

THE PREPARATION OF 1-METHYL- (AND ETHYL)-1,4-DIHYDRO-4-
OXO- AND 4-THIOXO-3-QUINOLINESULFONAMIDES FROM 4-AMINO-
3-QUINOLINESULFONAMIDES *

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Abstract - Basic hydrolysis of 1-methyl or 1-ethyl-4-amino-3-aminosulfonylquinolinium alkyl sulfates (4) obtained from 4-amino-3-quinolinesulfonamides (2) yields 1-methyl- and 1-ethyl-1,4-dihydro-4-oxo-3-quinolinesulfonamides (5). Salts (4) reacted with sodium hydrosulfide to give sulfur analogs of the compounds (5), i.e., 1-alkyl-1,4-dihydro-4-thioxo-3-quinolinesulfonamides (7).

INTRODUCTION

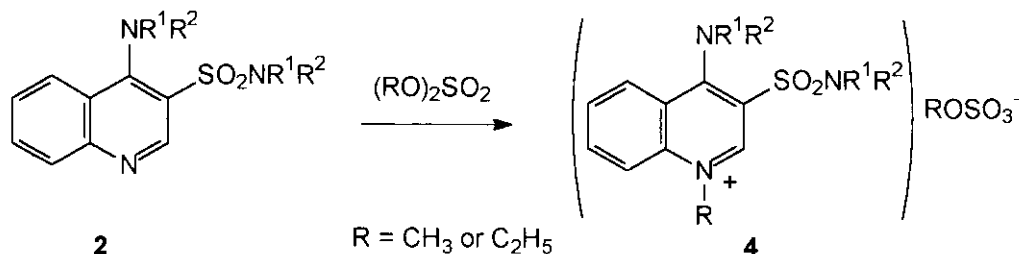
Antihypertensive activity ^{1,2} of 1,4-dihydro-4-oxo-3-quinolinesulfonamides (5) resulted in a considerable interest in the effective synthetic methods facilitating these compounds. We reported previously a synthesis of 1-nonsubstituted and 1-alkyl-1,4-dihydro-4-oxo-3-quinolinesulfonamides (5) from 4-chloro-3-quinolinesulfonamides (1).³ The compounds (5) can be obtained by the hydrolysis of the quinolinium salts (3) resulting from the quaternization of 4-chloro-3-quinolinesulfonamides (1) or by acid hydrolysis of chloroquinoline (1).³ 1-Nonsubstituted 1,4-dihydro-4-oxo-3-quinolinesulfonamides were also synthesized from 4-amino-3-quinolinesulfonamides (2).⁴

The reactants for the synthesis of 4-chloro- and 4-amino-3-quinolinesulfonamides (1, 2) were obtained in a three step process starting from quinoline *via* thioquinanthrene and 4-chloro-3-quinolinesulfonyl chloride.⁵ Till now some 1-alkyl-1,4-dihydro-4-thioxo-3-quinolinesulfonamides (7) were synthesized in the reaction of salts (3) with hydrogen sulfide.²

Because the majority of 4-amino-3-quinolinesulfonamides (2) can be synthesized directly from 4-chloro-3-quinolinesulfonyl chloride providing higher yields than respective 4-chloro-3-quinolinesulfonamides (1),^{3,4} a synthetic route is planned to obtain 4-quinolinone-3-sulfonamides (5) and 4-quinolinethione-3-sulfonamides (7) *via* quinolinium salts (4) deriving from 4-amino-3-quinolinesulfonamides (2).

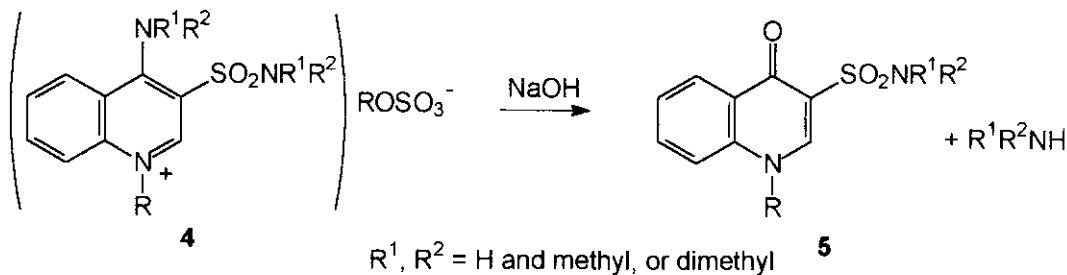
RESULTS AND DISCUSSION

1-Alkyl-4-amino-3-aminosulfonylquinolinium alkyl sulfates (**4**) were obtained similarly as the salts (**3**)³ i.e., in a reaction of 4-amino-3-quinolinesulfonamides (**2**) with the excess of dialkyl (dimethyl or diethyl) sulfate. After the removal of the excess of dialkyl sulfate the salts (**4**) were reacted further without purification. The higher basicity of 4-amino-3-quinolinesulfonamides (**2**), in comparison to the respective chloro analogs (**1**) allows one to perform quaternarization with full consumption of reactants.

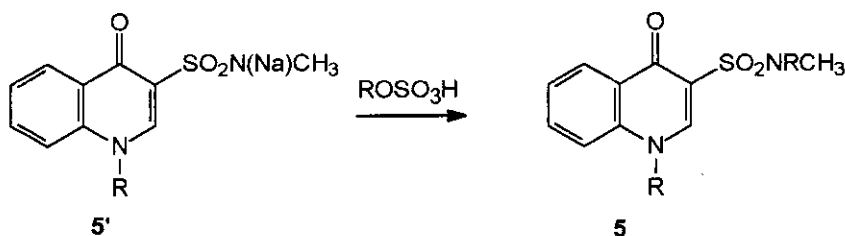


Synthesis of 1-alkyl-1,4-dihydro-4-oxo-3-quinolinesulfonamides (**5**).

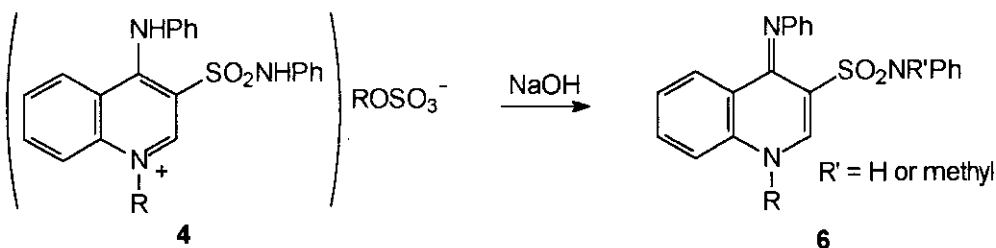
Salts (**4**) derived from the primary and secondary aliphatic (methyl or dimethyl) amines or primary aromatic amine (aniline) were hydrolyzed in basic solution to form 1-alkyl-1,4-dihydro-4-oxo-3-quinoline-sulfonamides (**5**). Basic hydrolysis has been applied before to transform the 2- or 4-dimethylaminopyridinium salts into the substituted 2- or 4-pyridones.^{6,7} Acid hydrolysis of salts (**4**) seemed improper because it has been found that *N*-monosubstituted 4-amino-3-quinolinesulfonamides (**2**) do not react in the reaction conditions.⁴ As expected a hydrolysis of salts (**4**) derived from aliphatic amines gives quinolonesulfonamides (**5**) in a good yield.



N,N-Disubstituted quinolones (**5b** and **5d**) were also isolated in the reaction of derivatives (**4a** and **4b**) of methylamine, respectively. A partial alkylation of the formed sodium salt of 1-alkyl-1,4-dihydro-*N*-methyl-4-oxo-3-quinolinesulfonamides (**5a** and **5c**) by alkyl hydrogen sulfate can probably explain that fact, because till now the alkylation of sulfonamide group has not been observed during a formation of salt (**3**).³



In contrast with the aliphatic amine derivatives, hydrolysis of salts (**4e** and **4f**) derived from aniline terminated on the imine (**6**) level:



Moreover, the methylated product (**6b**) in the sulfonamide group in imine (**6a**) was observed in a moderate amount. Compounds (**6a** and **6c**) were practically insoluble in alkaline solutions. Imines (**6**) were not hydrolyzed even if heated for long periods with 18% hydrochloric or 50% sulfuric acid, which complies with the results of the acidic hydrolysis of 4-phenylamino-3-quinolinesulfonamide.⁴

The results of the reactions performed are given in Table 1.

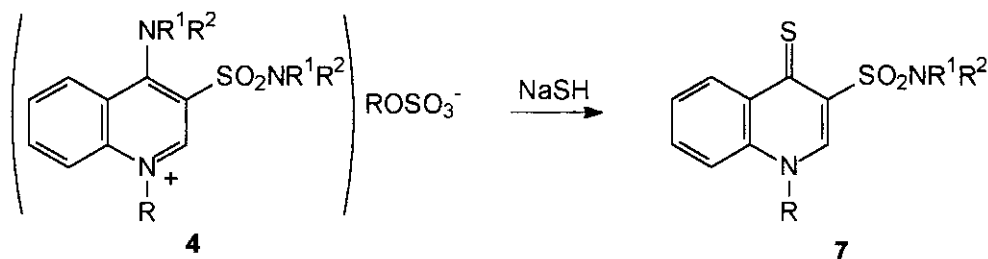
Table 1

Substrate	Salt 4	R	R ¹	R ²	Yield (%) of alkylation product	
					Monoalkylation product	Dialkylation product
2a	4a	CH ₃	H	CH ₃	5a 62	5b 26
2a	4b	CH ₂ CH ₃	H	CH ₃	5c 87	5d 3
2b	4c	CH ₃	CH ₃	CH ₃	5b 73	-
2b	4d	CH ₂ CH ₃	CH ₃	CH ₃	5e 84	-
2c	4e	CH ₃	H	C ₆ H ₅	6a 38	6b 53
2c	4f	CH ₂ CH ₃	H	C ₆ H ₅	6c 87	0

The results of hydrolysis of salts (**4**) obtained from the selected 4-amino-3-quinolinesulfonamides (**2**) indicate that 1,4-dihydro-4-oxo-3-quinolinesulfonamides (**5**) can be synthesized only from the primary and secondary aliphatic amines.

Synthesis of 1-alkyl-1,4-dihydro-4-thioxo-3-quinolinesulfonamides (7)

The hydrolysis of 1-alkyl-4-amino-3-aminosulfonylquinolinium alkyl sulfates (4) shows that salts (4) should react with nucleophiles stronger than those containing nucleophilic oxygen. Therefore, it is decided to investigate the reaction of compounds (4) with sodium hydrosulfide which in comparison to hydrogen sulfide is a reactant much more convenient to handle. Positive results will provide a new synthetic method facilitating 1-alkyl-1,4-dihydro-4-thioxo-3-quinolinesulfonamides (7):³



Moreover, the investigation should answer a question how salts (5) deriving from aniline, which hydrolysis terminated on the imine (6) level, would react with sodium hydrosulfide. A reaction of 1-methyl-4-methylamino-*N*-methyl-3-aminosulfonylquinolinium methyl sulfate (4a), forms a model for the investigation performed in boiling water, pyridine, 1-propanol and dioxane as well as DMSO at 100 °C.

The expected 1-methyl-1,4-dihydro-*N*-methyl-4-thioxo-3-quinolinesulfonamide (7a) was isolated selectively with very high yields in water (dielectric constant 80.2) and DMSO (dielectric constant 46.7). Quinolinethione (7a) is formed also in pyridine (dielectric constant 12.4), but in this particular case it was very difficult to purify the product obtained. Salt (4a) reacted with sodium hydrosulfide in 1-propanol (dielectric constant 20.3) to form not only the expected thione (7a) (26%), but also dealkylated product - the substrate (2a) was isolated (58%). Salt (4a) does not react with sodium hydrosulfide in dioxane probably because of the lower polarity of the solvent (dielectric constant 2.24).

It has been decided to investigate the reactivity of salts (4) deriving from the broader spectrum of aliphatic amines and aniline. The reaction was performed in DMSO. It could have been used for reacting salts (3) resulted from the reaction of chloro derivatives (1) with sodium hydrosulfide, which would eliminate a treatment with hydrogen sulfide. Water if used could have promoted hydrolysis of salt (3). Table 2 gives the results of the reaction of quinolinium salts (4) with sodium hydrosulfide in DMSO at 100 °C.

Table 2

	Product 7			Yield (0.5 h)	Yield (3 h)
	R	R ₁	R ₂	%	%
7a	CH ₃	H	CH ₃	73	-
7b	CH ₂ CH ₃	H	CH ₃	76	-
7c	CH ₃	CH ₂ CH ₃	CH ₂ CH ₃	85	-
7d	CH ₂ CH ₃	CH ₂ CH ₃	CH ₂ CH ₃	89	-
7e	CH ₃	-CH ₂ CH ₂ -O-CH ₂ CH ₂ -		33	65
7f	CH ₂ CH ₃	-CH ₂ CH ₂ -O-CH ₂ CH ₂ -		42	71
7g	CH ₃	H	C ₆ H ₅	57	81
7h	CH ₂ CH ₃	H	C ₆ H ₅	56	73

Slightly lower yields for the morpholine and aniline derivatives (33%-57%) can result from the fact that relatively large groups can form a steric hindrance blocking the access of the hydrosulfide anion to the position 4 of quinoline ring. This explanation can be proved by extending the reaction time from 0.5 h to 3 h, which results in the significant higher yield of thiones (7e - 7h) (65%-81%).

The results of the reaction of primary amines with sodium hydrosulfide indicating the lack of alkylation of the sulfonamide group prove that such alkylation does not proceed during a formation of salts (4).

In this particular case alkyl hydrogen sulfides formed probably, react with the excess of sodium hydrosulfide, which prevents alkylation of the products (7a, 7b, 7g and 7h) formed. It is worth noticing that salts (4) derived from aniline react with sulfur nucleophile (SH⁻ anion) to liberate aniline in contrast to hydrolysis reaction (OH⁻ anion) which terminated on the imine level.

EXPERIMENTAL

Melting points were determined in open capillary tubes on a Boetius mp apparatus and are uncorrected. The ¹H NMR spectra were recorded on a Bruker MSL 300 (300 MHz) spectrometer with tetramethylsilane as the internal standard. Chemical shifts are reported in ppm (δ) and *J* values in Hz. EIMS were run on a LKB GC 2091 spectrometer at 70 eV and 15 eV. CIMS spectra were recorded on a Finnigan MAT 95 spectrometer using isobutane as a reagent and temperature of ion source of 180 °C.

1-Alkyl-4-amino-3-sulfonylaminoquinolinium alkyl sulfates (4). General procedure:

4-Amino-3-quinolinesulfonamides (2) (2 mmol) and dimethyl sulfate (0.57 mL, 6 mmol) or diethyl sulfate (0.66 mL, 6 mmol) was heated at 94 °C for 1.5 h (dimethyl sulfate) or 20 h (diethyl sulfate). The mixture was then cooled down to rt. An excess of dialkyl sulfate was removed by three-fold trituration with ether

(4 mL) followed by decantation. The resulted salts (**4**) were reacted further without purification.

1-Alkyl-1,4-dihydro-4-oxo-3-quinolinesulfonamides (**5**). General procedure:

1-Alkyl-4-amino-3-aminosulfonylquinolinium alkyl sulfates (**4a** - **4d**) (~2 mmol) were dissolved in water (20 mL) and sodium hydroxide (2 g, 50 mmol) was added. The solution obtained was refluxed for 0.5 h or 3 h. After cooling to rt quinolones (**5b**, **5d** and **5e**) were filtered off and washed with water. The filtrate was acidified with 10% hydrochloride acid to pH 4-6 and products formed were filtered off. The compounds (**5a**, **5c**) obtained were crystallized from aqueous ethanol. The results of the experiments are given in Table 1.

1,4-Dihydro-1-alkyl-4-phenylimino-3-quinolinesulfonanilides (**6a**, **6b** and **6c**).

1-Alkyl-4-phenylamino-3-anilinosulfonylquinolinium alkyl sulfates (**4e** and **4f**) (~2 mmol) were treated with 10% sodium hydroxide (20 mL, 55 mmol). The resulted suspension was refluxed for 0.5 h. After cooling to rt the mixture is acidified with 15% hydrochloride acid and the products (**6a** and **6b**) were extracted of chloroform (2x 10 mL) and separated on chromatographic column (neutral aluminium oxide/chloroform), while the product (**6c**) was filtered off. The obtained products were recrystallized from ethanol. The results of the experiments are given in Table 1.

1,4-Dihydro-4-thioxo-3-quinolinesulfonamides (**7**). General procedure:

The obtained 1-alkyl-4-amino-3-aminosulfonylquinolinium alkyl sulfates (**4**) (~2 mmol) were dissolved in DMSO (10 mL) and hydrated sodium hydrosulfide (1 g) ($\text{NaSH} \times n\text{H}_2\text{O}$) was added. The mixture was heated at 100 °C for 0.5 h. After cooling the solution was poured into water (100 mL) and products (**7**) were filtered off and washed with water and ethanol (5 mL). 1,4-Dihydro-4-thioxo-3-quinolinesulfonamides (**7**) were crystallized from acetic acid. The results of the experiments are given in Table 2.

1,4-Dihydro-1,*N*-dimethyl-4-oxo-3-quinolinesulfonamide (**5a**) mp 258-259 °C, lit.,³ mp 258-260 °C.

1,4-Dihydro-1,*N,N*-trimethyl-4-oxo-3-quinolinesulfonamide (**5b**) mp 239-240 °C. EI MS (70 eV), (*m/z*): 266(M^+ , 1.1%), 159(100%). CI MS (*m/z*): 267($\text{M}^+ + 1$, 100%). ¹H NMR, δ : 2.80[s, 6H, $\text{N}(\text{CH}_3)_2$]; 3.96(s, 3H, CH_3); 7.52-7.58(m, 1H, **H6**); 7.78-7.81(m, 1H, **H8**); 7.84-7.94(m, 1H, **H7**); 8.24-8.27(m, 1H, **H5**); 8.62(s, 1H, **H2**). Anal. Calcd for $\text{C}_{12}\text{H}_{14}\text{N}_2\text{O}_3\text{S}$: C 54.12, H 5.30, N 18.02, S 12.04. Found: C 54.41, H 5.52, N 17.92, S 12.14.

1-Ethyl-1,4-dihydro-*N*-methyl-4-oxo-3-quinolinesulfonamide (**5c**) mp 194-195 °C, lit.,³ mp 196-197 °C.

1,*N*-Diethyl-1,4-dihydro-*N*-methyl-4-oxo-3-quinolinesulfonamide (**5d**) oil, EI MS (70 eV), (*m/z*): (M^+ , 0.3%). ¹H NMR, δ : 1.13(t, *J*=7.1 Hz, 3H, NCH_2CH_3); 1.44(t, *J*=7.1 Hz, 3H, $1\text{-CH}_2\text{CH}_3$); 2.87(s, 3H, NCH_3); 3.28(q, *J*=7.1 Hz, 2H, NCH_2CH_3); 4.52(q, *J*=7.1 Hz, 2H, $1\text{-CH}_2\text{CH}_3$); 7.56-7.64(m, 1H, **H6**); 7.88-7.91(m, 2H, **H7**, **H8**); 8.30-8.33(m, 1H, **H5**); 8.71(s, 1H, **H2**).

1-Ethyl-1,4-dihydro-*N,N*-dimethyl-4-oxo-3-quinolinesulfonamide (**5e**) mp 144-145 °C. EI MS (70 eV),

(*m/z*): 280(M^+ , 0.5%), 173(100%). ^1H NMR, δ : 1.47(t, $J=7.2$ Hz, 3H, CH_2CH_3); 2.89[s, 6H, $\text{N}(\text{CH}_3)_2$]; 4.23(q, $J=7.2$ Hz, 2H, CH_2CH_3); 7.58-7.65(m, 1H, **H6**); 7.85-7.91(m, 2H, **H7**, **H8**); 8.30-8.34(m, 1H, **H-5**); 8.68(s, 1H, **H2**). *Anal.* Calcd for $\text{C}_{13}\text{H}_{16}\text{N}_2\text{O}_3\text{S}$: C 55.70, H 5.75, N 9.99, S 11.44. Found: C 55.88, H 5.60, N 10.18, S 11.51.

1,4-Dihydro-1-methyl-4-phenylimino-3-quinolinesulfonanilide (**6a**) mp 213-214 °C. EI MS (70 eV), (*m/z*): 389(M^+ , 100%). ^1H NMR, δ : 3.71(s, 3H, CH_3); 6.69-6.71(m, 2H, **H**_{arom.}); 6.86-6.92(m, 1H, **H**_{arom.}); 6.97-7.02(m, 2H, **H**_{arom.}); 7.21-7.35(m, 7H, **H**_{arom.}); 7.46-7.53(m, 2H, **H**_{arom.}); 8.30(s, 1H, **H2**); 9.41(s, 1H, **NHPh**). *Anal.* Calcd for $\text{C}_{22}\text{H}_{19}\text{N}_3\text{O}_2$: C 67.85, H 4.92, N 10.79, S 8.23. Found: C 67.98, H 4.74, N 10.55, S 8.41.

1,4-Dihydro-1,*N*-dimethyl-4-phenylimino-3-quinolinesulfonanilide (**6b**) mp 179-180 °C. EI MS (15 eV), (*m/z*): 403(M^+ , 7.0%), 233(100%). ^1H NMR, δ : 3.38(s, 3H, N-CH_3); 3.67(s, 3H, 1-CH_3); 6.69-6.72(m, 2H, **H**_{arom.}); 6.91-7.00(m, 2H, **H**_{arom.}); 7.13-7.18(m, 1H, **H**_{arom.}); 7.28-7.38(m, 7H, **H**_{arom.}); 7.48-7.55(m, 2H, **H**_{arom.}); 8.15(s, 1H, **H2**). *Anal.* Calcd for $\text{C}_{23}\text{H}_{21}\text{N}_3\text{O}_2\text{S}$: C 68.46, H 5.25, N 10.41, S 7.95. Found: C 68.56, H 5.11, N 10.29, S 8.03.

1-Ethyl-1,4-dihydro-4-phenylimino-3-quinolinesulfonanilide (**6c**) mp 192-193 °C. EI MS (15 eV), (*m/z*): 403(M^+ , 73.3%), 247(100%). ^1H NMR, δ : 1.23(t, $J=7.1$ Hz, 3H, CH_2CH_3); 4.22(q, $J=7.1$ Hz, 2H, CH_2CH_3); 6.66-6.68(m, 2H, **H**_{arom.}); 6.83-6.89(m, 1H, **H**_{arom.}); 6.93-6.99(m, 2H, **H**_{arom.}); 7.18-7.33(m, 7H, **H**_{arom.}); 7.43-7.50(m, 2H, **H**_{arom.}); 8.28(s, 1H, **H2**); 9.40(**NHPh**). *Anal.* Calcd for $\text{C}_{23}\text{H}_{21}\text{N}_3\text{O}_2\text{S}$: C 68.46, H 5.25, N 10.41, S 7.95. Found: C 68.31, H 5.31, N 10.22, S 7.81.

1,4-Dihydro-1,*N*-dimethyl-4-thioxo-3-quinolinesulfonamide (**7a**) mp 242-243 °C (decomp), lit.,² mp 242-243 °C (decomp).

1-Ethyl-1,4-dihydro-*N*-methyl-4-thioxo-3-quinolinesulfonamide (**7b**) mp 237-238 °C (decomp). EI MS (15 eV), (*m/z*): 282(M^+ , 18.7%), 189(100%). ^1H NMR, δ : 1.45(t, $J=7.0$ Hz, 3H, CH_2CH_3); 2.38(d, $J=5.2$ Hz, 3H, NHCH_3); 4.63(q, $J=7.1$ Hz, 2H, CH_2CH_3); 7.06(q, $J=5.1$ Hz, 1H, NHCH_3); 7.64-7.69(m, H, **H6**); 7.92-7.97(m, H, **H7**); 8.04-8.07(m, 1H, **H8**); 8.79(s, 1H, **H2**); 8.92-8.95(m, 1H, **H5**). *Anal.* Calcd for $\text{C}_{12}\text{H}_{14}\text{N}_2\text{O}_2\text{S}_2$: C 51.04, H 5.00, N 9.92, S 22.71. Found: C 50.89, H 5.21, N 9.68, S 22.60.

N,N-Diethyl-1,4-dihydro-1-methyl-4-thioxo-3-quinolinesulfonamide (**7c**) mp 191-192 °C (decomp), lit.,² mp 191-192 °C (decomp).

1,*N,N*-Triethyl-1,4-dihydro-4-thioxo-3-quinolinesulfonamide (**7d**) mp 121-123 °C (decomp). EI MS (15 eV), (*m/z*): 324(M^+ , 1.6%), 99(100%). ^1H NMR, δ : 1.05[t, $J=7.0$ Hz, 6H, $(\text{CH}_2\text{CH}_3)_2$]; 1.43(t, $J=6.9$ Hz, 3H, CH_2CH_3); 3.35[q, $J=7.0$ Hz, 4H, $(\text{CH}_2\text{CH}_3)_2$]; 4.58(q, $J=6.9$ Hz, 2H, CH_2CH_3); 7.58-7.65(m, 1H, **H6**); 7.87-7.92(m, 1H, **H7**); 7.98-8.01(m, 1H, **H8**); 8.81(s, 1H, **H2**); 8.89-8.92(m, 1H, **H5**). *Anal.* Calcd for $\text{C}_{15}\text{H}_{20}\text{N}_2\text{O}_2\text{S}_2$: C 55.53, H 6.21, N 8.63, S 19.76. Found: C 55.41, 6.37, 8.90, S 19.57.

1,4-Dihydro-1-methyl-4-thioxo-3-quinolinesulfonmorpholide (**7e**) mp 200-202 °C (decomp). EI MS (15 eV), (m/z): 324(M⁺, 3.2%), 48(100%). ¹H NMR, δ: 3.41-3.44(m, 4H, -CH₂-N-CH₂-); 3.41-3.44(m, 4H, -CH₂-O-CH₂-); 4.15(s, 3H, 1-CH₃); 7.71-7.74(m, H, **H6**); 8.00-8.02(m, 2H, **H7**, **H8**); 8.94(s, 1H, **H2**); 8.98-9.01(m, 1H, **H5**). *Anal.* Calcd for C₁₄H₁₆N₂O₃S₂: C 51.83, H 4.97, N 8.64, S 19.76. Found: C 51.98, H 5.12, N 8.45, S 19.91.

1-Ethyl-1,4-dihydro-4-thioxo-3-quinolinesulfonmorpholide (**7f**) mp 180-181 °C (decomp). EI MS (15 eV), (m/z): 338(M⁺, 11.2%), 189(100%). ¹H NMR, δ: 1.41(t, J=7.0 Hz, 3H, CH₂CH₃); 3.29-3.33(m, 4H, -CH₂-N-CH₂-); 3.29-3.33(m, 4H, -CH₂-O-CH₂-); 4.54(q, J=7.0 Hz, 2H, CH₂CH₃); 7.56-7.61(m, H, **H6**); 7.85-7.91(m, 1H, **H7**); 7.96-7.99(m, 1H, **H8**); 8.75(s, 1H, **H2**); 8.88-8.91(m, 1H, **H5**). *Anal.* Calcd for C₁₅H₁₈N₂O₃S₂: C 53.23, H 5.36, N 8.28, S 18.95. Found: C 53.03, H 5.58, N 8.32, S 18.74.

1,4-Dihydro-1-methyl-4-thioxo-3-quinolinesulfonanilide (**7g**) mp 217-218 °C (decomp). EI MS (15 eV), (m/z): 330(M⁺, 52.9%), 238(100%). ¹H NMR, δ: 4.06(s, 3H, 1-CH₃); 6.96-7.00(m, 1H, p-C₆H₅); 7.07-7.28(m, 4H, C₆H₄); 7.62-7.68(m, H, **H6**); 7.87-7.90(m, 2H, **H7**, **H8**); 8.83(s, 1H, **H2**); 8.83-8.87(m, 1H, **H5**); 9.87(s, 1H, NHPh). *Anal.* Calcd for C₁₆H₁₄N₂O₂S₂: C 58.16, H 4.27, N 8.48, S 19.41. Found: C 58.41, H 4.39, N 8.61, S 19.30.

1-Ethyl-1,4-dihydro-4-thioxo-3-quinolinesulfonanilide (**7h**) mp 253-255 °C (decomp). EI MS (15 eV), (m/z): 344(M⁺, 51.1%), 252(100%). ¹H NMR, δ: 1.43(t, J=7.0 Hz, 3H, CH₂CH₃); 4.65(q, J=7.0 Hz, 2H, CH₂CH₃); 7.08-7.14(m, 1H, p-C₆H₅); 7.22-7.35(m, 4H, C₆H₅); 7.65-7.70(m, H, **H6**); 7.96-8.05(m, 2H, **H7**, **H8**); 8.92(s, 1H, **H2**); 8.94-8.97(m, 1H, **H5**); 9.91(s, 1H, NHPh). *Anal.* Calcd for C₁₇H₁₆N₂O₂S₂: C 59.28, H 4.68, N 8.13, S 18.62. Found: C 59.50, H 4.81, N 8.01, S 18.90.

REFERENCES

* Part LXII in the series of Azinyl Sulfides.

1. R. V. Davies, J. Fraser, and K. J. Nicol, European Pat. 0 206 616 A2, (09.06.1986) (*Chem. Abstr.*, 1987, **107**, P 58881g).
2. L. Skrzypek, J. Folwarczna, W. Janiec, I. Kaczmarczyk-Sedlak, A. Maślankiewicz, and M. Pytlik, *Polish. J. Chem.* 1998, **72**, 1127.
3. L. Skrzypek and A. Maślankiewicz, *Heterocycles*, 1997, **45**, 2015.
4. L. Skrzypek, *Heterocycles*, 1998, **48**, 1249.
5. A. Maślankiewicz and L. Skrzypek, *Heterocycles*, 1994, **38**, 1317.
6. J. Pernak and L. Michalak, *Heterocycles*, 1994, **37**, 311.
7. E. W. Rodd, *Chemistry of Carbon Compounds IV^F - Heterocyclic Compounds*, II-Edition, S. Cofey, New York, 1976.