# SYNTHESIS AND REACTIONS OF 2,3-DIHYDROCYCLOHEPTA[b][1,4]-THIAZINES AND 2,3-DIHYDRO-1H-CYCLOHEPTA[b]PYRAZINES[1]

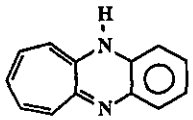
Tetsuo NOZOE*, Sumio ISHIKAWA , and Kimio SHINDO*†
Tokyo Research Laboratories, Kao Corporation, 1-3 Bunka,
Sumida-ku, Tokyo 131
†Department of Chemistry, Faculty of Science, Josai University,
Sakado, Saitama 350-02

**Abstract** - The reaction of 2-methoxytropone with ethylenediamine gave 2-(2-aminoethyl)aminotropone and 2,2'-(1,2-ethanediamino)-bis(tropone), and the former afforded 2,3-dihydro-1H-cycloheptа[b]pyrazine (13) on heating. N-Methyl compound 14 of 13 was also obtained by the similar method. 14 was led to the dimethyl cation 18b, which gave exclusively 7-bromo compound 24 with bromine in acetic acid. 18b and 24 rearranged to 1,2,3,4-tetrahydro-1,4-dimethylquinoxaline-6-carbaldehyde with alkali, while 13 rearranged to 1-phenylimidazolin-2-one on treatment with $H_2O_2$. The reaction of 2-chlorotropone with 2-aminoethanethiol rapidly afforded 2-(2-aminoethylthio)tropone (35a), which gradually changed to 2-[2-(2-troponyl)thioethylamino]tropone (37a) and N,N'-bis(2-troponyl)-2-aminoethanedisulfide (39a) via unstable 2-(2-mercaptoethyl)-aminotropone (38a). Hydrochloride of 35a gave, upon heating, 2,3-dihydrocyclohepta[b][1,4]thiazine (15), which gave N-methyl cation 40 on treatment with magic methyl. 40 gradually changed with cold alkali to the disulfide 39b, via 35b, 37b, and 38b, in a manner similar to the case of their parent compounds (35a, 37a, and 38a). Possible pathways of these reactions, especially the facile exchange of the difunctionalized side-chains, are discussed.

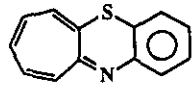
---

Dedicated to Professor Sir Derek Barton on the occasion of his 70th birthday.

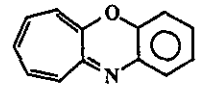
In the course of our recent reinvestigation of benzo[b]tropazine (1)[2] and benzo-[b]tropothiazine (2)[3], we synthesized various derivatives of cyclohepta[b][1,4]-benzoxazine (3)[4] and its S- (2)[5] and N-analogue (1)[6,7].



1

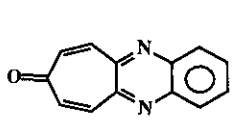


2

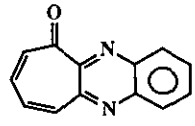


3

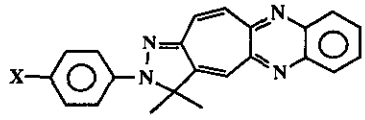
Various heterocyclic compounds having quinoxalotropone moiety have also been reported: namely, 4-8 and their O- and S-analogues 9-12 (Chart 1).



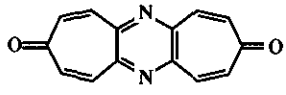
4[8]



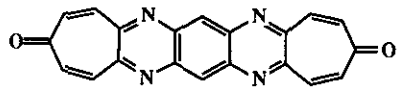
5[9]



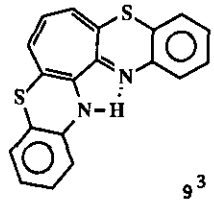
6[10]



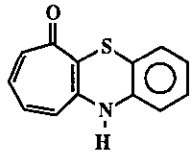
7[11]



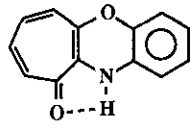
8[12]



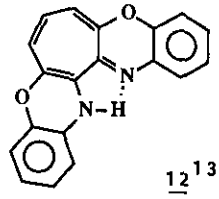
9[3]



10[3]



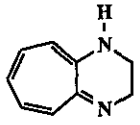
11[13]



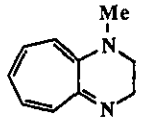
12[13]

Chart 1

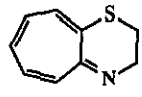
The interesting aspects of these compounds of type 1-3 prompted us to synthesize their parent compounds (13-16) and to compare their properties with each other and those with their respective benzologues 1-3, which we wish to report in this



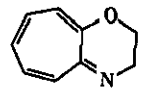
13



14

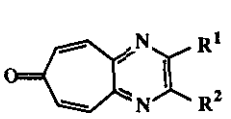


15

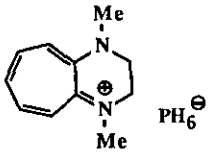


16

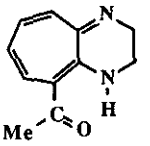
communication. In connection with these ring-system, there have been reported the syntheses of pyrazinotropones 17a-c ($R^1$,$R^2$=H or Me)[14,15], N,N'-dimethyl-2,3-dihydrocyclohepta[b][1,4]pyrazinium salt 18a[16], 5-acetylcyclohepta[b]pyrazine 19[17], and 2,3-dihydrocyclohepta[b][1,4]oxazine 16[18].



17a-c



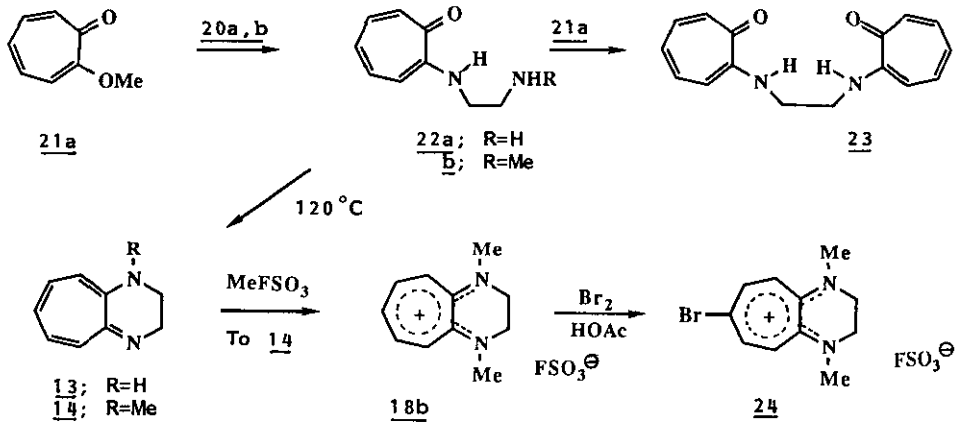
18a



19

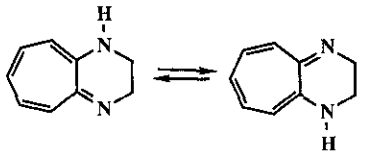
20a; X=$NH_2$
b; X=NHMe
c; X=OH
d; X=SH

2-(2-Aminoethylamino)tropone (22a: R=H)[19] (95% yield; N-Acetamide, yellow needles, mp 124 °C) and 2,2'-(1,2-ethanediamino)-bis(tropone) (23)[20] (4%, mp 230 °C) were obtained when an ethanolic solution of 2-methoxytropone (21a) was refluxed with four equiv. of ethylenediamine (20a) for 45 min. However, on heating 22a in ethanol for 6 h at 120 °C (sealed tube), 2,3-dihydro-1H-cyclohepta[b]pyrazine (13)[21] (pale yellow needles, mp 134 °C) was obtained in 98% yield (Scheme 1).

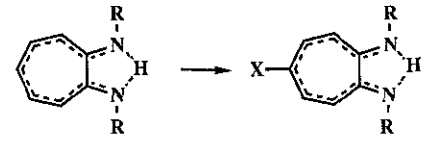



Scheme 1

Compound 13 exhibited $^1$H nmr signals at 3.53 (4H) due to methylene protons and at 6.08 (1H), 6.21 (2H), and 6.51 (2H) due to 7-membered ring protons, thus indicating that 13 exists in rapidly interchanging tautomeric forms 13A and 13B (hydrogen atom being on either one of the two N atoms) in $CDCl_3$ at 27 °C. In this regard, it has been noted[22] that orange-colored 2-aminotroponeimines 25 (R=Me or aryl) possess the symmetrical hydrogen-bonded structure and give various highly colored metal complexes and substitution products.

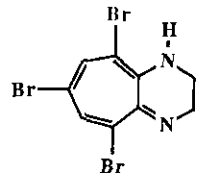


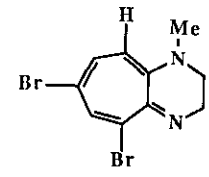
13A 13B



25 26

Similarly, 2-(2-methylaminoethyl)aminotropone (22b)[23] was prepared from 21a and N-methylethylenediamine (20b: X=NHMe); at a high temperature (120 °C in sealed tube) N-methyl compound 14[24] was obtained by ring-closure (70% yield). Methylation of 14 with methyl fluorosulfate (magic methyl) gave N,N'-dimethyl cation 18b (yellow needles, mp 165 °C)[25]. Interestingly, cation 18b rapidly afforded 7-bromo compound 24 (yellow solid, mp 227 °C)[26] almost quantitatively on treatment with excess bromine in acetic acid, in a manner similar to the facile cationoid substitution reaction of 25 to give exclusively 26 (X=Br and arylazo)[22]. Similar treatment of 13 and 14 with excess bromine in acetic acid afforded tribromo 27 ($X^1$=$X^2$=$X^3$=Br) and dibromo compound 28 ($X^1$=$X^2$=Br, $X^3$=H), respectively, as the main products

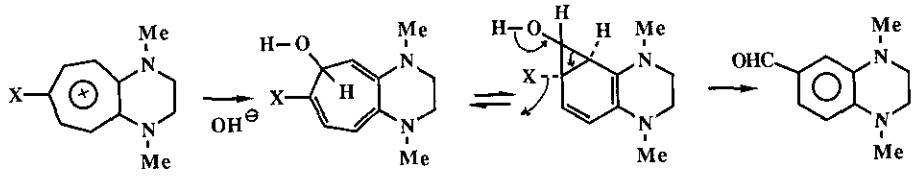




27 28

besides small amounts of mono-, di-, and tri-bromo compounds. These results suggest that the exclusive formation of 7-bromo compound 24 from 18b is mostly due to the steric effect of the two N-methyl groups.

With hot alkali, cation 18 and its bromo compound 24 rearranged to 1,2,3,4-tetrahydro-1,4-dimethylquinoxaline-6-carbaldehyde 29[27] (Scheme 2), while 14



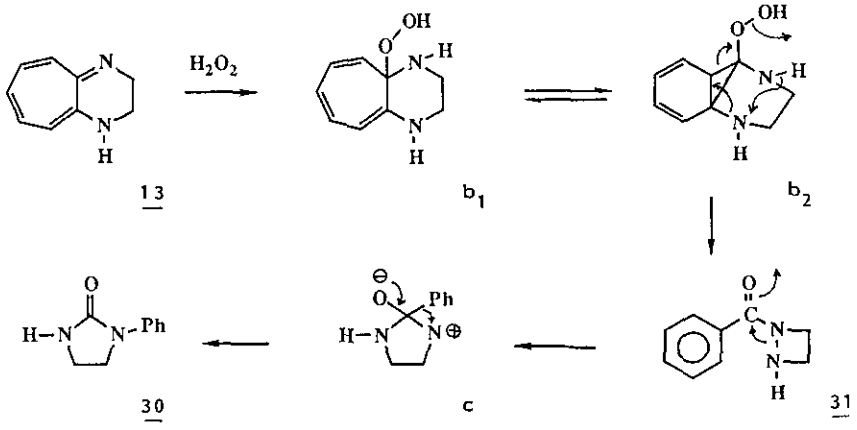
18; X=H
24; X=Br

$a_1$ $a_2$ 29

Scheme 2

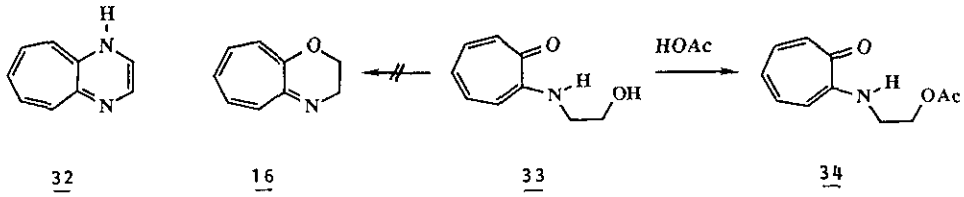
decomposed into tropolone via 22b. Treatment of 13 with $H_2O_2$ in methanol produced

1-phenylimidazolin-2-one (30)[28]; a possible pathway of the rearrangement involving unstable 1-benzoyldiazetidine 31 is shown in Scheme 3. Attempted dehydrogenation

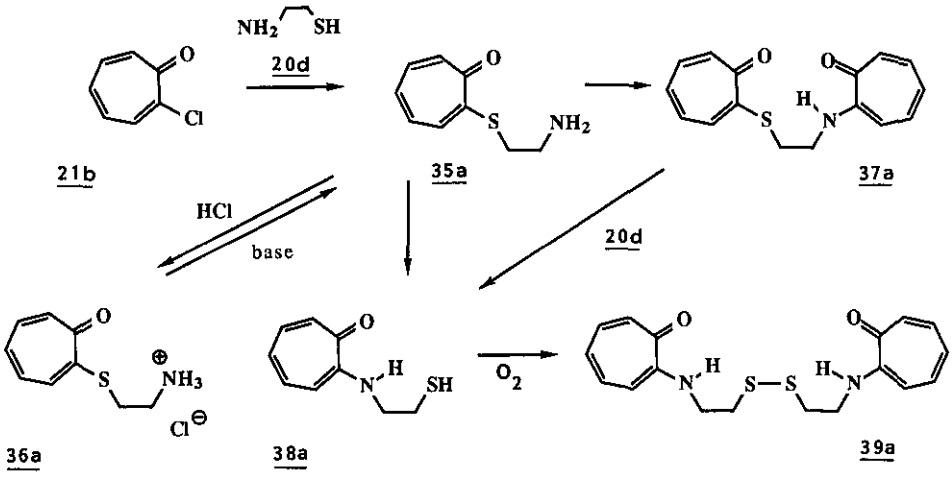



*Scheme 3*

of 13 by using DDQ or trityl fluoroborate resulted in the formation of only a resinous compound *without affording cyclohepta[b][1,4]pyrazine* (32). 2-(2-Hydroxyethylamino)tropone (33)[29], which was obtained from 21a and 2-aminoethanol (20c, X=OH), did not give 16 on heating at 100-120 °C either in ethanol or acetic acid but afforded only acetate 34 in the latter solvent.




Hydrochloride 36a[30] (yellow needles) of 2-(2-aminoethylthio)tropone 35a (mono-, brown oil, and diacetate, brown needles, mp 105 °C), was immediately obtained in 75% yield by adding 2-3 drops of conc. HCl to a mixture of 2-chlorotropone (21b) and 2-aminoethanethiol (20d, X=SH)) at 0-5 °C. 2-[2-(2-Troponyl)thioethylamino]-tropone (37a)[31] was immediately obtained in 83% yield, when a methanolic solution of free 35a (obtained by neutralizing 36a with triethylamine) was treated with 21b. N,N'-Bis-(2-troponyl)-2-aminoethanedisulfide (39a)[32] was obtained via unstable 2-(2-mercaptoethylamino)tropone (38a), when free amine 35a was allowed to stand for 1 day, or when a methanolic solution of 37a and 20d was left in open air




*Scheme 4*

for several hours (Scheme 4). Time-dependent HPLC chromatograms of the above reactions are shown in Figs 1 and 2.

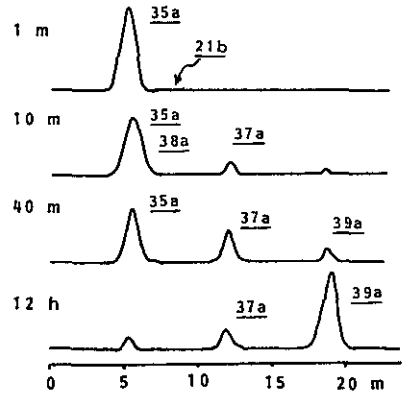



Fig 1. Time-dependent HPLC chromatograms of the reaction of 21b with 20d in MeOH at r.t.

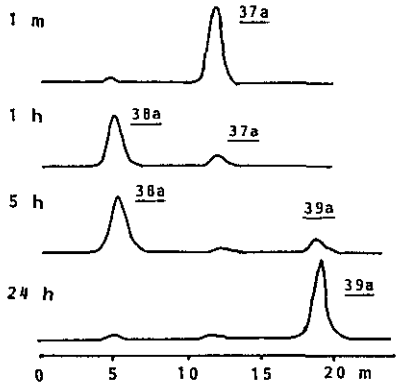
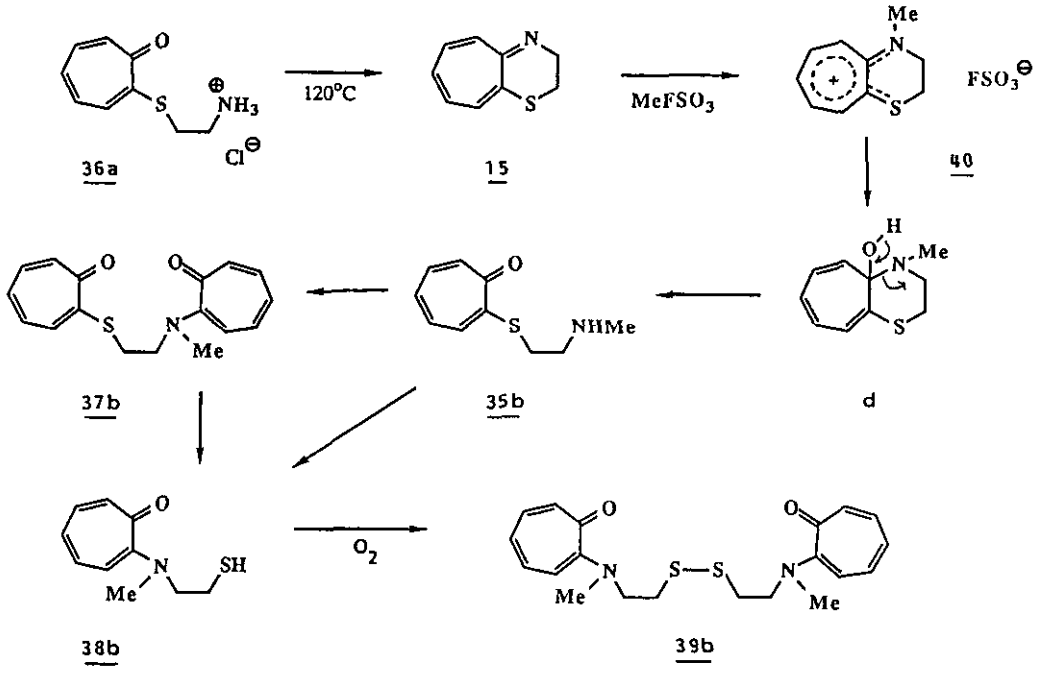



Fig 2. Time-dependent HPLC chromatograms of the reaction of 37a with 20d in MeOH at r.t.

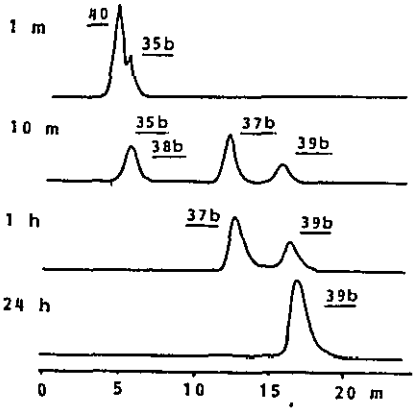
Upon heating in ethanol for 2 h at 120 °C (sealed tube), the HCl salt 36a afforded 2,3-dihydrocyclohepta[b][1,4]thiazine (15)[33], which turns out to be stable to alkali as in the case of its benzologue 2[5]. Treatment of 15 with magic methyl for 15 h at room temperature gave N-methyl cation 40[34] (52%) (Scheme 5). With alkali, 40 underwent ring-opening to give 35b, which was transformed into 38b via 37b[35]. Compound 38b, which is very unstable in air, converted to disulfide 39b[36] on

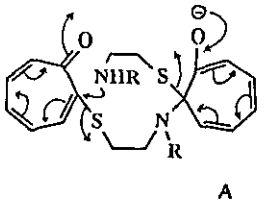
standing or during attempted isolation (Scheme 5). Time-dependent HPLC diagrams of these reactions are shown in Fig 3. The reactions of the ring-opened product 35b




Scheme 5

to yield 39b, which closely resembles those of 35a to 39a via 37a (Scheme 4), are likely to proceed through the bimolecular (A) or intramolecular intermediate (B), because the rearrangement of 35b to 38b undergoes without addition of extra 20d.



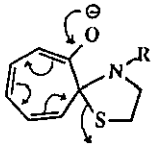




Fig 3. Time-dependent HPLC chromatograms of the reaction of 40 with sodium hydroxide in MeOH at r.t.

These unprecedented, facile intermolecular (via A) or intramolecular (via B) exchange of the bifunctionalized side-chain (Scheme 4 or 5), which could be explained in terms of HSAB principle, is considered one of the characteristic features of polarizable troponoid system.

We wish to thank Professor Hiroshi Yamamoto (Okayama Univ.) for his helpful discussion.

**REFERENCES AND NOTES**

1. Partly presented at the 45th National Meeting of the Chemical Society of Japan, Tokyo, April 1982 (Abstr. No 2D10), and at the 47th Meeting, Tokyo, April 1983 (Abstr. No 4F34).
2. T. Nozoe, T. Kitahara, K. Takase, and M. Sasaki, Proc. Japan Acad., **32**, 349 (1956).
3. T. Nozoe, T. Asao, and K. Takahashi, Bull. Chem. Soc. Jpn., **34**, 146 (1961), ibid., **39**, 1980 (1966).
4. T. Nozoe, H. Okai, and T. Someya, Bull. Chem. Soc. Jpn., **51**, 2185 (1978).
5. K.Shindo, S.Ishikawa, and T.Nozoe, Bull. Chem. Soc. Jpn., **58**, 165 (1985).
6. T. Nozoe, Pure Appl. Chem., **54**, 975 (1982); T. Nozoe, Chemistry (Chinese, Chem. Soc., Taiwan), **41**, A43 (1983).
7. T. Nozoe, S. Ishikawa, and K. Shindo, Chem. Lett., **1988**, 1593; K. Shindo, S. Ishikawa, and T. Nozoe, submitted for publication.
8. T. Nozoe, M.Sato, and T. Matsuda, Sci. Rep. Tohoku Univ., **37**, 407 (1953).
9. M. Hirama, A. Kawamata, and S. Ito, Chem. Lett., **1979**, 855.
10. T. Nozoe, T. Ikemi, and T. Ozeki, Proc. Jpn. Acad., **31**, 455 (1955).
11. T. Asao, Bull. Chem. Soc. Jpn., **34**, 151 (1961).
12. H. Takeshita, A. Mori, T. Nagao, and T. Nagamura, Chem. Lett., **1988**, 175.
13. T. Nozoe, H. Okai, and T. Someya, Bull. Chem. Soc. Jpn., **52**, 1156 (1979); T. Someya, H. Okai, H. Wakabayashi, and T. Nozoe, ibid., **56**, 2756 (1983); T. Nozoe, H. Okai, H. Wakabayashi, and S. Ishikawa, Chem. Lett., **1984**, 1145.
14. S. Itô, Sci. Rep. Tohoku Univ., **42**, 247 (1963).
15. S. Sunagawa, Y. Sato, and H. Watatani, Chem. Pharm. Bull. (Tokyo)., **11**, 142 (1963).
16. J. D. Wilson, C. F. Hobbs, and H. Weingarten, J. Org. Chem., **35**, 1542 (1970).

17. Y. Sudoh, K. Onitsuka, K. Imafuku, and H. Matsumura, Bull. Chem. Soc. Jpn., **56**, 3358 (1983).

18. A. Zask, N. Gonella, K. Nakanishi, C. J. Turner, S. Imajo, and T. Nozoe, Inorg. Chem., **1986**, 3400.

19. 22a: Yellow oil; uv (MeOH) 244, 334, and 399 nm (log ε 4.37, 4.04, and 4.00); $^1$H nmr (100 MHz in $CDCl_3$) δ =1.90 (2H, br, $NH_2$), 3.07 (2H, t, J=6 Hz, $CH_2$), 3.41 (2H, q, J=6 Hz, $CH_2$), 6.64 (2H, m, ar-H), 7.20 (3H, m, ar-H), and 7.48 (1H, br, NH). Found: m/z 164.0953. Calcd for $C_9H_{12}N_2O$: M, 164.0947. Picrate, mp 226 °C.

20. 23: Yellow needles; uv (MeOH) 244, 338, and 407 nm (log ε 4.68, 4.35, and 4.35); ir (KBr) 3270 (NH) and 1600 $cm^{-1}$ (C=O); $^1$H nmr (100 MHz in DMSO-$d_6$) δ = 3.64 (4H, s, $CH_2$), 6.56-7.36 (10H, m, ar-H), and 7.97 (2H, s, NH); MS (rel. intensity) m/z 268 ($M^+$, 3), 148 (11), 147 (55), 146 (10), 135 (42), 134 (100), 122 (12), 106 (19), and 77 (22). Anal. Calcd for $C_{16}H_{12}N_2O$: C, 71.62; H, 6.01; N, 10.44. Found: C, 71.69; H, 6.23; N, 10.51.

21. 13: Uv (MeOH) 254, 366, and 424 nm (log ε 4.37, 3.88, and 3.80); $^1$H nmr (100 MHz in $CDCl_3$) δ =3.53 (4H, s, $CH_2$), 6.08 (1H, t, J=9 Hz, H-7), 6.21 (2H, d, J=10 Hz, H-5,9), and 6.51 (2H, dd, J=10 and 9 Hz, H-6,8); MS m/z 146 ($M^+$). Anal. Calcd for $C_9H_{10}N_2$: C, 73.94; H, 6.89; N, 19.16. Found: C, 73.76; H, 6.95; N, 19.31.

22. W. R. Brasen, H. E. Halinquish, and R. E. Benson, J. Am. Chem. Soc., **83**, 3125 (1961); W. R. Brasen and R. E. Benson, ibid., **83**, 3135 (1961).

23. 22b: Red-brown oil; uv (MeOH) 247, 337, and 404 nm, (MeOH + HCl) 247, 336, and 370 nm; ir 3320 $cm^{-1}$ (NH); $^1$H nmr (270 MHz in $CDCl_3$) δ=1.96 (1H, br, NH), 2.47 (3H, s, $CH_3$), 2.95 (2H, t, J=5.9 Hz, $CH_2$), 3.44 (2H, q, J=5.9 Hz, $CH_2$), 6.57 (1H, d, J=11 Hz, H-7), 6.67 (1H, t, J=9.5 Hz, H-5), 7.14 (1H, d, J= 11.7 Hz, H-3), 7.22 (1H, dd, J=11.0 and 9.5 Hz, H-6), 7.26 (1H, dd, J=11.7 and 9.5 Hz, H-4), and 7.45 (1H, br, NH). Found: m/z 178.1105. Calcd for $C_{10}H_{14}N_2O$: M, 178.1103. Picrate: yellow plates, mp 212 °C.

24. 14: Red-brown oil; Uv (MeOH) 257, 464, 405, and 429 nm (log ε 4.13, 3.73, 3.65, and 3.57); $^1$H nmr (270 MHz in $CDCl_3$) δ=3.07 (3H, s, $CH_3$), 3.33 (2H, t, J=5.1 Hz, $CH_2$), 3.82 (2H, t, J=5.1 Hz, $CH_2$), 5.81 (1H, d, J=10.3 Hz, H-9), 6.10 (1H, dd, J=10.3 and 7.3 Hz, H-7), 6.54 (1H, t, J=10.3 Hz, H-8), 6.60 (1H, dd, J=11.7 and 7.3 Hz, H-6), and 6.68 (1H, d, J=11.7 Hz, H-5). Found: m/z

160.0981. Calcd for $C_{10}H_{12}N_2$: M, 160.0998. Picrate: brown needles, mp 189-192 °C.

25. 18b: Uv (MeOH) 267, 361, and 440 nm (log$\varepsilon$ 4.46, 4.03, and 3.96); $^1$H nmr (270 MHz in $CD_3CN$) $\delta$=3.31 (6H, s, $CH_3$), 3.85 (4H, s, $CH_2$), 7.01 (1H, t, J=9.5 Hz, H-7), 7.06 (2H, d, J=11.0 Hz, H-5,9), and 7.45 (2H, dd, J=11.0 and 9.5 Hz, H-6,8); $^{13}$C nmr (67.8 MHz in $CD_3CN$) $\delta$=42.3 (C-2,3), 51.7 ($CH_3$), 118.8 (C-5,9), 127.2 (C-7), 139.7 (C-6,8), and 151.5 (C-4a,9a). Anal. Calcd for $C_{11}H_{15}N_2FO_3S$: C, 48.16; H, 5.51; N, 10.21. Found: C, 48.02; H, 5.79; N, 9.93.

26. 24: Uv (MeOH) 273, 373, and 460 nm; $^1$H nmr (270 MHz in DMSO-$d_6$) $\delta$=3.35 (6H, s, $CH_3$), 3.92 (4H, s, $CH_2$), 6.97 (2H, d, J=11.4 Hz, H-6,8), and 7.78 (2H, d, J=11.4 Hz, H-5,9). Anal. Calcd for $C_{11}H_{14}N_2BrFSO_3$: C, 37.41; H, 4.00; N, 7.93. Found: C, 37.15; H, 3.94; N, 7.58.

27. 29: Yellow oil; uv (MeOH) 228, 276, 318, and 377(sh) nm, (MeOH + HCl) 257 and 323 nm; ir ($CHCl_3$) 2840, 2745, and 1665 cm$^{-1}$ (CHO); $^1$H nmr (270 MHz in $CDCl_3$) $\delta$=2.93 (3H, s, $CH_3$), 3.01 (3H, s, $CH_3$), 3.27 (2H, t, J=5 Hz, $CH_2$), 3.55 (2H, t, J=5 Hz, $CH_2$), 6.52 (1H, d, J=8 Hz, H-8), 7.07 (1H, d, J=2 Hz, H-5), 7.24 (1H, dd, J=8 and 2 Hz, H-7), and 9.67 (1H, s, CHO). Found: m/z 190.1119. Calcd for $C_{11}H_{14}N_2O$: M, 190.1107.

28. S. Gabriel and G.Eshenback, Ber., **30**, 2495 (1897); A. F. Mackay, W. R. R. Park, and S. J. Viron, J. Am. Chem. Soc., **72**, 3659 (1950). 30 : Colorless plates; mp 161 °C (Ref. 160-161 °C); uv (MeOH) 244 nm; ir (KBr) 3260 (NH) and 1680 cm$^{-1}$; $^1$H nmr (100 MHz in $CDCl_3$) $\delta$=3.56 (2H, m, $CH_2$), 3.95 (2H, m, $CH_2$), 5.27 (1H, br, NH), 7.05 (1H, tt, J=7.1 and 1.5 Hz, H-4'), 7.34 (2H, t, J=7.1 Hz, H-3',5'), and 7.55 (2H, dd, J=7.1 and 1.5 Hz, H-2',6'); MS m/z 162 ($M^+$).

29. 33: Yellow needles; mp 88 °C; uv (MeOH) 247, 336, and 404 nm (log$\varepsilon$ 4.40, 4.09, and 4.06); ir (KBr) 3260 (OH) and 3240 cm$^{-1}$ (NH); $^1$H nmr (100 MHz in $CDCl_3$) $\delta$=3.48 (1H, s, OH), 3.53 (2H, q, J=5 Hz, $CH_2$-1'), 4.01 (2H, t, J=5 Hz, $CH_2$-2'), 6.6-6.8 (2H, m, ar-H), 7.1-7.4 (3H, m, ar-H), and 7.95 (1H, br, NH); MS m/z 165 ($M^+$). Found: m/z 165.0785. Calcd for $C_9H_{11}NO_2$: M, 165.0789.

30. 36a: mp 152 °C; uv (MeOH) 228, 247, 270, 310, and 380 nm (log$\varepsilon$ 3.88, 4.01, 3.78, 3.79, and 3.69); ir (KBr) 1620 cm$^{-1}$ (C=O); $^1$H nmr (270 MHz in DMSO-$d_6$) $\delta$=3.05 (2H, t, J=7.7 Hz, N-$CH_2$), 3.25 (2H, t, J=7.7 Hz, S-$CH_2$), 6.95 (1H, d, J=11.7 Hz, H-7), 7.10 (1H, dd, J=10.3 and 8.2 Hz, H-5), 7.22 (1H, td, J=10.3

and 1.5 Hz, H-4), 7.39 (1H, ddd, J=11.7, 8.2, and 1.5 Hz, H-6), 7.52 (1H, d, J=10.3 Hz, H-3), and 8.36 (3H, br, $NH_3$); MS m/z 181 ($M^+$-HCl). Anal. Calcd for $C_9H_{12}NClSO$: C, 49.65; H, 5.56; N, 6.43. Found: C, 49.45; H, 5.73; N, 6.33.

31. 37a: Brown needles, mp 148 °C; uv (MeOH) 246, 336, and 402 nm (log ε 4.45, 4.19, and 4.12); ir (KBr) 3260 (NH) and 1600 $cm^{-1}$(C=O); $^1H$ nmr (270 MHz in $CDCl_3$) δ=3.32 (2H, t, J=6.8 Hz, S-$CH_2$), 3.72 (2H, q, J=6.8 Hz, N-$CH_2$), 6.57 (2H, d, J=10.3 Hz, H-7,7'), 6.76 (1H, dd, J=7.3 and 2.4 Hz, ar-H), and 6.91-7.34 (8H, m, ar-H and NH); MS m/z 285 ($M^+$). Anal. Calcd for $C_{14}H_{15}NO_2S$: C, 67.45; H, 5.30; N, 4.91. Found: C, 67.43; H, 5.48; N, 4.85.

32. 39a: Brown needles; mp 166 °C; uv (MeOH) 243, 335, 386, and 403 nm (log ε 4.44, 4.17, 4.00, and 4.12); ir (KBr) 3260 (NH) and 1620 $cm^{-1}$ (C=O); $^1H$ nmr ($CDCl_3$) δ=2.99 (4H, t, J=6.8 Hz, S-$CH_2$), 3.69 (4H, q, J=6.8 Hz, N-$CH_2$), 6.56 (2H, d, J=10.8 Hz, H-7,7'), 6.75 (2H, dd, J=7.5 and 2.7 Hz, H-3,3'), and 7.13-7.41 (8H, m, ar-H and NH); MS m/z 360 ($M^+$; 1.5), 215 (4.4), 213 (47), 181 (24), 180 (7), 149 (24), 148 (100), 135 (11), 134 (92), 106 (17), 77 (23), and 65 (11). Anal. Calcd for $C_{18}H_{20}N_2O_2S$: C, 59.97; H, 5.59; N, 7.77. Found: C, 60.15; H, 5.72; N, 7.68.

33. 15: Yellow solid; uv (MeOH) 243, 268, and 377 nm (log ε 4.07, 3.99, and 3.75, (MeOH+HCl) 240, 271, and 385 nm; $^1H$ nmr (270 MHz in $CD_3CN$) δ=2.94 (2H, t, J= 5 Hz, $CH_2$), 3.80 (2H, t, J=5 Hz, $CH_2$), 6.28-6.42 (3H, m, H-7,8,9), and 6.48-6.58 (2H, m, H-5,6), (270 MHz in 20% $CF_3COOD$-$CD_3CN$) δ=3.21 (2H, t, J=5 Hz, $CH_2$), 3.93 (2H, t, J=5 Hz, $CH_2$), 7.38-7.53 (3H, m, ar-H), 7.68 (1H, ddd, J=12, 8, and 2 Hz, H-6 or 8), and 7.98 (1H, dd, J=9 and 1.5 Hz, H-5 or 9); $^{13}C$ nmr (67.8 MHz in $CD_3CN$) δ=30.7, 50.9, 125.4, 129.8, 129.9, 131.0, 134.0, 136.6, and 162.1, (67.8 MHz in 20% $CF_3COOD$-$CD_3CN$) δ=24.6, 44.5, 131.1, 137.7, 138.9, 142.8, 142.9, 144.3, and 162.6; MS. m/z 163 ($M^+$). Anal. Calcd for $C_9H_9NS$: C, 65.84; H, 5.53; N, 8.53%. Found: C, 65.78; H, 5.65; N, 8.49%. Picrate, mp 164 °C.

34. 40: Yellow needles, mp 103-104 °C; uv (MeOH) 276 and 390 nm (log ε 4.24 and 3.90); $^1H$ nmr (270 MHz in $CD_3CN$) δ=3.46 (2H, t, J=5.0 Hz, $CH_2$), 3.50 (3H, s, $CH_3$), 4.12 (2H, t, J=5.0 Hz, $CH_2$), 7.29 (1H, d, J=12.1 Hz, H-5), 7.42 (2H, m, H-7,9), 7.74 (1H, m, H-6), and 7.82 (1H, m, H-8); $^{13}C$ nmr (67.8MHz in $CD_3CN$) δ=29.6, 44.5, 57.6, 124.4, 136.5, 137.3, 137.8, 141.9, 143.9, and 162.7.

Anal. Calcd for $C_9H_9NFO_3S_2$: C, 43.29; H, 4.36; N, 5.05. Found: C, 43.03; H, 4.12; N, 4.79.

35. 37b: Brown oil; uv (MeOH) 253, 350, and 375 nm; $^1$H nmr (270 MHz in $CDCl_3$) $\delta$ = 3.14 (3H, s, $CH_3$), 3.32 (2H, t, J=7.8 Hz, $CH_2$), 3.82 (2H, t, J=7.8 Hz, $CH_2$), 6.91-7.26 (9H, m, ar-H), and 7.58 (1H, d, J=9.4 Hz, H-3); MS m/z 299 ($M^+$, 9), 162 (43), 161 (66), 148 (67), 120 (19), and 77 (20). Found: m/z 299.0974. Calcd for $C_{17}H_{17}NO_2S$: M, 299.0979.

36. 39b: Yellow solid; uv (MeOH) 254, 354, and 408 nm; $^1$H nmr (270 MHz in $CDCl_3$) $\delta$=2.99 (4H, t, J=7.5 Hz, $CH_2$), 3.06 (6H, s, $CH_3$), 3.84 (4H, t, J=7.5 Hz, $CH_2$), 6.56 (2H, d, J=10.4 Hz, H-3,3'), 6.59 (2H, dd, J=10.4 and 8.2 Hz, H-5,5'), 6.97 (2H, d, J=11.5 Hz, H-7,7'), 7.04 (2H, t, J=10.4 Hz, H-4,4'), and 7.08 (2H, dd, J=11.5 and 8.2 Hz, H-6,6'); MS m/z 388 ($M^+$, 9), 227 (21), 195 (11), 194 (179), 163 (19), 162 (100), 148 (87), 120 (12), 105 (13), and 77 (25). Found: m/z 388.1289. Calcd for $C_{20}H_{24}N_2O_2S_2$: M, 388.1280.

Received, 4th October, 1988