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OBSERVATIONS ON THE VILSMEIER REACTION Part 2. THE ANOMALOUS REACTION OF N-BENZYL N-CYANOETHYL-4-METHYLANILINE DERIVATIVES

Andrew P. Shawcross and Stephen P. Stanforth*

Department of Chemical and Life Sciences
Newcastle upon Tyne Polytechnic
Newcastle upon Tyne NE1 8ST

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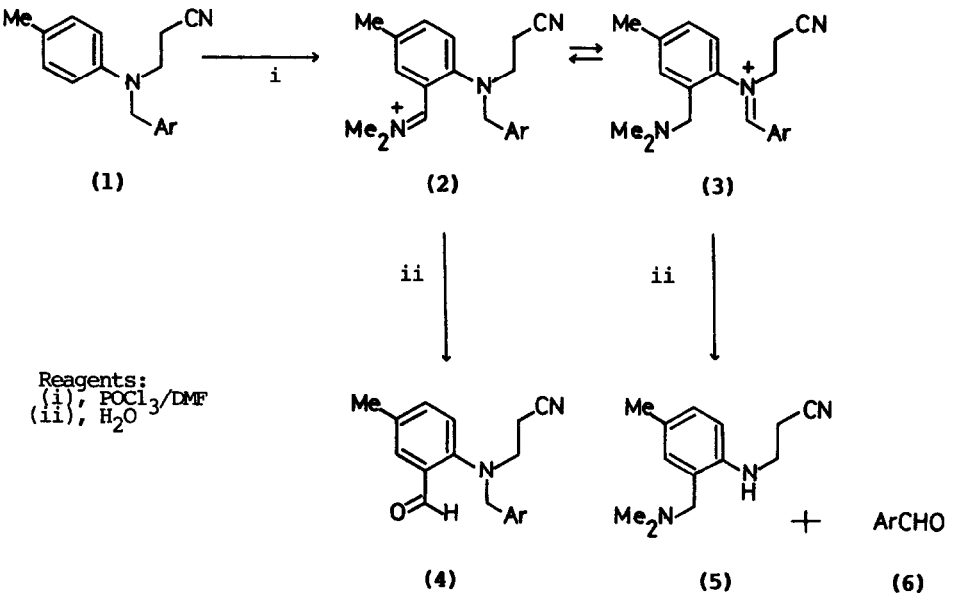
Abstract: The reaction of a series of the title anilines **(1)** with variously substituted benzyl groups under Vilsmeier conditions was investigated. Only perfluorobenzyl derivatives showed normal formylation while other fluoro derivatives gave mixed results and other substituents gave solely the anomalous amine **(5)** together with the aldehyde **(6)** derived from the benzyl group.

In Part 1 [1] we described the reactions of compounds **(1a)** and **(1d)** under Vilsmeier conditions which yielded, after hydrolysis, the debenzylated 2-dimethylaminomethylated derivative **(5)**. The benzyl group was transformed into the benzaldehydes **(6a)** and **(6d)**. The mechanism proposed for these transformations (Scheme 1) involves formation of the iminium salts **(2a)** and **(2d)** respectively followed by a [1,5]-H shift yielding the corresponding iminium salts **(3a)** and **(3d)**. Hydrolysis of these iminium salts then affords the reaction products. None of the aldehydes **(4a)** and **(4d)** which would be associated with the normal Vilsmeier formylation process were isolated in these reactions. In an extension to our original investigations we have now prepared a series of compounds **(1)** in order to determine the effect of substituents in the aryl-ring on the course of the reaction. The vinylogue **(7)** of compound **(1a)** was also prepared.

Preparation of Compounds (1) and (7)

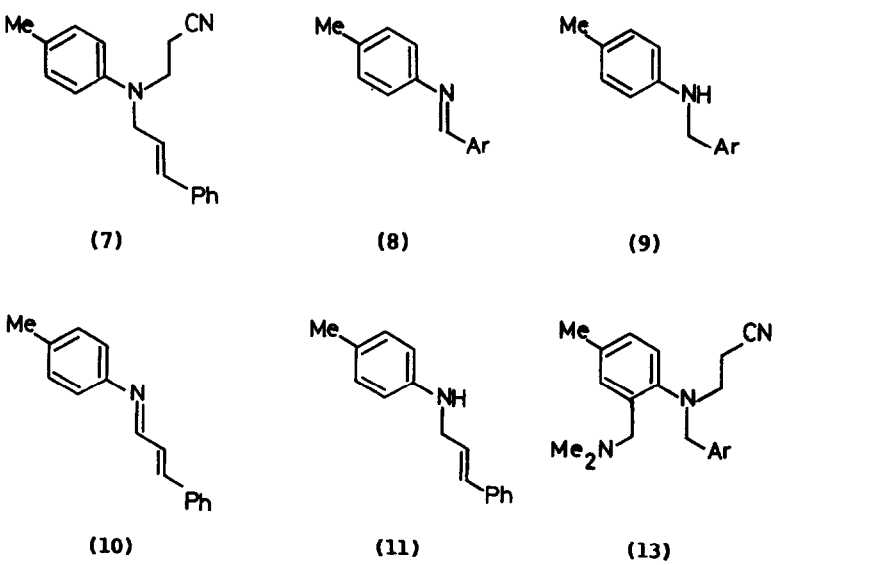
The preparation of compounds **(1a)** and **(1d)** have already been described [1] and compounds **(1b)**, **(1c)** and **(1e-1p)** were prepared by a similar procedure. Thus, reaction of 4-methylaniline with the appropriate aldehyde **(6)** yielded the Schiff bases **(8)** which were reduced giving the amines **(9)**. Cyanoethylation of amines **(9)** with acrylonitrile in the presence of copper(I)chloride [2] afforded compounds **(1)** (32-97% yield). Compound **(7)** was similarly prepared *via* compounds **(10)** and **(11)**. When the aryl-substituent was 4-dimethylamino [compound **(9i)**] only N,N-di(2-cyanoethyl)-4-methylaniline **(12)** was obtained under these cyanoethylation conditions presumably by the mechanism depicted in Scheme 2.

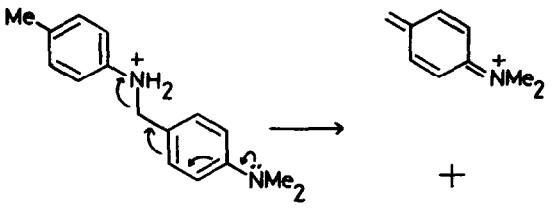


Aryl=

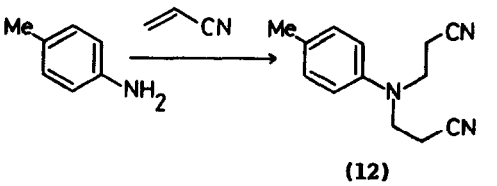
a	phenyl	f	4-bromophenyl	k	2-thienyl
b	3-methylphenyl	g	3-methoxyphenyl	l	3-fluorophenyl
c	4-methylphenyl	h	4-methoxyphenyl	m	4-fluorophenyl
d	4-chlorophenyl	i	4-N,N-dimethylaminophenyl	n	2,4-difluorophenyl
e	3-bromophenyl	j	4-nitrophenyl	o	3,5-difluorophenyl
				p	2,3,4,5,6-pentafluoro-pheny

Scheme 1





(9i)



(12)

Scheme 2

Entry	Compound /	Yield (%) of aldehyde **(4)**	Yield (%) of aldehyde **(6)**	Yield (%) of amine **(5)**
1	**(1b)**	--	92	79
2	**(1c)**	--	88	76
3	**(1e)**	--	71	58
4	**(1f)**	--	82	62
5	**(1g)**	--	89	80
6	**(1h)**	--	76	74
7	**(1i)**	--	30	not isolated
8	**(1k)**	--	47	59
9	**(1l)**	13	40	49
10	**(1m)**	--	71	82
11	**(1n)**	42.5	30	39
12	**(1o)**	35	32	39
13	**(1p)**	32, 67*	--	--
14	**(7)**	--	40	24

* a ten-fold excess of $POCl_3$ to compound **(1p)** was used

Table 1

Vilsmeier Reaction of Compounds **(1)** and **(7)**

The results of our investigations are summarised in Table 1. In all cases a 2-3 times excess of $POCl_3$ [relative to compound **(1)**] was mixed with dimethylformamide with cooling and then compound **(1)** was added. The mixture was then heated (5-6 hours) at 90° C and the resulting iminium salts **(2)** and/or **(3)** were hydrolysed and the products isolated as described in the Experimental Section. In entries 1-8 and 10 we isolated only the products **(5)** and **(6)** associated with the [1,5]-H shift and these observations complement our previous investigations [1]. The N-cinnamyl derivative **(7)** (entry 14) similarly yielded amine **(5)** and cinnamaldehyde. We had anticipated that when the aryl-group in formula **(1)** was electron-deficient then the [1,5]-H shift would be precluded because the formation of the iminium salt **(3)** would not be favoured. Thus, the pentafluoro derivative **(1p)** (entry 13) gave only the formylated product **(4p)** as expected and no amine **(5)** or pentafluorobenzaldehyde **(6p)** associated with a [1,5]-H shift was observed. In contrast, the nitro-derivative **(1j)** gave amine **(5)** and 4-nitrobenzaldehyde **(6j)**. In entries 11 and 12

competing reaction pathways were evident for the difluoro derivatives **(1n)** and **(1o)** and the corresponding products **(5)** and **(6)** resulting from a [1,5]-H shift together with product **(4)** were isolated. Similarly, competing reactions were observed for the 3-fluoro derivative **(11)** (entry 9). The formation of aldehyde **(41)** from the Vilsmeier reaction of compound **(11)** was exceptional in comparison to the mono-halogenated compounds **(1d-1f)** and **(1m)** where only products derived from a [1,5]-H shift were isolated.

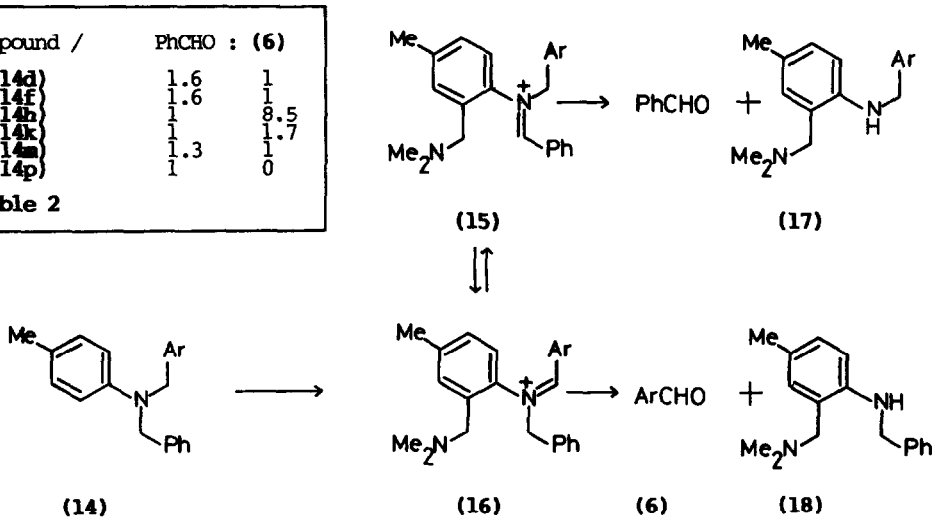
In support of the mechanistic proposals depicted in Scheme 1, iminium salts **(3c)** and **(3h)** could be reduced in situ with sodium borohydride giving the corresponding products **(13c)** and **(13h)** (39% and 76% yield respectively).

Competitive [1,5]-H Shifts

Supporting evidence for the mechanism depicted in Scheme 1 was also obtained from a study of the Vilsmeier reaction of compounds **(14)**. These compounds **(14)** were readily prepared (32-66% yield) by treatment of amines **(9)** with benzyl bromide in the presence of potassium carbonate. Treatment of compounds **(14)** under Vilsmeier conditions would be expected to yield iminium salts **(15)** and/or **(16)** (Scheme 3) with the ratio **(15)**: **(16)** depending upon the nature of the aryl-group in formula **(14)**. Thus, compounds **(14)** under Vilsmeier conditions gave benzaldehyde and/or aldehyde **(6)** (Table 2) and the ratio of these two aldehydes (determined by ^{1}H-nmr spectroscopy) clearly reflects the expected order of stability of the iminium salts **(15)** and **(16)**. The ratio of amines **(17)** and **(18)** could not be accurately determined in entries 1-5 because of nearly coincident nmr signals and separation of these amines by chromatography was not possible. Amine **(17p)** was the only product formed in the Vilsmeier reaction of compound **(14p)** and was isolated satisfactorily.

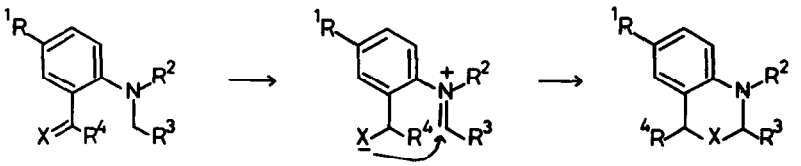
Entry	Compound /	PhCHO :	(6)
1	**(14d)**	1.6	1
2	**(14f)**	1.6	1
3	**(14h)**	1	8.5
4	**(14k)**	1	1.7
5	**(14m)**	1.3	1
6	**(14p)**	1	0

Table 2



Scheme 3

Reinhoudt and co-workers [3,4] have recently reported the synthesis of a number of heterocycles **(21)** (Scheme 4) from the corresponding compounds **(19)** (X=O,S,NR^5,CR^6R^7). These transformations occur via the dipolar intermediates **(20)** which are formed from precursors **(19)** by a [1,5]-H shift. The reactions we have described (Scheme 1) are related mechanistically to those depicted in Scheme 4.



(19) **(20)** **(21)**

Scheme 4

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Experimental

General experimental directions are given in Part 1 [1].

Preparation of Schiff Bases **(8)** and **(10)**. General Method: To a solution of 4-methylaniline in ethanol was added the appropriate aromatic aldehyde (1 equivalent). The mixture was either kept at room temperature or heated under reflux (1.0hr) and then allowed to cool to room temperature. With the exception of compounds **(8b)** and **(8g)** all the Schiff bases crystallised upon standing. In the cases of compounds **(8b)** and **(8g)** the ethanol was removed by evaporation under reduced pressure yielding the Schiff bases as oils. The following compounds have been reported previously: compound **(8b)** [5], compound **(8c)** [6], compound **(8f)** [7], compound **(8h)** [6], compound **(8i)** [8], compound **(8j)** [9], compound **(8k)** [10], compound **(8l)** [11], compound **(8m)** [12], compound **(8p)** [13] and compound **(10)** [14].

Compound **(8e)**: 4-Methylaniline (4.4g) and 3-bromobenzaldehyde (7.4g) at room temperature gave N-(3-bromobenzylidene)-4-methylaniline **(8e)** (9.4g; 83%) as cream rhombs, m.p. 52-54°C (ethanol). [Found: C,61.3; H,4.3; N,4.8; Br,29.3. $C_{14}H_{12}BrN$ requires C,61.3; H,4.4; N,5.1;Br,29.2%]. ν_{max} 1625 cm^{-1}. δ 8.38(1H,s,-N=CH-), 8.07(1H,t,J 1.5Hz,Ar-H), 7.9-7.0(7H,m,Ar-H) and 2.37(3H,s,-CH_3).

Compound **(8g)**: 4-Methylaniline (10.7g) and 3-methoxybenzaldehyde (13.6g) were mixed at room temperature (1.0hr). The ethanol was removed by evaporation under reduced pressure giving N-(3-methoxybenzylidene)-4-methylaniline **(8g)** as an oil which was used without further purification. δ 8.35(1H,s,ArC<u>H</u>=), 7.50-6.70(8H,m,Ar-<u>H</u>), 3.80(3H,s,Ar-OC<u>H</u>$_3$) and 2.35(3H,s,Ar-C<u>H</u>$_3$).

Compound **(8n)**: 4-Methylaniline (10.7g) and 2,4-difluorobenzaldehyde (14.2g) were stirred at room temperature (0.5hr) giving N-(2,4-difluorobenzylidene)-4-methylaniline **(8n)** as yellow crystals (18.7g; 81%), m.p.57-58°C (ethanol). [Found: C,72.5; H,4.7; N,6.1; F,16.4. $C_{14}H_{11}F_2N$ requires C,72.7; H,4.8; N,6.1; F,16.4%]. V_{max} 1625, 1505, 1135, and 860 cm^{-1}. δ 8.70(1H,s,-N=C<u>H</u>-), 8.20(1H,m,Ar-<u>H</u>), 7.20(4H,s, Ar-<u>H</u>), 6.90(2H,m,Ar-<u>H</u>) and 2.40(3H,s,-C<u>H</u>$_3$).

Compound **(8o)**: 4-Methylaniline (10.7g) and 3,5-difluorobenzaldehyde (14.2g) were stirred at room temperature (0.5hr). The mixture was concentrated by evaporation under reduced pressure giving N-(3,5-difluorobenzylidene)-4-methylaniline **(8o)** (17.4g; 75%); as yellow crystals, m.p.43-45°C. [Found: C,72.3; H,4.7; N,6.0; F,16.4. $C_{14}H_{11}F_2N$ requires C,72.7; H,4.8; N,6.1; F,16.4%]. V_{max} 1625, 1590, 1320, and 1120 cm^{-1}. δ 8.35(1H,s,-N=C<u>H</u>-), 7.45-6.90(7H,m,Ar-<u>H</u>), and 2.40(3H,s,-C<u>H</u>$_3$).

Preparation of Amines **(9)** and **(11)**. General Method:

To a stirred solution of the appropriate Schiff bases **(8)** or **(10)** in methanol or ethanol was added sodium borohydride (1-1.5 equivalents) portionwise. The mixture was cooled if necessary to control the exothermic reaction. After the vigorous reaction had subsided the solution was heated under reflux (1-2hr), allowed to cool to room temperature and then poured into water. The mixture was extracted several times (dichloromethane or ether) and the combined organic extracts were washed with water, dried ($MgSO_4$) and evaporated under reduced pressure. The following compounds have been reported previously: compound **(9b)** [15], compound **(9c)** [15], compound **(9h)** [16], compound **(9i)** [17], compound **(9j)** [18], compound **(9k)** [19] and compound **(11)** [14].

Compound **(9e)**: Compound **(8e)** (4.1g) gave N-(3-bromobenzyl)-4-methylaniline **(9e)** (3.6g; 87%) as white needles, m.p. 36°C (ethanol). [Found: C,60.8; H,5.1; N,4.9; Br,29.0. $C_{14}H_{14}BrN$ requires C,60.9; H,5.1; N,5.1; Br,28.9%]. V_{max} 3410 (>NH) and 1520 cm^{-1}. δ 7.6-7.1(4H,m,Ar-<u>H</u>), 6.95(2H,d,<u>J</u> 9Hz,Ar-<u>H</u>), 6.52(2H,d,<u>J</u> 9Hz,Ar-<u>H</u>), 4.28(2H,s,>C<u>H</u>$_2$), 4.0-3.5(1H,broad s,>N<u>H</u>) and 2.20(3H,s,-C<u>H</u>$_3$).

Compound **(9f)**: Compound **(8f)** (41.4g) gave N-(4-bromobenzyl)-4-methylaniline **(9f)** (34.9g; 84%) as lime-green platelets m.p.90-92°C (ethanol). [Found: C,61.2; H,5.0; N,5.2; Br,28.8. $C_{14}H_{14}BrN$ requires C,60.9; H,5.1; N,5.1; Br,28.9%]. V_{max} 1515, 1070, 1110 and 810 cm^{-1}. δ 7.40(2H,d,<u>J</u> 7Hz,Ar-<u>H</u>), 7.10(2H,d,<u>J</u> 7Hz,Ar-<u>H</u>), 6.95(2H,d,<u>J</u> 7Hz,Ar-<u>H</u>), 6.45(2H,d,<u>J</u> 7Hz,Ar-<u>H</u>), 4.20(2H,s,>C<u>H</u>$_2$), 3.80(1H,s,>N<u>H</u>) and 2.20(3H,s,-C<u>H</u>$_3$).

Compound **(9g)**: Compound **(8g)** (22.5g) gave N-(3-methoxybenzyl)-4-methylaniline **(9g)**

[21.67g; 95% (from 3-methoxybenzaldehyde)] as an oil. [Found: C,79.5; H,7.7; N,6.2. $C_{15}H_{17}NO$ requires C,79.3; H,7.5; N,6.2%]. ν_{max} (liquid film) 3410 (>NH), 1610, 1520, and 1265 cm^{-1}. δ 7.25-6.30(8H,m,Ar-H), 4.15(2H,s,>CH_2), 3.65(4H,broad s,-OCH_3 and >NH) and 2.20(3H,s,-CH_3).

Compound **(91)**: Compound **(81)** (12.1g) gave N-(3-fluorobenzyl)-4-methylaniline **(91)** (12.1g; 98%) as an oil. [Found: C,78.3; H,6.6; N,6.6; F,9.0. $C_{14}H_{14}FN$ requires C,78.1; H,6.6; N,6.5; F,8.8%]. ν_{max} (liquid film) 3410 (>NH), 1610, 1520, 1265 and 810 cm^{-1}. δ 7.25-6.35(8H,m,Ar-H), 4.20(2H,s,>CH_2), 3.85(1H,s,>NH) and 2.20(3H,s,-CH_3).

Compound **(9m)**: Compound **(8m)** (7.8g) gave N-(4-fluorobenzyl)-4-methylaniline **(9m)** (7.12g; 91%) as white crystals, m.p. 27-28°C (ethanol). [Found: C,78.4; H,6.5; N,6.4; F,8.9. $C_{14}H_{14}FN$ requires C,78.1; H,6.6; N,6.5; F,8.8%]. ν_{max} 3415 (>NH), 1620, 1510, 1225 and 810 cm^{-1}. δ 7.35-6.40(8H,m,Ar-H), 4.15(2H,s,>CH_2), 3.80(1H,s,>NH) and 2.20(3H,s,-CH_3).

Compound **(9n)**: Compound **(8n)** (17.5g) gave N-(2,4-difluorobenzyl)-4-methylaniline **(9n)** (16.1g; 91%) as an oil. [Found: C,72.0; H,5.6; N,6.3; F,16.6. $C_{14}H_{13}F_2N$ requires C,72.1; H,5.6; N,6.0; F,16.3%]. ν_{max} (liquid film) 3420 (>NH), 1530, and 1510 cm^{-1}. δ 7.40-7.10(2H,m,Ar-H), 6.95(2H,d,J 9Hz,Ar-H), 6.80(1H,s,Ar-H), 6.50(2H,d,J 9Hz,Ar-H), 4.30(2H,s,>CH_2), 3.70(1H, broad s,>NH) and 2.20(3H,s,-CH_3).

Compound **(9o)**: Compound **(8o)** (16.5g) gave N-(3,5-difluorobenzyl)-4-methylaniline **(9o)** (15.05g; 90%) as an oil. [Found: C,71.9; H,5.6; N,6.3; F,16.4. $C_{14}H_{13}F_2N$ requires C,72.1; H,5.6; N,6.0; F,16.3%]. ν_{max} (liquid film) 3420 (>NH), 1520, 1120 and 615 cm^{-1}. δ 7.00-6.45(7H,m,Ar-H), 4.25(2H,s,>CH_2), 3.85(1H,broad s,>NH) and 2.20(3H,s-CH_3).

Compound **(9p)**: Compound **(8p)** (20.0g) gave N-(2,3,4,5,6-pentafluorobenzyl)-4-methylaniline **(9p)** (19.67g; 98%) as white platelets, m.p.62-63°C (ethanol). [Found: C,58.3; H,3.4; N,4.6. $C_{14}H_{10}F_5N$ requires C,58.5; H,3.5; N,4.9%]. ν_{max} 3370 (>NH), 1520 and 1500 cm^{-1}. δ 7.20(2H,d,J 9Hz,Ar-H), 6.85(2H,d,J 9Hz,Ar-H), 4.30(2H,s,>CH_2) and 2.20(3H,s,-CH_3).

Preparation of Compounds **(1)**, **(7)** and **(12)**. General Method:

The method reported in Part 1 [1] was used to prepare compounds **(1)**, **(7)** and **(12)**.

Compound **(1b)**: Compound **(9b)** (9.0g), acrylonitrile (16cm^3) and CuCl (2.75g) gave N-(3-methylbenzyl) N-(2-cyanoethyl)-4-methylaniline **(1b)** (7.53g; 67%) as an oil after purification by column chromatography (silica gel, eluent petroleum ether b.p. 40/60°C : ethyl acetate 5:1). [Found C,81.5; H,7.8; N,10.7. $C_{18}H_{20}N_2$ requires C,81.8; H,7.6; N,10.6%]. ν_{max} (liquid film) 2250 (weak,-CN) cm^{-1}. δ 7.20-6.90(6H,m,Ar-H), 6.60(2H,d,J 8Hz,Ar-H), 4.50(2H,s,>CH_2) 3.70(2H,t,J 7Hz,>NCH_2CH_2CN), 2.50(2H,t,J 7Hz,>NCH_2CH_2CN) 2.30(3H,s,-CH_3) and 2.20(3H,s,-CH_3).

Compound **(1c)**: Compound **(9c)** (9.0g), acrylonitrile (16cm^3) and CuCl (2.75g) gave N-(4-methylbenzyl) N-(2-cyanoethyl)-4-methylaniline **(1c)** (6.84g; 61%) as an oil after

purification by column chromatography (silica gel, eluent petroleum ether b.p 40/60°C : ethyl acetate 5:1). [Found: C,81.7; H,7.8; N,10.9. $C_{18}H_{20}N_2$ requires C,81.8; H,7.6; N,10.6%]. V_{max} (liquid film) 2250 (-CN) cm^{-1}. δ 7.10(4H,s,Ar-H), 7.00(2H,d, J 9Hz,-ArH), 6.60(2H,d,J 9Hz,Ar-H), 4.50(2H,s,>CH_2) 3.65(2H,t,J 7Hz,>NCH_2CH_2CN), 2.50(2H,t,J 7Hz,>NCH_2CH_2CN), 2.30(3H,s,-CH_3) and 2.20(3H,s,-CH_3).

Compound **(1e)**: Compound **(9e)** (3.3g), acrylonitrile (8cm^3) and CuCl (1.07g) gave N-(3-bromobenzyl) N-(2-cyanoethyl)-4-methylaniline **(1e)** (1.8g; 46%) as an oil after purification by chromatography (silica gel, eluent petroleum ether b.p. 40/60°C : ethyl acetate 5:1). [Found: C,62.0; H,5.0; N,8.3; Br,24.6. $C_{17}H_{17}N_2Br$ requires C,62.0; H,5.2; N,8.5; Br,24.3%]. V_{max} 2250 (weak,-CN) cm^{-1}. δ 7.3-6.4(8H,m,Ar-H), 4.35(2H,s,-CH_2Ar), 3.50(2H,t,J 7Hz,>NCH_2CH_2CN), 2.40(2H,t,J 7Hz,>NCH_2CH_2CN) and 2.14(3H,s,-CH_3).

Compound **(1f)**: Compound **(9f)** (9.0g), acrylonitrile (18cm^3) and CuCl (2.75g) gave N-(4-bromobenzyl) N-(2-cyanoethyl)-4-methylaniline **(1f)** (5.0g; 47%) as white needles, m.p.79-80°C. [Found: C,61.7; H,5.0; N,8.3; Br,24.5. $C_{17}H_{17}BrN_2$ requires C,62.0; H,5.2; N,8.5; Br,24.3%]. V_{max} 2250 (weak,-CN) cm^{-1}. δ 7.50-6.45(8H,m,Ar-H), 4.40(2H,s,-CH_2Ar), 3.60(2H,t,J 7Hz,>NCH_2CH_2CN), 2.50(2H,t,J 7Hz,>NCH_2CH_2CN) and 2.20(3H,s,-CH_3).

Compound **(1g)**: Compound **(9g)** (10.0g), acrylonitrile (16cm^3) and CuCl (2.75g) gave N-(2-cyanoethyl) N-(3-methoxybenzyl)-4-methylaniline **(1g)** (6.3g; 51%) as white needles, m.p.65-66°C. [Found: C,77.4; H,7.4; N,10.2. $C_{18}H_{20}N_2O$ requires C,77.1; H,7.2; N,10.0%]. V_{max} 2250 (-CN) cm^{-1}. δ 7.20-6.35(8H,m,Ar-H), 4.40(2H,s,-CH_2Ar), 3.70(3H,s,-OCH_3), 3.60(2H,t,J 7Hz,>NCH_2CH_2CN), 2.50(2H,t,J 7Hz,>NCH_2CH_2CN) and 2.20(3H,s,-CH_3).

Compound **(1h)**: Compound **(9h)** (9.0g), acrylonitrile (18cm^3) and CuCl (2.75g) gave N-(2-cyanoethyl) N-(4-methoxybenzyl)-4-methylaniline **(1h)** (6.6g; 59%) as white needles, m.p.69°C. [Found: C,76.9; H,7.3; N,10.0. $C_{18}H_{20}N_2O$ requires C,77.1; H,7.2; N,10.0%]. V_{max} 2250 (weak,-CN) cm^{-1}. δ 7.20-6.60(8H,m,Ar-H), 4.40(2H,s,-CH_2Ar), 3.75(3H,s,-OCH_3), 3.60(2H,t,J 7Hz,>CH_2CH_2CN), 2.50(2H,t,J 7Hz,>NCH_2CH_2CN) and 2.25(3H,s,-CH_3).

Compound **(1j)**: Compound **(9j)** (9.0g), acrylonitrile (18cm^3) and CuCl (2.75g) gave N-(2-cyanoethyl) N-(4-nitrobenzyl)-4-methylaniline **(1j)** (6.0g; 55%) as orange needles, m.p.67-68°C. [Found: C,68.9; H,5.7; N,14.2. $C_{17}H_{17}N_3O_2$ requires C,69.1; H,5.8; N,14.2%]. V_{max} 2250 (-CN) cm^{-1}. δ 8.15-6.50(8H,m,Ar-H), 4.46(2H,s,-CH_2Ar), 3.75(2H,t,J 7Hz,>NCH_2CH_2CN), 2.60(2H,t,J 7Hz,>NCH_2CH_2CN) and 2.25(3H,s,-CH_3).

Compound **(1k)**: Compound **(9k)** (4.5g), acrylonitrile (9cm^3) and CuCl (1.4g) gave N-(2-cyanoethyl) N-(2-thienylmethyl)-4-methylaniline **(1k)** (2.3g; 41%) as white needles, m.p.50-51.5°C. [Found: C,70.5; H,6.4; N,11.0; S,12.6. $C_{15}H_{16}NS$ requires C,70.3; H,6.3; N,10.9; S,12.6%]. V_{max} 2250 (weak,-CN) cm^{-1}. δ 7.20-6.50(7H,m,Ar-H), 4.60(2H,s,-CH_2Ar), 3.60(2H,t,J 7Hz,>NC_2CH_2CN), 2.50(2H,t,J 7Hz,>NCH_2CH_2CN) and 2.20(3H,s,-CH_3).

Compound **(1l)**: Compound **(9l)** (9.0g), acrylonitrile (16cm^3) and CuCl (2.75g) gave N-(2-cyanoethyl) N-(3-fluorobenzyl)-4-methylaniline **(1l)** (8.85g; 79%) as an oil after purification by chromatography (silica gel, eluent CH_2Cl_2). [Found: C,75.8; H,6.5; N,10.6;

F,7.4. $C_{17}H_{17}FN_2$ requires C,76.1; H,6.4; N,10.4; F,7.1%]. ν_{max} (liquid film) 2250 (-CN) cm^{-1}. δ 7.25-6.60(8H,m,Ar-H), 4.50(2H,s,-CH_2Ar), 3.60(2H,t,J 7Hz,>NCH_2CH_2CN), 2.60(2H,t,J 7Hz,>NCH_2CH_2CN) and 2.25(3H,s,-CH_3).

Compound **(1m)**: Compound **(9m)** (5.0g), acrylonitrile (8cm^3) and CuCl (1.4g) gave N-(2-cyanoethyl) N-(4-fluorobenzyl)-4-methylaniline **(1m)** (3.5g; 56%) as pale green needles, m.p.61-62°C. [Found: C,76.2; H,6.3; N,10.6; F,7.2. $C_{17}H_{17}FN_2$ requires C,76.1; H,6.3; N,10.4; F,7.1%]. ν_{max} 2250 (-CN) cm^{-1}. δ 7.25-6.40(8H,m,Ar-H), 4.40(2H,s,-CH_2Ar), 4.40(2H,t,J 7Hz,>NCH_2CH_2CN), 2.50(2H,t,J 7Hz,>NCH_2CH_2CN) and 2.20(3H,s,-CH_3).

Compound **(1n)**: Compound **(9n)** (9.0g), acrylonitrile (16cm^3) and CuCl (2.75g) gave N-(2,4-difluorobenzyl) N-(2-cyanoethyl)-4-methylaniline **(1n)** (5.12g; 46%) as white microcrystals, m.p.75.5-76°C. [Found: C,71.1; H,5.6; N,9.6. $C_{17}H_{16}F_2N_2$ requires C,71.3; H,5.6; N,9.8%]. ν_{max} 2250 (-CN) cm^{-1}. δ 7.25-6.50(3H,m,Ar-H), 7.00(2H,d,J 7Hz,Ar-H), 6.60(2H,d,J 7Hz,Ar-H), 4.50(2H,s,>CH_2), 3.70(2H,t,J 7Hz,>NCH_2CH_2CN), 2.60(2H,t,J 7Hz,>NCH_2CH_2CN) and 2.20(3H,s,-CH_3).

Compound **(1o)**: Compound **(9o)** (9.0g), acrylonitrile (16cm^3) and CuCl (2.75g) gave N-(3,5-difluorobenzyl) N-(2-cyanoethyl)-4-methylaniline **(1o)** as an oil (7.56g; 68%) after purification by column chromatography (silica gel, eluent petroleum ether b.p. 40/60°C : ethyl acetate 5:1). The oil crystalised upon standing giving a white solid m.p.66-67°C. [Found: C,71.2; H,5.9; N,9.8. $C_{17}H_{16}F_2N_2$ requires C,71.3; H,5.6; N,9.8%]. ν_{max} 2250 (-CN) cm^{-1}. δ 7.20-6.50(7H,m,Ar-H), 4.50(2H,s,>CH_2), 3.70(2H,t,J 7Hz,>NCH_2CH_2CN), 2.60(2H,t,J 7Hz,>NCH_2CH_2CN) and 2.25(3H,s,-CH_3).

Compound **(1p)**: Compound **(9p)** (8.0g), acrylonitrile (16cm^3) and CuCl (2.75g) gave N-(2,3,4,5,6-pentafluorobenzyl) N-(2-cyanoethyl)-4-methylaniline **(1p)** as white microcrystals, m.p.71-72°C. [Found: C,59.8; H,3.8; N,8.15; F,28.1. $C_{17}H_{13}F_5N_2$ requires C,60.0; H,3.8; N,8.2; F,27.9%]. ν_{max} 2250 (-CN) cm^{-1}. δ 7.10(2H,d,J 9Hz,Ar-H), 6.75(2H,d,J 9Hz,Ar-H), 4.55(2H,s,>CH_2), 3.60(2H,t,J 7Hz,>NCH_2CH_2CN), 2.55(2H,t,J 7Hz,>NCH_2CH_2CN) and 2.25(3H,s,-CH_3).

Compound **(7)**: Compound **(11)** (4.0g), acrylonitrile (9cm^3) and CuCl (1.07g) gave N-cinnamyl N-(2-cyanoethyl)-4-methylaniline **(7)** (5.0g; 100%) as cream needles, m.p. 80-82°C (ethanol). [Found: C,82.6; H,7.3; N,10.1. $C_{19}H_{20}N_2$ requires C,82.6; H,7.3; N,10.1%]. ν_{max} 2245 (-CN), 1620, 1520, 1350, 1180 and 970 cm^{-1}. δ 7.4-6.0(11H,m,Ar-H and-CH=CH-), 4.08(2H,d,J 6Hz,>CH_2), 3.68(2H,t,J 7Hz,>NCH_2CH_2CN), 2.57(2H,t,J 7Hz,>NCH_2CH_2CN) and 2.27(3H,s,-CH_3).

Compound **(12)**: Compound **(9i)** (8.0g), acrylonitrile (16cm^3) and CuCl (2.75g) gave N,N-di(2-cyanoethyl)-4-methylaniline **(12)** [2] (1.84g; 26%) after column chromatography (silica gel, eluent CH_2Cl_2).

Vilsmeier Reactions of Compounds **(1)** and **(7)**. General Method:

The Vilsmeier reactions of compounds **(1)** and **(7)** were carried out as described in Part [1]. The reaction products were isolated as follows. The cooled reaction mixture was poured into water and a few drops of dilute hydrochloric acid solution were added. Aldehydes **(6)** and/or **(4)**, together with unreacted compound **(1)** were then isolated by ether or dichloromethane extraction. In the case of formation of more than one product the products were separated by column chromatography. The aqueous fraction was then basified by the addition of dilute sodium hydroxide solution and amine **(5)** was isolated by extraction into ether or dichloromethane.

Compound **(1b)** (1.5g) and $POCl_3$ (1.74g) gave amine **(5)** (0.97g; 79%) and 3-methylbenzaldehyde (0.63g; 92%).

Compound **(1c)** (1.5g) and $POCl_3$ (1.74g) gave amine **(5)** (0.94g; 76%) and 4-methylbenzaldehyde (0.60g; 88%).

Compound **(1e)** (0.6g) and $POCl_3$ (0.70g) gave amine **(5)** (0.23g; 58%) and 3-bromobenzaldehyde (0.24g; 71%).

Compound **(1f)** (1.5g) and $POCl_3$ (1.4g) gave amine **(5)** (0.61g; 62%) and 4-bromobenzaldehyde (0.69; 82%).

Compound **(1g)** (1.0g) and $POCl_3$ (1.09g) gave amine **(5)** (0.62g; 80%) and 3-methoxybenzaldehyde (0.43; 89%).

Compound **(1h)** (1.0g) and $POCl_3$ (1.64g) gave amine **(5)** (0.42g; 74%) and 4-methoxybenzaldehyde (0.57; 76%).

Compound **(1j)** (1.5g) and $POCl_3$ (1.6g) gave amine **(5)** (0.48g; 43%) and a 3:1 mixture (by ^{1}H-nmr spectroscopy) (0.29g) of 4-nitrobenzaldehyde and compound **(1j)** after column chromatography (silica gel, eluent petroleum ether b.p. 40/60°C : ethyl acetate 1:1).

Compound **(1k)** (1.0g) and $POCl_3$ (1.20g) gave amine **(5)** (0.5g; 59%) and, after column chromatography (silica gel, eluent petroleum ether b.p. 40/60°C : ethyl acetate 4:1), thiophene-2-carboxaldehyde (0.23g; 47%).

Compound **(1l)** (1.5g) and $POCl_3$ (1.71g) gave amine **(5)** (0.60g; 49%) and two aldehydes. This mixture was fractionated by column chromatography (silica gel, eluent CH_2Cl_2) giving 3-fluorobenzaldehyde (0.28g; 40%) and N-(2-cyanoethyl) N-(3-fluorobenzyl)-2-amino -5-methylbenzaldehyde **(4l)** (0.22g; 13%) as a colourless oil. ν_{max} (liquid film) 2250 (-CN) and 1680 (-CHO) cm^{-1}. δ 10.50(1H,s,-CHO), 7.60-7.0(7H,m,Ar-H), 4.30(2H,s,$>CH_2$), 3.40(2H,t,J 7Hz,$>NCH_2CH_2CN$), 2.40(2H,t,J 7Hz,$>NCH_2CH_2CN$) and 2.35(3H,s,$-CH_3$). Compound **(4l)** gave a 2,4-dinitrophenylhydrazone derivative, m.p. 177°C (ethanol). [Found: C,60.4; H,4.4; N,17.5. $C_{24}H_{21}FN_6O_4$ requires C,60.5; H,4.4; N,17.6%].

Compound **(1m)** (1.0g) and $POCl_3$ (1.5g) gave amine **(5)** (0.61g; 82%) and 4-fluorobenzaldehyde (0.33; 71%).

Compound **(1n)** (1.5g) and $POCl_3$ (2.41g) gave amine **(5)** (0.44g; 39%) and a mixture of two aldehydes together with unreacted compound **(1n)**. This mixture was fractionated by column chromatography (eluent, petroleum ether b.p. 40/60°C : ethyl acetate 9:1) giving

2,4-difluorobenzaldehyde (0.22g; 30%), compound **(1n)** (0.03g; 2%) and N-(2-cyanoethyl) N-(2,4-difluorobenzyl)-2-amino-5-methylbenzaldehyde **(4n)** as a colourless liquid (0.70g; 42.5%). ν_{max} (liquid film) 2250 (-CN) and 1680 (-CHO) cm^{-1}. δ 10.45(1H,s,-CHO), 7.70(1H,m,Ar-H), 7.45-6.80(5H,m,Ar-H), 4.25(2H,s,$>CH_2$), 3.40(2H,t,J 7Hz,$>NCH_2CH_2CN$), 2.50(2H,t,J 7Hz,$>NCH_2CH_2CN$) and 2.35(3H,s,$-CH_3$). Compound **(4n)** gave a 2,4-dinitrophenylhydrazone derivative, m.p. 167-168.5°C (ethanol). [Found: C,58.0; H,4.9; N,16.8; F,7.5. $C_{24}H_{20}F_2N_6O_4$ requires C,58.3; H,4.1; N,17.0; F,7.7%].

Compound **(1o)** (1.5g) and $POCl_3$ (2.4lg) gave amine **(5)** (0.44g; 39%) and a mixture of two aldehydes together with unreacted compound **(1o)**. This mixture was fractionated by column chromatography (silica gel, eluent petroleum ether b.p. 40/60°C : ethyl acetate 9:1) giving 3,5-difluorobenzaldehyde (0.24g; 32%), compound **(1o)** (0.07g; 5%) and N-(2-cyanoethyl) N-(3,5-difluorobenzyl)-2-amino-5-methylbenzaldehyde **(4o)** (0.57g; 35%) as lime rhombs, m.p.69-70°C (ethanol). ν_{max} 2250 (-CN) and 1680 (-CHO) cm^{-1}. δ 10.5(1H,s,-CHO), 7.65(1H,m,Ar-H), 7.45-6.75(5H,m,Ar-H), 4.30(2H,s,$>CH_2$), 3.40(2H,t,J 7Hz,$>NCH_2CH_2CN$), 2.50(2H,t,J 7Hz,$>NCH_2CH_2CN$) and 2.35(3H,s,$-CH_3$). Compound **(4o)** gave a 2,4-dinitrophenylhydrazone derivative, m.p. 182-183.5°C (ethanol). [Found: C,58.6; H,4.1; N,16.8; F,7.5. $C_{24}H_{20}F_2N_6O_4$ requires C,58.3; H,4.1; N,17.0; F,7.7%].

Compound **(1p)** (1.0g) and $POCl_3$ (0.9g) gave unreacted compound **(1p)** (0.39g) and N-(2-cyanoethyl) N-(2,3,4,5,6-pentafluorobenzyl)-2-amino-5-methylbenzaldehyde **(4p)** (0.35g; 32%) as pink crystals, m.p. 114-115°C (ethanol) after column chromatography (silica gel, eluent CH_2Cl_2). [Found: C,58.5; H,3.6; N,7.5; F,25.9. $C_{18}H_{13}F_5N_2O$ requires C,58.7; H,3.6; N,7.6; F,25.8%]. ν_{max} (liquid film) 2250 (-CN) and 1680 (-CHO) cm^{-1}. δ 10.40(1H,s,-CHO), 7.70(1H,m,Ar-H), 7.50-7.05(2H,m,Ar-H), 4.40(2H,s,$>CH_2$), 3.45(2H,t,J 7Hz,$>NCH_2CH_2CN$), 2.50(2H,t,J 7Hz,$>NCH_2CH_2CN$) and 2.35(3H,s,$-CH_3$). When compound **(1p)** (1.0g) was reacted with $POCl_3$ (4.5g) compound **(4p)** (0.73g; 67%) was isolated without the need of column chromatography.

Compound **(7)** (1.4g) and $POCl_3$ (2.0g) gave amine **(5)** (0.26g; 24%) and cinnamaldehyde (0.27g; 40%).

N-(2-Cyanoethyl) N-(4-methylbenzyl)-2-dimethylaminomethyl-4-methylaniline **(13c)** and N-(2-Cyanoethyl) N-(4-methoxybenzyl)-2-dimethylaminomethyl-4-methylaniline **(13h)**.

To cooled (ice-bath) DMF ($10cm^3$) was added $POCl_3$ (2.6g) dropwise with stirring keeping the temperature below 15°C. The mixture was stirred in the cold (10mins) and compound **(1c)** (1.5g) was added. The mixture was heated (5hrs) at 90°C and then allowed to cool to room temperature. The mixture was poured into DMF ($50cm^3$) and sodium borohydride (3.5g) was added portionwise. The mixture was then heated (1hr) at 80°C, allowed to cooled to room temperature, poured into water and extracted with ether. The combined ethereal extracts were washed with water, dried ($MgSO_4$) and evaporated under reduced pressure yielding a

yellow oil which was fractionated by column chromatography (eluent, petroleum ether b.p. 40/69°C : ethyl acetate 4:1) giving N-(2-cyanoethyl) N-(4-methylbenzyl)-2-dimethylaminomethyl-4-methylaniline **(13c)** (0.72g; 39%) as colourless rhombs, m.p. 118.5-119°C (ethanol). [Found: M 321.2244 $C_{21}H_{27}N_3$ requires M 321.2199]. V_{max} 2375, 2250 (weak,-CN) and 1170 cm^{-1}. δ 7.30-7.10(7H,m,Ar-H), 4.20(2H,s,$>CH_2$), 4.00(2H,s,$>CH_2$), 3.15(2H,t,J 7Hz,$>NCH_2CH_2CN$), 2.55(6H,s,$-NMe_2$), 2.30(8H,overlapping s and t,2X-CH_3 and $>NCH_2CH_2CN$).

N-(2-Cyanoethyl) N-(4-methoxybenzyl)-2-dimethylaminomethyl-4-methylaniline **(13h)** (0.91g; 76%) was similarly obtained from compound **(1h)** (1.0g), $POCl_3$ (1.64g) and $NaBH_4$ (2.5g) as colourless rhombs, m.p. 132-133°C (ethanol). [Found: M 337.2198 $C_{21}H_{27}N_3O$ requires M 337.2148]. V_{max} 2380, 2250 (weak,-CN), 1515 and 1170 cm^{-1}. δ 7.30-7.05(7H,m,Ar-H), 4.20(2H,s,$>CH_2$), 3.95(2H,s,$>CH_2$), 3.80(3H,s,$-OCH_3$), 3.15(2H,t,J 7Hz,$>NCH_2CH_2CN$), 2.50(6H,s,$-NMe_2$), 2.30(5H,overlapping s and t,$-CH_3$ and $>NCH_2CH_2CN$).

Preparation of Compounds **(14)**. General Method:

A mixture of compound **(9)**, benzyl bromide, potassium carbonate and sodium iodide (catalytic amount) in anhydrous tetrahydrofuran ($40cm^3$) was heated under reflux (5-6hrs). The reaction mixture was allowed to cool to room temperature and then poured into water. The mixture was extracted several times with ether and the combined organic extracts were washed with water, dried ($MgSO_4$) and evaporated under reduced pressure. Except for compound **(14k)**, the resulting oils or solids were crystallised from ethanol. By this method the following transformations were achieved:

Compound **(14d)**: Compound **(9d)** (6.1g), benzyl bromide (4.51g) and potassium carbonate (7.72g) gave N-benzyl N-(4-chlorobenzyl)-4-methylaniline **(14d)** (5.31g; 63%) as pale yellow platelets, m.p. 83-84.5°C. [Found: C,78.6; H,6.3; N,4.2; Cl,11.1. $C_{21}H_{20}ClN$ requires C,78.4; H,6.3; N,4.35; Cl,11.0%]. V_{max} 1620, 1520 and 805 cm^{-1}. δ 7.25(9H,s,Ar-H), 6.95(2H,d,J 8Hz,Ar-H), 6.60(2H,d,J 8Hz,Ar-H), 4.55(4H,broad s,$>CH_2$) and 2.20(3H,s,$-CH_3$).

Compound **(14f)**: Compound **(9f)** (5.52g), benzyl bromide (3.42g) and potassium carbonate (5.52g) gave N-benzyl N-(4-bromobenzyl)-4-methylaniline **(14f)** (4.0g; 55%) as white platelets, m.p. 92-93.5°C. [Found: C,69.1; H,5.6; N,3.7; Br,21.6 $C_{21}H_{20}BrN$ requires C,68.9; H,5.5; N,3.8; Br,21.8%]. V_{max} 1615, 1520 and 800 cm^{-1}. δ 7.50-6.60(8H,m,Ar-H), 7.20(5H,s,Ph-H), 4.55(2H,s,$>CH_2$), 4.50(2H,s,$>CH_2$) and 2.20(3H,s,$-CH_3$).

Compound **(14h)**: Compound **(9h)** (6.0g), benzyl bromide (4.52g) and potassium carbonate (7.3g) gave N-benzyl N-(4-methoxybenzyl)-4-methylaniline **(14h)** (5.55g; 66%) as white crystals, m.p. 43-43.5°C. [Found: C,83.5; H,7.5; N,4.4. $C_{22}H_{23}NO$ requires C,83.2; H,7.3; N,4.4%]. V_{max} 1610, 1510 and 1240 cm^{-1}. δ 7.25(5H,s,Ph-H), 7.10(2H,d,J 8Hz,Ar-H), 6.95(2H,d,J 8Hz,Ar-H), 6.80(2H,d,J 8Hz,Ar-H), 6.60(2H,d,J 8Hz,Ar-H), 4.60(4H,d,$>CH_2$), 3.75(3H,s,$-OCH_3$) and 2.20(3H,s,$-CH_3$).

Compound **(14k)**: Compound **(9k)** (7.0g), benzyl bromide (5.9g) and potassium carbonate (9.52g) gave N-benzyl N-(2-thienylmethyl)-4-methylaniline **(14k)** as a yellow oil (5.42g; 54%) after column chromatography (silica gel, eluent petroleum ether b.p. 40/60°C : ethyl acetate 9:1). [Found: M 293.1271. $C_{19}H_{19}NS$ requires M 293.1234]. ν_{max} (liquid film) 1620, 1520 and 615 cm^{-1}.δ 7.30(5H,s,Ph-H), 7.25-6.75(7H,m,Ar-H), 4.75(2H,s,$>CH_2$), 4.60(2H,s,$>CH_2$) and 2.30(3H,s,$-CH_3$).

Compound **(14m)**: Compound **(9m)** (6.0g), benzyl bromide (4.77g) and potassium carbonate (7.7g) gave N-benzyl N-(4-fluorobenzyl)-4-methylaniline **(14m)** (4.07g; 48%) as white microcrystals, m.p. 57-58.5°C. [Found: C,82.3; H,6.5; N,4.3; F,6.5. $C_{21}H_{20}FN$ requires C,82.6; H,6.6; N,4.6; F,6.2%]. ν_{max} 1620, 1520, 1155 and 800 cm^{-1}.δ 7.25(5H,s,Ph-H), 7.20-6.60(8H,m,Ar-H), 4.55(4H,s,$>CH_2$) and 2.20(3H,s,$-CH_3$).

Compound **(14p)**: Compound **(9p)** (6.0g), benzyl bromide (3.57g) and potassium carbonate (5.77g) gave N-benzyl N-(2,3,4,5,6-pentafluorobenzyl)-4-methylaniline **(14p)** (2.50g; 32%) as white platelets, m.p. 82-83°C. [Found: C,66.6; H,4.2; N,3.5. $C_{21}H_{16}F_5N$ requires C,66.8; H,4.3; N,3.4%]. ν_{max} 1520, 1500 and 800 cm^{-1}.δ 7.25(5H,s,Ph-H), 7.00(2H,d,J 8Hz,Ar-H), 6.60(2H,d,J 8Hz,Ar-H), 4.55(2H,s,$>CH_2$), 4.45(2H,s,$>CH_2$) and 2.25(3H,s,$-CH_3$).

Competative Reactions of Compounds **(14)**. General Method:

The Vilsmeier reaction of compounds **(14)** and isolation of products was achieved using a similar procedure to that described above for compounds **(1)**. With the exception of compound **(14p)** a mixture of aldehyde products and amine products were obtained. The ratio of aldehyde products are given in Table 2. The ratio of amine products could not be determined satisfactorily (see text). Compound **(14p)** gave benzaldehyde and N-(2,3,4,5,6-pentafluorobenzyl)-2-dimethylaminomethyl-4-methylaniline **(17p)** (47%) as an oil. [Found: M 344.1365. $C_{17}H_{17}F_5N_2$ requires M 344.1308]. ν_{max} 3250, 1500, 1110, 1030 and 940 cm^{-1}. δ 7.20-6.65(3H,m,Ar-H), 4.40(2H,s,$>CH_2$), 3.30(2H,s,$>CH_2$), 2.20(3H,s,$-CH_3$) and 2.10(6H,s,$-NMe_2$).

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