Thermolytic Ring Closure Reactions of 4-Azido-3-phenylsulfanyl- and 4-Azido-3-phenylsulfonyl-2-quinolones to 12*H*-Quinolino-[3,4-*b*][1,4]benzothiazin-6(5*H*)-ones [1]

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4-Hydroxy-3-phenylsulfanyl-2-quinolones **2** and 4-hydroxy-3-sulfonyl-2-quinolones **7**, which are readily accessible from 4-hydroxy-2-quinolones **1** and diphenyldisulfide or thiophenol, can be converted to 4-azido-3-phenylsulfanyl-2-quinolones **10** or 4-azido-3-phenylsulfonyl-2-quinolones **12** *via* 4-chloro-3-phenylsulfanyl-2-quinolones **5** or 4-chloro-3-phenylsulfonyl-2-quinolones **9**, respectively. Thermolysis of the azides **10** and **12** results in a cyclization reaction to give quinolino[3,4-*b*][1,4]benzothiazinone **11** and quinolino[3,4-*b*][1,4]benzothiazinone dioxides **13**, respectively. The conditions for thermolysis have been studied by differential scanning calorimetry (DSC).

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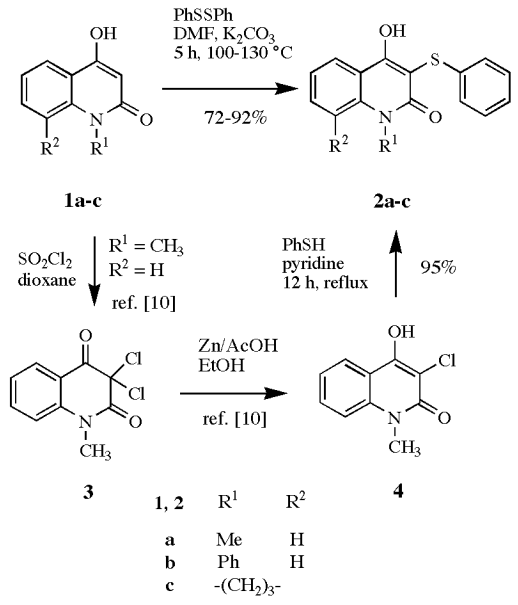
Organic azides with reactive *ortho*-groups such as aryl-, heteroaryl- or acyl groups are known to decompose on thermolysis or photolysis followed by a cyclization to heterocycles, either *via* a nitrene or an electrocyclic mechanism [2]. Mainly, this cyclization type leads to five-membered heterocycles. Two typical examples are the attack of the azide nitrogen either to the 2-position of a phenyl ring in *ortho*-position to the azide forming indoles [3], or by attack of the azide nitrogen to e.g. the oxygen atom of a carbonyl group in *ortho*-position to the azide forming isoxazoles [4]. Only in a few cases, the formation of six-membered heterocycles is reported [2], *e.g.* with a benzyl substituent in *ortho*-position of the azido group; in this way we obtained from 4-azido-3-benzyl-2-quinolones in good yields dibenzo[*b*,*h*][1,6]naphthyridin-6-ones [5]. Similarly, the phenylsulfanyl group, Ph-S, or their oxidized variants, the phenylsulfoxide group, Ph-SO, and the phenylsulfonyl group, Ph-SO_2, seemed to be good candidates for such a thermal azide cyclization.

Recently a direct sulfenylation of 4-hydroxy-2-quinolones by the action of diphenyl disulfide has been developed in our group [6,7]. This reaction sequence was used, in this contribution, in order to obtain 4-azido-2-quinolones with phenylsulfanyl groups in 3-position as suitable starting materials for the planned thermal cyclization of azides to six-membered heterocycles. The reaction of 4-hydroxy-2-quinolones **1** with diphenyl disulfide was carried out as described in references [6,7] under basic conditions. During the reaction the thiophenolate anion was formed, which was oxidized by oxygen back to diphenyl disulfide. In contrast to the earlier described method [7], we obtained better results when the air for oxidation was not bubbled through the reaction mixture, but compressed air was blown onto the mixture with a tube ending above the surface of the reaction mixture. This was because the inlet pipe often was clogged when air was bubbled through the mixture. In this way the amount of employed diphenyl disulfide could be reduced to a half-molar amount and the 3-phenylsulfanyl-2-quinolones **2a-c** were obtained in good to excellent yields. There is also the possibility to obtain the thioethers **2** from thiophenol and 3-chloro-4-hydroxyquinolones **4** in pyridine as basic solvent in excellent yields, however this method needs two more steps.

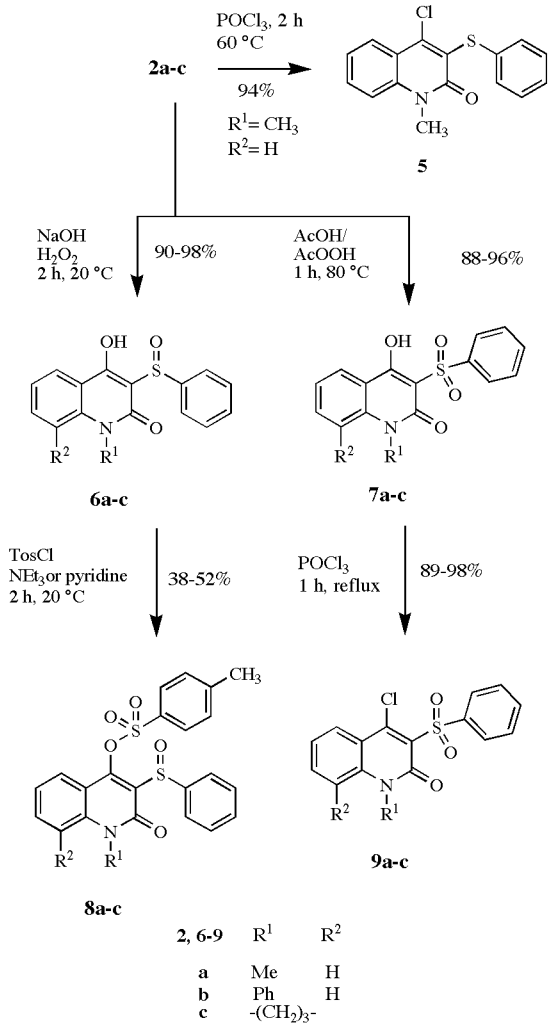
Scheme 1



To obtain the desired azides, 4-hydroxy-3-phenylsulfanyl-2-quinolones **2** were converted in the next step to reactive intermediates. The reaction of **2a** with phosphoryl chloride gave in excellent yields 4-chloro-1-methyl-3-phenylsulfanyl-2-quinolone (**5**). The oxidation of the thioethers **2a-c** gave depending on the conditions either in alkaline hydrogen peroxide solution the sulfoxides **6a-c** or with peracetic acid the sulfones **7a-c**. The oxidation to the sulfoxides **6a-c** needed some care, because higher temperatures and longer reaction

times caused partial oxidation to the sulfones **7** that gave a mixture which was difficult to separate. Keeping the temperature at 20 °C by slow addition of hydrogen peroxide minimized by-products. The reaction of the sulfones **7a-c** with phosphoryl chloride using triethylamine to destroy hydrogen bondings between the hydroxy and the sulfonyl group gave in excellent yields 4-chloro-3-phenylsulfonyl-2-quinolones **9a-c**. However, the sulfoxides **6** could not be converted to 4-chloroquinolones, because a large number of unseparable byproducts were formed. So the tosylates **8a-c**, another reactive class of compounds, were synthesized by reaction of the sulfones **6** with tosylchloride in a basic solvent.

Scheme 2

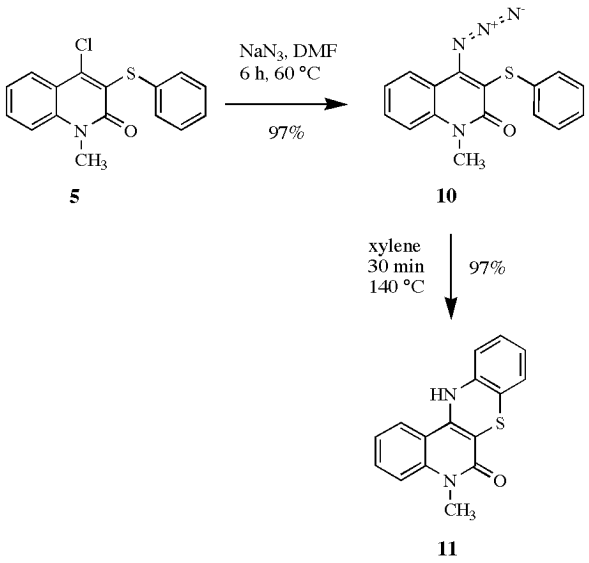


2, 6-9	R^1	R^2
a	Me	H
b	Ph	H
c	-$(CH_2)_3$-	

Nucleophilic substitution of the chloro atom in 4-chloro-1-methyl-3-phenylsulfanyl-2-quinolone (**5**) with the azide anion was performed by reaction with sodium azide in dimethyl formamide at 60 °C in nearly quantitative yield. Data about the thermal behavior of 4-azido-1-methyl-3-phenylsulfanyl-2-quinolone (**10**) were obtained using differential scanning calorimetry. The diagrams revealed that the azidoquinolone **10** started to decompose without a melting area at about 140 °C. The reaction enthalpy (-190 mcal/mg) is rather high [1] which needs safety precautions for larger reaction scales. After the reaction peak no decomposition signals were visible and at 325 °C a small melting area could be observed which could be assigned to the cyclized follow-up product. This observation gave hints that the reaction product was stable at higher temperatures without decomposition.

The cyclization was performed in a preparative manner using xylene as the solvent following hints from the DSC diagram. After a reaction time of 10 minutes, a light brown solid began to be precipitated, and after 30 minutes the reaction was finished. The reaction product was the expected 5-methyl-12*H*-quinolino[3,4-*b*][1,4]benzothiazino-6(5*H*)-one (**11**) which could be confirmed by spectra and analytical data. The spectral data are also in agreement with literature data of this compound obtained from 4-hydroxy-1-methyl-2-quinolone (**1a**) and 2-aminothiophenol under acidic conditions [8].

Scheme 3



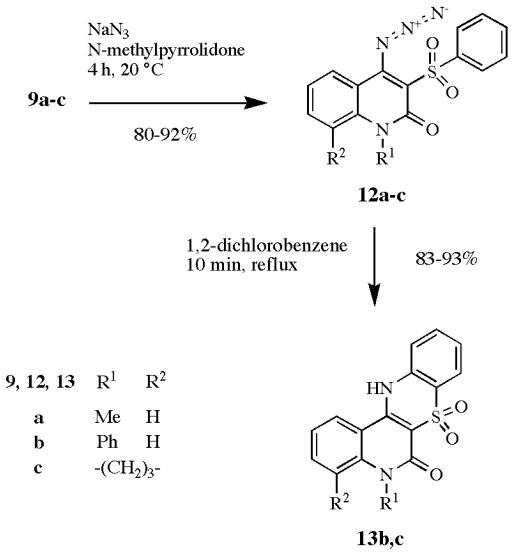
The reaction of the 3-phenylsulfinyl-4-tosyloxyquinolones **8a-c** with sodium azide gave no synthetic useable results. At low temperatures no reaction could be observed, and at elevated temperatures decomposition to a mixture of compounds took place.

The exchange of the chloro group in 4-chloro-3-phenylsulfonylquinolones **9a-c** could be easily achieved already at room temperature using a small excess of sodium azide in *N*-methylpyrrolidone as the solvent to give 4-azido-3-phenylsulfonyl-2-quinolones **12a-c** in excellent yields. The data from differential scanning calorimetry (DSC)

showed only a single signal with onsets between 156-187 °C, without further decomposition and melting peaks. The reaction enthalpies range between -127 and -160 mcal/mg, which is similarly high as in the azide **10**, and again with larger scales some safety precaution should be considered. Thermogravimetric analyses of **12b** show the cleavage of nitrogen (mass defect 7% or 28 g/mol) between 177-183 °C, followed by a horizontal line until 250 °C which indicates a stable area, and then again continuous decomposition.

The synthetic thermolysis of the azides **12b,c** was performed in refluxing 1,2-dichlorobenzene according to the onset temperatures of 154-160 °C obtained from DSC data; after 10 minutes the evolution of nitrogen gas had stopped and the reaction mixture was worked up. The spectral and microanalytical data were in agreement with the structures of 5-phenyl-12*H*-quinolino[3,4-*b*][1,4]benzothiazin-6(5*H*)-one 7,7-dioxide (**13b**) and 4,5,6,14-tetrahydrobenzo[9,10]quinolizino[3,2-*b*][1,4]benzothiazin-8-one 9,9-dioxide (**13c**), a hitherto unknown class of compounds.

Scheme 4



EXPERIMENTAL

Melting points were determined on a Gallenkamp Melting Point Apparatus, Mod. MFB-595 in open capillary tubes. Calorimetric data were obtained on a Rheometric Scientific DSC-Plus instrument with the differential scanning calorimetry software V5.42. The differential scanning calorimetry plots were recorded between 25 - 400 °C, with a heating rate of 2-10 °C/min, and 1.5-3 mg compound in sealed aluminium crucibles (11 bar). Thermogravimetric data were obtained with a Perkin Elmer Thermogravimetric Analyzer TGA7. The plots were recorded between 30-450 °C, with a heating rate of 10 °C/min, 5-12 mg compound in platinum crucibles and a slow stream of nitrogen in the thermobalance. The ^{1}H nmr spectra were recorded on a Bruker AM 360 instrument (360 MHz). The solvent for nmr spectra was deuteriochloroform unless otherwise stated. Chemical shifts are reported in ppm from internal tetramethylsilane standard and are given in δ-units. Infrared spectra were taken on a Perkin-Elmer 298 spectrophotometer or a Galaxy Series FTIR 7000 in potassium bromide pellets. Elemental analyses were performed on a Fisons elemental analyzer, Mod. EA 1108 and are within ±0.4 of the theoretical percentages. All reactions were monitored by thin layer chromatography carried out on 0.2 mm silica gel F-254 (Merck) plates using uv light (254 and 366 nm) for detection. Common reagent-grade chemicals are either commercially available and were used without further purification or prepared by standard literature procedures.

4-Hydroxy-2-quinolones (**1a-c**) were obtained from the corresponding anilines and diethyl malonate in a three step reaction according to an earlier reported procedure [9]. 3,3-Dichloro-1-methyl-quinoline-2,4(1*H*,3*H*)-dione (**3**) and 3-chloro-4-hydroxy-1-methyl-quinolin-2(1*H*)-one (**4**) were obtained using the methods described in reference [10].

General Procedure for the Synthesis of 4-Hydroxy-3-phenylsulfanylquinolin-2(1*H*)-ones **2a-c**.

A solution of the corresponding 4-hydroxy-2-quinolone **1a-c** (50-60 mmol) in dimethylformamide (100 mL) was combined with an excess of dry potassium carbonate (10 g) and diphenyldisulfide (25-30 mmol). The mixture was heated to 100-130 °C and stirred for 5 hours. During the reaction time a stream of compressed air was blown onto the mixture, using a tube which ended above the surface of the reaction mixture to avoid blocking of the inlet pipe, to oxidize the formed waste thiophenol back to diphenyldisulfide. The reaction mixture was cooled to room temperature and diluted with water (500 mL) and excess diphenyldisulfide was filtered off. The filtrate was acidified with 6 *N* hydrochloric acid to pH = 1 (attention: strong foaming) and the resulting precipitate was separated. To avoid bad smell from thiophenol residues, the filtrate was oxidized using sodium hypochlorite solution.

4-Hydroxy-1-methyl-3-phenylsulfanylquinolin-2(1*H*)-one (**2a**).

Method a.

Compound **2a** was obtained according to the general procedure from 4-hydroxy-2-quinolone **1a** (10.51 g, 60 mmol) and diphenyldisulfide (6.55 g, 30 mmol); the yield was 15.60 g (92%), colorless prisms, mp 230 °C (ethanol).

Method b.

A solution of 3-chloro-4-hydroxy-1-methyl-2-quinolone (**4**) (5.25 g, 25 mmol) and thiophenol (2.8 g, 25 mmol) in pyridine (20 mL) was heated for 12 hours under reflux. Then the mixture was poured onto ice-water and acidified to pH = 1. The resulting oily product was stirred in water until solid, and then collected by suction filtration. The yield was 7.77 g (95%), colorless platelets, mp 230 °C (ethanol); lit mp 230-232 °C [7].

4-Hydroxy-1-phenyl-3-phenylsulfanylquinolin-2(1*H*)-one (**2b**).

Compound **2b** was obtained from 4-hydroxy-2-quinolone **1b** (11.85 g, 50 mmol) and diphenyldisulfide (5.45 g, 25 mmol); the yield was 12.44 g (72%), colorless prisms, mp 181 °C (toluene); lit mp 180-183 °C [7].

1-Hydroxy-2-phenylsulfanyl-6,7-dihydro-5*H*-benzo[*ij*]quinolizin-3-one (**2c**).

Compound **2c** was obtained from 1-hydroxybenzoquinolizin-3-one (**1c**) (10.0 g, 50 mmol) and diphenyldisulfide (5.45 g, 25

mmol); the yield was 14.08 g (91%), colorless prisms, mp 174-175 °C (ethanol); ir: 1620 m, 1580 m cm^{-1}; ^1H nmr (deuteriodimethylsulfoxide): δ 2.05 (q, *J* = 6 Hz, CH_2), 3.00 (t, *J* = 6 Hz, Ar-CH_2), 4.05 (t, *J* = 6 Hz, NCH_2), 7.10-7.20 (m, 4 ArH), 7.25-7.35 (m, 2 ArH), 7.45 (d, *J* = 7 Hz, H-8), 7.9 (dd, *J* = 2+7.5 Hz, H-10).

Anal. Calcd. for $C_{18}H_{15}NO_2S$: C, 69.88; H, 4.89; N, 4.53; S 10.36. Found: C, 69.97; H, 4.86; N, 4.49; S 10.40.

4-Chloro-1-methyl-3-phenylsulfanylquinolin-2(1*H*)-one (**5**).

A mixture of 4-hydroxy-1-methyl-3-phenylsulfanyl-2-quinolone (**2a**) (2.83 g, 10 mmol) in phosphoryl chloride (30 mL) was warmed to 60 °C for 2 hours. After cooling to room temperature the excess phosphoryl chloride was removed *in vacuo* and the residue poured onto ice/water (200 mL). The mixture was brought to pH = 6 with sodium carbonate, the resulting oily product stirred with water until solid and collected by filtration. The yield was 2.05 g (94%), yellow plates, mp 169-171 °C (ethanol); ir: 1650 s cm^{-1}; ^1H nmr: δ 3.72 (s, NCH_3), 7.31 (m, 7 ArH), 7.63 (t, *J* = 8 Hz, 1 ArH), 8.12 (dd, *J* = 2+8 Hz, 5-H).

Anal. Calcd. for $C_{16}H_{12}ClNOS$: C, 63.68; H, 4.00; N, 4.64. Found: C, 63.57; H, 3.82; N, 4.52.

General Procedure for the Synthesis of 4-Hydroxy-3-phenylsulfinylquinolin-2(1*H*)-ones **6a-c**.

To a solution of the corresponding 4-hydroxy-3-phenylsulfanyl-2-quinolone **2a-c** (10-20 mmol) in 1 *N* aqueous sodium hydroxide solution (40-80 mL) in a 500 mL flask, hydrogen peroxide (30%, 20-40 mL) was added slowly to keep the temperature at room temperature. After stirring for further 2 hours at room temperature the mixture was brought to pH = 5-6 with 6 *N* hydrochloric acid and the formed precipitate separated by filtration.

4-Hydroxy-1-methyl-3-phenylsulfinylquinolin-2(1*H*)-one (**6a**).

Compound **6a** was obtained from 4-hydroxy-3-phenylsulfanyl-2-quinolone **2a** (5.67 g, 20 mmol) and hydrogen peroxide (40 mL) in sodium hydroxide (80 mL); the yield was 5.76 g (97%), colorless prisms, mp 175 °C (ethanol); lit mp 175-176 °C [7].

4-Hydroxy-1-phenyl-3-phenylsulfinylquinolin-2(1*H*)-one (**6b**).

Compound **6b** was obtained from 4-hydroxy-3-phenylsulfanyl-2-quinolone **2b** (3.45 g, 10 mmol) and hydrogen peroxide (20 mL) in sodium hydroxide (40 mL). The yield was 3.53 g (98%), colorless prisms, mp 192 °C (toluene); 1640 s, 1560 s cm^{-1}; ^1H nmr (deuteriodimethylsulfoxide): δ 6.56 (d, *J* = 8.5 Hz, 1 ArH), 7.24 (d, *J* = 6.8 Hz, 1 ArH), 7.31-7.39 (m, 2 ArH), 7.54-7.64 (m, 7 ArH), 7.93-7.96 (m, 2 ArH), 8.01 (dd, *J* = 1.2+8 Hz, 1 ArH).

Anal. Calcd. For $C_{21}H_{15}NO_3S$: C, 69.79; H, 4.18; N, 3.88; S, 8.87. Found: C, 69.77; H, 3.94; N, 3.76; S, 8.56.

1-Hydroxy-2-phenylsulfinyl-6,7-dihydro-5*H*-benzo[*ij*]quinolizin-3-one (**6c**).

Compound **6c** was obtained from 1-hydroxy-2-phenylsulfanylbenzoquinolizin-3-one **2c** (3.09 g, 10 mmol) and hydrogen peroxide (20 mL) in sodium hydroxide (40 mL). The yield was 2.92 g (90%), colorless prisms, mp 175 °C (ethanol); ir: 1620 m, 1580 m cm^{-1}; ^1H nmr: δ 2.00-2.15 (m, CH_2), 2.85-3.00 (t, *J* = 6.5 Hz, Ar-CH_2), 4.05 (t, *J* = 6.5 Hz, NCH_2), 7.05-7.50 (m, 5 ArH), 7.80-8.05 (m, 3 ArH).

Anal. Calcd. for $C_{18}H_{15}NO_3S$: C, 66.44; H, 4.64; N, 4.30; S, 9.85. Found: C, 66.28; H, 4.81; N, 4.27; S, 9.70.

General Procedure for the Synthesis of 4-Hydroxy-3-phenylsulfonylquinolin-2(1*H*)-ones **7a-c**.

A solution of the corresponding 4-hydroxy-3-phenylsulfanyl-2-quinolone **2a-c** (20-30 mmol) in glacial acetic acid (55-80 mL) was heated to 50 °C. Then, peracetic acid (40%, 20-30 mL) was added at a rate such that the temperature did not exceed 75-80 °C. The reaction mixture was then stirred at that temperature for 1 hour. The mixture was cooled to room temperature, poured onto ice/water (300 mL) and the solid collected by suction filtration.

4-Hydroxy-1-methyl-3-phenylsulfonylquinolin-2(1*H*)-one (**7a**).

Compound **7a** was obtained from 4-hydroxy-3-phenylsulfanyl-2-quinolone **2a** (5.67 g, 20 mmol) and peracetic acid (20 mL) in glacial acetic acid (55 mL); the yield was 5.46 g (88%), colorless prisms, mp 246 °C (toluene); ir: 3000-3200 br, 1640 s, 1620 s cm^{-1}; ^1H nmr: δ 3.44 (s, NCH_3), 7.38 (t, *J* = 7.3 Hz, 1 ArH), 7.55 (d, *J* = 8.6 Hz, 1 ArH), 7.62 (t, *J* = 8.4 Hz, 2 ArH), 7.72 (t, *J* = 7.5 Hz, 1 ArH), 7.82 (t, *J* = 7 Hz, 1 ArH), 8.70 (d, *J* = 7.5 Hz, 2 ArH), 8.14 (d, *J* = 7 Hz, 1 ArH).

Anal. Calcd. for $C_{16}H_{13}NO_4S$: C, 60.94; H, 4.16; N, 4.44. Found: C, 60.61; H, 4.00; N, 4.35.

4-Hydroxy-1-phenyl-3-phenylsulfonylquinolin-2(1*H*)-one (**7b**).

Compound **7b** was obtained from 4-hydroxy-3-phenylsulfanyl-2-quinolone **2b** (6.91 g, 20 mmol) and peracetic acid (20 mL) in glacial acetic acid (55 mL); the yield was 6.94 g (92%), colorless needles, mp 253 °C (acetic acid); ir: 2900-3100 br, 1660 s, 1620 s cm^{-1}; ^1H nmr: δ 6.51 (d, *J* = 8.5 Hz, 1 ArH), 7.23 (d, *J* = 7 Hz, 2 ArH), 7.36 (t, *J* = 7 Hz, 1 ArH), 7.51-7.62 (m, 6 ArH), 7.71 (t, *J* = 7 Hz, 1 ArH), 8.04 (d, *J* = 7 Hz, 2 ArH), 8.16 (d, J = 7 Hz, 1 ArH).

Anal. Calcd. for $C_{21}H_{15}NO_4S$: C, 66.83; H, 4.01; N, 3.71; S, 8.50. Found: C, 66.97; H, 3.87; N, 3.64; S, 8.42.

1-Hydroxy-2-phenylsulfonyl-6,7-dihydro-5*H*-benzo[*ij*]quinolizin-3-one (**7c**).

Compound **7c** was obtained from 1-hydroxy-2-phenylsulfanylbenzo[*ij*]quinolizinone **2c** (9.28 g, 30 mmol) and peracetic acid (30 mL) in glacial acetic acid (80 mL); the yield was 9.37 g (96%), colorless needles, mp 215-216 °C (dimethylformamide/water); ir: 1640 s cm^{-1}; ^1H nmr: δ 2.00 (q, *J* = 6.7 Hz, CH_2), 2.90 (t, *J* = 6.7 Hz, $ArCH_2$), 4.00 (t, *J* = 6.7 Hz, NCH_2), 7.10-7.70 (m, 5 ArH), 8.00-8.20 (m, 3 ArH), 12.20 (s, OH).

Anal. Calcd. for $C_{18}H_{15}NO_4S$: C, 63.33; H, 4.43; N, 4.10; S, 9.39. Found: C, 62.98; H, 4.62; N, 4.11; S, 9.43.

1-Methyl-4-(4-methylphenylsulfonyloxy)-3-phenylsulfinylquinolin-2(1*H*)-one (**8a**).

A mixture of 4-hydroxy-3-phenylsulfinylquinolone **6a** (1.50 g, 5 mmol) and *p*-toluenesulfonyl chloride (1.33 g, 7 mmol) in dry pyridine (20 mL) was stirred at room temperature for 2 hours. The reaction mixture was then poured onto ice/water (200 mL) and formed a precipitate which was collected by suction filtration and dried *in vacuo*; the yield was 0.87 g (38%), yellow prisms, mp 180 °C (toluene); ^1H nmr: δ 2.50 (s, CH_3), 3.75 (s, NCH_3), 7.15-7.45 (m, 10 ArH), 7.60-7.73 (m, 1 ArH), 7.85-8.05 (m, 2 ArH).

Anal. Calcd. for $C_{23}H_{19}NO_5S_2$: C, 60.91; H, 4.22; N, 3.09. Found: C, 60.70; H, 4.23; N, 3.25.

4-(4-Methylphenylsulfonyloxy)-1-phenyl-3-phenylsulfinylquinolin-2(1*H*)-one (**8b**).

A mixture of 4-hydroxy-3-phenylsulfinylquinolone **6b** (1.52 g, 8 mmol) and *p*-toluenesulfonyl chloride (1.90 g, 10 mmol) in dry triethylamine (20 mL) was reacted and worked up as described for **8a**; the yield was 1.34 g (52%), yellow-orange prisms, mp 192 °C (ethanol); ^{1}H nmr: δ 2.47 (s, CH_3), 6.60 (d, *J* = 8.5 Hz, 1 ArH), 7.11-7.68 (m, 15 ArH), 7.95 (d, *J* = 8 Hz, 1 ArH), 8.03 (d, *J* = 8 Hz, 1 ArH).

Anal. Calcd. for $C_{28}H_{21}NO_5S_2$: C, 65.23; H, 4.11; N, 2.72. Found: C, 64.85; H, 3.93; N, 3.11.

1-(4-Methylphenylsulfonyloxy)-2-phenylsulfinyl-6,7-dihydro-5*H*-benzo[*ij*]quinolizin-3-one (**8c**).

A mixture of 1-hydroxy-2-phenylsulfinylbenzoquinolizin-3-one **6c** (1.63 g, 5 mmol) and *p*-toluenesulfonyl chloride (1.33 g, 7 mmol) in dry pyridine (20 mL) was reacted and worked up as described for **8a**; the yield was 1.06 g (44%), colorless prisms, mp 217 °C (ethanol); ^{1}H nmr: δ 2.10 (q, CH_2), 2.45 (s, CH_3), 3.00 (t, *J* = 6 Hz, Ar-CH_2), 4.15 (t, *J* = 6 Hz, NCH_2), 7.10-7.45 (m, 9 ArH), 7.80-7.95 (m, 3 ArH).

Anal. Calcd. for $C_{25}H_{21}NO_5S_2$: C, 62.61; H, 4.41; N, 2.92. Found: C, 62.13; H, 4.76; N, 2.97.

4-Chloro-1-methyl-3-phenylsulfonylquinolin-2(1*H*)-one (**9a**).

Dry triethylamine (5 mL) was added to a solution of 4-hydroxy-3-phenylsulfonyl-2-quinolone **7a** (4.73 g, 15 mmol) in phosphoryl chloride (50 mL), the mixture was heated under reflux for 1 hour and then the excess phosphoryl chloride removed *in vacuo*. The residue was poured onto ice/water (300 mL) and brought to pH = 6 with concentrated aqueous sodium hydroxide. The precipitate was collected by suction filtration and washed with water; the yield was 4.90 g (98%), pale brown prisms, mp 217 °C (ethanol); ir: 1640 s, 1600 s 1530 m cm^{-1}; ^{1}H nmr (deuteriodimethylsulfoxide): δ 3.50 (s, NCH_3), 7.46 (t, *J* = 8 Hz, 1 ArH), 7.58-7.71 (m, 4 ArH), 7.86 (t, *J* = 8.5 Hz, 1 ArH), 8.00 (d, *J* = 7.3 Hz, 2 ArH), 8.31 (d, *J* = 8.3 Hz, 1 ArH).

Anal. Calcd. for $C_{16}H_{12}ClNO_3S$: C, 57.57; H, 3.62; N, 4.20. Found: C, 57.41; H, 3.59; N, 4.11.

4-Chloro-1-phenyl-3-phenylsulfonylquinolin-2(1*H*)-one (**9b**).

Compound **9b** was obtained from 4-hydroxy-3-phenylsulfonylquinolone **7b** (3.77 g, 15 mmol), dry triethylamine (4 mL) and phosphoryl chloride (40 mL) as described for **9a**; the yield was 3.30 g (89%), pale brown needles, mp 299 °C (toluene); ir: 3050 w, 1670 s, 1600 s 1530 m cm^{-1}; ^{1}H nmr (deuteriodimethylsulfoxide): δ 6.60 (d, *J* = 7.5 Hz, 1 ArH), 7.25-7.35 (m, 2 ArH), 7.45-7.70 (m, 8 ArH), 8.00 (d, *J* = 7.5 Hz, 2 ArH), 8.40 (d, *J* = 7.5 Hz, 1 ArH).

Anal. Calcd. for $C_{21}H_{14}ClNO_3S$: C, 63.72; H, 3.56; N, 3.54. Found: C, 64.06; H, 3.55; N, 3.46.

1-Chloro-2-phenylsulfonyl-6,7-dihydro-5*H*-benzo[*ij*]quinolizin-3-one (**9c**).

Compound **9c** was obtained from 1-hydroxy-2-phenylsulfonylbenzoquinolizin-3-one **7c** (3.25 g, 10 mmol), dry triethylamine (4 mL) and phosphoryl chloride (40 mL) as described for **9a**; the yield was 3.30 g (93%), pale colorless needles, mp 215 °C (ethanol); ir: 1640 s, 1530 s cm^{-1}; ^{1}H nmr (deuteriodimethylsulfoxide): δ 1.93-1.98 (m, CH_2), 2.92 (t, *J* = 6 Hz, Ar-CH_2), 3.90 (t, *J* = 6 Hz, NCH_2), 7.36 (t, *J* = 7.5 Hz, 1 ArH), 7.58-7.63 (m, 3 ArH), 7.67-7.71 (m, 1 ArH), 8.00 (d, *J* = 7 Hz, 2 ArH), 8.15 (d, J = 7.5 Hz, 1 ArH).

Anal. Calcd. for $C_{18}H_{14}ClNO_3S$: C, 60.08; H, 3.92; N, 3.89. Found: C, 59.79; H, 3.79; N, 3.81.

4-Azido-1-methyl-3-phenylsulfanylquinolin-2(1*H*)-one (**10**).

A mixture of 4-chloro-1-methyl-3-phenylsulfanylquinolin-2(1*H*)-one (**5**) (1.51 g, 5 mmol) and sodium azide (0.98 g, 15 mmol) in dimethylformamide (20 mL) was warmed to 60 °C for 6 hours. Then the mixture was cooled to room temperature and poured onto ice/water (150 mL), the formed precipitate was separated by filtration and washed with water (100 mL). The yield was 1.42 g (92%), colorless platelets, mp 152-153 °C (dec); calorimetric data for thermolysis: reaction/decomposition onset at 130 °C, peak maximum 149 °C, ΔH = -194 mcal/mg, mp 325.2 °C (**11**); ir: 2105 s, 1645 s; ^{1}H nmr: δ 3.72 (s, CH_3), 7.28 (m, 7 ArH), 7.63 (t, *J* = 8 Hz, 1 ArH), 8.04 (dd, *J* = 2+8 Hz, H-5).

Anal. Calcd. for $C_{16}H_{12}N_4OS$: C, 62.32; H, 3.92; N, 18.17. Found: C, 61.98; H, 3.74; N, 18.15.

5-Methyl-12*H*-quinolino[3,4-*b*][1,4]benzothiazin-6(5*H*)-one (**11**).

A solution of 4-azido-1-methyl-3-phenylsulfanyl-2-quinolone (**10**) (1.37 g, 4.4 mmol) in xylene (50 mL) was heated under reflux for 30 minutes. During this period, nitrogen was evolved and the color of the solution changed first to yellow and then a light brown solid precipitated. The solvent was removed *in vacuo* and the residue dried at 40 °C. The yield was 1.21 g (97%), light brown needles, mp 324-325 °C; lit mp. >310 °C [8]; ir: 3340 m, 1625 m, 1605 m, 1575 s; ^{1}H nmr (deuteriodimethylsulfoxide): δ 3.58 (s, CH_3), 6.89 (m, 4 ArH), 7.48 (m, 3 ArH), 8.11 (dd, *J* = 2+8 Hz, 1-H), 8.48 (s, 1 NH).

Anal. Calcd. for $C_{16}H_{12}N_2OS$: C, 68.55; H, 4.31; N, 9.99. Found: C, 68.30; H, 4.02; N, 9.89.

4-Azido-1-methyl-3-phenylsulfonylquinolin-2(1*H*)-one (**12a**).

A suspension of the 4-chloro-3-phenylsulfonyl-2-quinolone **9a** (1.67 g, 5 mmol) and sodium azide (0.50 g, 7 mmol) in *N*-methylpyrrolidone (30 mL) was stirred at room temperature for 4 hours. The reaction mixture was then poured onto ice/water (100 mL), the mixture was allowed to stand for 12 hours and then the precipitate was collected by suction filtration; the yield was 1.56 g (92%), pale brown prisms, mp 183 °C (dec) (toluene); calorimetric data for thermolysis: reaction/decomposition onset at 173 °C, peak maximum 183 °C, ΔH = -127 mcal/mg; ir: 3100 w, 2250 w, 2120 s, 1680 s cm^{-1}; ^{1}H nmr: δ 3.55 (s, NCH_3), 7.25-7.40 (m, 2 ArH), 7.50-7.80 (m, 4 ArH), 8.15 (d, *J* = 7.5 Hz, 2 ArH), 8.30 (d, *J* = 7.5 Hz, 1 ArH).

Anal. Calcd. for $C_{16}H_{12}N_4O_3S$: C, 56.46; H, 3.55; N, 16.46. Found: C, 56.85; H, 3.57; N, 16.16.

4-Azido-1-phenyl-3-phenylsulfonylquinolin-2(1*H*)-one (**12b**).

It was obtained from 4-chloro-3-phenylsulfonyl-2-quinolone **9b** (1.90 g, 5 mmol) according to the procedure described for **12a**; the yield was 1.69 g (84%), pale brown prisms, mp 190 °C (ethanol); calorimetric data for thermolysis: reaction/decomposition onset at 187 °C, peak maximum 190 °C, ΔH = -160 mcal/mg; ir: 3050 w, 2120 s, 1660 s cm^{-1}; ^{1}H nmr: δ 6.60 (d, *J* = 7.5 Hz, 1 ArH), 7.10 (d, *J* = 7.5 Hz, 2 ArH), 7.25-7.35 (m, 1 ArH), 7.40-7.60 (m, 7 ArH), 8.10 (dd, *J* = 1.5+7.5 Hz, 2 ArH), 8.30 (dd, J = 1.5+7.5 Hz, 5-H).

Anal. Calcd. for $C_{21}H_{14}N_4O_3S$: C, 62.68; H, 3.51; N, 13.92; S, 7.97. Found: C, 62.71; H, 3.60; N, 13.70; S, 7.82.

1-Azido-2-phenylsulfonyl-6,7-dihydro-5*H*-benzo[*ij*]quinolizin-3-one (**12c**).

Compound **12c** was obtained from 1-chloro-2-phenylsulfonylbenzoquinolizin-3-one **6c** (1.83 g, 5 mmol) according to the procedure described for **12a**; the yield was 1.46 g (80%), pale brown prisms, mp 164 °C (ethanol); calorimetric data for thermolysis: reaction/decomposition onset at 156 °C, peak maximum 164 °C, ΔH = -154 mcal/mg; ir: 2950 w, 2200 m, 2140 s, 1640 s cm^{-1}; ^{1}H-nmr: δ 1.95-2.05 (m, CH_2), 2.95 (t, *J* = 6 Hz, Ar-CH_2), 4.00 (t, *J* = 6 Hz, NCH_2), 7.15-7.25 (m, 1 ArH), 7.40-7.60 (m, 4 ArH), 8.00-8.20 (m, 3 ArH).

Anal. Calcd. for $C_{18}H_{14}N_4O_3S$: C, 59.01; H, 3.85; N, 15.29. Found: C, 59.15; H, 3.82; N, 15.22.

5-Phenyl-12*H*-quinolino[3,4-*b*][1,4]benzothiazin-6(5*H*)-one 7,7-dioxide (**13b**).

A suspension of 4-azidoquinolone **12b** (0.310 g, 0.8 mmol) in dichlorobenzene (3 mL) was heated under reflux for 10 minutes. During this time evolution of nitrogen gas could be observed. The mixture was cooled to room temperature and quenched with hexane. The formed solid was collected by suction filtration and washed with hexane; the yield was 0.250 g (83%), brown prisms, mp 210 °C (dimethylformamide); ir: 3320 m, 1660 s cm^{-1}; ^{1}H nmr (deuteriodimethylsulfoxide): δ 6.58 (d, *J* = 8.3 Hz, 1 ArH), 7.36 (d, *J* = 7.5 Hz, 1 ArH), 7.44 (t, *J* = 7.3 Hz, 2 ArH), 7.58-7.66 (m, 5 ArH), 7.74 (t, *J* = 7.3 Hz, 1 ArH), 7.84 (d, *J* = 8.3 Hz, 1 ArH), 7.95 (d, *J* = 8.0 Hz, 1 ArH), 8.60 (d, *J* = 8 Hz, 1 ArH), 10.90 (s, NH).

Anal. Calcd. for $C_{21}H_{14}N_2O_3S$: C, 67.37; H, 3.77; N, 7.48. Found: C, 67.04; H, 3.66; N, 7.44.

4,5,6,14-Tetrahydrobenzo[9,10]quinolizino[3,2-*b*][1,4]benzothiazin-8-one 9,9-Dioxide (**13c**).

A suspension of 1-azido-2-phenylsulfonylbenzoquinolizin-3-one (**12c**) (0.500 g, 1.4 mmol) in 1,2-dichlorobenzene (7 mL) was reacted and worked up as described for **12b**; the yield was 0.440 g (93%), brown prisms, mp 223 °C (dimethylformamide); ir: 3320 m, 1630 s cm^{-1}; ^{1}H nmr (deuteriodimethylsulfoxide): δ 2.00 (m, CH_2), 2.96 (m, Ar-CH_2), 4.00 (m, NCH_2), 7.30 (t, *J* = 7.5 Hz, 1 ArH), 7.39 (t, *J* = 7.5 Hz, 1 ArH), 7.56 (d, *J* = 7.1 Hz, 1 ArH), 7.68 (t, *J* = 7.5 Hz, 1 ArH), 7.77 (d, *J* = 8.3 Hz, 1 ArH), 7.92 (d, *J* = 7.6 Hz, 1 ArH), 8.39 (d, *J* = 8.7 Hz, 1 ArH), 10.70 (s, NH).

Anal. Calcd. for $C_{18}H_{14}N_2O_3S$: C, 63.89; H, 4.17; N, 8.28; S, 9.48. Found: C, 64.03; H, 4.26; N, 8.66; S, 9.83.

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