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Condensed Heterotricycles: Dibenz[*b*,*f*][1,4]oxazepin-11(10H)-thiones, 11-Substituted Dibenz[*b*,*f*][1,4]oxazepines & Dibenz[*b*,*f*][1,4]thiazepine Analogues*†

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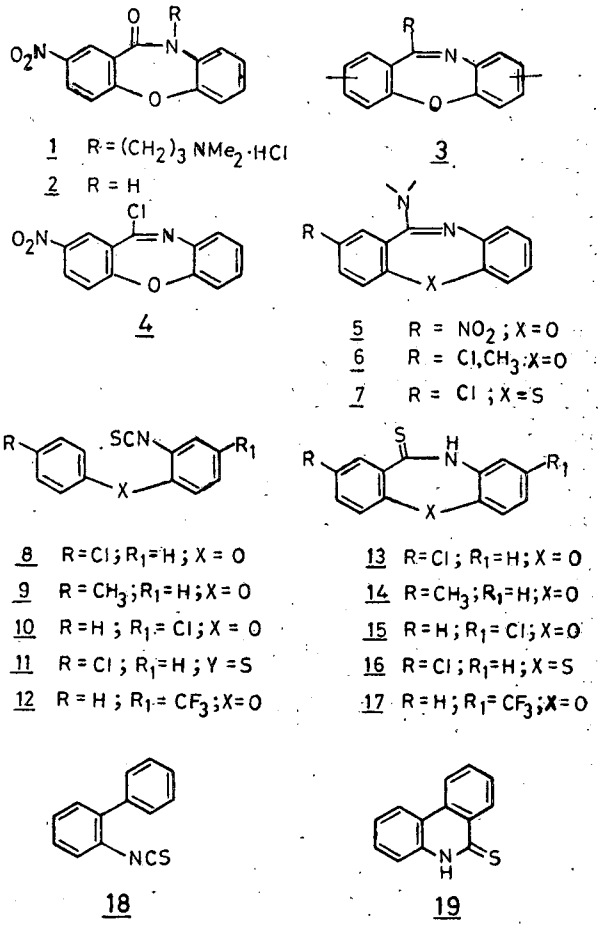
The reaction of iminochloride 4, obtained from 2-nitrodibenzoxazepinone (2), phosphorus oxychloride and dimethylaniline, with cyclic secondary bases, affords 11-amino derivatives 5, and with γ-dimethylaminopropanol, the amino-alkoxy derivative 23, isomeric with Sintamil‡ (1). Aluminium chloride-catalysed cyclizations of *o*-isothiocyanatodiphenyl ethers and diphenyl sulphides 8-11 yield dibenzoxazepine and thiazepinethiones 13-16, which are converted to 11-amino derivatives of the types 6 and 7 by reaction with amines and to 11-aminoalkylmercapto derivatives of type 20 by reaction with aminoalkylchlorides. Amidoxime 21 and azine 22 are obtained from thiones 15 and 13, by reaction with hydroxylamine and hydrazine respectively. 11-Dimethylaminomethyldibenzoxazepine (28) is obtained along with the ring-cleaved product 30, by cyclization of the amide 25 with PPA and $POCl_3$ mixture or by the conversion of the chloracetamide 24 to 27, followed by reaction with dimethylamine. Phenanthridinethione (19) is readily obtained by the cyclization of the isothiocyanate 18.

IN connection with our work on Sintamil (1)[2] described in other papers of this series[3-5], we wanted to prepare and evaluate biologically, 11-substituted derivatives of the general structure 3, wherein R was an amino, aminomethyl, aminoalkyloxy or aminoalkylmercapto group, and some dibenzo[*b*,*f*][1,4]thiazepine analogues. At the time we started our work, some 11-aminodibenz[*b*,*f*][1,4]-oxazepines and thiazepines were known[6]. Subsequently there have been some publications and patents in this field. The other types were undisclosed. Our work generated many unknown compounds which are reported in this paper, while their biological activity is described elsewhere[5].

For the synthesis of 11-amino-2-nitrodibenzoxazepines, we converted the readily available 2-nitrodibenzoxazepinone (2)[2] to the 11-chloro derivative 4 with $POCl_3$ in the presence of a small amount of dimethylaniline. In the absence of the last reagent, the conversion did not occur. Reaction of 4 with cyclic secondary amines like piperidine afforded compounds of the general structure 5. Among nine such compounds prepared, the N-methylpiperazino derivative has been subsequently disclosed in two patents[7,8]. In the preparations of 4 and 5, small amounts of interesting byproducts were obtained. These will be discussed in a subsequent paper, where reactions of 4 with other bases are described[9]. An attempt to prepare the 11-amino derivative (5: N<=NH_2) by the reaction of *o*-aminophenol and 2-chloro-5-nitrobenzonitrile was not successful.

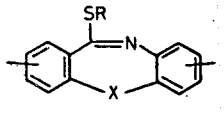
For the synthesis of some examples of 11-aminodibenzoxazepines (6) and thiazepines (7) not carrying nuclear nitro groups, we utilized the thiones 13-16, using an extension of the known synthesis of dibenzoxazepinones by the aluminium chloride-catalysed cyclization of *o*-isocyanatodiphenyl



*CIBA contribution No. 348.

†For a previous paper in this series, see K. Nagarajan *et al.*[1].

‡Sintamil—Registered trade name of CIBA of India for CIBA 2330-Go; 10-[3-(dimethylamino)propyl]-2-nitrodibenz-[*b*,*f*][1,4]oxazepin-11(10H)-one hydrochloride.



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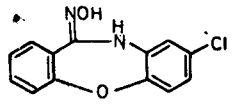

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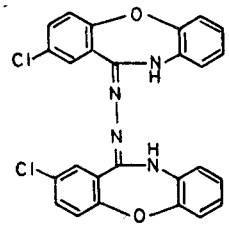

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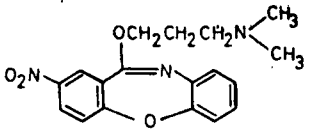

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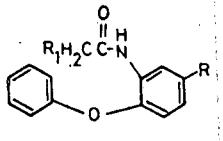
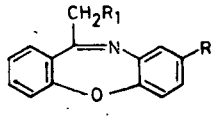
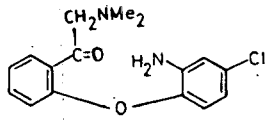


24 R = R_1 = Cl
25 R = Cl ; R_1 = NMe_2
26 R = CF_3 ; R_1 = NMe_2



27 R = R_1 = Cl
28 R = Cl ; R_1 = NMe_2
29 R = CF_3 ; R = NMe_2



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ethers[10]. Thus *o*-aminodiphenyl ethers and sulphides were converted to the isothiocyanates (8-11), and thence in good yields to the thiones 13-16 under controlled conditions using aluminium chloride as catalyst. Isothiocyanate 12 polymerized under these conditions and did not afford 17. Routes disclosed for such thiones, after our work was completed, involve fusion of dibenzthiazepinones with phosphorus pentasulphide[11] and PPA-catalysed cyclization of diphenyl ether dithiocarbamates and thioureas[12]. We extended our route to the synthesis of phenanthridinethione (19) from the readily prepared *o*-isothiocyanatodiphenyl (18). The method was found to be superior to the previous one for 19, which involves treatment of phenanthridinone with phosphorus pentasulphide[13].

Direct reaction of the thiones 13-16 with cyclic secondary bases like N-methylpiperazine afforded representative examples of 6 and 7 in good yields, thus obviating the need to convert thiones to their S-alkyl or S-aralkyl derivatives prior to displacement[11].

Treatment of the thiones with sodium hydride followed by an alkylating agent such as chloracetonitrile or dialkylaminoalkyl chloride led to S-alkylated products (20). These were sensitive to strong aq. acids and were cleaved to the respective lactams, showing thereby that they were S- and not N-alkyl derivatives. Thione 15 was transformed to the amidoxime 21 by hydroxylamine, while the reaction of thione 13 with hydrazine gave the azine 22. Treatment of iminochloride 4 with sodium dimethylaminopropyloxide afforded the dibenzoxazepine (23), which was different from 1. A very recent patent, details of which are not available, claims 11-aminoalkyloxy- and 11-aminoalkylmercapto-dibenzoxazepines and dibenzthiazepines[14].

The preparation of the 11-dimethylaminomethyldibenzoxazepine (28) was achieved by the cyclization of amide 25 with $POCl_3$+PPA. Either reagent alone did not bring about ring-closure. Alternatively, the chloracetyl derivative 24 could be cyclized by the mixture to the 11-chloromethyldibenzoxazepine (27), which upon further reaction with dimethylamine, led to 28. In the conversion of the dimethylaminoacetyl compound 25 to 28, a sizeable amount of a byproduct was obtained, which turned out to be 30 from analytical and spectral data. 30 cyclized back to 28 even during salt formation with mineral or organic acids. The formation of compounds like 30 in such cyclization reactions has been reported in a recent patent[15], although earlier publications in this area have not recorded[16-18] it. Cyclization of the trifluoromethyl derivative 26 did not yield 29, but led to resinification.

Experimental Procedure

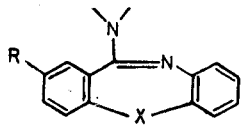
M.ps. are uncorrected. IR (nujol), UV (95% ethanol) and mass spectra were run respectively on a Perkin-Elmer infracord spectrophotometer, Beckmann DK 2A spectrometer and a Varian Mat CH7 mass spectrometer. NMR spectra were run on a Varian A60 spectrometer. Chemical shifts are quoted in ppm downfield from TMS as the internal standard.

2-Nitro-11-chlorodibenz[b,f][1,4]oxazepine (4) — A mixture of nitro lactam 2 (10 g, 40 mmole), $POCl_3$ (80 ml) and dimethylaniline (3 ml) was heated under reflux overnight. The excess $POCl_3$ was then removed *in vacuo*, using toluene to expel the last traces. Ice and water were added to the residue and the mixture extracted with ether-CH_2Cl_2. The latter extract was filtered from a small quantity of insoluble, unreacted 2 and the filtrate washed with water, dried and evaporated. The solid residue was triturated with a little CH_2Cl_2-hexane and filtered (filtrate-A) to give 4, m.p. 182-84° (CH_2Cl_2-hexane) (Found: C, 57·26; H, 2·81; N, 9·98. $C_{13}H_7ClN_2O_3$ requires C, 56·84; H, 2·57; N, 10·20%).

Filtrate-A was evaporated and the residue chromatographed over silica gel to give some more 4 in the earlier eluates and a byproduct in the latter eluates. In one experiment, the chromatography also afforded among the earlier fractions 2-nitro-11-ethoxydibenz[*b,f*][1,4]oxazepine, presumably by reaction of 4 with traces of ethanol in the ether used for extraction, m.p. 120-22° (hexane) (Found: C, 62·96; H, 4·17; N, 9·84. $C_{15}H_{12}N_2O_4$ requires C, 63·38; H, 4·26; N, 9·86%); MS: *m/e* 284 (M^+), 274, 267, 256, 240, 210, 194, 182, 154, 153; NMR ($CDCl_3$): 1·47 (*t*, J=7 Hz, CH_2-CH_3), 4·52 (*q*, J=7 Hz, OCH_2-CH_3).

2-Nitro-11-aminodibenz[b,f][1,4]oxazepines (5) — Iminochloride (4, 5·4 g, 20 mmoles), N-methylpiperazine (4·0 g, 40 mmoles) and benzene (50 ml) were heated under reflux for 6 hr. The separated solid was filtered and washed with water to give the product (4·2 g). The benzene layer in the filtrate was separated, washed with water, dried and evaporated to give more product (2·4 g). The total amount was crystallized from acetone-MeOH to give 2-nitro-11-(4-methylpiperazine-1-yl)dibenz[*b,f*][1,4]oxazepine (5·5 g), m.p. 188-91°; λ_{max} 258, 280 (inflex), 320 nm (sh) (log ϵ 4·28, 4·15, 3·83).

TABLE 1 — 11-AMINODIBENZOXAZEPINES AND THIAZEPINES



N	Crystallized from	m.p. °C	Mol. formula	N (%)* Found	N (%)* Reqd
		X = O; R = NO_2			
Pyrrolidino	MeOH	151-53	$C_{17}H_{15}N_3O_3$	13·64	13·59
N-methylpiperazino	EtOH	187-91	$C_{18}H_{18}N_4O_3$	16·44	16·56
Morpholino	Acetone-MeOH	187-90	$C_{17}H_{15}N_3O_4$	13·06	12·92
4-Methylpiperidino	do	166-68	$C_{19}H_{19}N_3O_3$	12·95	12·46
N-(2-methoxyphenylpiperazino)	do	187-89	$C_{24}H_{22}N_4O_4$	12·79	13·02
N-(*o*-tolylpiperazino)	do	191-93	$C_{24}H_{22}N_4O_3$	13·88	13·52
N-(*p*-fluorophenylpiperazino)	do	209-12	$C_{23}H_{19}FN_4O_3$	13·38	13·39
Imidazolo (HCl)	EtOH	>300	$C_{16}H_{11}ClN_4O_3$	16·35	16·35
		X = O; R = Cl			
N-methylpiperazino (HCl)	EtOH-Et_2O	270-72	$C_{18}H_{19}Cl_2N_3O.\frac{1}{2}H_2O$	11·35	11·26
		X = O; R = CH_3			
Morpholino	MeOH	143-44	$C_{16}H_{18}N_2O_2$	9·29	9·52
Piperidino	Acetone-MeOH	189-91	$C_{19}H_{20}N_2O$	9·49	9·58
		X = S; R = Cl			
N-methylpiperazino	Hexane	113-16	$C_{18}H_{18}ClN_3S$	12·65	12·22

*Satisfactory C and H analyses were also obtained.

11-Aminodibenzoxazepines thus made are listed in Table 1.

Dibenzoxazepine and dibenzthiazepinethiones—These were synthesized by the following typical procedure*. To 2-amino-4'-chlorodiphenyl ether (19·7 g, 90 m moles) in benzene (60 ml) cooled by ice-water, was added with stirring, $CSCl_2$ (31 g, 270 mmoles). After 1 hr at 0°, the mixture was heated under reflux for 16 hr. Solvent and the excess $CSCl_2$ were removed *in vacuo* and the residual oil distilled to give isothiocyanate 8 (21 g), b.p. 165-68°/1·5-2 mm.

8 (11·7 g, 45 mmoles) in *o*-dichlorobenzene (40 ml) was added during 15 min to a stirred suspension of anhyd. aluminium chloride (6·7 g, 50 mmoles) in the same solvent (40 ml) at 100°. The mixture was stirred at 100° for 1 hr and then decomposed with ice-cold dil. HCl to give a sticky mass which was triturated with hexane and filtered. The precipitate crystallized from chloroform to give thione 13 (10·3 g), m.p. 227-29° (Found: C, 59·87; H, 3·23; N, 5·26; S, 11·85. $C_{13}H_8ClNOS$ requires C, 59·67; H, 3·08; N, 5·36; S, 12·23%); ν_{max} 3165 cm^{-1} (NH); NMR (DMSO-d_6): 7·30 (*m*, C_6-*H*, C_7-*H*, C_8-*H* and C_9-*H*), 7·32 (*d*, *J*=9 Hz, C_4-*H*), 7·60 (*d* of *d*, *J*=9, 3 Hz, C_3-*H*), 8·02 (*d*, *J*=3 Hz, C_1-*H*), 12·5 (broad *s*, N*H*).

Similarly were prepared from appropriate isothiocyanates, thione 14, m.p. 177-79° ($CHCl_3$-hexane) (Found: C, 69·58; H, 4·74; N, 5·50; S, 13·45. $C_{14}H_{11}NOS$ requires C, 69·70; H, 4·59; N, 5·80; S, 13·26%); ν_{max} 3150 cm^{-1} (NH); thione 15, m.p. 232-35° ($CHCl_3$) (Found: C, 59·64; H, 3·22; N, 5·56. $C_{13}H_8ClNOS$ requires C, 59·67; H, 3·08; N, 5·36%); ν_{max} 3160 cm^{-1} (NH); and thione 16, m.p. 265-66° (THF-Et_2O) (Found: C, 56·29; H, 3·08; N, 5·29; S, 22·18. $C_{13}H_8ClNS_2$ requires C, 56·23; H, 2·90; N, 5·05; S, 23·05%); ν_{max} 3130 cm^{-1} (NH).

Reaction of thiones with amines — Experimental details for a typical reaction are as follows:

Thione 13 (5·2 g, 20 mmoles) and N-methylpiperazine (8 g, 80 mmoles) were heated together at 100° for 14 hr till evolution of H_2S ceased. Water was added to the residue which was then extracted with ether. The etherial layer was extracted with dil. HCl and then with water and dried. Evaporation gave negligible amount of neutral material. The acidic extract was basified and extracted with ether to give 2-chloro-11-morpholinodibenz[*b*,*f*][1,4]oxazepine which was converted into the HCl salt which crystallized from EtOH (6·3 g), m.p. 270-72° (after drying at 100° overnight); free base had m.p. 107-09° (Et_2O-hexane) (lit.[6], m.p. 108-10°); MS: *m/e* 329 (M^+, ^{37}Cl), 327 (M^+, ^{35}Cl), 259, 257, 230, 228, 193.

11-Aminodibenzoxazepines and dibenzthiazepine thus made are listed in Table 1.

Amidoxime 21 — Thione 15 (3·1 g, 12 mmoles) and hydroxylamine HCl (1·7 g, 24 mmoles) were heated together in pyridine (10 ml) at 100° overnight, when H_2S was evolved. The solution was diluted with water and the resultant precipitate crystallized from EtOH to give 21 (2·5 g), m.p. 202-04° (d) (Found: C, 60·13; H, 3·71; N, 10·76. $C_{13}H_9ClN_2O_2$ requires C, 59·89; H, 3·48; N, 10·75%); ν_{max} 1650 (C=N); 3380, 3150 and 3220 cm^{-1} (NH).

Azine 22 — Thione 13 (3·1 g, 12 mmoles) and hydrazine hydrate (3·0 g, 60 mmoles) were heated at 110° for 5 hr. The mixture was cooled, treated with water and the precipitate recrystallized from DMF to give 22 (1 g), m.p. >300° (Found: C, 64·23; H,

*This method has been used by Hunziker *et al.*, for the synthesis of dibenzodiazepinethiones[19].

3·58; N, 12·08. $C_{26}H_{16}Cl_2N_4O_2$ requires C, 64·07; H, 3·28; N, 11·49%); ν_{max} 3300 cm^{-1} (NH).

2-Nitro-11-(3-dimethylaminopropyl-1)oxydibenz[b,f]-[1,4]oxazepine (23) — To a stirred solution of 3-dimethylamino-1-propanol (2·06 g, 20 mmoles) in dry dioxane (15 ml) was added sodium hydride (50% suspension in mineral oil, 0·96 g, 20 mmoles) and the mixture stirred at 60° for 45 min. A solution of the imino chloride 4 (5·5 g, 20 mmoles) in dioxane (75 ml) was added dropwise during 20 min and the reaction mixture stirred at 60° overnight, cooled and filtered. The filtrate was evaporated *in vacuo* and the residue taken up in ether. The ether extract was filtered and the filtrate evaporated. The residual base was converted into a crystalline maleate which recrystallized from EtOH to give 23 maleate (3 g), m.p. 160-62° (Found: C, 58·11; H, 5·33; N, 8·95. $C_{22}H_{23}N_3O_8$ requires C, 57·76; H, 5·07; N, 9·19%); NMR of free base ($CDCl_3$): 2·15 (*qu*, J=7 Hz, C-CH_2-C), 2·27 (*s*, NMe_2), 2·50 (*t*, J=7 Hz, N-CH_2), 4·50 (*t*, J=7 Hz, OCH_2), 7·00-7·35 (*m*, C-4, C-6, C-7, C-8, C-9 protons), 8·22 (*d* of *d*, J=9, 3 Hz, C_3-*H*), 8·33 (*d*, J=3 Hz, C_1-*H*).

11-(Aminoalkyl)mercaptodibenzoxazepines and dibenzthiazepines — Details of synthesis of a typical example are as follows:

A solution of thione 13 (3·1 g, 12 mmoles) in dioxane (30 ml) was added to a stirred suspension of sodium hydride (50% suspension in mineral oil; 0·55 g, 14 mmoles) in dioxane (10 ml) and the mixture heated under reflux for 1 hr. 3-Dimethylamino-1-propyl chloride (1·7 g, 14 mmoles) in toluene (5 ml) was then added, the mixture heated under reflux overnight and filtered. The filtrate was concentrated *in vacuo* and the residue partitioned between ether and dil. HCl. The ether extract contained a neutral product (0·4 g). The acid extract was basified and extracted with ether to give the desired product (2·3 g), which was converted into a crystalline maleate. Recrystallization from ethanol-ether gave the maleate of the amino alkylmercapto derivative (1·6 g), m.p. 107-8°; λ_{max} 210, 240 (inflex), 288, 332 nm (log ϵ 4·64, 4·22, 3·84, 3·72).

These derivatives are listed in Table 2.

N-Chloracetyl-2-amino-4-chlorodiphenyl ether (24) — Chloracetyl chloride (2·3 g) was added dropwise with stirring and ice-cooling to 2-amino-4-chlorodiphenyl ether (4·4 g) in ether (75 ml) and sodium bicarbonate (2 g) in water (20 ml). The mixture was stirred for 2 hr at 0°. The etherial layer was separated, washed successively with water, dil. HCl and water, dried and evaporated to give 24 (6 g), m.p. 78°; ν_{max} 1670 (C=O), 3370 cm^{-1} (NH).

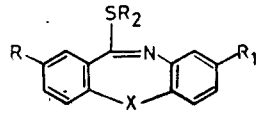
Similarly was prepared N-chloroacetyl-2-amino-4-trifluoromethyldiphenyl ether, m.p. 79-81° (hexane) (Found: C, 54·80; H, 3·66; N, 4·36. $C_{15}H_{11}ClF_3NO_2$ requires C, 54·64; H, 3·36; N, 4·25%); ν_{max} 1695 (C=O), 3420 cm^{-1} (NH).

N-(Dimethylamino)acetyl-2-amino-4-chlorodiphenyl ether (25) — Chloracetamide 24 (4·9 g) and dimethylamine (30 ml, 30% in EtOH) were heated under reflux for 16 hr. The solvent was evaporated off and dil. HCl and ether added to the residue. The HCl extract was basified with conc. aq. ammonia and the precipitated 25 filtered off (5·3 g), m.p. 85-86° (EtOH) (Found: C, 62·84; H, 5·78; N, 9·00. $C_{16}H_{17}ClN_2O_2$ requires C, 63·05; H, 5·62; N, 9·19%); ν_{max} 1675 (C=O), 3300 cm^{-1} (NH); NMR (CCl_4): 2·15 (*s*, NMe_2), 2·90 (*s*, CH_2), 6·75-7·50 (*m*, 6H, Ar-*H*), 8·55 (*d*, J=2·5 Hz, C_3-*H*), 9·45 (broad *s*, N*H*), HCl salt, m.p. 192-94° (EtOH).

Likewise was prepared 26, m.p. 78-80° (hexane) (Found: C, 60·73; H, 5·31; N, 8·16. $C_{17}H_{17}F_3N_2O_2$ requires C, 60·35; H, 5·00; N, 8·28%).

8-Chloro-11-chloromethyldibenz[b,f][1,4]oxazepine (27) — Chloracetamide 24 (6 g), PPA (50 g) and

TABLE 2 — 11-AMINOALKYLMERCAPTODIBENZOXAZEPINES AND THIAZEPINES



R_2	Crystallized from	m.p. (b.p./m) °C	Mol. formula	N (%)* Found	N (%)* Reqd
		X = O; R = Cl; R_1 = H			
$(CH_2)_3NMe_2$ (maleate)	EtOH-Et_2O	107-8	$C_{22}H_{23}ClN_2O_5S$	6·41	6·05
$(CH_2)_2NMe_2$ (HCl)	EtOH-Et_2O	191-3	$C_{17}H_{18}Cl_2N_2OS$	7·81	7·59
$(CH_2)_2NEt_2$	—	160-80/ 0·006 mm	$C_{19}H_{21}ClN_2OS$	7·42	7·76
$(CH_2)_2NEt_2$ (tosylate)	EtOH-Et_2O	145-47	$C_{26}H_{29}ClN_2O_4S_2$	5·27	5·26
		X = O; R = H; R_1 = Cl			
CH_2CN	C_6H_6-hexane	110-12	$C_{15}H_9ClN_2OS$	8·99	9·32
$(CH_2)_2NMe_2$	—	175-80/ 0·001 mm	$C_{17}H_{17}ClN_2OS$	8·12	8·42
$(CH_2)_2NMe_2$ (maleate)	EtOH-Et_2O	129-30	$C_{21}H_{21}ClN_2O_5S$	6·19	6·24
		X = S; R = Cl; R = H			
$(CH_2)_3NMe_2$ (HCl)	Acetone-Et_2O	242-44	$C_{18}H_{20}Cl_2N_2S_2$	7·31	7·02
Piperidinoethyl (HCl)	EtOH-Et_2O	230-32	$C_{20}H_{22}Cl_2N_2S_2$	6·72	6·59

*Satisfactory C and H analyses were also obtained.

$POCl_3$ (9 ml) were heated together at 130-40° with stirring for 2 hr under nitrogen atmosphere. The mixture was cooled and decomposed with ice. The resultant solution was made ammoniacal and extracted with ether. The ether extract was washed with water, dried and evaporated. The residue crystallized from ether-hexane to give 27 (4·5 g), m.p. 81-83° (Found: C, 60·19; H, 3·56; N, 5·05. $C_{14}H_9Cl_2NO$ requires C, 60·45; H, 3·26; N, 5·04%); ν_{max} 1610 cm^{-1} (C=N); NMR ($CDCl_3$): 4·63 (*s*, CH_2Cl), 7·00-7·70 (*m*, 7H, Ar-*H*).

11-(*Dimethylamino*)-*methyl*-8-*chlorodibenz*[*b*,*f*][1,4]-*oxazepine* (28): (a) *From chloromethyldibenzoxazepine* (27) — A mixture of 27 (2 g) and dimethylamine (25 ml, 33% solution in EtOH) was heated at 100° overnight in a sealed tube. The tube was cooled and opened. Ethanol was removed *in vacuo* and the residue separated into non-basic (0·45 g) and basic (1·4 g) portions. The basic part was an oil and was converted into a crystalline maleate (1·1 g), m.p. 178-80° (EtOH), (Found: C, 59·28; H, 5·02; N, 7·18. $C_{20}H_{19}ClN_2O_5$ requires C, 59·63; H, 4·75; N, 6·95%); NMR (CCl_4): 2·33 (*s*, NMe_2), 3·63 (*s*, CH_2), 6·80-7·80 (*m*, 7H, Ar-*H*).

(b) *From dimethylacetamide* 25 — 25 (5 g), PPA (40 g) and $POCl_3$ (7 ml) were heated with stirring at 130-40° under nitrogen atmosphere for 2 hr. The initial vigorous frothing subsided soon. The mixture was cooled and treated with ice-cold water. The aq. layer was decanted off from glassy hard, material (A) which stuck to the bottom of the reaction vessel. The aq. acidic decantate was basified with ammonia and extracted with ether. The etherial extract was evaporated to give a solid (1 g), which was separated into a part which was insoluble in cold hexane (B, 0·4 g), m.p. ~95° and another which was soluble. The latter gave a crystalline maleate (0·4 g), m.p. 178-80°; identical with the preparation from (a) above.

The glassy mass (A) was treated with hot water to give a solution which was cooled and basified. Extraction with ether gave a solid, which was triturated with hexane and filtered. The hexane filtrate gave 28 maleate (0·2 g). The hexane-insoluble part was combined with B and crystallized from ether to give the aminoketone (30), m.p. 111-15° (Found: C, 62·92; H, 5·67; N, 9·03. $C_{16}H_{17}ClN_2O_2$ requires C, 63·05; H, 5·62; N, 9·19%); ν_{max} 1670 (C=O); 3180, 3310 and 3400 cm^{-1} (NH); NMR ($CDCl_3$); 2·25 (*s*, NMe_2), 3·73 (*s*, CH_2), 4·45 (broad *s*, NH_2).

Phenanthridinethione (19)—*o*-Isothiocyanatodiphenyl (18) (3·2 g)[20] was cyclized using aluminium chloride (2·6 g) and *o*-dichlorobenzene (20 ml) as solvent to give 19 (2·4 g) (THF-ether), m.p. 280-82° (d); (lit.[13], m.p. 281-83°) (Found: C, 73·80; H, 4·57;, N, 6·92. $C_{13}H_9NS$ requires C, 73·92; H, 4·30; N, 6·63%).

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