# SYNTHESIS OF 3-ALKYLSULFINYL-4(1*H*)-QUINOLINONES FROM 4-METHOXY-3-ALKYLTHIOQUINOLINES #

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Abstract - Reactions of 4-methoxy- or 1,4-dihydro-4-oxo-3-alkylthioquinolines (**1**) and (**4**, **5**) with a nitrating mixture ran as the 3-alkylthio group *S*-monooxidation and led to the respective alkylsulfinyl derivatives (**2**, **3** or **6**). Hydrolysis of 4-methoxy-3-alkylsulfinylquinolines (**2**) with hydrochloric acid (1:1) at 65-68 °C gave 3-alkylsulfinyl-4(1*H*)-quinolinones (**3**).

## INTRODUCTION

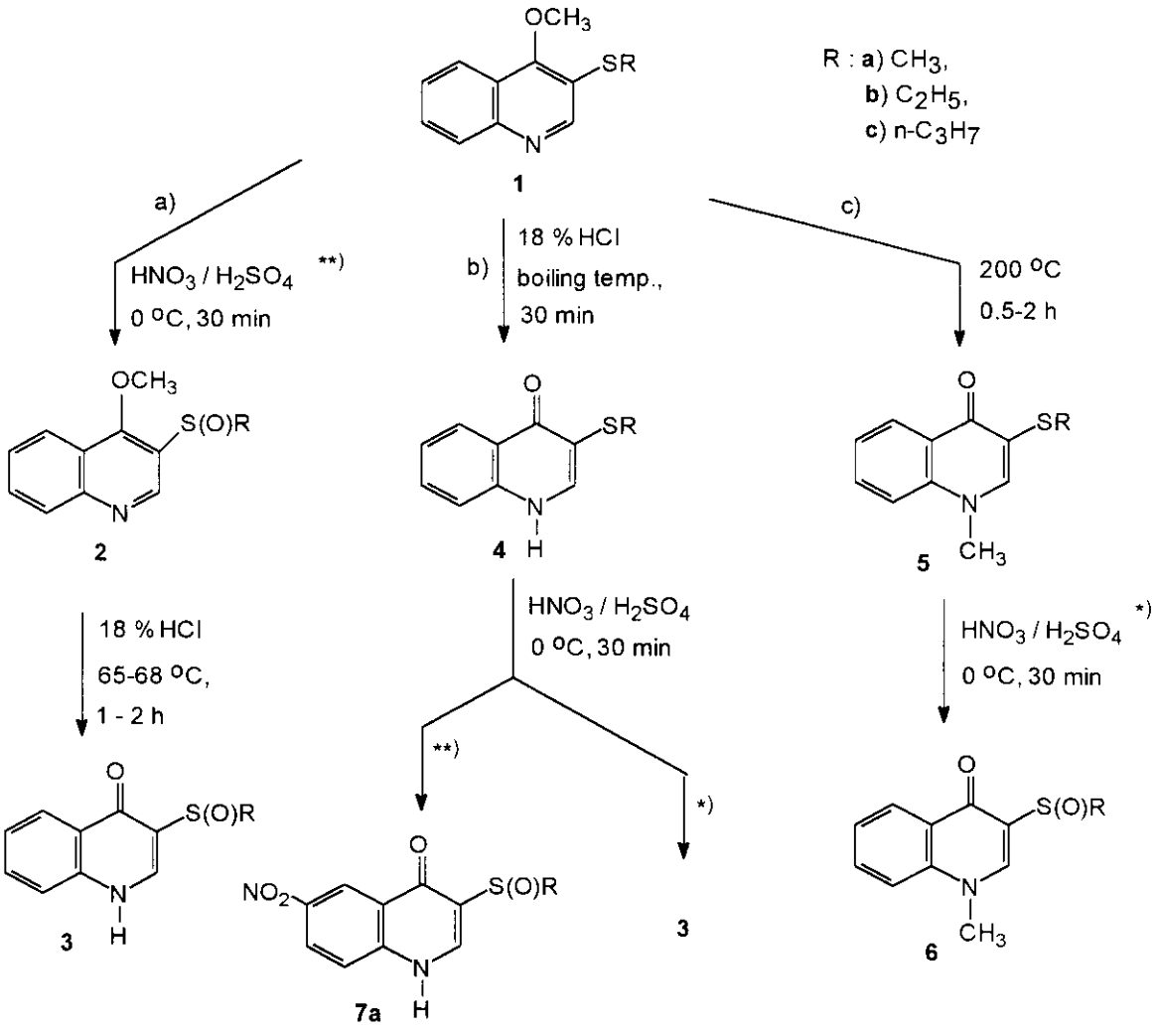
Flosequinan, i.e.7-fluoro derivative of 1-methyl-3-methylsulfinyl-4(1*H*)-quinolinone exhibits vasodilatory and antihypertensive activity.[1,2] As broadly demonstrated for fluoroquinolinone antibacterial drugs,[3] flosequinan may be prepared like other 4(1*H*)-quinolinones, *via* pyridine ring closure starting from respective benzene derivatives followed by sulfide group oxidation and *N*-methylation.[2,4] However, our previous studies on the 3,4-difunctionalization of quinoline *via* thioquinanthrene demonstrate 4-alkoxy-3-alkylthioquinolines (**1**) and 3-alkylthio-4(1*H*)-quinolinones (**4**) to be easily available.[5,6] Furthermore, cautious treatment of 4-substituted 3'-methylthio-3,4'-diquinolinyl sulfides with a nitrating mixture allows the methylthio group oxidation and gives high yield of corresponding 3'-methylsulfinyl-3,4'-diquinolinyl sulfides.[7] One would therefore expect to find a new way of preparing 3-alkylsulfinyl-4(1*H*)-quinolinones (**3**) or (**6**) starting from 4-alkoxy-3-(alkylthio)quinolines (**1**) by combining monooxidation of 3-alkylthio group and transformations of 4-methoxy group, as shown in the Scheme.

## RESULTS AND DISCUSSION

The key step in the preparation of 3-alkylsulfinyl-4(1*H*)-quinolinones (**3**) or (**6**) from 4-alkoxy-3-alkylthio quinolines (**1**) is oxidation of the 3-alkylthio function in **1**, **4** or **5** to sulfoxide one in compounds (**2**, **3** or **6**), respectively. However, in reactions with 4-substituted 3'-methyltio-3,4'-diquinolinyl sulfides, the nitrating mixture acts both as an oxidizing system and as a nitrating one.[7] To avoid nitration we choose 4-methoxy-3-methylthioquinoline (**1a**) as a model compound since 4-methoxyquinoline is less reactive than

4(1*H*)-quinolinone toward nitration with nitric acid / conc. sulfuric acid mixture.[8] In fact, treatment of sulfide (**1a**) with solution containing up to three molar equivalents of nitric acid (applied in the form of nitrating mixture) involved only *S*-monooxidation and gave mainly 4-methoxy-3-methylsulfinylquinoline (**2a**) (85 %) accompanied by some amounts of 3-methylsulfinyl-4(1*H*)-quinolinone (**3a**) (as hydrolysis product of **2a**). Similar results were obtained for sulfides (**1b** and **1c**).

Scheme




*) One molar equiv., **) three molar equivs of $HNO_3$ per sulfide group was used.

The aza-activated ether linkage in 4-alkoxyquinolines could be easily splitted giving respective 4(1*H*)-quinolinones by the action of hydrochloric or hydrobromic acid.[6,9] One would therefore expect hydrolysis of 4-methoxy-3-alkylsulfinylquinolines (**2**) into 3-alkylsulfinyl-4(1*H*)-quinolinones (**3**) by means of hydrochloric acid, as shown for transformation of 4-alkoxy-3-alkylthioquinolines (**1**) into 3-alkylthio-

4(1*H*)-quinolinones (**4**).[6] Easy deoxygenation of sulfoxides in the presence of hydrogen halides, both in aqueous and non-aqueous solutions has been, on the other hand, well documented.[10-12] Furthermore, Connor and Strandtmann [13] reported that the action of boiling 5N hydrochloric acid causes deoxygenation of 1-methyl-3-methylsulfinyl-4(1*H*)-quinolinone (**6a**) to 1-methyl-3-methylthio-4(1*H*)-quinolinone (**5a**), it even causes splitting of the whole methylsulfinyl group and formation of 1-methyl-4(1*H*)-quinolinone. Very close results, including transformation of methylsulfinyl group and hydrolysis of 4-methoxy group, were obtained in our studies concerning the behaviour of 4-methoxy-3-methylsulfinylquinoline (**2a**) in boiling hydrochloric acid (1:1) for 0.5 h. The main product was 3-methylthio-4(1*H*)-quinolinone (**4a**) (50%) accompanied by small amounts of 4(1*H*)-quinolinone. Also, as reported by Connor and Strandtmann [13] for **3a** or **6a** the balance of substrate-isolated products relation was below 60 %. Fortunately, treatment of **2a-c** with hydrochloric acid (1:1) at 65-68 $^{o}$C causes selective splitting of the ether linkage, leaving the sulfinyl group almost unaffected and gives the expected 3-alkylsulfinyl-4(1*H*)-quinolinones (**3a-c**), with 85-90 % yield. Comparison of the acid catalyzed hydrolysis ability of 4-methoxy-3-alkylthioquinolines (**1**) versus 4-methoxy-3-alkylsulfinylquinolines (**2**) shows that in the case when sulfoxides (**2**) were completely used up and converted into quinolinones (**3**) with in 85-90 % yield, the consumption of 4-methoxy-3-alkylthio-quinolines (**1**) (and the conversion of **1** to 3-alkylthio-4(1*H*)-quinolinones (**4**) ) amounted to 12 -14 % only.

Preparation of **3** presented above consists of oxidation step of **1** into **2** and hydrolysis of **2** into **3** (Scheme, route a). To avoid problems caused by instability of sulfoxides (**2**) in the presence of hydrochloric acid we decided to study a reverse reaction sequence starting from **1** but involving transformation of methoxyquinoline (**1**) to 4-quinolinones (**4**) or (**5**) and completing the process with oxidation of sulfides (**4**) or (**5**) to sulfoxides (**3**) or (**6**), respectively. However, the reaction of 3-methylthio-4(1*H*)-quinolinone (**4a**) with the mixture containing three molar equivalents of nitric acid proceeded as both *S*-oxidation and nitration to give 6-nitro-3-methylsulfinyl-4(1*H*)-quinolinone (**7a**) (R=Me) with 70% yield. On the other hand, analogical reaction of compounds (**4a-4c**) or (**5a-5c**) performed with the use of one molar equivalent of nitric acid gave only the sulfide group oxidation products (**3a-3c**) or (**6a-6c**) with 85-90 % or 85-97 % yield, respectively.

The $^{1}$H NMR spectra of methoxy-sulfoxides (**2**) related to the spectral data of sulfides (**1**) show characteristic changes (cf. ref.[7]) in the positions of H-2 protons shifted downfield by $\Delta\delta$ = 0.36- 0.45 ppm. On the other hand, the differences in the chemical shifts values $\Delta\delta_{sulfoxide\text{-}sulfide}$ for $SCH_2$ protons ($\Delta\delta$ = *ca.* 0.02 up to 0.40 ppm) and that for $SCH_3$ protons ($\Delta\delta$ up to 0.54 ppm) show non-identical spatial arrangement of alkylsulfinyl group in 3-methylsulfinylquinolines (**2a**), (**3a**) and (**6a**) and theirs higher alkyl

homologs (**2b**,**c**), (**3b**,**c**) and (**6b**,**c**), respectively.The assignment of the aromatic ring protons was performed by the use of COSY spectra as well as by $^1$H-$^1$H NOE experiments with methoxy group protons indicating the spectral position of H-5 proton signals.

## EXPERIMENTAL

All melting points are uncorrected. The $^1$H NMR spectra were recorded on a Bruker MSL 300 spectrometer at 300 MHz in deuteriochloroform or in hexadeuteriodimethyl sulfoxide solutions with tetramethylsilane as internal standard. The COSY and NOE correlation spectra diagrams were performed on the same samples that were used to determine $^1$H NMR spectra at 500 MHz (on a Bruker AM 500 spectrometer). IR spectra were taken on a UR-10 apparatus (Carl Zeiss, Jena) in KBr pellets. EI MS spectra were determined on a LKB 2091 spectrometer at 15 and 70 eV and Finnigan MAT 95 spectrometer at 70 eV.

TLC analyses were performed employing Merck's silicagel 60 $F_{254}$ plates and a solution of chloroform-methanol (25 : 2, v/v) as an eluent (system I) or Merck's aluminium oxide 60 $F_{254}$ neutral (type E) plates using mixture of chloroform - methanol (60:1, v/v) as an eluent (system II).

4-Methoxy-3-alkylthioquinolines (**1a**) (R=$CH_3$), (**1b**) (R=$C_2H_5$) and (**1c**) (R=n-$C_3H_7$) were prepared from thioquinanthrene and sodium methoxide followed by *S*-alkylation with alkyl iodide according to the "one pot" procedure reported previously.[5]

4-Methoxy-3-propylthioquinoline (**1c**)

This compound was obtained as an oil, bp 167-170 °C / 1 torr. $^1$H NMR ($CDCl_3$), δ : 1.01 (t, 3H, $J$ = 7.3 Hz, $CH_3CH_2$), 1.59-1.66 (sextet, 2H, $J$ = 7.3 Hz, $CH_2CH_2CH_3$), 2.95 (t, 2H, $J$ = 7.3 Hz, $SCH_2CH_2$), 4.13 (s, 3H, $CH_3$-O), 7.51-7.56 (m,1H, H-6), 7.65-7.70 (m,1H, H-7), 8.03-8.06 (m, 1H, H-8), 8.07-8.11 (m,1H, H-5), 8.84 (s, 1H, H-2). EI MS (70 eV) m/z (relative intensity): 233 (100, $M^+$). *Anal.* Calcd for $C_{13}H_{15}NOS$: C, 66.92; H, 6.48; N, 6.00; S, 13.74. Found: C, 67.00; H, 6.50; N, 5.90; S, 13.61.

1,4-Dihydro-4-oxo-3-alkylthioquinolines (**4a**) (R=$CH_3$), (**4b**) (R=$C_2H_5$), (**4c**) (R=n-$C_3H_7$) were prepared by hydrolysis of 4-methoxy-3-alkylthioquinolines (**1**) with boiling hydrochloric acid (1:1).[6] The properties of **4a** and **4b** were the same as reported previously.[6] 1,4-Dihydro-4-oxo-3-propylthioquinoline (**4c**) : mp 137-139 °C (ethanol), lit.,[15] mp 137-138 °C, yield 86%.

Thermal rearrangement of 4-methoxy-3-alkylthioquinolines (**1**) to 1-methyl-3-alkylthio-4-oxo-1,4-dihydroquinolines (**5**)

A glass test tube containing 100 mg of 4-methoxy-3-alkylthioquinoline (**1**) was inserted into a hot oil bath (200 °C) and then kept at this temperature for 0.5- 2 h. The products mixture was cooled down to rt. The

pure products (**5a**) (R=$CH_3$, 90%) and (**5b**) (R=$C_2H_5$, 96%) were obtained by recrystallization of crude material from 95% ethanol. n-Propyl derivative (**5c**) (R=n-$C_3H_7$) was isolated by means of column chromatography on silica gel (100-200 mesh) using a mixture of chloroform - 95% ethanol, 20 : 1, v/v, as an eluent and finally recrystallized from ethanol.

1-Methyl-3-methylthio-4-oxo-1,4-dihydroquinoline (**5a**) : mp 121-123 °C, lit.,[13] mp 123-124 °C. $^1$H NMR and TLC data of **5a** were identical as those reported previously.[16]

1-Methyl-3-ethylthio-4-oxo-1,4-dihydroquinoline (**5b**) : mp 114-116 °C, lit., [4] mp 115-117 °C.

1-Methyl-3-propylthio-4-oxo-1,4-dihydroquinoline (**5c**) : mp 75-77 °C, lit., [4] mp 74-76 °C, yield 86 %.

4-Methoxy-3-alkylsulfinylquinolines (**2**)

4-Methoxy-3-alkylthioquinoline (**1**) (9 mmol) was dissolved upon stirring in 96% sulfuric acid (25 mL) at 0° C. The nitrating mixture (fuming nitric acid, d=1.50, 1.4 mL, *ca.* 31 mmol of $HNO_3$ and 1.4 mL of conc. sulfuric acid) was then added dropwise at 0-5 °C. The mixture was maintained at 0° C for 1.5 h, and then cautiously poured on 300 g of ice, and neutralized at 0 °C with conc. aqueous ammonia, up to pH 6. The solid (in the case of **2a**) was filtered off, washed twice with cold water then with cold methanol, and air-dried. In the case of ethyl and propyl derivatives, the products (**2b**) or (**2c**) were isolated by extraction with chloroform (5 x 20 mL). Combined extracts were dried over anhydrous magnesium sulfate and then treated in a typical manner to give sulfoxides (**2b**) or (**2c**) as thick oils. Ethyl derivative (**2b**) (R=$C_2H_5$) and propyl one (**2c**) (R=n-$C_3H_7$) were separated by means of column chromatography on silica gel (100-200 mesh) using a mixture of chloroform (or methylene chloride) - 95% ethanol, 19 : 1, v/v, as an eluent.

4-Methoxy-3-methylsulfinylquinoline (**2a**).

This compound had mp 138-140 °C (ethanol), yield 85 %. $^1$H NMR ($CDCl_3$), δ : 2.90 (s, 3H, $CH_3SO$), 4.13 (4 (s, 3H, $CH_3$-O), 7.58 (ddd, 1H, $^3J$ = 6.9 Hz, $^3J$ = 8.4 Hz, $^4J$ =1.2 Hz, H-6),7.68 (ddd,1H, $^3J$ = 6.9 Hz, $^3J$ = 8.4 Hz, $^4J$ = 1.5 Hz, H-7), 7.99 (ddd, 1H, $^3J$ = 8.5 Hz, $^4J$ = 1.2 Hz , $^5J$ = 0.7 Hz, H-8), 8.05 (ddd, 1H, $^3J$ = 8.5 Hz, $^4J$ = 1.2 Hz, $^5J$ = 0.7 Hz, H-5), 9.49 (s, 1H, H-2). IR (KBr pellet), $\nu_{S=O}$ = 1055 cm$^{-1}$ . EI MS (70 eV) m/z (relative intensity): 221 (10, $M^+$), 204 (100, M - OH), 206 (51.1, M-$CH_3$). *Anal.* Calcd for $C_{11}H_{11}NO_2S$: C, 59.71; H, 5.02; N, 6.33; S, 14.46. Found: C, 59.63; H, 5.05; N, 6.18; S, 14.69.

4-Methoxy-3-ethylsulfinylquinoline (**2b**).

This compound was obtained as an oil, yield 89 %. $^1$H NMR ($CDCl_3$), δ : 1.26 (t, 3H, $J$ = 7.5 Hz, $CH_3CH_2$), 2.92-3.04 and 3.05-3.16 (2m, 2 x 1H, both from $CH_3CH_2$ group), 4.14 (s, 3H, $CH_3$-O), 7.62 (ddd, 1H, $^3J$ = 6.9 Hz, $^3J$ = 8.3 Hz, $^4J$ = 1.1 Hz, H-6), 7.80 (ddd, 1H, $^3J$ = 6.9 Hz, $^3J$ = 8.4 Hz, $^4J$ = 1.5

Hz, H-7), 8.09 (ddd, 1H, $^{3}J$ = 8.3 Hz, $^{4}J$ = 1.5 Hz, $^{5}J$ = 0.7 Hz, H-8), 8.17 (ddd,1H, $^{3}J$ = 8.5 Hz, $^{4}J$ = 1.1 Hz , $^{5}J$ = 0.7 Hz, H-5), 9.19 (s, 1H, H-2). IR (KBr pellet), $\nu_{S=O}$ = 1020, 1055 and 1075 $cm^{-1}$. EI MS (15 eV) m/z (relative intensity): 235 (12, $M^{+}$). *Anal.* Calcd for $C_{12}H_{13}NO_2S$: C, 61.25; H, 5.57; N, 5.96; S, 13.63. Found: C, 61.41; H, 5.40; N, 6.00; S, 13.79.

4-Methoxy-3-propylsulfinylquinoline (**2c**).

This compound was obtained as an oil, yield 88 %; $^{1}H$ NMR ($CDCl_3$), δ : 1.05 (t, 3H, $J$ = 7.4 Hz, $CH_2C\underline{H}_3$), 1.63-1.73 and 1.83-1.94 (2m, 2 x 1H, both from $CH_2C\underline{H}_2CH_3$ group), 2.94-3.03 (m, 2H, $SC\underline{H}_2CH_2$), 4.13 (s, 3H, $CH_3$-O), 7.59-7.62 (m, 1H, H-6), 7.76-7.81 (m, 1H, H-7), 8.07-8.11 (m, 1H, H-8), 8.14-8.17 (m, 1H, H-5), 9.21 (s, 1H, H-2). IR (KBr pellet), $\nu_{S=O}$ = 1025, 1041, 1061 and 1081 $cm^{-1}$. EI MS (15 eV) m/z (relative intensity): 249 (14, $M^{+}$), 207 (100, M - $C_3H_6$). *Anal.* Calcd for $C_{13}H_{15}NO_2S$: C, 62.63; H, 6.07; N, 5.62; S,12.84. Found: C, 62.80; H, 6.01; N, 5.70; S, 12.72.

1,4-Dihydro-4-oxo-3-methylsulfinyl-6-nitroquinoline (**7a**)

This compound was prepared from quinolinone (**4a**) according to the procedure for the preparation of **2a** followed by recrystallization from DMF to give **7a** with mp 242-243 °C in 70 % yield. $^{1}H$ NMR (DMSO-$d_6$), δ : 2.82 (s, 3H, $CH_3SO$), 7.82 (dd, 1H, $^{3}J$ = 9.1 Hz, $^{5}J$ = 0.5 Hz, H-8), 8.14 (s, 1H, H-2), 8.45 (dd, 1H, $^{3}J$ = 9.1 Hz, $^{4}J$ = 2.6 Hz, H-7), 8.78 (dd, 1H, $^{4}J$ = 2.6 Hz, $^{5}J$ = 0.5 Hz, H-5), 12.35 (s, 1H, $N_1$-H). IR (KBr pellet), $\nu_{S=O}$ = 1030 and 1070 $cm^{-1}$ , $\nu_{NO_2}$ = 1360 and 1560 $cm^{-1}$. EI MS (15 eV) m/z (relative intensity): 252 (22.5, $M^{+}$). *Anal.* Calcd for $C_{10}H_8N_2O_4S$: C, 47.62; H, 3.2; N, 11.11; S, 12.69. Found: C, 47.90; H, 3.01; N, 11.42; S, 12.90.

Oxidation of 3-alkylthio-4-oxo-1,4-dihydroquinolines (**4a-c**) and 1-methyl-3-alkylthio-4-oxo-1,4-dihydroquinolines (**5a-c**) leading to sulfoxides (**3**) or (**6**). (route b,c).

3-Alkylthio-4-oxo-1,4-dihydroquinoline (**4**) or (**5**) (9 mmol) was dissolved with stirring in 96% sulfuric acid (25 mL) at 0 °C. The nitrating mixture (fuming nitric acid, d=1.50, 0.43 mL, *ca.* 10 mmol of $HNO_3$ and 1.4 mL of conc. sulfuric acid) was then added dropwise at 0-5 °C. The addition of nitrating mixture was stopped when deep-cherry colored reaction mixture turned yellow. The mixture was then cautiously poured on 300 g of ice, and neutralized at 0 °C with conc. aqueous ammonia, up to pH 6.

The mixture (together with possible solid precipitates) was extracted with chloroform (4 x 20 mL). The combined extracts were washed with water and then dried over anhydrous sodium sulfate. Evaporation of the solvent left **3** or **6** as a solid. Crude product was recrystallized from ethyl acetate, ethyl acetate /hexane

or ethanol. For analytical purposes, compounds (**3a-c**) were purified by column chromatography (aluminium oxide, methylene chloride / 95% ethanol - 1 : 1, v/v)

1,4-Dihydro-4-oxo-3-methylsulfinylquinoline (**3a**) : mp 248-250 °C, lit., [13] mp 253-254 °C, yield 85 %; $^1$H NMR and IR data of **3a** were identical with those reported previously.[13]

1,4-Dihydro-4-oxo-3-ethylsulfinylquinoline (**3b**)

This compound had mp 65-66 °C (methanol), yield 90 %. $^1$H NMR ($CDCl_3$) : δ 1.28 (t, 3H, $J$ = 7.4 Hz, $CH_3CH_2$ ), 3.03-3.18 and 3.33-3.45 (2m, 2 x 1H, both from $CH_3CH_2$ group), 7.43 (ddd, 1H, $^3J$ = 7.0 Hz, $^3J$ = 8.1 Hz , $^4J$ = 1.1 Hz, H-6), 7.58 (ddd, 1H, $^3J$ = 8.3 Hz, $^4J$ = 1.1 Hz , $^5J$ = 0.5 Hz, H-8), 7.69 (ddd, 1H, $^3J$ = 7.0 Hz, $^3J$ = 8.3 Hz, $^4J$ = 1.2 Hz, H-7), 8.09 (d, 1H, $^3J$ = 3.1 Hz, H-2), 8.32 (ddd, 1H, $^3J$ = 8.1 Hz, $^4J$ = 1.2 Hz, $^5J$ = 0.5 Hz, H-5), 11.82 (br d, $^3J$ = 3 Hz, 1H, N-H). IR (KBr pellet), $\nu_{S=O}$ = 1030 and 1058 cm$^{-1}$; EI MS (15 eV) m/z (relative intensity): 221 (67.8, $M^+$). *Anal.* Calcd for $C_{11}H_{11}NO_2S$ : C, 59.71; H, 5.02; N, 6.33; S, 14.46. Found: C, 59.60; H, 5.10; N, 6.18; S, 14.71.

1,4-Dihydro-4-oxo-3-n-propylsulfinylquinoline (**3c**)

This compound had mp 88-91 °C (ethanol), yield 88 %. $^1$H NMR ($CDCl_3$), δ : 1.08 (t, 3H, $J$ = 7.4 Hz, $CH_3CH_2$), 1.69-1.79 and 1.87-1.97 (2m, 2 x 1H, both from $CH_2CH_2CH_3$ group), 2.95-3.02 and 3.36-3.43 (2m, 2 x 1H, both from $SCH_2CH_2$ group), 7.41-7.45 (m, 1H, H-6), 7.61-7.64 (m, 1H, H-8), 7.67- 7.71 (m, 1H, H-7), 8.13 (d, $J$ = 6.3 Hz, 1H, H-2), 8.31-8.34 (m, 1H, H-5), 12.19 (br d, $J$ = 6.2 Hz, 1H, N-H). IR (KBr pellet), $\nu_{S=O}$ = 1024 and 1057 cm$^{-1}$. EI MS (15 eV) m/z (relative intensity): 235 (59, $M^+$), 193 (100, M - $C_3H_6$). *Anal.* Calcd for $C_{12}H_{13}NO_2S$: C, 61.26; H, 5.57; N, 5.96; S,13.60; Found C, 61.01. H, 5.40; N, 6.10; S, 13.71.

1-Methyl-1,4-dihydro-4-oxo-3-methylsulfinylquinoline (**6a**)

This compound had mp 167-169 °C (ethanol / ethyl acetate), lit.,[17] mp 168-170 °C, yield 85 % .

1-Methyl-1,4-dihydro-4-oxo-3-ethylsulfinylquinoline (**6b**)

This compound had mp 159-161 °C (ethanol / ethyl acetate), lit.,[4] mp 160-163 °C, yield 97 % .

1-Methyl-1,4-dihydro-4-oxo-3-n-propylsulfinylquinoline (**6c**)

This compound had mp 154-155 °C (ethanol / ethyl acetate), lit.,[4] mp 153-155 °C, yield 87 % .

Hydrolysis of 4-methoxy-3-alkylsulfinylquinolines (**2**) with hydrochloric acid to 1,4-dihydro-4-oxo-3-alkylsulfinyl-quinolines (**3**)

A mixture of **2** (1 mmol) and hydrochloric acid (1:1) (7 mL) was heated under stirring at 65-68 °C for 1-2 h. The solution was then evaporated to dryness under vacuum at 60 °C. The residue was triturated with 2

mL of water and neutralized with 5% aqueous sodium bicarbonate to pH 5.5-6. The resultant solid was filtered off, washed with water and air-dried to give crude 4(1*H*)-quinolinone derivatives (**3**). Compounds (**3**) were finally recrystallized from ethanol.

| Results: | Substrate | Product (yield, mp) |
|---|---|---|
| | (**2a**) (R=$CH_3$), | (**3a**) (85, 238-240 °C) |
| | (**2b**) (R=$C_2H_5$) | (**3b**) (90, 65-6 °C) |
| | (**2c**) (R=n-$C_3H_7$), | (**3c**) (88, 136-8 °C) |

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