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Syntheses of Heterocyclic Compounds involving Sulfur. I. Syntheses of 1,3-Dihydro-2*H*-pyrimido[5,6,1-*kl*]phenothiazine, 1,2-Dihydro-3*H*-pyrazino[3,2,1-*kl*]phenothiazine and 1,2-Dihydroimidazo-[4,5,1-*kl*]phenothiazine

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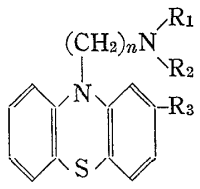
Reaction of 1-tosylaminomethylphenothiazine (VI) and methylene iodide gave 2-tosyl-1,3-dihydro-2*H*-pyrimido[5,6,1-*kl*]phenothiazine (VII). 3-Tosyl-1,2-dihydro-3*H*-pyrazino-[3,2,1-*kl*]phenothiazine (XIV) or 2-tosyl-1,2-dihydroimidazo[4,5,1-*kl*]phenothiazine (XVIII) was synthesized from 1-tosylaminophenothiazine (XIII) and ethylene bromide or methylene iodide. Detosylation of VII, XIV, and XVIII gave 1,3-dihydro-2*H*-pyrimido[5,6,1-*kl*]-phenothiazine (VIII), 1,2-dihydro-3*H*-pyrazino[3,2,1-*kl*]phenothiazine (XII), and 1,2-dihydroimidazo[4,5,1-*kl*]phenothiazine (XVII), respectively.

In addition, syntheses of these new four-ringed nitrogen heterocycles were studied by other routes.

Phenothiazine derivatives (I) have been well known as antihistaminic and tranquilizing agents. As a part of investigations on new chemotherapeutic agents, we studied the syntheses of 1,3-dihydro-2*H*-pyrimido[5,6,1-*kl*]phenothiazine (VIII), 1,2-dihydro-3*H*-pyrazino[3,2,1-*kl*]phenothiazine (XII) and 1,2-dihydroimidazo[4,5,1-*kl*]phenothiazine (XVII) in which the nitrogen containing group at 10-position is bonded to the benzene ring.



I

Synthesis of these compounds was effected by two routes as shown in Chart 1.

One is the lithium aluminum hydride reduction of the lactams obtained by the reactions of 1-aminomethylphenothiazine (III) and 1-aminophenothiazine (IX) with phosgene or oxalyl chloride (route A), and the other is the detosylation of cyclic tosylamines prepared by the reaction of 1-tosylaminomethylphenothiazine (VI) or 1-tosylaminophenothiazine (XIII) with methylene iodide or ethylene bromide (route B).

The preparation of 1,3-dihydro-2*H*-pyrimido[5,6,1-*kl*]phenothiazine (VIII) in Chart 2 was begun with the conversion of phenothiazine-1-carboxamide[2] (II) to III by its reduction with lithium aluminum hydride. Reaction of III and phosgene (route A) did not give a cyclized product, 1,3-dihydro-2*H*-pyrimido[5,6,1-*kl*]phenothiazin-1-one (IV) but N,N'-bis[(1-phenothiazinyl)methyl]urea (V), which was assumed to be formed by the reaction of two moles of the amine and one mole of phosgene, was obtained. The elementary analysis of V agreed well with the formula of $C_{27}H_{22}ON_4S_2$, and its infrared (IR) spectrum showed two NH streching vibrations at 3400 and 3280 cm^{-1}, and a carbonyl band at 1675 cm^{-1}, indicating that this compound is an N,N'-dimethylurea derivative. Tosylation of III with tosyl chloride (route B) provided 1-tosylaminomethylphenothiazine (VI). 2-Tosyl-1,3-dihydro-2*H*-pyrimido[5,6,1-*kl*]phenothiazine (VII) was obtained by the cyclization of VI with methylene iodide. Detosylation of VII with 90% sulfuric acid gave VIII.

1) Location: *1, Tanabedori 3-chome, Mizuho-ku, Nagoya.*
2) N.V. Savitskaya, *Z. Obshch. Khim.*, **24**, 152 (1954).

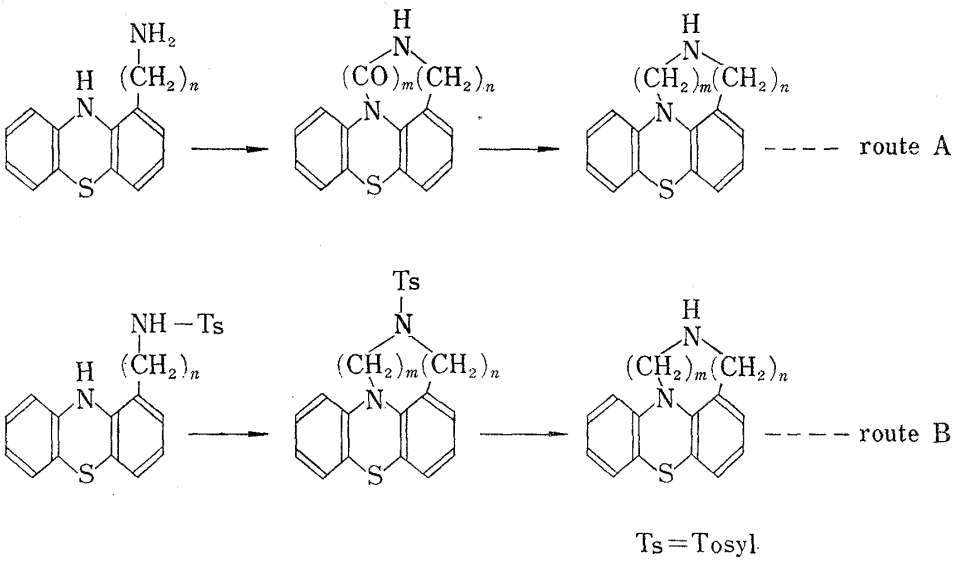


Chart 1

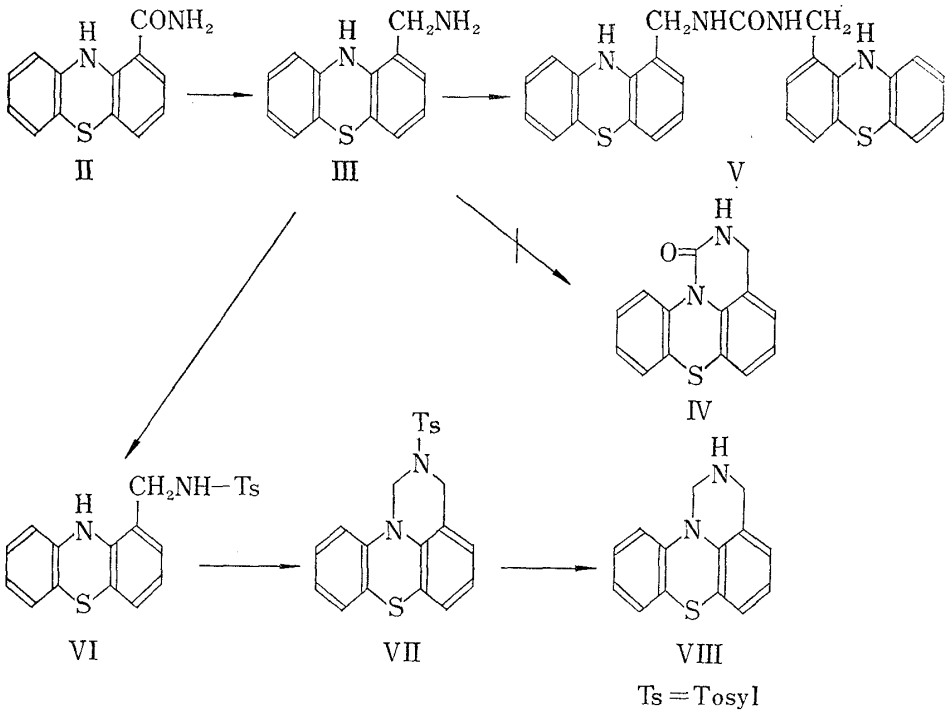


Chart 2

Synthesis of 1,2-dihydro-3*H*-pyrazino[3,2,1-*kl*]phenothiazine (XII) was carried out as shown in Chart 3. Treatment of 1-aminophenothiazine[3] (IX) with oxalyl chloride (route A) gave two products, yellow prisms (X), mp>300°, and yellow needles (XI), mp 268—269°. The elementary analysis of X agreed with the formula of $C_{14}H_8O_2N_2S$ and its IR spectrum showed NH streching vibration at 3440 cm^{-1} and two carbonyl bands at 1715 and 1695 cm^{-1}. From these facts, X is undoubtly 1,2-dihydro-3*H*-pyrazino[3,2,1-*kl*]phenothiazin-1,2-dione, the objective lactam. The structure of XI was concluded as N,N'-di(1-phenothiazinyl)oxalamide due to the facts that the composition agreed with the formula of $C_{26}H_{18}O_2N_4S_2$, and its

3) F. Kehrmann, *Compt. Rend.*, **225**, 578 (1947).

IR spectrum showed two NH streching vibrations at 3330 and 3250 cm^{-1}, and a carbonyl band at 1695 cm^{-1}, resembling the spectrum of N,N′-diphenyloxalamide. Reduction of X with lithium aluminum hydride in tetrahydrofuran gave XII as a yellow oil in a very low yield. This oil was identical with the sample obtained from route B described below. Treatment of the tosylate (XIII), obtained from IX, with ethylene bromide (route B) gave 3-tosyl-1,2-dihydro-3*H*-pyrazino[3,2,1-*kl*]phenothiazine (XIV). In this reaction, when the temperature was low, pale pink prisms (XV), mp 187.5—188.5°, were isolated as a by-product. The composition of XV agreed well with the formula of $C_{21}H_{19}O_2N_2SBr_2$, and its IR spectrum showed NH streching vibration at 3370 cm^{-1}. In addition, SO_2 streching vibration at 1350 and 1158 cm^{-1} had shifted respectively 27 and 3 cm^{-1} higher than these in XIII, and indicated characteristics of the tertiary sulfonamide. From all these data, XV is undoubtly 1-[N-tosyl-N-(2-bromoethyl)]aminophenothiazine, the intermediate to XIV. Detosylation of XIV with 90% sulfuric acid or its irradiation with 100W high-pressure mercury lamp in the presence of sodium carbonate and sodium borohydride gave XII.

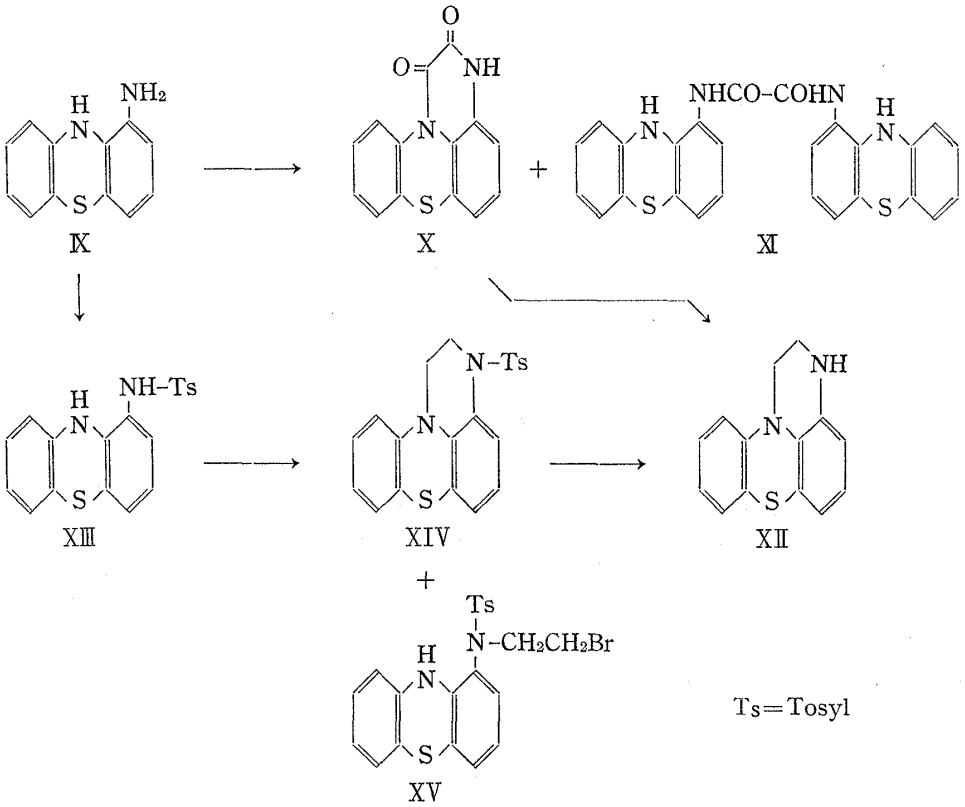


Chart 3

Finally, synthesis of 1,2-dihydroimidazo[4,5,1-*kl*]phenothiazine (XVII) was examined as outlined in Chart 4. Reaction between IX and phosgene (route A) gave a cyclized product, 1,2-dihydroimidazo[4,5,1-*kl*]phenothiazin-1-one (XVI). An attempt to prepare XVII by the reduction of XVI with lithium aluminum hydride did not succeed and a black tar was obtained. Cyclization of XIII with methylene iodide (route B) gave two kinds of product, 2-tosyl-1,2-dihydroimidazo[4,5,1-*kl*]phenothiazine (XVIII) and colorless prisms (XIX), mp 248.5—249.5°. The composition of XIX agreed with the formula of $C_{39}H_{32}O_4N_4S_4$, and its IR spectrum showed NH streching vibration at 3320 cm^{-1}. The SO_2 streching vibrations of this compound at 1355 and 1168 cm^{-1} shifted respectively 32 and 13 cm^{-1} higher than these in XIII. From these facts, XIX is bis[N-tosyl-N-(1-phenothiazinyl)amino]methane. Detosylation of XVIII with 90% sulfuric acid or 25% hydrochloric acid, or its irradiation with 100W high-pressure

mercury lamp in the presence of sodium carbonate and sodium borohydride gave imidazo[4,5,1-*kl*]phenothiazine (XX) to be accompanied with dehydrogenation. In these reactions, XVII was not obtained, and treatment of XVIII with lithium aluminum hydride in ether successfully gave XVII.

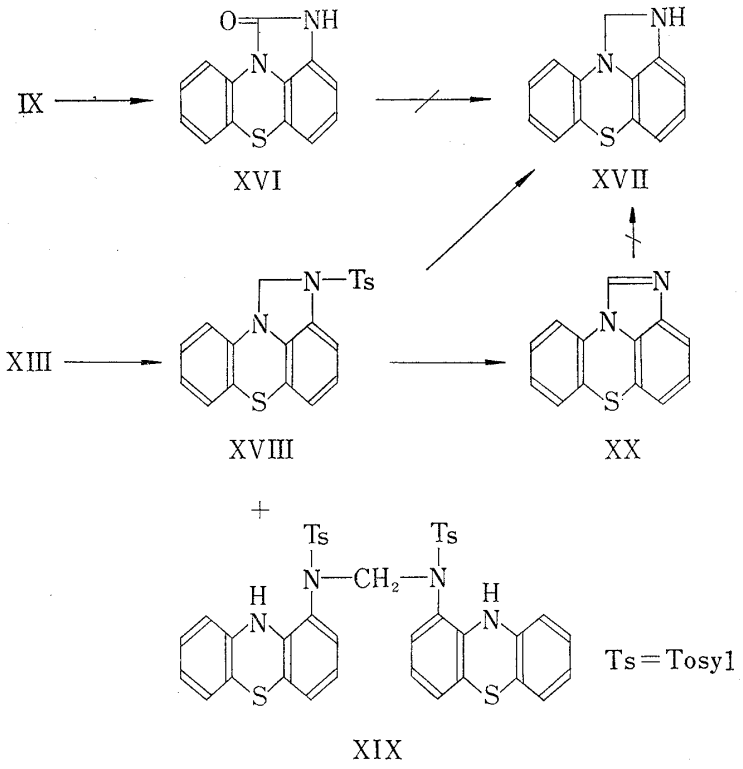


Chart 4

Further, catalytic hydrogenation of XX in the presence of palladium-charcoal or Adams' catalyst was examined, but XVII was not obtained and XX was recovered. It is considered that a fused imidazole ring conjugated with the phenothiazine ring contributes to stabilize the larger aromatic ring newly formed, resulting the resistance to catalytic hydrogenation.

The result of detosylation of the cyclized compounds, VII, XIV, and XVIII, with 90% sulfuric acid, or 25% hydrochloric acid, or irradiation with 100W high-pressure mercury lamp in the presence of sodium carbonate and sodium borohydride, is given in Table I.

Table I

Reagent	Condition	VII→VIII Yield (%)	XIV→XII Yield (%)	XVIII→XX Yield (%)
90% H_2SO_4	room temp. 7 day 105°	30	trace	trace
25% HCl	7 hr	recover	—	83
100W hν $NaBH_4$, Na_2CO_3 in 70% EtOH	20—25° 10 hr	recover	42	38

Experimental

1-Aminomethylphenothiazine (III)——A mixture of 4 g of phenothiazine-1-carboxamide[2] (II), 2.8 g of $LiAlH_4$, and 270 ml of dry ether was refluxed for 10 hr. An excess of $LiAlH_4$ was decomposed with H_2O and the resultant precipitate was filtered off. The filtrate was washed with H_2O, dried, and evaporated to

dryness, and the residue was purified by chromatography over Al_2O_3 in benzene to afford 2.9 g (76.5%) of III as a pale yellow oil. IR ν_{max}^{film} cm^{-1}: 3350 (NH), 3230, 3160 (NH_2). Recrystallization of the picrate from EtOH gave dark red needles, mp 223.5—225° (decomp.). *Anal.* Calcd. for $C_{19}H_{15}O_7N_5S$: C, 49.89; H, 3.31; N, 15.31. Found: C, 50.01; H, 3.38; N, 15.45.

N,N'-Bis[(1-phenothiazinyl)methyl]urea (V)——To a mixture of 300 mg of III, 300 mg of K_2CO_3, and 30 ml of dry ether was added 430 mg of 30% $COCl_2$–toluene solution at 0° and the mixture was stirred for 20 min at the same temperature, then at room temperature for 2 hr. The above solution was diluted with H_2O and extracted with ether. The extract was washed with 2% HCl and H_2O, and dried. The solvent was evaporated to dryness and the residue was recrystallized from EtOH to give 230 mg (72.5%) of V as yellow needles, mp 190—191°. *Anal.* Calcd. for $C_{27}H_{22}ON_4S_2$: C, 67.21; H, 4.60; O, 3.32; N, 11.61; mole. wt. 482.5. Found: C, 67.39; H, 4.66; O, 3.39; N, 11.45; mol. wt. 502 (Rast). IR ν_{max}^{KBr} cm^{-1}: 3400, 3280 (NH), 1675 (C=O).

1-Tosylaminomethylphenothiazine (VI)——To a solution of 2 g of III and 15 ml of dry pyridine was rapidly added a solution of 2 g of TsCl in 20 ml of dry pyridine and the mixture was warmed on a hot water bath for 5 min. The reaction mixture was poured into ice–water and extracted with ether. The extract was washed with dil. HCl and H_2O, and dried. The solvent was evaporated to dryness and the residue was recrystallized from benzene to give 2.7 g (81%) of VI as yellow needles, mp 183—184°. *Anal.* Calcd. for $C_{20}H_{18}O_2N_2S_2$: C, 62.80; H, 4.75; N, 7.32. Found: C, 62.73; H, 4.99; N, 7.39. IR ν_{max}^{KBr} cm^{-1}: 3380, 3260 (NH), 1325, 1150 (SO_2).

2-Tosyl-1,3-dihydro-2*H*-pyrimido[5,6,1-*kl*]phenothiazine (VII)——A mixture of 1.6 g of VI, 0.5 g of NaH (50% dispersion in mineral oil), and 30 ml of dry dimethyl sulfoxide was stirred at room temperature for 1 hr, and then at 50° for 1.5 hr in N_2 atmosphere. When cooled, 1.6 g of methylene iodide was added to this solution and stirred at room temperature for 30 min, and then at 80—85° for 3 hr. The reaction mixture was poured into 300 ml of H_2O containing 4 g of NH_4Cl, extracted with $CHCl_3$, which was washed with H_2O and dried. The solvent was evaporated and the residue was purified by chromatography over SiO_2 gel in $CHCl_3$ to give a yellow solid. Recrystallization from EtOH afforded 0.75 g (45.7%) of VII as pale yellow prisms, mp 214—215°. *Anal.* Calcd. for $C_{21}H_{18}O_2N_2S_2$: C, 63.95; H, 4.57; O, 8.11; N, 7.10. Found: C, 64.13; H, 4.75; O, 8.28; N, 7.20. IR ν_{max}^{KBr} cm^{-1}: 1340, 1160 (SO_2).

1,3-Dihydro-2*H*-pyrimido[5,6,1-*kl*]phenothiazine (VIII)——A mixture of 250 mg of VII and 15 ml of 90% H_2SO_4 was stirred in N_2 atmosphere at room temperature for 7 days. The reaction mixture was poured into 50 ml of ice–water, basified with NH_4OH, and extracted with ether. The extract was washed with H_2O and dried. The solvent was evaporated and the residue was purified by chromatography over Al_2O_3 in benzene to give a yellow solid. Recrystallization from EtOH afforded 35 mg (30%) of VIII as yellow needles, mp 102—103°. *Anal.* Calcd. for $C_{14}H_{12}N_2S$: C, 69.99; H, 5.02; N, 11.66. Found: C, 70.12; H, 5.15; N, 11.75. IR ν_{max}^{KBr} cm^{-1}: 3160 (NH). NMR τ (in $CDCl_3$): 2.72—3.43 (7H, multiplet, aromatic proton), 5.42 (2H, singlet, >N–CH_2–Ar), 6.10 (2H, singlet, >N–CH_2–), 8.00 (1H, singlet, NH). UV λ_{max}^{EtOH} mμ (log ε): 245 (shoulder 4.01), 269 (4.59), 328 (3.60).

1,2-Dihydro-3*H*-pyrazino[3,2,1-*kl*]phenothiazin-1,2-dione (X) and N,N'-Bi(1-phenothiazinyl)oxalamide (XI)——To a mixture of 1.5 g of 1-aminophenothiazine[3] (IX), 1.6 g of K_2CO_3, and 160 ml of dry ether was added a solution of 1 g of oxalyl chloride in 20 ml of dry ether with cooling in an ice–bath and the mixture was stirred at 5—10° for 3 hr. The reaction mixture was evaporated to dryness under reduced pressure and the residue was washed with 2% HCl and then with H_2O to give a tan powder. The powder was extracted with hot EtOH and the extract was evaporated to obtain a yellow powder. Recrystallization from EtOH afforded 120 mg (6.8%) of X as yellow prisms, mp >300°. *Anal.* Calcd. for $C_{14}H_8O_2N_2S$: C, 62.67; H, 3.01; O, 11.93; N, 10.45. Found: C, 62.45; H, 3.03; O, 11.71; N, 10.20. IR ν_{max}^{KBr} cm^{-1}: 3440 (NH), 1715, 1695 (C=O).

The residue from hot EtOH extraction was recrystallized from pyridine–H_2O to give 1.2 g (72%) of XI as yellow needles, mp 268—269°. *Anal.* Calcd. for $C_{26}H_{18}O_2N_4S_2$: C, 64.70; H, 3.76; O, 6.64; N, 11.61; mol. wt. 482. Found: C, 64.45; H, 3.81; O, 6.79; N, 11.93; mole. wt. 505 (Rast). IR ν_{max}^{KBr} cm^{-1}: 3330, 3250 (NH), 1695 (C=O).

1-Tosylaminophenothiazine (XIII)——To a mixture of 5 g of IX and 30 ml of dry pyridine was added a solution of 4.8 g of TsCl in 50 ml of dry pyridine and the mixture was warmed on a hot water bath for 5 min. The reaction mixture was poured into ice–water, the precipitate was collected by filtration, washed with dil. HCl and H_2O, and dried. Recrystallization from benzene afforded 6.5 g (75%) of XIII as colorless prisms, mp 162—163°. *Anal.* Calcd. for $C_{19}H_{16}O_2N_2S_2$: C, 61.93; H, 4.37; N, 7.60. Found: C, 62.15; H, 4.45; N, 7.65. IR ν_{max}^{KBr} cm^{-1}: 3370, 3310 (NH), 1323, 1155 (SO_2).

3-Tosy-1,2-dihydro-3*H*-pyrazino[3,2,1-*kl*]phenothiazine (XIV)——A mixture of 1.5 g of XIII, 0.8 g of NaH (50% dispersion in mineral oil), and 30 ml of dry dimethyl sulfoxide was stirred at 65—70° for 2 hr in N_2 atmosphere. When cooled, a solution of 2.7 g of ethylene bromide in 30 ml of toluene was added dropwise to this solution, and the mixture was stirred at 105—110° for 4 hr. The reaction mixture was poured into 300 ml of H_2O containing 4 g of NH_4Cl, extracted with $CHCl_3$, and the extract was washed with H_2O and dried. The solvent was evaporated and the residue was purified by chromatography over SiO_2

gel in $CHCl_3$ to give 0.67 g (43.5%) of XIV as colorless prisms (from EtOH), mp 105—106°. *Anal.* Calcd. for $C_{21}H_{18}O_2N_2S_2$: C, 63.95; H, 4.60; O, 8.12; N, 7.10. Found: C, 63.81; H, 4.71; O, 8.24; N, 7.15. IR ν_{max}^{KBr} cm^{-1}: 1355, 1165 (SO_2).

3-Tosyl-1,2-dihydro-3*H*-pyrazino[3,2,1-*kl*]phenothiazine (XIV) and 1-[N-Tosyl-N-(2-bromoethyl)]aminophenothiazine (XV)——A mixture of 2 g of XIII, 1.1 g of NaH (50% dispersion in mineral oil), and 40 ml of dry dimethyl sulfoxide was stirred at 65—70° for 2 hr in N_2 atmosphere. When cooled, a solution of 3.6 g of ethylene bromide in 40 ml of toluene was added dropwise to this solution and the mixture was stirred at 50—55° for 5 hr. The reaction mixture was poured into 400 ml of H_2O containing 5 g of NH_4Cl, extracted with $CHCl_3$, and the extract was washed with H_2O and dried. The solvent was evaporated and the residue was purified by chromatography over SiO_2 gel in $CHCl_3$. The first eluate gave 0.31 g (17%) of XV as pale pink prisms (from EtOH–benzene), mp 187.5—188.5°. *Anal.* Calcd. for $C_{21}H_{19}O_2N_2SBr_2$: C, 53.07; H, 4.02; O, 6.74; N, 5.90. Found: C, 53.21; H, 4.17; O, 6.89; N, 5.98. IR ν_{max}^{KBr} cm^{-1}: 3370 (NH), 1350, 1158 (SO_2).

The second eluate gave 0.6 g (29%) of XIV as colorless prisms (from EtOH), mp 105—106°, which was identified by IR spectrum.

1,2-Dihydro-3*H*-pyrazino[3,2,1-*kl*]phenothiazine (XII)——a) A mixture of 500 mg of XIV, 270 mg of $NaBH_4$, 210 mg of Na_2CO_3, and 120 ml of 70% EtOH was irradiated for 10 hr with 100W high-pressure mercury lamp at 20—25° in N_2 atmosphere. The reaction mixture was concentrated and the residue was acidified with 5% HCl to decompose an excess of $NaBH_4$. This solution was basified again with Na_2CO_3, extracted with ether, and the extract was washed with H_2O and dried. The solvent was evaporated and the residue was purified by chromatography over Al_2O_3 in benzene to afford 125 mg (42%) of XII as a yellow oil. IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 3400 (NH). NMR τ (in $CDCl_3$): 2.65—3.71 (7H, multiplet, aromatic proton), 6.20(2H, triplet, >N–C<u>H</u>$_2$–CH_2–NH–), 6.45 (2H, triplet, >N–CH_2–C<u>H</u>$_2$–NH–), 6.53 (1H, singlet, NH). UV λ_{max}^{EtOH} mμ (log ε): 244 (4.24), 270 (4.28), 324 (3.59). Recrystallization of the hydrochloride from EtOH gave colorless needles, mp 124—125.5° (decomp.). *Anal.* Calcd. for $C_{14}H_{13}N_2SCl$: C, 60.75; H, 4.75; N, 10.12. Found: C, 61.05; H, 4.87; N, 10.21.

b) A mixture of 150 mg of XIV and 10 ml of 90% H_2SO_4 was stirred in N_2 atmosphere at room temperature for 7 days. After addition of H_2O, the mixture was basified with NH_4OH, extracted with ether, and the extract was washed with H_2O and dried. The solvent was evaporated and the residue was purified by chromatography over Al_2O_3 in benzene to afford a trace of XII as a yellow oil, which was identified by IR spectrum.

1,2-Dihydroimidazo[4,5,1-*kl*]phenothiazin-1-one (XVI)——To a suspension of 1 g of IX and 0.9 g of K_2CO_3 in 100 ml of dry ether was added 1.9 g of 30% $COCl_2$–toluene solution at 0°, and the mixture was stirred at 5—10° for 2 hr. The solvent was evaporated to dryness under reduced pressure, the residue was washed with 5% HCl and H_2O to give a yellow powder. Recrystallization from AcOEt gave 0.4 g (35%) of XVI as colorless needles, mp 291—292°, which was identical with the sample obtained from the method of Savitskaya.[2]

2-Tosyl-1,2-dihydroimidazo[4,5,1-*kl*]phenothiazine (XVIII) and Bis[N-tosyl-N-(1-phenothiazinyl) amino]-methane (XIX)——A mixture of 1.5 g of XIII, 0.47 g of NaH (50% dispersion in mineral oil), and 30 ml of dry dimethyl sulfoxide was stirred at 65—70° for 2 hr in N_2 atmosphere. To the cooled mixture was added 1.45 g of methylene iodide, and the mixture was stirred at room temperature for 30 min and at 80—85° for 3 hr. The reaction mixture was poured into 300 ml of H_2O containing 4 g of NH_4Cl, extracted with $CHCl_3$, and the extract was washed with H_2O and dried. The solvent was evaporated and the residue was purified by chromatography over SiO_2 gel in $CHCl_3$. The first eluate gave 0.48 g (28%) of XVIII as yellow needles (from EtOH), mp 115—116°. *Anal.* Calcd. for $C_{20}H_{16}O_2N_2S_2$: C, 63.13; H, 4.23; O, 8.41; N, 7.36. Found: C, 63.21; H, 4.35; O, 8.62; N, 7.28. IR ν_{max}^{KBr} cm^{-1}: 1360, 1163 (SO_2).

The second eluate gave 0.23 g (15%) of XIX as colorless prisms (from benzene), mp 248.5—249.5°. *Anal.* Calcd. for $C_{39}H_{32}O_4N_4S_4$: C, 62.54; H, 4.31; O, 8.54; N, 7.48; mol. wt. 749. Found: C, 62.64; H, 4.42; O, 8.71; N, 7.53; mol. wt. 710 (Rast). IR ν_{max}^{KBr} cm^{-1}: 3320 (NH), 1355, 1168 (SO_2).

Imidazo[4,5,1-*kl*]phenothiazine (XX)——a) A mixture of 300 mg of XVIII, 30 ml of 25% HCl was heated at 105—110° for 7 hr in N_2 atmosphere with stirring. The cooled reaction mixture was filtered, the filtrate was basified with Na_2CO_3, extracted with $CHCl_3$, and the extract was washed with H_2O and dried. The solvent was evaporated and the residue was recrystallized from 50% EtOH to give 150 mg (83%) of XX as colorless needles, mp 177—178°. *Anal.* Calcd. for $C_{13}H_8N_2S$: C, 69.64; H, 3.57; N, 12.50. Found: C, 69.45; H, 3.72; N, 12.41. IR ν_{max}^{KBr} cm^{-1}: 1625 (C=N). NMR τ (in $CDCl_3$): 1.68 (1H, singlet, –CH=N–), 2.63—3.40 (7H, multiplet, aromatic proton). Mass Spectrum *m/e*: 224 (M^+). UV λ_{max}^{EtOH} mμ (log ε): 225 (4.48), 233 (4.42), 250 (4.25), 265 (4.05), 274 (3.99), 290 (3.76), 300 (3.89), 330 (3.92).

b) A mixture of 250 mg of XVIII, 150 mg of $NaBH_4$, 110 mg of K_2CO_3, and 50 ml of 70% EtOH was irradiated with 100W high-pressure mercury lamp at 20—25° for 10 hr in N_2 atmosphere. The reaction mixture was treated by the usual way to give 34 mg (38%) of XX as colorless needles, mp 177—178°, which was identified by IR spectrum.

c) A mixture of 100 mg of XVIII and 10 ml of 90% H_2SO_4 was stirred at room temperature for 7 days in N_2 atmosphere. The reaction mixture was treated by the usual way to give a trace of XX as colorless needles, mp 177—178°, which was identified by IR spectrum.

1,2-Dihydroimidazo[4,5,1-*kl*]phenothiazine (XVII)——A mixture of 400 mg of XVIII, 1 g of $LiAlH_4$, and 30 ml of dry ether was refluxed for 15 hr. An excess of $LiAlH_4$ was decomposed with H_2O and the resultant precipitate was filtered off. The filtrate was washed with H_2O and dried. The solvent was evaporated and the residue was purified by chromatography over Al_2O_3 in benzene to afford 180 mg (23.8%) of XVII as a yellow oil. IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 3250 (NH). NMR τ (in $CDCl_3$): 2.48—3.70 (7H, multiplet, aromatic proton), 4.88 (2H, singlet, $-CH_2-$), 6.08 (1H, singlet, NH). UV λ_{max}^{EtOH} mμ (log ε): 232 (4.37), 257 (4.31), 329 (3.78). Recrystallization of the hydrochloride from EtOH–ether gave colorless needles, mp 112—114° (decomp.). *Anal.* Calcd. for $C_{13}H_{11}N_2SCl$: C, 59.43; H, 4.19; N, 10.67. Found: C, 59.55; H, 4.25; N, 10.56.

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