SO_2Ph	H	4	73
$(CH_2)_2COOH$	Me	5	Cl	SO_2Ph	H	4	64

The use of methanol in place of DMSO reduces the yield of the desired product on account of partial destruction of the imidazole ring [32].

Unlike the monohalogenomethyl derivatives, the di- and trihalogenomethyl-substituted nitroimidazoles can be obtained easily by VNS [12, 33, 34]. Thus, from 1-benzyl-4-nitroimidazole and chloroform the corresponding 5-dichloromethyl derivative was obtained with an 82% yield, and it was then hydrolyzed to the relatively difficult to obtain 1-benzyl-4-nitroimidazole-5-carbaldehyde (yield 78%).



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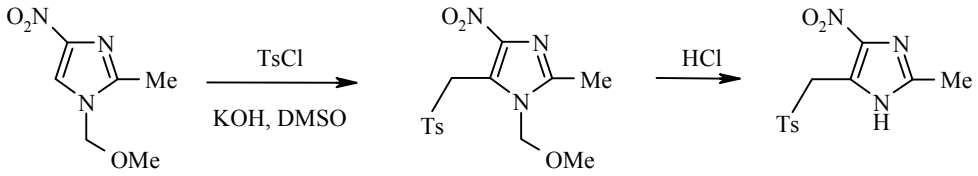
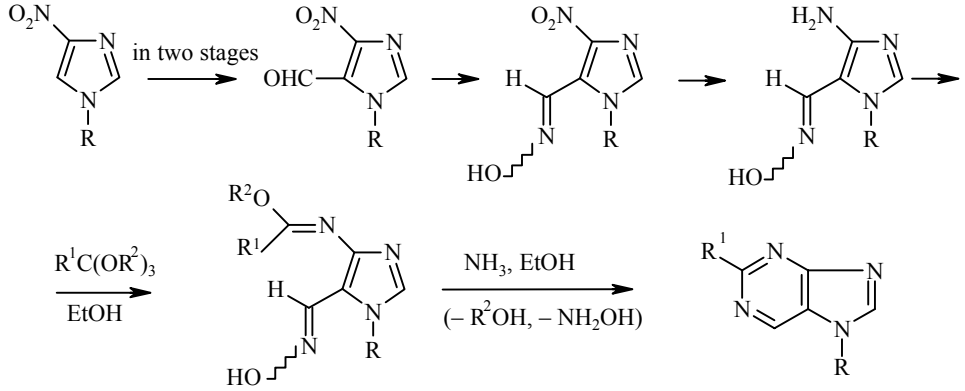
In 1,2-disubstituted 4-nitroimidazoles VNS takes place at the only accessible position 5 [18, 21].



Vicarious nucleophilic substitution is the key stage in the synthesis of N-7-substituted purines from 1-R-4-nitroimidazoles [35].



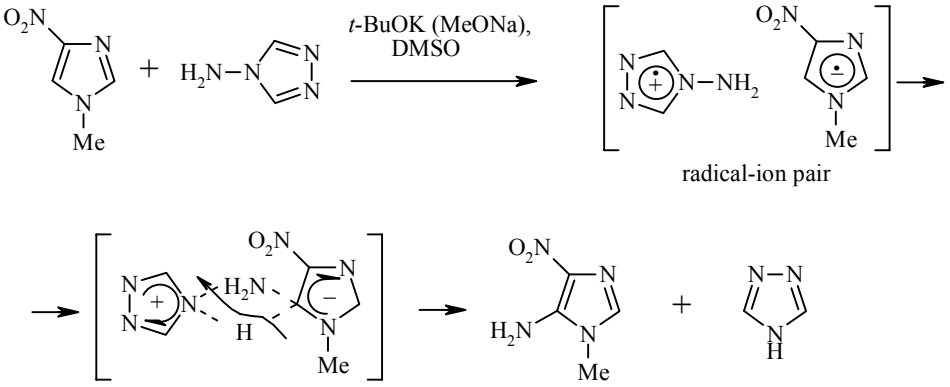
R, R^1, R^2: Me, H, Et; CH_2Ph, H, Et; Me, Me, Et; CH_2Ph, Me, Et; CH_2Ph, *n*-Bu, Me

In spite of such widespread usage of VNS its mechanism has still been investigated insufficiently. It was observed [2] that a blue-violet color appeared in the reaction mixture, and during VNS in 1-methyl-4-nitroimidazole by the action of aminating reagents (1,1,1-trimethylhydrazinium iodide and 4-amino-1,2,4-triazole) in the sodium methoxide–DMSO or potassium *tert*-butoxide–DMSO system we observed the appearance of a bright-blue color, which soon changed to red-brown, in the reaction mixture. This made it possible to propose the formation of intermediate radical-ion particles in the reaction [36, 37], which gave us grounds for turning to ESR to detect possible free-radical particles during the amination of nitroimidazoles [38]. In fact, signals with well resolved hyperfine structure were recorded in the ESR spectra during the reaction of 1-methyl-4-nitroimidazole, 1-methyl-4-nitropyrazole, and also nitrobenzene with the indicated aminating reagents [37]. The characteristics of the ESR signals make it possible to assign them unambiguously to the

primary radical-anion of the substrate [39],and this may indicate the presence of single-electron transfer in the reaction. Quantum-chemical calculation of the radical-anion of 1-methyl-4-nitroimidazole by the UHF/6-31G* method showed that the highest electron density is concentrated at position 5 of the imidazole ring [38].

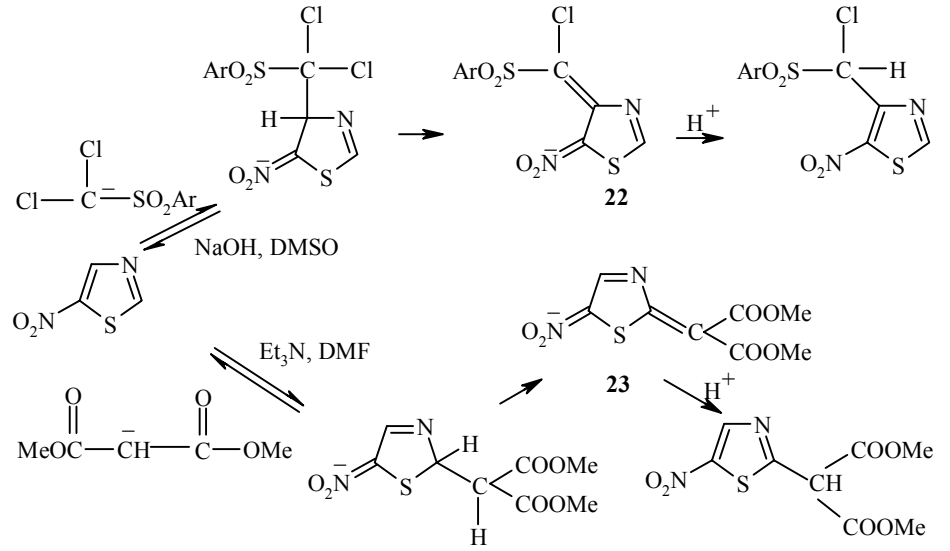
In the absence of C-amination (in the case of 2-methyl- and 1,2-dimethyl-4-nitroimidazoles) the ESR signals of the primary radical-anions were not recorded, in the same way that the ESR signals were not recorded in any of the blank experiments when even one of the components was absent from the reaction mixture [38].

The obtained results may indicate the presence in the reaction of a single-electron transfer channel and, thus, the vicarious C-amination of 1-methyl-4-nitroimidazole is probably realized by a radical-ion mechanism. The most likely reaction is not transfer of an electron along the chain [40] but "collapse" of the radical-ion pair [41, 42]. The escape of the free radical-ions "from the cage" into the solution is recorded by the ESR method. The proposed scheme for the reaction of 1-methyl-4-nitroimidazole with 4-amino-1,2,4-triazole is given below.



Thiazoles

Vicarious nucleophilic substitution in 2-chloro- and 2-bromo-5-nitrothiazole takes place at the only possible reaction center of the substrate – the $C_{(4)}$ atom [43]. At the same time in 5-nitrothiazole itself there are two possible reaction centers ($C_{(4)}$ and $C_{(2)}$). In the same paper a difference was found in the orientation of the process, depending on the nature of the employed reagent. Thus, 5-nitrothiazole reacts with the carbanion of chloromethyl methyl sulfone at position 4 and with the carbanion of dimethyl malonate at position 2.

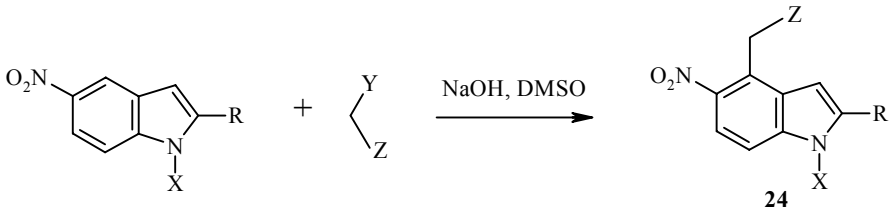


In the opinion of the authors such a significant difference in the direction of the reaction can be explained on the basis of the concept of kinetic or thermodynamic control of the determining stage. Nucleophilic addition at position 4 must take place more quickly in the unsymmetrical 5-nitrothiazole ring. However, the σ^n-adduct **22** formed here must be significantly less stable than the isomeric σ^n-adduct **23** formed at position 2 [43].

In the literature we did not find any example of the use of either vicinal or symmetrical triazoles as substrates in VNS reactions. Our own attempts to bring 1-methyl-3-nitro-1,2,4-triazole into such reactions were also unsuccessful. However, a paper recently appeared on the use of 1-phenylsulfinylmethyl-1,2,4-triazole (**11**) as alkylating agent in VNS with 1-methyl-4-nitropyrazole [21] (see above).

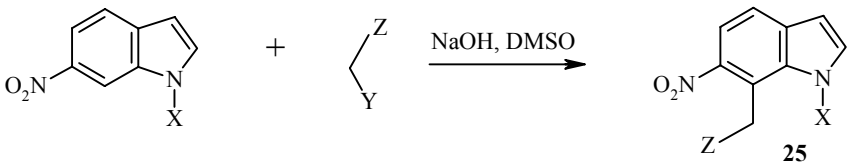
Indoles

Several examples of VNS in 1- and 1,2-disubstituted nitroindoles have been described [14, 18, 28, 44, 45]. If the NO_2 group is at position 5, the substituent enters at position 4, and if this group is at the $C_{(6)}$ atom substitution occurs at the $C_{(7)}$ atom.



24

R, X, Y, Z: H, CH_2OMe, Cl, Ts; H, CH_2Ph, OC_6H_4Cl-4, CN; H, CH_2Ph, Cl, Ts; Me, Me, OC_6H_4Cl-4, CN; Me, CH_2Ph, Cl, Ts; Me, Ts, OC_6H_4Cl-4, CN; Me, Ts, Cl, Ts. Yields of **24** 70–85%



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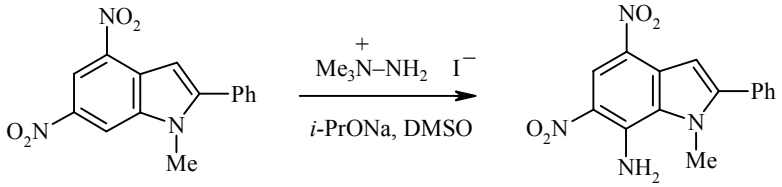
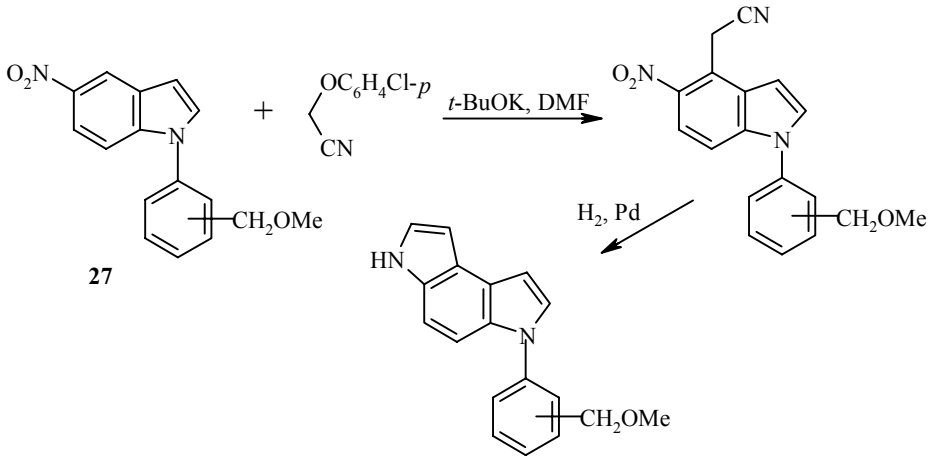
X, Y, Z: Me, Cl, Ts; CH_2OMe, OC_6H_4Cl-4, CN; CH_2OMe, Cl, *t*-$BuSO_2$; CH_2Ph, Cl, Ts; CH_2OMe, Cl, Ts; $CH_2C_6H_4OMe$-4, OC_6H_4Cl-4, CN; $CH_2C_6H_4OMe$-4, Cl, *t*-$BuSO_2$; $CH_2C_6H_4OMe$-4, Cl, Ts; $CH_2C_6H_4(OMe)_2$-3,4, Cl, Ts. Yields of **25** 70–91%

1-Methyl-4,6-dinitro-2-phenylindole and its *para*-diethylamino derivative are aminated by trimethylhydrazinium iodide exclusively at position 7 with the formation of 7-amino-substituted **26** [46].



26

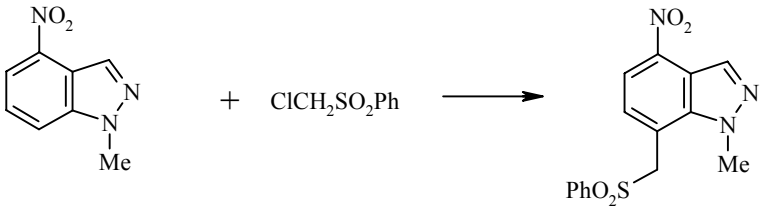
The cyanomethylation of the 1-substituted 5-nitroindole **27** by VNS is the key stage in the production of pyrrolo[3,2-*e*]indole – the initial heterocyclic fragment in the antitumor antibiotic CC-1065 [45].



27

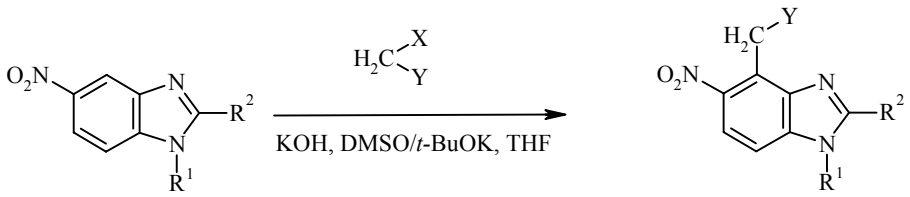
Benzazoles

In 4-nitroindazoles **28**, as in their 6-nitro isomers, VNS takes place at the $C_{(7)}$ atom [47]. The structure of the reaction product **29** was refined by X-ray crystallographic analysis [48].



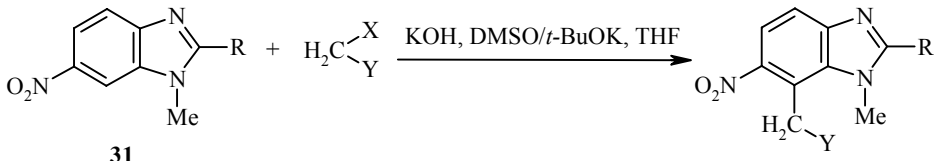
28 **29**

1-Substituted 5-nitrobenzimidazoles [18, 49], like their 6-nitro isomers **31** [49], enter ito VNS, although it was noticed here that their reactivity was rather lower than with nitroindazoles.



30 **32**

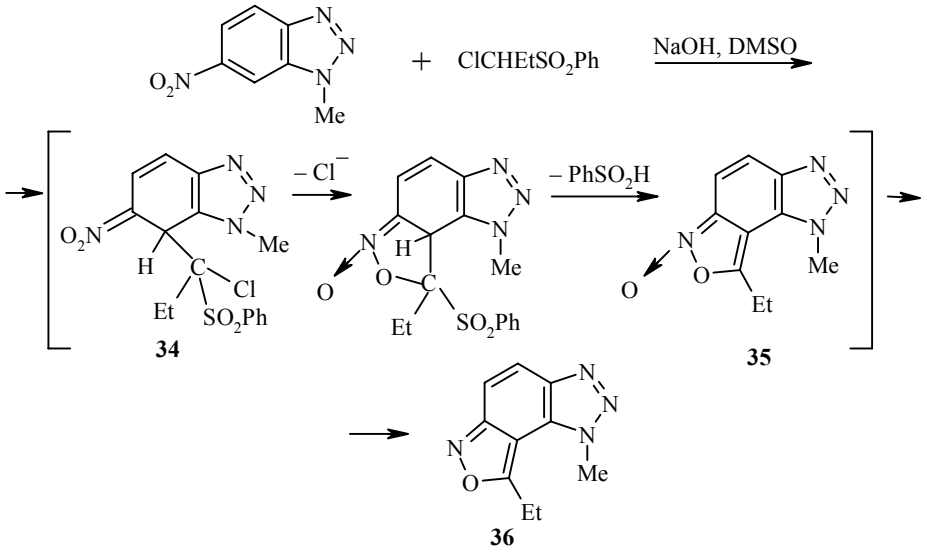
X = Cl, SPh; R^1, R^2, Y: H, CF_3, SO_2Ph; H, CF_3, CN. Yields of **32** 15–20%



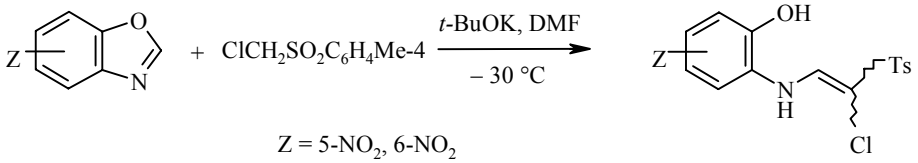
31 **33**

X = Cl, SPh; R, Y: H, SO_2Ph; CF_3, Ts. Yields of **33** 10–30%

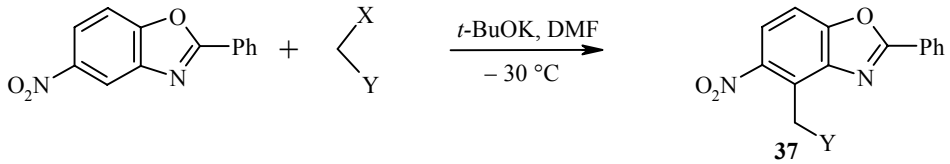
The nitro derivatives of benzotriazoles exhibit certain special features in VNS. The substituent occupies both the *ortho* and the *para* position [50] in relation to the nitro group or the *ortho* position exclusively [21]. It is assumed that the σ^n-adduct (**34**) is obtained from 1-methyl-6-nitrobenzotriazole and α-chloropropyl phenyl sulfone and then undergoes intramolecular cyclization with the formation of 8-ethyl-1-methylisoxazolo[4,3-*e*]-benzotriazole 6-oxide (**35**). By passing the reaction mixture through silica gel it was possible to isolate 8-ethyl-1-methylisoxazolo[4,3-*e*]benzotriazole (**36**) with a yield of 14% [50].



Benzoxazole unsubstituted at position 2 [51] and also its 5- or 6-nitro derivatives [52] react under the conditions of VNS with opening of the benzoxazole ring.

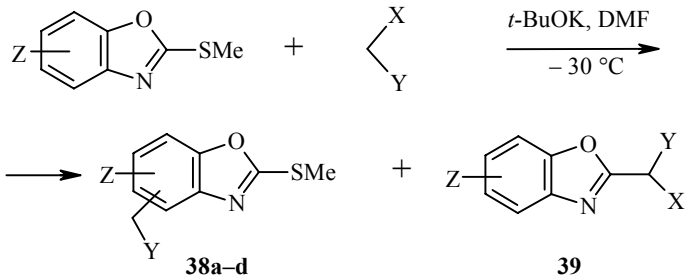


If position 2 in the substrate is blocked by a phenyl substituent, the bicyclic system is retained, and the reaction takes place at position 7.



37 (yield, %) X = Cl, Y = Ts (77); X = OC_6H_4Cl-4, Y = CN (82)

2-Methylthio-5-nitrobenzoxazole and its 6-nitro isomer form the products from substitution both in the phenylene (**38**) and in the oxazole (**39**) rings. It is interesting to note that in 2-methylthio-5-nitrobenzoxazoles VNS takes place at the $C_{(4)}$ atom while in the 6-nitro isomers it takes place at the $C_{(7)}$ atom [52].

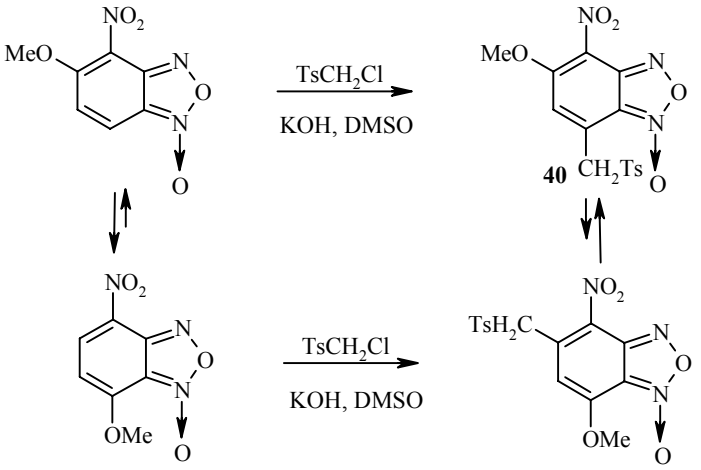


38a–d **39**

Z = 5-NO_2, 6-NO_2; X = Cl, OC_6H_4Cl-4; Y = Ts, CN;

CH_2Y, yield of **38,** %: 4-CH_2Ts, 23; 4-CH_2CN, 63; 7-CH_2Ts, 23; 7-CH_2CN, 60

4-Nitrobenzofuroxane and also its 5- and 7-methoxy derivatives react by the mechanism of VNS with chloromethyl phenyl sulfone, *para*-tolyl chloromethyl sulfone, and certain other derivatives in a superbasic medium at positions 5 or 7. In all cases the more stable 7-isomers **40** are formed as a result of a Bolton–Katritzky rearrangement [53].



Triazolo- and tetrazolopyridazines undergo VNS of hydrogen at the $C_{(8)}$ atom. The crystal structure of the reaction products was demonstrated by X-ray crystallographic analysis [54].

As follows from the presented data, VNS of hydrogen in activated heterocyclic compounds is a convenient and, in some cases, the only method for the introduction of various functional groups and substituents into activated heterocyclic systems. Thus, VNS is the key stage in the synthesis of purine bases from commercially available nitroimidazoles. It can be stated with certainty that the VNS of hydrogen will in the near future occupy a creditable position in the synthetic arsenal of researchers and will extend our ideas about the fine processes occurring in the synthesis of organic compounds.

REFERENCES

1. J. Golinski and M. Makosza, *Tetrahedron Lett.*, **37**, 3495 (1978).
2. M. Makosza (Makosha), *Usp. Khim.*, **58**, 1298 (1989).
3. M. Makosza (Makosha), *Izv. Akad. Nauk. Ser. Khim.*, No. 3, 531 (1996).
4. P. F. Pagoria, A. R. Mitchell, and R. D. Schmidt, *International Symposium on Energetic Material Technology*, Phoenix (1995), 6 [preprint UCRL-121967].

5. P. F. Pagoria, R. D. Schmidt, and A. R. Mitchell, *National Amer. Chem. Soc. Meeting*, Orleans, (1996), 1 [preprint UCRL-JC-122488].
6. P. F. Pagoria, A. R. Mitchell, R. D. Schmidt, and L. E. Fried, *Lawrence*, Livermore National Laboratory, (1997), 1 [preprint UCRL-ID-125792].
7. P. F. Pagoria, A. R. Mitchell, R. D.Schmidt, and L. E. Fried, *Chemistry & Materials Science Progress Report; Summary of Selected Research and Development Topics*, Univ. of California, Livermore, (1997), 28 [preprint UCID-20622-97].
8. B. N. Knyazev and V. N. Drozd, *Zh. Org. Khim.*, **31**, 3 (1995).
9. M. Makosza and J. Winiarski, *Acc. Chem. Res.*, **20**, 289 (1987).
10. M. Makosza (Makosha), in: *Modern Trends in Organic Synthesis* [Russian translation], Mir, Moscow (1986), p. 518.
11. M. Makosza, *Polish J. Chem.*, **66**, 3 (1992).
12. M. Makosza and K. Wojciechowski, *Lieb. Ann. Rec.*, 1805 (1997).
13. M. Makosza, *Synthesis*, 103 (1991).
14. M. Makosza and K. Wojciechowski, *Heterocycles*, **54**, 445 (2001).
15. M. Makosza and E. Slomka, *Bull. Pol. Acad. Sci. Chem.*, **32**, 69 (1984).
16. E. Kwast and M. Makosza, *Tetrahedron Lett.*, **31**, 121 (1990).
17. M. Makosza and E. Kwast, *Tetrahedron*, **51**, 8339 (1995).
18. M. K. Bernard, *Polish. J. Chem.*, **71**, 1413 (1997).
19. P. F. Pagoria, A. R. Mitchell, R. D. Schmidt, and L. E. Fried, *Chemistry & Materials Science Progress Report*, Weapons Research and Development and Laboratory Directed Research and Development, University of California, Livermore (1997), 7 [UCID-20622-96].
20. M. K. Bernard, M. Makosza, B. Szafran, and U. Wrzeciono, *Liebigs Ann. Chem.*, **6**, 545 (1989).
21. M. K. Bernard, *Tetrahedron*, **56**, 7273 (2000).
22. V. A. Lopyrev, V. N. Elokhina, O. V. Krylova, A. S. Nakhmanovich, L. I. Larina, M. S. Sorokin, and A. I. Vokin, *Khim. Geterotsikl. Soedin.*, 1254 (1999).
23. V. N. Elokhina, O. V. Krylova, L. I. Larina, A. S. Nakhmanovich, M. S. Sorokin, K. A. Volkova, and V. A. Lopyrev, *Khim. Geterotsikl. Soedin.*, 551 (2000).
24. P. F. Pagoria, A. R. Mitchell, and R. D. Schmidt, *J. Org. Chem.*, **61**, 2934 (1996).
25. A. R. Katritzky and K. S. Laurenso, *J. Org. Chem.*, **51**, 5039 (1986).
26. M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, V. G. Zakrzewski, J. A. Montgomery, Jr., R. E. Stratmann, J. C. Burant, S. Dapprich, J. M. Millam, A. D. Daniels, K. N. Kudin, M. C. Strain, O. Farkas, J. Tomasi, V. Barone, M. Cossi, R. Cammi, B. Mennucci, C. Pomelli, C. Adamo, S. Clifford, J. Ochterski, G. A. Petersson, P. Y. Ayala, Q. Cui, K. Morokuma, D. K. Malick, A. D. Rabuck, K. Raghavachari, J. B. Foresman, J. Cioslowski, J. V. Ortiz, A. Y. Baboul, B. B. Stefanov, G. Liu, A. Liashenko, P. Piskorz, I. Komaromi, R. Gomperts, R. L. Martin, D. J. Fox, T. Keith, M. A. Al-Laham, C. Y. Peng, A. Nanayakkara, C. Gonzalez, M. Challacombe, P. M. W. Gill, B. Johnson, W. Chen, M. W. Wong, J. L. Andres, M. Head-Gordon, E. S. Replogle, and J. A. Pople, *GAUSSIAN 98*, Revision A. 6, Gaussian, Inc., Pittsburgh, PA (1998).
27. M. Makosza and E. Kwast, *Bull. Pol. Acad. Sci. Chem.*, **35**, 287 (1987).
28. M. Makosza and M. Bialecki, *J. Org. Chem.*, **63**, 4878 (1998).
29. J. Suwinski and K. Swierczek, *Tetrahedron Lett.*, **51**, 7941 (1992).
30. J. Suwinski and K. Swierczek, *Tetrahedron*, **49**, 5339 (1993).
31. J. Suwinski, W. Pawlus, E. Salwinska, and K. Swierczek, *Heterocycles*, **37**, 1511 (1994).
32. J. Suwinski and K. Swierczek, *Khim. Geterotsikl. Soedin.*, 1214 (1996).
33. M. Makosza and Z. Owczarczyk, *J. Org. Chem.*, **54**, 5094 (1989).
34. S. Ostrowski, *Polish J. Chem.*, **68**, 2237 (1994).
35. S. Ostrowski, *Molecules*, **4**, 287 (1999).

36. M. Makosza, in: *Intern. Conf. Reaction Mechanisms and Organic Intermediates*, Saint-Petersburg, Russia, June 11-14, 2001, p. 69.
37. O. V. Donskaya, V. N. Elokhina, T. I. Vakul' skaya, A. V. Vokin, L. I. Larina, and V. A. Lopyrev, in: *Intern. Conf. Reaction Mechanisms and Organic Intermediates*, Saint-Petersburg, Russia, June 11-14, 2001, p. 96.
38. O. V. Donskaya. V. N. Elokhina, T. I. Vakul'skaya, A. V. Vokin, L. I. Larina, and V. A. Lopyrev, *Mendeleev Commun.*, in the press.
39. T. I. Vakul'skaya, L. I. Larina, O. B. Nefedova, L. P. Petukhov, M. G. Voronkov, and V. A. Lopyrev, *Khim. Geterotsikl. Soedin.*, 1398 (1979).
40. D. H. R. Barton, S. Greneur, and W. B. Motherwell, *Tetrahedron Lett.*, **24**, 1601 (1983).
41. O. Yu. Okhlobystin, *Electron Transfer in Organic Reactions* [in Russian], Izd. Rost. Un-ta, Rostov (1974).
42. Z. V. Todres, *Radical-Ions in Organic Synthesis* [in Russian], Khimiya, Moscow (1986).
43. M. Makosza, A. Rydz, and Z. Wrobel, *Polish J. Chem.*, **69**, 918 (1995).
44. K. Wojciechowski and M. Makosza, *Synthesis*, **2**, 106 (1989).
45. D. L. Boger and D. S Johnson, *Angew. Chem., Int. Ed. Engl.*, **35**, 1439 (1996).
46. V. V. Rozhkow, A. M. Kuvshinov, S. A. Shevelev, *Heterocycl. Commun.*, **6**, 525 (2000).
47. J. Dudzinska-Uzarewicz, U. Wrzeciono, A. Frankiewicz, E. Linkowska, T. Kohler, and P. Nuhn, *Pharmazie*, **43**, 611 (1988).
48. A. Gzella, U. Wrzeciono, J. Dudzinska-Uzarewicz, and T. Borowiak, *Acta Crystallogr.*, **45**, 642 (1989).
49. M. K. Bernard, *Polish J. Chem.*, **69**, 1120 (1995).
50. M. K. Bernard, C. Szoja, and U. Wrzeciono, *Liebigs Ann. Chem.*, 755 (1990).
51. M. Makosza, J. Golinski, and A. Rykowski, *Tetrahedron Lett.*, **24**, 3277 (1983).
52. M. Makosza and J. Stalewski, *Tetrahedron*, **51**, 7277 (1995).
53. S. Ostrowski and K. Wojciechowski, *Can. J. Chem.*, **68**, 2239 (1990).
54. A. A. Katrusiak, S. Baloniak, A. S. Katrusiak, *Polish J. Chem.*, **70**, 1279 (1996).