Polyhalogenoaromatic Compounds. Part 49.[1] Synthesis of Carbolines by the Reaction of Enamines with Tetrachloro-4-cyanopyridine

Hans Suschitzky, Basil J. Wakefield,* and Krzyzstof Walocha
The Ramage Laboratories, Department of Chemistry and Applied Chemistry, University of Salford, Salford M5 4WT
Nigel Hughes and Anthony J. Nelson
I.C.I., PLC, Organics Division, Research Department, Hexagon House, Blackley, Manchester M9 3DA

Reactions of tetrachloro-4-cyanopyridine with 1-(dialkylamino)cyclohexenes gave tetrahydro-5*H*-pyrido[3,2-*b*]indoles and tetrahydro-9*H*-pyrido[2,3-*b*]indoles, in proportions varying with the dialkylamino-group. The tetrahydrocarbolines could be dehydrogenated by treatment with 2,3-dichloro-5,6-dicyano-1,4-benzoquinone. 2,3-Dichloro-4-cyano-9-ethyl-9*H*-pyrido[2,3-*b*]indole was synthesised independently by photolysis of trichloro-4-cyano-6-(*N*-ethylanilino)pyridine.

Attempts to prepare carbolines by an extension of Blazejewski and Wakselman's synthesis [2] of tetrafluorotetrahydrocarbazoles (see Scheme) have met with only limited success. Thus, pentachloropyridine reacted only sluggishly with enamines and the products could not be made to cyclise; cyclisation was achieved in only one product from 3,5-dichlorotrifluoropyridine.[3] One analogous example involving pentafluoropyridine has also been reported.[2]

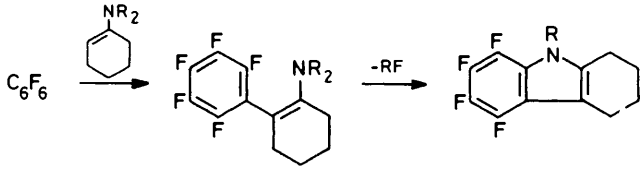
We have recently reported that ambident nucleophiles react with tetrachloro-4-cyanopyridine (1) at both the 2- and 3-positions.[1] Thus, compound (1) appeared to be a promising substrate for reactions with enamines.

The main product from a reaction in which compound (1) was heated with 1-morpholinocyclohexene *appeared* to be the desired tetrahydrocarboline (2) (*ca.* 60%). Minor products were the ketone (6) (5%), presumably arising from hydrolysis of the enamine (7), and the morpholinopyridine (8) (13%) (Table 1). The structure of the last product, compound (8), was assigned following its synthesis by the reaction of tetrachloro-6-morpholinopyridine (12) with cyanide ion, thus confirming that nucleophiles attack tetrachloro-4-cyanopyridine (1) initially at the 2-position.

Close investigation of the supposed tetrahydrocarboline (2) revealed the presence of *two* compounds which were separable by careful chromatography on alumina. The two compounds were isomers, having virtually identical mass spectra, and i.r. spectra differing only in the fingerprint region. Their ^{1}H n.m.r. spectra, however, showed small differences in the chemical shifts of the signals assigned to the NCH_2 of the side-chain (see Table 2).

We concluded that the two components were compound (2) and its isomer (13), and we provisionally assigned their structures from their n.m.r. spectra, on the basis that the chemical shift for the α-CH_2 moiety of the side-chain would be further downfield when *peri* to the cyano-group, as in compound (2). Further work, described below, confirmed this assignment.

Reactions of compound (1) with a series of enamines were carried out; the results are summarised in Table 1. The structures of the pairs of tetrahydrocarbolines were assigned from their n.m.r. spectra (Table 2) as described above for the case of compounds (2) and (13). With each enamine a similar range of products was obtained, but their proportions varied considerably. In the case of 1-(diethylamino)cyclohexene the minor product (16) was formed in only trace amounts and could not be fully characterised; the n.m.r. spectrum recorded in Table 2 was obtained from a mixture with its isomer (5). If all the products are formed *via* initial attack at C-2, then the tetrahydrocarbolines (2)—(5) and the ketone (6) arise from C-alkylation of the enamine, and the tetrahydrocarbolines (13)—(16) and the amines (8)—(11) arise from N-alkylation of the enamine. The factors governing C-*vs.* N-alkylation of enamines are not straightforward,[4] but our results show similar trends to those observed by Blazejewski and Wakselman.[2]



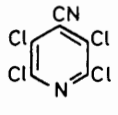
Scheme

The tetrahydrocarbolines (3), (5) and (14) were readily dehydrogenated by 2,3-dichloro-5,6-dicyano-*p*-benzoquinone (DDQ) [though not by chloranil (2,3,5,6-tetrachloro-*p*-benzoquinone)] to give the carbolines (17), (18), and (19), respectively. The carboline (20) was synthesised independently as follows. 2,3,5-Trichloro-4-cyano-6-(*N*-ethylanilino)pyridine (21) was prepared by the reaction of *N*-ethylaniline or *NN*-diethylaniline with tetrachloro-4-cyanopyridine (1). Photolysis of this intermediate (21) then gave the carboline (20) (*cf.* ref. 5). This carboline (20) differed from the one derived from the major product of the reaction of 1-(diethylamino)cyclohexene with tetrachloro-4-cyanopyridine (1); the latter carboline thus has structure (18), and its precursor tetrahydrocarboline must have structure (5). These unambiguous structure assignments confirmed our deductions from the n.m.r. spectra. In the case of the carbolines, a further indication was given by the lowest-field signals; for example, for the carboline (18) this was at δ 8.2, assigned to 9-H, whereas the corresponding (5-H) signal of the carboline (20) was shifted downfield to δ 8.4 owing to the proximity of the cyano-group.

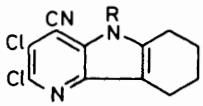
An attempt to prepare an enamine, or its cyclisation product, by the reaction of piperidine with the cyclohexanone (6) led instead to the 6-piperidino-derivative (22).

Tetrachloro-4-cyanopyridine (1) was readily oxidised to its *N*-oxide by peroxyacetic acid in the presence of sulphuric acid.[6] The *N*-oxide reacted with 1-piperidinocyclohexene mainly by N-alkylation, giving the amine (9) in 51% yield. C-Alkylation led not to a tetrahydrocarboline but to the cyclopentene (23), formed by the ring-contraction previously reported.[3]

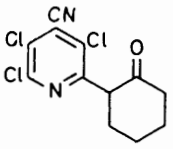
Preliminary experiments on the chemistry of the tetrahydrocarbolines have revealed that the side-chains are surprisingly unreactive. For example, when the compounds



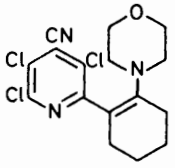
(1)



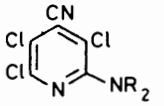
(2) R = $CH_2CH_2OCH_2CH_2Cl$
(3) R = $[CH_2]_5Cl$
(4) R = $[CH_2]_4Cl$
(5) R = Et



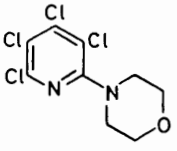
(6)



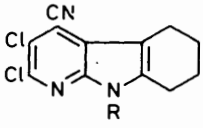
(7)



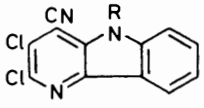
(8) R_2 =
(9) R_2 =
(10) R_2 =
(11) R = Et



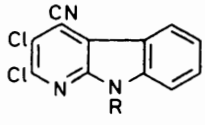
(12)



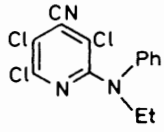
(13) R = $CH_2CH_2OCH_2CH_2Cl$
(14) R = $[CH_2]_5Cl$
(15) R = $[CH_2]_4Cl$
(16) R = Et



(17) R = $[CH_2]_5Cl$
(18) R = Et



(19) R = $[CH_2]_5Cl$
(20) R = Et



(21)

bearing *N*-(5-chloropentyl) substituents, (3) and (14), were heated with aqueous ethanolic alkali, neither this substituent nor a ring chlorine was affected. Instead, the cyano-group was hydrolysed, giving the amides, (24) and (25), respectively.

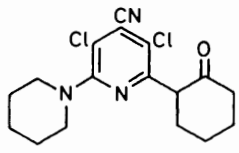
Experimental

N.m.r. spectra were recorded at 60, 80, or 90 MHz in $CDCl_3$ unless otherwise stated, with Me_4Si as internal reference.

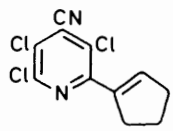
All new compounds showed the appropriate molecular-ion peaks in their mass spectra. The tetrahydrocarbolines all showed peaks at *m/z* 278 (α-cleavage of side-chain), 265 (loss of side-chain), 250 (278 − C_2H_4 by retro-Diels–Alder), and 237 (265 − C_2H_4 by retro-Diels–Alder). The carbolines all showed peaks at *m/z* 274 (α-cleavage of side-chain) and 261 (loss of side-chain).

Light petroleum refers to the fraction b.p. 60—80 °C unless otherwise stated.

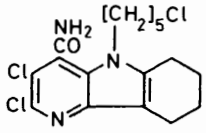
Tetrachloro-4-cyanopyridine (1) was prepared by chlorination of 4-cyanopyridine. Enamines were prepared by standard methods.[3]



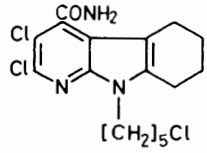
(22)



(23)



(24)



(25)

Reactions of Tetrachloro-4-cyanopyridine (1) *with Enamines.*—The freshly distilled enamine (0.01 mol) was added to a solution of tetrachloro-4-cyanopyridine (0.01 mol) in dry chlorobenzene (150 ml). The mixture was heated under reflux during 30 h and was then cooled and filtered. The filtrate was evaporated to dryness and the residue was dissolved in ethanol (50ml). The solution was cooled to −5 °C and was filtered. The components of the solid mixture thus obtained were separated by chromatography on alumina, using light petroleum–chloroform (3 : 1) as eluant. The products of the reaction are listed in Table 1 and their properties in Table 2.

2-Amino-3,5,6-trichloro-4-cyanopyridine Derivatives.—(*a*) Trichloro-4-cyano-6-piperidinopyridine (9) was prepared as previously described.[1]

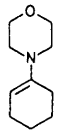
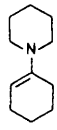
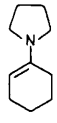
(*b*) To a stirred solution of tetrachloro-4-cyanopyridine (0.01 mmol) in ethanol (15 ml) was added a solution of pyrrolidine (0.01 mol) in ethanol (15 ml) during 30 min. The mixture was then heated under reflux during 8 h and was then cooled and poured into ice–water (100 ml). The resulting precipitate was filtered off, dried, and subjected to chromatography on silica. Gradient elution with light petroleum–toluene as eluant gave *trichloro-4-cyano-6-pyrrolidinopyridine* (10), m.p. 107.5—108.5 °C (from ethanol) with the properties listed in Table 2.

(*c*) A mixture of tetrachloro-4-cyanopyridine (0.01 mol), morpholine (0.02 mol), and acetone (100 ml) was stirred at room temperature during 30 min. The insoluble amine hydrochloride was removed by filtration and the filtrate was evaporated to dryness. The residue was recrystallised from ethanol to give *trichloro-4-cyano-6-morpholinopyridine* (8) (*ca.* quantitative) with the properties listed in Table 2.

(*d*) A mixture of tetrachloro-6-morpholinopyridine (12) (0.01 mol), potassium cyanide (0.02 mol), and dimethylformamide (200 ml) was stirred at room temperature during 24 h. The solution was filtered and the filtrate was evaporated to dryness. The residue was extracted with chloroform. The extract was evaporated to dryness and the residual brown oil was subjected to chromatography on alumina (10% methanol in light petroleum, b.p. 40—60 °C, as eluant, to give starting material (47%) and trichloro-4-cyano-6-morpholinopyridine (8) (12%), identical (m.p., mixed m.p.) with the material described above.

(*e*) A mixture of tetrachloro-4-cyanopyridine (0.01 mol), *N*-ethylaniline (0.01 mol), and 1,2,4-trichlorobenzene (100 ml) was heated under reflux during 24 h. The solvent was evaporated off under reduced pressure and the residue was dissolved in ethanol (50 ml). The solution was cooled to −5 °C and the product which crystallised out was isolated by

Table 1. Products from reactions of tetrachloro-4-cyanopyridine (1) with enamines

Enamine	Products [a]				Total products [a] from C-alkylation	Total products [a] from N-alkylation
	(2) 11	(6) 5	(13) 48	(8) 13	16	61
	(3) 42	(6) 0	(14) 41	(9) 8	42	49
	(4) 26	(6) 0	(15) 37	(10) 15	26	52
	(5) 31	(6) 8	(16) trace	(11) 25	39	25

[a] Isolated yields (%).

Table 2. Properties of products from reaction of tetrachloro-4-cyanopyridine with enamines

	M.p. (°C) [a]	^{1}H N.m.r. δ	Formula	Analyses (%) Found (Calculated) C	H	N
2,3-*Dichloro*-5-(5-*chloro*-3-*oxapentyl*)-4-*cyano*-6,7,8,9-*tetrahydro*-5H-*pyrido*[3,2-b]*indole* (2)	154	1.9 (total 4 H, m, 2 × CH_2), 2.8 (4 H, m, 2 × $=CCH_2$), 3.6 (4 H, t, 2 × OCH_2), 3.8 (2 H, t, CH_2Cl), and 4.5 (2 H, t, NCH_2)	$C_{16}H_{16}Cl_3N_3O$	51.4 (51.6)	4.3 (4.3)	11.3 (11.3)
2,3-*Dichloro*-5-(5-*chloropentyl*)-4-*cyano*-6,7,8,9-*tetrahydro*-5H-*pyrido*[3,2-b]*indole* (3)	126	1.6—1.9 (total, 10 H, m, 5 × CH_2), 2.75 (4 H, m, 2 × $=CCH_2$), 3.55 (2 H, t, CH_2Cl), and 4.3 (2 H, t, NCH_2)	$C_{17}H_{18}Cl_3N_3$	55.1 (55.1)	5.0 (4.9)	11.4 (11.3)
2,3-*Dichloro*-5-(4-*chlorobutyl*)-4-*cyano*-6,7,8,9-*tetrahydro*-5H-*pyrido*[3,2-b]*indole* (4)	143	1.7—1.9 (total 8 H, m, 4 × CH_2), 2.85 (4 H, m, 2 × $=CCH_2$), 3.55 (2 H, t, CH_2Cl), and 4.3 (2 H, t, NCH_2)	$C_{16}H_{16}Cl_3N_3$	54.0 (53.9)	4.3 (4.5)	11.8 (11.8)
2,3-*Dichloro*-4-*cyano*-5-*ethyl*-6,7,8,9-*tetrahydro*-5H-*pyrido*[3,2-b]*indole* (5)	159	1.4 (3 H, t, Me), 1.9 (total 4 H, m, 2 × CH_2), 2.75 (4 H, m, 2 × $=CCH_2$), and 4.35 (2 H, q, NCH_2)	$C_{14}H_{13}Cl_2N_3$	57.2 (57.2)	4.45 (4.45)	14.2 (14.3)
2,3-*Dichloro*-9-(5-*chloro*-3-*oxapentyl*)-4-*cyano*-5,6,7,8-*tetrahydro*-9H-*pyrido*[2,3-b]*indole* (13)	165	1.9 (total 4 H, m, 2 × CH_2), 2.9 (4 H, m, 2 × $=CCH_2$), 3.6 (4 H, t, 2 × OCH_2), 3.8 (2 H, t, CH_2Cl), and 4.35 (2 H, t, NCH_2)	$C_{16}H_{16}Cl_3N_3O$	51.7 (51.6)	4.4 (4.3)	11.3 (11.3)
2,3-*Dichloro*-9-(5-*chloropentyl*)-4-*cyano*-5,6,7,8-*tetrahydro*-9H-*pyrido*[2,3-b]*indole* (14)	139	1.6—1.9 (total 10 H, m, 5 × CH_2), 2.85 (4 H, m, 2 × $=CCH_2$), 3.5 (2 H, t, CH_2Cl), and 4.15 (2 H, t, NCH_2)	$C_{17}H_{18}Cl_3N_3$	55.0 (55.1)	5.1 (4.9)	11.5 (11.3)

Table 2 (*continued*)

	M.p. (°C) [a]	^{1}H N.m.r. δ	Formula	Analyses (%) Found (Calculated) C	H	N
2,3-*Dichloro*-9-(4-*chlorobutyl*)-4-*cyano*-5,6,7,8-*tetrahydro*-9H-*pyrido*[2,3-b]*indole* (15)	147	1.7—1.9 (total 8 H, m, 4 × CH_2), 2.9 (4 H, m, 2 × $=CCH_2$), 3.6 (2 H, t, CH_2Cl), and 4.2 (2 H, t, NCH_2)	$C_{16}H_{16}Cl_3N_3$	53.8 (53.9)	4.7 (4.5)	11.6 (11.8)
2,3-Dichloro-4-cyano-9-ethyl-5,6,7,8-tetrahydro-9*H*-pyrido[2,3-*b*]indole[8] (16)		1.3 (3 H, t, Me), 1.9 (total 4 H, m, 2 × CH_2), 2.75 (4 H, m, 2 × $=CCH_2$), and 4.2 (2 H, q, NCH_2)				
2-(*Trichloro*-4-*cyanopyridin*-2-*yl*)*cyclohexanone* (6)	150 [b]	1.7—2.7 (total 8 H, 4 × CH_2) and 4.2 (1 H, t, ArC*H*CO)	$C_{12}H_9Cl_3N_2O$	47.5 (47.5)	3.05 (3.0)	9.2 (9.2)
2,3,5-*Trichloro*-4-*cyano*-6-*morpholinopyridine* (8)	128	3.4 (4 H, t, 2 × OCH_2) and 3.8 (4 H, t, 2 × NCH_2)	$C_{10}H_8Cl_3N_3O$	41.1 (41.05)	2.7 (2.8)	14.3 (14.4)
2,3,5-Trichloro-4-cyano-6-piperidinopyridine (9)	96 [c]					
2,3,5-*Trichloro*-4-*cyano*-6-*pyrrolidinopyridine* (10)	107.5—108.5	2.00 (4 H, m, CCH_2CH_2C) and 3.85 (4 H, m, 2 × NCH_2)	$C_{10}H_8Cl_3N_3$	43.35 (43.4)	3.0 (2.9)	15.25 (15.2)
2,3-*Dichloro*-5-(5-*chloropentyl*)-4-*cyano*-5H-*pyrido*[3,2-b]*indole* (17)	168	1.5—2.1 (total 6 H, m, 3 × CH_2), 3.5 (2 H, t, CH_2Cl_2), 4.6 (2 H, t, NCH_2), 7.2—7.8 (total 3 H, 6-, 7-, and 8-H), and 8.3 (1 H, d [d], 9-H)	$C_{17}H_{14}Cl_3N_3$	55.6 (55.7)	3.9 (3.85)	11.3 (11.5)
2,3-*Dichloro*-4-*cyano*-5-*ethyl*-5H-*pyrido*[3,2-b]*indole* (18)	192	1.5 (3 H, t, Me), 4.6 (2 H, q, NCH_2), 7.2—7.8 (total 3 H, m, 6-, 7-, and 8-H), and 8.2 (1 H, d [d], 9-H)	$C_{14}H_9Cl_2N_3$	58.1 (57.95)	3.1 (3.1)	14.5 (14.5)
2,3-*Dichloro*-9-(5-*chloropentyl*)-4-*cyano*-9H-*pyrido*[2,3-b]*indole* (19)	159	1.5—2.0 (total 6 H, m, 3 × CH_2), 3.5 (2 H, t, CH_2Cl_2), 4.4 (2 H, t, NCH_2), 7.2—7.7 (total 3 H, m, 6-, 7-, and 8-H), and 8.4 (1 H, d [d], 5-H)	$C_{17}H_{14}Cl_3N_3$	55.7 (55.7)	4.0 (3.85)	11.3 (11.5)
2,3-*Dichloro*-4-*cyano*-9-*ethyl*-9H-*pyrido*[2,3-b]*indole* (20)	198	1.5 (3 H, t, Me), 4.5 (2 H, q, NCH_2), 7.2—7.8 (total 3 H, m, 6-, 7-, and 8-H), and 8.4 (1 H, d [d], 5-H)	$C_{14}H_9Cl_2N_3$	57.9 (57.95)	3.2 (3.2)	14.6 (14.5)

[a] From ethanol unless otherwise stated. [b] From hexane–toluene. [c] Lit., m.p. 90—92 °C (ref. 1). [d] Additional coupling unresolved at 90 MHz.

filtration to give *trichloro*-4-*cyano*-6-(N-*ethylanilino*)*pyridine* (21) (35%), m.p. 102 °C (from hexane); δ 1.3 (3 H, t), 4.0 (2 H, q), and 6.9—7.5 (5 H, m) (Found: C, 51.6; H, 3.1; N, 12.9. $C_{14}H_{10}Cl_3N_3$ requires C, 51.5; H, 3.1; N, 12.9%).

A similar experiment using *NN*-diethylaniline in place of *N*-ethylaniline gave the same compound (18%).

Dehydrogenation of Tetrahydrocarbolines.—The tetrahydrocarboline (0.01 mol) and DDQ (0.02 mol) were heated under reflux in chlorobenzene during 30 min. The solution was cooled and filtered, and the filtrate was evaporated to dryness. The residue was recrystallised from ethanol to give the carboline in *ca.* quantitative yield. The properties of the products (17)—(19) are listed in Table 2.

An attempted dehydrogenation with chloranil gave mainly recovered starting material, together with tars.

2,3-*Dichloro*-4-*cyano*-9-*ethyl*-9H-*pyrido*[2,3-b]*indole* (20).—A solution of trichloro-4-cyano-6-(*N*-ethylanilino)pyridine (21) (1 mmol) in dry diethyl ether (100 ml) was irradiated through a quartz filter by a medium-pressure mercury lamp during 4 h. The mixture was then evaporated to dryness and the product (87%) was purified by recrystallisation from ethanol to afford the α-*carboline* (20) with the properties listed in Table 2.

2-(3,5-*Dichloro*-4-*cyano*-6-*piperidinopyridin*-2-*yl*)*cyclohexanone* (22).—A mixture of 2-(trichloro-4-cyanopyridin-2-yl)cyclohexanone (6) (5 mmol), piperidine (5 mmol), piperidine hydrochloride (trace), and xylene (50 ml) was heated in a Dean-and-Stark apparatus during 5 h. The organic phase was then evaporated to dryness and the residue was recrystallised from ethanol to give the *title compound* (22) (68%), m.p. 157 °C; δ 1.7—2.2 (total 12 H, m, 6 × CH_2), 2.6 (2 H, t ($COCH_2$), 3.3 (4 H, m, CH_2NCH_2), and 4.1 (1 H, t, COC*H*Ar) (Found: C, 58.2; H, 5.35; N, 11.8. $C_{17}H_{19}Cl_2N_3O$ requires C, 58.0; H, 5.4; N, 11.9%).

Reaction of Tetrachloro-4-cyanopyridine N-*Oxide with Enamines.—Typical reaction.* To a refluxing solution of tetrachloro-4-cyanopyridine *N*-oxide[6] (0.01 mol) in dry chlorobenzene (150 ml) was added freshly distilled 1-piperidinocyclohexene (0.01 ml) and the mixture was heated under reflux during 30 h. The mixture was cooled and filtered and the filtrate was evaporated to dryness. Chromatography of the residue on alumina (3 : 1 light petroleum–chloroform as eluant) gave trichloro-4-cyano-6-piperidinopyridine (9) (51%) and 2,3,5-*trichloro*-4-*cyano*-6-*cyclopent*-1-*enylpyridine* (23) (15%), m.p. 108 °C (from hexane); δ 2.0 (2 H, q, $CH_2CH_2CH_2$), 2.6—3.0 (4 H, m, 2 × CH_2), and 6.95 (1 H, m, =CH) (Found: C, 48.3; H, 2.6; N, 10.4. $C_{11}H_7Cl_3N_2$ requires C, 48.3; H, 2.6; N, 10.2%).

Reactions of the Tetrahydrocarbolines (3) *and* (14) *with Alkali.*—To a solution of 2,3-dichloro-5-(5-chloropentyl)-4-cyano-6,7,8,9-tetrahydro-5*H*-pyrido[3,2-*b*]indole (3) (0.05 mol) in refluxing ethanol (500 ml) was added, dropwise, 10% aqueous potassium hydroxide (150 ml). The mixture was heated under reflux during 45 min. The solvent was then evaporated off and the residue was poured into water (500 ml). The insoluble product was recovered by filtration and was purified by chromatography on silica (9 : 1 dichloromethane–ethyl acetate as eluant) to give 2,3-*dichloro*-5-(5-*chloropentyl*)-6,7,8,9-*tetrahydro*-5H-*pyrido*[3,2-b]*indole*-4-*carboxamide* (24) (58%), m.p. 224 °C (from ethanol); $\nu_{max.}$ 3 300—3 100br and 1 690 cm^{-1}; δ 1.5—2.0 (total 10 H, m, 5 × CH_2), 2.7br (4 H, 2 × $=CCH_2$), 3.5 (2 H, t, CH_2Cl), 4.0 (2 H, t, NCH_2), and 6.1br and 6.5br (together 2 H, exchangeable with D_2O, NH_2) (Found: C, 52.5; H, 5.2; N, 10.8. $C_{17}H_{20}Cl_3N_3O$ requires C, 52.5; H, 5.2; N, 10.8%).

A similar experiment with the isomeric 9-(5-chloropentyl)-carboline (14) gave the corresponding *amide* (25) (84%), m.p. 160 °C (from ethanol); $\nu_{max.}$ 3 380, 3 200, and 1 640 cm^{-1}; δ 1.5—2.2 (total 10 H, m, 5 × CH_2), 2.7br (4 H, 2 × $=CCH_2$), 3.5 (2 H, t, CH_2Cl), 4.1 (2 H, t, NCH_2), and 6.1br (2 H, exchangeable with D_2O, NH_2) (Found: C, 52.6; H, 5.2; N, 10.8. $C_{17}H_{20}Cl_3N_3O$ requires C, 52.5; H, 5.2; N, 10.8%).

Acknowledgements

We thank I.C.I. plc for financial support and the Jagiellonian University, Krakow, for leave of absence (to K. W.).

References

1 Part 48, R. Dainter, L. Julia, H. Suschitzky, and B. J. Wakefield, *J. Chem. Soc., Perkin Trans. 1*, 1982, 2897.
2 J.-C. Blazejewski and C. Wakselman, *J. Chem. Soc., Perkin Trans. 1*, 1980, 2845.
3 H. Suschitzky, B. J. Wakefield, and J. P. Whitten, *J. Chem. Soc., Perkin Trans. 1*, 1980, 2709.
4 'Enamines: Synthesis, Structure, and Reactions,' ed. A. G. Cook, Marcel Dekker, New York, 1969; S. F. Dyke, 'The Chemistry of Enamines,' Cambridge University Press, Cambridge, 1973.
5 J. Bratt, B. Iddon, A. G. Mack, H. Suschitzky, J. A. Taylor, and B. J. Wakefield, *J. Chem. Soc., Perkin Trans. 1*, 1980, 648; E. P. Fokin, T. N. Gerasimova, T. V. Fomenko, and N. V. Semikolenova, *Zh. Org. Khim.*, 1978, **14**, 834.
6 R. Dainter, unpublished work; *cf.* G. E. Chivers and H. Suschitzky *J. Chem. Soc. C*, 1971, 2867.

Received 19*th July* 1982; *Paper* 2/1224