Tetrahedron. Vol. 29, pp. 177 to 184. Pergamon Press 1973. Printed in Great Britain

NEW ROUTES TO CONDENSED POLYNUCLEAR COMPOUNDS–VIII

SCOPE OF PHENANTHRIDINE SYNTHESIS THROUGH CYCLISATION OF HALOANILS

S. V. KESSAR,* D. PAL and M. SINGH†
Department of Chemistry, Panjab University, Chandigarh, India

(*Received in the UK* 12 *July* 1972; *Accepted for publication* 25 *August* 1972)

Abstract—The new phenanthridine synthesis based on reaction of haloanils with metal amides is of wide application. The cyclisation succeeds in presence of alkyl, alkoxy, dialkylamino, cyano, carboxy, halogeno and carbonyl groups but fails in case of nitro substituents.

The present work was undertaken to define the scope and limitations of the new phenanthridine synthesis.[1] A large number of aromatic *ortho* haloanils (**1**) or their derivatives (**4** and **7**) have been cyclised by treatment with metal amides in liquid ammonia. The results are summarised in Table 1. The substrates used for these cyclisations were either known compounds or were prepared by the methods outlined in Table 2.

It may be seen that phenanthridines bearing a variety of groups, e.g., alkyl, alkoxy, carboxyl and dimethylamino, can be obtained in excellent yields. In cyclisation of Schiff bases from *meta* substituted anilines, two products can arise due to ring closure at either of the positions *ortho* to the N atom. For instance, reaction of the anil **1h** gave a mixture of phenanthridines which, by NMR spectrometry, was found to contain 60% of 1-Me (δ2·93) and 40% of 3-Me (δ2·51) isomer.[18] Preference for cyclisation on the more hindered side, observed in the reaction of the *meta* cyano anil (**7c**) also, is rather surprising.

When electron withdrawing groups, like carbethoxy,‡ acetyl, cyano and chloro, are present on the ring undergoing electrophilic attack by benzyne, only slight lowering of the yield (~ 70%) results. However, the reaction fails with nitro anils. Free OH groups are also detrimental; the *ortho*-OH anil **1k** gave 4-hydroxyphenanthridine (**6n**) in low yield while no pure product could be obtained from the corresponding *p*-isomer. In these compounds, immediate conversion to a phenoxide should occur under the basic reaction conditions and a favourable effect on the cyclisation step could have been expected. Probably, amide ion addition to the —C═N-bond gets suppressed, to a rate below that essential[1] for the success of the reaction, since it leads to a doubly charged moiety.

Cyclisation of the anils having alkyl and alkoxy groups in the aldehyde part proceeds smoothly. However, in certain disubstituted cases§ (**1n** and **1o**, *R'* = 4,5-dimethoxy or methylenedioxy), the yield is modest. It could be due to decreased benzyne selectivity as presence of alkoxy groups is known[19] to cause such an effect by facilitating nucleophilic attack on this reactive intermediate. Thus, a larger proportion of the formed benzyne may be reacting with more abundant ammonia molecules instead of undergoing cyclisation. In the hope of achieving better discrimination, a reaction of **4b** (**4**, *R'* = 4,5-methylenedioxy) with potassium amide was carried in liquid ammonia cooled to −75°. However, no significant improvement in the yield was observed. Resort to the dihydro anil route also was unrewarding.‖ Considering this and the fact that the lowering of yield occurs only when the alkoxy groups are present in certain positions,§ the reasons for the adverse effect seem obscure.

Kondo and Uyeo[13] have reported the synthesis (1% yield) of phenanthridine **6o** (**6**, *R'* = 8,9-methylenedioxy, *R* = *R''* = H) by an Ullmann reaction of N-(6-bromo-3,4-methylenedioxybenzylidene)-*o*-bromo-aniline and give 181° as its m.p. Warren and Wright[14] have also assigned this structure to the base (m.p. 149°) secured by zinc dust distillation of Haemanthamine. The m.p. of the cyclisation product obtained in the present work is 138-9°. In view of this discrepency, its structure has been confirmed by mass spectrometry. The molecular ion peak at

---

*To whom all communication should be addressed.

†Taken in part from the Doctorate dissertation of M. Singh, Panjab University (1971).

‡Conversion to carboxamide occurs under the reaction conditions.

§The adverse effect is observed only when the two alkoxy groups are present contiguous to the formed benzyne. The cyclisation of other anils (IR = 5,6-dimethoxy and R = 4-methoxy) gives normal yields.

‖Thus any explanation of poor yield concerned with amide ion addition step seems untenable.

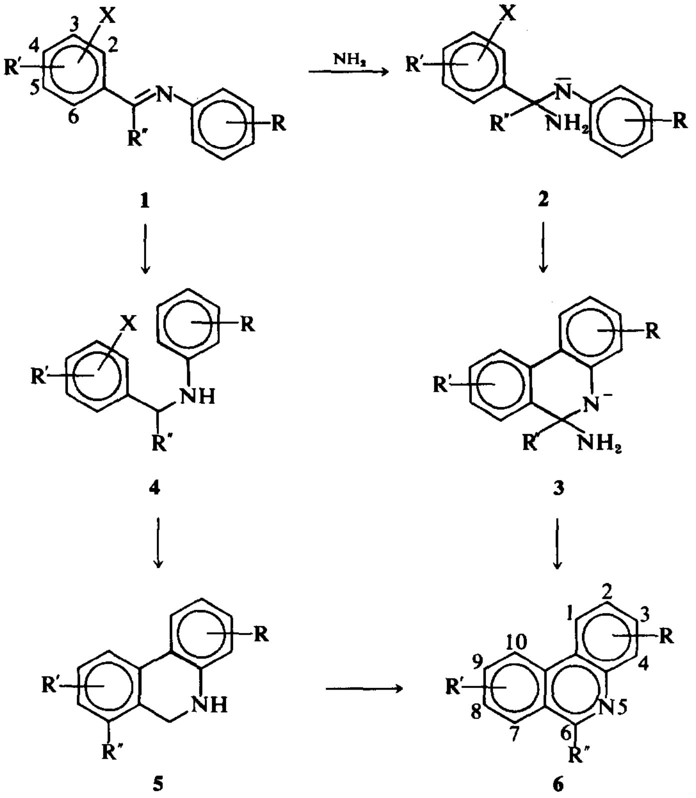
Table 1

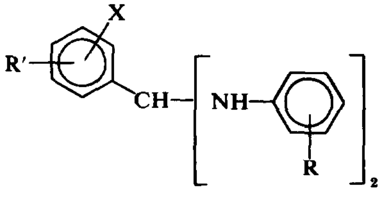
	Reactant				Reaction		Product^{a}			mp/bp	
	X	*R′*	*R″*	*R*	time		*R*	*R′*	*R″*	°C	Yield %
1a	2-Cl	H	H	H	$\frac{1}{2}$ hr	**6a**	H	H	H	105-6	> 90^{b}
1b^{2}	2-Cl	H	H	4-Me	$\frac{1}{2}$ hr	**6b**	2-Me	H	H	87-8^{3}	> 90^{b}
1c^{4}	2-Cl	H	H	2-Me	$\frac{1}{2}$ hr	**6c**	4-Me	H	H	93-4^{5}	> 90^{b}
1d^{2}	2-Cl	H	H	4-OMe	1 hr	**6d**	2-OMe	H	H	87-88	> 90^{b}
1e	2-Cl	H	H	2-OMe	$\frac{3}{4}$ hr	**6e**	4-OMe	H	H	96-7*	68^{c}
1f	2-Cl	H	H	4-COOH	1.5 hr	**6f**	2-COOH	H	H	304	> 90^{b}
1g^{7}	2-Cl	H	H	4-NMe$_2$	$\frac{1}{2}$ hr	**6g**	2-NMe$_2$	H	H	118-19	> 90^{b}
1h	2-Cl	H	H	3-Me	$\frac{3}{4}$ hr	**6h**	1-& 3-Me	H	H	40-2	70
7a	2-Cl	H	—	4-COOet	2 hr	**6i**	2-CONH$_2$	H	H	268-9	75^{c}
7b	2-Cl	H	—	4-COMe	1 hr	**6j**	2-COMe	H	H	144-45	57^{c}
1i	2-Cl	H	H	4-CN	$\frac{1}{2}$ hr	**6k**	2-CN	H	H	219-20	68^{c}
1j^{8}	2-Cl	H	H	4-Cl	$\frac{1}{2}$ hr	**6l**	2-Cl	H	H	155-6	58^{c}
7c	2-Cl	H	—	3-CN	$\frac{3}{4}$ hr	**6m**	1-CN	H	H	161-3	13^{c}
1k^{9}	2-Cl	H	H	2-OH	3 hr	**6n**	4-OH	H	H	188-89*	29^{c}
1l	2-Br	4-Me	H	H	$\frac{1}{2}$ hr	**6o**	H	9-Me	H	155-60/1mm 239-40 (picrate)^{10}	> 90^{b}
1m^{11}	3-Br	4-OMe	H	H	$\frac{1}{2}$ hr	**6p**	H	9-OMe	H	85-86 241-2 (B.HCl)^{12}	~ 90^{b}
1n	2-Cl	4,5-dimethoxy	H	H	2 hr	**6q**	H	8,9-dimethoxy	H	169-70	45^{c}
1o^{11}	2-Cl	4,5-methylenedioxy	H	H	$\frac{1}{2}$ hr	**6r**	H	8,9-methylenedioxy	H	138-9^{13,14}	13^{c}
7d	2-Br	5,6-dimethoxy	—	H	$\frac{3}{4}$ hr	**6s**	H	7,8-dimethoxy	H	121-2	69^{c}
1p	2-Cl	H	Me	H	1 hr	**6t**	H	H	6-Me	85^{15}	48^{c}
1q^{16}	2-Cl	H	Ph	H	3 hr	**6u**	H	H	6Ph	105-6^{17}	16^{c}

[a] Correct analytical data was obtained for all new products.
[b] The yield is of the crude product which was almost pure by the TLC and mp.
[c] The crude product was impure and the yield is for the pure crystallised material.
*Berlin *et al.*, report 140–2° as the m.p. of **6e**. Its structure was confirmed by demethylating it to **6n**.

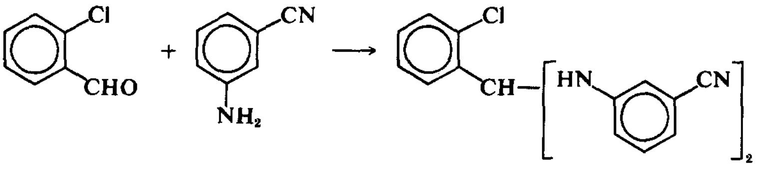
Table 2

	Product				Method of	m.p./b.p.		Analysis	
								Found	Required
	X	*R*	*R'*	*R''*	preparation	°C	Yield %	N%	N%
1e	2-Cl	2-OMe	H	H	C	155–60/1 mm	76	5·80	5·70
1f	2-Cl	4-COOH	H	H	B	218–19 (EtOH)	90	5·76	5·39
1g	2-Cl	4-NMe_2	H	H	B	67–8 (EtOH)[7]	85	11·24	10·83
1h	2-Cl	3-Me	H	H	A	154–6/2 mm	79	6·11	6·10
1i	2-Cl	4-CN	H	H	B	113–15 (EtOH)	63	7·70	7·10
1l	2-Br	H	4-Me	H	B	170–5/1 mm	89	6·28	5·11
1n	2-Cl	H	4,5-dimethoxy	H	B	102–3 (EtOH)	85	5·45	5·08
7a	2-Cl	4-COOet	H	—	B	95–6 (EtOH)	80	6·48	6·19
7b	2-Cl	4-COMe	H	—	B	113–5 (EtOH)	66	11·23	11·64
7c	2-Cl	3-CN	H	—	B	71–2 (EtOH)	80	15·66	15·63
7d	2-Br	H	5,6-dimethoxy	—	B	70-2 (pet. ether: ether)	85	6·88	6·78

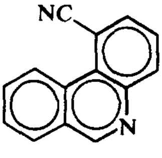




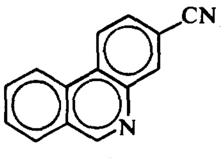
7



7c



6m

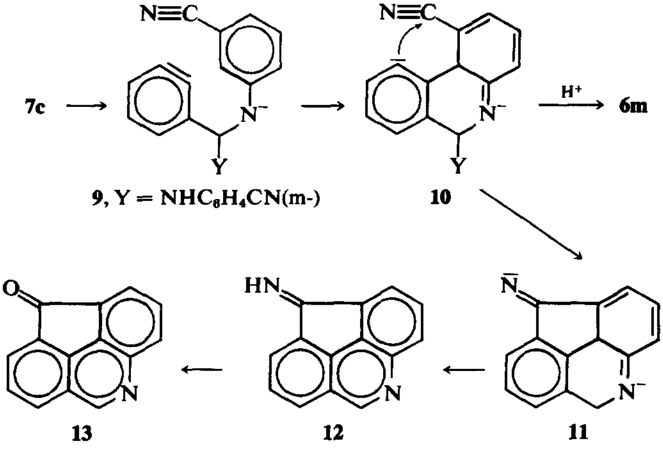


8

m/e 223 and a doubly charged ion (M^{++}) at 111·5 are very prominent in the spectrum.[20] Also the fragment corresponding to a loss of CH_2O (M-30) is clearly observable.[21]

The synthetic sequence starting with *m*-cyanoaniline has shown some unexpected results. Condensation of *o*-chlorobenzaldehyde and *m*-cyanoaniline gave the amine **7c**. By analogy with other such adducts,[1] reaction of this material with potassium amide in liquid ammonia was expected to give a mixture of 1- and 3-cyanophenanthridines. Indeed, two pure products (A and B) were isolated. One of these (A, m.p. 161–3°, 13% yield) was found to be a cyanophenanthridine; IR 2210 cm^{-1} (—C≡N); mass spectrum, m/e 204 (M^+), 177 (M-HCN) and 102 (M^{++}). A decision between structure **6m** and **8** for this compound (A) could be made on basis of two features of its NMR spectrum – a slightly broadened doublet (1H) at δ9·6 and absense of any singlet in δ8·2 region (characteristic for H-4 in phenanthridines). The former signal can arise from H-10 of structure **6m**, its exceptionally low field position being a consequence of close proximity to the cyano group. From the models it can be seen that the line joining this proton to the mid point of the cyano group, located at C-1, makes almost a right angle with the axis of the latter. If effects due to nitrogen are ignored and normal acetylenic anisotropy is assumed,[22] the proton (H-10) falls in a strongly deshielding region. In structure **8**, on the other hand, no signal below δ9·2 (H-6 signal) is expected.

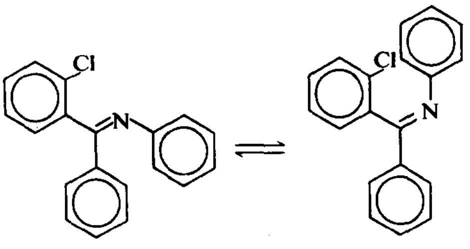
The IR spectrum of compound B (m.p. 245–6°) was devoid of any peak corresponding to a cyano group but exhibited absorption in the CO region. The molecular ion (M^+) in its mass spectrum appeared at m/e 205 instead of at m/e 204 calculated for a cyanophenanthridine. That the m/e 205 peak represented the molecular ion was confirmed by the presence of a strong doubly charged ion (M^{++}) at m/e 102·5. On basis of this and the analytical data, structure **13** was ultimately assigned to the compound B. The most abundant fragment, m/e 177 (M-28), in the mass spectrum of B can be easily visualised to arise from expulsion of a CO moiety[23] from **13**. Genesis of this fragment primarily through loss of H_2CN is unlikely as corresponding fragments in phenanthridines appear only in low inten-



sity.* Direct formation of the ion m/e 177 from the molecular ion is substantiated by observation of an appropriate metastable peak at m/e 152·9.

Formation of the tetracyclic compound **13** in reaction of **7c** with potassium amide can be rationalised in terms of a nucleophilic attack by the formed carbanion **10** on the proximate cyano group.† This type of cyclisation, entailing joining of both the benzyne carbons with two remote points on the side chain, does not seem to have been reported earlier. Its potential for synthesis of condensed polynuclear systems merits further investigation.

Cyclisation of Schiff bases in which the hydrogen of the azomethine linkage is replaced by an alkyl or aryl group was found to afford 6-substituted phenanthridines only in poor yields. It is interesting to note that, in contrast to **1**, the condensate from



1q **14**

o-chlorobenzophenone and aniline is likely to contain a substantial proportion of the *cis* isomer (**14**), yet the yield in its cyclisation is inferior. This offers indirect support for the postulated reaction mechanism[1] as an opposite trend should be observed if a direct cyclisation was taking place. The amide ion addition, on the other hand is expected to be less facile with the more substituted Schiff bases.

In view of the potential of this cyclisation as a commercial source for phenanthridine compounds, variation of the experimental conditions has been investigated to some extent. It was found that use of potassium or sodium amide caused no difference in the yield. Further, increase in concentration had little effect and 5 g batches of haloanils could be efficiently cyclised in 500 ml of liquid ammonia. Attempts to cyclise haloanils (**1**), or the dihydroderivatives (**4**), were unsuccessful when molten potassium hydroxide, potassium t-butoxide in DMSO or lithium piperidide in ether were used as bases. In reaction with a pre-formed complex of sodamide and sodium t-butoxide, a mixture of phenanthridine (**6a**) and 5,6-dihydrophenanthridine (**5a**) was obtained in a low yield.‡ Aprotic solvents are inferior for this cyclisation probably because of an unfavourable competition between the carbon and nitrogen, internal or external, nucleophiles for attack at the benzyne intermediate. It is well known that in protic solvents, as compared to aprotic ones, the proportion of attack by the less electronegative site of an ambident anion increases, presumably due to a differential protective solvation (hydrogen bonding) of the other.[24]

Ethylenediamine is a protic solvent, which can be easily handled at room temperature and has p*Ka*, dipole moment and dielectric constant similar to that of liquid ammonia.[25] In this medium reaction of the dihydroanil **4a** (**4**, X = 2-Cl, $R = R' = R'' = \mathrm{H}$) with sodamide gave a mixture (70% **5a** and 10% **6a**) from which, after oxidation with MnO_2, pure phenanthridine could be isolated in 62% yield. It seems that in some other benzyne reaction also ethylenediamine may prove a suitable alternate for liquid ammonia, especially when solubility of a large organic molecule is a concerned factor.

In the end it may be summarised that for obtaining many types of phenanthridine derivatives, reaction of haloanils with amide ions in liquid ammonia seems to be the most advantageous method.§ Experimentally the reaction is simple and pure products can often be obtained without resort to chromatography etc. Preliminary work has shown that reactions involving dehydroaromatic intermediates other than benzyne are feasible and cyclisation on to hetero rings is also successful.[26] A variety of new ring systems thus become readily accessible.

EXPERIMENTAL

M.p.'s and b.p.'s are uncorrected. NMR spectra were recorded on a Varian HA-100. Mass spectra (70 e/V) were recorded on a MS-9 spectrometer.

Preparation of anils

Method A. Equimolar amounts of the haloaldehyde and the aromatic amine were heated in a test tube at 110° (oil bath). Water started to condense on the sides of the test bue and was wiped off with a cotton plug. When the water formation stopped, the residue was distilled under reduced pressure. The distillate was used directly or crystallised from a suitable solvent.

Method B. A soln of equimolar quantities of the haloaldehyde and the amine in etOH was refluxed for 2 hr. It was concentrated and cooled to furnish the pure condensation product.

Method C. A toluene soln of the amine (1 mole) and excess haloaldehyde (2·5 mole) was refluxed for 8 hr in a Dean and Stark apparatus. Solvent was removed and the residue distilled to give the pure Schiff base. The distillate was used directly or crystallised from a suitable solvent.[27]

Cyclisation of haloanils (**1**). All cyclisations were

---

*The intensity of M-28 fragment in A is 4·5% as compared to 25% in B.

†The actual sequence of steps can be different from the one depicted e.g. attack on the cyano group may occur later than the aromatisation of the ring carrying this group.

‡Direct cyclisation of the anil **1a** was unsuccessful under these conditions.

§For a comparative study of already known routes: see Doctorate dissertation of M. Singh, Panjab University, 1971, p. 11.

carried according to the general procedure.[1] Cases where significant variations were employed in the work up procedure are described.

1- *and* 3-*Methylphenanthridine* (**6h**). Reaction of the anil **1h** (1 g, 4·36 mmole) with KNH$_2$ (from 1·014 g, 26·14 mmole, K metal) for 45 min gave an oil (820 mg), TLC (light petroleum : ether, 1 : 1) of which showed two spots (major ~ 80%). The mixture could not be separated by column chromatography. Part of the oil was then sublimed under reduced pressure and then crystallised from light petroleum containing a drop of Me$_2$CO to give a solid (one spot on TLC in several solvent systems); m.p. 40–42°; NMR (CDCl$_3$) δ2·93 (*s*, 1-CH$_3$),[18] δ2·51 (*s*, 3-CH$_3$). (Found: N, 7·76. C$_{14}$H$_{11}$N requires: N, 7·25%).

Phenanthridine-2-*carboxamide* (**6i**). The amine **2a** (0·5 g, 1·1 mmole) was treated with KNH$_2$ (from 407 mg, 10·43 mmole, K metal) for 2 hr. After work up the mixture was extracted with ether and the residue was filtered. Ether extract was washed with H$_2$O and dried. Removal of solvent afforded a gummy solid (280 mg). It was crystallised from light petroleum (residue – 40 mg) to give *p*-carbethoxy aniline (100 mg), m.p. 88–9°, undepressed on admixture with an authentic sample: (Lit.[28] mp 89–90°).

The combined residue was washed with H$_2$O and dried (183 mg, 75%). Crystallisation from EtOH afforded pure **6i**, m.p. 268–9°. (Found: N, 12·8. C$_{14}$H$_{10}$N$_2$O requires: N, 12·61%).

Reaction of N-(2-*chloro*-5-*nitrobenzylidene*)-*aniline* (**1s**) *with potassium amide*. The anil[29] **1s** (810 mg, 3·11 mmole) was treated with KNH$_2$ (from 728 mg, 18·66 mmole, K metal), for 45 min. A very deep red colour appeared immediately on addition of the anil. After the usual work up the mixture was extracted with EtOAc. The insoluble residue was filtered, washed with H$_2$O and dried. Evaporation of the EtOAc soln gave a dark oil. Both the oil and the residue gave positive Beilstein's test for halogens and were not investigated further.

Reaction of N-(2-*chlorobenzylidene*-p-*nitroaniline* (**1r**) *with potassium amide*. The anil[30] **1r** (0·5 g, 1·92 mmole) was treated with KNH$_2$ (from 0·75 g, 19·2 mmole, K metal) for 45 min. The usual work up afforded an oil giving a positive halogen test. It was found to contain (TLC) *p*-nitroaniline along with five other components.

Demethylation of 4-*methoxyphenanthridine* (**6e**). A soln of **6e** (100 mg) in 48% HI (3 ml) and AcOH (3 ml) was refluxed for 6 hr. The mixture was dried under vacuum and the gummy solid washed well with ether and H$_2$O. The residue was crystallised twice from Me$_2$CO to afford a white solid (20 mg), m.p. 185–6°.

4-*Hydroxyphenanthridine* (**6n**). The anil[9] **1k** (5 g, 21·6 mmole) was treated with KNH$_2$ (8·426 g, 0·216 mole, K metal) for 3 hr. To the residue left after the evaporation of NH$_3$, H$_2$O (100 ml) was added and the mixture filtered to get a solid (3·9 g). It was washed with ether (5 × 10 ml) and then taken up in Me$_2$CO. An insoluble material (700 mg) was filtered off and the filtrate concentrated and chilled to afford a solid (1·2 g, 29%, m.p. 182–5°) which was sublimed at 95°/1 mm and crystallised from Me$_2$CO to give pure **6n**, m.p. 188–9°. No m.p. depression was observed on admixture with the solid obtained above on demethylation of **6e**. (Lit.* m.p. 186–8°). (Found: N, 7·79; Calc. for C$_{13}$H$_9$NO: N, 7·17%).

Reaction of 4-[(2-*chlorobenzylidene*)*amino*]-*phenol* (**1t**) *with potassium amide*. Reaction of **1t** (1 g, 4·32 mmole) with KNH$_2$ (from 1·011 g, 25·92 mmole, K metal) gave an oil (562 mg) and a polymeric ether insoluble solid (m.p. > 310°). TLC (light petroleum : ether, 2 : 1) of the oil showed three major spots of nearly equal intensity. Its IR spectrum did not exhibit absorption corresponding to a dienone group[31] (near 1668 cm^{-1}).

8,9-*Methylenedioxyphenanthridine* (**6r**). Reaction of **1o** (2 g, 7·7 mmole) with KNH$_2$ (from 1·803 g, 46·24 mmole, K metal) gave a gummy solid (1·2 g) along with a considerable amount of tar. It was chromatographed over basic Al$_2$O$_3$ (30 g). Elution with light petroleum : benzene (10 : 1) afforded **6r** (225 mg, 13%); m.p. 138–39° (EtOH); (Lit.[13,14] m.p. 181°, m.p. 149°); mass spectrum (70 e/V) *m*/*e* (rel intensity) 224 (17·5), 223 (100), 193 (1·8), 167 (5·5), 166 (4), 165 (8·7), 164 (11), 139 (6·6), 138 (21), 137 (6·6), 128 (2·9), 112 (3·6), 111·5 (14·6), 111 (20). (Found: C, 74·6; H, 4·0; N, 6·71. Calc'd for C$_{14}$H$_9$NO$_2$ C, 75·34; H, 4·03; N, 6·28%).

8,9-*Methylenedioxyphenanthridine* (**6r**) *subjected to reaction conditions*. The phenanthridine **6r** (100 mg) was treated with KNH$_2$ (from 110 mg, K metal) for 1·5 hr and isolated according to the general procedure. The crude solid (90 mg, 137–9°) showed only one spot on TLC (light petroleum : ether, 1 : 1) and was identical with the starting material.

2-*Chloro*-4,5-*methylenedioxybenzylaniline* (**4**). A soln of **1o** (2 g, 7·7 mole) in EtOH (15 ml) was treated with NaBH$_4$ (320 mg, 8·47 mmole) and then heated at 50° for 2 hr. The mixture was decomposed with H$_2$O (100 ml) and extracted with ether. The ether extract was washed with H$_2$O and dried. The solvent was removed and the residual solid was crystallised from EtOH to give **4b** (1·71 g, 85%, m.p. 85–6°). (Found: N, 4·9, C$_{14}$H$_{12}$ClNO$_2$ requires: N, 5·35%).

Reaction of 2-*chloro*-4,5-*methylenedioxybenzylaniline* (**4b**) *with potassium amide*. Reaction of **4b** (1 g, 3·82 mmole) with KNH$_2$ (895 mg, 22·94 mmole, K metal) gave an oil (610 mg) along with considerable tarry material. TLC (light petroleum : ether, 1 : 1) of the crude oil showed 6 spots (major ~ 30%). The crude oil was chromatographed over basic Al$_2$O$_3$ (20 g). Elution with light petroleum : benzene (10 : 1) afforded **6r**: (128 mg, 15%); m.p. 138–9° (EtOH).

Reaction of N-(2-*chloro*-4,5-*methylenedioxybenzylidine*)-*aniline* (**1o**) *with potassium amide at* –75°. To a stirred suspension of KNH$_2$ (from 450 mg, 11·53 mmole, K metal) in liquid NH$_3$ cooled (–75°) by a Me$_2$CO-solid CO$_2$ bath, was added the anil **1o** (0·5 g, 1·92 mmole). The mixture was stirred for 3 hr and decomposed with NH$_4$Cl. NH$_3$ was evaporated, H$_2$O (200 ml) added and the suspension extracted with ether. Ether extract was washed with H$_2$O and dried. Solvent was removed to afford an oil (220 mg). The oil on TLC [light petroleum : ether : EtOAc, 1 : 1 : 5] showed a mixture similar to the one obtained in the reaction at – 33°.

1-*Cyanophenanthridine* (**6m**) and 9H-*cyclopenta*(1,m, n)*phenanthridin*-9-*one* (**13**). Reaction of **7c** (1·4 g, 3·9 mmole) with KNH$_2$ (1·817 g, 46·57 mmole, K metal) for 45 min using chloroform for extraction, gave a gummy solid (500 mg). TLC (light petroleum : ether, 1 : 1) of which showed six spots (two major ~ 35% each). It was chromatographed over basic Al$_2$O$_3$ (20 g). Elution with light petroleum : benzene (10 : 1) afforded a solid (100 mg, 13%); m.p. 161–3°. It was crystallised from light petroleum to give pure **6m**; m.p. 163°; IR (KBr) 2210 cm^{-1} (—C≡N); NMR (CDCl$_3$) δ9·6 (d, 1, J ~ 4 cs, H-10), δ9·2 (*s*, *l*, H-6), δ8·34 (*d*, *l*, *J* ~ 4 cs, H-4), δ8·04–7·6 (*m*, 5, H-2,3,7,8,9);

---

*Berlin *et al.*, report 140–2° as the m.p. of **6e**. Its structure was confirmed by demethylating it to **6n**.

mass spectrum (70 e/V) *m/e* (rel intensity) 205 (15·7), 204 (100), 203 (17·4), 177 (6·7), 176 (4·5), 102 (10), 75 (6·7), 28 (19·4). (Found: N, 13·87. $C_{14}H_8N_2$ requires N, 13·72%).

Further elution with light petroleum: benzene (10:2 and 10:3) gave a solid (165 mg, 21%); m.p. 243–5°. It was crystallised from EtOAc to give pure **13**, m.p. 245–6°; IR (KBr) 1700 cm^{-1} (C=O); mass spectrum (70 e/V) *m/e* (rel intensity) 205 (100), 177 (25), 176 (4), 150 (9), 110 (60), 102·5 (5·5), 75 (10), 28 (8·6). (Found: C, 81·51; H, 3·60; N, 6·86. $C_{14}H_7NO$ requires: C, 81·94, H, 3·44; N, 6·83%).

Authentic 6-*methylphenanthridine* (**6t**). The method has been adapted from the procedure of Gilman and Nelson[32] for the preparation of 6-phenylphenanthridine. To a stirred soln of phenanthridine (0·5 g, 2·79 mmole) in ether (15 ml), under dry N_2, was added MeLi (3·35 mmole) in ether (10 ml) over a period of 1 hr. On addition of excess MeLi the soln became clear having a bluish green fluorescence. It was stirred for 4 hr and decomposed with ice water. The ether layer was washed with H_2O, dried and the solvent was removed. Nitrobenzene (5 ml) was added to the residue and the mixture was refluxed for 30 min to oxidise any dihydro product formed during the reaction. The nitrobenzene was removed under reduced pressure (2 mm). The residue was taken up in MeOH and treated with charcoal and the solvent evaporated. The solid obtained was crystallised from light petroleum to afford **6t** (260 mg, 48%): m.p. 80–2°; (Lit.[15] m.p. 85°).

N-*(2-Chloro-α-methylbenzylidene)-aniline* (**1p**). Reaction of *o*-chloroacetophenone (8 g, 5·18 mmole) and ethyl orthoformate (8·5 g, 5·74 mmole) in EtOH (10 ml) containing a drop of HCl, according to the procedure of Claisen,[33] gave 2-chloroacetophenone acetal (6·4 g, 54%); b.p. 125°/15 mm.

A mixture of the above acetal (3·3 g, 14·44 mmole) and aniline (1·34 g, 14·44 mmole) was refluxed for 45 min.[34] It was then distilled under reduced pressure to give **1p** (2·5 g, 75%); b.p. 147–50°/0·5 mm. (Found: N, 5·87. $C_{14}H_{12}ClN$ requires: N, 6·1%).

6-*Methylphenanthridine* (**6t**). Reaction of **1p** (1 g, 4·36 mmole) with KNH_2 (1·02 g, 26·1 mmole, K metal) for 1 hr gave an oil (530 mg) along with some tar. TLC (light petroleum: ether, 1:1) showed five spots (major ~ 60%). It was chromatographed over basic Al_2O_3 (20 g). Elution with light petroleum afforded a solid (252 mg, 30%; m.p. 80–2°). Crystallisation from light petroleum gave pure **6t**, m.p. 85°, undepressed on admixture with the authentic sample prepared above.

6-*Phenylphenanthridine* (**6u**). Reaction of **1q**[16] (0·5 g, 1·72 mmole) with KNH_2 (401 mg, 10·42 mmole, K metal) for 3 hr gave an oil (250 mg) along with some tar. TLC (light petroleum: ether, 1:1) showed eight spots (major ~ 30%). It was chromatographed over basic Al_2O_3 (20 g). Elution with light petroleum: benzene (20:1) afforded a solid (70 mg, 16%), m.p. 103–5°. It was crystallised from light petroleum to give pure **6u**, m.p. 105–6°, undepressed on admixture with an authentic sample (Lit.[32] m.p. 105–6°).

Reaction of N-*phenyl-2-chlorobenzylamine* (**4a**) *with sodamide/sodium t-butoxide in tetrahydrofuran.* A. To a suspension of $NaNH_2$ (628 mg, 16·1 mmole) in anhyd THF (30 ml) was slowly added t-BuOH (425 mg, 5·74 mmole) in THF (4 ml), maintaining the temp. below 30°.[35] After the addition, stirring was continued for 2 hr at 45°. The amine **4a** (0·5 g, 2·3 mmole) in THF (5 ml) was then added quickly to the stirred mixture. A red colour appeared on addition which finally changed to deep brown. The mixture was stirred at 45° for 4 hr and decomposed with H_2O (100 ml). It was then extracted with ether, washed with H_2O and dried. Removal of solvent gave an oil (350 mg). TLC (light petroleum: ether, 2:1) showed it to be consisting of starting material (20%), **5a** (50%) and **6a** (15%).

The above material in $CHCl_3$ (10 ml) was stirred with MnO_2 (2 g) for 2 hr. It was filtered and the residue washed well with $CHCl_3$. Removal of solvent gave an oil (270 mg) which was chromatographed over basic Al_2O_3 (15 g). Elution with light petroleum (60–80°) afforded **6a** (150 mg, m.p. 101–3°, 36%). It was crystallised from light petroleum to afford pure **6a**: m.p. 104–5° B. The amine **4a** (0·5 g, 2·3 mmole) was treated with t-BuOH (425 mg, 5·74 mmole) and $NaNH_2$ (897 mg, 23 mmole) in THF (30 ml) for 6 hr according to the procedure described above. Removal of solvent gave an oil which on TLC (light petroleum: ether, 2:1) showed only 30% **6a**.

Reaction of N-*(2-chlorobenzylidene)-aniline* (**1a**) *with sodamide/sodium t-butoxide in tetrahydrofuran.* The anil **1a** (0·5 g, 2·32 mmole) was treated (5 hr) with $NaNH_2$ (726 mg, 18·6 mmole) and t-BuOH (429 mg, 5·8 mmole) according to the procedure described above. The usual work up gave an insoluble fluffy material (300 mg) and an oil. None of these revealed the presence of phenanthridine by TLC.

Reaction of N-*phenyl-2-chlorobenzylamine* (**4a**) *with sodamide in ethylenediamine.* A mixture of $NaNH_2$ (1·256 g, 32·2 mmole) and EDA (30 ml) was refluxed for 15 min. To this soln **4a** (1 g, 4·6 mmole) in EDA (5 ml) was added. After 30 min refluxing a 4 ml portion of the mixture was decomposed with H_2O (25 ml). It was extracted with ether, washed with H_2O and dried. TLC (light petroleum: ether, 2:1) showed the presence of **5a** (70%), benzylaniline (10%), **6a** (10%) and about 10% of the material remained at the base.

The remaining mixture on decomposition, after1 hr, with H_2O (200 ml) gave a gummy solid (959 mg), which was taken up in light petroleum and the residue (62 mg) was discarded. From the filtrate no solid could be obtained by crystallisation (light petroleum). The material was oxidised by stirring with MnO_2 in $CHCl_3$ and chromatographed over basic Al_2O_3 (40 g). Elution with light petroleum gave benzylaniline as an oil (60 mg). Further elution with light petroleum: benzene (5:1) gave **6a** (516 mg, 63%); mp 103–4° undepressed on admixture with an authentic sample.[17]

Reaction of N-*(2-chlorobenzylidene)-aniline* (**1a**) *with sodamide in ethylenediamine.* Reaction of **1a** (1 g, 4·64 mmole) with $NaNH_2$ (1·267 g, 32·48 mmole) in EDA (30 ml) according to the procedure described above for 1 hr gave an oil and considerable amount of an insoluble fluffy material. TLC (light petroleum: ether, 2:1) showed 3 spots (major ~ 50%) but none of these corresponded to **6a**.

REFERENCES

[1] S. V. Kessar, R. Gopal and M. Singh, *Tetrahedron.*

[2] M. Nakamura, K. Komatsu, Y. Gondo, H. Ohta and Y. Ueda, *Chem. Pharm. Bull. Tokyo* **15**, 585 (1967); *chem. Abstr.* **67**, 53450m (1967).

[3] C. L. Arcus and M. M. Coombs, *J. Chem. Soc.* 4319 (1954).

[4] S. M. Sherlin, *J. Gen. Chem. USSR* **6**, 508 (1936); *Chem. Abstr.* **30**, 5570 (1936).

[5] J. Kenner, W. H. Ritchie and F. S. Statham, *J. Chem. Soc.* 1169 (1937).

[6] A. Ya. Berlin and T. P. Sycheva, *Zh. Obshch. Khim.* **22**,

2003 (1952); *Chem. Abstr.* **47**, 9330b (1953).

[7] G. Ed. Utzinger and F. A. Regenass, *Helv. Chim. Acta* **37**, 1901 (1954).

[8] A. Hantzsch and O-Schwab, *Ber. Dtsch. Chem. Ges.* **34**, 832 (1901).

[9] F. Mayer, and A. Bansa, *Ibid.* **54**, 23 (1921).

[10] M. S. Gibson, *J. Chem. Soc.* 1076 (1956).

[11] T. S. Wheeler, and R. G. Naik, *Ibid.* 1780 (1938).

[12] T. R. Govindachari, B. R. Pai and V. N. Sundararajan, *Ibid.* 1715 (1950).

[13] H. Kondo and S. Uyeo, *Ber. Dtsch. Chem. Ges.* **68**, 1756 (1935).

[14] F. L. Warren and W. G. Wright, *J. Chem. Soc.* 4696 (1958).

[15] C. L. Arcus and M. M. Coombs, *Ibid.* 4319 (1954).

[16] C. Graebe and F. Keller, *Ber. Dtsch. Chem. Ges.* **32**, 1687 (1899).

[17] P. Friedlander and A. Weinberg, *Ibid.* **15**, 2679 (1882).

[18] B. R. T. Keene and P. Tissington, *J. Chem. Soc.* 3032 (1965).

[19] R. W. Hoffmann, *Dehydrobenzene and Cycloalkynes* p. 246. Academic Press, New York (1967); E. R. Biehl, E. Nieh and K. C. Hsu, *J. Org. Chem.* **34**, 3595 (1969).

[20] Q. N. Porter and J. Baldas, *Mass Spectrometry of Heterocyclic Compounds* p. 419. Wiley Interscience, New York (1971).

[21] M. Sainsbury, S. F. Dyke and B. J. Moon, *J. Chem. Soc.* (C), 1797 (1970).

[22a] L. M. Jackmann, *Applications of Nuclear Magnetic Resonance in Organic Chemistry* (1st Ed.) p. 18. Pergamon Press, New York (1964).

[b] K. D. Bartle and J. A. S. Smith, *Spectrochim. Acta* Part A, **23**, 1715 (1967); *Chem. Abstr.* **67**, 86364q (1967).

[23] J. H. D. Eland and C. J. Danby, *J. Chem. Soc.* 5937 (1965).

[24] N. Kornblum, R. A. Smiley, R. K. Blackwood and D. C. Iffland, *J. Am. Chem. Soc.* **77**, 6269 (1955).

[25a] C. D. Hodgman, *Handbook of Chemistry and Physics* (44th Ed.) p. 2631 and 2634. The Chemical Rubber Pub. Co., Ohio (1962).

[b] N. A. Lange, *Handbook of Chemistry* (8th Ed.) pp. 1253–4. Handbook Pub. Inc., Ohio (1952).

[26] S. V. Kessar, M. Singh, P. Jit, G. Singh and A. K. Lumb, *Tetrahedron Letters* 471 (1971).

[27] E. W. Nasiruddin and M. Latif, *Chem. Ind.* 51 (1969).

[28] I. Heilbron, *Dictionary of Organic Compounds* (4th Ed.) p. 338. Eyre and Spottis-woode, London (1965).

[29] Cohn and Blau, *Montash Chemi* **25**, 369 (1907).

[30] F. Mayer and B. Stein, *Ber. Dtsch. Chem. Ges.* **50**, 1306 (1917).

[31] D. H. Hey, J. A. Leonard, T. M. Moynehan and C. W. Rees, *J. Chem. Soc.* 232 (1961).

[32] H. Gilman, and R. D. Nelson, *J. Am. Chem. Soc.* **70**, 3316 (1948).

[33] L. Claisen, *Ber. Dtsch. Chem. Ges.* **40**, 3908 (1907).

[34] E. Knovenagel, *Ibid.* **55**, 1929 (1922).

[35] P. Caubere, and B. Loubinoux, *Bull. Soc. Chim. Fr.* 3858 (1968).