*Russian Chemical Reviews* **64** (2) 133 – 140 (1995)
©1995 Russian Academy of Sciences and Turpion Ltd

UDC 547.562

# The Smiles rearrangement of *o*-aminophenyl phenyl ethers

T N Gerasimova, E F Kolchina

## Contents


| | |
|---|---|
| I. Introduction | 133 |
| II. Rearrangement of *o*-aminophenyl phenyl ethers | 134 |
| III. The Smiles rearrangement of aromatic polyfluoro-compounds | 136 |


**Abstract. A systematic account is given of the literature data on the Smiles rearrangement of *o*-aminophenyl phenyl ethers including data obtained by means of model studies on polyfluoro-derivatives. Attention is concentrated on the influence of the structure of *o*-aminophenyl phenyl ethers on their reactivity. The bibliography includes 51 references.**

## I. Introduction

The Smiles rearrangement plays an important role in the synthesis of condensed heterocyclic systems comprising activated aromatic halo-compounds and asymmetric bifunctional nucleophiles. In a general form, it can be represented by Scheme 1, which includes the inversion of the side chain in a type **1** structure.[1-3] An activated aromatic or heteroaromatic ring is the migrating residue, while the side chain may be part of the aromatic system.

Scheme 1

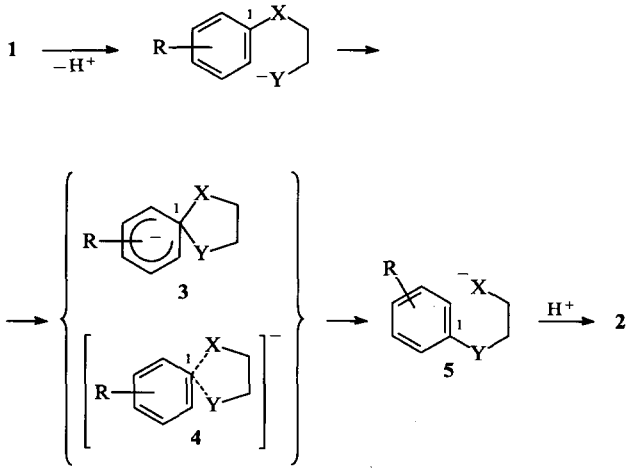


**1** **2**

Transformations of this kind were first investigated by Smiles and co-workers in 1931 in relation to *o*-hydroxy-derivatives of diaryl sulfones and sulfides.[4] Later the Smiles rearrangement was extended to a large number of aromatic derivatives with different combinations of groups X and YH and the most important factors affecting its rate were determined: activation of the migrating aromatic ring, mobility of the substituting group, nucleophilicity of the attacking centre, and acidity of the functional group YH.[1,2]

The Smiles rearrangement is usually carried out in a basic medium. The proposed reaction mechanism includes the YH ionisation stage and nucleophilic attack by the anion $Y^-$ on the 1-position in the aromatic ring accompanied by the formation of an intermediate Meisenheimer spiro-complex **3** or the transition state **4** (Scheme 2).[1,2]

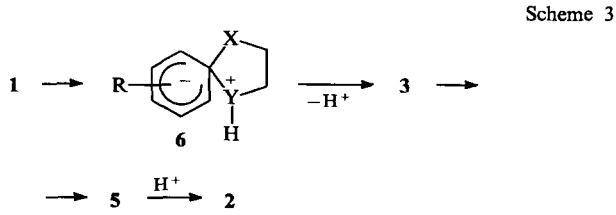
Scheme 2



The type **3** intermediates, including those with the functional groups X and Y linked by the *o*-phenylene fragment, were isolated or detected in solution by spectroscopic methods.[5-8] The Smiles rearrangement can occur as a reversible process,[1,2] which presupposes the irreversibility of the formation stages and of further reactions of the intermediate **3** and is most probable when the nucleophilicities of the centres X and Y are similar.[6]

Examples of the Smiles rearrangement which do not require the presence of bases and which occur without preliminary ionisation of the group YH are known. In such cases, the nucleophilic attack by the latter on the 1-position leads to the formation of a type **6** zwitterionic spiro-complex which is then converted into the intermediate **3** via deprotonation (Scheme 3).

Scheme 3



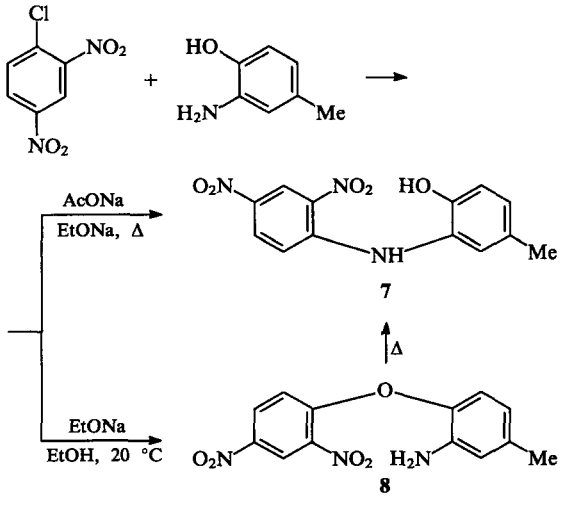
**T N Gerasimova, E F Kolchina** Laboratory of Organic Photosensitive Materials. Novosibirsk Institute of Organic Chemistry, Siberian Division of the Russian Academy of Sciences, prosp. akad. Lavrent'eva 9, 630090 Novosibirsk, Russian Federation. Fax (7-383) 235 47 52. Tel. (7-383) 235 79 96 (T N Gerasimova)

Received 12 December 1994
*Uspekhi Khimii* **64** (2) 142 – 149 (1995); translated by A K Grzybowski

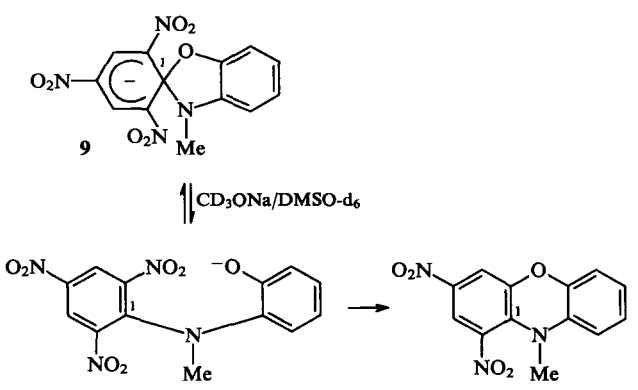
The rearrangement of *o*-aminophenyl phenyl ether to aryl(*o*-hydoxyaryl)amines, discovered and first investigated by Roberts and de Worms,[9] belongs to transformations of this kind. It has been demonstrated on numerous examples that this rearrangement plays a significant role in the synthesis of phenoxazines from aromatic polynitrohalo-compounds and *o*-aminophenols, preceding the final intramolecular cyclisation stage and determining the structure of the reaction products.[2,10,11] In the 1960s, a series of unexpected aspects of this reaction were discovered.[12,13] However, in a review[2] devoted to the Smiles rearrangement the data concerning the transformations of *o*-aminophenyl phenyl ethers were treated systematically to an inadequate extent. This factor as well as the results of our investigations in recent years, obtained by extending the Smiles rearrangements to aromatic polyfluoro-compounds,[14] led us to write the present review.

## II. Rearrangement of *o*-aminophenyl phenyl ethers

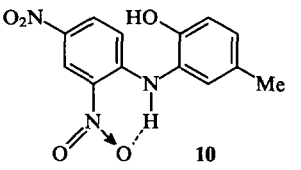
It was shown in 1934[9] that the interaction of 1-chloro-2,4-dinitrobenzene with 2-amino-*p*-cresol affords either the diphenylamine **7** or the diphenyl ether **8**, depending on the reaction conditions. On heating, compound **8** rearranges to the amine **7**. The reaction takes place in basic and hydroxyl-containing solvents (pyridine, aniline, alcohols, etc.) and is retarded in an alkaline [sic] medium. According to the authors,[9] the rearrangement of the ether **8** takes place without the preliminary ionisation of the amino-group, i.e. proceeds via Scheme 3.



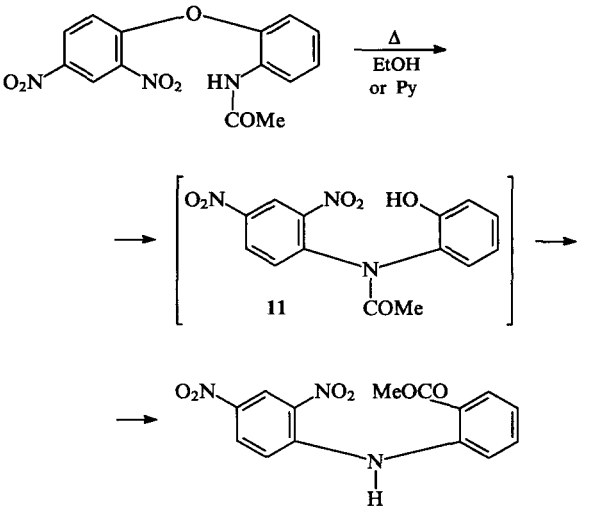

It is assumed that aryl(*o*-hydroxyaryl)amines do not undergo the Smiles rearrangement.[1,2,15-19] The reversible formation of the spirocyclic complex **9** from *N*-methyl-*N*-picryl-2-aminophenol has been established by spectroscopic methods.[5,20] Presumably the absence of the Smiles rearrangement in the given instance is due to the relative ease of the dissociation of the C(1)–O bond with formation of a stable phenoxide anion.




The rearrangement of the ether **8** to the amine **7** is not accompanied by cyclisation and the formation of a phenoxazine. This feature, which has been explained by the formation of an intramolecular hydrogen bond stabilising the unreactive structure **10**,[18,21,22] made it possible to observe the Smiles rearrangement 'in a pure form' and helped to discover the influence of the nature of the substituents at the nitrogen atom and in the aromatic rings on the rate of the transformation.

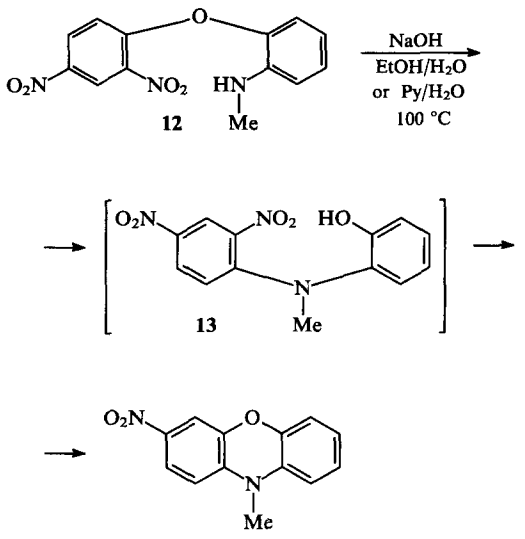


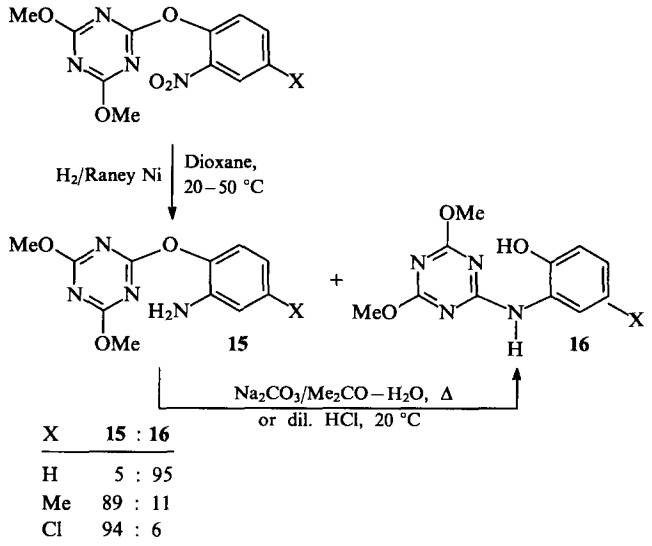

It has been shown that the higher the electron-accepting capacity of the acyl residue the greater the lowering of the rate of rearrangement caused by the *N*-acylation of *o*-aminophenyl ethers. Since the rearrangement of *o*-*N*-acyl-substituted diphenyl ethers takes place in a neutral medium, one may suggest that it takes place via Scheme 3.[9,23] The Smiles rearrangement is accompanied in this case by the migration of the acyl residue from the nitrogen atom to the oxygen atom, tentatively in accordance with a stepwise mechanism via the intermediate *o*-hydroxyamine **11**.[24]




The introduction of the electron-donating *N*-methyl group into the molecule of 2-aminophenyl 2,4-dinitrophenyl ether also lowers its capacity for the rearrangement. Thus compound **12** is stable under the conditions of the transformation of the $NH_2$ analogue and leads slowly to *N*-methyl-3-nitrophenoxazine only on heating in an alkaline solution.[25] The *para*-location of the nitro-group and of the heterocyclic nitrogen atom in the molecule of the phenoxazine formed indicate that the cyclisation stage is preceded by the rearrangement to the diphenylamine **13**. The latter is unstable under the reaction conditions because an intramolecular hydrogen bond, of the kind stabilising the $NH_2$ analogue, cannot be formed.[21,25]

Although the rearrangement of the *N*-methyl-substituted ether **12** requires an alkaline medium, its occurrence via Scheme 3 is most likely. The activating effect of alkali is apparently manifested in the stage involving the conversion of the zwitterionic type **6** spiro-complex into the intermediate **3**. The reaction mechanism involving the deprotonation of the spirocyclic complex as the rate-limiting stage had been established earlier as a result of a kinetic study of the rearrangement of 2-aminophenyl 2,4-dinitrophenyl sulfide[26] and of a series of similar processes.[8,27,28]

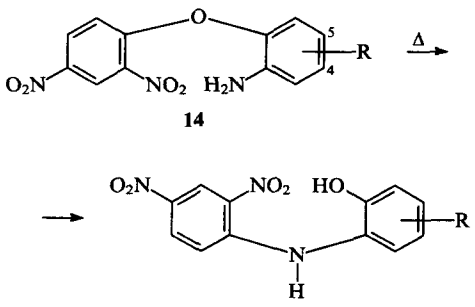




The influence of substituents in the ring carrying the amino-group on the rearrangement of *o*-aminophenyl phenyl ethers is fairly complex and not unambiguous. When Scheme 3 operates, the rearrangement should be facilitated by substituents increasing the basicity of the attacking amino-group or stabilising the phenoxide anion formed. The study of the rearrangement of type **14** ethers showed that the highest rate of transformation is attained for R = H; the introduction of a substituent of any kind into the *para*- or *meta*-position relative to the amino-group slows down the reaction, the greatest effect being manifested in the case of 5-methyl-substituted compounds (Table 1).[29,30]

**Table 1.** The durations of the rearrangement of the diphenyl ethers **14** in the 4:1 acetic acid–pyridine mixture at 50 °C.

| R | *t*/min | R | *t*/min | R | *t*/min |
|---|---|---|---|---|---|
| 4-H | 5 | 4-Cl | 60 | 5-H | 5 |
| 4-Me | 7 | 4-Br | 30 | 5-Me | 90 |
| 4-OMe | 13 | 4-I | 15 | 5-I | 7 |
| 4-$NH_2$ | 50 | | | | |

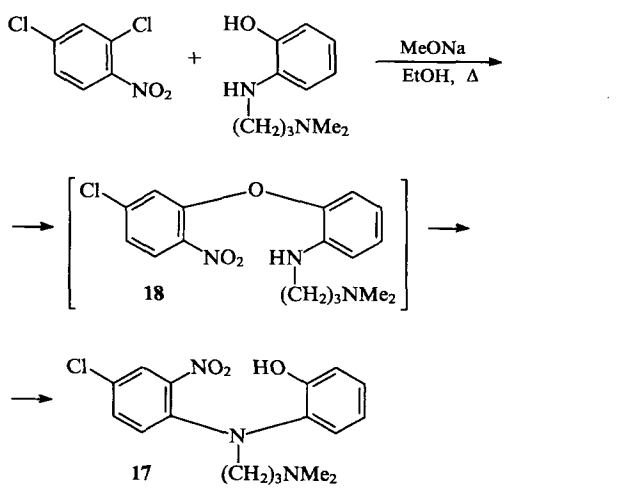


The direct dependence of the rate of rearrangement on the sum of the Hammett constants $(-\sigma_m + \sigma_p)$ of the substituent X has been discovered similarly for *o*-aminophenoxytriazines **15**, which are partly converted into the amines **16** during their synthesis by the reduction of the corresponding nitro-compounds: H(0) > Me (−0.101) > Cl (−0.146).[31]

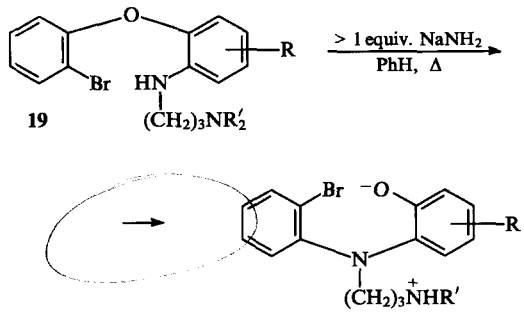
On this basis, the activation of the migrating aryl residue was recognised as the most important factor determining the possibility of the occurrence of the Smiles rearrangement.[1,2] The rearrangements of *o*-aminophenyl phenyl ethers were investigated mainly in relation to 2,4-dinitro-derivatives.[9,23,25] We are not aware of any attempts to achieve them for mononitro-analogues.

Data on the synthesis and reactions of the picryl ether of 2-amino-*p*-cresol, presented by Roberts and de Worms,[9] have been quite justifiably questioned by Drozd and coworkers.[20] As already mentioned above, the possibility of the occurrence of the Smiles rearrangement as a result of migration of an activated heterocyclic residue has been demonstrated in a number of studies.[31–33] Thus prolonged maintenance of the ether **15** (X = H) in acetone in the presence of sodium carbonate leads to its complete transformation into the amine **16**. A characteristic feature of the rearrangement in this case is the fact that it is catalysed not only by a base but also by an acid.[31] The catalytic effect of the acid is apparently associated with the enhancement of the electron-accepting capacity of the migrating ring by the protonation of the heterocyclic nitrogen atom.[34] The replacement of the methoxy-groups in compound **15** by the more electron-donating diethyl amino-groups suppresses the rearrangement.[31] However, the need for a high degree of activation of the migrating ring for the occurrence of the Smiles rearrangement of *o*-aminophenyl phenyl ethers was soon questioned.

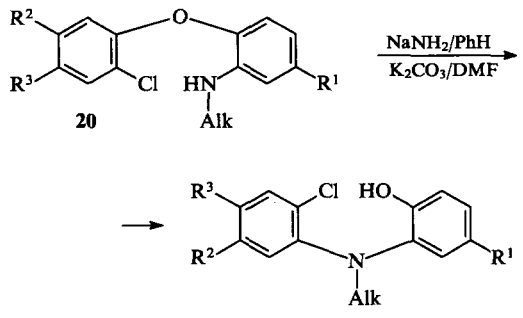
In 1961, Bonvicino et al.[22] suggested that the reaction involving the formation of aryl(*o*-hydroxyaryl)amino **17** from *o*-*N*-(3-dimethylaminopropyl)phenol and 2,4-dichloro-1-nitrobenzene involves the rearrangement of the intermediate ether **18**.



In conformity with this hypothesis, they carried out the rearrangement of the ether **19** by refluxing it in benzene in the presence of an excess of sodium amide.[12]




This is the first example of the Smiles rearrangement with a halogen atom as the activating group. According to the authors,[12] it is determined by the higher nucleophilicity of the N-anion formed from the *N*-alkylamino-group under the reaction conditions. Indeed, 2-amino-5-chlorophenyl 2-bromophenyl ether, which gives rise to a somewhat less nucleophilic N-anion, does not change on prolonged refluxing with sodium amide in xylene.[22] However, it was shown later that type **20** ethers, which also do not contain strong electron-accepting groups in the molecule, do undergo the rearrangement on refluxing in dimethylformamide (DMF) in the presence of potassium carbonate, i.e. under conditions which in all probability do not ensure the formation of N-anions.[13,35] Examples of the nonactivated Smiles rearrangement in the presence of a base have been described also for other classes of compounds, but have not so far been explained convincingly.[2,13,36,37]



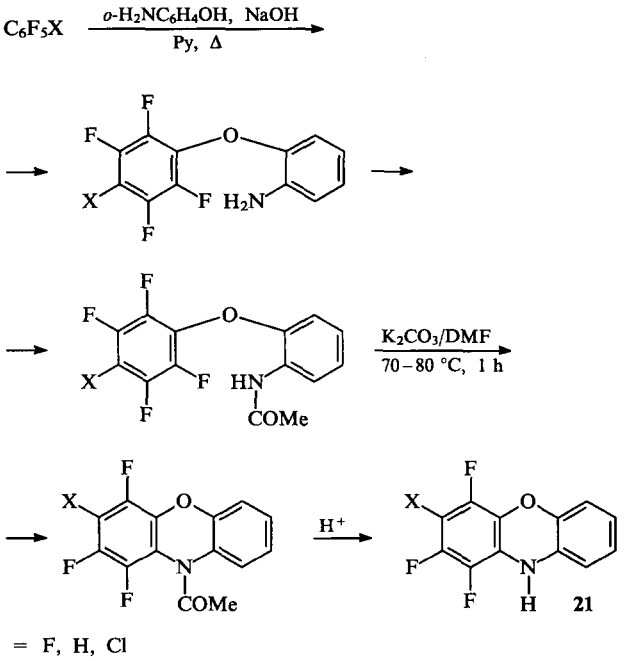

$R^1$, $R^2$, $R^3$ = H or Cl

Alk = $CH_2Ph$, $(CH_2)_3NMe_2$

On the whole, systematic studies by Roberts and also subsequent investigations quoted in the present review make it possible to outline the limits of the applicability of the Smiles rearrangement among *o*-aminophenyl phenyl ethers and to establish certain characteristics of the influence of structural factors on this process. However, the mechanism and elementary stages of the rearrangement remain unelucidated. There have also been no kinetic studies. This is partly due to the fact that in most cases the rearrangement of *o*-aminophenyl phenyl ethers is accompanied by side reactions, in the first place intramolecular nucleophilic cyclisation to phenoxazine derivatives.[2,10] There are not many examples of its observation 'in a pure form'. In our view, the problem of the synthesis of systems with a specified structure and the difficulty of analysing the reaction mixtures and of the determination of the structures of the product formed are also complicating factors. Polyfluoro-substituted *o*-aminophenyl phenyl ethers of the type $4\text{-}XC_6F_4OC_6H_4NHY\text{-}2'$, which can be readily synthesised from the simplest polyfluorobenzenes and *o*-aminophenol, are convenient objects from this point of view.[38-40] These ethers contain a fluorinated aromatic ring, the electron-accepting properties of which can be readily varied by altering the substituent X. The possibility of employing $^{19}F$ NMR spectroscopy for the analysis of the reaction mixtures and the identification of the products is a great advantage of the fluoro-compounds.

## III. The Smiles rearrangement of aromatic polyfluoro-compounds

The Smiles rearrangement of aromatic polyfluoro-compounds was first observed by the present authors in the synthesis of polyfluorinated derivatives of phenoxazine from the compounds $C_6F_5X$ and *o*-aminophenol.[41] It was shown with the aid of $^{19}F$ NMR spectroscopy that the molecule of the phenoxazine **21** (X = H or Cl) contains the OAr group and the substituent X in the *meta*-positions relative to one another. The change in the relative positions in the intramolecular cyclisation stage suggested that the formation of the phenoxazine system is preceded by the Smiles rearrangement.



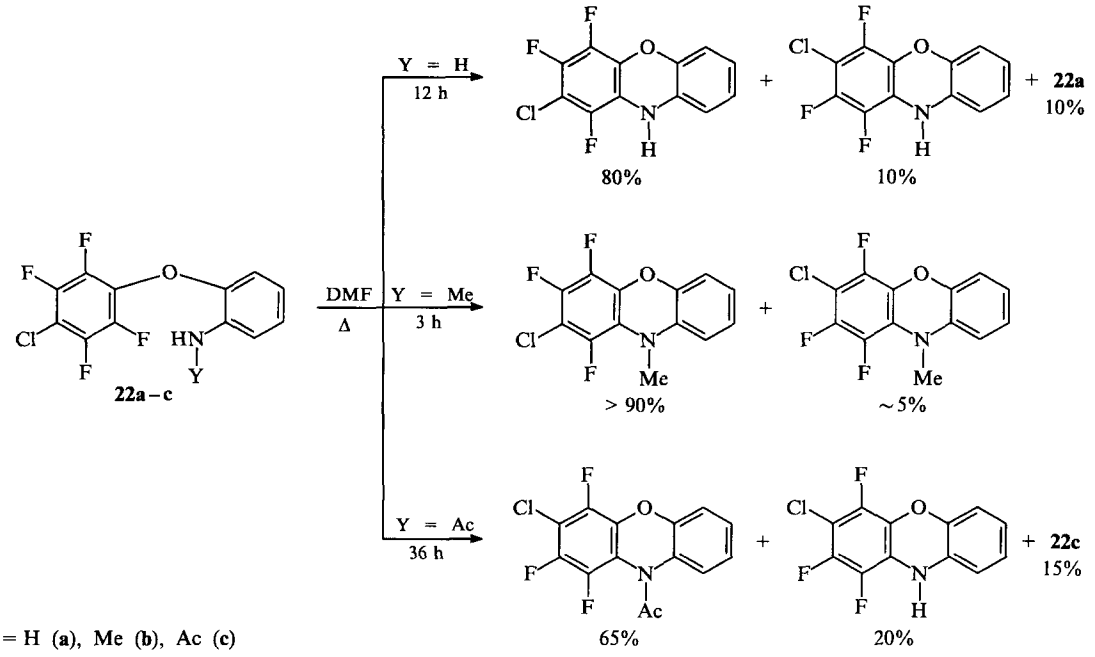

X = F, H, Cl

The transformations of polyfluorinated *o*-aminophenyl phenyl ethers have been investigated in detail in relation to compounds **22a-c** containing a chlorine atom in the fluorinated part of the molecule and the NHY group (Y = H, Me, Ac) in the nonfluorinated part.[14,42] It was shown that their refluxing in DMF leads to cyclisation to phenoxazines as a result of intramolecular nucleophilic substitution of the *ortho*-fluorine atom. The *N*-alkyl-substituted ether **22b** reacts faster, while the *N*-acetyl derivative **22c** reacts significantly more slowly than compound **22a**, which contains the $NH_2$ group (Scheme 4).

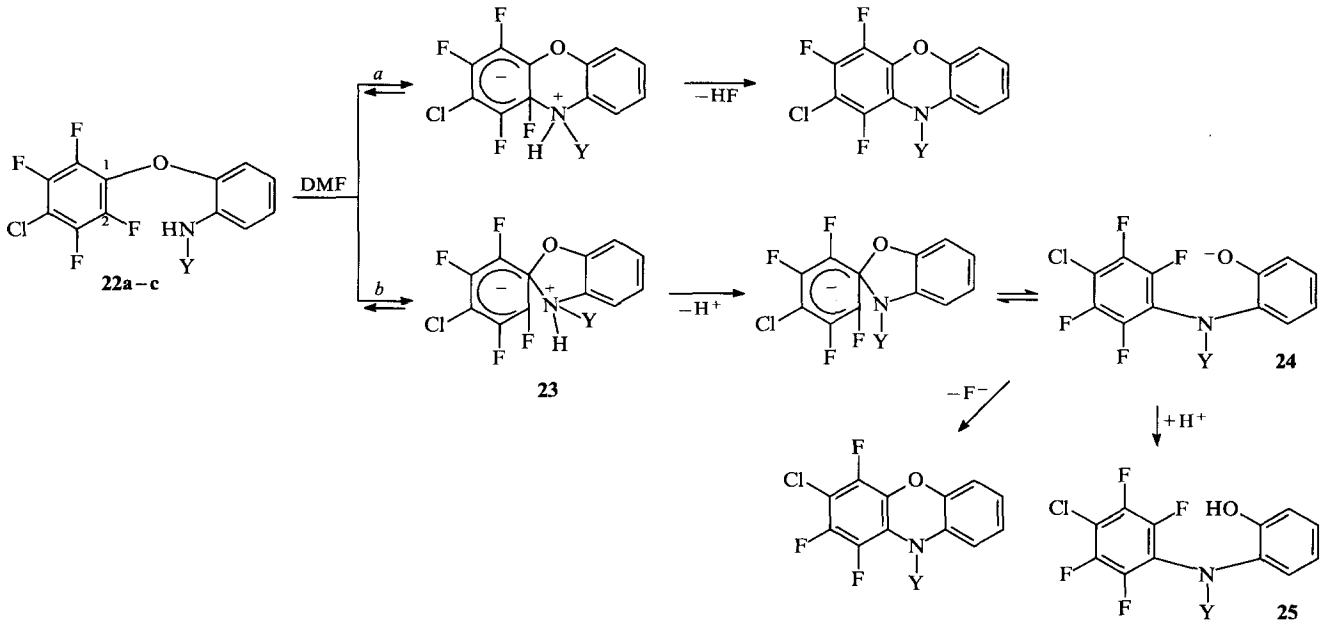
The structure of the phenoxazines formed indicates two reaction paths (Scheme 5): nucleophilic cyclisation as a result of the attack by the nitrogen atom on the 2-position with subsequent elimination of the fluoride ion (path *a*) and cyclisation with preceding Smiles rearrangement (path *b*). The second path is preferred because it involves the attack by the nucleophile on the most electrophilic C(1) carbon atom in the *para*-position relative to the chlorine atom, which agrees with the rules governing the directing effect in aromatic polyfluoro-compounds.[43,44]

The reaction path is determined by the nature of the group NHY. In the case of the ether **22c**, the molecule of which contains the comparatively weakly nucleophilic acetamido-group, the reaction proceeds wholly via path *b*. The diphenyl ethers **22a, b** are cyclised predominantly as a result of the

Scheme 4

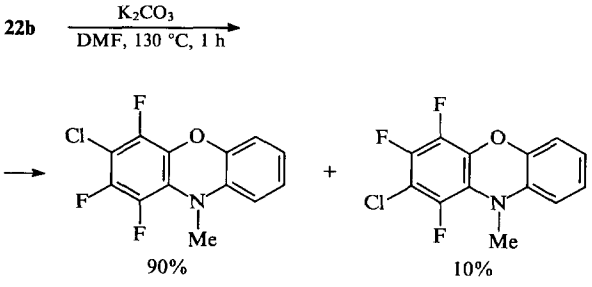



Scheme 5

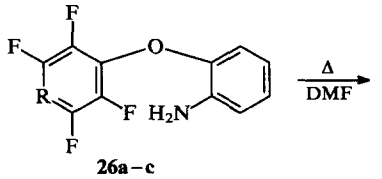



substitution of the fluorine atom in the 2-position in the fluorinated ring without the Smiles rearrangement. Such a change in the reaction path in the case of compounds containing more nucleophilic reaction centres ($NH_2$ and MeNH groups) is caused, in our view, by the greater difficulty in the second stage of process *b*, namely the deprotonation of the spiro-complex **23**. An essential condition for the occurrence of path *a* is the reversibility of the stage involving the formation of this complex.

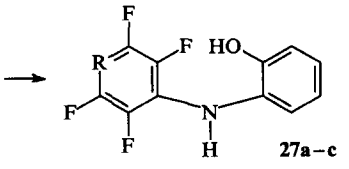
As already mentioned in the preceding section, examples of the Smiles rearrangement with deprotonation of the spiro-complex as the rate-limiting stage have been described in the literature. It has been shown that such processes are susceptible to general base catalysis.[26–28] Accordingly, the introduction of potassium carbonate into the reaction of the ether **22b** drives the process predominantly via path *b*.



The only argument in support of the occurrence of the Smiles rearrangement in the case of the ethers **22a–c** is the structure of the phenoxazine derivatives formed from them. The corresponding aryl(*o*-hydroxyaryl)amines **25**—the rearrangement products—were not detected in the reaction mixtures. Presumably the introduction into the *para*-position of the fluorinated aromatic ring of the diphenyl ether molecule of an additional electron-accepting group, increasing the electrophilicity of the reaction centre 1 compared with the centre 2, makes it possible to reduce the reaction temperature and to stop the process at the rearrangement stage. Indeed, heating in DMF of type **26** ethers, containing a powerful electron acceptor in the *para*-position relative to the oxygen atom, led to the formation of the isomeric aryl(*o*-hydroxyaryl)amine **27**. Analysis of the $^{19}F$ NMR spectra of the reaction mixtures showed that the rearrangement is the only type of reaction.[45,46]




**26a–c**




**27a–c**

R = C—$NO_2$, C—$CF_3$, N

This made it possible to measure the rate of reaction of the ethers **26** when they are kept in DMF in the temperature range 60–120 °C and to estimate in this way their relative capacities for the Smiles rearrangement. The reaction rate constants were calculated from the first-order equation

$$k = \frac{1}{t}\ln\left(\frac{c_0}{c}\right) = \frac{1}{t}\ln\left(1 + \frac{H_a}{H_e}\right),$$

where $t$ is the time, $H_a$ is the integral intensity at the signals due to the F(3) and F(5) atoms [or F(2) and F(6)] in the $^{19}F$ NMR spectrum of the amine **27**, and $H_e$ is the integral intensity of the signal due to the F(6) and F(5) atoms [or F(2) and F(6)] in the $^{19}F$ NMR spectrum of the ether **26** (Table 2).

**Table 2.** The rate constants for the rearrangement of the *o*-aminoaryl aryl ethers 4-$RC_6F_4OC_6H_4NH_2$-2′ **26a–c** in DMF.

| Compound **26** (R) | Temperature/°C | Reaction rate constant $10^4k/s^{-1}$ |
|---|---|---|
| **26a** (C–$NO_2$) | 60 | 2.17 |
| | 70 | 3.93 |
| | 80 | 7.59 |
| | 90 | 12.20 |
| **26b** (C–$CF_3$) | 90 | 0.12 |
| | 100 | 0.21 |
| | 110 | 0.53 |
| | 120 | 1.03 |
| **26c** (N) | 70 | 0.82 |
| | 80 | 1.66 |
| | 90 | 3.34 |
| | 100 | 7.21 |

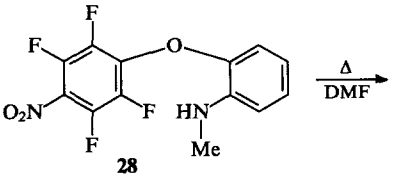
The activating effect of the group R in the rearrangement of the ether **26** increases in the sequence (the relative rate constants at 90 °C are indicated in brackets) C–$CF_3$(1) < N(27) < C–$NO_2$(100) and corresponds to the influence of these groups on the rate of the nucleophilic substitution of the fluorine atom by an amino-group in aromatic polyfluoro-compounds.[47,48]

Roberts and coworkers[9,29] noted the activating effect of water on the rearrangement of *o*-aminophenyl phenyl ethers in aprotic solvents. At the same time, it is known that the addition of water to polar aprotic solvents can reduce the rate of the Smiles rearrangement.[28] Kinetic measurements on the rearrangement of the ethers **26** in DMF containing 20% of water showed that its influence on the rate of reaction is determined by the nature of the substituent R (Table 3). A catalytic effect has been observed for compounds **26a, c**. As in the case of 2-amino-4-methylphenyl 2,4-dinitrophenyl ether,[9] it may be due to the formation of hydrogen bonds with a substituent and the consequent enhancement of its electron-accepting properties. In conformity with this hypothesis, the rate of rearrangement of the ether **26b**, containing the $CF_3$ group in the molecule, is somewhat lower in aqueous DMF than in dry DMF.[46]

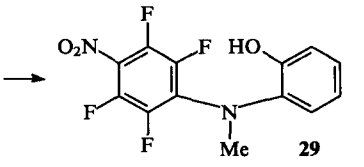
**Table 3.** The rate constants for the rearrangement of the *o*-aminoaryl aryl ethers 4-$RC_6F_4OC_6H_4NH_2$-2′ **26a–c** in the 80:20 DMF–$H_2O$ mixture.

| Compound **26** (R) | Temperature/°C | $10^4k/s^{-1}$ | $\frac{k_{DMF\cdot H_2O}}{k_{DMF}}$ |
|---|---|---|---|
| **26a** (C–$NO_2$) | 60 | 11.8 | 5.4 |
| **26b** (C–$CF_3$) | 100 | 0.15 | 0.7 |
| **26c** (N) | 70 | 1.01 | 1.2 |

The influence of *N*-substituents on the rearrangement of polyfluoro-substituted *o*-aminophenyl phenyl ethers has been investigated in relation to the derivatives of the ether **26a**.[14,42,48] The rate of rearrangement of the *N*-methyl-substituted ether **28**, which is unambiguously transformed into the isomeric amine **29** on heating in DMF, was measured by a procedure similar to that described for compound **26**.



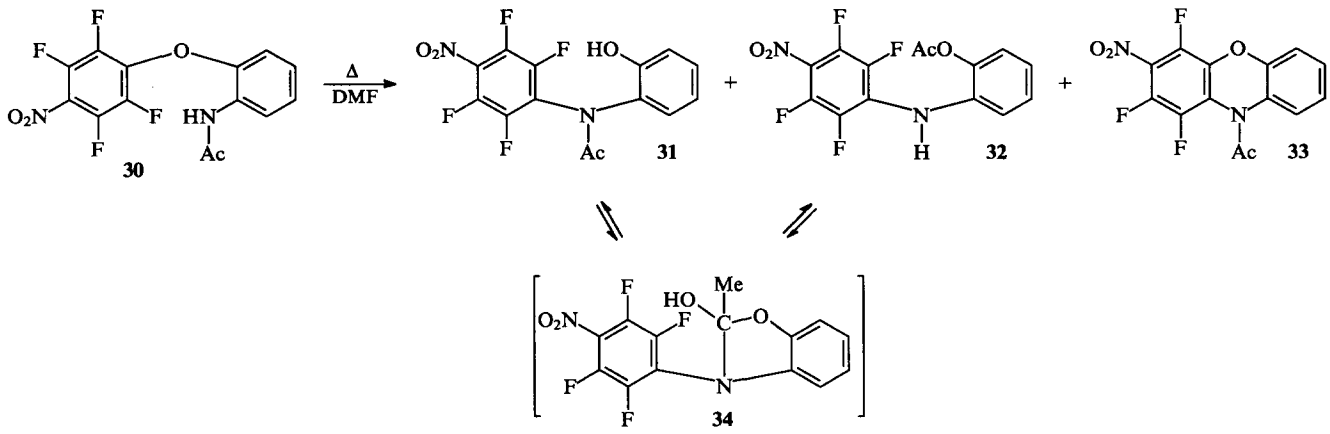

**28**




**29**

A mixture of three compounds (compounds **31–33**) has been obtained from the acetamido-substituted diphenyl ether **30**. The formation of the amine **31** indicates the occurrence of the Smiles rearrangement. The presence of compound **32** in the reaction mixture is evidence that the rearrangement is accompanied by the migration of the acetyl group from the nitrogen atom to the oxygen atom.[49,50] A similar rearrangement had been observed earlier for nonfluorinated compounds,[9,24,25] but, in contrast to its dinitro-analogue **11**, the amine **31** was not only detected in the reaction mixture but was also isolated in a pure form. The dissolution of any of the isomeric compounds **31** and **32** in DMF leads to the rapid (during the dissolution and measurement of the $^{19}F$ NMR spectra) formation of a **31**:**32** = 3:1 equilibrium

Scheme 6



mixture. The data of Pavlova and Rachinskii[51] suggest that the migration of the acetyl group from the N atom to the O atom, observed under these conditions, takes place via the cyclic structure **34** (Scheme 6).

The fact that heating of the diarylamine **31** in DMF under the conditions of the transformation of the ether **30** does not lead to the phenoxazine **33** is very interesting. The presence of the latter in the reaction mixture obtained from the ether **30** is in all probability caused by the cyclisation of the intermediate type **24** phenoxide anion (see Scheme 5).

The Smiles rearrangement precedes the formation of compounds **32** and **33**. This makes it possible to estimate its rate by studying the kinetics of the consumption of the initial ether **30**. The rate of its transformation was determined from the time variation of the integral intensities of the signals due to the fluorine atoms in the $^{19}F$ NMR spectrum. The rate constant was calculated from the first-order equation

$$k = \frac{1}{t}\ln\left(\frac{c_0}{c}\right) = \frac{1}{t}\ln\left(\frac{H_0}{H}\right),$$

where $t$ is the time, $H_0$ the initial integral intensity of the signals due to the F(3) and F(5) atoms [or F(2) and F(6)] in the $^{19}F$ NMR spectrum of the initial ether **30**, and $H$ is the integral intensity of the signals due to the same atoms in the $^{19}F$ NMR spectrum at time $t$. The rate constants found for the rearrangement of compounds **28** and **30** and the ether **26a** at 90 °C are presented in Table 4.[14]

**Table 4.** The rate constants for the rearrangement of the diaryl ethers 4-$NO_2C_6F_4OC_6H_4NHY$-2′ in DMF at 90 °C.[14]

| Compound | NHY group | Reaction rate constant, $10^4 k/s^{-1}$ |
|---|---|---|
| **26a** | $NH_2$ | 12.2 |
| **28** | NHMe | 7.40 |
| **30** | NHAc | 1.32 |

Thus both the *N*-methyl-substituted ether **28** and the *N*-acetyl derivative **30** rearrange in DMF more slowly than compound **26a** containing a free amino-group in the molecule. The observed effect of *N*-substitution may be interpreted within the framework of the mechanism based on Scheme 4 and agrees with the hypothesis, put forward above, that variation of the substituent alters the rate-limiting stage in the Smiles rearrangement. Whereas the rate-limiting stage for the acetamido-compound **30** in a neutral medium involves in all probability the formation of a type **23** zwitterionic complex, the rate of the process for compound **28**, containing the more nucleophilic *N*-methylamino-group, may be determined by deprotonation[28] and in both cases the introduction of a base into the reaction sphere should have an activating effect. Indeed the transformation of the ethers **28** and **30** in the presence of potassium carbonate takes place below room temperature. The rearrangement of the ether **26a** is apparently of an intermediate type.

Thus the use of model aromatic polyfluoro-systems combined with $^{19}F$ NMR spectroscopy made it possible to expand greatly the possibilities for the study of the Smiles rearrangement of *o*-aminophenyl phenyl ethers and to obtain primary kinetic data concerning the influence of the nature of the reactants on the rate of reaction. Further development of studies on these lines may not only make a significant contribution to investigations of the Smiles rearrangement, but will undoubtedly promote the practical employment of the reactions of aromatic polyfluoro-compounds with bifunctional nucleophiles in the synthesis of a wide variety of fluoro-substituted heteroaromatic systems.

## References


1. J F Bunett, R E Zahler *Chem. Rev.* **49** 362 (1951)
2. W E Truce, E M Kreider, W W Brand *Org. React.* **18** 99 (1970)
3. T S Stevens, W E Watts *Selected Molecular Rearrangements* (London, Beccles, Colchester: W Clowes, 1973) p. 119
4. A A Levi, L A Warren, S Smiles *J. Chem. Soc.* 3264 (1931)
5. V N Knyazev, V N Drozd, T Ya Mozhaeva *Zh. Org. Khim.* **15** 1107 (1979)
6. V N Knyazev, V N Drozd *Izv. Sib. Otd. Akad. Nauk SSSR, Ser. Khim. Nauk* (4) 43 (1983)
7. V N Knyazev, V N Drozd *Izv. Sib. Otd. Akad. Nauk SSSR, Ser. Khim. Nauk* (4) 92 (1990)
8. E Buncel, M R Crampton, M J Strauss, F Terrier *Electron Deficient Aromatic and Heteroaromatic-base Interactions* (Amsterdam: Elsevier, 1984)
9. K C Roberts, C G M de Worms *J. Chem. Soc.* 727 (1934)
10. M Ionescu, H Mantsch, in *Advances in Heterocyclic Chemistry* Vol. 8 (Eds A R Katritzky, A J Boulton) (New York: Academic Press, 1968) p. 83
11. V N Drozd *Zh. Vses. Khim. O-va im. D. I. Mendeleeva* **21** 266 (1976)
12. G E Bonvicino, L H Yogodzinski, R A Hardy Jr *J. Org. Chem.* **27** 4272 (1962)
13. M F Grundon, W L Matier *J. Chem. Soc. (B)* 266 (1966)
14. T N Gerasimova, E F Kolchina *J. Fluorine Chem.* **66** 69 (1994)
15. F Ullmann, S M Sane *Ber. Dtsch. Chem. Ges.* **44** 3730 (1911)
16. B Boothroyd, E R Clark *J. Chem. Soc.* 1499 (1953)
17. B Boothroyd, E R Clark *J. Chem. Soc.* 1504 (1953)
18. H Musso *Chem. Ber.* **96** 1927 (1963)
19. H J Shine, S Wu *J. Org. Chem.* **44** 3310 (1979)
20. V N Knyazev, V N Drozd, T Ya Mozhaeva *Zh. Org. Khim.* **16** 876 (1980)
21. O L Brady, C Waller *J. Chem. Soc.* 1218 (1930)

22. G E Bonvicino, L H Yogodzinski, R A Hardy Jr *J. Org. Chem.* **26** 2797 (1961)
23. K C Roberts, C G M de Worms *J. Chem. Soc.* 1309 (1935)
24. J Skarzewski, Z Skrowaczewska *Tetrahedron* **32** 1221 (1976)
25. K C Roberts, H B Clark *J. Chem. Soc.* 1312 (1935)
26. K Bowden, P R Williams *J. Chem. Soc., Perkin Trans. 2* 215 (1991)
27. A C Knipe, J Lound-Keast, N Sridhar *J. Chem. Soc., Perkin Trans. 2* 1885 (1984)
28. A C Knipe, N Sridhar, J Lound-Keast *J. Chem. Soc., Perkin Trans. 2* 1893 (1984)
29. K C Roberts, C G M de Worms, H B Clark *J. Chem. Soc.* 196 (1935)
30. K C Roberts, J A Rhys *J. Chem. Soc.* 39 (1937)
31. T Harayama, K Okada, S Sekiguchi, K Matsui *J. Heterocycl. Chem.* 7 981 (1970)
32. US P. 3 850 931; *Chem. Abstr.* **82** 140 165 (1975)
33. R Budziarek *J. Chem. Soc., Chem. Commun.* 1427 (1968)
34. O R Rodig, R E Collier, R K Schlatzer *J. Org. Chem.* **29** 2652 (1964)
35. D M Schmidt, G E Bonvicino *J. Org. Chem.* **49** 1664 (1984)
36. E A Nodiff, M Hausman *J. Org. Chem.* **29** 2453 (1964)
37. R R Gupta, M Kumar, in *Bioactive Molecules* Vol. 4 (Ed. R R Gupta) (Amsterdam: Elsevier, 1988) p. 19
38. G G Yakobson, G G Furin, L S Kobrina, N N Vorozhtsov, Jr *Zh. Obshch. Khim.* **37** 1285 (1967)
39. A E Borodin, B F Malichenko *Dokl. Akad. Nauk Ukr. SSR, Ser. B* 710 (1978)
40. T V Mikhalina, E F Kolchina, T N Gerasimova, E P Fokin *Izv. Sib. Otd. Akad. Nauk SSSR, Ser. Khim. Nauk* (1) 113 (1984)
41. E F Kolchina, I Yu Kargapolova, T N Gerasimova *Izv. Akad. Nauk SSSR, Ser. Khim.* 1855 (1986)
42. E F Kolchina, T N Gerasimova *Izv. Akad. Nauk, Ser. Khim.* 1101 (1993)
43. L S Kobrina *Fluorine Chem. Rev.* 7 1 (1974)
44. R D Chambers, D Close, D Lyn, H Williams *J. Chem. Soc., Perkin Trans. 2* 778 (1980)
45. T N Gerasimova, E F Kolchina, I Yu Kargapolova *Izv. Akad. Nauk SSSR, Ser. Khim.* 2814 (1987)
46. E F Kolchina, T N Gerasimova *J. Fluorine Chem.* **41** 345 (1988)
47. R D Chambers, P A Martin, J S Waterhouse, D L Williams, B Anderson *J. Fluorine Chem.* **20** 507 (1982)
48. V V Bardin, O N Loginova, G G Furin *Izv. Sib. Otd. Akad. Nauk SSSR, Ser. Khim. Nauk* (1) 77 (1988)
49. E F Kolchina, T N Gerasimova *Izv. Akad. Nauk SSSR, Ser. Khim.* 850 (1990)
50. E F Kolchina, T N Gerasimova *Izv. Akad. Nauk SSSR, Ser. Khim.* 846 (1990)
51. L V Pavlova, F Yu Rachinskii *Usp. Khim.* **37** 1369 (1968) [*Russ. Chem. Rev.* **37** 587 (1968)]