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CARBOCYCLIC PHENYLHYDRAZINES IN THE FISCHER INDOLE SYNTHESIS—I

REACTIONS WITH CYCLOALKANONES

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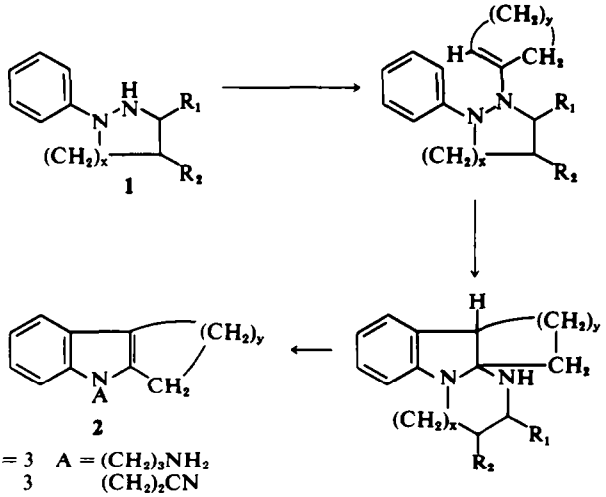
Abstract—Reactions of 1-phenylpyrazolidine with a variety of cycloalkanones yield 5-(3-aminopropyl)-cycloalk[b]indoles **2a**, **2c**, **2d**, **2e**, **2f**, **2g**; with N-benzoyl-4-piperidone the product is **3**; 2-methylcyclohexanone and 2-carbethoxycyclohexanone yield **4a** and **4b** resp. while 1,2-cyclohexanedione yields **5**.

Early in 1969 we began to investigate the use of 1-phenylpyrazolidine and some of its homologues for the preparation of substituted indoles via a modified Fischer Indole Synthesis.[1] The publication of two recent papers concerning similar work[2a,b] prompts us to disclose our own experiments.

The Fischer Indole Synthesis has been investigated extensively.[3] The great majority of the cases described in the literature deal with acyclic hydrazines which lose ammonia or the equivalent thereof during the course of the reaction with a carbonyl compound. We were interested in preventing the second nitrogen from being lost during the formation of the respective indole. This was accomplished by treating N,N′-carbocyclic phenylhydrazines e.g. 1-phenylpyrazolidines with a variety of ketones.

1-Phenylpyrazolidine **1a** (x = 1, $R_1 = R_2 = H$), although described in the literature,[4] was more conveniently prepared from the known 1-phenylpyrazolidine-3-one[5] via reduction with LAH. When equimolar amounts of 1-phenylpyrazolidine



2a:	y = 3	A = $(CH_2)_3NH_2$
2b:	3	$(CH_2)_2CN$
2c:	2	$(CH_2)_3NH_2$
2d:	4	$(CH_2)_3NH_2$
2e:	5	$(CH_2)_3NH_2$
2f:	9	$(CH_2)_3NH_2$
2g:	5	$CH_2CH(CH_3)CH_2NH_2$
2h:	3	$(CH_2)_4NH_2$
2i:	3	$(CH_2)_3CH(CH_3)NH_2$

Fig 1.

1a (as the base) and cyclohexanone were heated under reflux for 1 hr in toluene with concomitant azeotropic distillation of water,[6] 9-(3-aminopropyl)-1,2,3,4-tetrahydrocarbazole **2a** was isolated in 95% yield as the maleate salt. This compound, as well as the free base and its hydrochloride, was found to be identical in every respect (IR, NMR, UV, *m/e*, m.p. for the salts) with an authentic sample prepared by reduction of 9-(2-cyanoethyl)-1,2,3,4-tetrahydrocarbazole **2b**.[7] Similar yields of **2a** were obtained when the reactions were carried out in 95% ethanol.

The reaction between 1-phenylpyrazolidine **1a** and cyclopentanone proceeded under similar conditions as described for cyclohexanone in refluxing toluene to give 4-(3-aminopropyl)-1,2,3,4-tetrahydrocyclopent[b]indole **2c**, isolated in 85% yield as the maleic acid addition salt.

When compared with cyclohexanone, the reaction between 1-phenylpyrazolidine **1a** and cycloheptanone proceeded at a much slower rate, but it was found to be subject to acid catalysis. Therefore equimolar amounts of 1-phenylpyrazolidine **1a** hydrochloride[4] and cycloalkanones were refluxed in glacial acetic acid. The following compounds were isolated: **2a,d,e,f**.

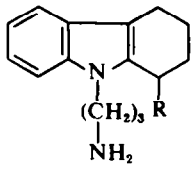
When 1 - phenyl - 4 - methyl - pyrazolidine hydrochloride **1b** (x = 1, R_1 = H, R_2 = Me) was treated with cyclooctanone the corresponding cyclooct [b]indole **2g** was isolated and characterized as the maleic acid salt in 55% yield.

9 - (4 - Aminobutyl) - 1, 2, 3, 4 - tetrahydrocarbazole **2h** was secured in good yield from the reaction between hexahydro - 1 - phenyl - pyridazine hydrochloride **1c** and cyclohexanone. Under similar conditions the same ketone yielded 9 - (4 - aminopentyl) - 1, 2, 3, 4 - tetrahydrocarbazole **2i** in 33% only when reacted with hexahydro - 1 - phenyl - 3 - methyl - pyridazine hydrochloride **1d** (x = 2, R_1 = Me, R_2 = H).

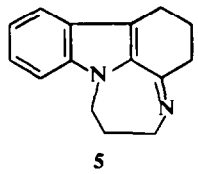
N - Benzoyl - 4 - piperidone was found to react smoothly with 1-phenylpyrazolidine **1a** (free base). The product, 5-(3-aminopropyl)-2-benzoyl-1, 2, 3, 4-tetrahydro-5H-pyrido [4,3-b] indole **3** was isolated and characterized as the maleic acid salt in good yield.

3

We now turned our attention to α-substituted cyclohexanones in the hope of learning something about the characteristics of the intermediary enehydrazine. 2-Methylcyclohexanone was refluxed with 1-phenylpyrazolidine hydrochloride **1a** in glacial acetic acid. 9-(3-Aminopropyl)-1-methyl-1, 2, 3, 4-tetrahydrocarbazole hydrochloride **4a** was isolated in 89% yield. The structure was assigned on the basis of its NMR spectrum (doublet for the methyl group at δ 1·28 ppm, J = 7 c/s). 2-Carbethoxycyclohexanone rearranged to 9-(3-aminopropyl)-1, 2, 3, 4-tetrahydrocarbazole-1-carboxylic acid ethyl ester **4b** in 82% yield when reacted with 1-phenylpyrazolidine hydrochloride **1a**.



4a: R = CH_3
4b: R = COOEt
4c: R = =O



5

The reaction between 1,2-cyclohexanedione and 1-phenylpyrazolidine hydrochloride **1a** seems to proceed in two steps. After the initial refluxing in glacial acetic acid, the crude product was treated with dry hydrogen chloride. Only then were we able to isolate 1, 2, 3, 5, 6, 7-hexahydro-[1, 4]diazepino[3, 2, 1-jk]carbazole hydrochloride **5** in reasonable yield (58%). Although analytical data is not satisfactory, spectral data nevertheless seems to indicate the presence of the tricyclic compound **4c** as the intermediate hydrochloride which slowly cyclizes to **5** in the absence of excess acid.

Table 1.

No.	m.p. of HCl salt °C	*m/e* [M⁺]	% yield
2a[a]	292	228	91
2d[b]	291	242	82
2e[c]	252	256	96
2f	236	312	90
2g	151*	270	55*
2h	186	242	67
2i	235	256	33

[a] Lit. m.p. of HCl 241°, Ref 9.
[b] Lit. m.p. of HCl 272°, Ref 8.
[c] Lit. m.p. of HCl 255°, Ref 8.
*Maleic acid addition salt.

DISCUSSION

Our experiments reacting 1-phenylpyrazolidine with cyclohexanone in toluene* clearly demonstrate that no acid is required for the formation of the enehydrazine and its subsequent [3,3] sigmatropic rearrangement to 9-(3-aminopropyl)-1, 2, 3, 4-tetrahydrocarbazole **2a**. These findings differ from what has previously been published by the Russian authors.[2a] We thus see the role of the acid

*95% ethanol may be used in place of toluene.

required in the reactions with medium sized ring ketones as that of a catalyst for the formation of the respective enehydrazines analogous to the formation of enamines.[10]

While indolization of 2-substituted cyclohexanone arylhydrazones using hydrogen chloride in acetic acid is reported to give mixtures of the corresponding indole and 3H-indole[1] we have isolated the indoles **4a** and **4b** (seemingly as the only products) in 89 and 82% yield resp.

EXPERIMENTAL

M.ps are determined on a Thomas Hoover capillary m.p. apparatus and are not corrected. NMR spectra were measured on either a Varian A-60 and/or T-60 spectrometer and are recorded in δ (ppm) values from TMS as internal standard. UV absorption spectra were measured in ethanol on a Cary spectrometer Model 14. IR spectra were taken on a Perkin-Elmer Model 257 or 457. Gas-liquid chromatography was carried out on a Hewlett-Packard 5750 Chromatograph. Mass spectra were taken on a LKB 9000 Mass spectrometer.

1-Phenylpyrazolidine **1a**. A soln of 50 g (0·31 mol) of commercial 1-phenyl-3-pyrazolidinone in 500 ml anhyd THF was added dropwise to a mixture of 15 g (0·4 mol) LAH in 150 ml THF under N_2. The resulting mixture was heated under reflux for 18 hr, cooled and then diluted with 500 ml ether. The excess reducing agent was decomposed by dropwise addition of 70 ml water. The resulting white ppt was filtered off and washed with ether. The combined filtrates were concentrated under reduced pressure leaving 45·2 g 1-phenylpyrazolidine. The free base was used without further purification; 1 component (GLC); *m/e* 148 [M⁺]. A soln of 26·5 g (0·18 mol) 1-phenylpyrazolidine in 100 ml EtOH was cooled in an ice bath and saturated with dry HCl. The product precipitated and was removed by filtration to give 30 g (91%) of **1a**.HCl, m.p. 167–168°, lit m.p. 167–168°.[4]

9-(3-Aminopropyl-1, 2, 3, 4-tetrahydrocarbazole **2a** *maleate*. A mixture of 4·5 g (0·03 mol) of **1a** and 3·0 g (0·03 mol) cyclohexanone in 75 ml toluene was heated under reflux under N_2 for 1 hr with azeotropic distillation of water.[6] To the cold soln 3·5 g (0·03 mol) maleic acid in MeOH was added. The product precipitated and was removed by filtration; yield 10·0 g (95%); m.p. 184–188°. Recrystallization from MeOH/ether gave 8·0 g (76%) of **2a**.maleate; m.p. 196–198°; *m/e* 228 [M⁺]; NMR ($CDCl_3$ + DMSO) δ 4·12 (t, 2, J = 7 c/s, indole N—CH_2) 6·14 (s, 2, CH maleic acid) 6·8–7·5 (m, 4, C_6H_4); IR (Nujol) 3100–3300 (NH) 1690; UV 228 nm (ϵ 36,300) 279 (6,500) Calcd for $C_{15}H_{20}N_2 . C_4H_4O_4$ (334·4): C, 66·3; H, 7·0; N, 8·1%.) The hydrochloride of **2a** was prepared in a similar way: m.p. 291–293°; IR (Nujol) 3000–3200 (NH); UV 231 nm (ϵ 32,800) 279 (6,350) 285 (7,040) 293 (6,450). (Found: C, 68·3; H, 8·2; N, 10·4; Cl, 13·7. Calcd for $C_{15}H_{20}N_2 . HCl$ (264·8): C, 68·0; H, 7·9; N, 10·7; Cl, 13·5%.)

A mixture of 7·4 g (0·05 mol) 1-phenylpyrazolidine and 5·5 g (0·058 mol) cyclohexanone in 80 ml toluene was refluxed for 5·5 hr with azeotropic distillation of water. The solvent was evaporated under reduced pressure and the product distilled *in vacuo*, the fraction boiling at 220–240°/0·03 mm being collected; yield 6·0 g (53%); *m/e* 228 [M⁺].

The same compound could be isolated from the acid addition salt described above following conventional procedures. NMR ($CDCl_3$) δ 1·03 (broad, 2, D_2O exchangeable, NH_2) 1·5–2·1 (m, 6) 2·4–2·9 (m, 6) 3·99 (t, 2, J = 7 c/s, indole N—CH_2) 6·8–7·6 (m, 4).

4-(3-Aminopropyl)-1, 2, 3, 4-tetrahydrocyclopent[b]*indole maleate* **2c**. A soln of 4·0 g (0·027 mol) of **1a** and 4·0 g (0·048 mol) cyclopentanone in 50 ml toluene was refluxed overnight under N_2 with azeotropic distillation of water. To the cold soln 4·0 g (0·035 mol) maleic acid in 20 ml MeOH was added to precipitate the product, m.p. 151–153°; yield 7·5 g (85%); recrystallization from MeOH/ether; m.p. 178–179°; *m/e* 214 [M⁺]; NMR $CDCl_3$ + DMSO) δ 1·8–3·2 (m, 10H) 4·11 (t, 2, J = 6·5 c/s, N—CH_2) 6·21 (s, 2, maleic acid) 6·8–7·2 (m, 4, C_6H_4); IR (Nujol) 2500–3300 (NH) 1620; UV 214 nm (ϵ 32,000) 231 (35,100) 279 (6,650) 284 (7,210) 292 (6,510). (Found: C, 65·3; H, 6·9; N, 8·4. Calcd for $C_{14}H_{18}N_2 . C_4H_4O_4$ (330·4): C, 65·4; H, 6·7; N, 8·5%).

5-(3-Aminopropyl)-5, 6, 7, 8, 9, 10-hexahydrocyclohept[b]*indole hydrochloride* **2d**. A mixture of 4·0 g (0·022 mol) of **1a** and 3·5 g (0·031 mol) cycloheptanone was refluxed in 50 ml glacial AcOH under N_2 for 1 hr. The product precipitated from the cold soln, the process brought to completion by the addition of ether; yield 5·0 g (82%); m.p. 283–284°; m.p. 290–292° after recrystallization from MeOH/ether; *m/e* 242 [M⁺]; NMR ($CDCl_3$ + DMSO) δ 1·4–2·4 (m, 8) 2·4–3·2 (m, 6) 4·23 (t, 2, J = 7 c/s, indole N—CH_2) 6·8–7·6 (m, 4, C_6H_4) 8·0–8·8 (3); IR (Nujol) 2300–3300 (NH) 1605; UV 230 nm (ϵ 32,000) 280 (6,200) 287 (7,140) 294 (6,940). (Found: C, 69·1; H, 8·3; N, 10·1; Cl, 12·6. Calcd for $C_{16}H_{22}N_2 . HCl$ (278·9): C, 68·9; H, 8·3; N, 10·0; Cl, 12·7%).

5-(3-Aminopropyl)-6, 7, 8, 9, 10, 11-hexahydro-5H-cyclooct[b]*indole hydrochloride* **2e**. Same procedure as above; yield 96%; m.p. 250–252°; *m/e* 256 [M⁺]; NMR ($CDCl_3$ + DMSO) δ 1·2–2·5 (m, 10) 2·5–3·2 (m, 6) 4·20 (t, 2, J = 7·5 c/s, N—CH_2) 6·8–7·7 (m, 4, C_6H_4) 8·0–8·8 (3); IR (Nujol) 2500-3250 (NH) 1600; UV 231 nm (ϵ 30,400) 280 (6,150) 287 (7,050) 294 (6,790). (Found: C, 69·2; H, 8·7; N, 9·6; Cl, 12·2. Calcd for $C_{17}H_{24}N_2 . HCl$ (292·85): C, 69·7; H, 8·6; N, 9·6; Cl, 12·1%).

5-(3-Aminopropyl)-6, 7, 8, 9, 10, 11, 12, 13, 14, 15-decahydro-5H-cyclodeca[b]*indole hydrochloride* **2f**. Same procedure as above; yield 90%; m.p. 234–236°; *m/e* 312 [M⁺]; NMR ($CDCl_3$ + DMSO) δ 1·0–2·5 (m, 18) 2·5–3·2 (m, 6) 4·24 (t, 2, J = 7·5 c/s, NCH_2) 6·8–7·7 (m, 4, C_6H_4) 8·1–8·8 (3); IR (Nujol) 2350–3250 (NH) 1620 (weak); UV 231 nm (ϵ 32,300) 280 (6,510) 286 (7,320) 294 (6,810). (Found: C, 71·6; H, 9·2; N, 8·1; Cl, 10·4. Calcd for $C_{21}H_{32}N_2 . HCl$ (348·96): C, 72·3; H, 9·5; N, 8·0; Cl, 10·2%).

1-Phenyl-4-methyl-pyrazolidine hydrochloride **1b**. Prepared from 1-phenyl-4-methyl-3-pyrazolidinone[11] following the procedures described for the preparation of **1a**; yield 71%; m.p. 202–204°; *m/e* 162 [M⁺]. (Found: C, 60·2; H, 7·5; N, 13·9; Cl, 18·0. Calcd for $C_{10}H_{14}N_2 . HCl$ (198·69): C, 60·4; H, 7·6; N, 14·1; Cl, 17·8%).

5-(3-Amino-2-methyl-propyl)-6, 7, 8, 9, 10, 11-hexahydro-5H-cyclooct[b]*indole maleate* **2g**. Same procedures as for **2f**; yield 55%; m.p. 150–151°; *m/e* 270 [M⁺]; NMR ($CDCl_3$ + DMSO) δ 1·0 (d, 3, J = 6 c/s, CH_3) 1·2–2·2 (m, 9) 2·6–3·2 (m, 6) 4·0 (d, 2, J = 7 c/s, N—CH_2—CH) 6·2 (s, 2, maleic acid) 6·9–7·6 (m, 4, C_6H_4); IR (Nujol) 2500–3200 (NH) 1610 (weak); UV 230 nm (ϵ 32,600) 280 (6,510) 288 (7,340) 295 (7,020). (Found: C, 67·7; H, 8·0; N, 7·2. Calcd for $C_{18}H_{26}N_2 . C_4H_4O_4$ (386·5): C, 68·4; H, 7·8; N, 7·3%).

1-Phenyl-hexahydropyridazine hydrochloride **1c**. Prepared from tetrahydro-1-phenyl-3,6-pyridazinedione[12] fol-

lowing the procedures described for the preparation of **1a**; yield 33%; m.p. 154–155°; *m/e* 162 [M⁺]. (Found: C, 60·2; H, 7·6; N, 13·9; Cl, 18·2. Calcd for $C_{10}H_{14}N_2$. HCl (198·7): C, 60·4; H, 7·6; N, 14·1; Cl, 17·8%).

9-(4-*Aminobutyl*)-1, 2, 3, 4-*tetrahydrocarbazole hydrochloride* **2h**. Same procedures as for the preparation of **2g**; yield 67%; m.p. 183–186°; *m/e* 242 [M⁺]; NMR (DMSO) δ 1·4–2·3 (m, 8) 2·3–3·1 (m, 6) 4·12 (t, 2, J = 7 c/s, N—CH_2) 6·8–7·6 (m, 4, C_6H_4). (Found: C, 69·0; H, 8·3; N, 10·0; Cl, 13·2. Calcd for $C_{16}H_{22}N_2$. HCl (278·9): C, 68·9; H, 8·3; N, 10·0; Cl, 12·7%).

1-*Phenyl*-3-*methyl-hexahydropyridazine hydrochloride* **1d**. Prepared from 4,5-dihydro-6-methyl-2-phenyl-3(2H)-pyridazinone[12] following the same procedures as described for the preparation of **1a**; yield 72%; m.p. 205–207°; *m/e* 176 [M⁺]. (Found: C, 62·4; H, 8·4; N, 13·0. Calcd for $C_{11}H_{16}N_2$. HCl (212·7): C, 62·1; H, 8·1; N, 13·2%).

9-(4-*Aminopentyl*)-1, 2, 3, 4-*tetrahydrocarbazole hydrochloride* **2i**. Same procedures as described for the preparation of **2h**; yield 33%; m.p. 233–235°; *m/e* 256 [M⁺]; NMR ($CDCl_3$ + DMSO) δ 1·22 (d, 3, J = 7 c/s, CH_3) 1·4–2·3 (m, 8) 2·3–3·5 (m, 5) 4·09 (t, 2, J = 6 c/s, N—CH_2) 6·8–7·6 (m, 4, C_6H_4) 8·2 (broad, 3); UV 231 nm (ε 33,430) 279 (6,180) 286 (6,940) 293 (6,560). (Found: C, 69·2; H, 8·7; N, 9·7; Cl, 12·7. Calcd for $C_{17}H_{24}N_2$. HCl (292·9): C, 69·7; H, 8·6; N, 9·6; Cl, 12·7%.)

5-(3-*Aminopropyl*-2-*benzoyl*-1, 2, 3, 4-*tetrahydro*-5H-*pyrido* [4, 3-*b*] *indole maleate* **3**. A mixture of 6·8 g (0·046 mol) of **1a** and 10·1 g (0·05 mol) N-benzoyl-4-piperidone was refluxed overnight under N_2 in 80 ml toluene with azeotropic distillation of water. When the cold soln was treated with 5·8 g (0·05 mol) maleic acid in MeOH the product precipitated, m.p. 170–172°, yield 15·0 g (73%). A pure sample was secured from MeOH/ether, m.p. 183–185°; NMR ($CDCl_3$ + DMSO) δ 1·8–2·4 (m, 2) 2·92 (t, 4, J = 7 c/s) 3·5–4·5 (m, 2) 4·20 (t, 2, J = 7·5 c/s, N—CH_2) 4·8 (m, 2) 6·18 (s, 2, maleic acid) 7·0–8·0 (m, 9, aromatic H); IR (Nujol) 2600–3300 (NH) 1700 (weak) 1610 (C=O); UV 225 nm (ε 22,700) 275 (7,640) 282 (7,810) 292 (6,500). (Found: C, 66·7; H, 6·0; N, 9·1. Calcd for $C_{21}H_{23}N_3O$. $C_4H_4O_4$ (449·5): C, 66·8; H, 6·1; N, 9·4%.)

9-(3-*Aminopropyl*)-1-*methyl*-1, 2, 3, 4-*tetrahydrocarbazole hydrochloride* **4a**. A mixture of 3·0 g (0·016 mol) of **1a** and 2·7 g (0·024 mol) 2-methylcyclohexanone was refluxed in 50 ml of glacial AcOH under N_2 for 1·5 hr. When the mixture was cooled the product started to precipitate. The process was completed by the addition of ether; yield 3·9 g (89%); m.p. 282–285°. After recrystallization from MeOH/ether m.p. 292–293°; yield 3·1 g (70%); a sample was dried at 110°/HV overnight; *m/e* 242 [M⁺]; NMR ($CDCl_3$ + DMSO) δ 1·28 (d, 3, J = 7 c/s, CH_3); IR (Nujol) 2500–3250 (NH) 1610 (weak); UV 231 nm (ε 30,450) 280 (6,350) 286 (7,000) 294 (6,350). (Found: C, 69·1; H, 8·2; N, 9·8. Calcd for $C_{16}H_{22}N_2$. HCl (278·8): C, 68·9; H, 8·3; N, 10·0%.)

The above hydrochloride was transferred into the maleic acid salt; m.p. 177–178°; NMR ($CDCl_3$ + DMSO) δ 1·27 (d, 3, J = 7 c/s; CH_3) 1·5–2·4 (m, 6) 2·4–3·3 (m, 5) 4·15 (t, 2, J = 7·5 c/s, N—CH_2) 6·21 (s, 2, maleic acid) 6·8–7·7 (m, 4, C_6H_4) 7·7–9·0 (3); IR (Nujol) 2650–3250 (NH) 1690 (weak); UV 230 nm (ε 36,400) 280 (7,380) 285 (7,930) 294 (7,100). (Found: C, 67·0; H, 7·3; N, 7·9. Calcd for $C_{16}H_{22}N_2$. $C_4H_4O_4$ (358·4): C, 67·0; H, 7·3; N, 7·8%.)

9-(3-*Aminopropyl*)-1, 2, 3, 4-*tetrahydrocarbazole*-1-*carboxylic acid ethyl ester hydrochloride* **4b**. A mixture of 3·0 g (0·016 mol) of **1a** and 4·0 g (0·024 mol) 2-carbethoxycyclohexanone was refluxed under N_2 in 50 ml glacial AcOH for 1·5 hr. From the cold soln the product was precipitated by the addition of ether; yield 4·5 g (82%); m.p. 163–166°. A sample was recrystallized from MeOH/ether (4x); m.p. 176–178°; *m/e* 300 [M⁺]; NMR ($CDCl_3$ + DMSO) δ 1·25 (t, 3, J = 7 c/s; CH_3) 1·5–2·5 (m, 6) 2·5–3·3 (m, 4) 3·3–3·7 (1) 3·7–4·5 (m, 4) 6·9–7·6 (m, 4, C_6H_4) 8·0–9·0 (3); IR (Nujol) 2500–3500 (NH) 1721 (C=O) 1616 (weak); UV 229 nm (ε 30,200) 279 (6,390) 285 (6,970) 293 (6,110). (Found: C, 64·0; H, 7·5; N, 8·1; Cl, 10·4. Calcd for $C_{18}H_{24}N_2O_2$. HCl (336·9): C, 64·2; H, 7·5; N, 8·3; Cl, 10·5%.)

The free base was obtained from the hydrochloride following the usual procedures; b.p. 200–230°/0·03 mm Hg; NMR ($CDCl_3$) δ 1·15 (s, 2, D_2O exchangeable, NH_2) 1·23 (t, 3, J = 7 c/s; CH_3) 1·6–2·6 (m, 6) 2·6–3·0 (m, 4) 3·8–4·4 (m, 5) 7·0–7·6 (m, 4, C_6H_4); IR (film) 3360 (NH) 1730 (C=O).

1, 2, 3, 5, 6, 7-*Hexahydro*-[1, 4]*diazepino*[3, 2, 1-jk]*carbazole* **5**. A mixture of 6·4 g (0·035 mol) of **1a** and 4·0 g (0·036 mol) 1,2-cyclohexanedione was refluxed in 80 ml of glacial AcOH under an N_2 for 2 hr. Upon the addition of ether 0·450 g product was precipitated, m.p. 282–284°, together with a dark oil which was redissolved in EtOH and treated with dry HCl. When ether was added 4·8 g product was collected as a solid; total yield 58%; m.p. 284–286°; *m/e* 224 [M⁺]. (Found: C, 69·0; H, 6·7; N, 10·4; Cl, 13·6. Calcd for $C_{15}H_{16}N_2$. HCl (260·8): C, 69·1; H, 6·6; N, 10·7; Cl, 13·6%.)

The free base was obtained from the hydrochloride following conventional procedures in 80% yield; m.p. 82–84°; NMR ($CDCl_3$) δ 1·8–2·5 (m, 4) 2·5–3·2 (m, 4) 3·9–4·4 (m, 4) 6·9–7·4 (m, 3, C_6H_3) 7·4–7·8 (m, 1, arom.) no D_2O exchangeable protons; IR (CH_2Cl_2) 1630 (C=N) 1609; UV 243 nm (ε 4,160) 311 (5,100) 340 (2,610). (Found: C, 80·0; H, 7·0; N, 12·4. Calcd for $C_{15}H_{16}N_2$ (224·3): C, 80·3; H, 7·2; N, 12·5%.)

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