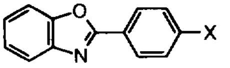
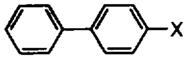
We have no direct evidence of the presence of ketimines **9**; on the other hand these compounds are known to be very sensitive to moisture.[10] Actually, ketimine **9b** was prepared and maintained at 60 °C in benzene solution in the presence of DPDC: under these conditions it quickly disappeared giving benzophenone **4b** (25%) and trace amounts of benzoxazoles **10a-b** and biphenyls **11a-b**.



10a,b

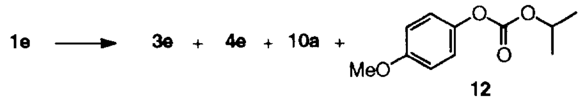


11a,b

Trace amounts of benzoxazoles and biphenyls were also found in all the reactions of imines **1a-e** with DPDC and this result is supporting the intervention of ketimines **9** in the reaction mechanism depicted in Scheme 2. As far as compounds **10** and **11** are concerned, they could arise from a 5-endo ring closure of phenoxyls **8** as previously suggested.[8]

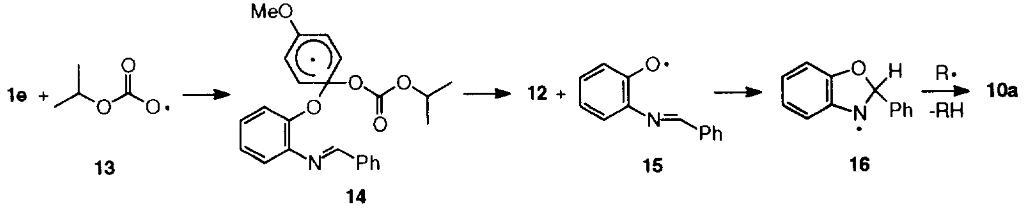
It is worth to point out that the reaction path leading from **5** to **8** entails a homolytic rearrangement that appears to our knowledge to be the first example of 1,5 radical translocation of an aryl group from an oxygen to a carbon atom.[11]

As far as imine **1e** is concerned, from Table 1 it can be noted that the yields of compounds **3e** and **4e** are significantly lower than the ones observed with the other imines; furthermore, it is worth to point out the presence of a greater amount of oxazole **10a** (6%), together with carbonate **12** (4%) (Scheme 3).



Scheme 3. Reaction products obtained from imine **1e**.

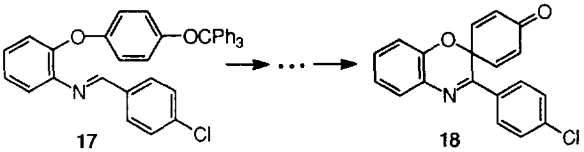
The formation of this compound could be rationalised by assuming an *ipso*-substitution process by *iso*-propoxycarbonyloxy radical **13**, arising from decomposition of DPDC, on the aromatic ring bearing the two oxygenated moieties (Scheme 4); this is probably due both to the electrophilic character of radical **13** and to the electron-donating substituents on the aromatic ring. In the case of imines **1a-d**, which are lacking in a so high electronic density on their aromatic rings, cognates of **12** were never obtained. The mechanism shown in Scheme 4 accounts for the increased yield of benzoxazole **10a** as well: together with **12**, the cyclohexadienyl **14** also affords the phenoxy radical **15**, which leads to **10a** through an easy aromatisation of the intermediate aminyl **16**.



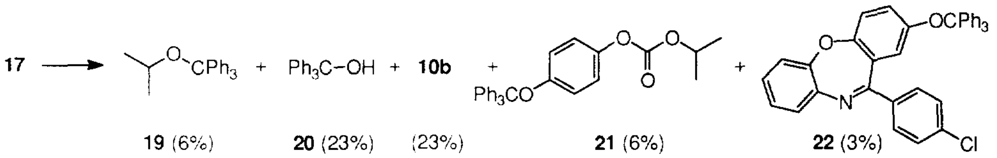
Scheme 4. Aromatic *ipso*-substitution of radical **13** on imine **1e**.

Many papers dealing with aromatic *ipso*-substitution of halogen atoms have appeared, but it is noteworthy that the process shown in the above Scheme seems to be the first example of substitution of an aryloxy group by an oxygen-centred radical.[12] An analogous substitution of the methoxy group was not observed, probably due to the greater stability of the aryloxyl **15** with respect to the methoxy radical.

In the attempt of giving evidence of the spirocyclohexadienyl radical **7** and on the basis of a previous related success,[2b] we allowed imine **17** to react under the same conditions with the aim of isolating the spirocyclohexadienone **18**.

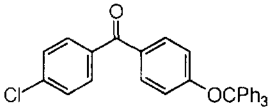


In Scheme 5 we report the products obtained from imine **17**.



Scheme 5. Reaction products obtained from imine **17**.

As it can be noted, unfortunately no cyclohexadienone **18** was obtained; on the other hand we isolated compounds (**19** and **20**[13]) that could be accounted for by assuming a homolytic cleavage of the triphenylmethyl-oxygen bond. In addition, the absence of benzophenone **23** and benzoxazole **24** (and their hydroxy derivatives, whose formation during column chromatography could be envisaged) let us suppose that the triphenylmethoxy group has a dramatic effect on the 6-membered-cyclisation intermediates.



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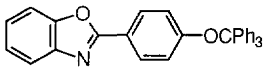
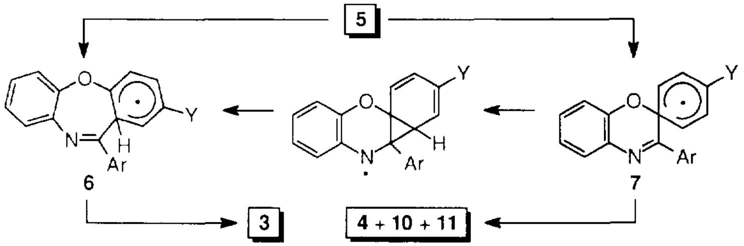


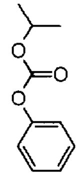
24

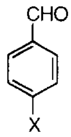
The presence of dibenzoxazepine **22**, which was obtained in almost identical yield as in the case of the analogous **3e** from imine **1e**, suggests that **22** is probably formed through a reaction pathway independent of the effect of the triphenylmethoxy substituent, *i.e.* a direct 7-membered ring closure. We actually did not rule out the possibility of formation of the dibenzoxazepines *via* a ring-expansion mechanism as shown in Scheme 6 but, mainly when Y is Ph_3C-O, it appears very unlikely that this route can efficiently compete with the other possible reactions of 7.[14]



Scheme 6. Ring-expansion mechanism for the formation of dibenzoxazepines **3**.

As far as compounds **10b** and **21** are concerned, they can be rationalised through the same *ipso*-substitution mechanism we have already described for the analogous derivatives **10a** and **12** obtained from imine **1e** (see Scheme 4). In all the reactions, besides the reported products, we also found the following ones, which have no relation with our study, and have been previously accounted for.[8]


25



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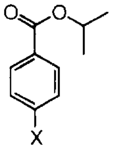

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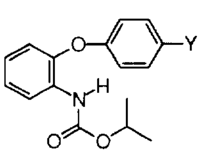

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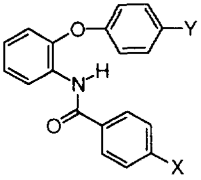
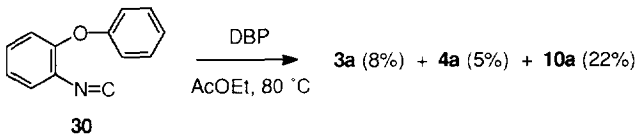


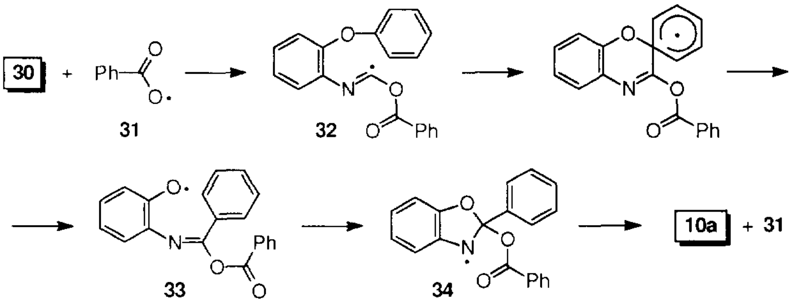
29

With the aim to obtain less complicated reaction mixtures, we tried to generate **5**-like imidoyls by radical addition to 2-phenoxyisocyanobenzene **30**. When **30** was allowed to react with dibenzoyl peroxide (DBP) in boiling ethyl acetate, we obtained the products reported in Scheme 7. Compounds **3a** and **4a** are easily accounted for by assuming an initial addition of a phenyl radical, generated by decomposition of DBP, to the carbon atom of the isonitrile; the resulting imidoyl **5a** evolves as we reported in Scheme 2 to give **3a** and **4a**. On the other hand, this mechanism does not rationalise the amount of **10a**, obtained only in traces when imidoyl **5a** was generated from the corresponding imine **1a**.



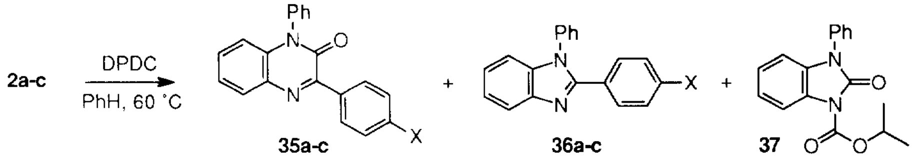
Scheme 7. Reaction products obtained from isonitrile **30**.

Since the β-fragmentation of benzoyloxy radical **31** is not very fast,[15] we suppose that also **31** could attack the isonitrile giving the intermediate imidoyl **32**; migration of the phenyl group through 6-membered *ipso*-substitution leads to phenoxyl **33**: 5-endo ring closure of **33** affords the cyclic aminyl **34**, which can easily aromatise *via* β-scission with expulsion of the relatively stable benzoyloxyl **31**; this radical behaves indeed like a catalyst in the formation of benzoxazole **10a** (Scheme 8). Another possibility entails hydrogen abstraction by **34** and loss of benzoic acid from the resulting dihydrobenzoxazole.



Scheme 8. Suggested mechanism of formation of **10a** from isonitrile **30** and DBP.

In support of the presence of the intermediate **32**, GC-MS analysis of the reaction mixture revealed small quantities of 2-phenoxyphenyl isocyanate, probably arising from **32** through β-scission with loss of a benzoyl radical; on the other hand, **32**-like imidoyls are known to fragment to isocyanates.[16] The reaction of isonitrile **30** shows once more the 1,5 migration of a phenyl radical from oxygen to carbon; in addition, the presence of a good radical leaving-group in the cyclic aminyls (**34** and **12**) favours the formation of benzoxazoles. As far as the isonitrile is concerned, further studies are in progress dealing with the addition of different radicals.Going from the oxygen- to the nitrogen-substituted imines **2a-c**, their behaviour is completely different. When **2a-c** were allowed to react in the same conditions, besides by-products **25**, **26**, and **27**, we got the compounds reported in Scheme 9 and Table 2.

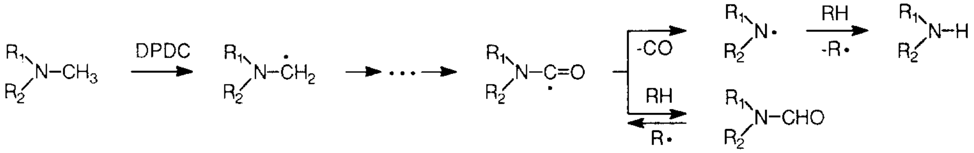


Scheme 9. Main products of the reaction of imines **2a-c** with DPDC.

Comp.	X	t (h)[a]	**35** (%)[a]	**36** (%)[a]	**37** (%)[a]	t (h)[b]	**35**(%)[b]	**36** (%)[b]	**37** (%)[b]
2a	H	30	20	14	14	18	25	18	18
2b	Cl	30	16	14	7	18	28	20	11
2c	OMe	26	16	9	12	18	25	15	18

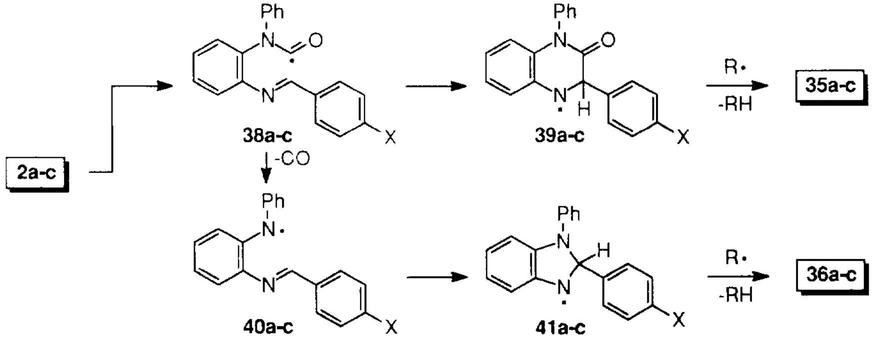
Table n. 2. All yields are for the starting imines.
a) Reactions carried out with 2 mmol of DPDC. b) Reactions carried out with 4 mmol of DPDC.

None of these products can be accounted for through the intervention of an imidoyl radical analogous to the oxygenated intermediate **5**; therefore, we need to postulate a different pathway and we imagine that DPDC can oxidise the methyl group linked to the nitrogen atom. This idea was confirmed by the reaction of *N*-methylcarbazole with DPDC, which gave in two hours *N*-formylcarbazole and carbazole, according to the general Scheme 10.



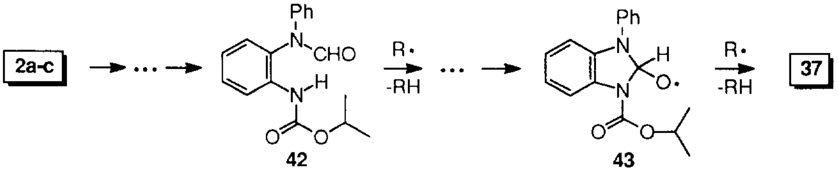
Scheme n. 10. Mechanism of oxidation of a methyl group by DPDC.

A so short reaction time for the oxidation of the methyl group let us think that this process should be faster than abstraction of the iminic hydrogen to form an imidoyl radical. Furthermore, this result leads us to suppose that compounds **35**, **36**, and **37** could be explained by the intermediacy of carbamoyl and aminyl radicals derived from oxidation of the methylamino moiety of imines **2a-c**. On these bases we suggest the formation of the intermediate carbamoyl radicals **38**, which can give a 6-endo cyclisation on the iminic double bond to furnish quinoxalinones **35** after hydrogen abstraction from **39**; radicals **38** can also loose carbon monoxide leading to aminyls **40**, which afford benzimidazoles **36** through a 5-endo cyclisation on the carbon-nitrogen double bond followed by hydrogen abstraction from **41** (Scheme 11).[17]



Scheme n. 11. Mechanism of formation of compounds **35** and **36**.

Furthermore, we could expect that also these imines can generate a carbamate analogous to compounds **28** obtained from imines **1**. We did not detect this product in the reaction mixtures, but we suppose that it can be oxidised to the formyl derivative **42**; hydrogen abstraction by DPDC eventually leads to radical **43** and then to **37** (Scheme 12).



Scheme 12. Mechanism of formation of compound **37**.

The reactions of imines **2** with DPDC afforded no traces of products arising from imidoyl radicals; we actually observed trace amounts of benzophenones **4a-c**, but the presence of these compounds is by no means important, because they were also detected in the same quantities when the corresponding aldehydes **26** were allowed to react in the same conditions.

In order to check the possibility of 1,5-aryl migration from nitrogen to carbon in imidoyl radicals derived from **2**-like imines, we are going to substitute the methyl with a further phenyl group. Studies are also in progress to investigate the reactivity in the gas phase of imidoyl radicals generated by Flash Vacuum Pyrolysis from appropriate precursors.

EXPERIMENTAL SECTION

General Procedures.

Melting points were determined on an Electrothermal capillary apparatus and are uncorrected. ^{1}H- and ^{13}C-NMR spectra were recorded in deuterochloroform on Varian EM 360L (60 MHz), Varian Gemini 200 (200 MHz), or Varian Gemini 300 (300 MHz) instruments, using tetramethylsilane as an internal standard. Mass spectra (MS) and high resolution mass spectra (HRMS) were performed with a VG 7070E spectrometer by electron impact with a beam energy of 70 eV. IR spectra were recorded in chloroform or tetrachloromethane on a Perkin-Elmer 257 spectrophotometer. GC-MS analyses were carried out on a Carlo Erba AUTO/HRGC/MS-QMD 1000 instrument equipped with a Quadrex capillary column (007, 25 m x 0.25 mm I.D.) and a NIST/NBS library. GC quantitative determinations (internal-standard method) were performed on a Varian Star 3400 CX gas chromatograph equipped with a FID and the same column described for GC-MS analyses. Column chromatography was carried out on silica gel (ICN Silica, 63-200, 60 A), basic aluminium oxide (Baker, Activity Grade III), or Florisil® (Aldrich, 100-200 mesh) using light petroleum (40-70 °C) and a light petroleum/diethyl ether gradient (from 0 up to 100% diethyl ether) as eluant. Previously reported reaction products were identified by spectral comparison and mixed mp determination with authentic specimens.

Starting Materials.

All reactions were carried out in benzene (Baker); the solvent was dried over sodium threads to minimise hydrolysis of the starting imines in the reaction mixtures. 2-Phenoxybenzenamine, benzaldehyde, 4-chlorobenzaldehyde, 4-methoxybenzaldehyde, benzoyl chloride, 4-chlorobenzoyl chloride, 4-methoxybenzoyl chloride, 2-aminophenol, benzophenone (**4a**), 4-chlorobenzophenone (**4b**), 4-methoxybenzophenone (**4c**), 2-chloronitrobenzene, and triphenylmethyl chloride (Aldrich) were commercially available.

4-Chloro-2'-nitrodiphenylether,[18] hydroquinone mono(2-aminophenyl)ether,[19] 2-(4-chlorophenoxy)-benzenamine,[18] *N*-(2-phenoxyphenyl)benzamide (**29a**),[20] *N*-[2-(4-methoxyphenoxy)phenyl]benzamide (**29c**),[21] 11-phenyldibenz[*b*,*f*][*1*,*4*]oxazepine (**3a**),[22] 2-methoxy-11-phenyldibenz[*b*,*f*][*1*,*4*]oxazepine (**3c**),[21] *N*-diphenylmethylene-2-aminophenol (**9a**),[10] 2-phenyl-benz[*d*][*1,3*]oxazole (**10a**),[23] 2-(4-chlorophenyl)benz[*d*][*1,3*]oxazole (**10b**),[23] 2-(4-methoxyphenyl)-benz[*d*][*1,3*]oxazole (**10c**),[23] *N*-(2-phenoxyphenyl)formamide,[18] 2-propyl benzoate (**27a**),[24] 2-propyl 4-chlorobenzoate (**27b**),[24] 2-propyl 4-methoxybenzoate (**27c**),[24] 2-propyl chloroformate,[25] *N*-methyl-*N*-phenylbenzen-1,2-diamine,[26] and di-*iso*-propyl peroxydicarbonate (DPDC)[27] were prepared according to the literature. DPDC was stored at 5 °C as a dry-benzene solution and the peroxide content was determined by iodometric titration.[28]

4-Methoxy-2'-nitrodiphenylether (mp = 73-75 °C, lit.[29] mp = 74.5-75.5 °C) and 2-(4-methoxyphenoxy)-benzenamine [bp (0.2 mmHg) = 128-130 °C, lit.[29] bp (0.2 mmHg) = 130 °C] were prepared according to Wardrop et al.[18]

Synthesis of the imines.

General Procedure. A benzene or toluene (50 mL) solution of the amine (25 mmol) and the aldehyde (25 mmol) was refluxed (2-6 h) with azeotropic removal of water in the presence of catalytic amounts of *p*-toluenesulfonic acid (0.1 g). The solvent was evaporated and the residue crystallised or distilled as appropriate. In a few cases, the attempted distillation caused partial decomposition of the imine, therefore the synthesis was repeated and the oily products were used in the subsequent reactions without further purification. Microanalyses of these oily compounds were not performed, but their ^{1}H-NMR spectra were in accordance with a very good sample homogeneity; their identity was also confirmed by HRMS analysis. The following imines were prepared according to this general procedure.

N-Phenylmethylene-2-phenoxybenzenamine (1a), yield = 80%, mp = 84-86 °C (after several washings with diethyl ether);[30] 200 MHz ^{1}H-NMR δ 6.90-7.50 (12H, m, Ar-*H*), 7.70-7.85 (2H, m, Ar-*H*), 8.48 (1H, s, -N=C*H*-); MS *m/e* (rel inten) 273 (M^+, 68), 272 (37), 196 (100), 77 (11); HRMS calcd for $C_{19}H_{15}NO$ 273.1154, found 273.1152.

N-(4-Chlorophenylmethylene)-2-phenoxybenzenamine (1b), yield = 55%, mp = 73-76 °C (from light petroleum/2-propanol 70:30 v/v);[31] 200 MHz ^{1}H-NMR δ 6.90-7.40 (11H, m + A part of AA'BB', *J* = 7.9 Hz, Ar-*H*), 7.67 (2H, B part of AA'BB', *J* = 7.9 Hz, Ar-*H*), 8.40 (1H, s, -N=C*H*-); MS *m/e* (rel inten) 309 (M^+ + 2, 17), 308 (M^+ + 1, 19), 307 (M^+, 50), 306 (30), 196 (100), 77 (15); HRMS calcd for $C_{19}H_{14}ClNO$ 307.0764, found 307.0761.

N-(4-Methoxyphenylmethylene)-2-phenoxybenzenamine (1c), yield = 51%, mp = 79-81 °C (from light petroleum/diethyl ether 70:30 v/v); 200 MHz ^{1}H-NMR δ 3.80 (3H, s, -O*Me*), 6.85-7.40 (11H, m, Ar-*H*), 7.70 (2H, B part of AA'BB', *J* = 8.3 Hz, Ar-*H*), 8.40 (1H, s, -N=C*H*-); MS *m/e* (rel inten) 303 (M^+, 100), 302 (86), 226 (12), 196 (94), 77 (18); HRMS calcd for $C_{20}H_{17}NO_2$ 303.1259, found 303.1258. Anal. calcd for $C_{20}H_{17}NO_2$: C, 79.19; H, 5.65; N, 4.62. Found: C, 79.40; H, 5.63; N, 4.63.

N-(Phenylmethylene)-2-(4-chlorophenoxy)benzenamine (1d), yield = 64%, bp (0.04 mbar) = 158-160 °C; 200 MHz ^{1}H-NMR δ 6.82-6.94 (3H, m + A part of AA'BB', *J* = 8.9 Hz, Ar-*H*), 7.04-7.30 (5H, m + B part of AA'BB', *J* = 8.9 Hz, Ar-*H*), 7.36-7.46 (3H, m, Ar-*H*), 7.72-7.82 (2H, m, Ar-*H*), 8.43 (1H, s, -N=C*H*-); MS *m/e* (rel inten) 309 (M^+ + 2, 22), 308 (M^+ + 1, 22), 307 (M^+, 66), 306 (34), 232 (34), 230 (100); HRMS calcd for $C_{19}H_{14}ClNO$ 307.0764, found 307.0765. Anal. calcd for $C_{19}H_{14}ClNO$: C, 74.15; H, 4.58; N, 4.55. Found: C, 74.40; H, 4.57; N, 4.56.

N-(Phenylmethylene)-2-(4-methoxyphenoxy)benzenamine (1e), yield = 20%, oil (after column chromatography on Florisil); 200 MHz ^{1}H-NMR δ 3.75 (3H, s, -O*Me*), 6.80-7.20 (9H, m + AA'BB', *J* = 8.9 Hz, Ar-*H*), 7.37-7.45 (2H, m, Ar-*H*), 7.80-7.88 (2H, m, Ar-*H*), 8.50 (1H, s, -N=C*H*-); MS *m/e* (rel inten) 303 (M^+, 33), 302 (15), 288 (2), 226 (100), 152 (6), 77 (9); HRMS calcd for $C_{20}H_{17}NO_2$ 303.1259, found 303.1258.

N-(4-Chlorophenylmethylene)-2-(4-hydroxyphenoxy)benzenamine, yield = 73% (reflux in toluene), mp = 138-140 °C (from light petroleum/diethyl ether 50:50 v/v); 300 MHz ^{1}H-NMR δ 5.13 (1H, bs, -O*H*); 6.74 (2H, A part of AA'BB', *J* = 9.0 Hz, Ar-*H*), 6.87 (2H, B part of AA'BB', *J* = 9.0 Hz, Ar-*H*), 6.90-6.96 (1H, m, Ar-*H*), 7.10-7.18 (3H, m, Ar-*H*), 7.40 (2H, A part of AA'BB', *J* = 8.4 Hz, Ar-*H*), 7.77 (2H, B part of AA'BB', *J* = 8.4 Hz, Ar-*H*), 8.47 (1H, s, -N=C*H*-); MS *m/e* (rel inten) 325 (M$^+$ + 2, 10), 324 (M$^+$ + 1, 10), 323 (M$^+$, 26), 322 (16), 230 (4), 212 (53), 100 (100); HRMS calcd for $C_{19}H_{14}ClNO_2$ 323.0713, found 323.0708. Anal. calcd for $C_{19}H_{14}ClNO_2$: C, 70.48; H, 4.36; N, 4.33. Found: C, 70.75; H, 4.35; N, 4.32.

N-(Phenylmethylene)-N'-methyl-N'-phenylbenzen-1,2-diamine (2a), oil that could not be distilled (reflux in toluene); 60 MHz ^{1}H-NMR δ 3.27 (3H, s, -*Me*), 6.04-7.17 (14H, m, Ar-*H*), 7.57 (1H, s, -N=C*H*-); MS *m/e* (rel inten) 286 (M$^+$, 100), 271 (13), 209 (26), 194 (15), 168 (9), 167 (12), 91 (16), 77 (18); HRMS calcd for $C_{20}H_{18}N_2$ 286.1470, found 286.1474.

N-(4-Chlorophenylmethylene)-N'-methyl-N'-phenylbenzen-1,2-diamine (2b), yield = 70%, bp (0.02 mbar) = 190-192 °C; 60 MHz ^{1}H-NMR δ 3.25 (3H, s, -*Me*), 6.58-7.64 (13H, m, Ar-*H*), 8.30 (1H, s, -N=C*H*-); MS *m/e* (rel inten) 322 (M$^+$ + 2, 45), 320 (M$^+$, 100), 306 (16), 305 (31), 304 (45), 303 (27), 228 (8), 197 (15), 196 (15), 195 (19), 181 (25), 168 (11), 77 (29); HRMS calcd for $C_{20}H_{17}ClN_2$ 320.1080, found 320.1084. Anal. calcd for $C_{20}H_{17}ClN_2$: C, 74.88; H, 5.34; N, 8.73. Found: C, 75.25; H, 5.33; N, 8.70.

N-(4-Methoxyphenylmethylene)-N'-methyl-N'-phenylbenzen-1,2-diamine (2c), oil that could not be distilled (reflux in toluene); 60 MHz ^{1}H-NMR δ 3.23 (3H, s, -*Me*), 3.73 (3H, s, -O*Me*), 6.50-7.83 (13H, m, Ar-*H*), 8.27 (1H, s, -N=C*H*-); MS *m/e* (rel inten) 316 (M$^+$, 100), 301 (17), 224 (14), 209 (14), 167 (10), 91 (11), 77 (15); HRMS calcd for $C_{21}H_{20}N_2O$ 316.1576, found 316.1578.

N-(4-Chlorophenylmethylene)-2-[4-(triphenylmethoxy)phenoxy]benzenamine (18). Following the procedure previously described,[2b] *N*-(4-chlorophenylmethylene)-2-(4-hydroxyphenoxy)benzenamine (9.89 g, 31 mmol) was added to a solution of sodium ethoxide (31 mmol) in absolute ethanol (200 mL) and the mixture was refluxed to complete dissolution of the imine. The solvent was removed, the residue suspended in dry benzene (100 mL), and a solution of triphenylmethyl chloride (8.53 g, 31 mmol) in dry benzene (100 mL) was added dropwise to the boiling mixture. After 2 hours of reflux the hot mixture was filtered, the solvent evaporated and the residue crystallised from ethyl acetate to give 10.48 g (62%) of the title imine, mp = 155-158 °C; 300 MHz ^{1}H-NMR δ 6.55-6.63 (4H, AA'BB', *J* = 9.1 Hz, Ar-*H*), 6.79-6.84 (1H, m, Ar-*H*), 7.04-7.14 (3H, m, Ar-*H*), 7.20-7.29 (9H, m, Ar-*H*), 7.39-7.46 (8H, m, Ar-*H*), 7.70-7.76 (2H, A part of AA'BB', *J* = 8.3 Hz, Ar-*H*), 8.38 (1H, s, -N=C*H*-); MS *m/e* (rel inten) 325 (10), 324 (8), 323 (23), 322 (15), 244 (70), 243 (67), 231 (19), 229 (54), 212 (53), 167 (42), 166 (36), 165 (100), 152 (14). Anal. calcd for $C_{38}H_{28}ClNO_2$: C, 80.63; H, 4.99; Cl, 6.26; N, 2.47. Found: C, 80.85; H, 5.00; Cl, 6.27; N, 2.46.

Synthesis of the amides.

General procedure. A solution of the amine (30 mmol), the aroyl chloride (30 mmol), and triethylamine (33 mmol) in benzene (100 mL) was refluxed to complete disappearance of the starting amine (3-4 h). The solvent was evaporated and the residue suspended in water and extracted with dichloromethane. The organic phase was dried over sodium sulfate, the solvent was evaporated, and the residue crystallised. The following amides were prepared according to this general procedure.

N-(2-Phenoxyphenyl)-4-chlorobenzamide (29b), yield = 91%, mp = 79-81 °C (from light petroleum/benzene 50:50 v/v); 200 MHz ^{1}H-NMR δ 6.89 (1H, dd, J_1 = 8.2 Hz, J_2 = 1.5 Hz, Ar-*H*), 7.00-7.22 (5H, m, Ar-*H*), 7.31-7.44 (4H, m + A part of AA'BB', *J* = 8.5 Hz, Ar-*H*), 7.71 (2H, B part of AA'BB', *J* = 8.5 Hz, Ar-*H*), 8.42 (1H, bs, -N*H*-), 8.57 (1H, dd, J_1 = 8.0 Hz, J_2 = 1.5 Hz, Ar-*H*); MS *m/e* (rel inten) 325

($M^+ + 2$, 12), 323 (M^+, 35), 232 (18), 230 (53), 141 (31), 139 (100), 113 (11), 111 (32); ν_{max} ($CHCl_3$) 3420, 1680, 1610, 1600, 1490, and 1450 cm^{-1}; HRMS calcd for $C_{19}H_{14}ClNO_2$ 323.0713, found 323.0712. Anal. calcd for $C_{19}H_{14}ClNO_2$: C, 70.48; H, 4.36; N, 4.33. Found: C, 70.72; H, 4.36; N, 4.34.

N-(2-Phenoxyphenyl)-4-methoxybenzamide (***29c***), yield = 95%, mp = 109-112 °C (from light petroleum/benzene 50:50 v/v); 200 MHz ^{1}H-NMR δ 3.82 (3H, s, -O*Me*), 6.85-7.22 (8H, m + A part of AA'BB', J = 8.8 Hz, Ar-*H*), 7.30-7.41 (2H, m, Ar-*H*), 7.74 (2H, B part of AA'BB', J = 8.8 Hz, Ar-*H*), 8.41 (1H, bs, -N*H*-), 8.60 (1H, dd, J_1 = 8.0 Hz, J_2 = 1.3 Hz, Ar-*H*); MS *m/e* (rel inten) 319 (M^+, 18), 226 (15), 135 (100), 92 (7), 77 (10); ν_{max} ($CHCl_3$) 3430, 1670, 1610, 1510, and 1450 cm^{-1}; HRMS calcd for $C_{20}H_{17}NO_3$ 319.1208, found 319.1205. Anal. calcd for $C_{20}H_{17}NO_3$: C, 75.22; H, 5.37; N, 4.39. Found: C, 75.50; H, 5.36; N, 4.39.

N-[2-(4-Chlorophenoxy)phenyl]benzamide (***29d***), yield = 83%, mp = 107-110 °C (from light petroleum/2-propanol 30:70 v/v); 200 MHz ^{1}H-NMR δ 6.86 (1H, dd, J_1 = 8.1 Hz, J_2 = 1.5 Hz, Ar-*H*), 6.98 (2H, A part of AA'BB', J = 9.0 Hz, Ar-*H*), 7.04 (1H, ddd, $J_1 = J_2$ = 8.1 Hz, J_3 = 1.5 Hz, Ar-*H*), 7.18 (1H, ddd, $J_1 = J_2$ = 8.1 Hz, J_3 = 1.5 Hz, Ar-*H*), 7.31 (2H, B part of AA'BB', J = 9.0 Hz, Ar-*H*), 7.39-7.57 (3H, m, Ar-*H*), 7.75-7.83 (2H, m, Ar-*H*), 8.42 (1H, bs, -N*H*-), 8.60 (1H, dd, J_1 = 8.1 Hz, J_2 = 1.5 Hz, Ar-*H*); MS *m/e* (rel inten) 325 ($M^+ + 2$, 28), 323 (M^+, 21), 196 (45), 105 (89), 77 (100), 51 (18); HRMS calcd for $C_{19}H_{14}ClNO_2$ 323.0713, found 323.0714. Anal. calcd for $C_{19}H_{14}ClNO_2$: C, 70.48; H, 4.36; N, 4.33. Found: C, 70.79; H, 4.35; N, 4.34.

Synthesis of the dibenzoxazepines.

General procedure. A mixture of the amide (6 mmol), polyphosphoric acid (10.20 g), and phosphorus oxychloride (3.41 g) was kept at 100 °C under magnetic stirring until the starting suspension turned to a yellow-orange solution (2-8 h). After cooling, the solution was poured into water, neutralised with 50% aqueous ammonia, and extracted with dichloromethane. The organic phase was dried over sodium sulfate, the solvent evaporated, and the residue chromatographed on silica gel and recrystallised. The following dibenzoxazepines were prepared according to this general procedure.

11-(4-Chlorophenyl)dibenz[b,f][1,4]oxazepine (***3b***), yield = 77%, mp = 153-155 °C (from ethanol);[32] 200 MHz ^{1}H-NMR δ 7.10-7.27 (6H, m), 7.34-7.52 (4H, m + A part of AA'BB', J = 8.6 Hz), 7.74 (2H, B part of AA'BB', J = 8.6 Hz); MS *m/e* (rel inten) 307 ($M^+ + 2$, 38), 306 ($M^+ + 1$, 46), 305 (M^+, 100), 304 (99), 270 (36), 241 (14), 240 (8), 139 (15), 120 (16); HRMS calcd for $C_{19}H_{12}ClNO$ 305.0607, found 305.0605.

11-(4-Methoxyphenyl)dibenz[b,f][1,4]oxazepine (***3c***), yield = 43%, mp = 118-121 °C (from ethanol);[32] 200 MHz ^{1}H-NMR δ 3.87 (3H, s, -O*Me*), 6.95 (2H, A part of AA'BB', J = 8.3 Hz, Ar-*H*), 7.10-7.52 (8H, m, Ar-*H*), 7.80 (2H, B part of AA'BB', J = 8.3 Hz, Ar-*H*); MS *m/e* (rel inten) 301 (M^+, 100), 300 (82), 286 (8), 270 (22), 257 (13), 151 (8), 139 (10); HRMS calcd for $C_{20}H_{15}NO_2$ 301.1103, found 301.1102.

2-Chloro-11-phenyldibenz[b,f][1,4]oxazepine (***3d***), yield = 37%, mp = 144-146 °C (from 2-propanol); 200 MHz ^{1}H-NMR δ 7.16-7.28 (5H, m), 7.40-7.54 (5H, m), 7.78-7.86 (2H, m); MS *m/e* (rel inten) 309 ($M^+ + 2$, 22), 308 ($M^+ + 1$, 22), 307 (M^+, 66), 306 (34), 232 (34), 230 (100); HRMS calcd for $C_{19}H_{12}ClNO$ 305.0607, found 305.0609. Anal. calcd for $C_{19}H_{12}ClNO$: C, 74.64; H, 3.96; N, 4.58. Found: C, 74.90; H, 3.96; N, 4.59.

Synthesis of the carbamates.

General procedure. A solution of the aniline (10 mmol), 2-propyl chloroformate (10 mmol), and pyridine (11 mmol) in benzene (50 mL) was kept at 90 °C to complete disappearance of the starting amine (1-4 h). Diethyl ether (30 mL) was added and the mixture was washed several times with water. The organic phase was dried over sodium sulfate, the solvent removed, and the residue chromatographed on silica gel. Microanalyses of the oily compounds were not performed but their ^{1}H-NMR spectra are in accordance with a very good sample homogeneity. Their identity was confirmed by HRMS analysis. The following carbamates were prepared according to this general procedure.

2-Propyl N-(2-phenoxyphenyl)carbamate (28a), yield = 28%, mp = 58-60 °C (from light petroleum); 200 MHz ^{1}H-NMR δ 1.28 (6H, d, *J* = 6.5 Hz, -CH*Me*$_2$), 5.02 (1H, sept, *J* = 6.5 Hz, -C*H*Me$_2$), 6.80-7.40 (9H, m, Ar-*H* + -N*H*-), 8.21 (1H, bd, *J* = 8.1 Hz, Ar-*H*); MS *m/e* (rel inten) 271 (M$^+$, 57), 229 (7), 212 (17), 211 (18), 185 (100), 108 (12), 77 (17), 43 (56); ν_{max} ($CHCl_3$) 3420, 1730, 1610, and 1450 cm^{-1}; HRMS calcd for $C_{16}H_{17}NO_3$ 271.1208, found 271.1207. Anal. calcd for $C_{16}H_{17}NO_3$: C, 70.83; H, 6.32; N, 5.16. Found: C, 71.20; H, 6.30; N, 5.18.

2-Propyl N-[2-(4-chlorophenoxy)phenyl]carbamate (28d), yield = 60%, oil; 200 MHz ^{1}H-NMR δ 1.25 (6H, d, *J* = 6.1 Hz, -CH*Me*$_2$), 5.00 (1H, sept, *J* = 6.1 Hz, -C*H*Me$_2$), 6.80 (1H, dd, J_1 = 7.7 Hz, J_2 = 1.3 Hz, Ar-*H*), 6.77-7.00 (3H, m + A part of AA'BB', *J* = 8.7 Hz, Ar-*H*), 7.05-7.17 (2H, m, Ar-*H* + -N*H*-), 7.28 (2H, B part of AA'BB', *J* = 8.7 Hz, Ar-*H*), 8.20 (1H, bd, *J* = 7.9 Hz, Ar-*H*); MS *m/e* (rel inten) 307 (M$^+$ + 2, 24), 305 (M$^+$, 71), 265 (4), 263 (11), 248 (7), 246 (21), 245 (8), 221 (31), 219 (100), 184 (9), 183 (19), 154 (9), 108 (15), 43 (88); HRMS calcd for $C_{16}H_{16}ClNO_3$ 305.0819, found 305.0819.

2-Propyl N-[2-(4-methoxyphenoxy)phenyl]carbamate (28e), yield = 96%, oil; 200 MHz ^{1}H-NMR δ 1.30 (6H, d, *J* = 6.5 Hz, -CH*Me*$_2$), 3.80 (3H, s, -O*Me*), 5.05 (1H, sept, *J* = 6.5 Hz, -C*H*Me$_2$), 6.73 (1H, dd, J_1 = 7.9 Hz, J_2 = 1.3 Hz, Ar-*H*), 6.85-7.12 (6H, m + AA'BB', *J* = 9.1 Hz, Ar-*H*), 7.28 (1H, bs, -N*H*-), 8.21 (1H, bd, *J* = 7.7 Hz, Ar-*H*); MS *m/e* (rel inten) 301 (M$^+$, 100), 259 (18), 242 (10), 241 (19), 226 (6), 215 (45), 200 (54), 183 (12), 43 (44); HRMS calcd for $C_{17}H_{19}NO_4$ 301.1314, found 301.1316.

N-(4-Chlorodiphenylmethylene)-2-aminophenol (9b). A solution of 2-aminophenol (1.09 g, 10 mmol) and 4-chlorobenzophenone (2.16 g, 10 mmol) in cumene (70 mL) was refluxed for 43 h, in the presence of catalytic amounts of *p*-toluenesulfonic acid, with azeotropic removal of water. The solvent was evaporated and the residue rapidly chromatographed on silica gel to give 1.27 g (41%) of the title imine, mp = 130-132 °C (after several washings with diethyl ether); 200 MHz ^{1}H-NMR δ 6.11-6.20 (1H, m, Ar-*H*), 6.40-6.54 (1H, m, Ar-*H*), 6.77 (1H, bs, -O*H*), 6.90-6.96 (2H, m, Ar-*H*), 7.07-7.18 (2H, m, Ar-*H*), 7.29-7.48 (5H, m, Ar-*H*), 7.61-7.72 (2H, m, Ar-*H*); MS *m/e* (rel inten) 309 (M$^+$ + 2, 26), 308 (M$^+$ + 1, 18), 307 (M$^+$, 76), 306 (8), 232 (34), 230 (100), 196 (100), 165 (9), 65 (19); HRMS calcd for $C_{19}H_{14}ClNO$ 307.0764, found 307.0762. Anal. calcd for $C_{19}H_{14}ClNO$: C, 74.15; H, 4.58; N, 4.55. Found: C, 74.41; H, 4.57; N, 4.55.

2-Phenoxyisocyanobenzene (30). A solution of *N*-(2-phenoxyphenyl)formamide (4.26 g, 20 mmol) and anhydrous triethylamine (5.80 mL, 42 mmol) in dry dichloromethane (20 mL) was stirred at 0 °C into a three-necked flask fitted with a reflux condenser maintained at -30 °C.[33] Diphosgene (1.21 mL, 10 mmol) in dry dichloromethane (4 mL) was added at 0 °C over one hour. After 30 min the solution was warmed to r.t. and extracted with water and 7.5% sodium bicarbonate solution. The organic phase was dried over 4-Å molecular sieves, the solvent evaporated, and the residue distilled: bp (0.2 mmHg) = 109-110 °C. A GC-MS analysis of the isonitrile showed the presence of significant amounts of *N*-(2-phenoxyphenyl)isocyanate, therefore the isonitrile was rapidly chromatographed on aluminium oxide. The final product (1 g, 26%) was completely isocyanate-free (GC-MS); MS *m/e* (rel inten) 195 (M$^+$, 100), 167 (38), 166 (10), 77 (50), 51 (31); ν_{max} (CCl_4) 2120 cm^{-1}; HRMS calcd for $C_{13}H_9NO$ 195.0684, found 195.0682. Anal. calcd for $C_{13}H_9NO$: C, 79.98; H, 4.65; N, 7.17. Found: C, 80.37; H, 4.66; N, 7.20.

Reactions of the imines with DPDC.

General procedure. A solution of the imine (1 mmol) and DPDC (2 or 4 mmol) in dry benzene (20 mL) was kept at 60 °C to complete disappearance of the starting material. The solvent was evaporated and the residue analysed by GC-MS and chromatographed or quantitatively analysed by GC, by the internal-standard method, using the authentic specimens prepared above. Besides the reported products, all the reactions afforded small quantities (1-2%) of 2-propyl esters **26**, traces of phenol, and variable amounts of phenyl 2-propyl carbonate, deriving from attack of the 2-propoxycarbonyloxy radicals to the solvent: these two compounds were also detected by decomposing DPDC in benzene in the absence of the imine. This reaction gave trace amounts of biphenyl as well and this accounts for the reported yields of the unsubstituted biphenyl, which are always slightly greater than those of the substituted ones. The following reactions were performed according to this general procedure.

From 1a and DPDC (2 mmol). A GC quantitative analysis gave (after 47 h) benzaldehyde (**26a**) (17%), biphenyl (**11a**) (1%), benzophenone (**4a**) (11%), 2-phenylbenz[*d*][*1,3*]oxazole (**10a**) (trace amounts), 2-propyl *N*-(2-phenoxyphenyl)carbamate (**28a**) (9%), 11-phenyldibenz[*b,f*][*1,4*]oxazepine (**3a**) (12%), and *N*-(2-phenoxyphenyl)benzamide (**29a**) (2%).

From 1a and DPDC (4 mmol). A GC quantitative analysis gave (after 25 h) **26a** (5%), **11a** (2%), **4a** (9%), **10a** (trace amounts), **28a** (2%), **3a** (10%), and **29a** (1%).

From 1b and DPDC (2 mmol). A GC quantitative analysis gave (after 70 h) 4-chlorobenzaldehyde (**26b**) (11%), **11a** (1%), 4-chlorobiphenyl (**11b**) (trace amounts), 4-chlorobenzophenone (**4b**) (11%), **10a** (trace amounts), 2-(4-chlorophenyl)benz[*d*][*1,3*]oxazole (**10b**) (trace amounts), **28a** (10%), 11-(4-chlorophenyl)-dibenz[*b,f*][*1,4*]oxazepine (**3b**) (17%), and *N*-(2-phenoxyphenyl)-4-chlorobenzamide (**29b**) (2%).

From 1b and DPDC (4 mmol). A GC quantitative analysis gave (after 18 h) **26b** (7%), **11a** (2%), **11b** (trace amounts), **4b** (8%), **10a** (trace amounts), **10b** (trace amounts), **28a** (1%), **3b** (8%), and **29b** (3%).

From 1c and DPDC (2 mmol). A GC quantitative analysis gave (after 48 h) 4-methoxybenzaldehyde (**26c**) (8%), **11a** (trace amounts), 4-methoxybiphenyl (**11c**) (trace amounts), 4-methoxybenzophenone (**4c**) (14%), **10a** (trace amounts), 2-(4-methoxyphenyl)benz[*d*][*1,3*]oxazole (**10c**) (1%), **28a** (5%), 11-(4-methoxyphenyl)dibenz[*b,f*][*1,4*]oxazepine (**3c**) (19%), and *N*-(2-phenoxyphenyl)-4-methoxybenzamide (**29c**) (2%).

From 1c and DPDC (4 mmol). A GC quantitative analysis gave (after 24 h) **26c** (3%), **11a** (1%), **11c** (trace amounts), **4c** (18%), **10a** (trace amounts), **10c** (trace amounts), **28a** (4%), **3c** (17%), and **29c** (1%).

From 1d and DPDC (2 mmol). A GC quantitative analysis gave (after 54 h) **26a** (15%), **11a** (1%), **11b** (trace amounts), **4b** (16%), **10a** (1%), **10b** (trace amounts), 2-propyl *N*-[2-(4-chlorophenoxy)-phenyl]carbamate (**28d**) (19%), 2-chloro-11-phenyldibenz[*b,f*][*1,4*]oxazepine (**3d**) (11%), and *N*-[2-(4-chlorophenoxy)phenyl]-benzamide (**29d**) (3%).

From 1d and DPDC (4 mmol). A GC quantitative analysis gave (after 24 h) **26a** (9%), **11a** (2%), **11b** (trace amounts), **4b** (13%), **10a** (2%), **10b** (trace amounts), **28d** (5%), **3d** (14%), and **29d** (1%).

From 1e and DPDC (4 mmol). A GC quantitative analysis gave (after 48 h) **26a** (4%), **11a** (2%), **4c** (4%), **10a** (6%), 2-propyl *N*-[2-(4-methoxyphenoxy)phenyl]carbamate (**28e**) (4%), 2-methoxy-11-phenyldibenz[*b,f*][*1,4*]oxazepine (**3e**) (3%), and *N*-[2-(4-methoxyphenoxy)phenyl]benzamide (**29e**) (trace amounts). The reaction was repeated on a 5-mmol scale and, by column chromatography on silica gel, we also isolated 2-propyl 4-methoxyphenyl carbonate (**12**) (4%), oil [300 MHz ^{1}H-NMR δ 1.31 (6H, d, J = 6.6 Hz, -CH*Me*$_2$), 3.79 (3H, s, -O*Me*), 4.95 (1H, sept, J = 6.6 Hz, -C*H*Me$_2$), 6.88 (2H, A part of AA'BB', J = 9.0 Hz, Ar-*H*), 7.09 (2H, B part of AA'BB', J = 9.0 Hz, Ar-*H*); MS *m/e* (rel inten) 210 (M$^+$, 3), 151 (4), 124 (100), 109 (57), 107 (10), 43 (28); HRMS calcd for $C_{11}H_{14}O_4$ 210.0892, found 210.0895]. The identity of this compound was also confirmed by the spectral analogies with the fully characterised carbonate **21** (see below).

From 17 and DPDC (4 mmol). The reaction was carried out on a 5-mmol scale with 20 mmol of DPDC. After 24 h a column chromatography of the reaction mixture gave 2-propyl triphenylmethyl ether (**19**) (6%), mp = 110-112 °C (from light petroleum) (lit.[34] mp = 111.7 °C), triphenylmethanol (**20**) (23%), mp = 160-162 °C (lit.[35] mp = 162-162.5 °C), **10b** (23%), mp = 150-151 °C (lit.[23] mp = 151-152 °C), 11-(4-chlorophenyl)-2-(triphenylmethoxy)dibenz[*b,f*][*1,4*]oxazepine (**22**) (3%), oil that could not be distilled [300 MHz ^{1}H-NMR δ 6.43 (1H, d, *J* = 2.6 Hz), 6.83 (1H, dd, J_1 = 8.7 Hz, J_2 = 2.6 Hz), 6.89 (1H, d, *J* = 8.7 Hz), 7.07-7.38 (20H, m + A part of AA'BB', *J* = 8.6 Hz), 7.44 (2H, B part of AA'BB', *J* = 8.6 Hz), 7.82 (1H, m); MS *m/e* (rel inten) 565 (M^+ + 2, <1), 564 (M^+ + 1, <1), 563 (M^+, <1), 562 (<1), 561 (<1), 323 (4), 322 (4), 321 (11), 320 (6), 304 (4), 286 (4), 243 (100), 228 (5), 165 (27). Anal. calcd for $C_{38}H_{26}ClNO_2$: C, 80.91; H, 4.65; N, 2.48. Found: C, 81.30; H, 4.66; N, 2.48], and 2-propyl 4-(triphenylmethoxy)phenyl carbonate (**21**) (6%), mp = 90-92 °C [300 MHz ^{1}H-NMR δ 1.33 (6H, d, *J* = 6.5 Hz, -CH*Me*$_2$), 4.92 (1H, sept, *J* = 6.5 Hz, -C*H*Me$_2$), 6.66 (2H, A part of AA'BB', *J* = 9.1 Hz, Ar-*H*), 6.80 (2H, B part of AA'BB', *J* = 9.1 Hz, Ar-*H*), 7.19-7.32 (9H, m, Ar-*H*), 7.42-7.48 (6H, m, Ar-*H*); MS *m/e* (rel inten) 244 (93), 243 (100), 242 (11), 241 (15), 228 (12), 165 (87), 43 (27). Anal. calcd for $C_{29}H_{26}O_4$: C, 79.43; H, 5.98. Found: C, 79.70; H, 6.00].

From 10b and DPDC (4 mmol). A GC quantitative analysis gave (after 24 h) **11a** (2%), **11b** (trace amounts), **4b** (25%), **10a** (trace amounts), and **10b** (trace amounts).

From 2a and DPDC (2 mmol).[36] Column chromatography gave (after 30 h) **26a** (4%), 1,2-diphenyl-1H-benzimidazole (**36a**) (14%), mp = 110-112 °C (from light petroleum) (lit.[37] mp = 111-112 °C), 1,3-diphenyl-1H-quinoxalin-2-one (**35a**) (20%), mp = 190-192 °C (from 2-propanol) (lit.[38] mp = 192 °C), and 3-phenylbenzimidazolin-2-one-1-carboxylic acid 2-propyl ester (**37**) (14%), mp = 115-117 °C (from light petroleum) [200 MHz ^{1}H-NMR δ 1.48 (6H, d, *J* = 6.4 Hz, -CH*Me*$_2$), 5.32 (1H, sept, *J* = 6.4 Hz, -C*H*Me$_2$), 6.96-7.03 (1H, m, Ar-*H*), 7.12-7.23 (2H, m, Ar-*H*), 7.42-7.60 (5H, m, Ar-*H*), 7.91-8.00 (1H, m, Ar-*H*); 200 MHz ^{13}C-NMR δ 22.35, 72.76, 109.19, 115.12, 123.35, 124.62, 126.69 (q), 127.02, 128.85, 130.12, 130.37 (q), 134.05 (q), 150.47 (q), 150.62 (q); MS *m/e* (rel inten) 296 (M^+, 25), 210 (100), 181 (16), 168 (5), 167 (8), 154 (5), 77 (10), 51 (7), 43 (24); ν_{max} ($CHCl_3$) 1790, 1750, 1600, 1480, 1390, 1370, 1320, and 1100 cm^{-1}; HRMS calcd for $C_{17}H_{16}N_2O_3$ 296.1161, found 296.1170. Anal. calcd for $C_{17}H_{16}N_2O_3$: C, 68.91; H, 5.44; N, 9.45. Found: C, 69.20; H, 5.42; N, 9.49].

From 2a and DPDC (4 mmol). Column chromatography gave (after 18 h) **26a** (2%), **36a** (16%), **35a** (25%), and **37**(18%).

From 2b and DPDC (2 mmol). Column chromatography gave (after 30 h) **26b** (17%), 2-(4-chlorophenyl)-1-phenyl-1H-benzimidazole (**36b**) (14%), mp = 140-141 °C (from light petroleum/benzene 95:5 v/v) (lit.[39] mp = 137.5-138 °C) [200 MHz ^{1}H-NMR δ 7.22-7.32 (7H, m), 7.48-7.55 (5H, m), 7.85-7.92 (1H, m); MS *m/e* (rel inten) 306 (M^+ + 2, 33), 305 (M^+ + 1, 43), 304 (M^+, 100), 303 (93), 268 (18), 77 (25); ν_{max} ($CHCl_3$) 1600 cm^{-1}; HRMS calcd for $C_{19}H_{13}ClN_2$ 304.0767, found 304.0766], 3-(4-chlorophenyl)-1-phenyl-1H-quinoxalin-2-one (**35b**) (20%), mp = 187-188 °C (from 2-propanol) [200 MHz ^{1}H-NMR δ 6.66-6.72 (1H, m), 7.30-7.50 (5H, m + A part of AA'BB', *J* = 8.7 Hz), 7.56-7.72 (4H, m), 7.96-8.04 (1H, m), 8.43 (2H, B part of AA'BB', *J* = 8.7 Hz); 300 MHz ^{13}C-NMR δ 115.45, 124.07, 128.31 (2C), 128.54, 130.12, 130.22, 130.39, 131.15, 132.95 (q), 134.22 (q), 136.05 (q), 136.79 (q), 153.04 (q), 154.48 (q); MS *m/e* (rel inten) 334 (M^+ + 2, 33), 332 (M^+, 100), 305 (28), 303 (85), 268 (12), 167 (10), 77 (28); ν_{max} ($CHCl_3$) 1660, 1610, and 1590 cm^{-1}; HRMS calcd for $C_{20}H_{13}ClN_2O$

332.0716, found 332.0717. Anal. calcd for $C_{20}H_{13}ClN_2O$: C, 72.18; H, 3.94; N, 8.42. Found: C, 72.41; H, 3.95; N, 8.46], and **37** (7%).

From 2b and DPDC (4 mmol). Column chromatography gave (after 18 h) **26b** (7%), **36b** (16%), **35b** (28%), and **37** (11%).

From 2c and DPDC (2 mmol). Column chromatography gave (after 26 h) **26c** (20%), 2-(4-methoxyphenyl)-1-phenyl-1H-benzimidazole (**36c**) (7%), mp = 135-137 °C (from light petroleum) (lit.[39] mp = 135-136 °C) [300 MHz ^{1}H-NMR δ 3.79 (3H, s, -O*Me*), 6.82 (2H, A part of AA'BB', *J* = 9.1 Hz, Ar-*H*), 7.21-7.35 (6H, m, Ar-*H*), 7.50 (4H, m + B part of AA'BB', *J* = 9.1 Hz, Ar-*H*), 7.85-7.90 (1H, m, Ar-*H*); MS *m/e* (rel inten) 300 (M$^+$, 90), 299 (100), 256 (40), 166 (9), 77 (13); ν_{max} ($CHCl_3$) 1600 cm^{-1}; HRMS calcd for $C_{20}H_{16}N_2O$ 300.1263, found 300.1266], 3-(4-methoxyphenyl)-1-phenyl-1H-quinoxalin-2-one (**35c**) (12%), mp = 217-219 °C (from 2-propanol) [300 MHz ^{1}H-NMR δ 3.88 (3H, s, -O*Me*), 6.64-6.68 (1H, m, Ar-*H*), 6.98 (2H, A part of AA'BB', *J* = 8.8 Hz, Ar-*H*), 7.29-7.37 (4H, m, Ar-*H*), 7.54-7.68 (3H, m, Ar-*H*), 7.94-7.98 (1H, m, Ar-*H*), 8.48 (2H, B part of AA'BB', *J* = 8.8 Hz, Ar-*H*); 200 MHz ^{13}C-NMR δ 55.87, 113.95, 115.78, 124.33, 128.81, 128.94, 129.86, 130.21, 130.80, 132.01, 133.54 (q), 134.41 (q), 136.74 (q), 154.80 (q), 162.11 (q); MS *m/e* (rel inten) 328 (M$^+$, 100), 300 (45), 299 (70), 256 (25), 77 (10); ν_{max} ($CHCl_3$) 1660, 1610, and 1590 cm^{-1}; HRMS calcd for $C_{21}H_{16}N_2O_2$ 328.1212, found 328.1214. Anal. calcd for $C_{21}H_{16}N_2O_2$: C, 76.81; H, 4.91; N, 8.53. Found: C, 77.25; H, 4.92; N, 8.56],[40] and **37** (12%).

From 2c and DPDC (4 mmol). Column chromatography gave (after 18 h) **26c** (6%), **36c** (13%), **35c** (21%), and **37** (18%).

Reaction of 2-phenoxyisocyanobenzene (30) with dibenzoyl peroxide (DBP). A solution of **30** (0.20 g, 1 mmol) and DBP (0.12 g, 0.5 mmol) in ethyl acetate (20 mL) was refluxed for 65 h adding, every 24 h, additional 0.5 mmol of DBP. The solvent was removed and the residue diluted with diethyl ether and washed with 10% aqueous sodium bicarbonate. The organic phase was dried and quantitatively analysed by GC giving **4a** (5%), **10a** (22%), **3a** (8%), and **29a** (15%). A qualitative analysis showed the presence of benzoic acid and trace amounts of a compound that seemed to be an unsubstituted dibenz[*b,f*][*1,4*]oxazepine: this last product was also obtained in the same amounts by refluxing the isonitrile in ethyl acetate in the absence of DBP.

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Isoquinoline Formation *via* Iminium Ions Cyclization: a Direct Approach to C-2' Functionalized 3-Aryltetrahydroisoquinolines

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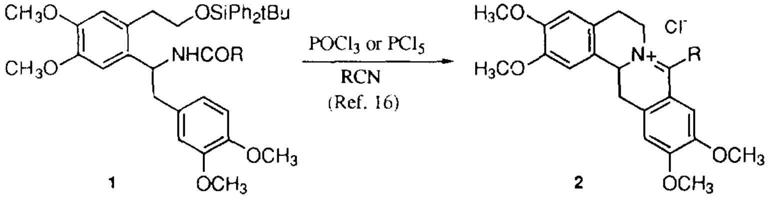
Abstract: 3-Aryltetrahydroisoquinoline derivatives can be efficiently prepared by titanium tetrachloride promoted cyclization of *N*-methoxymethyl-*N*-1,2-diarylethylamines *via* iminium ions. In the case of primary amines, the 1-aryl group prevents the alkylation of a second iminium ion, avoiding dimerization. The mild reaction conditions are compatible with the presence of acid sensitive groups; thus, the 2'-functionalized 3-aryltetrahydroisoquinoline **6a** could be prepared in high yield without desilylation. Therefore, this is a good alternative to the protic acid catalyzed Pictet-Spengler methodology, wich gives low yields of desilylated 3-aryltetrahydroisoquinolines **4** when applied to the 2'-functionalized amine **3a**.

The 3-arylisoquinolines are interesting heterocycles and attractive building blocks for alkaloid synthesis. The enamine moiety within the 1,2-dihydroisoquinolines or the fully aromatic derivatives can be utilized as an electron donor, or nucleophilic addition to the α-carbon can be effected by choosing the proper conditions.[1] Thus, the C-4 position of the heterocycle is susceptible of electrophilic substitution with aldehydes, alkyl halides, DMF or esters[2], and alkylation at C-3 can be carried out *via* the corresponding iminium ions. Alkylation/acylation at the nitrogen atom can also be carried out *via* nucleophilic substitution. These synthetically useful properties of the 3-arylisoquinolines have been used to synthesize more complex isoquinoline alkaloids, as spirobenzylisoquinolines,[3] isopavines,[4] protoberberines,[5] and benzo[c]phenanthridines.[6] In addition, the two last types of alkaloids are readily prepared in one step by the intramolecular cyclization 2'-functionalized 3-arylisoquinolines. However, only a few examples have been reported of the preparation and synthetic applications of 2'-functionalized 3-arylisoquinolines. Onda[7] and Hanaoka[8] have developed a biomimetic approach in which 2'-vinyl-3-aryl-1-isoquinolones are obtained by Hofmann degradation of protoberberinium salts and further cyclized to the benzo[c]phenanthridine skeleton photochemically or by derivatization of the vinyl group, respectively. Other approaches include the ammonolysis of benzopyrilium salts[9], $S_{RN}1$ reaction of iodobenzamides with 2-acetylhomoveratric acid enolates,[10] cycloadition of lithiated toluamides and benzaldimines[11] or cycloaddition of *N*-(2-ethenylbenzoyl)-*N*,2-dimethylbenzamide derivatives.[12]

We have previously reported that the Bischler-Napieralski and Pictet-Spengler methodologies are useful for the synthesis of 3-arylisoquinolines from 1,2-diarylethylamines[13], amides[14] or enamides[15] Recently, we enhanced the scope of this chemistry by describing a method for preparing 13,14-dihydroprotoberberines **2** by the treatment of 2'-(*tert*-butyldiphenylsilyloxyethyl)-1,2-diarylethylamides **1** under Bischler-Napieralski conditions ($POCl_3$ or PCl_5 using nitriles as solvents)[16] (Scheme 1). It has been demonstrated that these amides undergo a tandem cyclization in one pot *via* 3-aryl-3,4-dihydroisoquinolines. Therefore, we sought to develop methods to prepare 2'-functionalized 3-aryltetrahydro- or dihydroisoquinolines, which could provide a route to benzo[c]phenanthridines. The results of our studies on the preparation of these isoquinolines from 1,2-diarylethylamines are detailed below.



Scheme 1

As part of our initial studies, we decided to apply the Bischler-Napieralski reaction to *N*-substituted amides. We reasoned that a substituent at the nitrogen atom would avoid the second cyclization to the protoberberine skeleton and would direct the electrophile to C-4, after dehydrogenation of the formed heterocycle. Accordingly, the *N*-methyl amides prepared from 2'-(*tert*-butyldiphenylsilyloxyethyl)-1,2-diarylethylamides **1** (IMe/KOH/DMSO) were treated under the above described reaction conditions. All attempts to perform the reaction on the *N*-substituted amides always failed and desilylation, but no cyclization, was observed. To avoid desilylation, we tested milder reaction conditions. However, the use of CCl_4/Ph_3P[17,18] gave only stilbenes, probably formed *via* a retro-Ritter reaction, while using TFAA in ether[19] only starting material was recovered.

To find an efficient route to the desired 2'-functionalized 3-arylisoquinolines we treated the amine **3a** with formaldehyde, acetaldehyde, and benzaldehyde under Pictet-Spengler conditions, previously optimized in our laboratories.[13] The results are summarized in Table 1 (entries 1 and 2). Though the hydroxyl protecting group (*tert*-butyldiphenylsilyl) was chosen for its stability in acidic media[20] and it was previously tested in a model compound[21], this group turned out to be too labile under the reaction conditions. Thus, when **3a** was treated with formaldehyde in refluxing 3M HCl, desilylation was observed and only the tetrahydroisoquinoline **4a**, with a free hydroxyl group could be isolated in a low yield (14%) (Scheme 2). The use of milder conditions, such as lower concentrations of HCl, lower temperatures or switching to acetic acid in dioxane[22] gave similar results. Moreover, treatment of **3a** with acetaldehyde in 3M H_2SO_4 at 60-70°C gave even poorer results and a complex mixture of products was obtained. Only the reaction with benzaldehyde in 85% H_3PO_4 at 40°C gave the corresponding 1-phenyltetrahydroisoquinoline **4b** as a single diastereomer with a reasonable yield (58%), though desilylation also took place.