Synthesis and Properties of some Tetracyclic Derivatives of 9*H*-Carbazole, 10,11-Dihydro-5*H*-dibenz[*b*,*f*]azepine, and 5,11-Dihydrodibenz[*b*,*e*][1,4]oxazepine

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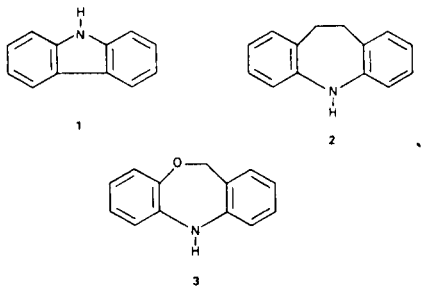
The behavior of 5,6-dihydro-4*H*-pyrido[3,2,1-*jk*]carbazol-4-one (**10**), 1,2,7,8-tetrahydro-3*H*-quino[1,8-*ab*][1]benzazepin-3-one (**11**), 1,2-dihydro-9*H*-[1]benzazepino[1,9-*ab*][4,1]benzoxazepin-4(3*H*)one (**13**), and 1,2-dihydro-8*H*-[1]benzazepino[1,9-*cd*][1,5]benzoxazepin-4(3*H*)one (**14**) towards the Schmidt reaction has been determined in polyphosphoric acid and in benzene- or chloroform-sulfuric acid. Evidence for the structure of the new heterocyclic systems obtained from these four compounds is presented.

J. Heterocyclic Chem., 13, 475 (1976).

Since it is often very difficult to predict, even with approximation, the products of a ring enlargement by the Schmidt reaction (1) owing to both the steric and electronic factors involved (2), in order to synthesize novel attractive intermediates of potential psychotherapeutic agents from 9*H*-carbazole (**1**), 10,11-dihydro-5*H*-dibenz[*b*,*f*]azepine (**2**), and 5,11-dihydrodibenz[*b*,*e*][1,4]oxazepine (**3**), we decided to investigate the reaction of 5,6-dihydro-4*H*-pyrido[3,2,1-*jk*]carbazol-4-one (**10**), 1,2,7,8-tetrahydro-3*H*-quino[1,8-*ab*][1]benzazepin-3-one (**11**), 1,2-dihydro-9*H*-[1]benzazepino[1,9-*ab*][4,1]benzoxazepin-4(3*H*)one (**13**), and 1,2-dihydro-8*H*-[1]benzazepino[1,9-*cd*][1,5]benzoxazepin-4(3*H*)one (**14**) (Table I) with hydrazoic acid.



As outlined in Scheme I, the tetracyclic ketone **10** was prepared from 9*H*-carbazole-9-propanoic acid (**8**) with trifluoracetic anhydride in benzene according to the procedure of Hromatka and Sauter (3). The ketocompound **11** (4) was obtained from 10,11-dihydro-5*H*-dibenz[*b*,*f*]-azepine-5-propanoic acid (**9**) (5) following the same procedure. The pmr spectrum of **11** showed a characteristic downfield one-proton quartet centered at δ 7.95 (J = 7 and 3 Hz) attributable to the deshielding influence of the carbonyl group on the adjacent aromatic proton at C-4, as it has been reported by Petigara and Yale (6) for analogous tetracyclic ketones. The cyclization of **9** was also accompanied by dehydrogenation (6) of **11** to give 7,8-dihydro-3*H*-quino[1,8-*ab*][1]benzazepin-3-one (**12**) whose structure followed from spectroscopic evidence. The ir spectrum showed a strong band at 1630 cm^{-1} for the carbonyl group and the pmr spectrum exhibited two doublets centered at δ 7.65 (J = 8 Hz) and δ 6.40 (J = 8 Hz) attributable to the protons at C-1 and C-2 respectively.

Scheme I

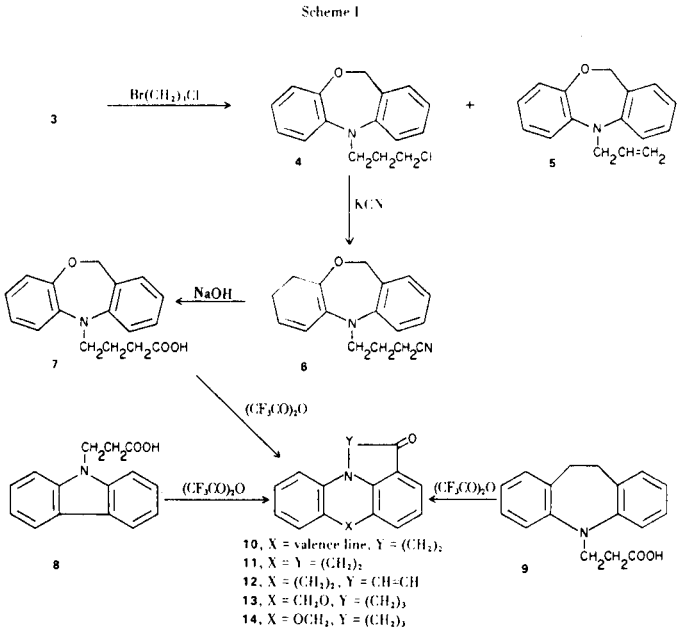
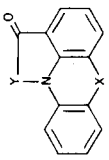


Table I.
Tetracyclic Ketones.



No	X	Y	M.P. °C	Crystallization Solvent (a)	Yield %(b)	Formula	% Carbon Calcd.	% Carbon Found	% Hydrogen Calcd.	% Hydrogen Found	% Nitrogen Calcd.	% Nitrogen Found
10	valence line	$(CH_2)_2$	95-97(c)	M	77	$C_{15}H_{11}NO$	81.43	81.27	5.01	5.04	6.33	6.39
11	$(CH_2)_2$	$(CH_2)_2$	93-95(d)	IS	62.5	$C_{17}H_{15}NO$	81.90	82.08	6.06	6.12	5.62	5.65
12	$(CH_2)_2$	CH=CH	128-130	IS	13.5	$C_{17}H_{13}NO$	82.57	82.51	5.30	5.25	5.66	5.61
13	CH_2O	$(CH_2)_3$	86-88(e)	B-P	22.5	$C_{17}H_{15}NO_2$	76.96	76.78	5.70	5.72	5.28	5.26
14	OCH_2	$(CH_2)_3$	116-118(f)	B-P	8	$C_{17}H_{15}NO_2$	76.96	76.85	5.70	5.74	5.28	5.31

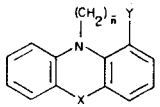
(a) M, methanol; IS, isopropyl ether; B, benzene; P, petroleum ether. (b) No attempts were made to optimize yields. (c) Lit. m.p. 92-96° (3). (d) Compound **11** was characterized by its oxime too, m.p. 202-204° [lit. m.p. 198-200° (4)] from methanol. (e) Ir: 1675 cm^{-1} (ν C=O); pmr: δ 7.65 (q, 1, J = 7 and 3 Hz, Ar-*H* at C-5). (f) Ir: 1675 cm^{-1} (ν C=O); pmr: δ 7.98 (q, 1, J = 7 and 3 Hz, Ar-*H* at C-5).

Using the procedure of Yale *et al.* (7), when **3** was allowed to react with an excess of 1-bromo-3-chloropropane for 28 hours a mixture of 5-(3-chloropropyl)-5,11-dihydrodibenz[*b*,*e*][1,4]oxazepine (**4**) and 5-allyl-5,11-dihydrodibenz[*b*,*e*][1,4]oxazepine (**5**) with a small amount of the starting material **3** was obtained. Attempts to purify **4** by column chromatography on Florisil were unsuccessful but this was not essential for the synthesis of 5,11-dihydrodibenz[*b*,*e*][1,4]oxazepine-5-butanenitrile (**6**). In fact, when the reaction mixture of **4** and **5** was treated with potassium cyanide (8) the derivative **6** was easily obtained.

Basic hydrolysis (9) of **6** and subsequent cyclization of 5,11-dihydrodibenz[*b*,*e*][1,4]oxazepine-5-butanoic acid (**7**) in benzene with trifluoroacetic anhydride (3) afforded a mixture of two isomeric ketones. The two isomers **13** and **14**, shown by pmr spectra and gc to be present in a 7:3 ratio, were separated by column chromatography on alumina and following crystallization from benzene-petroleum ether. The pmr spectra of the two isomers showed a downfield one-proton quartet attributable, as we said above, to the deshielding effect of the carbonyl group on the adjacent aromatic proton at C-5. Since it has been shown by Petigara and Yale (6) that the bridging CH_2O of analogous compounds causes significant shielding on the aromatic proton adjacent to the carbonyl group and placed in the ring containing the oxygen atom, the structure **13** was assigned to the isomer which showed the C-5 proton quartet centered at δ 7.65 (J = 7 and 3 Hz). Consequently, the structure **14** was assigned to the isomer showing the C-5 proton quartet centered at δ 7.98 (J = 7 and 3 Hz).

Treatment of **10** (Scheme II) with equimolar quantities of sodium azide in polyphosphoric acid at 60-70° for 4 hours (Method A) (10) did not give 6,7-dihydro[1,4]-diazepino[3,2,1-*jk*]carbazol-5(4*H*)one, but rather the isomeric lactam 6,7-dihydro[1,4]diazepino[6,7,1-*jk*]carbazol-4(5*H*)one (**15**), obtained as a result of alkyl migration due to the electronic effects of the nitrogen atom in the position ortho to the carbonyl group (11). The ir spectrum showed an amide carbonyl at 1650 cm^{-1} and the expected NH absorption. The pmr spectrum was in complete agreement with the structure **15**. In particular the two protons at C-6 were represented by a complex multiplet at δ 3.85-3.55 which showed marked variation by the addition of trifluoroacetic acid to the sample tube. Under similar reaction conditions **11** gave 1,2,8,9-tetrahydro[1]benzazepino[3,2,1-*jk*][1,4]benzodiazepin-4(3*H*)one (**16**) in high yield. When the Schmidt reaction was carried out in chloroform and in presence of the sulfuric acid (Method B) (1), **10** and **11** were recovered unchanged. As **13** and **14** are not stable in polyphosphoric acid, when they were treated with equimolar quantities of sodium

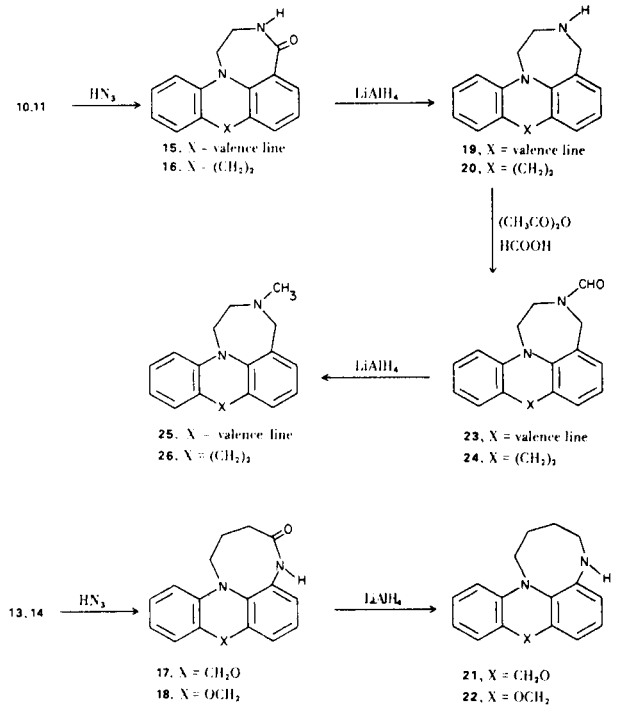
Table II.
Tetracyclic Lactames, Amines, and Formamides.



No	X	Y	n	Method (a)	M.P. °C	Crystallization Solvent (b)	Yield % (c)	Formula	% Carbon Calcd.	% Carbon Found	% Hydrogen Calcd.	% Hydrogen Found	% Nitrogen Calcd.	% Nitrogen Found
15	valence line	-NHCO	2	A	222-224	M	82	$C_{15}H_{12}N_2O$	76.25	75.98	5.12	5.12	11.86	11.90
16	$(CH_2)_2$	-NHCO	2	A	158-160	IS	79	$C_{17}H_{16}N_2O$	77.25	77.31	6.10	6.08	10.60	10.66
17	CH_2O	-CONH	3	B	198-200	B	52	$C_{17}H_{16}N_2O_2$	72.84	73.05	5.75	5.72	9.99	10.04
18	OCH_2	-CONH	3	B	213-215	B	48	$C_{17}H_{16}N_2O_2$	72.84	72.79	5.75	5.77	9.99	9.95
19	valence line	$-NHCH_2$	2		(d)		69.5(e)	(f)						
20	$(CH_2)_2$	$-NHCH_2$	2		(d)		82(e)	(g)						
21	CH_2O	-NH-	4		(h)		63(e)	(i)						
22	OCH_2	-NH-	4		(j)		75(e)	(k)						
23	valence line	$-N(CHO)CH_2$	2		(h)		95	(l)						
24	$(CH_2)_2$	$-N(CHO)CH_2$	2		(h)		92	(l)						
25	valence line	$-N(CH_3)CH_2$	2		97-99	B-P	81	$C_{16}H_{16}N_2$	81.32	81.27	6.83	6.81	11.86	11.91
26	$(CH_2)_2$	$-N(CH_3)CH_2$	2		(h)		87(e)	(m)						

(a) The Schmidt reaction was carried out in benzene-sulfuric acid (A) and in poliphosphoric acid (B). (b) M, methanol; IS, isopropyl ether; B, benzene; P, petroleum ether. (c) No attempts were made to optimize yields. (d) The compound was an oil; pmr: δ 4.30 (s, 2, $ArCH_2N$). (e) Yield calculated on the corresponding hydrochloride. (f) Characterized as hydrochloride, m.p. 259-261° dec. from ethanol-ethyl ether. *Anal.* Calcd. for $C_{15}H_{15}ClN_2$: C, 69.63; H, 5.84; Cl, 13.70; N, 10.83. Found: C, 69.81; H, 5.86; Cl, 13.61; N, 10.77. (g) Characterized as hydrochloride, m.p. 246-248° dec. from ethanol-ethyl ether. *Anal.* Calcd. for $C_{17}H_{19}ClN_2$: C, 71.19; H, 6.68; Cl, 12.36; N, 9.77. Found: C, 71.06; H, 6.72; Cl, 12.28; N, 9.73. (h) The compound was an oil. (i) Characterized as hydrochloride, m.p. 247-249° dec. from ethanol-ethyl ether. *Anal.* Calcd. for $C_{17}H_{19}ClN_2O$: C, 67.43; H, 6.32; Cl, 11.71; N, 9.25. Found: C, 67.61; H, 6.29; Cl, 11.67; N, 9.29. (j) The free base was an oil; pmr δ 7.25-6.40 (m, 7, Ar-*H*), 4.95 (s, 2, OCH_2), 4.05-3.30 (m, 4, $NCH_2CH_2CH_2CH_2N$), 2.15-1.50 (m, 4, $NCH_2CH_2CH_2CH_2N$). (k) Characterized as hydrochloride, m.p. 242-244° dec. from ethanol-ethyl ether. *Anal.* Calcd. for $C_{17}H_{19}ClN_2O$: C, 67.43; H, 6.32; Cl, 11.71; N, 9.25. Found: C, 67.27; H, 6.36; Cl, 11.75; N, 9.30. (l) Used in the next step without further purification. (m) Characterized as hydrochloride, m.p. 229-231° dec. from ethanol-ethyl ether. *Anal.* Calcd. for $C_{18}H_{21}ClN_2$: C, 71.87; H, 7.04; Cl, 11.78; N, 9.31. Found: C, 72.03; H, 7.08; Cl, 11.83; N, 9.27.

Scheme II



azide in polyphosphoric acid at 60-70° for 4 hours (Method A) an appreciable quantity of an intractable black tar was formed. The Schmidt reaction was then applied to **13** and **14** in benzene catalyzed by sulfuric acid (Method B), since these compounds were sufficiently stable in this medium. Although considerable amounts of starting materials were decomposed under similar conditions, it was possible to observe that the reaction proceeded to give the aryl migration. In fact, 2,3-dihydro-1*H*, 10*H*-[4,1]benzoxazepino[3,2,1-*jk*][1,6]benzodiazocin-4(5*H*)one (**17**) and 2,3-dihydro-1*H*,9*H*-[1,5]benzoxazepino [3,4,5-*kl*][1,6]benzodiazocin-4(5*H*)one (**18**) were the only products obtained from **13** and **14** respectively.

When the lithium aluminum hydride reduction of **15**, **16**, **17**, and **18** was carried out in refluxing tetrahydrofuran 4,5,6,7-tetrahydro[1,4]diazepino[6,7,1-*jk*]carbazole (**19**), 1,2,3,4,8,9-hexahydro[1]benzazepino[3,2,1-*jk*][1,4] benzodiazepine (**20**), 2,3,4,5-tetrahydro-1*H*, 10*H*-[4,1] benzoxazepino[3,2,1-*kl*][1,6]benzodiazocine (**21**), and 2,3,4,5-tetrahydro-1*H*, 9*H*-[1,5]benzoxazepino[3,4,5-*kl*] [1,6]benzodiazocine (**22**) were obtained. The pmr spectra of **19** and **20** showed a singlet at δ 4.30 for the newly formed two protons at C-4. The pmr spectra of **21** and **22** appeared to be in complete agreement with their structure. The pmr spectrum of **21** showed a singlet at δ 5.10 for the two protons at C-10, a complex multiplet at δ 4.05-3.30 for the protons at C-1 and C-4, and a complex multiplet at δ 2.15-1.50 for the protons at C-2 and C-3. The pmr spectrum of **22** had a singlet at δ 4.95 for the two protons at C-9 and same complex multiplets for the other protons.

Methylation of the basic nitrogen of **19** and **20** to give 4,5,6,7-tetrahydro-5-methyl[1,4]diazepino[6,7,1-*jk*]carbazole (**25**) and 1,2,3,4,8,9-hexahydro-3-methyl[1]benzazepino[3,2,1-*jk*][1,4]benzodiazepine (**26**) was achieved, in two steps, by lithium aluminum hydride reduction of the formamides prepared *via* reaction of **19** and **20** with formic acetic anhydride (12).

Data on compounds **15-26** are collected in Table II.

EXPERIMENTAL

The melting points were taken in open capillary tubes using a Tottoli apparatus (N. Büchi, Flawil, Switzerland) and are uncorrected. All intermediates and final products were examined by ir and pmr spectroscopy (Perkin-Elmer 257 and Varian T-60 A respectively) and their spectra were found to be in agreement with the assigned structures. Unless otherwise specified, the ir and pmr spectra were obtained for potassium bromide disks and for deuteriochloroform solutions with tetramethylsilane as internal reference respectively. The following notations are employed in the presentation of pmr spectra: s = singlet, d = doublet, t = triplet, q = quartet, sext = sextet, m = multiplet. "Alumina" refers to neutral aluminum oxide B. III from E. merck, Germany. "Florisil" refers to magnesium silicates (100-200 mesh) from Floridin Co., Pa. Thin layer chromatography (tlc) was carried out on precoated silica gel plates (Merck, F-254) and detection was effected by exposure to an iodine atmosphere.

5,11-Dihydrodibenz[*b*,*e*][1,4]oxazepine-5-butanenitrile (**6**).

A suspension of 100 g. (0.507 mole) of 5,11-dihydrodibenz-[*b*,*e*][1,4]oxazepine (**3**), 1250 ml. of 2-butanone, 310 g. (1.969 mole) of 1-bromo-3-chloropropane, and 153 g. of granular sodium hydroxide was heated under reflux for 7 hours. An additional 153 g. of granular sodium hydroxide was added and the mixture was refluxed for an additional 21 hours. The cooled reaction mixture was poured in ice-water and the 2-butanone layer separated, washed with 10% sodium chloride, dried over anhydrous sodium sulfate, and evaporated to dryness *in vacuo* to give 215 g. of a yellow oil which was chromatographed on a column of Florisil (ratio 1:30). Elution with petroleum ether-benzene (8:2) gave a 75:25 mixture (32 g.) of 5-(3-chloropropyl)-5,11-dihydrodibenz[*b*,*e*][1,4]oxazepine (**4**) and 5-allyl-5,11-dihydrodibenz [*b*,*e*][1,4]oxazepine (**5**). Continued elution with benzene permitted the recovery of 75 g. of the starting material **3**, m.p. 119-121° [lit. m.p. 118-118.5° (13)] from hexane. The percent composition of **4** and **5** was determined by integration of the pmr spectrum of their mixture after the two-protons quintet centered at δ 2.10 (J = 7 Hz) and the two-protons sextet centered at δ 4.40 (J = 5 and 2 Hz) were assigned to $NCH_2CH_2CH_2Cl$ of **4** and $NCH_2CH{=}CH_2$ of **5** respectively. The 75:25 mixture (32 g.) of **4** and **5** was added to a solution of 32 g. (0.491 mole) of potassium cyanide and 3 g. of potassium iodide in 500 ml. of 80% ethanol. The mixture was refluxed for 25 hours, cooled, poured in ice-water, and extracted with ethyl ether. The ether extract was dried over anhydrous sodium sulfate and evaporated. The 31.5 g. of oil obtained was chromatographed on a column of Florisil (ratio 1:30). Elution with petroleum ether-benzene (8:2) gave 7.5 g. (6%) of a yellow oil (**5**) which failed to crystallize; ir

(sodium chloride, neat): 1642 cm^{-1} (ν C=C); pmr: δ 7.40-6.65 (m, 8, Ar-*H*), 6.20-5.60 (m, 1, C*H*=CH_2), 5.50-5.05 (m, 4, OCH_2 and CH=CH_2), 4.40 (sext, 2, J = 5 and 2 Hz, CH_2CH=CH_2). Elution with benzene yielded 21 g. (15.5%) of 5,11-dihydrodibenz[*b*,*e*][1,4]oxazepine-5-butanenitrile (**6**) as an oil which did not crystallize and was used in the next step without further purification; ir (sodium chloride, neat): 2240 cm^{-1} (ν C≡N); pmr: δ 7.50-6.05 (m, 8, Ar-*H*), 5.30 (s, 2, OCH_2), 3.85 (t, 2, J = 6 Hz, NCH_2), 2.50-1.80 (m, 4, $CH_2CH_2C{\equiv}N$).

5,11-Dihydrodibenz[*b*,*e*][1,4]oxazepine-5-butanoic Acid (**7**).

A mixture of 32 g. (0.121 mole) of the nitrile **6**, 100 g. of sodium hydroxide, and 2000 ml. of 90% ethanol was heated under reflux for 6 hours. After evaporation of the solvent *in vacuo*, the residue was dissolved in 1500 ml. of water, filtered, and reprecipitated by addition of hydrochloric acid. The resulting solid was crystallized from aqueous methanol to give 30.8 g. (90%) of **7**, m.p. 179-181°.

Anal. Calcd. for $C_{17}H_{17}NO_3$: C 72.06; H 6.05; N 4.94. Found: C 71.87; H 6.07; N 4.92.

1,2,7,8-Tetrahydro-3*H*-quino[1,8-*ab*][1]benzazepin-3-one (**11**) and 7,8-Dihydro-3*H*-quino[1,8-*ab*][1]benzazepin-3-one (**12**) (Table I, **10-14**).

To a solution of 9.62 g. (0.036 mole) of 10,11-dihydro-5*H*-dibenz[*b*,*f*]azepine-5-propionic acid (**9**) in 960 ml. of benzene was added 8.6 ml. (0.061 mole) of trifluoroacetic anhydride. The solution, kept overnight at room temperature, was then heated under reflux for 5 hours, cooled, washed twice with 5% sodium bicarbonate and water, dried over anhydrous sodium sulfate, and evaporated to dryness *in vacuo* to give 8.9 g. of a red oil. Pmr and gc indicated a 75:25 mixture of **11** and **12** which were purified by column chromatography on alumina (ratio 1:30). The first component, eluted from the column using benzene as eluent, was crystallized from isopropyl ether to give 5.6 g. (62.5%) of **11**, m.p. 93-95°; ir: 1670 cm^{-1} (ν C=O); pmr: δ 7.95 (q , 1, J = 7 and 3 Hz, Ar-*H* at C-4), 7.35-6.70 (m, 6, Ar-*H*), 4.25-4.05 (m, 2, NCH_2), 3.20-2.80 (m, 6, CH_2CO and $ArCH_2CH_2Ar$). The second component, eluted from the column using chloroform as eluent, was crystallized from isopropyl ether to yield 1,2 g. (13.5%) of **12**, m.p. 128-130°; ir: 1630 cm^{-1} (ν C=O); pmr: δ 7.65 (d, 1, J = 8 Hz, NC*H*=CHCO), 6.40 (d, 1, J = 8 Hz, NCH=C*H*CO), 7.50-6.90 (m, 7, Ar-*H*), 3.25 (s, 4, $ArCH_2CH_2Ar$).

6,7-Dihydro[1,4]diazepino[6,7,1-*jk*]carbazol-4(5*H*)one (**15**) (Table II, **15** and **16**).

To a mixture of 3.54 g. (0.016 mole) of **10** in 210 g. of polyphosphoric acid, heated at 60-70°, 1.04 g. (0.016 mole) of sodium azide was added in small portions over 1 hour with slow agitation. The reaction temperature was maintained at 70° for 4 hours. The solution was then poured into ice-water, alkalinized with 50% sodium hydroxide, and extracted twice with chloroform. The chloroform extract was washed with water, dried over anhydrous sodium sulfate, and evaporated to dryness *in vacuo* to yield 3.45 g. of a crude oil, homogeneous on tlc (chloroform 98-acetic acid 2). The residual oil crystallized from methanol to give 3.1 g. (82%) of **15**, m.p. 222-224°; ir: 1650 cm^{-1} (ν C=O); pmr (DMSO-d_6): δ 3.85-3.55 (m, 2, CH_2NHCO). The complex CH_2 multiplet showed marked variation by the addition of trifluoroacetic acid to the sample tube.

2,3-Dihydro-1*H*,10*H*-[4,1]benzoxazepino[3,2,1-*jk*][1,6]benzodiazocin-4(5*H*)one (**17**) (Table II, **17** and **18**).

To a stirred mixture of 2.65 g. (0.010 mole) of **13** and 0.715 g. (0.011 mole) of sodium azide in 80 ml. of chloroform, cooled in an ice bath, 10 ml. of concentrated sulfuric acid was added dropwise. After 8 minutes the brownish green reaction mixture was poured into ice-water. The chloroform layer was separated and the aqueous layer was extracted twice with chloroform. The combined organic layer was washed successively with 10% sodium hydroxide and water, dried over anhydrous sodium sulfate, and concentrated *in vacuo* to afford 2.2 g. of a 75:25 mixture of **17** and the starting material **13**. The mixture was separated by column chromatography on alumina (ratio 1:50) using benzene-chloroform (7:3) as eluent. The first component to be eluted was **13** (0.35 g., m.p. 85-87°). Fractions containing **17** were combined, evaporated to dryness; the residue was crystallized from benzene to give 1.45 g. (52%) of pure product, m.p. 198-200°; ir (chloroform): 3390 (ν NH), 1670 cm^{-1} (ν C=O).

2,3,4,5-Tetrahydro-1*H*,10*H*-[4,1]benzoxazepino[3,2,1-*kl*][1,6]-benzodiazocine Hydrochloride (**21**·HCl) [Table II, (**19-22**)·HCl].

A solution of 3.083 g. (0.011 mole) of **17** in 150 ml. of dry tetrahydrofuran was added dropwise to a stirred suspension of 1.152 g. (0.033 mole) of lithium aluminum hydride and 100 ml. of dry tetrahydrofuran. The reaction mixture was then refluxed 4 hours. After cooling, the excess of lithium aluminum hydride was decomposed by the addition of water. A 10% solution of sodium hydroxide was added until the gelatinous precipitate became granular. The precipitate was filtered and washed with tetrahydrofuran. The combined extract was dried over anhydrous sodium sulfate and evaporated *in vacuo*. The oil residue was treated with hydrochloric acid-ethyl ether to give a white solid, which was crystallized from ethanol-ethyl ether to yield 2.1 g. (63%) of **21**·HCl, m.p. 247-249° dec.; pmr (on the free base): δ 7.30-6.35 (m, 7, Ar-*H*), 5.10 (s, 2, CH_2O), 4.05-3.30 (m, 4, $NCH_2CH_2CH_2CH_2N$), 2.15-1.50 (m, 4, $NCH_2CH_2CH_2CH_2N$).

4,5,6,7-Tetrahydro[1,4]diazepino[6,7,1-*jk*]carbazole-5-carboxaldehyde (**23**) (Table II, **23** and **24**).

A mixture of 0.953 g. (0.004 mole) of **19**, 0.5 ml. of 98% formic acid and 1.2 ml. of acetic anhydride was allowed to stand at room temperature for 20 hours. It was then poured into ice-water and extracted with benzene. The benzene extract was washed with water, dried over anhydrous sodium sulfate, and evaporated to dryness *in vacuo* to give 0.950 g. (95%) of a yellow oil (**23**), homogeneous on tlc (benzene 80-methanol 15-acetic acid 5) and used in the next step without further purification.

4,5,6,7-Tetrahydro-5-methyl[1,4]diazepino[6,7,1-*jk*]carbazole (**25**) (Table II, **25** and **26**).

Following the procedure above described for preparing **21**, compound **23** gave **25** (81%), m.p. 97-99° from benzene-petroleum ether; ir: 2800-2760 cm^{-1} (ν NCH_3); pmr: δ 8.20-7.10 (m, 7, Ar-*H*), 4.30-4.05 (m, 4, $CH_2CH_2N(CH_3)CH_2$), 3.35-3.10 (m, 2, $CH_2CH_2N(CH_3)CH_2$), 2.55 (s, 3, CH_3).

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