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Easy Photochemical Preparation of 2-Dimethylaminophenylfurans, -Pyrroles and -Thiophenes

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Abstract—2-(4-*N*,*N*-dimethylaminophenyl) heterocycles are smoothly obtained from the photolysis of 4-chloro-*N*,*N*-dimethylaniline in acetonitrile in the presence of furan, pyrrole, thiophene and some of their methyl derivatives bearing a free α-position. With 2,5-dimethyl heterocycles the arylation occurs with equal efficiency in the β position. In the case of furan, when the irradiation is carried out in methanol, *cis*/*trans* 2-aryl-5-methoxy-2,5-dihydro adducts are obtained. The reaction is rationalized as involving heterolytic cleavage of the C–Cl bond in the triplet state of the aniline. The intermediacy of the thus formed triplet aryl cation explains the observed high regio- and chemoselectivity of the process. © 2000 Elsevier Science Ltd. All rights reserved.

Introduction

There is an increasing interest in arylated five-membered heterocycles. Known examples are present among natural products[1] as well as in some oil shale raffinates[2] and have been prepared for uses ranging from components of switchable molecular wires[3] to compounds with optical non linearity.[4] The synthesis is mainly based on the application of one of the general methods of building the heterocyclic ring starting from the appropriate arylated open chain precursor.[5] The direct formation of the aryl-heterocycle carbon–carbon bond has found relatively few applications. These generally involve the reaction between a (hetero)aryl halide and a metallated (hetero)arene, in most cases under catalyzed conditions.[6] The attack of an aryl cation onto the electron-rich heterocycle is an attractive alternative, in view of the facile reaction of electrophiles with such derivatives. This contrasts with the fact that there are practically no methods for the generation of aryl cations except those of purely spectroscopic interest.[7] The decomposition of aryldiazonium salts[8] or of *N*-nitroso-*N*-arylamides[9] in the presence of thiophene, furan or pyrrolecarboxylate does give the arylated heterocycles, but the reaction involves the aryl radical rather than the cation.[10]

However, we recently found that irradiation of chloro and fluoroanilines causes efficient heterolysis of the carbon–halogen bond and the resulting aminophenylium cation can be trapped in the presence of benzene.[11] Therefore, we thought it worthwhile to extend the reaction to five-membered heterocycles, in view both of the interest of a synthesis of aminophenylheterocycles and of the support that such reactions could give for understanding the chemistry of a little investigated intermediate such as the phenylium cation.

Results

As has been previously reported,[11] photolysis of 4-chloro-*N*,*N*-dimethylaniline (**1**) in a polar solvent caused cleavage of the C–Cl bond and gave *N*,*N*-dimethylaniline (**5**) along with 2-(4′-*N*,*N*-dimethylaminophenyl)-4-chloroaniline (**6**, see Scheme 1). The irradiation was now carried out in acetonitrile in the presence of 1 M pyrrole (**2a**). Acidity was increased during the photoreaction and this caused the formation of colored products and of a polymeric film on the reactor wells, resulting in the interruption of the reaction because of the light-filter effect. However, acidity could be controlled either by adding 0.1 M triethylamine or by stirring solid potassium carbonate in the reaction vessel during the irradiation. Under these conditions coloration was minimized, the reaction proceeded with up to 85% conversion and 2-(4-dimethylaminophenyl)pyrrole (**3a**) was formed and isolated in good yield (64%, see Scheme 1 and Table 1). Careful analysis of the raw photolysed mixture showed that isomeric 3-(4-dimethylaminophenyl)pyrrole (**4a**) was also present, though in a much lesser amount (1%). The yield of non heterocycle-containing products, the above mentioned anilines **5** and **6**, was much reduced with respect to that observed in neat acetonitrile.

When 2,4-dimethylpyrrole (**2b**) was used, the course of the reaction was similar and again arylation took place at the α position yielding the 2,3,5-trisubstituted pyrrole **3b**. With both α positions blocked as in 2,5-dimethylpyrrole (**2f**),

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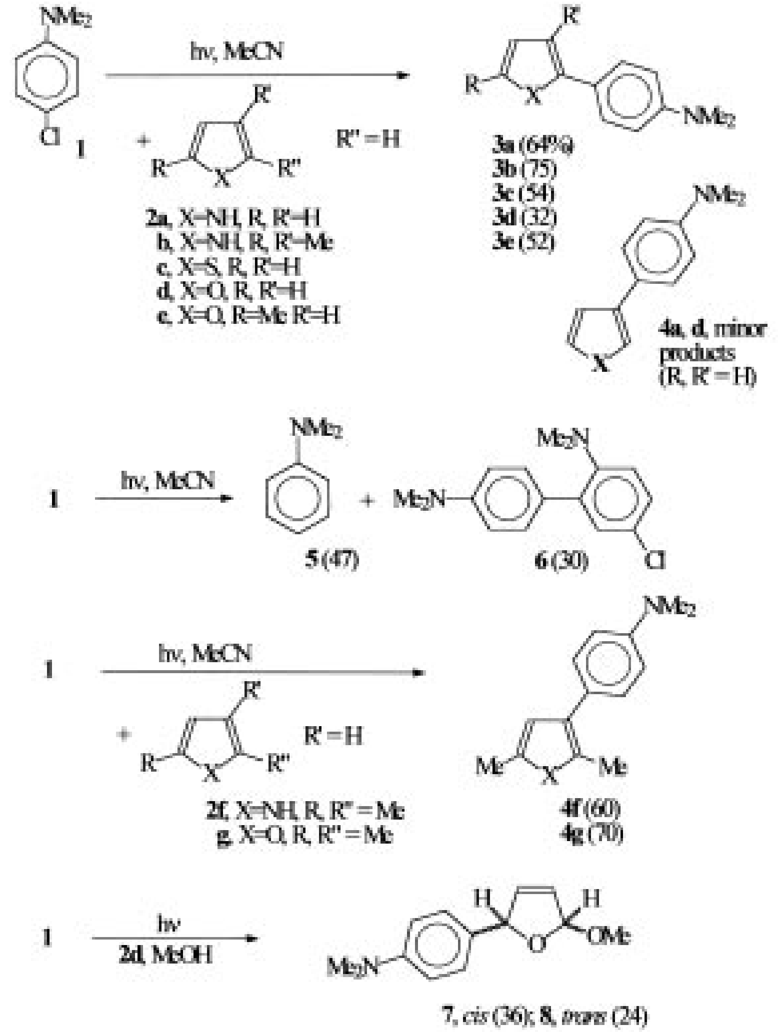


Scheme 1.

however, arylation in β occurred with reasonable yield to give product **4f**.

Similar irradiation in the presence of thiophene (**2c**) led again to α-arylation (product **3c**) and in this case the β isomer was not measurably formed in our experiments. With this heterocycle the arylation proceeded with almost the same yield also in the absence of buffering agents.

Table 1. Products from the irradiation of 4-chloro-*N*,*N*-dimethylaniline in acetonitrile in the presence of five-membered heterocycles (1 M)

Heterocycle	Products (% yield)			
	Arylated heterocycles		Further products	
None			**5** (47)	**6** (30)
2a	**3a** (64)	**4a** (1)	**5** (10)	**6** (tr)
2b	**3b** (75)		**5** (12)	**6** (7)
2c	**3c** (54)		**5** (15)	**6** (5)
2d[a]	**3d** (32)	**4d** (1)	**5** (4)	**6** (3)
2d[b]	**7** (36)	**8** (24)	**5** (10)	**6** (tr)
2e	**3e** (52)		**5** (10)	**6** (5)
2f	**4f** (60)		**5** (16)	**6** (7)
2g	**4g** (70)		**5** (6)	**6** (9)

[a] At 50% conversion.

[b] In methanol.

The reaction in the presence of furan (**2d**) was less satisfactory due to the enhanced sensitivity to acids of this substrate. Under the above conditions polymerization was not completely avoided and the substrate conversion could not be driven to the same extent. However, at 50% conversion the 2-arylfuran **3d** was formed and could be isolated in a reasonable yield (32%); analysis of the photolysate showed the presence of a detectable (1%) amount of isomeric **4d**. The reaction could be completed with the more acid-resistant 2-methylfuran (**2e**), again with arylation in α, while 2,5-dimethylfuran (**2g**) gave, as in the case of the corresponding pyrrole, the β-arylated derivative **4g**.

The reaction of furan was also tested in methanol as the solvent. In this case, the two isomeric 2-aryl-5-methoxy-2,5-dihydrofurans **7** and **8** were obtained. Only a few related 2-(aryl),[12] -(heteroaryl)[13] or -(alkyl)[14] -2,5-dihydrofurans are known, and the stereochemistry was generally not assigned. In the present case, however, the two isomers could be separated and the steric arrangement unambiguously assigned on the basis of NOESY experiments (see

Experimental). The reaction with pyrrole in methanol gave again aromatic **3a**, however, with no solvent addition.

Irradiation in the presence of 1 M methyl furan-2-carboxylate (**2h**) did not lead to new products in a significant amount and the reaction proceeded in the same way as in the absence of this additive to give products **5** and **6** and likewise no adduct was formed with furfural (**2i**, some competitive light absorbance in this case). Experiments in the presence of indole were unsatisfactory because competitive light-absorption by this heterocycle drastically slowed the reaction. However, GC–MS examination of the irradiated solution showed the presence of two peaks with the molecular weight and fragmentation expected for dimethylaminophenylindoles.

Importantly, apart from the case of indole, the time required for the photochemical conversion of aniline **1** did not change significantly when the irradiation was carried out in neat solvent or in the presence of the heterocycles considered (1 M).

Discussion

The photodecomposition of chloroanililine **1** in the presence of five-membered heterocycles (**2**) leads to efficient aminoarylation of these substrates. This smooth reaction gives selectively the 2-aryl substituted heterocycles in a reasonable yield and appears to be a viable entry to such derivatives, which may be valuable in view of the fact that related derivatives are of current interest for their non linear optical properties.[4] Furthermore, in the case of furan the irradiation in methanol gives arylated 2,5-dihydrofurans strictly related to compounds known for their anti HIV activity.[13] When both α positions are substituted, β arylation occurs in a similar yield. The reaction is successful with all the methyl substituted heterocycles we tried, but fails with electron-withdrawing substituted derivatives such as ester **2h** or aldehyde **2i**. Under the mild conditions of the photochemical reaction the arylation occurs with no significant side path except for some reductive dechlorination to give **5** and competing arylation of the aniline to form **6**, both processes however occurring only to a limited extent in the presence of 1 M heterocycles.

Mineral acidity is evolved as indicated by the stoichiometry of the reaction. This has little effect in the case of the rather acid-resistant thiophene, while in the other cases acid-induced polymerisation occurs to some degree. However, this is easily taken care of by buffering the acidity either by adding an amine or by stirring solid potassium carbonate. Only in the case of highly acid-sensitive furan this precaution is not fully satisfactory and the yield of the arylated product **3d** is limited to 32%.

The key mechanistic features of the aminoarylation can be deduced from the observed behavior. Chloroaniline **1** is photodecomposed only in polar solvents, with a quantum yield of reaction of ca. 0.8 in acetonitrile (≤0.02 in cyclohexane).[11] The efficiency of the reaction is not significantly affected by the presence of the additives (≤10% effect), while the product distribution completely changes from anilines **5** and **6** in neat MeCN to the aminoarylated heterocycles **3** as the main products with 1 M **2**. At a lower concentration of **2**, however (e.g. 0.1 M) the effect is small and the yield of products **5** and **6** is affected only to a minor degree.

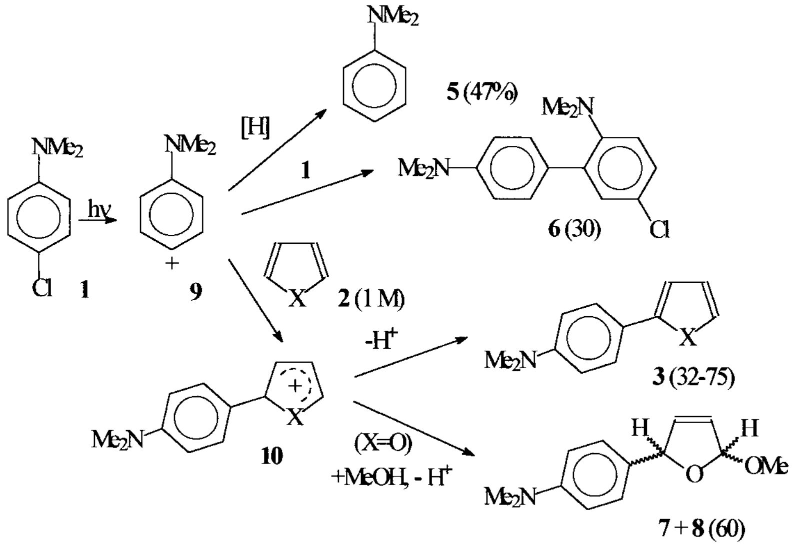
Thus, unimolecular decomposition of the aniline leads in every case to a single intermediate that either is reduced to **5** or adds to undecomposed chloraniline to form diamine **6** in neat acetonitrile. This is trapped in the presence of a sufficient amount of five-membered heterocycles **2**. As for the nature of this intermediate, the requirement of a polar medium suggests that it arises from a heterolytic fragmentation and the chemical evidence strongly supports such a view. Only electron rich substrates, such as furan, pyrrole, thiophene and their alkyl derivatives are effective traps, competing with another electron-rich trap, aniline **1**. This holds also for indole, as far as competitive light absorption allows to judge, but not for less electron-rich substrates such as **2h**, **i** (whereas radical arylation does occur with such derivatives).[9b] Thus, an electrophilic reaction is involved and the intermediate is the 4-(*N*,*N*-dimethylamino)-phenyl carbocation **9** formed by photoinduced heterolysis of the C–Cl bond from the aniline (see Scheme 2).

The course of the reaction follows in fact the expected course of electrophilic reactions with five-membered heterocycles, resulting in aromatic substitution via the usual addition-elimination mechanism involving π cationic adduct **10** and its deprotonation. With furan, cation **10** undergoes addition of a nucleophile rather than deprotonating when the latter is available, and the 2,5-dihydro-5-methoxy adducts **7** and **8** are obtained in methanol, while with the more aromatic pyrrole the substitution reaction occurs also in methanol. Again, this difference is in accordance with the well understood reactivity (substitution vs addition) of these heterocycles with electrophiles.[15]

Thus, the reaction is rationalized according to Scheme 2 with phenyl cation **9** as the key intermediate. The regio- and chemoselectivity observed require some further discussion, however, in order to place the present results in the frame of the current view on aryl cations.

First, in the present reaction heterocycles are arylated with a very high regioselectivity (α/β ratio ≥98). Speranza and coll. noticed[7] that the decomposition of 1,4-ditritiobenzene in the presence of heterocycles led to α/β ratios higher than expected from the 'hard' nature of the phenyl cation (4.7 for **2a**, 3.4 for **2c**, 5.3 for **2d**), but these were not as high as observed here. This may be in part due to the different structure of the cation (in the present case amino substituted) and to the different condition (MeCN or MeOH solutions rather than neat heterocycle), but a very high α/β ratio is typical of the phenyl radical,[8–10] rather than of the cation. This contrasts with the fact that the above-mentioned characteristics of the reaction clearly indicate the cation as the intermediate.

Second, the work by Schuster and colleagues[16] where the 4-diethylamino- and the 4-morpholinophenyl cations have been produced by photodecomposition of the corresponding diazonium tetrafluoroborate in trifluoroethanol showed that



Scheme 2.

the generated species were indiscriminate electrophiles, leading to the trifluoroethyl ethers as the virtually exclusive products. On the contrary, the photodecomposition of chloroaniline **1** does not give ethers neither in methanol nor in trifluoroethanol, leading in both cases, though in a different proportion, to reduced aniline **5** and to diamine **6**.[17]

A rationalization of these discrepancies is that both β-decay from ditritiobenzene (via the ground state) and direct photolysis of the diazonium salt (via the singlet excited state) lead to singlet phenyl cation. On the contrary, intersystem crossing (ISC) is deemed to be very efficient in aniline[18] and even more with chloro substituted **1** (Φ_{ISC} ca. 0.9, $k_{ISC} > 1\times10^9\ s^{-1}$).[19] Thus, photodecomposition of **1** is expected to occur in the triplet manifold (see Scheme 3) and to give cation **9** in the triplet state. Differently from parent phenyl cation, the 4-aminophenyl cation has been calculated to be the ground state species.[20] The triplet state has a large contribution of the diradicalic $\pi^5\sigma^1$ structure, rather than maintaining the pure $\pi^6\sigma^0$ character of the singlet cation (see Scheme 4). This makes such a species a less indiscriminate electrophile and a more easily reduced species (there is computational support for hydrogen transfer in the intramolecular case, with 2-propylphenyl cation),[21] explaining the high proportion of dehalogenated aniline **5** in neat MeCN.

The partial radical character of the triplet cation $\mathbf{9}^3$ explains the poor reactivity with σ nucleophiles and the efficient addition to excellent π nucleophiles such as the present five-membered heterocycles. The observed regioselectivity can be rationalized on the basis of the radical character of the reacting center (see Scheme 4). Alternatively, this may be due to initial electron transfer to give a pair of odd-electron species (see Scheme 4), a hypothesis which is again in accord with the better efficiency of π rather than σ nucleophiles in view of the lower ionization potential of the first reagents as compared e.g. to alcohols. In the latter mechanism, the regioselectivity is dictated by the spin density in the radical cation of the heterocycle, known to be much higher in the α position.[22] An electron transfer step has been previously proposed by Speranza and colleagues[7] in order to explain the high α/β ratio under their conditions.[23]

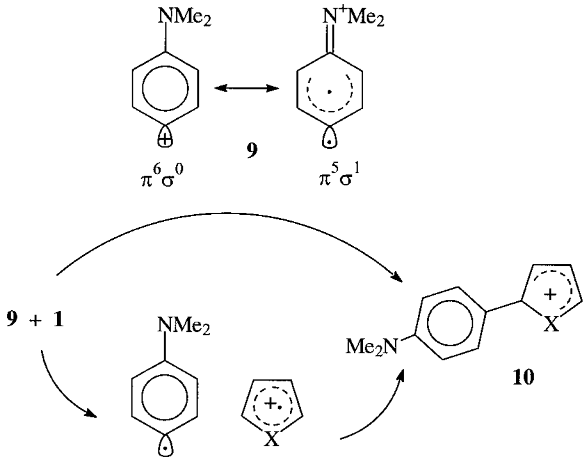
$$R_2NC_6H_4N_2^+BF_4^- \xrightarrow{h\nu,\ -N_2} \underset{\mathbf{9}^1}{R_2NC_6H_4^{+(1)}}$$

$$R_2NC_6H_4Cl \xrightarrow{h\nu,\ ISC} R_2NC_6H_4Cl^{3*} \xrightarrow{-Cl^-} \underset{\mathbf{9}^3}{R_2NC_6H_4^{+(3)}}$$

Scheme 3.

Whatever the exact mechanism, the addition to π nucleophiles is consistently an effective reaction and, as shown in the experiments with substrates **2f** and **2g**, it occurs efficiently at the β position when both α positions are substituted, again consistently with the general pattern of electrophilic substitution with electron-rich heterocycles.[15]

In conclusion, this study shows that arylated heterocycles can be smoothly obtained through a photochemical reaction via a highly regioselective reaction. Furthermore, the results



Scheme 4.

suggest that triplet aryl (or at least aminophenyl) cations can be generated photochemically and are promising synthetic intermediates in view of their peculiar chemoselectivity.

Experimental

General

4-Chloro-*N*,*N*-dimethylaniline (**1**, prepared by methylation of the aniline) and methyl furan-2-carboxylate (**2h**, prepared by methylation of the acid) and the other reagents (of commercial origin) were distilled or recrystallised before use. For the irradiations, spectroscopic grade solvents were used as received.

^{1}H and ^{13}C NMR spectra were recorded by means of a Brucker 300 MHz spectrometer and the chemical shifts are reported relative to TMS. Elemental analyses were effected by a Carlo Erba 1106 elemental analyser. The GC–MS analyses were performed using a IS40 instrument fitted with a J&W DB-5 column, 30 m×0.25 mm with film thickness 0.25 μm. The carrier was helium at 0.6 mL/min and samples (1 μl) were injected by splitless injection. The total run time was 30 min with the initial oven temperature 80°C (4 min), rising at a rate of 10°C/min to 250°C.

Preparative irradiations

In a typical experiment a solution of 780 mg aniline **1** (0.05 M) in 100 mL acetonitrile containing one of heterocycles **2** (1 M) was irradiated for 3 h in an immersion well apparatus fitted with an high pressure mercury arc (125 W, water-cooled through a quartz jacket) after 15 min flushing with argon and maintaining a slow gas flux during the irradiation. Anhydrous potassium carbonate (2 g) was added and the solution magnetically stirred during the experiment. In an alternative procedure, irradiations were carried out by using 20 mL portions of the same solutions in a number of quartz tubes which were capped after flushing with argon for 15 min and externally irradiated by means of 6×15 W phosphor coated lamps for 3 h. In this case, the solution was made 0.1 M triethylamine. The progress of the reaction was monitored by GC and GC–MS.

Products isolation and identification

The irradiated solution was evaporated under reduced pressure and the residue chromatographed on silica gel 60 HR by eluting with cyclohexane–ethyl acetate mixtures. The arylated heterocycles were obtained as solids or oils from the fractions (by repeating the chromatography in the case of unsatisfactory separation) and characterised by elemental analysis, GC–MS and NMR as detailed in the following.

The structures were deduced from the results of ^{1}H, ^{13}C, DEPT-135 and 2D correlated experiments.

2-(4′-*N*,*N*-Dimethylaminophenyl)-4-cloroaniline (6). Colourless oil which solidifies on standing, mp 40–42°C, lit.[24] oil; [Found: C, 77.82, H, 7.83, N, 10.05. $C_{16}H_{19}N_2Cl$ requires C, 77.87, H, 7.76, N, 10.19%]; δ_{H} (300 MHz $CDCl_3$) 2.55 (*s*, 6H, NMe_2), 3.05 (*s*, 6H, $-NMe_2$), 6.9 (*d*, *J*=8 Hz, 1H), 6.72 and 7.45 ($AA'XX'$, 4H, aromatics), 7.14 (*dd*, *J*=2, 8 Hz, 2H), 7.18 (*dd*, *J*=2 Hz, 1H). δ_{C} (300 MHz $CDCl_3$): 40.4 (NMe_2), 43.1 (NMe_2), 112.3 (CH), 118.6 (CH), 126.3, 126.5 (CH), 128,9, 129.0 (CH), 130.9 (CH), 135.8, 149.4, 149.8.

2-(4′-*N*,*N*-Dimethylaminophenyl)pyrrole (3a). Light yellow solid, mp dec. >160°C; [Found: C, 77.25, H, 7.45, N, 15.30. $C_{12}H_{14}N_2$ requires C, 77.38, H, 7.58, N, 15.04%]; δ_{H} (300 MHz $CDCl_3$): 3.02 (*s*, 6H, $-NMe_2$), 6.27 (*dd*, *J*=6, 2.5 Hz, 1H, H-4), 6.35 (*m*, 1H, H-3), 6.81 (*m*, 1H, H-5), 6.75 and 7.35 ($AA'XX'$, 4H, aromatics), 8.3 (*broad*, exch, 1H, NH). δ_{C} (300 MHz $CDCl_3$): 40.55 (NMe_2), 103.8 (CH), 109.6 (CH), 112.8 (2 CH), 117.5 (CH), 121.7, 124.9 (2 CH), 132.7, 149.1. GC/MS: t_{R} 15.18 min: *m*/*z* (EI) 186 (100), 171 (30), 144 (18), 115 (15), 63 (8). The analysis of the photolysed solution revealed traces (<2%) of a peak at t_{R} 16.00 min with fragmentation *m*/*z* (EI) 186 (100), 171 (35), 144 (18), 115 (25), 63 (8). In view of the similarity with spectrum of **3a** (see above), this was attributed to **3-(4′-*N*,*N*-dimethylaminophenyl)pyrrole (4a)**.

2-(4′-*N*,*N*-Dimethylaminophenyl)-3,5-dimethylpyrrole (3b). Light yellow solid, mp 92–94°C; [C, 78.36, H, 8.59, N, 13.05. $C_{14}H_{18}N_2$ requires C, 78.46, H, 8.47, N, 13.07%]; δ_{H} (300 MHz $CDCl_3$): 2.15 (*s*, 3H, CH_3), 2.25 (*s*, 3H, CH_3), 2.95 (*s*, 6H, $-NMe_2$), 5.8 (*s*, 1H, H-4), 6.8 and 7.2 ($AA'XX'$, 4H, aromatics), 7.8 (*broad*, exch, 1H, NH). The chemical shift of the signal attributed to H-4 (5.8 ppm) was characteristic of a hydrogen in β position. The value fits with that of the other pyrrole derivatives obtained, where the hydrogens in the β position were consistently shielded as compared to those in the α position. δ_{C} (300 MHz $CDCl_3$): 12.1 (CH_3), 12.9 (CH_3), 40.6 (NMe_2), 109.5 (CH), 111.4, 112.7 (2 CH), 114.4, 122.6, 126.1, 127.2 (2 CH), 148.6.

2-(4′-*N*,*N*-Dimethylaminophenyl)thiophene (3c). Colourless solid, mp 118–120°C, CH_3OH, lit.[25] 121–122°C; [C, 70.85, H, 6.52, N, 6.83. $C_{12}H_{13}$ NS: C, 70.90, H, 6.45, N, 6.89%]; δ_{H} (300 MHz $CDCl_3$): 3.02 (*s*, 6H, $-NMe_2$), 6.8 and 7.5 ($AA'XX'$, 4H, aromatics), 7.05 (*t*, *J*=4 Hz, 1H, H-4), 6.81 (*m*, 2H, H-3 and H-5); δ_{C} (300 MHz $CDCl_3$): 40.4 (NMe_2), 112.5 (2 CH), 120.8 (CH), 122.6 (CH), 126.8 (2 CH), 127.7 (CH), 138.2, 145.1, 149.8. GC/MS: t_{R} 15.17 min; *m*/*z* 203 (100), 187 (33), 205 (15), 115 (38). In the GC–MS analysis of the photolyzed solution no traces of the 3-substituted derivative was found.

2-(4′-*N*,*N*-Dimethylaminophenyl)furan (3d). Colourless solid, mp 65–67°C; [Found: C, 76.75, H, 7.12, N, 7.41. $C_{12}H_{13}$ NO requires: C, 76.98, H, 7.00, N, 7.48%]; δ_{H} (300 MHz $CDCl_3$): 3.05 (*s*, 6H, $-NMe_2$), 6.45 (*m*, 2H, H-3 and H-4), 7.42 (*t*, *J*=2 Hz, 1H, H-5), 6.8 and 7.6 ($AA'XX'$, 4H, aromatics); δ_{C} (300 MHz $CDCl_3$): 40.4 (NMe_2), 101.9 (CH), 111.3 (CH), 112.3 (2 CH), 119.7, 124.9 (2 CH), 140.6 (CH), 149.7, 154.7. GC/MS: t_{R} 13.01 min; *m*/*z* 187 (100), 172 (12), 171 (18), 158 (25), 144 (14), 115 (30). The analysis of the photolysed solution revealed traces (<1%) of a peak at t_{R} 13.10 min with fragmentation *m*/*z* 187 (100), 171 (55), 144 (45), 115 (40). In view of the similarity to the above spectrum of **3d**, this was recognised as **3-(4′-*N*,*N*-dimethylaminophenyl)furan (4d)**.

2-(4′-*N*,*N*-Dimethylaminophenyl)-5-methylfuran (3e). White solid, mp 68–70°C (CH_3OH); [C, 77.62, H, 7.45, N, 6.42. $C_{13}H_{15}NO$ requires C, 77.58, H, 7.51, N, 6.96%]; δ_H (300 MHz $CDCl_3$): 2.4 (*s*, 3H, CH_3), 3.01 (*s*, 6H, $-NMe_2$), 6.4 (*d*, *J*=3 Hz, 1H, H-3), 6.4 (*d*, *J*=3 Hz, 1H, H-4), 6.8 and 7.6 (AA′XX′, 4H, aromatics); δ_C (300 MHz $CDCl_3$): 13.6 (CH_3), 40.4 (NMe_2), 102.7 (CH), 107.2 (CH), 112.4 (2 CH), 120.2, 124.4 (2 CH), 149.4, 150.3, 153.0.

3-(4′-*N*,*N*-Dimethylaminophenyl)-2,5-dimethylpyrrole (4f). Light yellow solid, mp 90–92°C; [C, 78.25, H, 8.52, N, 12.97. $C_{14}H_{18}N_2$ requires C, 78.46, H, 8.47, N, 13.07%]; δ_H (300 MHz $CDCl_3$): 2.15 (*s*, 3H, CH_3), 2.25 (*s*, 3H, CH_3), 3.02 (*s*, 6H, $-NMe_2$), 6.0 (*s*, 1H, H-4), 6.8 and 7.2 (AA′XX′, 4H, aromatics), 7.6 (*broad*, exch, 1H, NH); δ_C (300 MHz $CDCl_3$): 12.8 (CH_3), 13.3 (CH_3), 41.3 (NMe_2), 106.7 (CH), 112.9 (2 CH), 114.6, 118.2, 122.2, 125.3, 128.2 (2 CH), 148.5.

3-(4′-*N*,*N*-Dimethylaminophenyl)-2,5-dimethylfuran (4g). Colourless solid, mp 38–41°C; [C, 78.25, H, 8.05, N, 6.45. $C_{14}H_{17}NO$ requires C, 78.10, H, 7.96, N, 6.51%]; δ_H (300 MHz $CDCl_3$): 2.2 (*s*, 3H, CH_3), 2.25 (*s*, 3H, CH_3), 3.0 (*s*, 6H, $-NMe_2$), 6.1 (*s*, 1H, H-4), 6.85 and 7.22 (AA′XX′, 4H, aromatics); δ_C (300 MHz $CDCl_3$): 12.8 (CH_3), 13.3 (CH_3), 40.6 (NMe_2), 106.9 (CH), 112.7 (2 CH), 121.1, 122.8, 128.0 (2 CH), 144.5, 148.9, 149.2.

(2*S*,5*R*)/(2*R*,5*S*) 2-(4′-*N*,*N*-Dimethylaminophenyl)-5-methoxy-2,5-dihydrofuran (7). Colourless oil; [Found: C, 71.35, H, 7.77, N, 6.34. $C_{13}H_{17}NO_2$ requires C, 71.21, H, 7.81, N, 6.39%]; δ_H (300 MHz $CDCl_3$): 2.15 (*s*, 6H, NMe_2), 3.45 (*s*, 3H, OMe), 5.62 (*m*, 1H, H-2), 5.76 (*dt*, *J*=1.3 and 1.2 Hz, 1H, H-5), 5.86 (*ddd*, *J*=6, 1.2 and 2.3 Hz, 1H, H-3), 6.14 (*dt*, *J*=6 and 1.2 Hz, 1H, H-4), 6.9 and 7.2 (AA′XX′, 4H, aromatics); δ_C (300 MHz $CDCl_3$): 40.5 (NMe_2), 54.8 (OMe), 87.6 (CH-2), 109.3 (CH-5), 112.3 (CH), 125.5 (CH), 128.0, 128.07 (CH), 135.7, 150.4. A NOESY experiment showed a NOE correlation between the methoxy group and the aromatic hydrogens at 7.2 ppm, thus identifying the stereochemistry.

(2*R*,5*R*)/(2*S*,5*S*) 2-(4′-*N*,*N*-Dimethylaminophenyl)-5-methoxy-2,5-dihydrofuran (8). Colourless oil; [Found: C, 71.32, H, 7.88, N, 6.32. $C_{13}H_{17}NO_2$ requires C, 71.21, H, 7.81, N, 6.39%]; δ_H (300 MHz $CDCl_3$): 2.15 (*s*, 6H, NMe_2), 3.4 (*s*, 3H, OMe), 5.8 (*m*, 1H, H-2), 5.9 (*ddd*, *J*=6, 1.2 and 2.4 Hz, 1H, H-3), 5.94 (*dt*, *J*=4 and 1.2 Hz, 1H, H-5), 6.2 (*dt*, *J*=6 and 1.2 Hz, 1H, H-4), 6.9 and 7.2 (AA′XX′, 4H, aromatics); δ_C (300 MHz $CDCl_3$): 40.9 (NMe_2), 54.4 (OMe), 87.03 (CH-2), 109.2 (CH-5), 112.5 (CH), 125.9 (CH), 127.2, 127.7 (CH), 136.2, 150.6. The fact that the coupling constant between H-2 and H-5 (4 Hz) was larger than that observed with isomer **7** (1.2 Hz) supported a *trans* arrangement for these two protons. No significant NOE correlation was found in the NOESY experiment.

Attempted reaction with indole. GC–MS analysis of the photolised solution of **1** in the presence of 1 M indole showed the presence of two new peaks, at t_R 17.44 min with fragmentation *m*/*z* 236 (100), 219 (5), 191 (7), 163 (3) and at t_R 19.45 min with fragmentation *m*/*z* 236 (100), 220 (3), 191 (3), 163 (3), respectively, both consistent with a structure of 4-(4′-*N*,*N*-dimethylaminophenyl)indole. The slow progress of the reaction discouraged preparative efforts.

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