Vol. 5, No. 4, 2011 Chemistry

Rostyslav Musyanovych

REACTIONS OF SULFENYL CHLORIDES OF SUBSTITUTED 1,4-NAPHTHOQUINONE

Lviv Polytechnic National University,
12, Bandera str., 79013 Lviv, Ukraine; vnovikov@polynet.lviv.ua

Received: April 30, 2010 / Revised: May 05, 2011 / Accepted: May 31, 2011

Abstract. Conditions of sulfenyl chlorides of substituted 1,4-naphthoquinone reactions with unsaturated compounds with the formation of new sulfides, thiones and 2-thiabicyclo[2.2.1]heptene and thiopyrane substances have been investigated.

Keywords: sulfenyl chlorides, thiones, sulfides, thiocyclic derivatives.

1.Introduction

Many derivatives of 1,4-naphthoquinone exhibit antibacterial, fungicidal, and insecticidal activity. Derivatives of 1,4-naphthoquinone with antiviral, antiphthisic, antibiotic, and antimalarial action were found among them and can be used for pharmacological treatment of different types of respiratory diseases [1-9]. Preparations on the basis of 1,4-naphthoquinone derivatives are effectively used for the treatment of brain function disorders (cerebral infarction, cerebral hemorrhage, atherosclerosis), and also have high antioxidant, cytolytic and cytostatic activity [10]. A number of compounds which contain a sulfide fragment are used in agriculture as effective pesticides, acaricides, insecticides, and defoliants (Chlorbenzide, Benthiocarb, Desmetryne, Ethiphencarb, Methomile, Aldicarb) [11, 12]. In the recent years researches of biological activity of sulfides were directed towards the search of the new [13, 14] as well modification of already known pesticide preparations with the purpose of decreasing of their toxicity for the warm-blooded [15-29]. Antiprotease preparations (derivates of flumenaminic acids) [20], calcium ions antagonists (derivatives of 4-phenyl-1,4-dihydropyridine) [30], and radioprotectors (tetrazolium and metadiazine derivatives) containing a sulfide group are known among pharmaceutical preparations [31].

The first representatives of thiosubstituted of 1,4-naphthoquinone were synthesized in 1940–1947 [32]. During 1947–2005 synthesis and biological researches mainly of the asymmetrical sulfides of 1,4-naphthoquinone were carried out. Compounds with strongly pronounced fungicidal action [33] against the various cultures of pathogenic fungi such as *C. albicans, C. neoformans, M. cannis, A. fumigatus, and T. mentagraphtes*; antitumoral activity against sarcoma *Walker 256* and lymphoid leukemia P 388 [33, 34]; antimicrobial action against *S. faecalis, K. pneumonia, E. coli, Ps. aeruginosa,* and *S. aureus* [33, 35]; and antiviral activity against the viruses *of Influenza-A*, herpes simplex (*HSV-1*), poliovirus type 2 infected *HeLa cells* [33, 36] were found. The synthesis of 1,4-naphthoquinone sulfides was carried out by two ways: by interaction of 2-substituted-3-chloro-1,4-naphthoquinones, 3-chloro-1,4-naphthoquinone, and 2,3-dichloro-1,4-naphthoquinone (DCNQ) with alkyl and aromatic thiols and by interaction of 2-substituted-1,4-naphthoquinones with sulfur monochloride [37]. In the mentioned works [38, 39] synthesis of symmetric sulfides and mechanism of polysulfides formation is suggested.

Simple thioketones are unstable compounds and until recent were known as dimers, trimers and polymers [40-43]. However lately due to the development of laboratory researches technique and understanding of the nature of C=S bond [44] a large number of simple aliphatic and alicyclic thioketones have been synthesized [45-49]. There are some representatives of this class which are stable crystalline compounds (thiocamphora, thiophenhone, adamantanethioketone) [50]. Crystalline thiobenzophenone (known from 1920) is sufficiently stable and its three-dimensional form is unknown [40]. Greater stability is usually characteristic of aromatic thioketones, which is caused by including of thiocarbonic group in the coupling system [50]. Synthesis methods of thioketones are varied and sometimes many-staged, which considerably reduces the yield of the product [50]. Formation of intermediate compound of thio-1,4-benzoquinonic structure was discovered in the reaction of 2,5-di-*tert*-butyl-4-chlorosulfanylphenol [51]. Thioketones

on the basis of 1,4-naphthoquinone were unknown and unreported in the literature.

In view of the special importance of derivatives of 1,4-naphthoquinone and thiocontaining compounds the interest in the researches of the synthesis of new sulfides derivatives of 1,4-naphthoquinone is obvious. The synthesis of new asymmetrical sulfides of 2-substituted-1,4-naphthoquinones with different pharmacophore groups on the basis of the reactions of addition of early obtained sulfenyl chlorides of 1,4-naphthoquinone [52] as well as investigation of thioketones formation and their interaction with unsaturated compounds is the continuation of the researches at the Department of Technology of Biologically Active Substances, Pharmacy and Biotechnology.

2. Experimental

Melting points were measured on a Nagema melting-point apparatus. ^{1}H NMR spectra were recorded on Varian VXR (300 MHz) spectrometer (DMSO-d_6 was a solution and TMS was the internal standard). IR spectra were recorded on Specord M80 in KBr tablets.

2.1. Materials

Sulfenyl chlorides [36], 2-hydroxy-3-mercapto-1,4-naphthoquinone [52] were the materials.

2.2. General Method of Sulfenyl Chlorides Interaction with Unsaturated Substances

An equivalent amount of an unsaturate compound was added to benzoic solution of 0.02 mol of sulfenylchloride at stirring and room temperature. The reaction mixture was left at constant stirring and room temperature for 3 h and then warmed up to 318–323 K during 1 h. Reactionary mixture was evaporated in vacuum and filtered. The residue was washed by water and recrystallized from benzene:hexane (4:1) mixture (Table 1).

3-Thioxonaphthalene-1,2,4-trione (5a). An equivalent amount of chlorosuccinimide was added to the cooled (268–263 K) suspension of 0.0016 mol of 2-hydroxy-3-mercapto-1,4-naphthoquinone in CCl_4 at constant stirring and left for 2 h at cooling. The reactionary mixture was filtered. The filtrate was evaporated and the residue was dried in vacuum. Then it was dissolved in chloroform and 0.0016 mol of triethylamine was dropped. The reaction mixture was filtered and immediately used for the synthesis of the compound **(6a).**

2-(3,5-Di-*tert*-butyl-4-oxocyclohexa-2,5-dienylidene)-3-thioxo-2,3-dihydro-1,4-naphthoquinone (5g). An equivalent amount of triethylamine was added to the solution of 0.005 mol of 2-(2,6-di-*tert*-butyl-4-hydroxyphenyl)-3-sulfenylchloride-1,4-naphthoquinone in chloroform at 263 K and constant stirring. The reaction mixture was left for 3 h and then concentrated in vacuum. Precipitated (**5g**) was removed by filtration and immediately used for the synthesis of the compound (**6g**).

2-(3,5-Di-*tert*-butyl-4-oxocyclohexa-2,5-dienylidene)-3-(bicyclo-[2.2.1]-5-thiohept-2-enyl)-naphthalene (6a). An equivalent amount of cyclopentadiene (or dimethylbutadiene) was added to the solution of 0.008 mol of compound (**5a**) in chloroform at constant stirring and cooling to 263 K. The reactionary mixture was left for 2 h, and then was evaporated in vacuum. The residue did not need purification.

1,2,4-Trione-3-(bicyclo[2.2.1]-5-thiohepto-2-enyl)-naphthalene (6g). The preparation is similar to the compound **5g**.

3-(3,5-Di-*tert*-butyl-4-oxocyclohexa-2,5-diene-1-ylidene)-4',5'-dimethyl-3',6'-dihydro-1H-spyro[naphtho-2,2'-thiopiran]-1,4(3H)-dione (7a). The preparation is similar to the compound **6a**.

Table 1

Yields, data of elemental analysis and spectral data of sulfides

No	Formula	Mp, K	Yield, %	Calculated, found, %					^{1}H NMR (δ, ppm)	IR, cm^{-1}
				C	H	S	N	Cl		
1	2	3	4	5	6	7	8	9	10	11
2	$C_{15}H_{10}NSClO_2$	358	57	58.92 58.98	3.96 3.89	10.49 10.52	4.58 4.62	11.59 11.62	8.15; 8.07 (2H, dd, CH_{Ar}); 7.77; 7.67 (2H, td, CH_{Ar}), 7.45 (2H, s, NH_2); 6.35-6.38 (2H, m, CH=); 4.80-4.84(1H, m, CH-C-); 4.61-4.64(1H, m, CH-Cl); 2.40-2.56 (2H, m, CH_2);	3330 (NH_2); 1620 (C=O); 1310(HC=CH)

Continuation of Table 1

1	2	3	4	5	6	7	8	9	10	11
3a	$C_{23}H_{23}NSClO_2$	376	64	68.65 68.67	4.32 4.30	7.64 7.67	3.34 3.31	8.44 8.45	8.32; 8.26 (2H, dd, CH_{Ar}); 7.84; 7.71 (2H, td, CH_{Ar}), 7.36 (2H, m, CH_{Ar}); 7.11-7.22 (5H, m, CH_{Ar}); 4.81(1H, s, OH); 1.10 (18H, s, $2C(CH_3)_3$)	3595(OH); 1655 (C=O); 1390($2C(CH_3)_3$)
3b	$C_{22}H_{18}NSClO_3$	360	63	64.55 64.51	5.18 5.20	7.49 7.51	3.27 3.29	8.28 8.24	8.11; 8.02 (2H, dd, CH_{Ar}); 7.45 (2H, s, NH_2); 7.26-7.42(5H, m, CH_{Ar}); 7.09-7.21 (5H, m, CH_{Ar}); 4.02-4.08 (1H, m, CH); 3.69-3.79 (2H, m, CH_2);	3330 (NH_2); 1654 (C=O); 1510(Ar); 1480 (CH_2)
4a	$C_{27}H_{28}SClO_4$	385	62	66.86 66.89	6.03 6.00	6.61 6.64		7.31 7.40	10.8 (1H, s, H-C=O); 8.33; 8.37 (2H, dd, CH_{Ar}); 7.81; 7.69 (2H, m, CH_{Ar}); 7.17 (2H, m, CH_{Ar}); 4.91(1H, s, OH); 4.04-4.08 (1H, m, CH); 3.68-3.82 (2H, m, CH_2); 1.19 (18H, s, $2C(CH_3)_3$)	3610(OH); 1650 (C=O); 1385($2C(CH_3)_3$)
4c	$C_{19}H_{13}NSClO_3$	408	59	61.37 61.42	3.80 3.75	8.62 8.64	3.77 3.79	9.53 9.49	9.5(1H, s, H-C=O); 8.31; 8.05 (2H, dd, CH_{Ar}); 7.86; 7.77 (2H, m, CH_{Ar}); 7.08-7.25 (5H, m, CH_{Ar}); 4.08-4.11 (1H, m CH); 3.80-3.92 (2H, m, CH_2);	1650 (C=O); 1591(CH_{Ar}); 1490 (CH_2);
4d	$C_{18}H_{17}SClO_3$	360	60	59.42 59.46	4.99 5.01	8.81 8.79	3.85 3.84	9.74 9.80	10.71 (1H, s, H-C=O), 8.33; 8.37 (2H, dd, CH_{Ar}); 7.81; 7.69 (2H, m, CH_{Ar}); 7.17 (2H, m, CH_{Ar}); 4.04-4.08 (1H, m, CH); 3.68-3.82 (2H, m CH_2); 1.96-2.41(4H, m, $N(CH_2)_2$); 1.09-1.52 (6H, m, $3CH_2$)	1661 (C=O); 1539 (*tert*-N); 1485 (CH_2)
4e	$C_{24}H_{25}SClO_3$	375	69	62.94 62.97	5.28 5.36	7.00 6.98	3.06 3.10	7.74 7.82	9.35 (1H, c, OH); 8.23; 8.09 (2H, dd, CH_{Ar}); 7.75; 7.69 (2H, td, CH_{Ar}); 7.56 (1H, s, NH); 7.15-7.35 (5H, m, CH_{Ar}); 4.78-4.82 (1H, s, CH-Cl); 3.74-3.87 (2H, m, C-CH_2); 3.64-3.67 (2H, m, N-CH_2); 1.94-1.84 (1H, m, CH); 1.03-1.06 (6H, m, $2CH_3$);	3610(OH); 3320 (-NH-); 1655 (C=O); 1575 (CH_{Ar})
4f	$C_{16}H_{17}SNO_3Cl$	378	64	54.63 54.71	4.01 4.06	9.11 9.04	3.98 3.86	10.08 10.12	10.1 (1H, s, H-C=O); 9.61 (1H, s, OH); 7.71; 7.64 (2H, m, CH_{Ar}); 8.15; 8.09 (2H, m, CH_{Ar}); 7.56 (1H, s, NH); 4.80-4.82 (1H, m, CH-Cl); 3.78-3.84 (2H, m, C-CH_2); 1.76(3H, s, CH_3);	3625(OH); 3285 (-NH-); 1612 (C=O)

Table 2

Yields, elemental analysis data and spectral data of the synthesized compounds

No.	Formula	Mp, K	Yield, %	Calculated, found, %			^{1}H NMR (δ, ppm)	IR, cm^{-1}
				C	H	S		
5a	$C_{24}H_{24}SO_3$	368	67	73.44 73.47	6.16 6.21	8.17 8.14	8.29; 8.12 (2H, dd, CH_{Ar}); 7.93; 7.72 (2H, td, CH_{Ar}); 7.36 (2H, m, CH_{Ar}); 2.79 (18H, s, 2C$(CH_3)_3$)	1655 (C=O); 1395 (C$(CH_3)_3$)
6a	$C_{29}H_{30}SO_3$	358	71	75.96 76.01	6.59 6.62	6.99 6.91	8.06; 8.12 (2H, dd, CH_{Ar}); 7.92; 7.89 (2H, td, CH_{Ar}); 7.36 (2H, m, CH_{Ar}); 6.33 (1H, m, CH=); 5.98 (1H, m, CH=); 4.09 (1H, m, CH); 4.55 (1H, m, CH); 2.76 (18H, s, 2C$(CH_3)_3$); 2.54 (2H, m, CH_2)	1655 (C=O); 1398 (C$(CH_3)_3$); 1497 (CH_2)
6g	$C_{15}H_{10}SO_3$	345	68	66.96 66.99	3.73 3.68	11.86 12.00	7.20; 7.24 (2H, td, CH_{Ar}); 7.11; 7.18 (2H, dd, H_{Ar}); 6.47(1H, m, CH=); 5.70(1H, m, CH=); 4.54 (1H, m, CH); 3.64 (1H, m, CH); 2.35(2H, m, CH_2)	1648 (C=O); 1487 (CH_2)
7a	$C_{30}H_{34}O_3S$	441	35	75.97 75.91	6.98 7.12	6.85 6.76	8.36 (1H, d, ^4J = 25, CH_{ap}); 8.25 (2H, m, CH_{Ar}); 7.81 (2H, m, CH_{aAr}); 7.70 (1H, d, ^4J = 25, CH_{ap}); 3.45(2H, dd, ^2J = 17.94, ^5J=2.00, CH_2); 3.05 (2H, dd, ^2J=18.70, ^5J = 1,50, CH_2); 1.73 (3H, s, CH_3); 1.69 (3H, s, CH_3); 1.17 (18H, s, CH_3)	1655 (C=O); 1398 (C$(CH_3)_3$)
7g	$C_{16}H_{14}O_3S$	458	47	66.86 67.11	4.28 4.93	12.05 11.99	8.09 (2H, m, $CH_{аром}$); 7.85 (2H, m, CH_{Ar}); 3.53 (2H, dd, ^2J=17.94, ^5J=3.00, CH_2); 2.81 (2H, dd, ^2J = 16.54, ^5J = 3.00 CH_2); 1.78 (3H, s, CH_3); 1.70 (3H, s, CH_3).	1652 (C=O); 1493 (CH_2)

4',5'-Dimethyl-3',6'-dihydro-1H-spyro[naphtho-2,2'-thiopyran]-1,3,4-trione (7g). The preparation is similar to the compound **6g**.

Yields, elemental analysis data and spectral data of the synthesized compounds (**5g**, **6a,g**, **7a,g**) are shown in Table 2.

3. Results and Discussion

Compounds of bivalent sulphur – sulfenyl chlorides – high reactivity, which causes their wide application in organic synthesis.

Due to high polarity and lability of S-Cl bonds they easily react both with nucleophilic and electrophilic reagents and may thus be used for the synthesis of compounds with the bonds like S–C, S=N, S–O, S–S, S–P, S=O, *etc*.[53].

In this work addition and elimination reactions of sulfenyl chlorides [52] with the formation of corresponding sulfides and thiocyclic compounds were carried out.

The addition reactions of sulfenyl chlorides pass by the mechanism of Ad_E2 [50], and the presence of quinonic conjugation in a molecule leads to the relative addition rate increase. Styrene and acrolein aldehyde were added to sulfenyl chlorides of substituted 1,4-naphthoquinone according to Markovnikov rule [50, 54] with the formation of the sulfides **2-4** (Scheme 1). The structure of the sulfides **3a,b** was also confirmed by alternative synthesis which consisted in the interaction of 2-R-3-mercapto-1,4-naphthoquinones [38, 55] with 2-chloro-1-phenylethanole with subsequent treatment of the product by thionyl chloride. Addition of cyclopentadiene to 2-amino-3-sulfenyl-1,4-naphthoquinone **2** took place in positions 1 and 4 of cyclopentadiene fragment [56].

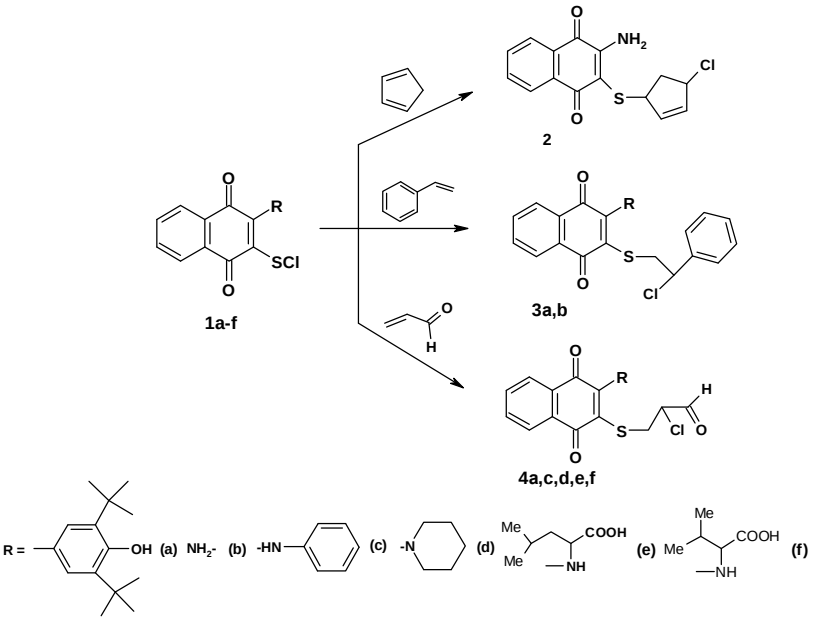
As it is known that the formation of thioketones can take place in the elimination reactions [50] and with the purpose of synthesis of new thioketones on the basis of substitutes 1,4-naphthoquinone the reactions of 2-hydroxy- **1g** and 2-(2,3-di-*tert*-butyl-4-hydroxyphenyl)-3-sulfenylchloride-1,4-naphthoquinone **1a** [52] with a triethylamine were carried out and the reaction products were investigated (Scheme 2).

Formation of thioketone **5a** from 2-hydroxy-3-sulfenylchloride-1,4-naphthoquinone **1a** took place at cooling to 268–263 K and addition of triethylamine for the elimination of HCl as a result of high mobility of hydroxylic hydrogen, lability of S–Cl bond and influence of the conjugating system. This compound exists *in situ* and during short time and at a room temperature forms the mixture of dimers, trimers and polymers, which was confiremd by the results of ^{1}H NMR. However, though it was not obtained in the monomeric form, cyclopentadiene or dimethylbutadiene was used for its catching by adding to cooled reactionary mixture (Scheme 2). In the ^{1}H NMR spectrum of 1,2,4-trione-3-(bicyclo[2.2.1]-5-thiohept-2-enyl)-naphthalene **6g** characteristic signals of CH_2 groups at 2.35 ppm and of four CH groups at 4.54, 3.64, 6.47, and 5.70 ppm respectively, are present, which testify to the formation of the thiocyclic compound. Another picture is observed at the interaction of 2-(2,3-di-*tert*-butyl-4-hydroxyphenyl)-3-sulfenylchloride-1,4-naphthoquinone **1a** with a triethylamine. The crystals of 2-(3,5-di-*tert*-butyl-4-oxocyclohexa-2,5-dienylidene)-3-thioxo-2,3-dihydro-1,4-naphthoquinone **5g** were isolated from the filtrate. The obtained thioketone **5a** is relatively stable and isolated in contrast to 3-thioxonaphthalene-1,2,4-trione **5a** in the crystalline monomer form, which can be explained by the shielding of *tert*-butyl fragment.

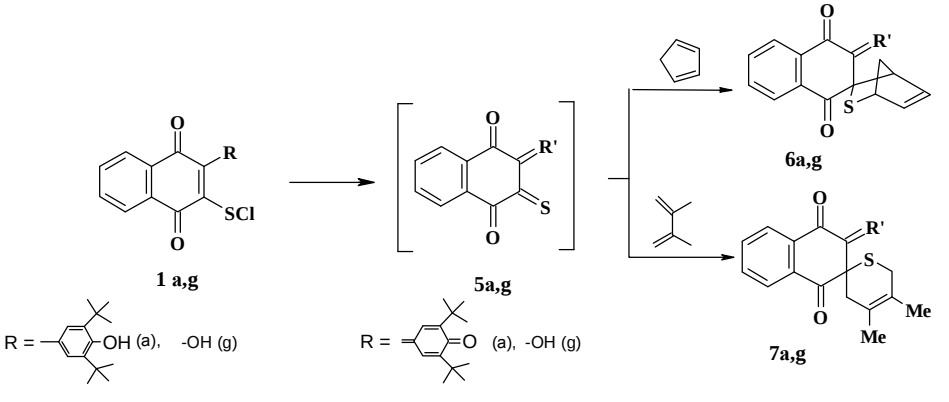
Compared to 2-(2,6-di-*tert*-butyl-4-hydroxyphenyl)-3-sulfenylchloride-1,4-naphthoquinone a peak of hydroxyl-group in ^{1}H NMR spectrum and IR of the compound (**5a**) is absent [52].

At heating in heptane of 2-(3,5-di-*tert*-butyl-4-oxocyclohexa-2,5-dienylidene)-3-thioxo-2,3-dihydro-1,4-naphthoquinone **5a** during 30 min. the mixture of thioketone and polymer compounds is opbtained and broadening of the peaks in ^{1}H NMR spectrum is observed.

Addition of cyclopentadiene to chloroform solution of the compound **5a** after recrystallization from heptane gave the 10–15 % yield of the product **6a.**



Scheme 1



Scheme 2

As a result of the carried out reactions of interaction of the synthesized *in situ* thioketones **5a,g** at cooling of the reactionary mixture to 268–263 K and addition of the proper unsaturated compound the formation of 2-thiabicyclo[2.2.1]heptene **6a,g** and thiopyrane **7a,g** derivatives of substitutes 1,4-naphthoquinone took place.

4. Conclusions

It was determined that the addition reactions of sulfenyl chlorides to styrene, acrolein aldehyde, and cyclopentadiene pass to form the corresponding substituted sulfides. New thiopyrane and thioheptene derivatives of 1,4-naphthoquinone were synthesized by interaction of sulfenyl chlorides in the presence of trietylamine with dimethylbutadiene or cyclopentadiene.

References

[1]Zakharova O., Goryunov L., Troshkova N. e*t al.*: Eur. J. Med. Chem., 2010, **45,** 270.
[2] Khalifa M., Ismail M. and Noaman E.: Bull. Pharmaceut. Sci., 2008, **31,** 69.
[3] Tandon V., Singh R. and Yadav D.: Bioorg. Med. Chem. Lett., 2004, **11,** 2901.
[4] Oku H. and Ishiguro K.: Biol. Pharmaceut. Bull., 2002, **25,** 658.
[5] Checker R., Sharma D., Sandur S. *et al.*: Int. Immunopharm, 2009, **9**, 949.
[6] Fry M. and Pudney M.: Biochem Pharmacol, 1992, **43,** 1545.
[7] Ferreira S., da Silva F., Bezerra F. *et al.*: Arch. Pharmazie, 2010, **343,** 81.
[8] Kim H., Lee C. and Lee H.: J. Food. Sci. Biotechnol., 2009, **18**, 755.
[9] Santos M., Faria N., Iley J. *et al.*: Bioorg. Med. Chem. Lett., 2010, **20,** 193.
[10] Kartoflytskaya A., Stepanyuk H., Yushkova V. *et al.*: Khym. Farmats. Zh., 1997, **31**, 130.
[11] Melnikov N., Novozhylov K. and Pylova T.: Khimicheskie Sredstva Zashchity Rastenij. Khimiya, Moskwa 1980.
[12] Shamshurin A. and Krimer M.: Phiziko-Khimicheskie Svojstva Pesticidov, Khimiya, Moskwa 1976.
[13] Koval I. and Panasenko T.: Ukr. Khim. Zh., 1990, **56**, 638.
[14] Koval I. and Panasenko T.: Zh. Org. Khimii, 1992, **28**, 325.
[15] Mastrukova T. and Kabachnik M.: Agrokhimiya, 1983, **6**, 76.
[16] Hartmann A., Heywang G., Kuehle E. *et al.*: Pat. DE 3215256, Publ. Oct. 27, 1983.
[17] Siegle P., Kuehle E., Hammann I. *et al.*: Pat. DE 2434184, Publ. Febr. 05, 1976.
[18] Siegle P., Kuehle E., Hammann I. *et al.*: Pat. DE 2254359, Publ. May 16, 1976.
[19] Hartmann A., Kuehle E., Hammann I. *et al.*: Pat. DE 2600981, Publ. July 21, 1978.
[20] Siegle P., Kuehle E., Hammann I. *et al.*: Pat. DE 2609830, Publ. Sept. 15, 1977.
[21] Siegle P., Kuehle E., Hammann I. *et al*: Pat. Eur. 49684. Chem. Abstr., 1982, **97**, 91977.
[22] Thurman D.: Pat. USA 4315928, Publ. Febr. 16, 1982.
[23] Drabek J. and Boger M.: Pat. USA 4413008, Publ. Nov. 01, 1983.
[24] Siegle P., Kuehle E., Hammann I. *et al.*: Pat. DE 2344175, Publ. March 27, 1975.
[25] Brown M. and Kohn G.: Pat. USA 3812174, Publ. May 21, 1974.
[26] Brown M. and Kohn G.: Pat. USA 3920830, Publ. Nov. 18, 1975.
[27] Stetter J., Homeyer B. and Hammann I.: Pat. DE 2824394, Publ. Dec. 13, 1979.
[28] Hoffmann H., Hammann I. and Homeyer B.: Pat. DE 2737606, Publ. March 01, 1979.
[29] Kuhle E. and Klauke E.: Angew. Chem., 1977, **89**, 797.
[30] Yagupolsky L.: Aromaticheskie i Heterocyclicheskie Soedineniya s Ftorsoderzhashchimi Zamestitelyami, Naukova dumka, Kiev 1988.
[31] Golomolzin B., Tarakhtij E., Tregubenko I. *et al.*: Khim.-Pharm. Zh., 1988, **22**, 839.
[32] Fieser L. and Brown R.: J. Am. Chem. Soc., 1949, **71**, 3609.
[33] Tandon V., Singh R. and Yadav D.: Bioorg. Med. Chem. Lett., 2004, **14**, 2901.
[34] Tandon V., Chhor R., Singh R. *et al.*: *ibid*, 1079.
[35] Tandon V., Yadav D., Singh R. *et al.*: Bioorg. Med. Chem. Lett., 2005, **15**, 5324.
[36] Tandon V., Yadav D., Singh R. *et al.*: *ibid*, 3463.
[37] Schoberl A. and Wagner A.: Methoden der Organischen Chemie (Houben-Weyl), V. VII/4. Thieme Verlag, Stuttgart 1968.
[38] Stasevych M., Plotnikov M., Platonov M. *et al.*: Heteroatom. Chem., 2005, **3**, 205.
[39] Stasevych M.: Ph.D thesis. Lviv Polytechnic National University, Ukraine, Lviv 2006.
[40] Campaign E.: Chem. Rev., 1946, **39**, 1.
[41] Schoberl A. and Wagner A.: Methoden der Organischen Chemie (Hoben-Weyl), V. 9. Berlin 1955.
[42] Reid E.: Organic Chemistry of Bivalent Sulfur, V. 3. Chemical Publishing Co, New York 1960.
[43] Campaigne E.: The Chemistry of the Carbonyl Group. Interscience, New York 1966.
[44] Mayer R.: Organosulfur Chemistry. Interscience, New York 1967.
[45] McKenzie S.: Organic Compounds of Sulfur, Selenium and Tellerium, V. 1. The Chem. Soc., London 1970.
[46] Duus F.: Organic Compounds of Sulfur, Selenium and Tellerium, V. 2. The Chem. Soc., London 1973.
[47] Duus F.: Organic Compounds of Sulfur, Selenium and Tellerium, V. 3. The Chem. Soc., London 1975.
[48] Paquer D.: Int. J. Sulfur Chem., 1972, **7**, 269.
[49] Paquer D.: Int. J. Sulfur Chem.,1973, **8**, 173.
[50] Hogg D.: Obschaya Organicheskaya Khimiya. Khimiya, Moskwa 1983.
[51] Novikov E., Chumachenko N. and Kopel'tsev Y.: Mendeleev Commun., 1996, **6,** 103.
[52] Stasevych M., Musyanovych R., Plotnikov M. *et al.*: Heteroatom. Chem., 2005, **16**, 587.
[53] Koval I.: Uspekhi Khimii, 1995, **64**, 781.
[54] Yanilkin R., Gryaznov P., Efremov Yu. and Bodrikov I.: Zh. Org. Khim., 1990, **60**, 2470.
[55] Stasevych M., Chervetsova V., Plotnikov M. *et al.*: Ukrainika Biorganica Acta, 2006, **4**, 33.
[56] Brintzinger H. and Ellwanger H.: Chem. Ber., 1954, **87**, 300.

РЕАКЦІЇ СУЛЬФЕНІЛХЛОРИДІВ ЗАМІЩЕНОГО 1,4-НАФТОХІНОНУ

Анотація. *Досліджено умови перебігу реакцій сульфенілхлоридів заміщеного 1,4-нафтохінону з ненасиченими сполуками з утворенням нових сульфідів, тіокетонів та 2-тіабіцикло[2.2.1]гептенових та тіопіранових сполук.*

Ключові слова: *сульфенілхлориди, тіокетони, сульфіди, тіоциклічні похідні.*