

ELECTROREDUCTIVE ADDITIONS OF AROMATIC DICHALCOGENIDES TO FLUORINATED ETHENES

David DVORAK^{b1}, Eva NEUGEBAUEROVA^a, Frantisek LISKA^{a1} and Jiri LUDVIK^{b2,*}

^a Department of Organic Chemistry, Prague Institute of Chemical Technology, 166 28 Prague 6, Czech Republic; e-mail: ¹ frantisek.liska@vscht.cz

^b J. Heyrovsky Institute of Physical Chemistry, Academy of Sciences of the Czech Republic, 182 23 Prague 8, Czech Republic; e-mail: ¹ david.dvorak@post.cz, ² ludvik@jh-inst.cas.cz

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Intermediates and products formed during the electrochemical reduction of diphenyl disulfide (**1**) add to chlorotrifluoroethene (**3**) under the formation of 2-chloro-1,1,2-trifluoroethyl phenyl sulfide (**5**) and the *E/Z* isomers of 2-chloro-1,2-difluoroethyl phenyl sulfide (**6**). The analogous reaction with 1,2-dichlorodifluoroethene (**4**) led to a mixture of *E/Z* isomers of **6**. Electrochemically reduced diphenyl diselenide (**2**) reacted with **3** giving rise to 2-chloro-1,1,2-trifluoroethyl phenyl selenide (**7**) whereas the reaction with **4** does not proceed. Addition of disulfide **1** to **4** gives evidence of the participation of the radical PhS[•]. With diselenide **2**, an analogous radical addition reaction was not observed. This is consistent with other experiments suggesting different mechanisms of reductive cleavage of the S–S and Se–Se bonds and the absence of radicals PhSe[•] in the latter.

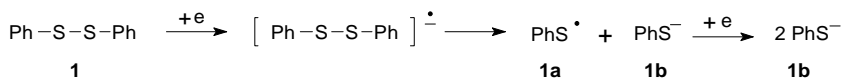
Key words: Electrochemistry; Diphenyl dichalcogenides; Diphenyl disulfide; Diphenyl diselenide; Chlorofluoroethenes; Electroreductive addition.

When investigating electrochemical reduction of dichalcogenides on mercury electrodes in nonaqueous solutions different reduction patterns are observed¹ for diphenyl disulfide (**1**) and diphenyl diselenide (**2**). It has been demonstrated that **1** undergoes a two-electron reduction by the ECE (electrode–chemical–electrode) mechanism, *i.e.*, the first electron transfer to **1** is followed by the decay of the formed radical anion to the phenylsulfanyl radical **1a** and anion **1b**. Polarographic (cyclic voltammetric) treatment gives a single irreversible two-electron wave (peak). The existence of radical **1a** has been proved by electrochemically generated luminiscence² (ECL). Accepting a further electron, radical **1a** transforms to anion **1b** (Scheme 1).

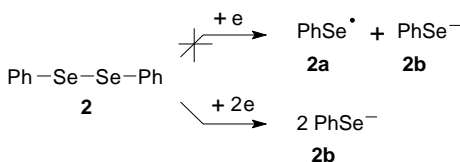
Electrochemical reduction of diphenyl diselenide (**2**) is also associated with the transfer of two electrons. In contrast to the disulfide case, the reduction of **2** takes place

* The author to whom correspondence should be addressed.

in two reversible waves¹. The formation of phenylselanyl radical **2a** has not been proved yet, only anion **2b** as the final product has been found³ (Scheme 2).

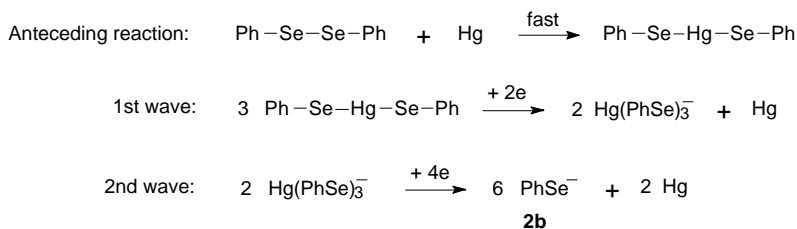


SCHEME 1



SCHEME 2

The difference in the dichalcogenide reduction pathways is due to the fact that whereas disulfide **1** (or the product of its interaction with mercury) is adsorbed on the mercury electrode, diselenide **2** reacts with mercury in nonaqueous medium spontaneously⁴ giving rise to Ph-Se-Hg-Se-Ph, which is in turn reduced to selanyl anion **2b**. (Scheme 3).



SCHEME 3

Phenylsulfanyl anion **1b** formed during the cathodic reduction can be employed in alkylation and acylation reactions⁵, the analogously formed phenylselanyl anion **2b** has been used in alkylations and in ring opening of oxiranes⁶, in nucleophilic additions to α,β -unsaturated carbonyl compounds⁷ or in aromatic substitutions proceeding by the $S_{RN}1$ mechanism^{8,9}.

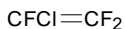
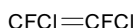
Fluorinated alkenes generally undergo additions of compounds of various kinds under conditions of radical, nucleophilic, electrophilic and cycloaddition reactions¹⁰⁻¹³. Chlorotrifluoroethene $\text{CFCl}=\text{CF}_2$ (**3**) affords addition products in all of these reaction types. This compound also enters into addition reactions with ketyl radicals formed by reduction of acetone at a mercury cathode under acidic conditions¹⁴, and the product is the same as that formed in the photochemical¹⁵ and radiation-induced¹⁶ addition of propen-2-ol.

Unlike **3**, 1,2-dichlorodifluoroethene (**4**) is nonreactive in nucleophilic additions; this fact has been used, for instance, in separation of a mixture¹⁷ where symmetric alkene **4**

was accompanied by its nonsymmetric isomer $\text{CF}_2=\text{CCl}_2$; only the latter undergoes nucleophilic addition of alcohols.

Regarding organic chalcogen compounds, radical¹⁸ and nucleophilic^{19–21} additions of alkanethiols and arenethiols to ethene **3** have been examined. In both cases, the transient alkylsulfanyl radicals RS^\bullet or alkylsulfanyl or arylsulfanyl anions (RS^- , ArS^-) were added to the CF_2 groups of **3**. Alkyl or aryl 2-chloro-1,1,2-trifluoroethyl sulfides were the major products. In addition, telomers have also been isolated from the products of the photochemically initiated reactions¹⁸. Corresponding chlorofluoroethyl phenyl sulfides and selenides are also formed by the electrophilic addition of chloro(phenyl)sulfanes and chloro(phenyl)selenanes to **3** (ref.²²). On the other hand, alkyl 1,2-dichloro-1,2-difluoroethyl sulfides, formed as sole products in the radiation-initiated addition of alkanethiols to **4**, have been identified and described unambiguously²³.

Two goals were pursued in the present work: (i) the synthetic goal, aimed at employing the reductive addition of electrochemically generated intermediates to fluoroenes for the synthesis of fluorinated sulfides and selenides, and (ii) the mechanistic goal, giving the opportunity to prove the occurrence of radical intermediates chemically and thus to evidence different pathways of cathodic reduction of dichalcogenides **1** and **2**. Chlorotrifluoroethene (**3**) and 1,2-dichlorodifluoroethene (**4**) were chosen as the substrates. Note that as a prerequisite for the reaction to occur, the two dichalcogenides must be reduced at appreciably more positive potentials than the fluorinated ethenes: $E_{1/2}\mathbf{1} = -0.91$ V, $E_{1/2}\mathbf{2} = -0.32$ V (1st wave), or -0.905 V (2nd wave), $E_{1/2}\mathbf{3} = -1.95$ V, $E_{1/2}\mathbf{4} = -2.49$ V vs saturated calomel electrode²⁴ (SCE). This allows the reagent to be generated in the mixture selectively, without reducing substrate **3** or **4**.

**3****4**

EXPERIMENTAL

Apparatus and Chemicals

The potentiostatic electrolyses were performed in a special three-compartment electrochemical cell with a working volume of 20 ml, enabling voltammetric measurements during the electrolysis. A stirred mercury pool (mercury for polarography, Merck, Germany) served as the working electrode, the reference electrode was SCE and the auxiliary electrode was a platinum sheet. Electrochemical potentiostat PAR Model 173 and 175 interfaced to a Model 178 integrator were employed for the controlled potential electrolysis and charge consumption monitoring. Electroadditions proceeded in anhydrous acetonitrile (VEB Apolda, Germany), which was purified by a proven procedure²⁵. Tetraethylammonium perchlorate and tetraethylammonium hexafluorophosphate (Fluka, Switzerland, used as received), both at a concentration of 0.2 mol l^{-1} , were used as the supporting electrolyte. Oxygen was removed from the solution by argon purging (Linde). Cyclic voltammetry was performed with a Metrohm hanging mercury drop electrode (HMDE) in a 5 ml cell (SCE – reference electrode, Pt wire – auxiliary electrode) using the same potentiostat at velocities 50 to 500 mV s^{-1} .

Diphenyl disulfide and diphenyl diselenide (both Merck, Germany) were used as received, in concentrations about 2.10^{-2} mol l^{-1} . Chlorotrifluoroethene was obtained from Spolchemie Usti nad Labem, Czech Republic, and 1,2-dichlorodifluoroethene was prepared following ref.²⁴.

TLC analyses were performed on silica gel 60 F₂₅₄ aluminium sheets (Merck, Germany). NMR spectra in deuterochloroform were scanned on a Bruker AM 400 MHz spectrometer; working frequencies for ¹H, ¹⁹F and ⁷⁷Se were 400.13, 376.50 and 76.31 MHz, respectively. Tetramethylsilane, trichlorofluoromethane and diphenyl diselenide served as the respective internal standards. Chemical shifts (δ -scale) are in ppm, coupling constants (J) in Hz. Infrared spectra were run on a Nicolet FTIR instrument, wavenumbers are in cm^{-1} . Melting points were not corrected.

Procedure

Electrolyses proceeded roughly to 95% conversion of the starting dichalcogenide (polarographically monitored). Fluorinated ethene **3** or **4** was fed into the solution in the gaseous state during the electrolysis, acetonitrile was distilled off and diethyl ether was added to the residue. The precipitated electrolyte was filtered off and the ethereal solution was evaporated to dryness. After dissolution in hexane, the products were separated by column chromatography on silica gel. The products were chromatographically homogeneous (TLC, GC) oils.

2-Chloro-1,1,2-trifluoroethyl Phenyl Sulfide (**5**)

GC: >95%. ¹⁹F NMR spectrum: -85.1 ddd, 1 F, ³ J (HF) = 4.6, ³ J (FF) = 19.4, ² J (FF) = 222.0 (CF-F); -90.3 ddd, 1 F, ³ J (HF) = 7.4, ³ J (FF) = 18.1, ² J (FF) = 221.3 (CF-F); -148.0 dt, 1 F, ³ J (FF) = 19.5, ² J (HF) = 48.2 (CFHCl).

2-Chloro-1,2-difluoroethyl Phenyl Sulfide (**6**)

GC: >95% of the *E/Z* mixture. ¹H NMR spectrum: 7.36 m, 3 H (H-2,4,6); 7.45 dd, 2 H, ³ J (HH) = 8.0, ⁴ J (HH) = 1.7 (H-3,5). ¹⁹F NMR spectrum, (*Z*)-isomer: -86.9 d, 1 F, ³ J (FF_{cis}) = 17.1 (S-CF); -112.8 d, 1 F, ³ J (FF_{cis}) = 17.1 (=CFCl); (*E*)-isomer: -104.1 d, 1 F, ³ J (FF_{trans}) = 140.6 (S-CF); -123.7 d, 1 F, ³ J (FF_{trans}) = 140.7 (=CFCl).

2-Chloro-1,1,2-trifluoroethyl Phenyl Selenide (**7**)

GC: >95%. ¹H NMR spectrum: 6.06 ddd, 1 H, ³ J (HF) = 4.1, ³ J (HF) = 9.0, ² J (HF) = 48.2 (CHFCI); 7.34–7.45 m, 3 H (H-2,4,6); 7.74 d, 2 H, ³ J (HH) = 7.0 (H-3,5). ¹⁹F NMR spectrum: -83.3 ddd, 1 F, ³ J (HF) = 4.1, ³ J (FF) = 20.8, ² J (FF) = 222.5 (CF-F); -89.1 ddd, 1 F, ³ J (HF) = 8.4, ³ J (FF) = 18.9, ² J (FF) = 222.6 (CF-F); -146.6 dt, 1 F, ³ J (FF) = 19.5, ² J (HF) = 47.2 (CHFCI). ⁷⁷Se NMR spectrum: 391.2 t, ² J (SeF) = 30.7. IR spectrum: 1 044 m, 1 096 s, 1 186 s, 1 271 w, 1 330 w, 1 440 m, 1 478 m, 2 855 w, 2 928 w, 3 012 w, 3 065 w. All the spectra were in accord with the published data (ref.²²).

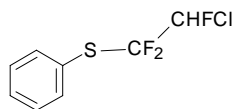
1,2-Bis(phenylselanyl)-2-chloro-1,1,2-trifluoroethane (**8**)

GC: >95%. ¹H NMR spectrum: 7.38 ddd, 2 H, ³ J (HH) = 7.2, ³ J (HH) = 7.0, ⁴ J (HH) = 1.3 (H-3,5); 7.46 m, 1 H (H-4); 7.76 dd, 2 H, ³ J (HH) = 7.1, ⁴ J (HH) = 1.5 (H-2,6). ¹⁹F NMR spectrum: -76.7 dd, 1 F, ³ J (FF) = 20.3, ² J (FF) = 207.0 (CF-F); -77.5 dd, 1 F, ³ J (FF) = 21.9, ² J (FF) = 207.7 (CF-F); -90.6 t, 1 F, ³ J (FF) = 21.1 (CFCl). ⁷⁷Se NMR spectrum: 550.9 s (SeCF₂); 637.7 d, ² J (SeF) = 47.3 (SeCFCl). IR spectrum: 1 022 s, 1 063 s, 1 166 s, 1 216 w, 1 305 w, 1 441 s, 1 477 s, 1 579 w, 1 735 w, 2 850 w, 2 928 w, 3 065 w. All the spectra were in accord with the published data (ref.²²).

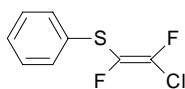
RESULTS

Addition of two dichalcogenides, diphenyl disulfide (**1**) and diphenyl diselenide (**2**), was achieved by electrolysis of their solutions in the presence of chlorotrifluoroethene (**3**) or 1,2-dichlorodifluoroethene (**4**) in acetonitrile at -1.10 V vs SCE. The addition of **1** to **3** gave mainly 2-chloro-1,1,2-trifluoroethyl phenyl sulfide (**5**) and a mixture of stereoisomeric (*Z*)- and (*E*)-2-chloro-1,2-difluoroethenyl phenyl sulfides (**6**) with the *E/Z* ratio 64 : 36 (determined on the basis of ^{19}F NMR spectra).

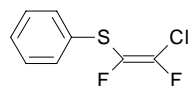
The analogous addition of **1** to **4**, the used ethene consisting of the *E* and *Z* isomers in the 48 : 52 ratio, also gave a mixture of the *E* and *Z* stereoisomers of the sulfide **6** with the *E/Z* ratio 55 : 45.



5



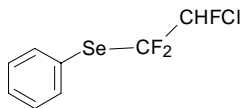
(E)-6



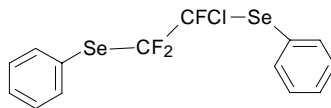
(Z)-6

A mixture of 2-chloro-1,1,2-trifluoroethyl phenyl selenide (**7**) and 1,2-bis(phenylselenyl)-2-chloro-1,1,2-trifluoroethane (**8**) was the major product of the addition of **2** to **3**.

The addition of **2** to **4** was conducted analogously, but instead of an addition product, only the starting diselenide and its complex with mercury having a melting temperature of $138\text{--}142$ °C (ref.¹) were obtained.



7



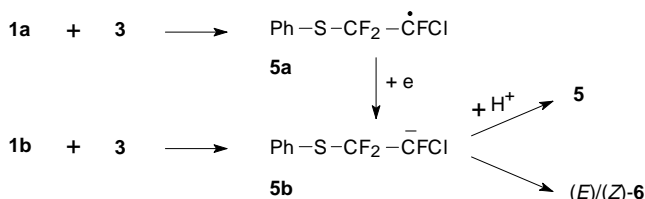
8

The structure of the reaction products **5–8** reflects the nature of the electrochemically generated intermediates which add to the double bond of the alkenes and is consistent with the observed different course of the reduction of the dichalcogenides **1** and **2** themselves. Both radical **1a** and anion **1b** can participate in the formation of products **5** and **6**. Addition of radical **1a** to **3** results in the formation of adduct-radical **5a** which is reduced further to carbanion **5b**. The latter can also arise in the nucleophilic addition of anion **1b** to **3**. Protonation transforms **5b** into adduct **5**, and the unsaturated sulfide **6** arises from the elimination of the fluoride ion from the neighbouring carbon (Scheme 4).

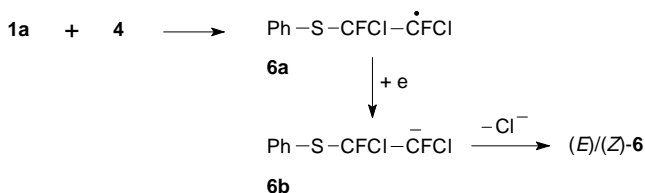
With **4**, we assume that only radical **1a** can participate in the formation of sulfide **6**: addition of **1a** to **4** gives first adduct-radical **6a**, which is reduced at the cathode to carbanion **6b**, and this is in turn transformed to sulfide **6** by elimination of the chloride ion from the neighbouring carbon (Scheme 5).

The pathway of the reductive addition of **1** to **4** is also supported by cyclic voltammetry patterns in dependence on temperature. The shape of the cyclic voltammogram of

1 does not change with temperature. The anodic-to-cathodic peak current ratio $i_{pa} : i_{pc}$ decreases on addition of **4** suggesting a consecutive reaction of intermediate **1a** with



SCHEME 4

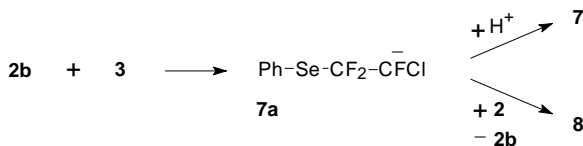


SCHEME 5

substrate **4**. This decrease is low at room temperature because the alkene concentration is low as well (compound **4** boils at 20 °C). This concentration however, increases by lowering the temperature to -20 °C, which is accompanied by an additional decrease in the anodic peak in the cyclic voltammogram (Table I).

The formation of products **7** and **8** is associated with the nucleophilic addition of phenylselenanyl anion **2b** to **3**. The adduct-anion **7a** formed in this step gives selenide **7** by protonation or diselenide **8** by reaction with additional diphenyl diselenide (Scheme 6).

The fact that no addition product is formed in the electroreductive addition of Ph_2Se_2 (**2**) to $\text{CFCl}=\text{CFCl}$ (**4**) indicates that (in contrast to the Ph_2S_2 case) in the reduction of **2**, the phenylselenanyl radical PhSe^\bullet (**2a**) is not formed as an intermediate, and the only intermediate is anion PhSe^- (**2b**) not reacting with **4**.



SCHEME 6

The results of electrolyses are given in Table II. The structure of reaction products **5–8** was proved by their ^1H , ^{13}C , ^{19}F and ^{77}Se NMR spectra.

CONCLUSIONS

The electroreductive addition of PhSSPh (**1**) and PhSeSePh (**2**) to $\text{CFCl}=\text{CF}_2$ (**3**) or $\text{CFCl}=\text{CFCl}$ (**4**) was investigated. To identify the nature of the reacting electrochemically generated intermediates, same reactivity of the two alkenes in radical additions and different reactivity in nucleophilic additions (where the symmetric $\text{CFCl}=\text{CFCl}$ is nonreactive) were utilized. The results give evidence that the electroreduction of the

TABLE I

Peak potentials and anodic-to-cathodic peak current ratios in cyclic voltammetry of PhSSPh (**1**) and its mixture with $\text{CFCl}=\text{CFCl}$ (**4**)

Compound	E_{pc} , V vs SCE	E_{pa} , V vs SCE	i_{pa}/i_{pc}	Temperature, °C
1	-0.99	-0.88	0.53	20
1	-1.05	-0.92	0.54	-20
1 + 4	-0.96	-0.85	0.40	20
1 + 4	-0.93	-0.775	0.28	-20

TABLE II

Reaction conditions and the yield of cathodic addition of PhSSPh (**1**) and PhSeSePh (**2**) to $\text{CFCl}=\text{CF}_2$ (**3**) and $\text{CFCl}=\text{CFCl}$ (**4**) in acetonitrile/ $\text{Et}_4\text{N}^+\text{ClO}_4^-$. The alkenes were fed to the electrolyzed mixture in the gaseous state

Dichalcogenide mmol	Alkene	Working potential V vs SCE	n_{app}^a	Product	Yield, %
1 0.312	3	-1.10	2.09	5	30
				6^b	32
1 0.325	4	-1.10	1.98	6^c	17
2 1.436	3	-1.10	2.05	7	57
				8	5
2 0.440	4	-1.10	1.99	<i>d</i>	<i>d</i>

^a n_{app} (Apparent value of n) number of F mol⁻¹ observed in coulometry. ^b E/Z ratio 64 : 36. ^c E/Z ratio 55 : 45. ^d No addition products were observed.

disulfide gives rise to radical intermediate **1a**, whereas in the electroreduction of **2** the analogous radical **2a** is not involved.

Electroreductive addition of dichalcogenides offers an alternative way of synthesis of aryl fluoroalkyl sulfides and selenides. The currently established synthetic procedure for sulfide **5** is base-catalyzed addition of benzenethiol to **3** (ref.²⁰) or the reaction of sodium benzenethiolate with 1,1,2-trichlorotrifluoroethane²⁶. Sulfide **6** can be prepared by dehydrofluorination of **5** (ref.²⁷) or by dehalogenation of 1,2-dibromo-2-chloro-1,2-difluoroethyl phenyl sulfide²⁸. Diselenide **8** has been so far prepared²² by thermally initiated radical addition of **2** to **3**. The electrochemical procedure is convenient in that only the desired reactant is selective generated at the cathode at a certain constant potential, the reactions proceed under mild conditions (room temperature and atmospheric pressure) and the addition products are relatively easy to isolate from the reaction mixture. In view of the fact that other aromatic and aliphatic diselenides are reduced electrochemically in a similar way^{1,4}, it is reasonable to assume that such additions can generally be conducted with other substitution derivatives as well.

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REFERENCES

1. Ludvik J., Nygaard B.: *Electrochim. Acta* **1996**, *41*, 1661.
2. Pragst F.: *J. Electroanal. Chem.* **1981**, *119*, 315.
3. Degrand C.: *Tetrahedron* **1990**, *46*, 5237.
4. Ludvik J., Nygaard B.: *J. Electroanal. Chem.* **1997**, *423*, 1.
5. Iversen P. E., Lund H.: *Acta Chem. Scand., Ser. B* **1974**, *28*, 8227.
6. Inokuchi T., Kusomoto M., Torii S.: *J. Org. Chem.* **1990**, *55*, 1548.
7. Torii S., Inokuchi T.: *Chem. Lett.* **1980**, 639.
8. Degrand C.: *J. Org. Chem.* **1987**, *52*, 1421.
9. Genesty M., Thobie C., Gautier A., Degrand C.: *J. Appl. Electrochem.* **1993**, *23*, 1125.
10. Hudlicky M.: *Chemistry of Organic Fluorine Compounds*, 2nd ed. Wiley & Sons, New York 1976.
11. Chambers R. D., Hobbs R. H.: *Adv. Fluorine Chem.* **1965**, *4*, 50.
12. Paleta O.: *Chem. Listy* **1996**, *60*, 1363.
13. Perry D. R. A.: *Fluorine Chem. Rev.* **1967**, *1*, 253.
14. Liska F., Dedek V., Nemeč M.: *Collect. Czech. Chem. Commun.* **1974**, *39*, 689.
15. Dedek V., Liska F.: *Collect. Czech. Chem. Commun.* **1967**, *32*, 4297.
16. Liska F., Nemeč M., Dedek V.: *Collect. Czech. Chem. Commun.* **1972**, *37*, 2091.
17. Barta M., Fikar J., Hemer I., Linhart I., Liska F., Dedek V.: *Czech. J. Chem.* **1984**, *101*, 54543.
18. Harris J. F., Stacey F. W.: *J. Am. Chem. Soc.* **1961**, *83*, 840.
19. Terrel R. C., Ucciardi T., Vitcha J. F.: *J. Org. Chem.* **1965**, *80*, 4011.
20. Knunyants I. L., Fokin A. V.: *Izv. Akad. Nauk SSSR* **1952**, 261.
21. Rapp K. E., Pruett R. L., Barr J. T., Bahner C. T., Gibson J. D., Cafferty R. H., Jr.: *J. Am. Chem. Soc.* **1950**, *72*, 8642.

22. Pietre S., De Cock C., Merenyi R., Viehe H. G.: *Tetrahedron* **1987**, 43, 4309.
23. Inukai K., Ueda T., Muramatsu H.: *Bull. Chem. Soc. Jpn.* **1966**, 89, 2191.
24. a) Neugebauerova E.: *M.S. Thesis*. Prague Institute of Chemical Technology, Prague 1995.
b) Dvorak D.: *Ph.D. Thesis*. Prague Institute of Chemical Technology, Prague 1995.
25. Walter R., Ramaley L.: *Anal. Chem.* **1973**, 45, 165.
26. Li X., Pan H., Fu W., Siang X.: *J. Fluorine Chem.* **1986**, 31, 213.
27. Sauvetre R., Normant J. F.: *Bull. Soc. Chim. Fr.* **1972**, 3202.
28. Yagupolskii L. M., Aleksandrov A. M.: *Zh. Obshch. Khim.* **1969**, 39, 765.
29. Urban J., Polasek M., Cisarova I., Ludvik J.: Unpublished results.