Journal of Organometallic Chemistry 694 (2009) 2476–2479

Contents lists available at ScienceDirect

Journal of Organometallic Chemistry

journal homepage: www.elsevier.com/locate/jorganchem

1-Fluorosilatrane synthesis from SiF_4 complexes and its properties

Sergey A. Lermontov [a,*], Alena N. Malkova [a], El'mira Kh. Lermontova [b], Andrei V. Churakov [b]

[a] Institute of Physiologically Active Compounds of Russian Academy of Sciences, Severny proezd 1, 142432 Chernogolovka, Moscow region, Russia
[b] N.S. Kurnakov Institute of General and Inorganic Chemistry of Russian Academy of Sciences, Leninskii Prospect 31, 119991 Moscow, Russia

ARTICLE INFO

Article history:
Received 18 February 2009
Received in revised form 13 April 2009
Accepted 17 April 2009
Available online 23 April 2009

Keywords:
Silicon tetrafluoride
1-Fluorosilatrane
Silicon dioxide

ABSTRACT

A new method of 1-fluorosilatrane synthesis on the basis of silicon tetrafluoride complexes obtained from SiO_2 is offered. Chemical properties of 1-fluorosilatrane in reactions of nucleophilic substitution are investigated. It is shown that fluorine can be substituted by O-nucleophiles (lithium methoxide, isopropoxide and phenoxide) and C-nucleophile (lithium phenylacetylenide).

1. Introduction

Silicon halides SiX_4 (X = Cl, Br, I), especially $SiCl_4$, are widely used as starting materials for the preparation of different organosilicon compounds [1]. The use of SiF_4 in organoelement synthesis is practically not investigated. It is known that SiF_4 reacts slowly with alcohols in a presence of bases forming silicon esters in a low yield [2] and reacts with Grignard reagents affording mainly triorganofluorosilanes [3] (Scheme 1).

We could find only a few examples of SiF_4 application in organic synthesis: as a catalyst in carbohydrates chemistry [4], a reagent for a mild epoxide ring opening [5] and for a preparation of alkylfluorides from orthoformates [6].

We have shown recently that SiO_2 easily reacts with alcoholic solutions of hexafluoropropene oxide or carbon acids fluoroanhydrides at room temperature with a formation of SiF_4 alcoholic complexes **1** [7]. These complexes can be further transformed into **2–3** type SiF_4 derivatives (Scheme 2).

Different SiF_4 complexes are well documented in literature [8,9], but we could not find any data concerning the use of such complexes in organoelement synthesis. The main goal of this work is the use of complexes **1–3** in organosilicon chemistry. In a case of success it could give a possibility of low temperature SiO_2 application as a starting material for a preparation of organosilicon compounds.

2. Results and discussion

2.1. 1-Fluorosilatrane synthesis

The main problem in silicon tetrafluoride chemistry is that SiF_4 is a very stable molecule (Si–F bond energy is 585 kJ/mol) and its destruction can be achieved only by a formation of some even more stable substances. We came to a conclusion that silatranes –pentacoordinate silicon compounds, stabilized by intramolecular Si–N bond – can be the desired type of strong silicon compounds (Fig. 1).

We have found that **1–3** complexes prepared from SiO_2 react with triethanolamine with the formation of hardly available 1-fluorosilatrane **4**. The reaction proceeds at 160–170 °C in a presence of SiO_2 affording compound **4** in a high yield (up to 86%) (Scheme 3). SiO_2 serves as a silicon source and as an acceptor of excessive fluoride; as a result all silicon in 1-fluorosilatrane **4** is taken from SiO_2. Tetraethylorthosilicate can also be used as fluoride acceptor. In this case only 25% of silicon in 1-fluorosilatrane **4** is taken from SiO_2 but the reaction proceeds at lower temperature (reflux in ethanol) (Scheme 3).

Earlier 1-fluorosilatrane was prepared by the nucleophilic substitution of ethoxy-groups in ethoxysilatrane [10–12]. Works describing the preparation of 1-fluorosilatrane from phenyltrifluorosilane [13] or gaseous SiF_4 [14] and triethanolamine show very few experimental details and 1-fluorosilatrane identification. A very convenient preparative 1-fluorosilatrane synthesis using $Si(OEt)_4$ as a silicon source have been recently published by Voronkov et al. [15].

* Corresponding author. Tel./fax: +7 496 524 9508.
E-mail addresses: lermon@ipac.ac.ru, malkova@ipac.ac.ru (S.A. Lermontov).

0022-328X/$ - see front matter © 2009 Elsevier B.V. All rights reserved.
doi:10.1016/j.jorganchem.2009.04.016

$$3\ SiF_4 + 4\ ROH \longrightarrow Si(OR)_4 + 2\ H_2SiF_6$$
$$SiF_4 + 3\ PhMgBr \longrightarrow FSiPh_3 + 3\ MgFBr$$

Scheme 1.

2.2. 1-Fluorosilatrane properties

1-Fluorosilatrane **4** properties were almost not studied. It was shown earlier that it is slightly soluble in methyl alcohol.

We have found that 1-fluorosilatrane **4** is a colorless stable compound, soluble in water, dimethylformamide, dimethylsulfoxide, slightly soluble in methyl and ethyl alcohols, tetrahydrofuran, CH_3CN и $CHCl_3$. It can be easily purified by sublimation in vacuum. Its ^{19}F NMR spectrum in D_2O differs significantly from that in Me_2SO-d_6 and CD_3CN probably due to hydrogen bonding.

1-Fluorosilatrane **4** is soluble in hexafluoroisopropyl alcohol at heating, but after the solvent removal solvates of 1-fluorosilatrane **4** with hexafluoroisopropyl alcohol are formed. These solvates are quite stable at room temperature but are destroyed at heating up to 100 °C in vacuum.

We decided to study chemical properties of 1-fluorosilatrane **4** to understand whether it is possible to use this easily obtained from SiO_2 compound in organosilicon synthesis. The main interest for us was a possibility of nucleophilic substitution of fluorine atom in **4** that could give the way to different silatranes.

The silatranes' structure determines their rather low reactivity in nucleophilic substitution reactions [10,16]. The classical S_N2 substitution mechanism can not be applied because a backside attack of a nucleophile is impossible.

Earlier nucleophilic substitution reactions of halogen at silicon atom were studied for iodo-, bromo- and chlorosilatranes [11,17], and it was shown that 1-iodosilatrane had the highest reactivity. The reactivity of 1-bromo- and 1-chlorosilatranes is essentially lower. We expected that 1-fluorosilatrane **4** would have the lowest reactivity among other halosilatranes and it would be necessary to use specific conditions for a nucleophilic substitution of fluorine atom.

We have found that 1-fluorosilatrane **4** reacts with lithium methoxide in methyl alcohol and with lithium isopropoxide in isopropyl alcohol at 220 °C forming 1-metoxysilatrane **5** and 1-isopropoxysilatrane **6** in a good yield (86% and 57%, respectively) (Scheme 4). Our attempt to reduce the reaction temperature to 170 °C resulted in an essential yield decrease. It is interesting to note that sodium methoxide did not react with **4** at all.

1-Fluorosilatrane **4** reacts also with lithium phenoxide but under even more rigid conditions. Reaction in methyl alcohol at 220 °C did not give even traces of 1-phenoxysilatrane **7**. 1-Phenoxysilatrane **7** was prepared by heating of solid reagents in a glass ampoule at 220 °C in a 85% yield (Scheme 4).

We have also found that 1-fluorosilatrane **4** reacts with a C-nucleophile – lithium phenylacetylenide. This reaction proceeds at room temperature and results in a formation of the substituted silatrane **8**, containing Si–C bond (Scheme 4).

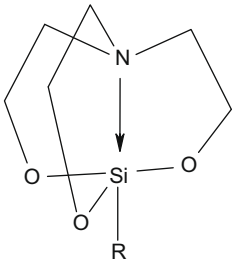


Fig. 1. General silatrane formula.

In accordance with our expectations the 1-fluorosilatrane **4** reactivity is lower than that of other 1-halosilatranes. The following conclusions can be made:

1. The cation role is very important. Lithium ion which forms insoluble lithium fluoride renders an electrophilic assistance to an elimination of fluorine atom. This conclusion is confirmed by a high yield in a reaction with lithium methoxide and by the absence of 1-methoxisilatrane in a reaction with sodium methoxide.
2. The rate limiting step is a Si–O bond cleavage leading to an intermediate silatrane ring opening. The O–C–C fragment is a leaving group at this step; it is easily substituted by a much stronger nucleophile (LiC≡CPh) at room temperature, but very rigid reaction conditions are needed for the substitution by a weaker phenolate anion (Scheme 5).

3. Conclusion

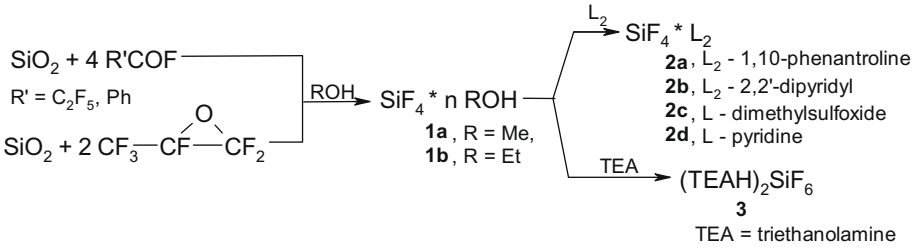
1-Fluorosilatrane **4** easily prepared from SiO_2 is a quite suitable compound for a synthesis of different silatranes containing organic substituent at a silicon atom. It is necessary to note that alkoxy- and aroxysilatranes prepared from 1-fluorosilatrane **4** can be easily transformed into organosilicon compounds without a silatranyl fragment [17a,18]. It makes 1-fluorosilatrane **4** a possible intermediate in organosilicon synthesis based on SiO_2.

4. Experimental

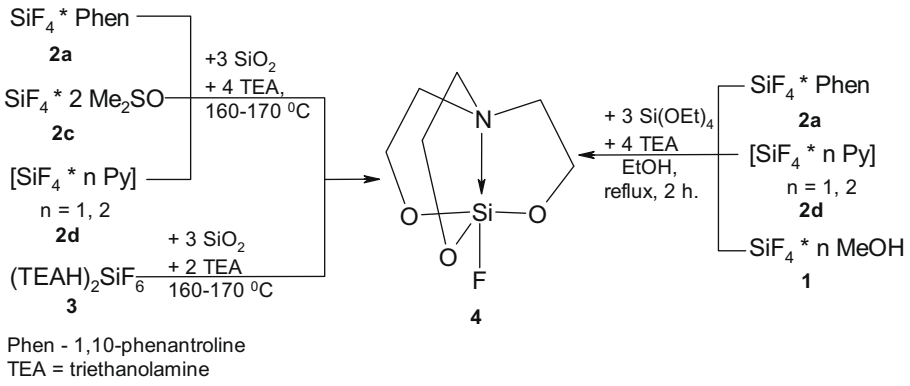
4.1. General

NMR spectra were recorded on a Bruker DPX-200 spectrometer. Proton shifts are reported in δ units downfield from Me_4Si, with the solvent as the reference signal. $CClF_3$ was used as a reference for the ^{19}F NMR. Mass spectra were recorded on a Finnigan MATINCOS 50 mass spectrometer (70 eV) by the direct inlet method.

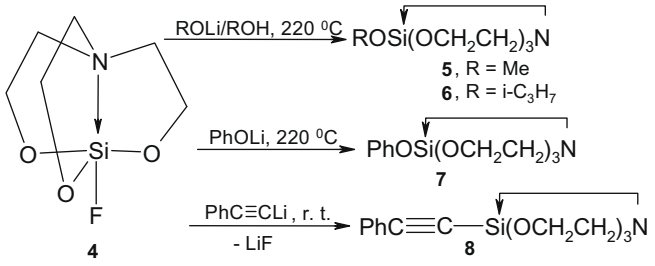
X-ray analysis was performed on a Bruker SMART APEX II diffractometer using graphite monochromatized Mo Kα radiation (λ = 0.71073 Å, ω-scan).



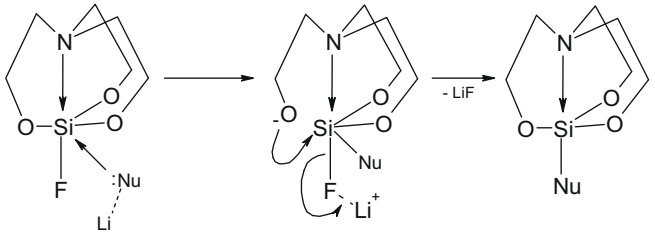
Scheme 2.



Scheme 3.



Scheme 4.



Scheme 5.

Hexafluoropropene oxide (HFPO) was a commercial product from Kirovo-Chepetsk chemical plant (Russia, 99.7% purity). Amorphous silicagel (Chemapol, L 100/250, for chromatography) was pre-dried at 150 °C during 2 h before a reaction. Triethanolamine (Merck), tetraethylorthosilicate (Merck), anhydrous methyl alcohol (Aldrich, 0.05% water content) and isopropyl alcohol (Acros, 0.1% water content) were used as purchased. Other solvents and reagents were purified and dried by standard procedures.

4.2. 1-Fluorosilatrane **4** synthesis

4.2.1. Synthesis of **1a** Intermediate

Anhydrous MeOH (10 mL) and SiO_2 (0.6 g, 0.01 mol) were placed in a PTFE flask equipped with a PTFE gas-injection tube, and hexafluoropropene oxide (HFPO) (3.32 g, 0.02 mol, determined from the weight increase) was introduced with magnetic stirring at room temperature. The reaction was slightly exothermic. After the end of HFPO addition the reaction mixture was stirred during 1 h (the whole amount of SiO_2 was dissolved).

4.2.2. Synthesis of **2a**, **2c**, **2d**, **3** complex-Intermediates

A solution of 1,10-phenanthroline (1,8 g, 0.01 mol) or Me_2SO (1.56 g, 0.02 mol) or pyridine (1.58 g, 0.02 mol) or triethanolamine (2.98 g, 0.02 mol) in anhydrous MeOH (5 mL) was added to a **1a** solution. Precipitates of compounds **2a**, **2d** and **3** were formed immediately, stored during 1 h, separated by filtration, washed with MeOH, and dried *in vacuo*. Compound **2c** was soluble in MeOH and after a solvent removal was purified by crystallization from toluene.

4.2.3. Synthesis of **4** from **2a**, **2c**, **2d**, **3** complex-Intermediates and SiO_2

SiO_2 (0.36 g, 0.006 mol), SiF_4*Phen (**2a**) (0.002 mol) (or SiF_4*2-Me_2SO (**2c**) or SiF_4*n Py (**2d**) or $(TEAH)_2SiF_6$ (**3**)) and triethanolamine (5 mL) were placed in a glass flack equipped with a reflux condenser. The reaction mixture was heated on an oil bath at 160–170 °C during 2 h with water vapor removal. After cooling the reaction mixture was treated twice by hot acetone for tar removal and a white precipitate was dried *in vacuo*. Yield: 48% from **2a**, 44% from **2c**, 86% from **2d**, 71% from **3**. Compound **4** was purified by sublimation in vacuum (1–2 mm Hg), m.p. > 235 °C. Anal. Calc. for $C_6H_{12}NO_3SiF$: C, 37.29; H, 6.29; F, 9.83. Found: C, 37.34; H, 6.34; F, 9.46%. ^{1}H NMR (200 MHz, Me_2SO-d_6): δ 2.9 (t, $^3J_{H,H}$ = 6.1 Hz, 6H, NCH_2), 3.7 (t, $^3J_{H,H}$ = 6.1 Hz, 6H, OCH_2). ^{19}F NMR (188 MHz, Me_2SO-d_6): δ −135.3 (s). $J(^{29}Si–F)$ = 125.5 Hz. ^{19}F NMR (188 MHz, D_2O): δ−120.7 (s). Mass spectrum coincided with a literature one [19].

4.2.4. Synthesis of **4** from $Si(OEt)_4$ and **2a**, **2d** complexes

$Si(OEt)_4$ (1.19 g, 0.006 mol), SiF_4*Phen (**2a**) (0.002 mol) (or SiF_4*nPy (**2d**)), anhydrous ethyl alcohol (20 mL) and triethanolamine (1.14 g, 0.008 mol) were placed in a glass flack equipped with a reflux condenser and a drying tube. The reaction mixture was refluxed during 2 h. A precipitate was separated by filtration, washed with EtOH, and dried *in vacuo*. Yield: 56% from **2a**, 94% from **2d**.

4.2.5. Synthesis of **4** from **1a**, $Si(OEt)_4$ and triethanolamine

Complex **1a**, obtained from SiO_2 (0.3 g, 0.005 mol) and hexafluoropropene oxide (1.66 g, 0.01 mol) in anhydrous MeOH (10 mL) was placed in a quartz flack. Then $Si(OEt)_4$ (3.12 g, 0.015 mol) and triethanolamine (2.92 g, 0.02 mol) were added. The reaction mixture was refluxed during 2 h. A precipitate of **4** was separated by filtration, washed with EtOH, and dried in vacuum. Yield 92%.

4.3. 1-Fluorosilatrane **4** properties

4.3.1. Nucleophilic substitution of fluorine atom by O-nucleophiles

Li (0.018 g, 0.0026 mol) was dissolved in anhydrous methyl or isopropyl alcohol (10 mL) and the solution was added to 1-fluorosilatrane **4** (0.5 g, 0.0026 mol). The reaction mixture was heated in a stainless steel autoclave at 220 °C during 5 h.

4.3.1.1. Compound 5 (1-metoxysilatrane). The product content in the reaction mixture was 86% (according to ^{1}H NMR data). Compound **5** was purified by a crystallization from xylene. Yield: 43%, m.p. 155–157 °C (literature data m.p. 155–156 °C [20]). ^{1}H NMR (200 MHz, $CDCl_3$): δ 2.8 (t, $^3J_{H,H}$ = 6.0 Hz, 6H, NCH_2), 3.3 (s, 3H, OCH_3), 3.7 (t, $^3J_{H,H}$ = 5.9 Hz, 6H, OCH_2). EI-MS: *m*/*z* (relative abundance, %) 205 (23) [M^+], 174 (97) [M^+–OCH_3], 162 (100), [M^+–C_2H_3O].

4.3.1.2. Compound 6 (1-isopropoxysilatrane). The product content in the reaction mixture was 57% (according to ^{1}H NMR data). Compound **6** was purified by a crystallization from xylene), m.p. 128–130 °C (literature data m.p. 129.5–131 °C) [19]. ^{1}H NMR (200 MHz, $CDCl_3$): δ 1.2 (d, $^3J_{H,H}$ = 6.05 Hz, 6H, CH_3), 2.9 (t, $^3J_{H,H}$ = 5.8 Hz, 6H, NCH_2), 3.9 (t, $^3J_{H,H}$ = 5.8 Hz, 6H, OCH_2), 4.1 (heptet, 1H, O–CH). EI-MS: *m*/*z* (relative abundance, %) 233 (25) [M^+], 218 (38) [M^+–CH_3], 190 (14) [M^+–C_2H_3O] and 174 (100) [M^+–OC_3H_7].

4.3.1.3. Compound 7 (1-phenoxysilatrane). 1-Fluorosilatrane **4** (0.5 g, 0.0026 mol) and lithium phenolate (0.26 g, 0.0026 mol) (prepared from phenol and lithium in methanol) were sealed in a glass ampoule and the ampoule was heated at 220 °C during 6 h. After cooling the ampoule was opened and the reaction mass was extracted by CH_3CN. The solvent and excessive phenol were removed *in vacuo*. The yield of crude **7** was 86%.

Compound **7** was purified by a crystallization from xylene, m.p. 228–229 °C (literature data m.p. 228–229.5 °C [21]). ^{1}H NMR (200 MHz, $CDCl_3$): δ 2.9 (t, $^3J_{H,H}$ = 6.1 Hz, 6H, NCH_2), 3.9 (t, $^3J_{H,H}$ = 6.1 Hz, 6H, OCH_2), 6.9 (t, 1H), 7.1 (d, 2H), 7.2 (t, 2H). EI-MS: *m*/*z* (relative abundance, %) 267 (18) [M^+] and 174 (100) [M^+–PhO].

4.3.2. Nucleophilic substitution of fluorine atom by C-nucleophile-lithium phenylacetylenide

Lithium phenylacetylenide was prepared from butyl lithium (0.003 mol of 0.77 M) and phenylacetylene (0.26 g, 0.0026 mol) in tetrahydrofuran at ambient temperature. 1-Fluorosilatrane **4** (0.5 g, 0.0026 mol) was added and the reaction mixture was stirred during 24 h.

4.3.2.1. Compound 8. Compound **8** was isolated after filtration and solvent removal in a 75% yield. It was purified by a crystallization from benzene. ^{1}H NMR (200 MHz, $CDCl_3$): δ 2.9 (t, $^3J_{H,H}$ = 5.9 Hz, 6H, NCH_2), 3.9 (t, $^3J_{H,H}$ = 5.9 Hz, 6H, OCH_2), 7.3 (m, 3H); 7.6 (m, 2H). EI-MS: *m*/*z* (relative abundance, %) 275 (78) [M^+], 232 (10) [M^+–C_2H_3O] and 174 (12) [M^+–PhC≡C].

A single crystal structure of compound **8** was determined by X-ray diffraction and was found to be the same as the previous literature data [22].

References

[1] D. Neville Jones (Ed.), Comprehensive organic chemistry, Pergamon Press Ltd., 1979, vol. 3, Selenium, Silicon, Boron, Compounds.
[2] (a) West Germany Patent DE 946893, 9.08.1956.;
(b) West Germany Patent DE 1002748, 25.07.1957.;
(c) West Germany Patent DE 955236, 3.01.1957.;
(d) British Patent GB 901676, 25.07.1962.;
(e) British Patent GB 866766, 3.05.1961.
[3] (a) G.V. Medoks, N.Z. Kotelkov, Russ. J. Gen. Chem. (RUS) 7 (1937) 2007–2008. CA 32 (1938) 531–534;
(b) G.V. Medoks, Russ. J. Gen. Chem. (RUS) 8 (1938) 291–293. CA 32 (1938) 5392–5393;
(c) J.A. Gierut, F.J. Sowa, J.A. Nieuwland, JACS 58 (1936) 897–898.
[4] S. Hashimoto, M. Hayashi, R. Noyori, Tetrahedron Lett. 25 (1984) 1379–1382.
[5] M. Shimuzu, H. Yoshioka, Tetrahedron Lett. 30 (1989) 967–970.
[6] K.G. Mason, J.A. Sperry, E.S. Stern, J. Chem. Soc. (1963) 2558–2559.
[7] (a) Russian Patent RU No. 2319665, 26.05.2006.;
(b) A.S. Lermontov, A.N. Malkova, Russ. Chem. Bull. 56 (2007) 435–437.
[8] A.A. Ennan, B.M. Kats, Russ. Chem. Rev. 43 (1974) 539–550.
[9] M.G. Voronkov, L.I. Gubanova, Main Group Met. Chem. 10 (1987) 209–286.
[10] C.L. Frye, G.A. Vincent, W.A. Finzel, J. Am. Chem. Soc. (1971) 6805–6811.
[11] M.G. Voronkov, V.P. Baryshok, L.P. Petukhov, V.I. Rakhlin, R.G. Mirskov, V.A. Pestunovich, J. Organomet. Chem. 358 (1988) 39–55.
[12] M.G. Voronkov, G.A. Kuznetsova, A.A. Trukhina, Russ. J. Gen. Chem. 76 (2006) 1968–1969.
[13] M.G. Voronkov, A.I. Albanov, E.A. Grebneva, O.M. Trofimova, N.F. Chernov, N.N. Chipanina, Russ. J. Gen. Chem. 76 (2006) 1854–1859.
[14] M.G. Voronkov, E.A. Grebneva, O.M. Trofimova, A.I. Albanov, N.F. Chernov, N.N. Chipanina, Russ. J. Gen. Chem. 76 (2006) 1851–1853.
[15] M.G. Voronkov, T.A. Kochina, D.V. Vrazhnov, M.Yu. Litvinov, Russ. J. Gen. Chem. 78 (2008) 2160–2161.
[16] M.G. Voronkov, V.M. Djakov, Silatranes (RUS), Novosibirsk, Nauka, 1978, p. 206.
[17] (a) C. Chuit, R.J.P. Corriu, C. Reye, J.C. Young, Chem. Rev. 93 (1993) 1371–1448;
(b) G. Cerveau, C. Chuit, R.J.P. Corriu, N.K. Nayyar, C. Reye, J. Organomet. Chem. 389 (1990) 159–168.
[18] T. Kemmitt, W. Henderson, Aust. J. Chem. 51 (1998) 1031–1035.
[19] L. Parkanyl, P. Hencsei, L. Binatsi, T. Muller, J. Organomet. Chem. 269 (1984) 1–9.
[20] M.G. Voronkov, G.I. Zelchan, Chem. Heterocycl. Compd. 1 (1965) 137–140.
[21] M.G. Voronkov, G.I. Zelchan, Chem. Heterocycl. Compd. 2 (1967) 381–384.
[22] A.A. Selina, S.S. Karlov, E.V. Gauchenova, A.V. Churakov, L.G. Kuz'mina, J.A.K. Howard, J. Lorberth, G.S. Zaitseva, Heteroat. Chem. 15 (2004) 43–56.