Chemistry of Heterocyclic Compounds, Vol. 46, No. 4, 2010

S- AND N,S-CONTAINING HETEROCYCLES BASED ON SULFENYL CHLORIDES OF SUBSTITUTED 1,4-NAPHTHOQUINONE

I. R. Buchkevych[1], M. V. Stasevych[1], R. Ya. Musyanovych[1], V. I. Lubenets[1], and V. P. Novikov[1]*

Keywords: 1,4-naphthoquinone, sulfenyl chlorides, thiazines, thioketones, thiopyrans.

We have carried out for the first time the synthesis of thiopyran and thiazine derivatives of 1,4-naphthoquinone by the reaction 3-hydroxy- (**1**), 3-(3,5-di-*tert*-butyl-4-hydroxyphenyl)- (**2**), 3-amino- **(3)**, 3-[(4-methylphenyl)amino]-2-chlorosulfenyl-1,4-naphthoquinones (**4**) [1, 2] in the presence of equimolar amounts of trimethylamine with dimethylbutadiene and styrene in chloroform at a temperature of -5 to -10°C for 5 h. During the reaction unstable intermediate thioketones **5′**,**6′** or iminothioketones **7′**,**8′** were formed which reacted *in situ* with dimethylbutadiene or styrene to give the adducts **5**,**6** and **7**,**8** respectively. On evaporating the chloroform the compounds **5**,**6** were isolated as needle-like crystals which were purified by crystallization from hexane, while the isomeric compounds **7a,b** and **8a,b** were separated by column chromatography (eluent 3:1 benzene–ethyl acetate).

In the ^{1}H NMR spectra of the synthesized naphthoquinones **7a,b** characteristic multiplet signals of the protons of the naphthoquinone fragment and the phenyl substituent are observed at weak field in the 7.08 to 8.11 ppm range, while the multiplet of the CH proton of the thiazine ring depends on the nature of the heteroatom in the α-position.

When the methine proton is next to the sulfur atom of the naphthothiazine fragment in compounds **7a**, **8a** it is shifted to weaker field at 5.23 and 5.16 ppm respectively, in comparison with the signals of the regioisomers **7b, 8b** where the peaks are observed at 4.00 and 4.82 ppm. In our view, such shifts of the signals of the methine proton are determined by the electron-donor influence of the NR substituent and the -C effect of the sulfur atom, and the presence of vacant *d*-orbitals ($2p_x$-$3d$ interaction).

So stable thiopyran **5,6** and thiazine **7, 8** derivatives of 1,4-naphthoquinone have been synthesized for the first time.

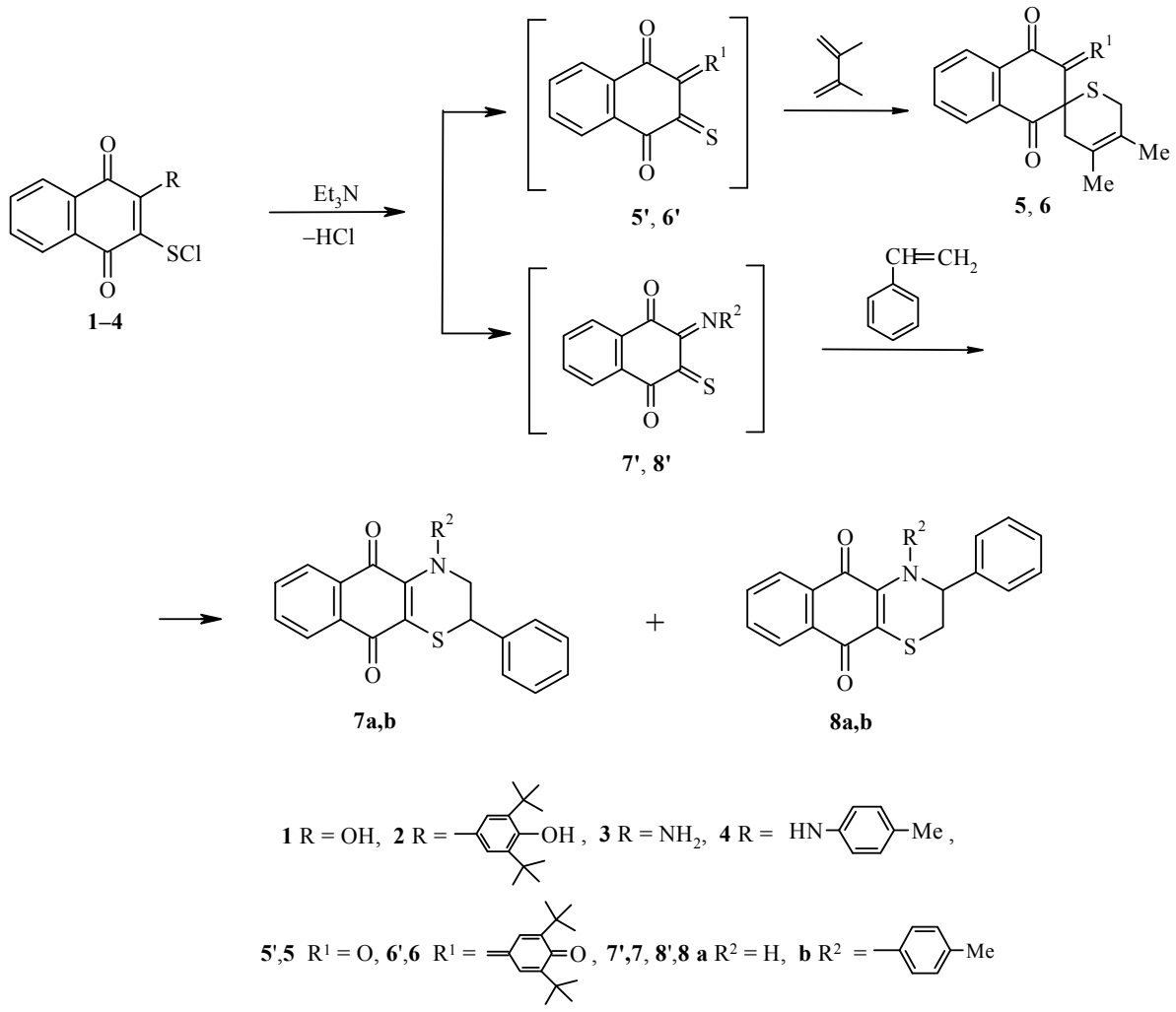
^{1}H NMR spectra of DMSO-d_6 solutions with TMS as internal standard were measured with a Bruker MSL-400 (400 MHz) instrument at 25°C.

4',5'-Dimethyl-3',6'-dihydro-1H-spiro[naphtho-2,2'-thiopyran]-1,3,4-trione (5). Yield 47%; mp 185-187°C. ^{1}H NMR spectrum, δ, ppm (*J*, Hz): 8.09 (2H, m, CH, Ar); 7.85 (2H, m, CH, Ar); 3.53 (2H, dd, ^2J = 17.9, ^5J = 3.0, CH_2); 2.81 (2H, dd, ^2J = 16.5, ^5J = 3.0, CH_2); 1.78 (3H, s, CH_3); 1.70 (3H, s, CH_3). Found, %: C 66.86; H 4.28; S 12.05. $C_{16}H_{14}O_3S$. Calculated, %: C 67.11; H 4.93; S 11.20.

* To whom correspondence should be addressed, e-mail: vnovikov@polynet.lviv.ua.

[1] Lviv Polytechnic National University, Lviv 79013, Ukraine.

Translated from Khimiya Geterotsiklicheskikh Soedinenii, No. 4, 632-634, April, 2010. Original article submitted March 16, 2010.



3-(3,5-Di(tert-butyl)-4-oxocyclohexa-2,5-dien-1-ylidene)-4',5'-dimethyl-3',6'-dihydro-1H-spiro-[naphtho-2,2'-thiopyran]-1,4(3H)-dione (6). Yield 35%; mp 168-170°C. ^{1}H NMR spectrum, δ, ppm (*J*, Hz): 8.36 (H, d, ^4J = 2.5, CH Ar); 8.25 (2H, m, CH Ar); 7.81 (2H, m CH Ar); 7.70 (H, d, ^4J = 2.5, CH Ar); 3.45 (2H, dd, ^2J =17.9, ^5J = 2.0, CH_2); 3.05 (2H, dd, ^2J = 18.7, ^5J = 1.5, CH_2); 1.73 (3H, s, CH_3); 1.69 (3H, s, CH_3); 1.17 (18H, s, CH_3). Found, %: C 75.97; H 6.98; S 6.85. $C_{30}H_{34}O_3S$. Calculated, %: C 75.91; H 7.22; S 6.76.

2-Phenyl-3,4-dihydro-2H-naphtho[2,3-*b*]-1,4-thiazine-5,10-dione (7a). Yield 32%; mp 180-181°C. ^{1}H NMR spectrum, δ, ppm (*J*, Hz): 8.11 (2H, m, CH Ar); 7.68 (2H, m, CH Ar); 7.48 (1H, s, NH); 7.08 (5H, m, CH Ar), 5.23 (1H, m, CH); 3.51 (2H, m, CH_2). Found, %: C 71.14; H 4.53; N 4.43; S 9.94. $C_{18}H_{13}NO_2S$. Calculated, %: C 70.34; H 4.26; N 4.56; S 10.43.

4-(4-Methylphenyl)-2-phenyl-3,4-dihydro-2H-naphtho[2,3-*b*]-1,4-thiazine-5,10-dione (7b). Yield 7%; mp 183-184°C. ^{1}H NMR spectrum, δ, ppm (*J*, Hz): 8.07 (2H, dd, ^3J = 7.7, ^5J = 0.6, CH Ar); 7.73 (2H, m, CH Ar); 7.35 (4H, m, CH Ar); 7.09 (5H, m, CH Ar); 5.38 (1H, m, CH_2); 4.96 (1H, m, CH); 4.69 (1H, m, CH_2); 2.31 (3H, s, CH_3). Found, %: C 76.01; H 4.14; N 3.55; S 8.12. $C_{25}H_{19}NO_2S$. Calculated, %: C 75.54; H 4.82; N 3.52; S 8.07.

3-Phenyl-3,4-dihydro-2H-naphtho[2,3-*b*]-1,4-thiazine-5,10-dione (8a). Yield 45%; mp 189-192°C. ^{1}H NMR spectrum, δ, ppm (*J*, Hz): 8.09 (2H, dd, ^3J = 7.7, ^5J = 0.6, CH Ar); 7.69 (2H, m, CH Ar); 7.28 (5H, m, CH Ar); 6.67 (1H, s, NH); 5.16 (1H, m, CH); 3.76 (2H, dd, ^2J = 1.7, ^3J = 3.5, CH_2). Found, %: C 70.28; H 4.45; N 4.62; S 9.91. $C_{18}H_{13}NO_2S$. Calculated, %: C 70.34; H 4.26; N 4.56; S 10.43.

4-(4-Methylphenyl)-3-phenyl-3,4-dihydro-2H-naphtho[2,3-*b*]-1,4-thiazine-5,10-dione (8b). Yield 5%; mp 192-193°C. ^{1}H NMR spectrum, δ, ppm (*J*, Hz): 8.07 (2H, m, CH Ar); 7.75 (2H, m, CH Ar); 7.65 (2H, m, CH Ar); 7.34 (7H, m, CH Ar); 5.57 (1H, m, CH); 4.195 (2H, dd, ^2J = 1.7, ^3J = 3.5, CH_2); 2.29 (3H, s, CH_3); Found, %: C 75.94; H 4.24; N 3.65, S 8.22. $C_{25}H_{19}NO_2S$. Calculated, %: C 75.54; H 4.82; N 3.52; S 8.07.

Supported by a Ukraine-Lithuania agreement M/43-2009.

REFERENCES

1. D. Hogg (editor). *General Organic Chemistry* [Russian translation], Khimiya (1983), Vol. 5, p. 445.
2. M. V. Stasevich, I. R. Mandzya, M. I. Semenyuk, O. I. Kuzik, G. B. Velichko, and R. Ya. Musyanovich, *Vestn. Nats. Un-ta "L'vovskaya Politekhnika",* No. 590, 128 (2007).