THE PREPARATION OF 1-NONSUBSTITUTED AND 1-METHYL- (AND ETHYL)-1,4-DIHYDRO-4-OXO-3-QUINOLINESULFONAMIDES FROM 4-CHLORO-3-QUINOLINESULFONAMIDES [1]

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Abstract 4-Chloro-3-quinolinesulfonamides (**1**) were hydrolysed to 1,4-dihydro-4-oxo-3-quinolinesulfonamides (**2**) with boiling 18% hydrochloric acid. *N*-Alkyl-1,4-dihydro-4-oxo-3-quinolinesulfonamides (**3**) were prepared by quaternization of compounds (**1**) with dialkyl (methyl or ethyl) sulfate followed by hydrolysis of the quinolinium salt (**4**) formed.

INTRODUCTION

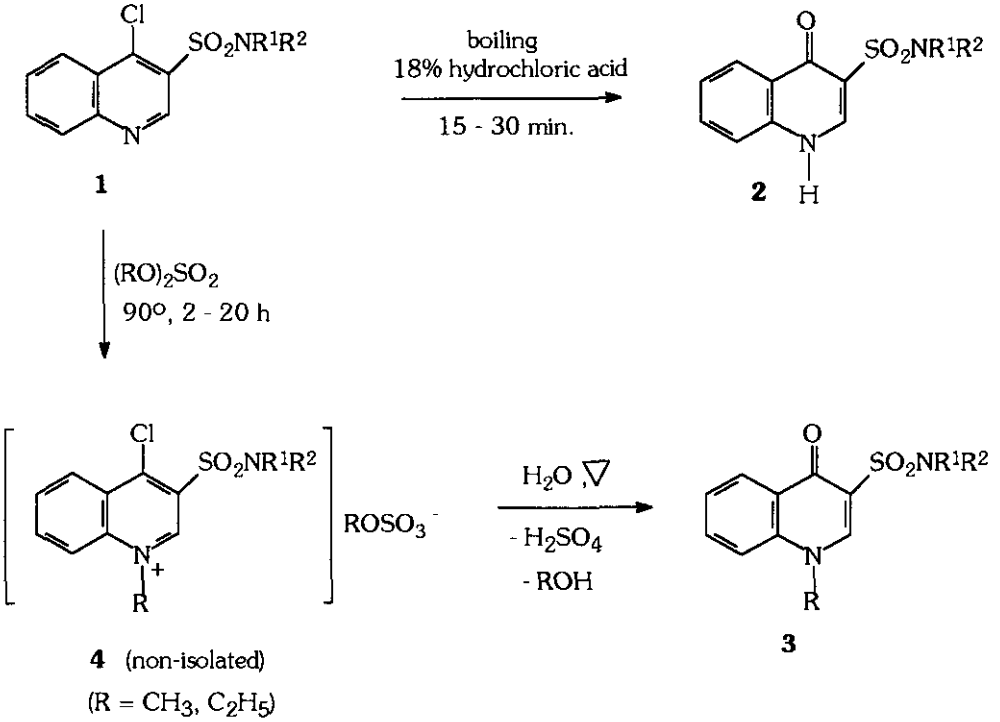
In the preceding paper we reported a two-step preparation of 4-chloro-3-quinolinesulfonyl chloride from quinoline.[2] Depending on the reaction procedure and amine structure, aminolysis of 4-chloro-3-quinolinesulfonyl chloride led to 4-amino-3-quinolinesulfonamides, 4-chloro-3-quinolinesulfonamides (**1**) (for ammonia and *N*-methylaniline) or the mixture of 4-amino-3-quinolinesulfonamide (the major product) and 4-chloro-3-quinolinesulfonamide (**1**) (the minor product).[2] The chloroquinolines (**1**) appeared to be unstable compounds and in the presence of atmospheric moisture they underwent partial hydrolysis to 4(1*H*)-quinolinones (**2**).

Literature search revealed that 1,4-dihydro-4-oxo-3-quinolinesulfonamides (**2**) could be prepared either *via* pyridine ring closure starting from appropriate benzene derivatives [3-5] or by sulfonation of 4(1*H*)-quinolinones.[4] N_1-Alkyl derivatives (**3**) were also prepared by N_1-alkylation of the corresponding 4(1*H*)-quinolinones. [3,4]

In this paper we would like to present a new way of preparing 4-oxo-3-quinolinesulfonamides (**2**) by hydrolysis of 4-chloro-3-quinolinesulfonamides (**1**) as well as a new approach to endocyclic-nitrogen atom substituted 4(1*H*)-quinolinones (**3**) *via* alkylation of (**1**) followed by hydrolysis of the formed *N*-alkylquinolinium salt (**4**).

RESULTS AND DISCUSSION

4-Chlorine substituent in 4-chloro-3-quinolinesulfonamides (**1**) is strongly activated toward nucleophilic displacement both by ring nitrogen (aza-activation) and by ortho electron-withdrawing sulfonamide group. Thus, 4-chloroquinolines (**1**) undergo partial hydrolysis even in atmospheric moisture at room temperature. For preparative purposes, compounds (**1**) were treated with hot 18% hydrochloric acid. It causes complete hydrolysis of (**1**) to (**2**) within 15-30 min and 1,4-dihydro-4-oxo-3-quinolinesulfonamides (**2**) were obtained in high yields (79-91%) as well as with good purity.



Taking into account high nucleophilic susceptibility of chlorine substituent in (**1**) as well as nitrogen-base type properties of (**1**) we consider to prepare 4-quinolinone-3-sulfonamide (**3**) by means of quaternization of (**1**) followed by hydrolysis of the formed *N*-alkyl-quinolinium salt (**4**). In fact, the reactions of compounds (**1**) with dialkyl sulfates proceed (90°C, 2 h for R = CH_3 or 20 h for R = C_2H_5) with complete consumption of quinoline substrate (**1**) (except 4-chloro-3-quinolinesulfonanilide, see Experimental) to form the salt (**4**) almost quantitatively. However, due to instability of quinolinium methyl (or ethyl) sulfates (**4**), we could not isolate them in a pure state. The s alts (**4**) were readily hydrolysed even in a weak aqueous acidic medium to form 1-methyl(ethyl)-4-quinolinone-3-sulfonamide (**3**). Yanagisawa *et al.* described that methylation of quinolinone-3-sulfonamide (**2a**) by means of methyl iodide / silver oxide system took place simultanously both at endocyclic and at sulfonamide nitrogens.[3] In the reaction of (**1**) with dialkyl sulfates no formation of products resulting from alkylation at sulfonamide nitrogen was observed.

Table

Product			Yield
	R^1	R^2	[%]
2a	H	H	90
2b	H	CH_3	87
2c	CH_3	CH_3	79
2d	H	CH_2CH_3	89
2e	CH_2CH_3	CH_2CH_3	81
2f	$-CH_2CH_2OCH_2CH_2-$		93
2g	$-CH_2(CH_2)_3CH_2-$		90
2h	H	Ph	91
2i	CH_3	Ph	89

Product				Yield
	R	R^1	R^2	[%]
3a	CH_3	H	H	82
3b	CH_2CH_3	H	H	81
3c	CH_3	H	CH_3	81
3d	CH_2CH_3	H	CH_3	80
3e	CH_3	$-CH_2CH_2OCH_2CH_2-$		84
3f	CH_2CH_3	$-CH_2CH_2OCH_2CH_2-$		83
3g	CH_3	H	Ph	79
3h	CH_2CH_3	H	Ph	ca. 20
3i	CH_3	CH_3	Ph	81
3j	CH_2CH_3	CH_3	Ph	88

EXPERIMENTAL

Melting points were determined in open capillary tubes on a Boetius melting point apparatus and are *uncorrected*. *The* ^{1}H *NMR spectra were recorded on a Bruker MSL 300 (300 MHz) spectrometer in* dimethyl sulfoxide-d_6 solutions with tetramethylsilane as the internal standard and chemical shifts are reported in ppm (δ) and *J* values in Hz. EIMS spectra were run on a LKB GC 2091 spectrometer at 70 eV and 15 eV. CIMS spectra were recorded with Finnigan MAT 95 spectrometer using isobutane as a reagent gas and temperature of ion source of 180 °C. TLC was performed on aluminium oxide using a mixture of chloroform - ethanol (10:1 v/v) as an eluent.

4-Chloro-3-quinolinesulfonamides (**1a-i**) were prepared by amination of 4-chloro-3-quinolinesulfonyl chloride with appropriate amine as described previously.[2]

1,4-Dihydro-4-oxo-3-quinolinesulfonamides (**2**)

The mixture of 4-chloro-3-quinolinesulfonamide (**1a-i**) (2 mmol) and 10 mL of 18% hydrochloric acid was refluxed for 0.5 h and cooled down to rt. The solid was filtered off, then washed twice with 2 mL of water and air-dried. It was recrystallized from ethanol or aqueous ethanol to give white crystals of 1,4-dihydro--4-oxo-3-quinolinesulfonamide (**2a-i**) (79-91%). *The results are collected in the Table.*

1,4-Dihydro-4-oxo-3-quinolinesulfonamide (**2a**)

mp 291-293 °C, lit.,[3] mp 303-305 °C.

1,4-Dihydro-*N*-methyl-4-oxo-3-quinolinesulfonamide (**2b**)

mp 263-265 °C. EI MS (15 eV), (m/z): 238(M^+, 78.28%), 145(100%). ^{1}H NMR, δ: 2.40(d, *J*=5.1 Hz, 3H, NHC**H**$_3$); 6.68(q, *J*=5.1 Hz, 1H, N**H**CH$_3$); 7.55-7.60(m, 1H, **H**-6); 7.78-7.81(m, 1H, **H**-8); 7.85-7.91(m, 1H, **H**-7); 8.27-8.30(m, 1H, **H**-5); 8.58(d, *J*=6.6 Hz, 1H, **H**-2; 12.66(d, *J*=6.3 Hz, 1H, N_1-**H**). *Anal.* Calcd for $C_{10}H_{10}N_2O_3S$: C 50.41; H 4.23; N 11.76; S 13.46. Found: C 50.52; H 4.41; N 1.64; S 13.54.

1,4-Dihydro-*N,N*-dimethyl-4-oxo-3-quinolinesulfonamide (**2c**)

mp 287-289 °C. EI MS (15 eV), (m/z): 252(M^+, 45.0%). ^{1}H NMR, δ: 2.89(s, 6H, 2 x C**H**$_3$); 7.53-7.59(m, 1H, **H**-6); 7.76-7.79(m, 1H, **H**-8); 7.84-7.89(m, 1H, **H**-7); 8.24-8.27(m, 1H, **H**-5); 8.58(s, 1H, **H**-2). *Anal.* Calcd for $C_{11}H_{12}N_2O_3S$: C 52.37; H 4.79; N 11.10; S 12.71. Found: C 52.45; H 4.64; N 11.22.

1,4-Dihydro-*N*-ethyl-4-oxo-3-quinolinesulfonamide (**2d**)

mp 252-253 °C. EI MS (15 eV), (m/z): 252(M^+, 77.89%), 145(100%). ^{1}H NMR, δ: 1.08(t, *J*=7.2 Hz, 3H, CH_2C**H**$_3$); 2.86-2.95(m, 2H, C**H**$_2$CH$_3$); 6.91(t, *J*=5.9 Hz, 1H, N**H**CH$_2$-); 7.54-7.59(m, 1H, **H**-6); 7.77-7.80 (m, 1H, **H**-8); 7.85-7.90(m, 1H, **H**-7); 8.27-8.30(m, 1H, **H**-5); 8.59(s, 1H, **H**-2); 12.60(s, 1H, N_1-**H**). *Anal.* Calcd for $C_{11}H_{12}N_2O_3S$: C 52.37; H 4.79; N 11.10; S 12.71. Found: C 52.30; H 4.58; N 11.15; S 12.64.

1,4-Dihydro-*N,N*-diethyl-4-oxo-3-quinolinesulfonamide (**2e**)

mp 271-273 °C. EI MS (15 eV), (m/z): 280(M^+, 100%). ^{1}H NMR, δ: 1.15(t, *J*=7.0 Hz, 6H, 2 x CH_2C**H**$_3$); 3.41(q, *J*=7.0 Hz, 4H, 2 x C**H**$_2$CH$_3$); 7.51-7.57(m, 1H, **H**-6); 7.76-7.82(m, 1H, **H**-8); 7.84-7.88(m, 1H, **H**-7); 8.24-8.27(m, 1H, **H**-5); 8.60(d, *J*=6.3 Hz, 1H, **H**-2); 12.59(d, *J*=6.3 Hz, 1H, N_1-**H**). *Anal.* Calcd for $C_{13}H_{16}N_2O_3S$: C 55.70; H 5.75; N 9.99; S 11.44. Found: C 55.60; H 5.84; N 10.06; S 11.24.

1,4-Dihydro-4-oxo-3-quinolinesulfonmorpholide (**2f**)

mp 297-298 °C. EI MS (15 eV), (m/z): 294(M^+, 46.9%), 86(100%). ^{1}H NMR, δ: 3.27-3.30(m, 4H, C**H**$_2$-N-C**H**$_2$); 3.68-3.71(m, 4H, C**H**$_2$-O-C**H**$_2$); 7.54-7.60(m, 1H, **H**-6); 7.77-7.79(m, 1H, **H**-8); 7.85-7.91 (m, 1H, **H**-7); 8.25-8.28(m, 1H, **H**-5); 8.59(s, 1H, **H**-2). *Anal.* Calcd for $C_{13}H_{14}N_2O_4S$: C 53.05; H 4.79; N 9.52; S 0.89. Found: C 53.18; H 4.65; N 9.72; S 10.99.

1,4-Dihydro-4-oxo-3-quinolinesulfonpiperidide (**2g**)

mp 295-297 °C. EI MS (15 eV), (m/z): 292(M^+, 35.2%), 84(100%). ^{1}H NMR, δ: 1.54-1.64(m, 6H, C-C**H**$_2$-C); 3.24-3.27(m, 4H, C**H**$_2$-N-C**H**$_2$); 7.53-7.58(m, 1H, **H**-6); 7.75-7.78(m, 1H, **H**-8); 7.83-7.88 (m, 1H, **H**-7); 8.24-8.27(m, 1H, **H**-5); 8.57(d, *J*=6.7 Hz, 1H, **H**-2); 12.61(d, *J*=6.3 Hz, 1H, N_1-**H**). *Anal.* Calcd for $C_{14}H_{16}N_2O_3S$: C 57.52; H 5.52; N 9.58; S 10.97. Found: C 57.64; H 5.61; N 9.48; S 11.03.

1,4-Dihydro-4-oxo-3-quinolinesulfonanilide (**2h**)

mp 264-265 °C. EI MS (15 eV), (m/z): 300(M^+, 39.65%), 93(100%). ^{1}H NMR, δ: 6.95-7.20(m, 5H,

C_6H_5); 7.41-7.48(m, 1H, **H**-6); 7.63-7.66(m, 1H, **H**-8); 7.71-7.78(m, 1H, **H**-7); 8.14-8.17(m, 1H, **H**-5); 8.58(s, 1H, **H**-2); 9.91(s, 1H, NHPh); 12.57(s, 1H, N_1-**H**). *Anal.*Calcd for $C_{15}H_{12}N_2O_3S$: C 59.99; H 4.03; N 9.33; S 10.67. Found: C 60.04; H 4.12; N 9.53; S 10.59.

1,4-Dihydro-*N*-methyl-4-oxo-3-quinolinesulfonanilide (**2i**)

mp 250-251 °C. EI MS (15 eV), (m/z): 314(M^+, 11.96%), 107(100%). ^{1}H NMR, δ: 3.50(s, 3H, NCH_3Ph); 7.12-7.31(m, 5H, C_6H_5); 7.44-7.50(m, 1H, **H**-6); 7.62-7.66(m, 1H, **H**-8); 7.72-7.78(m, 1H, **H**-7); 8.18-8.21(m, 1H, **H**-5); 8.32(s, 1H, **H**-2); 12.48(s, 1H, N_1-**H**). *Anal.* Calcd for $C_{16}H_{14}N_2O_3S$: C 61.13; H 4.49; N 8.91; S 10.20. Found: C 61.01; H 4.31; N 8.84; S 10.31.

The reaction of 4-chloro-3-quinolinesulfonamides (**1**) with dialkyl sulfates

A suspension of 2.5 mmol of finely powdered 4-chloro-3-quinolinesulfonamide (**1**) and 10 mmol of dialkyl sulfate was heated at 90°C for 2 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 3 mL of benzene followed by decantation. The oily residue was kept at 40 °C under vacuum to give, almost quantitatively, crude 1-alkyl-4-chloro-3-aminosulfonylquinolinium alkyl sulfate (**4**) as a solid or syrupy semi-solid material.

Determination of sulfate content, performed as presented below, indicates 97-98 % of salt (**4**) in crude material. In order to analyse sulfate content, the sample of alkyl sulfate (**4**) was hydrolysed [as presented for the preparation of (**3**)] to the mixture of quinolinone (**3**), sulfuric acid and alcohol. Quinolinone (**3**) was removed by filtration and washed with water. Aqueous filtrate and washings were combined and then neutralized with sodium bicarbonate solution and finally treated with 5 % barium chloride aqueous solution to precipitate barium sulfate.

Due to instability of quinolinium methyl (or ethyl) sulfates (**4**), they could not be isolated in a pure state. Crude salt (**4**) was used for the preparation of compound (**3**).

1,4-Dihydro-1-methyl(ethyl)-4-oxo-3-quinolinesulfonamides (**3**)

a) General procedure:

Quinolinium salt (**4**) (*ca.* 2.5 mmol) [prepared as above from compound (**1**)] was suspended in 10 mL of water. The mixture was refluxed for 1 h and then cooled down to rt.The solid was filtered off, washed with water and air-dried. It was recrystallized from ethanol or aqueous ethanol to give white crystals of 1,4-dihydro-1-methyl(ethyl)-4-oxo-3-quinolinesulfonamide (**3**) (79-88%). The results are collected in the Table.

b) Procedure for the conversion of 4-chloro-3-quinolinesulfonamide (**1f** or **1i** to **3e**, **3f** or **3i**, **3j**) without isolation of quinolinium salts (**4**).

The reaction of 4-chloro-3-quinolinesulfonamide (**1**) with dialkyl sulfate was performed as in procedure a). Salts (**4**) containing *N,N*-dialkylsulfonamide moiety are partially soluble in benzene. In these cases the mixture resulting from the reaction of (**1**) with excess of dialkyl sulfate was directly subjected to hydrolysis.

The compounds (**3**) were isolated as in procedure a).

c) Reaction of 4-chloro-3-quinolinesulfonanilide (**1h**) with diethyl sulfate.

The reaction of (**1h**) with diethyl sulfate proceeded very slowly, after 20 h only 10% conversion of (**1h**) was observed, 40% conversion of (**1h**) was reached after 100 h. The mixture was subjected to hydrolysis as in procedure b). 1-Ethyl-4-quinolinonesulfonanilide (**3h**) was isolated by column chromatography on aluminium oxide and solution of chloroform - ethanol (20 : 1, v/v) as an eluent.

1,4-Dihydro-1-methyl-4-oxo-3-quinolinesulfonamide (**3a**)

mp 244-245 °C, lit.,[4] mp 230-231 °C or lit.,[3] mp 244-246 °C.

1-Ethyl-1,4-dihydro-4-oxo-3-quinolinesulfonamide (**3b**)

mp 228-230 °C. EI MS (15 eV), (m/z): 252(M^+, 100%). ^{1}H NMR, δ: 1.37(t, J=6.9 Hz, 3H, CH_2CH_3); 4.49(q, J=6.9 Hz, 2H, CH_2CH_3); 6.85(s, 2H, NH_2); 7.52-7.57(m, 1H, **H**-6); 7.86-7.92(m, 1H, **H**-8); 7.86-7.92(m, 1H, **H**-7); 8.29-8.32(m, 1H, **H**-5); 8.69(s, 1H, **H**-2). *Anal.* Calcd for $C_{11}H_{12}N_2O_3S$: C 52.37; H 4.79; N 11.10; S 12.71. Found: C 51.81; H 4.46; N 10.86; S 12.60.

1,4-Dihydro-1,*N*-dimethyl-4-oxo-3-quinolinesulfonamide (**3c**)

mp 258-260 °C, lit.,[4] mp 248-250 °C or lit.,[3] mp 254-261 °C.

1-Ethyl-1,4-dihydro-*N*-methyl-4-oxo-3-quinolinesulfonamide (**3d**)

mp 196-197 °C. CI MS (m/z): 267(M^++1, 100%). ^{1}H NMR, δ: 1.38(t , J=7.1 Hz, 3H, CH_2CH_3); 2.41(d, J=5 Hz, 3H, $NHCH_3$); 4.48(q, J=7.1 Hz, 2H, CH_2CH_3); 6.74(q, J=5 Hz, 1H, $NHCH_3$); 7.50-7.58(m, 1H, **H**-6); 7.81-7.92(m, 2H, **H**-7, **H**-8); 8.26-8.30(m, 1H, **H**-5); 8.64(s, 1H, **H**-2). *Anal.* Calcd for $C_{12}H_{14}N_2O_3S$: C 54.12; H 5.30; N 10.53; S 12.02. Found: C 53.96; H 5.15; N 10.27; S 12.21.

1,4-Dihydro-1-methyl-4-oxo-3-quinolinesulfonmorpholide (**3e**)

mp 279-280 °C. CI MS (m/z): 309(M^++1, 100%). ^{1}H NMR, δ: 3.16-3.21(m, 4H, CH_2-N-CH_2); 3.59-3.62(m, 4H, CH_2-O-CH_2); 3.97(s ,3H, N_1-CH_3); 7.54-7.59(m, 1H, **H**-6); 7.79-7.81(m, 1H, **H**-8); 7.85-7.91(m, 1H, **H**-7); 8.24-8.27(m, 1H, **H**-5); 8.63(s, 1H, **H**-2). *Anal.* Calcd for $C_{14}H_{16}N_2O_4S$: C 54.53; H 23; N 9.08; S 10.40. Found: C 54.04; H 5.13; N 8.92; S 10.56.

1-Ethyl-1,4-dihydro-4-oxo-3-quinolinesulfonmorpholide (**3f**)

mp 186-188 °C. CI MS (m/z): 323(M^++1, 100%). ^{1}H NMR, δ: 1.39(t, J=7.0 Hz, 3H, CH_2CH_3); 3.16-3.21 (m, 4H, CH_2-N-CH_2); 3.59-3.62(m, 4H, CH_2-O-CH_2); 4.47(q, J=7.0 Hz, 2H, CH_2CH_3); 7.52-7.57(m, 1H, **H**-6); 7.83-7.91(m, 2H, **H**-7, **H**-8); 8.26-8.29(m, 1H, **H**-5); 8.65(s, 1H, **H**-2). *Anal.* Calcd for $C_{15}H_{18}N_2O_4S$: C 55.89; H 5.63; N 8.69; S 9.94. Found: C 56.02; H 5.89; N 8.54.

1,4-Dihydro-1-methyl-4-oxo-3-quinolinesulfonanilide (**3g**)

mp 281-283 °C. EI MS (15 eV), (m/z): 314(M^+, 100%). ^{1}H NMR, δ: 3.94(s, 3H, N_1-CH_3); 6.90-6.96(m, 1H, p-C_6H_5); 7.14-7.20(m, 4H, C_6H_4); 7.49-7.53(m, 1H, **H**-6); 7.71-7.74(m, 1H, **H**-8); 7.80-7.85(m, 1H,

H-7); 8.22-8.24(m, 1H, **H**-5); 8.73(s, 1H, **H**-2); 9.96(s, 1H, N**H**Ph). *Anal.* Calcd for $C_{16}H_{14}N_2O_3S$: C 61.13; H 4.49; N 8.91; S 10.20. Found: C 61.31; H 4.67; N 9.11; S 10.40.

1-Ethyl-1,4-dihydro-4-oxo-3-quinolinesulfonanilide (**3h**)

mp 254-255 °C. EI MS (15 eV), (m/z): 328(M^+, 100%). ^{1}H NMR, δ: 1.29(t, *J*=7.2 Hz, 3H, CH_2CH_3); 4.47(q, *J*=7.2 Hz, 2H, CH_2CH_3); 6.91-6.96(m, 1H, p-C_6H_5); 7.12-7.16(m, 4H, C_6H_5); 7.50-7.54(m, 1H, **H**-6); 7.82-7.84(m, 1H, **H**-8); 7.82-7.85(m, 1H, **H**-7); 8.24-8.26(m, 1H, **H**-5); 8.74(s, 1H, **H**-2); 9.99(s, 1H, N**H**Ph). *Anal.* Calcd for $C_{17}H_{16}N_2O_3S$: C 62.18; H 4.91; N 8.53; S 9.76. Found: C 62.40; H 4.70; N 8.67; S 9.84.

1,4-Dihydro-1,*N*-dimethyl-4-oxo-3-quinolinesulfonanilide (**3i**)

mp 178-180 °C. CI MS (m/z): 329(M^++1, 100%). ^{1}H NMR, δ: 3.89(s, 3H, N_1-CH_3); 3.48(s, 3H, NCH_3Ph); 7.26-7.31(m, 1H, p-C_6H_5); 7.12-7.16(m, 4H, C_6H_5); 7.53-7.58(m, 1H, **H**-6); 7.73-7.76(m, 1H, **H**-8); 7.83-7.88(m, 1H, **H**-7); 8.27-8.30(m, 1H, **H**-5); 8.52(s, 1H, **H**-2). *Anal.* Calcd for $C_{17}H_{16}N_2O_3S$: C 62.18; H 4.91; N 8.53; S 9.76. Found: C 61.42; H 4.88; N 8.37.p

1-Ethyl-1,4-dihydro-*N*-methyl-4-oxo-3-quinolinesulfonanilide (**3j**)

mp 187-189 °C. CI MS (m/z): 343(M^++1, 100%). ^{1}H NMR, δ: 1.23(t, *J*=7.0 Hz, 3H, CH_2CH_3); 3.47(s, 3H, NCH_3Ph); 4.39(q, *J*=7.0 Hz, 2H, CH_2CH_3); 7.13-7.19(m, 1H, p-C_6H_5); 7.25-7.30(m, 4H, C_6H_5); 7.51-7.57(m, 1H, **H**-6); 7.83-7.85(m, 2H, **H**-7, **H**-8); 8.28-8.30(m, 1H, **H**-5); 8.47(s, 1H, **H**-2). *Anal.* Calcd. for $C_{18}H_{18}N_2O_3S$: C 63.14; H 5.30; N 8.18; S 9.36. Found: C 62.94; H 5.51; N 8.27; S 9.46.

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Received, 17th June, 1997