Chemistry of 1,2,3-Thiadiazole. IV. Synthesis of [1]Benzoxepino-[3,4-*d*][1,2,3]thiadiazole, [1]Benzothiepino-[3,4-*d*][1,2,3]thiadiazole, [1]Benzothiepino[4,3-*d*][1,2,3]thiadiazole, [1]Benzoxepino[4,3-*d*]oxazole and [1]Benzoxepino[4,3-*d*]oxazole. Four Novel Heterocycles.

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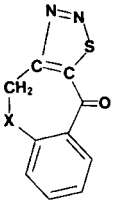
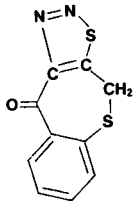
Starting from the readily available 4-bromomethy-5-carbethoxy1,2,3-thiadiazole (V), 5-bromomethy-4-carbethoxy-1,2,3-thiadiazole (IX) and ethyl 2-aryl-5-bromomethyloxazole-4-carboxylate (XIV), 4,10-dihydro-10-oxo[1]benzoxepino[3,4-*d*][1,2,3]thiadiazole (Ia), 4,10-dihydro-10-oxo[1]benzothiepino[3,4-*d*][1,2,3]thiadiazole (Ib), 4,10-dihydro-4-oxo[1]benzothiepino[4,3-*d*] [1,2,3]thiazole (II), 2-aryl-4,10-dihydro-4-oxo[1]benzoxepino[4,3-*d*]oxazoles (XIXa-XIXc) and 2-aryl-4,10-dihydro-4-oxo[1]benzothiepino[4,3-*d*]oxazoles (XIXd-XIXf) were prepared.

J. Heterocyclic Chem., **18**, 899 (1981).

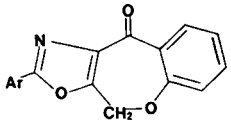
In continuation of the study on the chemistry of 1,2,3 -thiadiazole (1-3), and as part of a program to synthesize derivatives of benzoxepins and benzothiepins with possible antiinflammatory activity (4-6), it became necessary to synthesize 4,10-dihydro-10-oxo[1]benzoxepino[3,4-*d*][1,2,3] thiadiazole(Ia) 4,10-dihydro-10-oxo[1]benzothiepino[3,4-*d*] [1,2,3]thiadiazole (Ib), 4,10-dihydro-4-oxo[1]benzothiepino-[4,3-*d*][1,2,3]thiadiazole (II), 2-aryl-4,10-dihydro-4-oxo[1]-benzoxepino[4,3-*d*]oxazole (III) and 2-aryl-4,10-dihydro-4-oxo[1]benzothiepino[4,3-*d*]oxozole (IV).



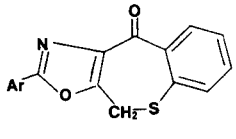
Ia , X=O
Ib , X=S



II



III

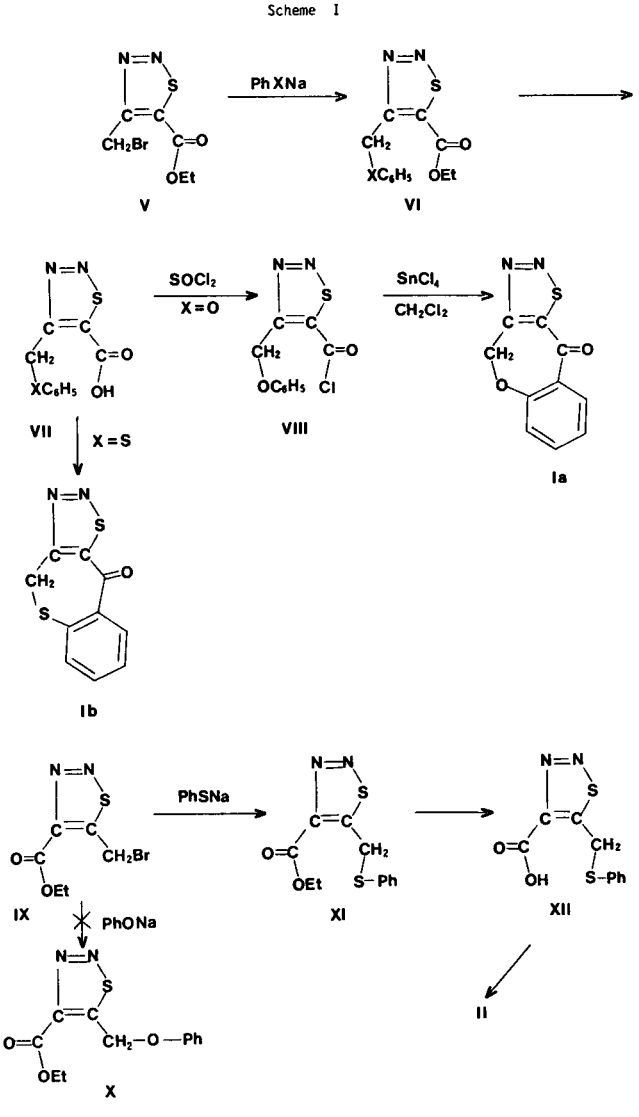


IV

A possible route for the formation of compound Ia and Ib in shown in Scheme I.

Reaction of 4-bromomethyl-5-carbethoxy-1,2,3,-thiazole (V) (2) with phenol and potassium carbonate according to the procedure reported previously (5) did not give the desired compound 4-phenoxymethyl-5-carbethoxy-1,2,3-thiazole (VI, X = 0). However, the latter compound could be obtained in high yield using sodium phenoxide in

Scheme I



butanone. Alkaline hydrolysis of compound VI (X = 0) afforded the acid VII (X = 0). The acid VII (X = 0) was con-

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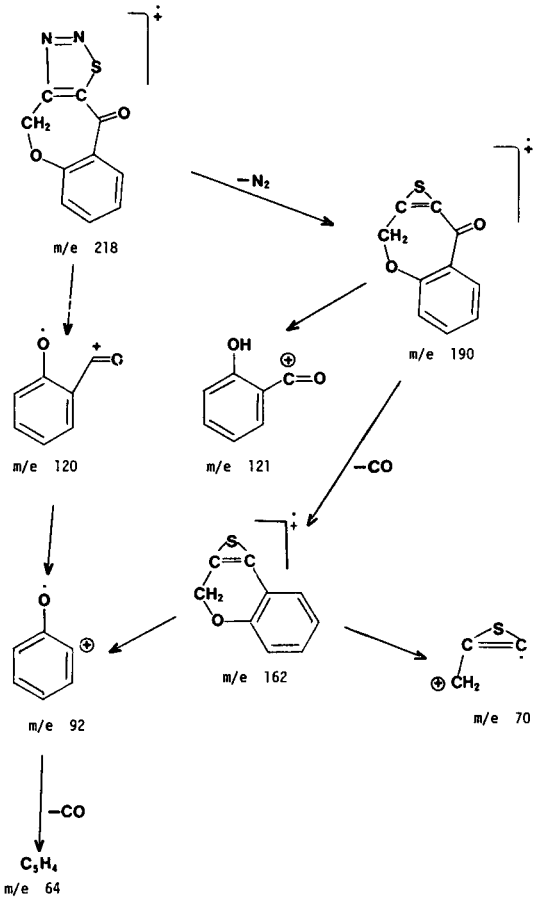
verted to acid chloride VIII with thionyl chloride and this product was cyclized with stannic chloride to provide compound Ia (7). The mass spectra fragmentation Pattern of compound Ia as summarized in Scheme II is in a good agreement with the suggested structure.

Scheme II



Reaction of compound V with sodium thiophenolate in ethanol afforded 4-phenylthiomethyl-5-carbethoxy-1,2,3--thiadiazole (VI, X = S). An initial attempt to cyclize this acid with stannic chloride according to the litterature (7) failed. This was remedied by cyclizing the acid with polyphosphoric acid to give the desired compound Ib in moderate yield. The mass spectra fragmentation pattern of compound Ib was similar to Ia and was in good agreement with the suggested structure. In the mass spectrum, in addition to a strong molecular ion peak at 234, ions at 206 (m-N_2), 178 [m-(N_2 + CO], 137 (C_6H_4 ), 136 (C_6H_4 ), 108 [$(C_6H_4S)^+$] and 69 (C_3HS) were observed.

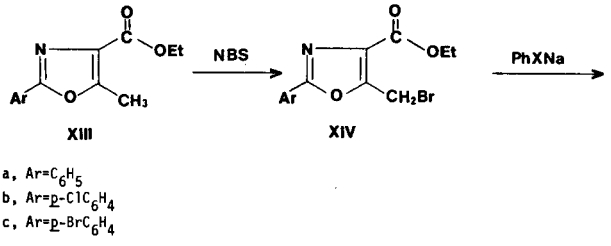
Reaction of phenol or sodium phenoxide with 5-bromomethyl-4-carbethoxy-1,2,3-thiadiazole under different experimental conditions did not give the desired product 4--carbethoxy-5-phenoxymethyl-1,2,3-thiadiazole (X). In all cases either the starting material or a mixture of compounds were obtained. None of these compounds was the desired compound X.

Reaction of compound IX with sodium thiophenolate in ethanol afforded 4-carbethoxy-5-phenylthiomethyl-1,2,3--thiadiazole (XI) in good yield. Hydrolysis followed by cyclization with polyphosphoric acid gave compound II (see Scheme I).

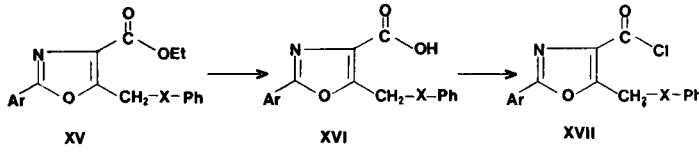
Reaction of *N*-bromosuccinimide with ethyl 2-aryl-5--methyloxazole-4-carboxylate (XIII) (8) gave ethyl 2-aryl-5--bromomethyloxazole-4-carboxylate (XIV) in high yield. Reaction of the latter with sodium phenoxide in butanone afforded ethyl 2-aryl-5-phenoxymethyloxazole-4-carboxylate (XV) in good yield. However, in the case of XIVb (Ar = *p*-ClC_6H_4) the yield of the desired product XVb was only 10%. In this case the major product was ethyl 2-*p*-chlorophenyl-5-acetoxymethyl-oxazole-4-carboxylate (XVIII). The yield of the desired compound XVb could be improved by using tetrahydrofuran instead of butanone as a solvent. Alkaline hydrolysis of compound XV gave the acid XVI which was converted to the final product XIX (X = O) by the stannic chloride method (7). The thia-analog of compound XIX was prepared in a similar manner (Scheme II).

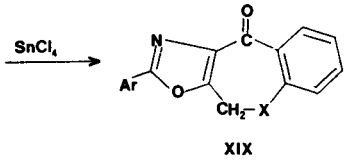
The physical data of the compounds prepared are summarized in Tables I, II, and III.

Scheme III



a, Ar=C_6H_5
b, Ar=p-ClC_6H_4
c, Ar=p-BrC_6H_4





a, X=O, Ar=C_6H_5
b, X=O, Ar=p-ClC_6H_4
c, X=O, Ar=p-BrC_6H_4
d, X=S, Ar=C_6H_5
e, X=S, Ar=p-ClC_6H_4
f, X=S, Ar=p-BrC_6H_4

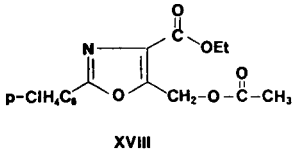
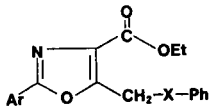


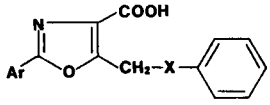
Table I



Compound	Ar	X	Yield %	M.p. °C(a)	Formula	C %		H %		N %	
						Calcd.	Found	Calcd.	Found	Calcd.	Found
XVa	C_6H_5-	0	90	50-52	$C_{19}H_{17}NO_4$	70.59	70.78	5.26	5.08	4.33	4.51
XVb	*p*-ClC_6H_4-	0	90 (b)	54-56	$C_{19}H_{16}ClNO_4$	63.78	63.94	4.48	4.29	3.92	3.98
XVc	*p*-BrC_6H_4-	0	95	94-96	$C_{19}H_{16}BrNO_4$	56.72	56.58	3.98	3.86	3.48	3.63
XVd	C_6H_5-	S	85	56-58	$C_{19}H_{17}NO_3S$	67.26	67.05	5.01	4.86	4.13	4.01
XVe	*p*-ClC_6H_4-	S	90	90-91	$C_{19}H_{16}ClNO_3S$	61.04	60.88	4.28	4.39	3.75	3.94
XVf	*P*-BrH_6H_4-	S	95	76-78	$C_{19}H_{16}BrNO_3S$	54.55	54.76	3.83	3.95	3.35	3.56

(a) All compounds were crystallized from ether. (b) The yield was 10% in butanone as a solvent for preparation, and 90% in tetrahydrofuran (see Experimental).

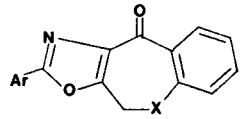
Table II



Compound	Ar	X	Yield %	M.p. °C(a)	Formula	C %		H %		N %	
						Calcd.	Found	Calcd.	Found	Calcd.	Found
XVIa	C_6H_5-	0	85	180-182	$C_{17}H_{13}NO_4$	69.15	69.01	4.41	4.63	4.75	4.56
XVIb	*p*-ClC_6H_4-	0	95	189-191	$C_{17}H_{12}ClNO_4$	61.91	61.75	3.64	3.83	4.25	4.36
XVIc	*p*-BrC_6H_4-	0	90	178-180	$C_{17}H_{12}BrNO_4$	54.55	54.73	3.21	3.40	3.74	3.92
XVId	C_6H_5-	S	90	186-188	$C_{17}H_{13}NO_3S$	65.59	65.78	4.18	4.01	4.50	4.63
XVIe	*p*-ClC_6H_4-	S	95	195-197	$C_{17}H_{12}ClNO_3S$	59.04	59.21	3.47	3.65	4.05	3.86
XVIf	*p*-BrC_6H_4-	S	95	185-187	$C_{17}H_{12}BrNO_3S$	52.31	52.18	3.08	2.89	3.59	3.78

(a) All compounds were crystallized from ethanol-water.

Table III



Compound	Ar	X	Yield %	M.p. °C(a)	Formula	C %		H %		N %	
						Calcd.	Found	Calcd.	Found	Calcd.	Found
XIXa	C_6H_5-	0	45	168-170	$C_{17}H_{11}NO_3$	73.65	73.84	3.97	3.74	5.05	5.24
XIXb	*p*-ClC_6H_4-	0	40	186-188	$C_{17}H_{10}ClNO_3$	65.49	65.65	3.21	3.01	4.49	4.38
XIXc	*p*-BrC_6H_4-	0	40	185-187	$C_{17}H_{10}BrNO_3$	57.30	57.18	2.81	2.65	3.93	3.71
XIXd	C_6H_5-	S	50	206-208	$C_{17}H_{11}NO_2S$	69.62	69.81	3.75	3.94	4.78	4.95
XIXe	*p*-ClC_6H_4-	S	40	148-150	$C_{17}H_{10}ClNO_3S$	62.29	62.43	3.05	3.21	4.27	4.35
XIXf	*p*-BrC_6H_4-	S	45	145-147	$C_{17}H_{10}BrNO_2S$	54.84	54.65	2.69	2.43	3.76	3.58

(a) All compounds were crystallized from ether.

EXPERIMENTAL

Melting points were taken on a Kofler hot stage microscope and were uncorrected. The ir spectra were obtained on a Perkin Elmer Model 267 spectrograph (potassium bromide). Nmr spectra were determined using a Varian T-60 spectrometer and chemical shifts (δ) are in ppm relative to internal tetramethylsilane. Mass spectra were run on a Varian MAT-311 spectrometer at 70 eV.

4-Phenoxymethyl-5-carbethoxy-1,2,3-thiadiazole VI (X = O).

A mixture of V (2.51 g., 0.01 mole) (2) and sodium phenoxide (1.28 g., 0.011 mole) in butanone (40 ml.) was stirred and refluxed overnight. The mixture was filtered and the solvent was evaporated. To the residue, water was added and the aqueous solution was extracted with chloroform. The chloroform was dried, filtered and evaporated. The residue was distilled under reduced pressure to give 2.38 g. (90%) of VI (X = O) b.p. 138-140° (4mm); nmr (deuteriochloroform): 7.67-6.67 (m, 5H, aromatic), 5.73 (s, 2H, CH_2), 4.43 (q, 2H, CH_2) and 1.33 ppm (t, 3H, CH_3).

Anal. Calcd. for $C_{12}H_{12}N_2O_3S$: C, 54.55; H, 4.55; N, 10.61. Found: C, 54.68; H, 4.71; N, 10.43.

4-Phenoxymethyl-1,2,3-thiadiazole-5-carboxylic Acid (VIII, X = O).

To a stirring and refluxing solution of VI (X = O, 2.64 g., 0.01 mole) in 30 ml. of ethanol, a solution of sodium hydroxide (0.44 g., 0.011 mole) in 5 ml. of water was added dropwise. After the addition was complete, heating was continued for 15 minutes. The solvent was evaporated. The

residue was dissolved in water and acidified with hydrochloric acid. The precipitate was crystallized from ethanol-water to give 2.12 g. (90%) of VII (X = O), m.p. 159-161°; ir: 1730 cm^{-1} (carbonyl).

Anal. Calcd. for $C_{10}H_8N_2O_3S$: C, 50.85; H, 3.39; N, 11.86. Found C, 50.67; H, 3.21; N, 11.98.

4,10-Dihydro-10-oxo[1]benzoxepino[3,4-*d*][1,2,3]thiadiazole (Ia).

To a mixture of VII (X = O, 236 mg., 1 mmole) in benzene (5 ml.), 0.5 ml. of thionyl chloride was added. The mixture was refluxed for 5 hours. The solvent was evaporated to give 4-phenoxymethyl-1,2,3-thidiazole-5--carboxy chloride (VIII), m.p. 79-81°; ir: 1745 cm^{-1}(carbonyl). To a stirring solution of the latter in 20 ml. of anhydrous methylene chloride, stannic chloride (261 mg., 1 mmole) in 5 ml. of methylene chloride was added. Stirring was continued at ambient temperature overnight and the mixture was refluxed for an additional 2 hours. The solvent was evaporated. To the residue, ice-water was added and the aqueous solution was extracted with chloroform. The chloroform was dried, filtered and evaporated. The residue was purified by tlc (silica gel, chloroform) and the desired compound was crystallized from ether to give 87 mg. (40%) of Ia, m.p. 90-92°; ir: 1622 cm^{-1}(carbonyl); nmr (deuteriochloroform): 7.53-6.83 (m, 4H, aromatic), and 5.67 ppm (s, 2H, CH_2); ms: m/e (relative intensity) 218 (M^+, 27), 190 (15), 162 (5), 121 (100), 120 (50), 92 (79), 70 (72), and 64 (48).

Anal. Calcd. for $C_{10}H_6N_2O_2S$: C, 55.05; H, 2.75; N, 12.84. Found: C, 54.91; H, 2.63; N, 12.67.

4-Phenylthiomethyl-5-carbethoxy-1,2,3-thiadiazole (VI, X = S).

To a stirring solution of sodium thiophenolate (0.01 mole), prepared from sodium (0.23 g., 0.01 mole), thiophenol (1.1 g., 0.01 mole) and ethanol (20 ml.), a solution of V (2.51 g., 0.01 mole) in 20 ml. of ethanol was added. After 1 hour the mixture was refluxed for 5 hours. The solvent was evaporated. To the residue, ice-water was added and the aqueous solution was extracted with chloroform. The chloroform was dried, filtered and evaporated, and the residue was distilled under reduced pressure to give 2.52 g. (90%) of VI (X = S), b.p. 148-150° (4mm); nmr (deuteriochloroform): 7.67-7.27 (m, 5H, aromatic), 4.92 (s, 2H, CH_2), 4.43 (q, 2H, CH_2), and 1.40 ppm (t, 3H, CH_3).

Anal. Calcd. for $C_{12}H_{12}N_2O_2S_2$: C, 51.43; H, 4.29; N, 10.00. Found: C, 51.28; H, 4.18; N, 10.18.

4-Phenylthiomethyl-1,2,3-thiadiazole-5-carboxylic Acid (VII, X = S).

This compound was prepared in a manner similar to the preparation of VII (X = O) in 85% yield, m.p. 129-130° (ethanol-water); ir: 1730 cm^{-1}(carbonyl).

Anal. Calcd. for $C_{10}H_8N_2O_2S_2$: C, 47.62; H, 3.17; N, 11.11. Found: C, 47.81; H, 3.01; N, 10.98.

4,10-Dihydro-10-oxo[1]benzothiepino[3,4-*d*][1,2,3]thiazole (Ib).

A mixture of VII (X = S, 252 mg., 1 mmole) and polyphosphoric acid (3 ml.) was heated in an oil bath at 120° for 2 hours. After cooling, ice-water was added, and the solution was neutralized with an aqueous solution of sodium bicarbonate. The mixture was then extracted with chloroform. The chloroform was dried, filtered and evaporated. The residue was purified by tlc (silica gel, chloroform) and the desired compound was crystallized from ether to give 82 mg. (35%) of Ib, m.p. 111-112°; ir: 1635 cm^{-1}(carbonyl); nmr (deuteriochloroform): 7.67-7.17 (m, 4H, aromatic) and 4.57 ppm (s, 2H, CH_2); ms m/e (relative intensity) 234 (M^+, 98), 206 (22), 178 (25), 137 (100), 108 (97), 69 (80) and 58 (46).

Anal. Calcd. for $C_{10}H_6N_2OS_2$: C, 51.28; H, 2.56; N, 11.97. Found: C, 51.45; H, 2.38; N, 11.79.

4-Carbethoxy-5-phenylthiomethyl-1,2,3-thiadiazole (XI).

This compound was prepared from 4-carbethoxy-5-bromomethyl-1,2,3--thiadiazole (IX) (2) in a manner similar to the preparation of VII (X = S) in 70% yield; b.p. 149-151° (4 mm); nmr (deuteriochloroform): 7.27 (s, 5H, aromatic), 4.73 (s, 2H, CH_2), 4.45 (q, 2H, CH_2) and 1.50 ppm (t, 3H, CH_3).

Anal. Calcd. for $C_{12}H_{12}N_2O_2S_2$: C, 51.43; H, 4.29; N, 10.00. Found: C, 51.26; H, 4.15; N, 9.88.

5-Phenylthiomethy-1,2,3-thiadiazole-4-carboxylic Acid (XII).

This compound was prepared in a manner similar to the preparation of VII (X = O) in 85% yield, m.p. 64-65° (ethanol-water); ir: 1700 cm^{-1}(carbonyl).

Anal. Calcd. for $C_{10}H_8N_2O_2S_2$: C, 47.62; H, 3.17; N, 11.11. Found: C, 47.46; H, 3.02; N, 11.28.

4,10-Dihydro-4-oxo[1]benzothiepino[4,3-*d*][1,2,3]thiadiazole (II).

This compound was prepared in a manner similar to the preparation of Ib in 20% yield; m.p. 98-99° (ether); ir: 1645 cm^{-1}(carbonyl).

Anal. Calc. for $C_{10}H_6N_2OS_2$: C, 51.28; H, 2.56; N, 11.97. Found: C, 51.09; H, 2.74; N, 11.75.

Ethyl 2-Phenyl-5-bromomethyloxazole-4-carboxylate (XIVa).

A mixture of XIIIa (2.31 g., 0.01 mole)(8) and *N*-bromosuccinimide (1.96 g., 0.11 mole) in 30 ml. of carbon tetrachloride was irradiated with a 500 W (G. E. photospot) lamp while heating and stirring at reflux temperature for 4 hours. The mixture was cooled and filtered. The solvent was evaporated and the residue was purified by tlc (silica gel, chloroform), and crystallized from ether to give 1.55 g. (50%) of XIVa, m.p. 87-89°; nmr (deuteriochloroform): 8.27-8.03 (m, 2H, aromatic), 7.67-7.10 (m, 3H, aromatic), 4.88 (s, 2H, CH_2), 4.47 (q, 2H, CH_2), and 1.42 ppm (t, 3H, CH_3).

*Anal.*Calcd. for $C_{13}H_{12}BrNO_3$: C, 50.32; H, 3.87; N, 4.52. Found: C, 50.18 H, 3.96; N, 4.71.

Ethyl 2-*p*-Chlorophenyl-5-bromomethyloxazole-4-carboxylate (XIVb).

This compound was prepared in a manner similar to the preparation of XIVa in 60% yield, m.p. 103-104° (ether); nmr (deuteriochloroform): 8.10 (d, 2H, aromatic), 7.47 (d, 2H, aromatic), 4.9 (s, 2H, CH_2), 4.50 (q, 2H, CH_2) and 1.45 ppm (t, 3H, CH_3).

Anal. Calcd. for $C_{13}H_{11}BrClNO_3$: C, 45.28; H, 3.19; N, 4.06. Found: C, 45.43; H, 3.36; N, 4.01.

Ethyl 2-*p*-Bromophenyl-5-bromomethyloxazole-4-carboxylate (XIVc).

This compound was prepared in a manner similar to the preparation of XIVa in 60% yield, m.p. 108-109° (ether); nmr (deuteriochloroform): 8.07 (d, 2H, aromatic), 7.67 (d, 2H, aromatic), 4.93 (s, 2H, CH_2), 4.47 (q, 2H, CH_2) and 1.47 ppm (t, 3H CH_3).

Anal. Calcd. for $C_{13}H_{11}Br_2NO_3$: C, 40.10; H, 2.83; N, 3.60. Found: C, 40.25; H, 2.96; N, 3.87.

Ethyl 2-Phenyl-5-phenoxymethyloxazole-4-carboxylate (XVa).

A mixture of XIVa (3.10 g., 0.01 mole) and sodium phenoxide 1.28 g., 0.011 mole) in butanone (40 ml.) was stirred and refluxed overnight and worked up as in the case of VI (X = O) to give 2.91 g. (90%) of XVa; m.p. 50-52° (ether); nmr (deuteriochloroform): 8.30-8.10 (m, 2H, aromatic), 7.67-7.00 (m, 8H, aromatic), 5.57 (s, 2H, CH_2), 4.57 (q, 2H, CH_2) and 1.50 ppm (t, 3H, CH_3).

Anal. Calcd. for $C_{19}H_{17}NO_4$: C, 70.59; H, 5.26; N, 4.33. Found: C, 70.78; H, 5.08; N, 4.51.

Compounds XVb and XVc were prepared similarly (Table I). In the case of XVb, this method gave only a 10% yield and the major product was compound XVIII (80%), m.p. 59-60° (ether); ir: 1730 (carbonyl), 1700 cm^{-1}(carbonyl); nmr (deuteriochloroform): 8.07 (d, 2H, aromatic), 7.43 (d, 2H, aromatic), 5.43 (s, 2H, CH_2), 4.37 (q, 2H, CH_2), 2.08 (s, 3H, CH_3) and 1.42 ppm (t, 3H, CH_3); ms: m/e (%) 325 (M + 2, 33), 323 (M^+, 100), 280 (99), 264 (23), 235 (99), 207 (27), 139 (98), and 111 (24).

Anal. Calcd. for $C_{15}H_{14}ClNO_5$: C, 55.64; H, 4.33; N, 4.33. Found: C, 55.54; H, 4.12; N, 4.51.

Ethyl 2-*p*-Chlorophenyl-5-Phenoxymethyloxazole-4-carboxylate (XVb). Method B.

A mixture of XIVb (3.45 g., 0.01 mole) and sodium phenoxide (1.28 g., 0.011 mole) in tetrahydrofuran (60 ml.) was stirred and refluxed overnight and worked up as in XVa to give 3.2 g. (90%) of XVb, m.p. 54-56°

(ether).

Ethyl 2-Phenyl-5-phenylthiomethyloxazole-4-carboxylate (XVd).

To a stirring solution of sodium thiophenolate (0.01 mole); prepared from sodium (0.23 g., 0.01 mole), thiophenol (1.1 g., 0.01 mole) and ethanol (20 ml.), a solution of XIVa (3.10 g., 0.01 mole) in 20 ml. of ethanol was added and the procedure was continued in a manner similar to the preparation of VI (X = S) to give 2.69 g. (85%) of XVd, m.p. 56-58° (ether-petroleum ether); nmr (deuteriochloroform): 8.27-7.93 (m, 2H, aromatic), 7.93-7.17 (m, 8H, aromatic), 4.53 (s, 2H, CH_2), 4.33 (q, 2H, CH_2) and 1.37 ppm (t, 3H, CH_3).

Anal. Calcd. for $C_{19}H_{17}NO_3S$: C, 67.26; H, 5.01; N, 4.13. Found: C, 67.05; H, 4.86; N, 4.01.

Compounds XVe and XVf were prepared similarly (see Table I).

2-Phenyl-5-phenoxymethyloxazole-4-carboxylic Acid (XVIa).

To a stirring and refluxing solution of XVa (3.23 g., 0.01 mole) in 30 ml. of ethanol, a solution of sodium hydroxide (0.44 g., 0.011 mole) in 5 ml. of water was added dropwise and the procedure was continued as in the case of VII (X = O) to give 2.51 g. (85%) of XVIa, m.p. 180-182°; ir: 1700 cm^{-1}(carbonyl).

Anal. Calcd. for $C_{17}H_{13}NO_4$: C, 69.15; H, 4.41; N, 4.75. Found: C, 69.01; H, 4.63; N, 4.56.

Compounds XVIb to XVIf were prepared similarly.

2-Phenyl-4,10-dihydro-4-oxo[1]benzoxepino[4,3-*d*]oxazole (XIXa).

To a mixture of XVIa (295 mg., 1 mmole) in benzene (5 ml.), thionyl chloride (0.5 ml.) was added. The mixture was refluxed for 5 hours. The solvent was evaporated to give 2-Phenyl-5-phenoxymethyloxazole-4--carboxy chloride (XVIIa); ir: 1760 cm^{-1}(carbonyl). To a stirring solution of the latter in 20 ml. of anhydrous methylene chloride, stannic chloride (261 mg., 1 mmole) in 5 ml. of methylene chloride was added and the procedure was continued in a manner similar to the preparation of Ia to give 125 mg. (45%) of XIXa, m.p. 168-170°; 1645 cm^{-1}(carbonyl); nmr (deuteriochloroform): 8.30-8.00 (m, 2H, aromatic), 7.63-7.10 (m, 7H, aromatic) and 5.32 ppm (s, 2H, CH_2); ms: m/e (%) 277 (M^+, 100), 249 (33), 121 (52), 106 (100), and 78 (49).

Anal. Calcd. for $C_{17}H_{11}NO_3$: C, 73.65; H, 3.97; N, 5.05. Found: C, 73.84; H, 3.74; N, 5.24.

Compounds XIXb-XIXf were prepared similarly (see Table III).

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