Cyclohepta[*b*][1,4]benzothiazines and Their Diazine Analogues. 1. Formation and Reactions of Cyclohepta-[*b*][1,4]benzothiazines[1)]

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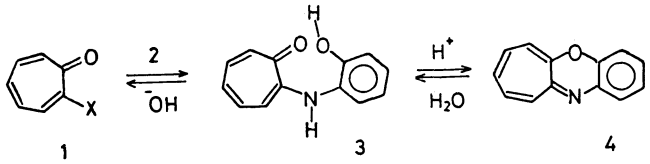
2-Chlorotropone reacted with *o*-aminobenzenethiol to give 2-(*o*-aminophenylthio)tropone, which readily cyclized in dilute methanolic HCl to afford the title benzothiazine (**9**). Although **9** was stable under basic conditions, its *N*-methyl cation reversibly afforded the ring-opened 2-[*o*-(methylamino)phenylthio]tropone in alkali. Oxidation of **9** with hydrogen peroxide in methanol underwent a rearrangement reaction to afford (exclusively) phenothiazine and its 1-formyl derivative. A similar H_2O_2 oxidation of 10-methoxycyclohepta[*b*][1,4]benzothiazine gave mainly methyl phenothiazine-1-carboxylate and 3-formyl-1-methoxy phenothiazine. Further oxidation of these products with hydrogen peroxide yielded thier *S*-oxides and *S,S*-dioxides. The reactivities of these cycloheptabenzothiazines are discussed in connection with those of the O- and N-analogues.

It was recently reported[2)] by one of us (T.N.) that the condensation of 2-chloro- or 2-methoxytropone (**1a, b**) with *o*-aminophenol (**2**) gave 2-(*o*-hydroxyanilino)-tropone (**3**), which cyclized in acid to afford cyclohepta-[*b*][1,4]benzoxazine (**4**). Compound **4** and its derivatives were generally unstable in alkali (or, in some cases, even to the moisture in solvents) and readily reverted to **3** and further hydrolyzed to tropolone (**1**: X=OH) upon heating with an excess of alkali.[2,3)]



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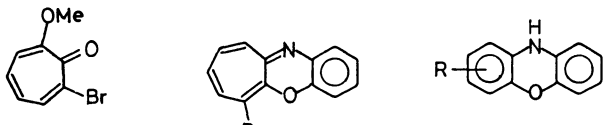

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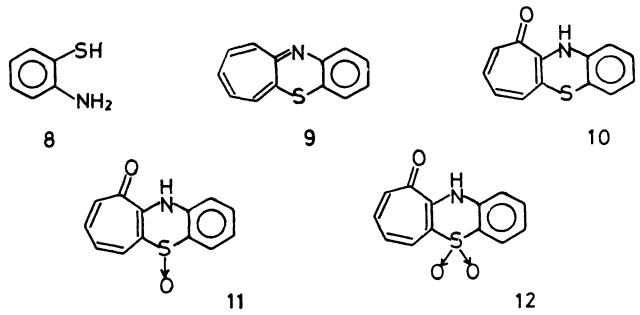
Moreover, reactive troponoids bearing two leaving groups, such as **5** and its isomers, were also found[4)] to condense with **2**, to provide 6-bromocyclohepta[*b*]-[1,4]benzoxazine (**6**) and its isomers, which were then transformed into a wide variety of interesting derivatives of cycloheptabenzoxazine **4** and phenoxazine **7**.

This evidence led us to investigate the synthesis and properties of the S- and N-analogues of **4** in order to make a systematic study of these reactive troponoids fused with heterocycles.[5)] Although the formation of cyclohepta[*b*][1,4]benzothiazine (**9**), corresponding 10(11*H*)-one **10**, and some of their derivatives from **1** (or **5**) and *o*-aminobenzenethiol (**8**), as well as the oxidative formation of *S*-oxide (**11**) and dioxide (**12**) with hydrogen peroxide, had been briefly reported earlier,[6,7)] we now wish to describe their detailed preparation and



8 9 10

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some new reactions of the title compound **9** and its derivatives.

Results and Discussion

We first studied the reaction of **1a** and **8** in methanol by means of reversed-phase, high-pressured liquid chromatography (HPLC). A stopped-flow apparatus was used to identify every product formed during the reaction[8)] (see Fig. 1). It was found that an intermediate substance **14** that was formed at an early stage of the reaction was gradually transformed almost solely into the final product **9**. Besides these, the only remaining product detected was disulfide **13** from **8**. When the condensation of **1a** with **8** was conducted in the presence of an alkali in order to neutralize the liberated HCl, compound **14** (isolable as yellow needles, mp 120.5 °C) was produced exclusively. The 2-(*o*-aminophenylthio)tropone structure was unambiguously assigned to **14** on the basis of its IR, UV, NMR, and mass spectra as well as elemental analysis (for assignments of the spectral signals, see Experimental part). That the condensation of **1a** with **8** apparently took place by a nucleophilic attack of SH (rather than NH_2) group of **8** was in conformity with the generally known order of the nucleophilicity of these groups towards halotropones.[9)]

The action of a trace amount of acid on **14** facilitated

cyclization to yield **9**, which remained stable and, in marked contrast to the afore-mentioned **4**, did not revert to **14** upon heating with methanolic potassium hydroxide. In a strong acid, compound **9** gave the red-colored monocation **9a** of a tropylium form as in the case of cation **4a** from **4**. It should be noted that these cationic species (**4a**,**9a**) are apparently different from the dark green-colored cation **15a** having a peripheral π-electron system which had been derived[5,10] from the N-analogue **15** in a strong acid.

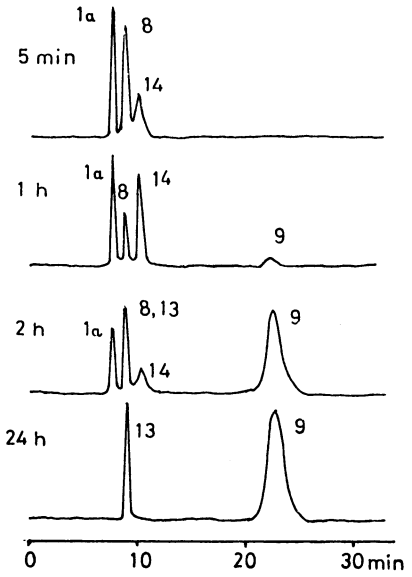
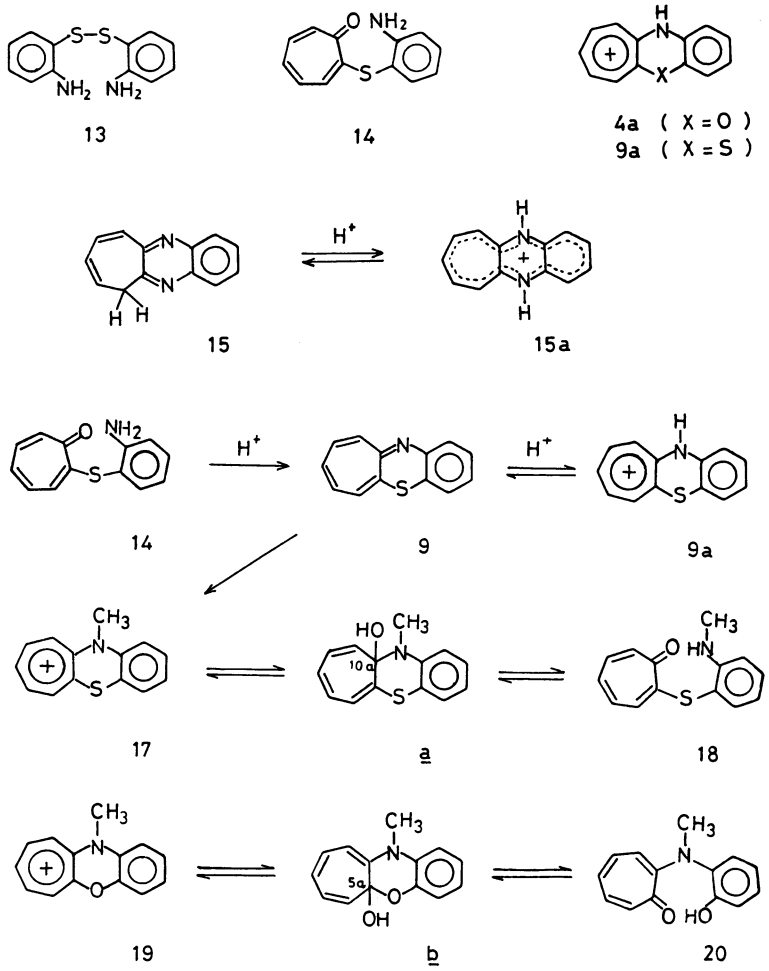


Fig. 1. Time dependent HPLC chromatogram of reaction of **1a** and **8** in MeOH at R.T.

The treatment of **9** with methyl fluorosulfate (magic methyl) yielded an inseparable mixture of the *N*-methyl cation **17** (see below) and **9a**, which, on basification, gave yellow needless **18**, along with recovered **9**. The structure of **18** was established on the basis of the spectral data (see Experimental) which closely resembled those of **14**, except for the presence of the *N*-methyl proton signal (NMR) at δ 2.09. Upon acidification, **18** gave the cyclized product **17**, isolable as the dark red BF_4^- salt. An appreciable down-field shift of the proton signals of the seven-membered ring in the NMR spectrum was strongly indicative of the cation **17**, predominantly in the tropylium form.

When **4** was likewise treated with magic methyl for comparison, a mixture of a similar cation **19** and **4a** was produced, which in turn led to aminotropone **20** and **4** upon basification. The structure of **20** was derived from the spectral data. On acidification, **20**



was found to cyclize to give **19** (isolable as BF_4^- salt) much faster than the case of **18** to **17**. The fact that the cation **17** was susceptible to a nucleophilic attack by OH^- at the 10*a*-position to give thiotropone **18** *via* an intermediate a, whereas its O-analogue **19** afforded aminotropone **20** *via* intermediate b by the OH^- attack at the 5*a*-position, is in accord with the results of theoretical calculations regarding the reactivities of these systems.[11]

We then studied the behaviors of **4** and the S-analogue **9** towards hydrogen peroxide. Treatment of compound **4** with H_2O_2 in methanol gave mainly cyclohepta[*b*][1,4]benzoxazin-10(11*H*)-one (**21**), along with small proportions of the hydrolyzed product **3** (*ca.* 3%) and the rearranged 1-formylphenoxazine[4] (**22**) (<1%). In contrast to oxazine **4**, compound **9** was

21 22

found exclusively to give a wide variety of rearrangement products. A close examination of this reaction using time-dependent HPLC (see Fig. 2) revealed that at the initial stage of the reaction, two main peaks (due to intermediates **23** and **24**) were observed. These gradually transformed into **23a** and **24a** and a small proportion of an additional product (**25**), and then finally gave products **23a** and **24a,b** as the main products. Presumable sequences of this oxidation reaction are summarized in Scheme 1. Although

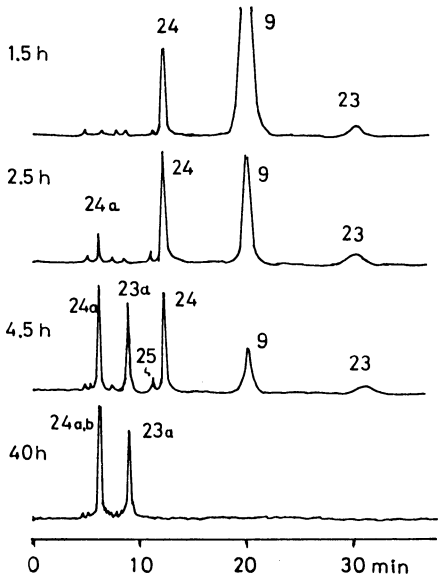


Fig. 2. Time dependent HPLC chromatogram of reaction of **9** and H_2O_2 in MeOH at R.T.

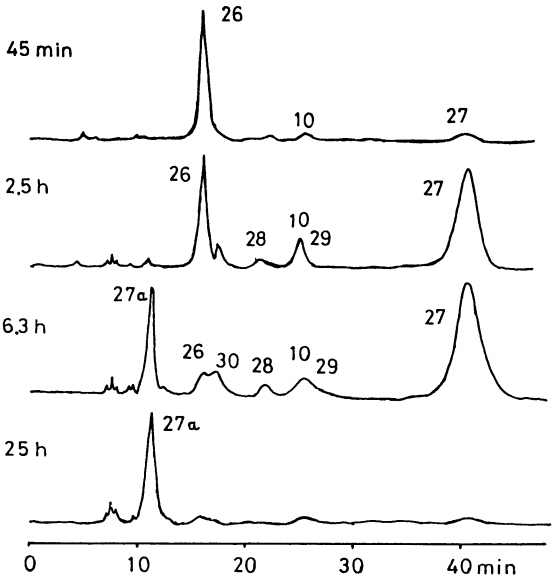
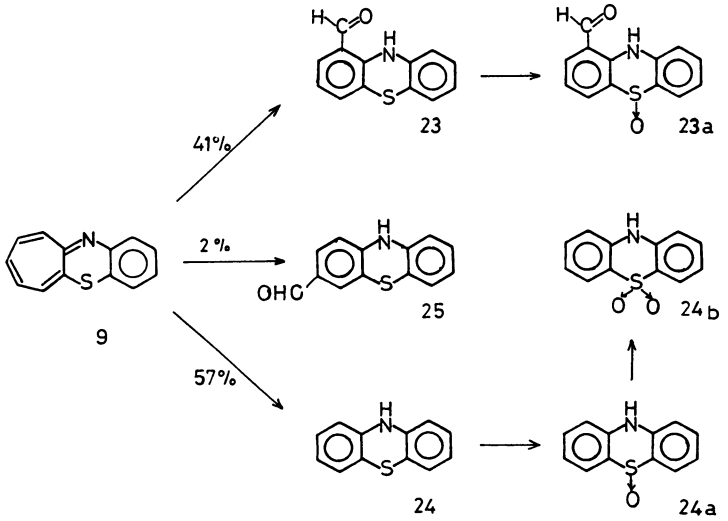


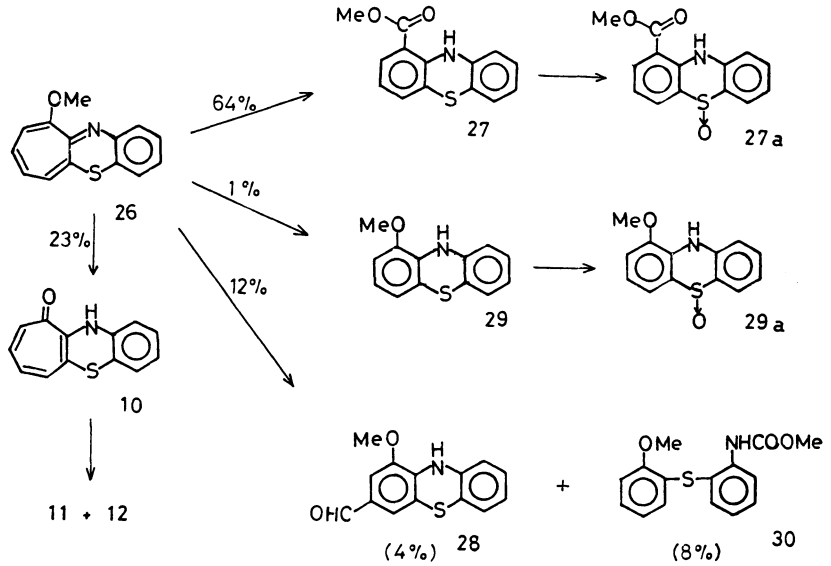
Fig. 3. Time dependent HPLC chromatogram of reaction of **26** and H_2O_2 in MeOH at R.T.



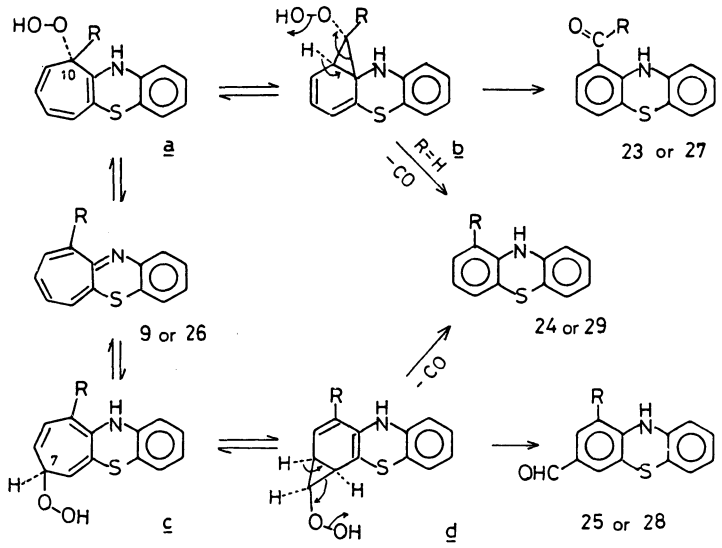
Scheme 1. H_2O_2 oxidation products from **9** in MeOH

compounds **23** and **25** both showed their molecular ion peaks at m/z 227 in the mass spectrum, the former (**23**) showed an IR absorption at 3300 cm^{-1} (NH) and characteristic ^{1}H-NMR signals at δ 10.00 (NH), 9.79 (CHO) and 7.17 (1H, dd, J=7.8 and 2.0 Hz), whereas the latter (**25**) showed the NH absorption at 3360 cm^{-1} and NMR signals at δ 8.90 (NH), 9.64 (CHO), and 7.30 (1H, d, J=1.8 Hz), thus permitting the assignments of 1-[12] and 3-formylphenothiazine structures to these products, respectively. Compound **24** was identified spectroscopically to be the known parent phenothiazine,[13] and **24a** and **24b** its *S*-monoxide and *S*,*S*-dioxides,[13] respectively. These *S*-oxides reverted to **23** and **24** upon redution with zinc duct.

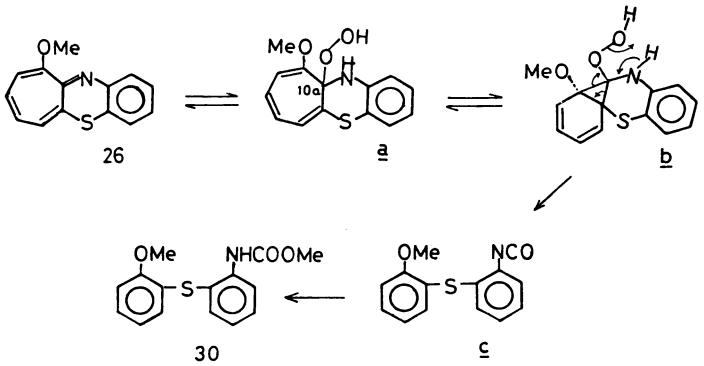
In order to clarify the site of the H_2O_2 attack on the seven-membered ring of **9**, compound **26** (bearing a methoxyl group at the 10-position) was subjected to similar oxidation. The reaction was again monitored by periodical HPLC checking (see Fig. 3). Although the reaction appeared to be somewhat more complex compared with the oxidation of **9**, a transient product **27** and the final product **27a** were mainly formed. These compounds were identified by the spectral evidence to be methyl 1-phenothiazinecarboxylate[14] (**27**) and its *S*-oxide (**27a**). The probable sequences of this oxidation to yield these compounds and several minor products (**28**—**30**) are summarized in Scheme 2. The structure of 3-formyl-1-methoxyphenothiazine for **28** was derived from the NMR spectrum which showed two characteristic doublets at δ 7.12 and 7.04 (with J=1.5 Hz) due to isolated ring-protons, in addition to a singlet (δ 3.92) of a MeO group. Com ound **29** was identified to be 1-methoxyphenothia-



Scheme 2. H_2O_2 oxidation products from **26** in MeOH



Scheme 3. R=H, OMe



Scheme 4.

zine[15] on the evidence of IR, NMR, and mass spectra. Oxidation of **29** was found to afford *S*-oxide **29a**. Compound **30** was assigned to be methyl 2-(*o*-methoxyphenylthio)phenylcarbamate from the IR, NMR, and MS spectra. In addition to these oxidation products, the hydrolyzed product **10** was also isolated.

Possible Reaction Pathways for the Oxidation of Cyclohepta[b][1,4]benzothiazines. The ring-contraction of **9** and **26** to **23—28** are most likely to proceed by a nucleophilic attack of H_2O_2 preferentially at the 10- and then, to a considerably less extent, 7-positions to yield the intermediates a and c, followed by the sequential steps illustrated in Scheme 3. On the other hand, the oxidative degradation of **26** to **30** is considered to be initiated by an attack of hydrogen peroxide at the 10*a* position, followed by similar ring-contraction (illustrated in Scheme 4). This order of reactivities of cycloheptabenzothiazines towards nucleophiles is generally in agreement with predictions based on theoretical calculations.[11]

Although the exact mechanism of these oxidations accompanied by such a variety of facile rearrengements (as well as other reactivities of the title compounds and their N-analogues) are currently under detailed investigation. The present experimental results further demonstrate a part of the diversity of chemical reactions involving troponoid compounds, particularly when fused with certain heterocycles.

Experimental

Melting points were determined with a Yanagimoto MP-3S and are uncorrected. The IR spectra were taken on a Shimazu IR-400 or IR-450, and the UV spectra were recorded with a Shimazu UV-202 or a Hitachi 557 spectrometer. The NMR spectra were recorded with JEOL JNM-PS100 (100-MHz) and GX270 (270-MHz) spectrometers using TMS as the internal standard. The mass spectra were taken on Shimazu LKB9000 and JEOL JMS-01SG mass spectrometers. The HPLC was carried out with Hitachi gel #3011 with MeOH–hexane (9:1) as the solvent. The UV spectra in acid and alkali were taken after adding a drop of 3M HCl or 3M NaOH (1M=1 mol dm^{-3}) to the sample solution. TLC analyses were carried out with Merk Kieselgel 60F-254 and Alminium oxide F-254 plates.

2-(o-Aminophenylthio)tropone (14). A solution of **1a** (200 mg, 1.4 mmol) in methanol (1 ml) was slowly added, with stirring at 0 °C, to a solution of **2** (200 mg, 1.6 mmol) and sodium hydroxide (170 mg, 4.2 mmol) in methanol (2 ml), and the mixture was allowed to stand for one day at −5—0 °C. The precipitates were collected and recrystallized from acetone to give **14** (304 mg, 93%) as yellow needles; mp 120.5 °C; UV (MeOH) 243, 340, and 367 nm (log ε 4.34, 3.98, and 3.97); IR (KBr) 3430, 3340 (NH_2), and 1610 cm^{-1} (C=O); ^{1}H NMR (270 MHz in C_6D_6) δ=3.55 (2H, br, NH_2), 5.93—5.98 (2H, m, H-4,5), 6.28 (1H, dd, *J*=8 and 1.5 Hz, H-3′), 6.31 (1H, m, H-6), 6.54 (1H, d, *J*=10 Hz, H-3), 6.55 (1H, m, *J*=8.8 and 1.5 Hz, H-5′ or 4′), 6.96 (1H, d, *J*=12 Hz, H-7), 7.01 (1H, m, *J*=8.8 and 1.5 Hz, H-4′ or 5′), and 7.28 (1H, dd, *J*=8 and 1.5 Hz, H-6′), (270 MHz in $CDCl_3$) δ=4.33 (2H, br, NH_2), 6.68 (1H, m, H-5 or 4), 6.80 (1H, t, *J*=8 Hz, H-5′), 6.88—6.92 (2H, H-3 and H-4 or 5), 6.86 (1H, d, *J*=8 Hz, H-3′), 7.13 (1H, d, *J*=12 Hz. H-7), 7.22 (1H, m, H-6), 7.30 (1H, t, *J*=8 Hz, H-4′), and 7.38 (1H, d, *J*=8 Hz, H-6′); ^{13}CNMR (67.8 MHz in $CDCl_3$) δ=183.5, 157.4, 149.3, 137.5, 136.4, 135.5, 132.8, 132.0, 130.5, 128.5, 115.7, and 112.2; MS *m/z* 229 (M^+);

Anal. ($C_{13}H_{11}NSO$) C, H, N.

N-Acetyl Derivative; Yellow plates; mp 150.5 °C; UV (MeOH) 243, 342, and 367 nm (log ε 4.34, 3.95, and 3.96); IR (KBr) 3305 (NH), 1690 (C=O), and 1610 cm^{-1} (C=O); ^{1}H NMR (100 MHz in $CDCl_3$) δ=2.08 (3H, s, CH_3), 6.45—7.59 (8H, m, ar-H), 8.10 (1H, s, NH), and 8.55 (1H, d, *J*=9 Hz, H-3′); MS *m/z* 271 (M^+);

Anal. ($C_{15}H_{13}NSO$) C, H, N.

Cyclohepta[b][1,4]benzothiazine (9). A solution of **14** (30 mg, 0.13 mmol), in methanol (2 ml) containing a drop of conc hydrochloric acid was allowed to stand for 30 min at 20 °C. After removal of the solvent *in vacuo*, the residue was neutralized with aqueous $NaHCO_3$ and extracted with benzene. The extracts were combined, dried (Na_2SO_4), and evaporated *in vacuo*, thus giving **9** (27 mg, 97%) as red plates; mp 87 °C (from acetone), (lit,[6] 86—87 °C); ^{1}H NMR (250 MHz in $CDCl_3$) δ=6.04 (1H, dd, *J*=8.5 and 1.0 Hz, H-6), 6.12 (1H, ddt, *J*=11.0, 7.3 and 1.0 Hz, H-8), 6.14 (1H, d, *J*=12.0 Hz, H-10), 6.25 (1H, dddd, *J*=11.0, 8.5, 1.4, and 1.0 Hz, H-7), 6.31 (1H, ddd, *J*=12.0, 7.3, and 1.4 Hz, H-9), 6.79 (1H, ddd, *J*=7.5, 1.6 and 0.6 Hz, H-4), 6.92 (1H, td, *J*=7.5, 7.0, and 1.8 Hz, H-3), 7.01 (1H, td, *J*=7.5, 7.0, and 1.6 Hz, H-2), and 7.07 (1H, ddd, *J*=7.5, 1.8, and 0.6 Hz, H-1). (250 MHz in CF_3COOD) δ=6.74—6.82 (2H, m), 6.81 (1H, d, *J*=11 Hz, H-10 or 6), 7.03—7.14 (3H, m), 7.17 (1H, dd, *J*=10 and 1.5 Hz, H-6 or 10), 7.22 (1H, td, *J*=10 and 1 Hz, H-7 or 9), and 7.36 (1H, ddd, *J*=11, 10, and 1 Hz, H-9 or 7). ^{13}C-NMR (67.8 MHz in

$CDCl_3$) δ=125.5 (d), 126.5 (d), 127.5 (d), 127.6 (d), 128.7 (d), 131.4 (d), 133.5 (d), 133.6 (d), 134.2 (d), 134.4 (s), 143.4 (s), and 159.4 (s).

2-[o-(Methylamino)phenylthio]tropone (18). A solution of **9** (50 mg, 0.24 mmol) and methyl fluorosulfate (200 mg, 1.75 mmol) in dichloromethane (0.5 ml) was allowed to stand in a sealed flask for 48 h at room temperature. After removing the solvent and the excess sulfate *in vacuo*, the residue was diluted with aqueous $NaHCO_3$ and then extracted with $CHCl_3$. The extracts were combined and evaporated *in vacuo*. The residue was chromatographed on silica-gel thin-layer plates with 10:1 benzene–MeOH as the eluant, thus giving **18** (36 mg, 63%) and unreacted **9** (15 mg).

18: Yellow needles (from $CHCl_3$); mp 156—157 °C; UV (MeOH) 248, 277sh, 324, 340, 366, and 384 nm (log ε 4.33, 3.78, 3.92, 3.96, 3.92, and 3.83), (MeOH+HCl) 242, 282, 342, and 454 nm (log ε 4.27, 4.13, 3.93, and 3.61); IR (KBr) 3350 (NH) and 1620 cm^{-1} (C=O); ^1H NMR (270 MHz in C_6D_6) δ=2.09 (3H, s, CH_3), 4.53 (1H, s, NH), 5.92 (1H, ddd, *J*= 10.4, 8.0, and 1.5 Hz, H-4) 5.95 (1H, ddd, *J*=10.4, 7.0, and 1.5 Hz, H-5), 6.30 (1H, m, H-6), 6.35 (1H, d, *J*=8.0 Hz, H-3′ or 6′), 6.57 (1H, dd, *J*=8.0 and 1.5 Hz, H-3), 6.59 (1H, td, *J*=8.0 and 1.5 Hz, H-5′ or 4′), 6.98 (1H, d, *J*= 11.7 Hz, H-7), 7.17 (1H, td, *J*=8.0 and 1.5 Hz, H-4′ or 5′), and 7.36 (1H, dd, *J*=8.0 and 1.5 Hz, H-6′ or 3′).

Found: *m/z* 243.0688. Calcd for $C_{14}H_{13}NSO$: M, 243.0816.

2-(N-Methyl-o-hydroxyanilino)tropone (20). The reaction of **4** and methyl fluorosulfate was conducted in a manner similar to that for **9** described above, thus giving **20** in 50% yield: Yellow meedles (from $CHCl_3$); mp 132—133 °C; UV (MeOH) 246, 344, and 410 nm (log ε 4.24, 4.02, and 3.93), (MeOH+HCl) 228, 262, 272, 320, and 428 nm, (log ε 4.42 4.33, 4.39, 3.89, and 3.95); IR (KBr) 3420 (OH) and 1600 cm^{-1} (C=O); ^1H NMR (270 MHz in C_6D_6) δ=2.64 (3H, s, CH_3), 6.12 (1H, t, *J*=9 Hz, H-5), 6.28 (1H, d, *J*=10 Hz, H-3), 6.41 (1H, t, *J*=10 and 9 Hz, H-4), 6.44 (1H, ddd, *J*=12, 9, and 1.5 Hz, H-6), 6.58 (1H, dd, *J*=8 and 2 Hz, H-3′ or 6′), 6.61 (1H, td, *J*=8 and 1.5 Hz, H-4′ or 5′), 6.85 (1H, d, *J*=12 Hz, H-7), 6.96 (1H, td, *J*=8 and 2 Hz, H-5′ or 4′), and 7.18 (1H, dd, *J*=8 and 1.5 Hz, H-6′ or 3′).

Found: *m/z* 227.0928. Calcd for $C_{14}H_{13}NO_2$: M, 227.0942.

11-Methylcyclohepta[b][1,4]benzothiazinium Tetrafluoroborate (17). To a solution of **18** (10 mg) in methanol (1 ml) was added 42% HBF_4 (40 mg), and the mixture was set aside at room temperature, depositting crystals after several hours. The precipitates were filtered off, giving **17** (11 mg, 85%, combined with the second crop): Dark red needles; mp 162—164 °C; UV (MeOH) 240, 282, 340, and 452 nm (log ε 4.39, 4.26, 4.04, and 3.68); ^1H NMR (270 MHz in CD_3CN) δ=3.75 (3H, s, CH_3), 7.21 (1H, dd, *J*=7 and 1.5 Hz, H-4 or 1), 7.29 (1H, dd, *J*=7 and 1.5 Hz, H-1 or 4), 7.34 (1H, td, *J*=7 and 1.5 Hz, H-3 or 2), 7.39 (1H, td, *J*=7 and 1.5 Hz, H-2 or 3), 7.46 (1H, d, *J*=12 Hz, H-10 or 6), 7.57 (1H, td, *J*=8 and 3 Hz, H-8), 7.73 (1H, td, *J*=8 and 1.5 Hz, H-7 or 9), 7.76 (1H, dd, *J*=8 and 3 Hz, H-6 or 10), and 7.91 (1H, m, *J*=12, 8, and 1.5 Hz, H-9 or 7).

Anal. ($C_{14}H_{12}BF_4NO$) C, H, N.

11-Methylcyclohepta[b][1,4]benzoxazinium Tetrafluoroborate (19). The same treatment of **20** with HBF_4 as above gave **19** (89%) as dark red needles; mp 156—157 °C; UV (MeOH+HBF_4)[16] 228, 264, 272, 320, and 428 nm (log ε 4.31, 4.22, 4.31, 3.78, and 3.83); ^1H NMR (270 MHz in CD_3CN) δ=3.31 (3H, s, CH_3), 6.79 (1H, m, H-4 or 1), 6.99—7.08 (3H, m, H-2, 3, and 1 or 4), 7.10 (1H, d, *J*=12 Hz, H-6 or 10), 7.15 (1H, d, *J*=12 Hz, H-10 or 6), 7.26 (1H, t, *J*=9.5 Hz, H-8), 7.55 (1H, ddd, *J*=12, 9.5, and 1.5 Hz, H-7 or 9), and 7.75 (1H, ddd, *J*=12, 9.5, and 1.5 Hz, H-9 or 7).

Anal. ($C_{14}H_{12}BF_4NO$) C, H, N.

Oxidation of 9 with H_2O_2. Compound **9** was treated with various molar ratios (1:4—10) of 28% H_2O_2 in methanol at room temperature. Each product was identified by means of periodical checking using HPLC and TLC; most of the products were separated by preparative HPLC, and the yields were based on the peak areas.

1-Formylphenothiazine (23): Orange needles (from EtOH–$CHCl_3$); mp 80.5—81.0 °C (lit,[12] 80—81 °C); UV (MeOH) 240, 288, and 431 nm (log ε 4.46, 3.83, and 3.60); IR (KBr) 3300 (NH), 2860, 2760, and 1665 cm^{-1} (CHO); ^1H NMR ($CDCl_3$) δ=6.55—7.07 (6H, m), 7.17 (1H, dd, *J*=7.8 and 2.0 Hz, H-2), 9.79 (1H, s, CHO), and 10.10 (1H, br, NH); (Found: C, 68.70; H, 3.80; N, 6.63%; M^+ 227).

1-Formylphenothiazine 5-Oxide (23a): Yellow needles (from EtOH); mp 196—197 °C; UV (MeOH) 228, 305, and 375 nm (log ε 3.98, 3.70, and 3.57); IR (KBr) 3250 (NH), 2870, 2780, and 1665 cm^{-1} (CHO); ^1H NMR ($CDCl_3$) δ=7.24—7.41 (3H, m, H-3,7,9), 7.64 (1H, t, *J*=8 Hz, H-8), 7.97 (2H, d, *J*=8 Hz, H-4,6), 8.23 (1H, d, *J*=8 Hz, H-2), 10.09 (1H, s, CHO), and 11.67 (1H, br, NH); MS, *m/z* 243 (M^+).

Anal. ($C_{13}H_9NSO_2$) C, H, N.

3-Formylphenothiazine (25): Yellow needles (from MeOH); mp 194.5—196 °C; UV (MeOH) 242, 288, and 405 nm (log ε 4.39, 4.49, and 3.93); IR (KBr) 3320 (NH), 2850, 2760, and 1660 cm^{-1} (CHO); ^1H NMR ($CDCl_3$) δ=6.64—6.97 (5H, m, H-1,6,7,8,9), 7.30 (1H, d, *J*=1.8 Hz, H-4), 7.46 (1H, dd, *J*=8.2 and 1.8 Hz, H-2), 8.90 (1H, br, NH), and 9.64 (1H, s, CHO); MS, *m/z* 227 (M^+).

Anal. ($C_{13}H_9NSO$) C, H, N.

Phenothiazine 5-Oxide (24a): Pale yellow needles (from EtOH); mp 246—247 °C (lit,[13] 242—242.5 °C); ^1H NMR (DMSO-d_6) δ=7.17 (2H, ddd, *J*=7.8, 6.8, and 1.5 Hz, H-3,7), 7.38 (2H, dd, *J*=8.3 and 1.5 Hz, H-1,9), 7.56 (2H, ddd, *J*=8.3, 6.8, and 1.5 Hz, H-2,8), 7.86 (2H, dd, *J*=7.8 and 1.5 Hz, H-4,6), and 10.78 (1H, br, NH).

Reaction of 10-Methoxycyclohepta[b][1,4]Benzothiazine (26) with H_2O_2. Compound **26** was prepared from 7-methoxy-2-bromotropone and *o*-aminobenzenethiol according to the reported method.[6] The reaction of **26** with H_2O_2 was conducted in a manner similar to that described earlier for **9**, thus giving **10—12** and **27—30**.

26: Red oil; ^1H NMR ($CDCl_3$) δ=3.89 (3H, s, OCH_3), 6.08—6.38 (4H, m), and 7.01—7.36 (4H, m); MS, *m/z* 241 (M^+). Picrate, mp 183—184 °C (lit,[6] 184—185 °C).

Methyl 1-Phenothiazinecarboxylate (27): Yellow needles (from $CHCl_3$); mp 113.1—114.4 °C (lit,[14] 113—113.5 °C); UV (MeOH) 210, 240, 256, 316, and 388 nm (log ε 4.58, 4.56, 4.57, 3.62, and 3.87); IR (KBr), 3300 (NH) and 1680 cm^{-1} (C=O); ^1H NMR ($CDCl_3$) δ=3.89 (3H, s, CH_3), 6.51—7.11 (6H, m), 7.67 (1H, dd, *J*=7.8 and 1.5 Hz, H-2), and 9.91 (1H, br, NH); (Found: C, 65.62; H, 4.31; N, 5.62%; M^+, 257).

Methyl 10H-Phenothiazine-1-carboxylate 5-Oxide (27a): Yellow needles (from $CHCl_3$); mp 167.0—169.2 °C; UV (MeOH) 209, 229, 250, 296, and 361 nm (log ε 4.34, 4.33, 4.04, 4.09, and 3.87); IR (KBr) 3260 (NH) and 1690 cm^{-1} (C=O); ^1H NMR ($CDCl_3$) δ=4.01 (3H, s, OCH_3), 7.21 (1H, dd, *J*=7.8 and 6.8 Hz, H-7), 7.28 (1H, t, *J*=7.8 Hz, H-3), 7.33 (1H, d, *J*=8.3 Hz, H-9), 7.61 (1H, ddd, *J*=8.3, 6.8, and 1.5 Hz, H-8),

7.93 (1H, d, J=7.8 Hz, H-6), 8.17 (1H, dd, J=7.8 and 1.5 Hz, H-2 or 4), 8.34 (1H, dd, J=7.8 and 1.5 Hz, H-4 or 2), and 11.58 (1H, br, NH); MS, m/z 273 (M^+).

Anal. ($C_{10}H_{11}NSO_3$) C, H, N.

*3-Formyl-1-methoxyphenothiazine (**28**)*: Yellow needles (from MeOH) mp 121 °C; UV (MeOH) 207, 246, 298, and 407 nm (log ε 4.38, 4.41, 4.35, and 3.82); IR (KBr) 3300 (NH) and 1660 cm^{-1} (C=O); ^1H NMR ($CDCl_3$) δ=3.92 (3H, s, OCH_3), 6.57 (1H, d, J=6.8 Hz, H-6 or 9), 6.61 (1H, br, NH), 6.88 (3H, m, H-7,8, and 9 or 6), 7.04 (1H, d, J=1.5 Hz, H-2 or 4), 7.12 (1H, d, J=1.5 Hz, H-4 or 2), and 9.68 (1H, s, CHO); MS, m/z 257 (M^+).

Anal. ($C_{14}H_{11}NSO_2$) C, H, N.

*Methyl 2-(o-Methoxyphenylthio)phenylcarbamate (**30**)*: Pale yellow needles (from $CHCl_3$); mp 93.0 °C; UV (MeOH) 209, 239, and 289 nm (log ε 4.60, 4.26, and 3.79); IR (KBr) 3370 (NH) and 1740 cm^{-1} (C=O); ^1H NMR ($CDCl_3$) 3.73 (3H, s, OCH_3), 3.92 (3H, s, OCH_3), 6.79—7.63 (7H, m), 8.07 (1H, br, NH), and 8.21 (1H, dd, J=8.3 and 1.5 Hz, H-3 or 6); MS (70 eV), m/z (rel intensity) 290 (18), 289 (100; M^+), 258 (12), 257 (62), 214 (10), 200 (16), 199 (25), 198 (21), 186 (15), 167 (8), 150 (43), and 77 (8).

Anal. ($C_{15}H_{15}NSO_3$) C, H, N.

*Cyclohepta[b][1,4]benzothiazin-10(11H)-one (**10**)*: Red needles (from MeOH); mp 168—169 °C (lit,[6] 168—169 °C); ^1H NMR (270 MHz in C_6D_6) δ=5.74 (1H, m, H-4), 5.84 (1H, dd, J=11.0 and 8.8 Hz, H-7) 6.22 (1H, d, J=11.0 Hz, H-6), 6.25 (1H, dd, J=11.7 and 8.8 Hz, H-8), 6.45—6.50 (3H, m, H-1,2,3), 6.99 (1H, d, J=11.7 Hz, H-9), and 8.74 (1H, s, NH).

*Cyclohepta[b][1,4]benzothiazin-10(11H)-one 5-Oxide (**11**)*: Yellow needles (from EtOH); mp 196—197 °C (lit,[7] 207 °C); ^1H NMR (270 MHz in C_6D_6) δ=6.17 (1H, dd, J=11.0 and 8.8 Hz, H-7), 6.24 (1H, d, J=8.1 Hz, H-1), 6.56 (1H, dd, J=11.7 and 8.8 Hz, H-8), 6.74 (1H, dd, J=8.1 and 7.3 Hz, H-3), 6.84 (1H, dd, J=8.1 and 7.3 Hz, H-2), 7.04 (1H, d, J=11.7 Hz, H-9), 7.29 (1H, d, J=11.0 Hz, H-6), 7.55 (1H, d, J=8.1 Hz, H-4), and 10.12 (1H, s, NH).

*Cyclohepta[b][1,4]benzothiazin-10(11H)-one 5,5-Dioxides (**12**)*: Yellow needles (from AcOH); mp 264—265 °C (lit,[7] 266 °C); ^1H NMR (270 MHz in C_6D_6) δ=6.17 (1H, dd, J=11.0 and 8.8 Hz, H-7), 7.27 (1H, d, J=11.7 Hz, H-9), 7.53 (1H, t, J=8.0 Hz, H-2 or 3), 7.64 (1H, dd, J=11.7 and 8.8 Hz, H-8), 7.81 (1H, t, J=8.0 Hz, H-3 or 2), 7.85 (1H, d, J=11.7 Hz, H-6), 8.03 (1H, d, J=8.0 Hz, H-1 or 4), 8.21 (1H, d, J=8.0 Hz, H-4 or 1), and 11.45 (1H, s, NH).

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