$AlCl_3$-mediated migration of the benzamido group of *N*-phenoxybenzamide derivatives to the phenyl group

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$AlCl_3$-mediated decomposition of *N*-phenoxybenzamide derivatives in dichloromethane mainly leads to regioselective intramolecular migration of the benzamido group from the oxygen to the *ortho* position of the phenyl group *via* electron-deficient nitrogen intermediates.

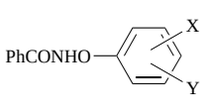
Previously we reported $AlCl_3$-mediated regioselective migration of the methoxy group of *N*-methoxy-*N*-phenylamides from the nitrogen to the *ortho* position of the phenyl group.[1] This rearrangement reaction suggests generation of an *N*-acyl-*N*-arylnitrenium ion[2] and subsequent nucleophilic migration of the methoxy group to the *ortho* position of the phenyl group *via* a tight ion pair intermediate.

In an extension of this work, we have investigated the reaction of *N*-phenoxybenzamide derivatives (**1**) with $AlCl_3$. Treatment of *N*-phenoxybenzamide (**1a**) with $AlCl_3$ (5 equiv.) in CH_2Cl_2 for 1 h at room temperature gave *N*-(2-hydroxyphenyl)-benzamide (**2a**) (85%). Several ring substituted phenoxyamines were synthesized by the literature and patent methods[3] and reacted with benzoyl chloride in pyridine with cooling to give **1**. Compounds **1** thus obtained were reacted with $AlCl_3$ in this way, and the results are presented in Table 1.

We have investigated the reaction of **1** with various Lewis acids [$AlCl_3$, $BF_3{\cdot}OEt_2$, $AlMe_3$ and $La(OTf)_3$] in aprotic solvents (CH_2Cl_2 and benzene) and found that $AlCl_3$-mediated decomposition of **1** leads (*i*) to the electrophilic intramolecular migration of the benzamido group from the oxygen to the *ortho* position of the phenyl ring to give **2** as major products, (*ii*) to the *ipso* position of the phenolic moiety followed by loss of the oxygen from the molecule to give **3**, and (*iii*) in the case of **1i** to the fluorine substituted carbon through 'back-donation'[4] by fluorine atom, followed by migration of the fluorine atom and subsequent elimination of hydrogen fluoride in the molecule to give **2l**, as a minor product (Table 1). Proposed reaction mechanisms are shown in Schemes 1 and 2. There was no migration of the benzamido group to the *para* position. The structure of **2l** was confirmed by spectral analyses and chemical transformation. Thus, it was hydrogenated over 10% palladium on carbon in ethyl acetate in the presence of triethylamine (2.8 equiv.) for 3 h to give **2g** in 73% yield.

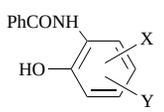
Five equiv. of $AlCl_3$ to **1** were needed to obtain a high yield of **2** and **3**, and starting compound (**1e**) was recovered by use of 2 equiv. of $AlCl_3$ in 1 h (76%). Use of $BF_3{\cdot}OEt_2$ instead of $AlCl_3$ required prolonged reaction time (2–3 days at room temperature) and in this case the carbonyl oxygen rather than the benzamido nitrogen migrated to the phenyl group which upon hydrolysis gave 2-hydroxy-5-methylphenyl benzoate (**5a**) in yields of 62% in CH_2Cl_2 and 74% in benzene. It seems that the rearrangement proceeds in a concerted mechanism *via* a six-membered cyclic transition state. In the case of $La(OTf)_3$ starting compound (**1e**) was recovered quantitatively. Reactions of **1** with $AlMe_3$ gave *N*-methylbenzamide (**6**) and the rearrangement products; production of **6** indicates that *N*-benzoylnitrenium ion was generated and trapped by $AlMe_3$. The results are presented in Table 2.

N-(4-Methylphenoxy)acetamide (**7**) reacted with $AlCl_3$ at room temperature for 1 h to give *N*-(2-hydroxy-5-methylphenyl)acetamide (**8**) (26%) and starting compound (**7**, 33%). It seems that the benzamido group migrates more easily than the acetamido group.



1

a X = H, Y = H
b X = 3-F, Y = H
c X = 2-Cl, Y = H
d X = 3-Cl, Y = H
e X = 4-Cl, Y = H
f X = 2-Me, Y = H
g X = 4-Me, Y = H
h X = 2-Cl, Y = 4-Cl
i X = 2-F, Y = 5-Br
j X = 2-Br, Y = 5-Br



2

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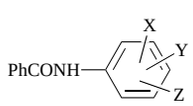
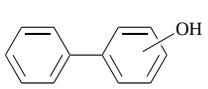
b X = 4-F, Y = H
c X = 6-F, Y = H
d X = 3-Cl, Y = H
e X = 4-Cl, Y = H
f X = 6-Cl, Y = H
g X = 5-Cl, Y = H
h X = 3-Me, Y = H
i X = 5-Me, Y = H
j X = 3-Cl, Y = 5-Cl
k X = 3-F, Y = 6-Br
l X = 4-Br, Y = 5-Cl
m X = 3-Br, Y = 6-Br

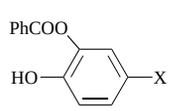


3

a X = Y = Z = H
b X = 2-Cl, Y = 4-Cl, Z = H
c X = 4-Me, Y = 5-Cl, Z = H
d X = 2-Cl, Y = 4-Cl, Z = 6-Cl
e X = 2-Br, Y = 4-Cl, Z = 5-Br

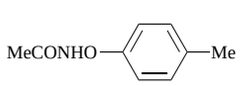


4a 2-OH
b 4-OH

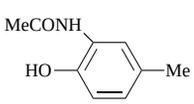


5a X = Me
b X = H

6



7



8

Structural elucidation of the products was performed by the measurements of IR, NMR and mass spectra, and elemental analyses. The key feature of the assignments is that in NMR spectra *N*-(2-substituted phenoxy)amide derivatives exhibit signals at unusually low field for the H-6 proton owing to steric effects[5] and intramolecular hydrogen bonding between the amide N–H proton and an *ortho* substituent.[6] In the case of *N*-(2-substituted phenoxy)amide derivatives, the H-6 proton appeared down field and reasonable correspondence of the chemical shift of H-6 proton to these structures was observed,

Table 1 Reaction of *N*-phenoxybenzamides (**1**) with $AlCl_3$ (5 equiv.) in CH_2Cl_2 at room temperature

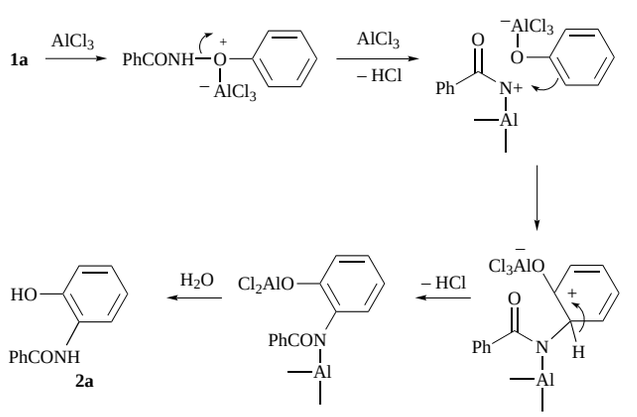
Entry	Starting compound	*t*/h	Product (yield, %)	
1	**1a**	1	**2a** (85)	
2	**1b**	3[a]	**2b** (48), **2c** (22)	
3	**1c**	0.5	**2d** (49),	**3b** (19)
4	**1d**	1[a]	**2e** (53), **2f** (20)	
5	**1e**	0.8	**2g** (65),	**3b** (20)
6	**1f**	0.5	**2h** (58)	
7	**1g**	1	**2i** (69),	**3c** (9)
8	**1h**	1.5	**2j** (44),	**3d** (25)
9	**1i**	5.5	**2k** (19), **21** (46)	
10	**1j**	4.5	**2m** (22),	**3e** (13)

[a] Reflux.

Table 2 Reaction of *N*-phenoxybenzamides (**1**) with $AlMe_3$ (5 equiv.) in CH_2Cl_2 at room temperature

Entry	Starting compound	*t*/h	Product (yield, %)
1	**1c**	2[a]	**2d** (4), **6** (74), **1c** (7)
2	**1e**	4	**2g** (46), **6** (14), **1e** (9)
3	**1f**	4	**2h** (52), **6** (13), **1f** (4)
4	**1g**	0.5[a]	**2i** (71), **6** (4), **1g** (4)

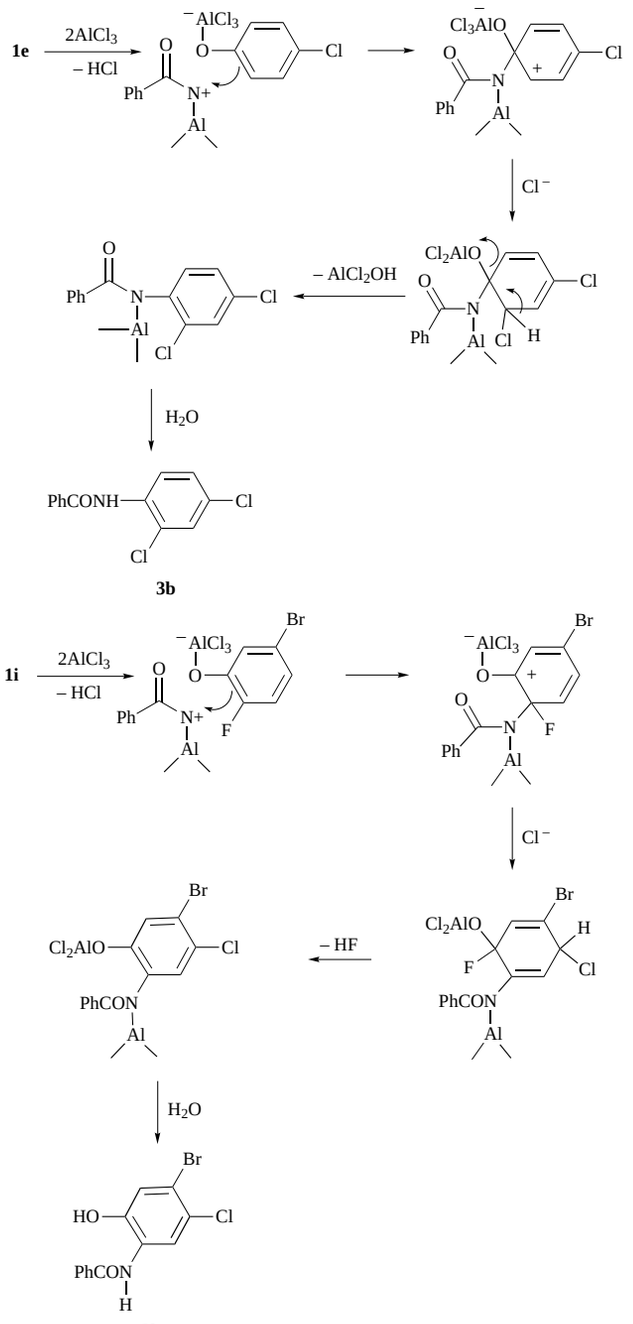
[a] Ice cooling.



Scheme 1 Proposed mechanism (main route)

except the case of entries 9 and 10 in Table 3. Thus, introduction of a methyl group at the 3 or 4 position causes pronounced up field shifts of the *ortho* proton resonances, the reason for which is not fully understood at present. It was reported that this *ortho* effect cannot be extended to *ortho* substituted phenolic esters.[5b] Indeed, the H-6 proton of **5a** showed an usual chemical shift (δ 6.96–7.03). Therefore, to confirm the structures of **2h** and **2i**, these were hydrolyzed[7] by heating in aqueous NaOH which transformed them into the corresponding aniline derivatives.

To investigate the mechanistic aspects of the rearrangement, we have undertaken to study this reaction using benzene as solvent. Treatment of **1a** with $AlCl_3$ (5 equiv.) in benzene for 1 h at room temperature gave **2a** (36%) and benzanilide (**3a**) (58%). Evidently, coordination of $AlCl_3$ with the phenoxy oxygen induces heterolytic cleavage of the N–O bond to give an *N*-acylnitrenium ion and a phenoxide anion. The positive charge thus produced was trapped intramolecularly by a phenoxide anion and canonical forms involving the benzene ring to give **2a** or trapped intermolecularly by benzene to give **3a**. It is very difficult to prove the presence of an acylnitrenium ion; however, a concerted mechanism is less favorable because thermodynamically unstable four-membered cyclic transition state must be considered in the case of production of *ortho* migration products.

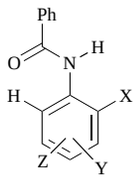


Scheme 2 Proposed mechanism (minor route)

In contrast, Shudo and co-workers have previously reported the reaction of the same compound **1a** with a strong protonic acid.[8] Treatment of **1a** with a mixture of trifluoroacetic acid (TFA) and trifluoromethanesulfonic acid (TFSA) in benzene gave 2- and 4-hydroxybiphenyls (**4a** and **4b**) (6% and 3%, respectively) and 2-hydroxyphenyl benzoate (**5b**) (43%). Protonation of the amide carbonyl of **1a** and subsequent heterolytic cleavage of the N–O bond brought about formation of a phenoxenium ion, which was trapped intermolecularly by benzene to give **4a** and **4b** or trapped intramolecularly by the carbonyl oxygen to give **5b**. It is interesting to note that the mode of cleavage of the N–O bond was completely dependent on the kind of acid used and that an *N*-acylnitrenium ion or a phenoxenium ion is produced from the same compound by use of a Lewis acid or a strong protonic acid, respectively (Scheme 3).

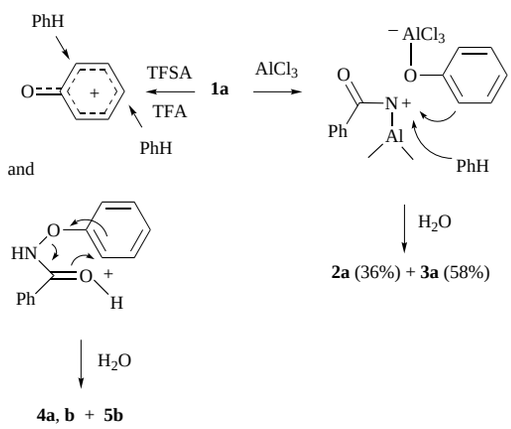
In conclusion, it is assumed that successful use of $AlCl_3$ for the generation of acylnitrenium ions and subsequent electrophilic migration to the phenyl ring is due mainly to the fact that the acylnitrenium–$AlCl_3$ complex will be sufficiently stable and

Table 3 ^{1}H NMR chemical shift data for H-6 in benzanilides



Entry	Compound	X	Y	Z	δ_H H-6	NH	OH
1	**3a**	H	H	H	7.53–7.61	7.76–7.86	—
2	**3b**	Cl	4-Cl	H	8.07	9.01	—
3	**3e**	Br	4-Cl	5-Br	8.96	8.40	—
4	**2a**	OH	H	H	7.88	9.24	8.99
5	**2b**	OH	4-F	H	7.70	9.66	9.47
6	**2d**	OH	3-Cl	H	7.42–7.66	8.36	7.81–8.00
7	**2e**	OH	4-Cl	H	7.82	9.47	9.13
8	**2g**	OH	5-Cl	H	7.91–8.13	9.47	9.31
9	**2h**	OH	3-Me	H	7.07	8.59	8.10
10	**2i**	OH	5-Me	H	7.37	8.94	8.59
11	**2j**	OH	3-Cl	5-Cl	7.87	9.67	—[a]
12	**2l**	OH	4-Br	5-Cl	8.24	9.87	9.31

[a] Signal not identified in the spectrum.



Scheme 3

long-lived enough to react with a phenyl ring, since arylnitrenium–$AlCl_3$ complexes[9] are reported to be more stable than the nitrenium ions themselves.

Experimental

Melting points are uncorrected and were taken on a Yanagimoto hot-stage melting point apparatus. ^{1}H NMR spectra were measured on a JEOL JNM-PMX60SI spectrometer with tetramethylsilane (Me_4Si) as an internal reference and $CDCl_3$ as the solvent. *J* values are given in Hz. Infrared (IR) spectra were recorded on a JASCO IR810 spectrometer. Low and high resolution mass spectra (MS) were obtained with a JEOL JMS-DX300 spectrometer with a direct inlet system at 70 eV. Elemental analyses were performed in the microanalytical laboratory of this University.

Compounds **1** were synthesized by benzoylation of phenoxyamines with benzoyl chloride in pyridine with ice cooling later at room temperature for periods ranging from several hours to overnight in 70–90% yields. Spectral data for new compounds are listed in Table 4. **1a**, mp 138–140 °C (benzene), lit.,[10] mp 137–138 °C (EtOH); **1d**, mp 109.5–110 °C (benzene), lit.,[10] mp 102–103 °C (CH_2Cl_2–hexane); **1e**, mp 121–122 °C (benzene), lit.,[10] mp 117–118 °C (CH_2Cl_2–hexane); **1g**, mp 131–133 °C (benzene), lit.,[10] mp 137–138 °C (benzene); **2a**, mp 171–173 °C (EtOH), lit.,[11] mp 169–170 °C; **2e**, mp 233–235 °C (AcOEt), lit.,[12] mp 231–232 °C; **2f**, mp 161–162 °C (AcOEt), lit.,[13] mp 155 °C; **2g**, mp 239–240 °C (AcOEt), lit.,[14] mp 229–230 °C; **2i**, mp 198–201 °C (AcOEt), lit.,[15] mp 191–192 °C; **2j**, mp 215–218 °C (AcOEt), lit.,[14] mp 215–216 °C; **3b**, mp 118–119 °C (benzene), lit.,[16] mp 115 °C; **3c**, mp 123–125 °C (AcOEt), lit.,[17] mp 122 °C; **3d**, mp 175–178 °C (benzene), lit.,[18] mp 175 °C; **6**, mp 81–82 °C (hexane), lit.,[19] mp 80–81 °C; **8**, mp 159–160 °C (benzene), lit.,[20] mp 159–160 °C.

Reaction of *N*-phenoxybenzamide derivatives (1) with $AlCl_3$ in CH_2Cl_2. Typical procedure

To **1a** (200 mg, 0.94 mmol) in CH_2Cl_2 (8 cm^3) was added $AlCl_3$ (625 mg, 4.69 mmol) with cooling. After stirring the reaction mixture for 1 h at room temperature, 10% HCl (10 cm^3) was added with cooling. The aqueous layer was extracted with CH_2Cl_2 (30 $cm^3 \times 2$), and the combined organic layer was washed with brine (30 cm^3), dried over Na_2SO_4 and concentrated. The residue was chromatographed on a column of silica gel with benzene–ethyl acetate (10 : 1) as an eluent to give **2a** (170 mg, 85%), mp 167–169 °C, which was recrystallized from EtOH, mp 171–173 °C (lit.,[11] mp 169–170 °C).

Physical and spectral data of all new compounds are listed in Tables 4 and 5.

Reaction of *N*-phenoxybenzamide derivatives (1) with $AlMe_3$ in CH_2Cl_2. Typical procedure

To **1f** (100 mg, 0.4 mmol) in CH_2Cl_2 (4 cm^3) was added a solution of $AlMe_3$ in hexane (1.01 M, 2.18 cm^3, 2.18 mmol) with cooling. After stirring the reaction mixture for 4 h at room temperature, 10% HCl (10 cm^3) was added with cooling. The aqueous layer was extracted with ethyl acetate (30 $cm^3 \times 2$), and the combined organic layer was washed with brine (30 cm^3), dried over Na_2SO_4 and concentrated. The crude products were chromatographed on a flash column of silica gel. First elution with diethyl ether–light petroleum (1 : 2) afforded **1f** (4 mg, 4%) and **2h** (52 mg, 52%), mp 168–169 °C (AcOEt) (Found: C, 73.77; H, 5.80; N, 6.03. $C_{14}H_{13}NO_2$ requires C, 73.99; H, 5.77; N, 6.16%); *m*/*z* 227 M^+; ν_{max}(KBr)/cm^{-1} 3320, 3260 (OH, NH), 1640 (CON); δ_H($CDCl_3$) 6.82 (1H, t, Ph), 6.93 (1H, d, Ph), 7.07 (1H, d, Ph), 7.47–7.65 (3H, m, Ph), 8.10 (1H, br s, NH), 8.59 (1H, s, OH). Further elution with the same solvent mixture (5 : 1) afforded **6** (8 mg, 13%), mp 80–81 °C (benzene) (lit.,[19] mp 80–81 °C).

Table 4 Spectral data for new compounds

Compound	ν_{max}/cm^{-1}	δ_H	*m/z* (M^+)
1b	3150, 1660	6.10–7.90 (9H, m, Ph) 9.83 (1H, br s, NH)	231 (M^+, 15%)
1c	3150, 1650	6.60–7.97 (9H, m, Ph) 9.12 (1H, br s, NH)	247 (M^+, 27%) 249 ($M^+ + 2$, 10%)
1f	3130, 1650	2.23 (3H, s, CH_3) 6.50–7.93 (9H, m, Ph) 9.23 (1H, br s, NH)	227 (M^+, 39%)
1h	3150, 1670	6.73–7.93 (8H, m, Ph) 9.93 (1H, br s, NH)	281 (M^+, 11%) 283 ($M^+ + 2$, 7%) 285 ($M^+ + 4$, 1%)
1i	3120, 1660	6.03–8.07 (8H, m, Ph) 9.17 (1H, br s, NH)	309 (M^+, 7%) 311 ($M^+ + 2$, 7%)
1j	3180, 1660	6.73–8.00 (8H, m, Ph) 9.10 (1H, br s, NH)	369 (M^+, 6%) 371 ($M^+ + 2$, 11%) 373 ($M^+ + 4$, 6%)
2b	3420, 3050 1640	6.65 (1H, ddd, *J* 9.5, 8.0, 2.8, Ph) 6.73 (1H, dd, *J* 9.5, 2.8, Ph) 7.48–7.66 (3H, m, Ph) 7.70 (1H, dd, *J* 8.0, 6.1, Ph) 7.96–8.09 (2H, m, Ph) 9.47 (1H, br s, NH) 9.66 (1H, br s, OH)	231 (M^+, 16%)
2c	3400, 3250, 1650	6.72 (1H, t, *J* 9.8, Ph)[a] 6.87 (1H, d, *J* 8.4, Ph) 7.05–7.16 (1H, m, Ph) 7.48–7.69 (3H, m, Ph) 7.87–7.99 (2H, m, Ph) 8.20 (1H, br s, NH) 9.76 (1H, br s, OH)	231 (M^+, 15%)
2d	3430, 3200, 1665	6.91 (1H, t, *J* 8.1, Ph) 7.08–7.22 (2H, m, Ph) 7.42–7.66 (3H, m, Ph) 7.81–8.00 (3H, m, Ph + NH) 8.36 (1H, br s, NH)	247 (M^+, 17%) 249 ($M^+ + 2$, 6%)
2k	3330, 3060, 1640	6.95 (1H, t, *J* 9.3, Ph) 7.14 (1H, dd, *J* 8.8, 4.8, Ph) 7.50–7.72 (3H, m, Ph) 7.94–8.07 (2H, m, Ph) 8.47 (1H, br s, NH) 9.89 (1H, br s, OH)	309 (M^+, 8%) 311 ($M^+ + 2$, 8%)
2l	3425, 3200, 1660	7.30 (1H, s, Ph)[a] 7.47–7.70 (3H, m, Ph) 7.99–8.07 (2H, m, Ph) 8.24 (1H, s, Ph) 9.31 (1H, br s, NH) 9.87 (1H, br s, OH)	325 (M^+, 5%) 327 ($M^+ + 2$, 7%) 329 ($M^+ + 4$, 2%)
2m	3290, 3080, 1640	7.08 (1H, d, *J* 8.6, Ph) 7.37 (1H, d, *J* 8.6, Ph) 7.51–7.76 (3H, m, Ph) 7.97–8.07 (2H, m, Ph) 8.45 (1H, br s, NH) 10.32 (1H, br s, OH)	369 (M^+, 3%) 371 ($M^+ + 2$, 6%) 373 ($M^+ + 4$, 3%)
3e	3290, 1660	7.50–7.67 (3H, m, Ph) 7.68 (1H, s, Ph) 7.89–7.95 (2H, m, Ph) 8.40 (1H, br s, NH) 8.96 (1H, s, Ph)	387 (M^+, 3%) 389 ($M^+ + 2$, 7%) 391 ($M^+ + 4$, 5%) 393 ($M^+ + 6$, 1%)
7	3120, 1670	1.98 (3H, s, CH_3) 2.25 (3H, s, CH_3) 6.53–7.25 (4H, m, Ph)	165 (M^+, 46%)

[a] $[^2H_6]$Acetone.

Reaction of *N*-(4-methylphenoxy)benzamide (1g) with $BF_3{\cdot}OEt_2$ in CH_2Cl_2

To **1g** (200 mg, 0.88 mmol) in CH_2Cl_2 (8 cm^3) was added $BF_3{\cdot}OEt_2$ (0.54 cm^3, 4.40 mmol) with cooling. After stirring the reaction mixture for 3 days at room temperature, 10% HCl (10 cm^3) was added with cooling. The aqueous layer was extracted with ethyl acetate (50 $cm^3 \times 2$), and the combined organic layer was washed with brine (50 cm^3), dried over Na_2SO_4 and concentrated. The residue was chromatographed on a column of silica gel with benzene–ethyl acetate (20 : 1) as an eluent to give **5a** (124 mg, 62%), mp 169–171 °C (MeOH–H_2O) (Found: C, 73.55; H, 5.26. $C_{14}H_{12}O_3$ requires C, 73.67; H, 5.30%); *m/z* 228

Table 5 Physical constants and microanalytical data of new compounds

Compound	Mp/°C	Solvent	Molecular formula	Found (%)			Required (%)		
				C	H	N	C	H	N
1b	92–93	AcOEt–hexane	$C_{13}H_{10}FNO_2$	67.41	4.48	5.96	67.53	4.36	6.06
1c	141–143	benzene	$C_{13}H_{10}ClNO_2$	63.02	4.23	5.56	63.04	4.07	5.66
1f	139–142	benzene	$C_{14}H_{13}NO_2$	73.92	5.84	6.11	73.99	5.77	6.16
1h	132–133	benzene	$C_{13}H_9Cl_2NO_2$	55.15	3.33	4.91	55.35	3.22	4.96
1i	123–123.5	benzene	$C_{13}H_9BrFNO_2$	50.28	2.99	4.32	50.35	2.93	4.52
1j	145–146	benzene	$C_{13}H_9Br_2NO_2$	42.09	2.53	3.58	42.08	2.45	3.78
2b	220–222	AcOEt	$C_{13}H_{10}FNO$	67.51	4.45	5.89	67.53	4.36	6.06
2c	145–146	AcOEt	$C_{13}H_{10}FNO$	67.42	4.49	5.93	67.53	4.36	6.06
2d	141–143	AcOEt	$C_{13}H_{10}ClNO_2$	62.96	4.22	5.72	63.04	4.07	5.66
2k	125–126	AcOEt	$C_{13}H_9BrFNO$	50.24	3.03	4.45	50.35	2.93	4.52
2l	248–251	AcOEt	$C_{13}H_9NO_2BrCl$	47.77	2.86	4.28	47.81	2.78	4.29
2m	177.5–178	benzene	$C_{13}H_9Br_2NO$	42.02	2.49	3.72	42.08	2.45	3.78
3e	178–180	AcOEt	$C_{13}H_8Br_2ClNO$	40.02	2.28	3.64	40.31	2.07	3.62
7	144–146	benzene	$C_9H_{11}NO_2$	65.36	6.71	8.37	65.44	6.71	8.48

(M^+); ν_{max}(KBr)/cm^{-1} 3400 (OH), 1725 (COO); δ_H($CDCl_3$) 2.31 (3H, s, CH_3), 5.29 (1H, s, OH), 6.96–7.03 (3H, m, Ph), 7.48–7.59 (2H, m, Ph), 7.61–7.72 (1H, m, Ph), 8.19–8.26 (2H, m, Ph).

Reaction of *N*-phenoxybenzamide (1a) with $AlCl_3$ in benzene

To **1a** (200 mg, 0.94 mmol) in benzene (8 cm^3) was added $AlCl_3$ (625 mg, 4.69 mmol) with cooling. After stirring the reaction mixture for 1 h at room temperature, 10% HCl (10 cm^3) was added with cooling. The aqueous layer was extracted with ethyl acetate (30 $cm^3 \times 2$), and the combined organic layer was washed with brine (30 cm^3), dried over Na_2SO_4 and concentrated. The crude products were chromatographed on a column of silica gel. First elution with benzene–ethyl acetate (20 : 1) afforded **3a** (101 mg, 58%), mp 162–164 °C (lit.,[21] mp 164–166 °C). Further elution with the same solvent mixture afforded **2a** (71 mg, 36%), mp 168–169 °C (lit.,[11] mp 169–170 °C).

References

1 Y. Kikugawa and M. Shimada, *J. Chem. Soc.*, *Chem. Commun.*, 1989, 1450.
2 R. A. Abramovitch and R. Jeryaraman, in *Azides and Nitrenes*, ed. E. F. V. Scriven, Academic Press, New York, 1984, pp. 297–357.
3 E. Miyazawa, T. Sakamoto and Y. Kikugawa, *Org. Prep. Proced. Int.*, 1997, **29**, 594, and references cited therein.
4 G. A. Olah, B. P. Singh and G. Liang, *J. Org. Chem.*, 1984, **49**, 2922; G. T. Tisue, M. Grassmann and W. Lwowski, *Tetrahedron*, 1968, **24**, 999; L. H. Horner and H. Steppan, *Liebigs Ann. Chem.*, 1957, **606**, 24.
5 (*a*) A. Ribera and M. Rico, *Tetrahedron Lett.*, 1968, 535; (*b*) M. Zanger, W. W. Simons and A. R. Gennaro, *J. Org. Chem.*, 1968, **33**, 3673.
6 R. F. C. Brown, L. Radom, S. Sternhell and I. D. Rae, *Can. J. Chem.*, 1968, **46**, 2577; J. R. Bartels-Keith and R. F. W. Cieciuch, *Can. J. Chem.*, 1968, **46**, 2593; B. D. Andrews, I. D. Rae and B. E. Reichert, *Tetrahedron Lett.*, 1969, 1859; J. M. Appleton, B. D. Andrews, I. D. Rae and B. E. Reichert, *Aust. J. Chem.*, 1970, **23**, 1667; G. W. Gribble and F. P. Bousquet, *Tetrahedron*, 1971, **27**, 3785.
7 K. Paluch, *Rocz. Chem.*, 1965, **39**, 744 (*Chem. Abstr.*, 1965, **63**, 8250).
8 Y. Endo, K. Shudo and T. Okamoto, *J. Am. Chem. Soc.*, 1982, **104**, 6393.
9 H. Takeuchi, M. Maeda, M. Mitani and K. Koyama, *J. Chem. Soc.*, *Perkin Trans. 1*, 1987, 57.
10 Y. Endo, K. Shudo and T. Okamoto, *Synthesis*, 1980, 461.
11 A. Ito, *Yakugaku Zassi*, 1962, **82**, 875.
12 J. T. Edward, *J. Chem. Soc.*, *Chem. Commun.*, 1956, 222.
13 G. R. Clemo and A. F. Daglish, *J. Chem. Soc.*, *Chem. Commun.*. 1950, 1481.
14 R. Adams and J. M. Stewart, *J. Am. Chem. Soc.*, 1952, **74**, 5876.
15 L. C. Raiford and J. Couture, *J. Am. Chem. Soc.*, **46**, 2305.
16 F. D. Chattaway, K. J. P. Orton and W. H. Hurtley, *Chem. Ber.*, 1899, **32**, 3635.
17 J. P. Wibaut, *Recl. Trav. Chim. Pays-Bas*, **32**, 244 (*Chem. Abstr.*, 1914, **8**, 1268).
18 M. P. Grammaticakis, *Bull. Soc. Chim. Fr.*, 1949, 761.
19 A. W. Titherley, *J. Chem. Soc.*, 1901, **79**, 391.
20 E. Nöelting and O. Kohn, *Ber.*, 1884, **17**, 351.
21 C. G. Derick and J. H. Bornmann, *J. Am. Chem. Soc.*, 1913, **35**, 1269.

Paper 7/06488H
Received 16*th June* 1997
Accepted 8*th September* 1997