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Received June 29, 1981

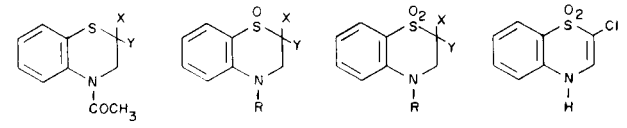
A series of derivatives of 4*H*-2,3-dihydrobenzo-1,4-thiazine has been prepared. 4-Acetyl-2,3-dihydrobenzo-1,4-thiazine undergoes self-condensation by *n*-butylmagnesium bromide affording the corresponding 4-acetoacetyl-2,3-dihydrobenzo-1,4-thiazine, which, is converted to 5*H*-1,4-thiazino[2,3,4-*ij*]quinolin-5-one. Halogenation of the acetyl derivative takes place at the position 2 of the heterocyclic ring and oxidation leads to 1-oxides and 1,1-dioxides.

J. Heterocyclic Chem., **19**, 237 (1982).

4-Substituted-2,3-dihydrobenzo-1,4-thiazines have been reported to exhibit blood pressure reducing properties on experimental animals (1). Because of this antihypertensive activity, new 1,4-benzothiazine derivatives are of considerable interest.

This paper describes the synthesis and some aspects of the reactivity of a number of new 4-substituted-2,3-dihydrobenzo-1,4-thiazines **1** as well as new derivatives of 4*H*-2,3-dihydrobenzo-1,4-thiazine 1-oxides and 1,1-dioxides **2, 3** and **4**.

All the new compounds were synthesized starting from **1a** (2), prepared from *o*-aminothiophenol and 1,2-dibromoethane or 1,2-dichloroethane under basic conditions by both routes (a) and (b) (see Scheme I). As for route (b), no thiazine ring opening (3) occurred during the acetylation, in accordance with what reported by Prasad (2).



1

a, X = Y = H
b, X = H; Y = Cl
c, X = H; Y = OCH_3
d, X = Y = Cl
e, X = Y = OCH_3

2

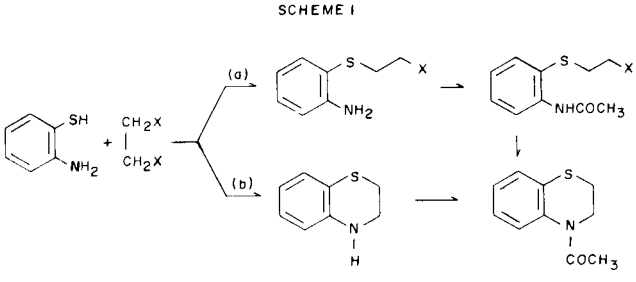
a, R = $COCH_3$; X = H; Y = Cl
b, R = $COCH_3$; X = Y = Cl
c, R = X = H; Y = Cl
d, R = H; X = Y = Cl

3

a, R = $COCH_3$; X = Y = H
b, R = $COCH_3$; X = H; Y = Cl
c R = $COCH_3$; X = Y = Cl
d, R = X = Y = H
e, R = X = H; Y = Cl
f, R H; X = Y = Cl

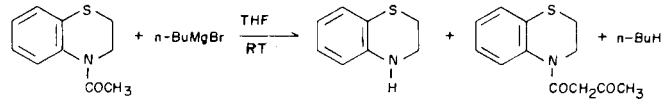
4

SCHEME I



Acetyl derivative **1a**, on treatment with *n*-butyl magnesium bromide in THF or ether at room temperature, afforded the unsubstituted dihydrobenzothiazine **5** and the β-ketoamide **6** (Scheme II). This result appeared to us rather surprising since carboxamides have been reported to react with organometallic reagents in a quite different way (4). The procedure is simple, convenient and requires very mild conditions, while attempts to synthesize **6** from **5** and ethyl acetocetate, according to Knorr's method (5), were unsuccessful. It is very likely that a Claisen-type condensation mechanism (4) is operating in this reaction, which is, as said above, rather unusual for carboxamides.

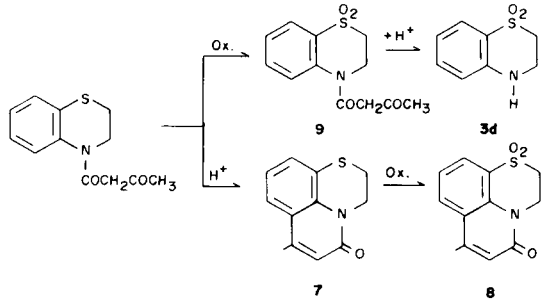
SCHEME II



1a 5 6

β-Ketoamide **6** is promptly and quantitatively cyclized by concentrated sulfuric acid to 5*H*-1,4-thiazino-[2,3,4-*ij*]quinolin-5-one (**7**); this, in turn, is readily oxidized to the corresponding 1,1-dioxide **8** by *m*-chloro-perbenzoic acid in dichloromethane, while attempts to cyclize **9**, obtained by oxidation of **6**, failed because of its easy deacylation to **3d** (4) (Scheme III). Compounds **6, 7, 8** and **9**, all unknown, might be of interest in the pharmaceuticals area.

SCHEME III

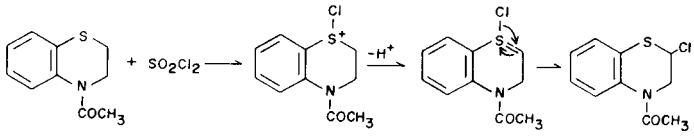


9 3d 7 8

Halogenation of **1a** with sulphuryl chloride occurs very easily at position 2 of the heterocyclic ring furnishing, depending on the reaction conditions, **1b** and **1d** in

satisfactory yields. A chlorosulphonium salt is probably an intermediate (2); this undergoes a Pummerer-type rearrangement affording the aforementioned **1b** and **1d** (Scheme IV). A bright yellow solid forms immediately after mixing the reagents; this dissolved on heating and could not be isolated. Failure of attempts to chlorinate the corresponding 1,1-dioxide **3a** under the same conditions supports this hypothesis.

SCHEME IV



Compounds **1b** and **1d** undergo monomethoxy- and dimethoxy-dehalogenation, respectively, leading to **1c** and **1e**, simply on heating at reflux in methanol or more quickly in the presence of sodium methoxide. No dehydrohalogenation has been observed under the experimental conditions and the amide function was in all cases unaffected. The remarkable mobility of the halogens in position 2 might be exploited to synthesize other 1,4-benzothiazines substituted in the 2-position.

Compounds **1** can be oxidized either to the 1-oxides **2** or the 1,1-dioxides **3** with hydrogen peroxide in water/methanol or with *m*-chloro-perbenzoic acid in dichloromethane, while oxidation of the unsubstituted benzo-thiazine **5** gives a brown mixture (quinones) (3). Hydrogen peroxide and solvents such as water and methanol must be avoided with **1b** and **1d**, because, in these cases, the oxidation reaction is accompanied by the aforementioned dehalogenation.

Monoxides **2a,b** and dioxides **3a,b,c** undergo rapid deacylation on heating in methanol or more rapidly in the presence of small amounts of sodium methoxide at room temperature, affording **2c,d** and **3d,e,f**, respectively. Details of this reaction are reported elsewhere (6). None of the halomonoxides **2a,b** or halodioxides **3b,c** undergo dehalogenation or dehydrohalogenation, in accordance with what has been found for α-halosulfoxides and α-halosulfones (7). However, **3c**, under rather severe conditions (see Experimental) suffers dehydrohalogenation together with deacylation giving compound **4**, which is unknown and, as reported for the bromo counterpart (8), is otherwise difficult to synthesize.

EXPERIMENTAL

All melting points were taken on Electrothermal apparatus and are uncorrected. The ir spectra were determined on Perkin Elmer 177 spectrophotometer. The H-nmr spectra were performed with a Varian EM 360A spectrometer, using tetramethylsilane as internal standard.

2-Aminophenyl-2-chloroethyl-sulphide.

To 5 g (0.04 mole) of *o*-aminothiophenol and 40 g (0.4 mole) of 1,2-dichloroethane at reflux was added 0.14*N* sodium methoxide (30 ml, 0.04 mole) dropwise under nitrogen and refluxing was continued for 3 hours. The reaction mixture was cooled, poured into water and extracted with dichloromethane. The organic phase was then washed with sodium bicarbonate (saturated solution), dried over sodium sulfate and evaporated leaving 6.3 g (84%) of yellow oil; ^{1}H-nmr (deuteriochloroform): δ 7.5-6.9 (m, 4H), 4.2 (b, s, 2H), 3.4 (t, 2H), 2.9 (t, 2H).

Anal. Calcd. for $C_8H_{10}ClNS$: C, 51.2; H, 5.3; N, 7.54. Found: C, 51.4; H, 5.3; N, 7.45.

2-Acetamidophenyl-2-chloroethyl-sulphide.

2-Aminophenyl-2-chloroethyl-sulphide (10.4 g, 0.055 mole) and 10 g (0.098 mole) of acetic anhydride were refluxed for 3 hours. The cooled mixture was poured into water (200 ml), extracted with 2*M* hydrochloric acid and dried over sodium sulfate. Evaporation of the solvent left a residue of 8.4 g (66%), mp 118° (methanol); ^{1}H-nmr (deuteriochloroform): δ 8.4 (b, d, 1H), 7.2-7.1 (m, 4H), 3.4 (t, 2H), 3.0 (t, 2H), 2.2 (s, 3H); ir: intense peak at 1680 cm^{-1}.

Anal. Calcd. for $C_{10}H_{12}ClNSO$: C, 52.3; H, 5.2; N, 6.1. Found: C, 52.4; H, 5.3; N, 6.1.

4*H*-2,3-Dihydrobenzo-1,4-thiazine.

o-Aminothiophenol (10g, 0.08 mole) in 10 ml of methanol and 66 g (0.35 mole) of 1,2-dibromoethane were heated at reflux under nitrogen. Then 0.8 *N* sodium methoxide (100 ml, 0.08 mole) was added and heating was continued for 2 hours. The reaction mixture was then poured into (10%) sodium bicarbonate, extracted with dichloromethane dried over sodium sulfate and the solvent evaporated leaving 11.1 g of yellow oil. This oil 10.6 g in 300 ml of methanol and 14 g sodium carbonate were then refluxed with stirring for 3 hours. The mixture was poured into water and extracted with dichloromethane. Removal of the solvent gave 6.9 g (58%) of yellow oil, bp 0.3 mm Hg, 118-120°; ^{1}H-nmr (deuteriochloroform): δ 6.9-6.2 (m, 4H), 4.7 (b, s, 1H), 3.5-3.3 (m, 2H), 2.8-2.7 (m, 2H) (which disappears by adding deuteriumoxide) lit (2).

Anal. Calcd. for C_8H_9NS: C, 63.5; H, 5.9; N, 9.3. Found: C, 63.7; H, 5.9; N, 9.2.

4-Acetyl-2,3-dihydrobenzo-1,4-thiazine (**1a**).

To 8 g (0.035 mole) of 2-acetamidophenyl-2-chloroethyl-sulphide in 200 ml of *t*-butyl alcohol and potassium *t*-butoxide (4.5 g, 0.037 mole) in 50 ml of *t*-butyl alcohol was added slowly with stirring at 45°. The reaction, followed by tlc (ether), was over in 15 minutes. After pouring into water and acidifing (hydrochloric acid), the mixture was extracted with dichloromethane, dried over sodium sulfate and the solvent removed *in vacuo* leaving a solid residue (7.5 g). This residue was chromatographied on a column (ether, silica gel) giving a solid 5.5 g. (81%), mp 55-56° [lit (2), mp 56-57°] (1:1 ether-light petroleum). Alternatively **1a** was synthesized as follows: to 0.3 g (0.002 mole) of 4*H*-2,3-dihydrobenzo-1,4-thiazine in 10 ml of dry pyridine at -10° was added acetyl chloride (0.2 g, 0.0025 mole) dropwise while stirring. The mixture was then poured into water, extracted with dichloromethane, washed many times with 2*M* hydrochloric acid, dried over sodium sulfate and the solvent removed *in vacuo*, leaving 0.32 g (84%) of a crystalline compound, mp 55-56.5° (ether/light petroleum).

4-Acetyl-2-chloro-2,3-dihydrobenzo-1,4-thiazine (**1b**).

To 7 g (0.036 mole) of **1a** in 300 ml of carbon tetrachloride, was added 2.91 ml (0.036 mole) of sulfuryl chloride in 35 ml of carbon tetrachloride dropwise with stirring at 60°. The reaction, followed by tlc (ether), was over in 1 hour. After removing the solvent, 9 g of an oil were obtained. The oil crystallised from ether (7 g, 85%) mp 71-72°; ^{1}H-nmr (deuteriochloroform): δ 7.7 (s, 4H), 5.1-5.6 (m, 1H), 4.9-4.4 (c, m, 1H), 4.1-3.7 (m, 1H), 2.2 (s, 3H).

Anal. Calcd. for $C_{10}H_{10}ClNSO$: C, 52.7; H, 4.4; N, 6.1. Found: C, 52.5; H, 4.5; N, 6.0.

4-Acetyl-2-methoxy-2,3-dihydrobenzo-1,4-thiazine (**1c**).

To 1.66 g (0.0073 mole) of **1b** in 30 ml of methanol was added 0.5*N* sodium methoxide (22 ml, 0.011 mole) at 25°. The reaction, followed by

tlc (ether), was quenched after 1 hour by pouring into water (250 ml) and extracted with dichloromethane. Evaporation afforded an oil (1.56 g, 96%) which solidified mp 99-100° (ethanol); ^{1}H-nmr (deuteriochloroform): δ 7.2 (s, 4H), 5.4-5.2 (t, 1H), 4.1 (b, s, 1H), 3.4 (s, 3H), 2.2 (s, 3H).

Anal. Calcd. for $C_{11}H_{13}NSO_2$: C, 59.2; H, 5.8; N, 6.3. Found: C, 59.3; H, 5.9; N, 6.3.

Alternatively **1c** can be obtained simply on heating **1b** in dry methanol.

4-Acetyl-2,2-dichloro-2,3-dihydrobenzo-1,4-thiazine (**1d**).

To 5g (0.026 mole) of **1a** in 100 ml of carbon tetrachloride 10 ml of sulfuryl chloride (excess) in 25 ml of carbon tetrachloride was added with stirring. A yellow solid appeared after mixing the reactants; it dissolved later on heating at reflux. The reaction, monitored by tlc (ether), was complete in 40 minutes.After removal of the solvent under reduced pressure, 7 g of yellow oil was obtained which was crystallized from ether (5.8 g, 85%) mp 78-79°; ^{1}H-nmr (deueriochloroform): δ 7.3-7.1 (m, 4H), 4.6 (s, 2H), 2.3 (s, 3H).

Anal. Calcd. for $C_{10}H_9Cl_2NSO$: C, 45.8; H, 3.4; N, 5.3. Found: C, 45.8; H, 3.5; N, 5.2.

4-Acetyl-2,2-dimethoxy-2,3-dihydrobenzo-1,4-thiazine (**1e**).

To 5.2 g (0.02 mole) of **1d** in 100 ml of methanol 0.3*N* sodium methoxide (85 ml, 0.026 mole) was added slowly with stirring at 35°. The reaction was complete in 30 minutes. The mixture was then poured into water and extracted with dichloromethane. Evaporation left a red oil (3.5 g),which was purified by column chromatography (ether, silica gel), giving 4 g (80%) of yellow solid mp 65.2° (ethanol); ^{1}H-nmr (deuteriochloroform): δ 7.2 (s, 4H), 4.1 (s, 2H), 4.4 (s, 3H).

4-Acetyl-2-chloro-2,3-dihydrobenzo-1,4-thiazine 1-oxide (**2a**).

Compound **1b** (4 g, 0.0176 mole) and 3.04 g (0.0176 mole) of *m*-chloroperbenzoic acid in 150 ml of carbon tetrachloride were kept at 40° for 20 hours. The solution was then washed with 3% sodium thiosulfate, 3% sodium bicarbonate, water and dried over sodium sulfate. Evaporation of the solvent left a crystalline residue (3.6 g, 84%) mp 128-129° (ethanol); ^{1}H-nmr (deuteriochloroform): δ 7.9-7.3 (c, m, 4H), 5.0-4.6 (c, m, 2H), 4.4-4.0 (m, 1H), 2.3 (s, 3H).

Anal. Calcd. for $C_{10}H_{10}ClNSO_2$: C, 49.2; H, 4.1; N, 5.7. Found: C, 49.1; H, 4.2; N, 5.6.

4-Acetyl-2,2-dichloro-2,3-dihydrobenzo-1,4-thiazine 1-Oxide (**2b**).

Compound **1d** (4 g, 0.0153 mole) and 2.8 g (0.0162 mole) of *m*-chloroperbenzoic acid in 150 ml of carbon tetrachloride were heated at 40° for 20 hours. The solution was then washed with aqueous 3% sodium thiosulfate, 3% sodium bicarbonate and water and dried over sodium sulfate. Removal of the solvent under reduced pressure gave 4 g (95%) of solid mp 99-100° ethanol); ^{1}H-nmr (deuteriochloroform): δ 7.9-7.3 (m, 4H), 5.3-5.0 (d, 1H), 4.3-4.0 (d, 1H), 2.3 (s, 3H).

Anal. Calcd. for $C_{10}H_9Cl_2NO_2S$: C, 43.1; H, 3.2; N, 5.0. Found: C, 42.9; H, 3.2; N, 5.0.

4*H*-2-Chloro-2,3-dihydrobenzo-1,4-thiazine 1-Oxide (**2c**).

Compound **2a** (1 g, 0.0041 mole) was dissolved in methanol and was treated with 0.44*N* sodium methoxide (10 ml, 0.0041 mole) at room temperature. The reaction was quenched after 10 minutes by pouring into water and extraction with dichloromethane. Evaporation gave 0.8 (96%) of a solid mp 194-195° (ethanol); ^{1}H-nmr (deuteriochloroform): δ 7.8-7.3 (c, m, 2H), 7.0-6.7 (c, m, 2H), 4.9-4.8 (d, d, 1H), 4.5-4.2 (d, d, 1H), 3.5-3.1 (d, d, 1H) (the N-H is hidden by the double doublets, and disappears by adding deuterium oxide).

Anal. Calcd. for C_8H_8ClNOS: C, 47.7; H, 4.0; N, 6.9. Found: C, 47.8; H, 4.1; N, 6.8.

4*H*-2,2-Dichloro-2,3-dihydrobenzo-1,4-thiazine-1-Oxide (**2d**).

To 1 g (0.0036 mole) of **2b** in 50 ml of methanol was added 0.44*N* sodium methoxide (10 ml, 0.0044 mole) at room temperature. The reaction was complete after 10 minutes; the solution was then poured into water, extracted with dichloromethane and dried over sodium sulfate. Removal of the solvent left 0.82 g (96%) of a white solid mp 156-157° (ethanol); ^{1}H-nmr (deuteriochloroform): δ 7.6-7.2 (m, 2H), 6.9-6.6 (m, 2H), 5.2 (b, s, 1H), 4.4-4.1 (d, d, 1H), 3.8-3.5 (d, d, 1H).

Anal. Calcd. for $C_8H_7Cl_2NOS$: C, 40.7; H, 3.0: N, 5.9. Found: C, 40.6; H, 3.0; N, 5.8.

4-Acetyl-2,3-dihydrobenzo-1,4-thiazine 1,1-dioxide (**3a**).

Compound **1a** (1.3 g, 0.0067 mole) in 40 ml of methanol, 0.92 g (0.0047 mole) of ammonium molybdate in 10 ml of water and 1.3 ml of 30% hydrogen peroxide in 15 ml of methanol were kept at room temperature overnight. After pouring into water, extraction with dichloromethane and removal of the solvent, 1.2 g (79%) of a solid mp 117-118° (from methanol) was obtained; ^{1}H-nmr (deuteriochloroform): δ 7.9-7.3 (m, 4H), 4.5-4.3 (t, 2H), 4.7-4.6 (t, 2H), 2.2 (s, 3H); ir: intense peak at 1140 and 1290 (SO_2), 1680 cm^{-1} (>C=O).

Anal. Calcd. for $C_{10}H_{11}NSO_3$: C, 53.3; H, 4.8; N, 6.2. Found: C, 53.5; H, 4.8; N, 6.2.

4-Acetyl-2-chloro-2,3-dihydrobenzo-1,4-thiazine 1,1-Dioxide (**3b**).

Compound **1b** (1.64 g, 0.0072 mole) and 3 g (0.017 mole) of *m*-Chloroperbenzoic acid were kept at room temperature overnight with stirring. Then the solution was washed with 3% sodium thiosulfate, 3% sodium bicarbonate and water. Evaporation of the solvent left an oil (1.5 g) which was chromatographied (silica gel, ether/acetone 9/1) in column, giving 1.5 g (80%) of a solid mp 115-116° (from ethanol); ^{1}H-nmr (deuteriochloroform): δ 8.1-7.5 (m, 4H), 5.3-4.7 (c, m, 2H), 4.5-4.2 (d, d, 1H), 2.3 (s, 3H); ir: intense peaks at 1670 cm^{-1} (>C=O), 1330 cm^{-1} (-SO_2).

Anal. Calcd. for $C_{10}H_{10}ClNO_3S$: C, 46.0; H, 3.9; N, 5.3. Found: C, 45.9; H, 4.1; N, 5.3.

4-Acetyl-2,2-dichloro-2,3-dihydrobenzothiazine 1,1-Dioxide (**3c**).

Compound **1d** (2.5 g, 0.009 mole) and 4 g (0.023 mole) of *m*-chloroperbenzoic acid in 30 ml of carbon tetrachloride were kept at 45° overnight. The solution was then washed with 3% sodium thiosulfate, 3% sodium bicarbonate and water. Removal of the solvent left 3.2 g (100%) of crystalline compound mp 134° (ethanol); ^{1}H-nmr (deuteriochloroform): δ 8.0-7.5 (m, 4H), 4.9 (s, 2H), 2.3 (s, 3H); ir: intense peaks at 1670 cm^{-1} (>C=O) and 1340, 1170 cm^{-1} (SO_2).

Anal. Calcd. for $C_{10}H_9Cl_2NSO_3$: C, 40.9; H, 3.1; N, 4.7. Found: C, 41.0; H, 3.3; N, 4.7.

4*H*-2,3-Dihydrobenzo-1,4-thiazine 1,1-dioxide (**3d**).

Compound **3a** (0.2 g, 0.0009 mole) in 15 ml of methanol was added to 0.3*N* sodium methoxide (15 ml, 0.0012 mole) at 25°. The reaction, complete after 10 minutes, was quenched by pouring into water and extracted with dichloromethane. Evaporation of the solvent left 0.16 g (100%) of crystalline compound mp 143-144° (ethanol) [lit (7) mp 144°]; ^{1}H-nmr (deuteriochloroform): δ 7.8-6.6 (m, 4H), 4.6 (b, s, 1H), 4.0-3.7 (m, 2H), 3.3-3.1 (m, 2H); ir: N-H at 3400, intense peaks at 1285 and 1135 cm^{-1} (SO_2).

4*H*-2-Chloro-2,3-dihydrobenzo-1,4-thiazine 1,1-Dioxide (**3e**).

Compound **3b**, (0.2 g, 0.0008 mole) in 20 ml of methanol was treated with 0.22*N* sodium methoxide (20 ml, 0.087 mole) at 35° for 10 minutes. The solution was then diluted with water and extracted with dichloromethane. Removal of the solvent gave 0.10 g (100%) of white crystals mp 137-138° (ethanol); ^{1}H-nmr (deuteriochloroform); δ 7.7-6.8 (m, 4H), 4.8-4.0 (c, m, 4H), ir: N-H at 3420, intense peaks at 1300 and 1130 cm^{-1} (SO_2).

Anal. Calcd. for $C_8H_8ClNSO_2$: C. 44.2; H, 3.7; N, 6.4. Found: C, 44.2; H, 3.8; N, 6.4.

4*H*-2,2-Dichloro-2,3-dihydrobenzo-1,4-thiazine 1,1-Dioxide (**3f**).

To 0.2 g (0.00076 mole) of **3c** in 15 ml of methanol, 0.3*N* sodium methoxide (15 ml, 0.0009 mole) was added at 25°. The reaction, over in 15 minutes, was quenched by pouring into water and extracted with

dichloromethane; evaporation of the solvent left 0.18 g (94%) of a white solid mp 192-193° (ethanol); H-nmr (deuteriochloroform): δ 7.6-6.6 (c, m, 4H), 4.8 (b, s, 1H), 4.3 (d, 2H); ir: N-H at 3400, intense peak at 1320 and 1150 cm^{-1} (-SO_2-).

Anal. Calcd. for $C_8H_7Cl_2NSO_2$: C, 38.1; H, 2.8; N, 5.6; Found: C, 38.2; H, 3.0; N, 5.7.

4*H*-2-Chlorobenzo-1,4-thiazine 1,1-Dioxide (**4**).

To 0.3 g (0.001 mole) of **3c** in 40 ml of *t*-butyl alcohol was added dropwise and with stirring at 35° 0.33 g (0.03 mole) of potassium *t*-butyl alcohol in 20 ml *t*-butyl alcohol. The reaction, complete after 1.5 hours, was quenched by pouring into water, neutralised with dilute hydrochloric acid and extracted with dichloromethane. Evaporation of the solvent gave 0.2 g (91%) of a solid mp 243-244° (ethanol); ^{1}H-nmr (DMSO-d_6): δ 7.8-7.4 (m, 5H, 4H belonging to the phenyl group, 1H to the vinyl), (b, d, 1H); ir N-H at 3380, intense peaks at 1280 and 1190 cm^{-1} (-SO_2).

Anal. Calcd. for $C_8H_6ClNSO_2$: C, 44.5; H, 2.8; N, 6.5. Found: C, 44.7; H, 2.9; N, 6.4.

4-Acetoacetyl-2,3-dihydrobenzo-1,4-thiazine (**6**).

To Compound **1a** (1 g, 0.0055 mole) in 50 ml of dry THF was added 6.5 ml of 0.85*N* *n*-butylmagnesium bromide (0.006 mole) with stirring and under nitrogen at room temperature. Stirring was continued until tlc (3:7 ether-light petroleum) showed the complete disappearance of the starting material. Then the solution was quenched with ammonium chloride (saturated solution), extracted with ether, the organic layer separated, dried over sodium sulfate and the solvent removed *in vacuo* leaving a residue (1.1 g, oil) which was a mixture of two products. These were separated by column chromatography. The first product (0.4 g, oil) was the unsubstituted 2,3-dihydrobenzo-1,4-thiazine **5** (ir and nmr consistent) The second product (0.5 g, oil, 83%) was the compound **6**; ir and nmr spectra clearly indicated the presence of an enolic form in equilibrium with the carbonyl form; ir: C=O stretchings at 1720 and 1640 cm^{-1}; ^{1}H-nmr (deuteriochloroform): δ carbonyl form, 2.2 (s, 3H), 3.1-3.3 (m, 2H), 3.7 (s, 2H), 3.9-4.1 (m, 2H), 7.1-7.3 (m, 4H); enolic form: 1.9 (s, 3H), 3.1-3.3 (m, 2H), 3.9-4.1 (m, 2H), 5.3 (s, 1H), 7.1-7.3 (m, 4H), 14.5 (b, s, 1H).

Anal. Calcd. for $C_{12}H_{13}NO_2S$: C, 61.0; H, 5.9; N, 5.5. Found: C. 60.9; H, 5.9; N, 5.6.

5*H*-1,4-thiazino[2,3,4-*ij*]quinolin-5-one (**7**).

Compound **6** 0.2 g (0.00085 mole) was treated with 5 ml of concentrated sulfuric acid and the yellow solution kept at room temperature for 1 hour. Then the reaction mixture was quenched by pouring into cold water and extracted with ether. The usual work-up gave 0.18 g (100%) of a solid mp 129-130° (ethanol); ^{1}H-nmr (deuteriochloroform): δ 2.4 (s, 3H), 2.9-3.2 (m, 2H), 4.4-4.7 (m, 2H), 6.6 (s, 1H), 6.9-7.6 (m, 3H).

Anal. Calcd. for $C_{12}H_{11}NOS$: C, 66.4; H; 5.1; N, 6.4. Found: C, 66.3; H, 5.0; N, 6.4.

5*H*-1,4-Thiazino[2,3,4-*ij*]quinolin-5-one 1,1-Dioxide (**8**).

Compound **7** 0.6 g (0.0027 mole) in 15 ml of dichloromethane was added to 2 g (0.011 mole) of *m*-chloroperbenzoic acid in 100 ml of dichloromethane and the solution was kept at room temperature overnight. Then the solution was washed with 5% sodium thiosulfate, 5% sodium dicarbonate and water. Removal of the solvent gave 0.6 g (87% of a solid mp 262-266° (ethanol); ir: C=O stretching at 1670, SO_2 stretching at 1100 and 1280 cm^{-1}; ^{1}H-nmr (deuteriochloroform): δ 2.5 (s, 3H), 3.4-3.7 (m, 2h), 4.8-5.1 (m, 2H), 6.7 (s, 1H), 7.3-8.3 (c, m, 3H).

Anal. Calcd. for $C_{12}H_{11}NO_3S$: C, 57.8; H, 4.4; N, 5.6. Found: C, 57.9; H, 4.5; N, 5.6.

4-Acetoacetyl-2,3-dihydrobenzo-1,4-thiazine 1,1-Dioxide (**9**).

m-Chloro-perbenzoic acid 0.8 g (0.0046 mole) was added to 0.4 g (0.0017) of **6** in 10 ml of dichloromethane and the mixture kept at room temperature overnight. Then the solution was washed first with 5% sodium thiosulfate, 5% sodium bicarbonate and finally with water. Removal of dichloromethane *in vacuo* left 0.37 g (82%) of an oil; ir and nmr spectra clearly indicate the presence of an enolic and a carbonyl form; ir: C=O stretchings at 1640 and 1730, SO_2 stretchings at 1130 and 1270 cm^{-1}; ^{1}H-nmr (deuteriochloroform): δ carbonyl form: 2.2 (s, 3H), 3.4-3.65 (m, 2H), 3.7 (s, 2H), 4.3-4.6 (m, 2H), 7.3-8.1 (c, m, 4H); enolic form: 1.9 (s, 3H), 3.4-3.65 (m, 2H), 4.3-4.6 (m, 2H), 5.3 (s, 1H), 7.3-8.1 (c, m, 4H), 13.9 (s, 1H).

Anal. Calcd. for $C_{12}H_{13}NO_4S$: C, 53.9; H, 4.9; N, 5.2. Found: C, 54.0; H, 5.0; N, 5.2.

Acknowledgement.

This work has been carried out during the tenure of a visiting fellow funded by the ICI Joint Research Scheme. We thank Dr. Marshall (Bangor) for valuable discussions.

REFERENCES AND NOTES

(1) R. N. Prasad, *J. Med. Chem.*, **12**, 290 (1969).

(2) R. N. Prasad, K. Tietje, *Can. J. Chem.*, **44**, 1247 (1966).

(3) R. Fusco, G. Palazzo, *Gazz. Chim. Ital.*, **81**, 735 (1951).

(4) F. Ciminale, L. Di Nunno, S. Florio, *Tetrahedron Letter*, **21**, 3001 (1980); F. Babudri, F. Ciminale, L. Di Nunno, S. Florio, *Tetrahedron*, in the press.

(5) L. Knorr, *Ann.*, **245**, 378 (1888).

(6) S. Florio, J. L. Leng, C. J. M. Stirling, *J. Heterocyclic Chem.*, **18**, 1273 (1981).

(7) N. Kharasch, "Organic Sulfur Compounds", Vol. 1, Pergamon Press, New York, 1961, p 150.

(8) G. Pagani, S. Bradamante Pagani, *Tetrahedron Letters*, **9**, 1041 (1968)