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Electrochemical dimerization of phenacyl bromides *N*-acylhydrazones—a new way to 1-*N*-acylamino-2,5-diaryl-pyrroles

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Abstract—Cathodic reduction of phenacyl bromides *N*-acyl hydrazones lead to dimeric 1,4-diaryl-1,4-butanedione di-*N*-acylhydrazones, which give the corresponding 1-*N*-acylamino-2,5-diarylpyrroles in good yields.

1. Introduction

1-Aminopyrroles and *N*-substituted-1-aminopyrroles are a class of useful intermediates in organic chemistry which possess a wide range of the properties expected for *N*,*N*-disubstituted hydrazines.[1] Furthermore, 1-*N*-carbalkoxyaminopyrroles undergo efficient Diels–Alder reaction with electron deficient olefins.[2] Some 1-*N*-substitutedaminopyrroles and their derivatives have shown antibacterial activity.[3] 1-*N*-Aminoacetamido-2,5-dialkylpyrroles have exhibited analgesic and anesthetic properties.[4] 1-*N*-Carbalkoxyaminopyrroles have been used in synthesis of anxiolytic agents.[5] Systems based on the reaction of iron salts with heterocyclic hydrazines have been used in photothermographic processes.[6]

Recent advances in electroorganic chemistry have provided organic chemists with a new versatile synthetic device of a great promise.[7] Despite the long history of electroorganic chemistry, most of the electroorganic reactions that could provide product selectivity have been developed within the last twenty five years.[8] Research of various applications has spread gradually to cover many areas of fundamental and industrial organic chemistry.

Among them the cathodic reduction of α-halocarbonyl compounds has proved to be a very good tool in organic synthesis.[9] We have prepared electrochemically in such manner several classes of compounds such as 4-aryl-2-methylfurans,[10] imidazo[2,1-*b*][1,3,4]-oxadiazines,[11] [1,3]oxathiolan-5-ones,[12] tetrahydrofuran-2-ols,[13] 3-chloro-1,4-disubstituted-2(1*H*)-quinolinones.[14]

Several years ago, we reported the cathodic reduction of phenacyl bromide semicarbazones leading to the dimeric semicarbazones which were converted into either 1,4-diaryl-1,4-butanediones and 2,5-diarylfuranes[15] or 3,6-diarylpyridazines.[16]

In the present study we wish to report a facile and convenient way to 1-*N*-acylamino-2,5-diarylpyrroles starting from phenacyl bromides **1a**–**f**, which first were converted into phenacyl bromide *N*-acylhydrazones **2a**–**f**. The electrochemical reduction of phenacyl bromide *N*-acylhydrazones led to the dimeric 1,4-diaryl-1,4-butanedione di-*N*-acylhydrazones **3a**–**f**. Heating of dimers **3a**–**f** gave the corresponding 1-*N*-acylamino-2,5-diarylpyrroles **4a**–**f**. Our syntheses are summarized in Scheme 1.

2. Results and discussion

Acylhydrazones **2a**–**f** were obtained in nearly quantative yields using a modified known procedure.[17] Electroreduction of **2a**–**f** was accomplished in a divided cell on the mercury cathode. The first step in this process apparently involves two-electron cleavage of the carbon–bromine bond with the formation of anion A and bromide anion (Scheme 2).[18] Subsequent nucleophilic attack of anion A on the molecule of starting substrate **2a**–**f** lead to dimeric

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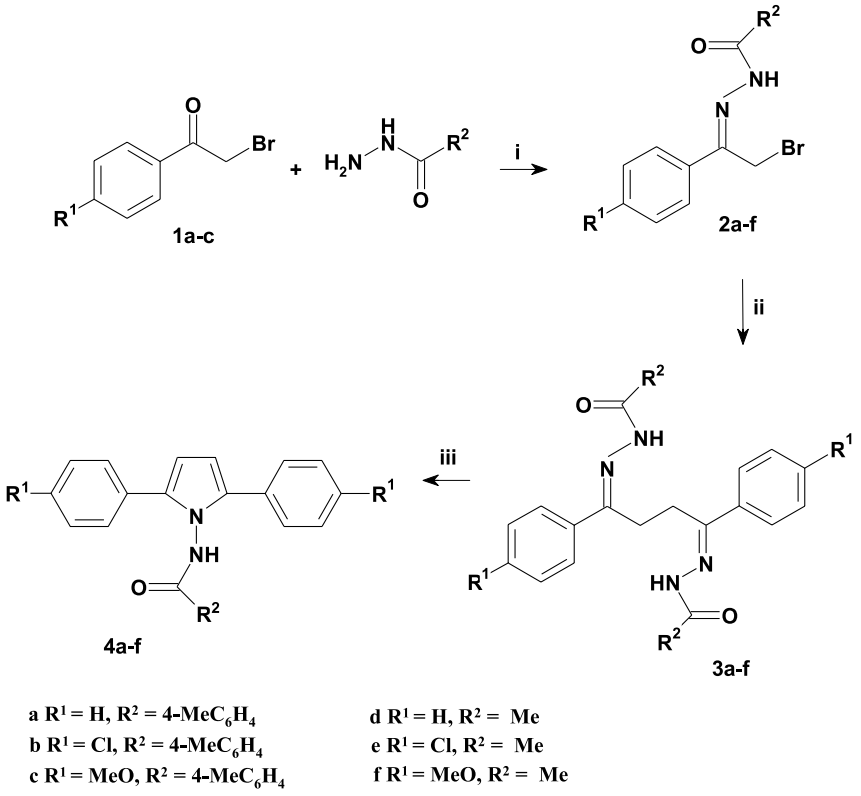
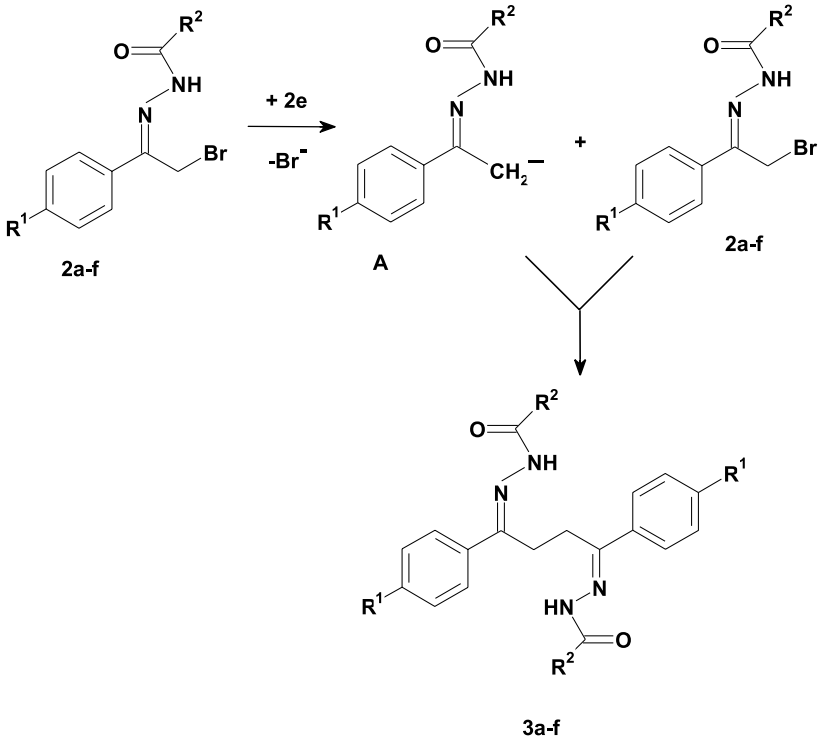


Scheme 1. (i) H^+, MeOH/H_2O; (ii) electrochemical dimerization; Hg-cathode, solvent–DMF, supporting electrolyte $LiClO_4$, divided cell; (iii) DMF reflux 1 h, or AcOH/EtOH, reflux 4 h.

compounds **3a–f** (Table 1). Similar dimers were obtained earlier by reduction of phenacyl bromides semicarbazones in a divided cell.[15,16] Further heating of **3a–c** in refluxing dimethylformamide (method A, Table 1) resulted in the formation of cyclic pyrroles **4a–c** in good yield. In contrast to **3a–c**, dimers **3d–f** were stable in boiling dimethylformamide. It should be mentioned that dimers of phenacyl bromides semicarbazones, that is, 1,4-diaryl-1,4-butanedione disemicarbazones in boiling dimethylformamide were converted into 3,6-diarylpyridazines.[16] Cyclization of **3d–f**



Scheme 2.

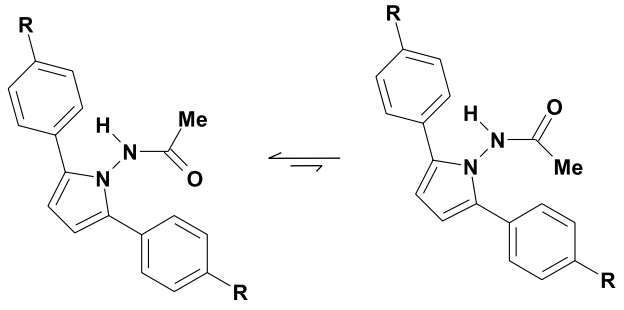
Table 1. Synthesis of 1-*N*-acylamino-2,5-diarylpyrroles

N-Acyl hydrazones	Di-*N*-acyl hydrazones	Yield (%)[a]	Method of cyclization	Pyrrole	Yield (%)[a]
2a	**3a**	69	**A** and **B**	**4a**	73 and 71
2b	**3b**	64	**A** and **B**	**4b**	76 and 72
2c	**3c**	62	**A** and **B**	**4c**	63 and 65
2d	**3d**	81	**B**	**4d**	87
2e	**3e**	85	**B**	**4e**	78
2f	**3f**	82	**B**	**4f**	72

[a] Isolated yields.

into the corresponding pyrroles **4a–f** was achieved in good yields by refluxing in the mixture of acetic acid/ethanol (1:1) (method B, Table 1). Dimers **3a–c** were also transformed into pyrroles **4a–c** using method B.

The ^{1}H NMR and ^{13}C NMR spectra of pyrroles **4d–f** showed the presence of two isomers for each compound (Scheme 3). The ratio of isomers depends on the solvent (Table 2). It is known that in a few cases single bond rotation is so slow that (*E*)- and (*Z*)-isomers can be detected on the NMR time scale even where no double bond exists,[19] for example, thioamides and certain amides,[20] because resonance gives the single bond some double bond character and slows rotation.[21]



4d-f

d R = H, e R = Cl, f R = OMe

Scheme 3.

Table 2. Ratio of isomer in 1-*N*-acetylamino-2,5-diarylpyrroles[a]

1-*N*-Acetyl-aminopyrrole	$CDCl_3$	Acetone-d_6	DMSO-d_6
4d	4:3	5:1	7:1
4e	2:1	7:1	10:1
4f	6:5	7:2	6:1

[a] ^{1}HMR data at 25 °C.

Table 3. ^{1}H NMR characteristic signals in $CDCl_3$ for isomers of 1-*N*-acetylamino-2,5-diarylpyrroles[a]

1-*N*-Acetyl-aminopyrrole	NH	CH═	CH_3
4d	7.77; *8.29*	6.35; *6.41*	1.89; *1.38*
4e	7.77; *8.26*	6.32; *6.61*	1.92; *1.36*
4f	7.64; *8.11*	6.25; *6.30*	1.90; *1.39*

[a] Signals of minor isomer in italics.

The (*Z*)-structures of **4d–f** main isomer were established by NOE experiments which show the close proximity of the amide proton and the methyl group (Table 3). For **4a–c** the ^{1}H NMR spectra show a single absorption for the NH, olefinic, and methyl protons due to the rapid interconversion of the *Z* and *E* isomers. This could be because conjugation between the carbonyl group and the benzene ring weakens the double bond character of the carbon–nitrogen bond.

As to our knowledge only one 1-*N*-acylamino-2,5-diarylpyrrole, namely 1-*N*-acetylamino-2,5-diphenylpyrrole is known in the chemical literature.[22,23] In both cases it was synthesized by action of acetyl anhydride on 1-amino-2,5-diphenylpyrrole.

3. Conclusion

Thus the electrochemical dimerization of phenacyl bromides *N*-acylhydrazones into dimeric 1,4-diaryl-1,4-butanedione di-*N*-acylhydrazones and further cyclization of dimers gives 1-*N*-acylamino-2,5-diarylpyrroles in good yields. This constitutes a facile and efficient method for the transformation of phenacyl bromides into 1-*N*-acylamino-2,5-diarylpyrroles, which are convenient and useful intermediates for organic chemistry and synthesis of pharmacology active agents.

The procedure uses inexpensive reagents, it is easily carried out, and the work up is very simple.

4. Experimental

The electrolyses were carried out using an Amel potentiostat Model 552 with electronic integrator Amel Model 721. Mass spectra (EI, ionizing voltage 70 eV) were determined using a Hewlett–Packard Model 5988A mass-selective detector equipped with a Hewlett–Packard Ms Chem Station. IR spectra of the compounds were recorded as dispersions in KBr on a Perkin–Elmer Model 583 spectrometer. ^{1}H and ^{13}C NMR spectra for **2a–f** and **3a–f** were recorded in $CDCl_3$ on Varian Unity 300 (300 MHz) spectrometer, for **4a–f** on Varian Unity 500-PLUS (500 MHz) spectrometer with tetramethylsilane (TMS) as the internal standard. All melting points were measured on a Reichert Thermovar microhot stage apparatus and are uncorrected.

4.1. General procedure for the preparation of phenacyl bromides *N*-acylhydrazones 2a–f

Phenacyl bromides (20 mmol) were slowly added in solid

state (**1a** as a solution in 20 ml of MeOH) to a solution of hydrazone (40 mmol) and 2 ml of 5% HCl in 60 ml of a mixture of MeOH/H_2O under rapid stirring below 5 °C. The stirring was maintained for 24 h to complete the reaction. The quantitatively precipitated solid was isolated by filtration. The precipitate was washed consequently with chloroform and hexane (**2a–c**) or with hexane only (**2d–f**) and used for the next reaction without further purification.

4.1.1. Phenacyl bromide *N*-(4-methylbenzoyl)hydrazone 2a. Yield 6.09 g (92%), mp 133–134 °C. ^{1}H NMR ($CDCl_3$): δ 2.34 and 2.41 (s, 3H), 4.34 and 4.42 (s, 2H), 7.15–7.80 (m, 9H), 9.03 and 9.18 (bs, 1H). IR: 3469, 3299, 3028, 1655, 1535, 1468, 1272, 1178, 831, 770. Anal. Calcd for $C_{16}H_{15}BrN_2O$: C, 58.02; H, 4.56; Br, 24.12; N, 8.46. Found: C, 57.83; H, 4.65; Br, 23.89; N, 8.37.

4.1.2. 4-Chlorophenacyl bromide *N*-(4-methylbenzoyl)-hydrazone 2b. Yield 6.87 g (94%), mp 144–146 °C. ^{1}H NMR ($CDCl_3$): δ 2.36 and 2.42 (s, 3H), 4.36 and 4.44 (s, 2H), 7.20–7.80 (m, 8H), 9.11 and 9.25 (bs, 1H). IR: 3466, 3154, 3009, 1646, 1506, 1455, 1280, 1129, 995, 830, 752. Anal. Calcd for $C_{16}H_{14}BrClN_2O$: C, 52.56; H, 3.86; Br, 21.85; Cl, 9.70; N, 7.66. Found: C, 52.37; H, 3.72; Br, 21.89; Cl, 9.53; N, 7.51.

4.1.3. 4-Methoxyphenacyl bromide *N*-(4-methyl-benzoyl)hydrazone 2c. Yield 6.57 g (91%), mp 118–120 °C. ^{1}H NMR ($CDCl_3$): δ 2.35 and 2.41 (s, 3H), 3.82 and 3.86 (s, 3H), 4.32 and 4.41 (s, 2H), 6.90–7.80 (m, 8H), 9.15 and 9.36 (bs, 1H). IR: 3467, 3153, 2995, 1640, 1609, 1455, 1249, 1174, 829, 751. Anal. Calcd for $C_{17}H_{17}BrN_2O_2$: C, 56.52; H, 4.74; Br, 22.12; N, 7.75. Found: C, 56.63; H, 4.85; Br, 21.89; N, 7.53.

4.1.4. Phenacyl bromide *N*-acetylhydrazone 2d. Yield 4.49 g (88%), mp 126–128 °C. ^{1}H NMR ($CDCl_3$): δ 2.41 (s, 3H), 4.29 (s, 2H,), 7.41 (m, 3H), 7.75 (m, 2H), 9.35 (bs, 1H). IR: 3466, 3199, 3044, 1669, 1553, 1260, 1119, 1003, 776, 690. Anal. Calcd for $C_{10}H_{11}BrN_2O$: C, 47.08; H, 4.35; Br, 31.32; N, 10.98. Found: C, 47.22; H, 4.39; Br, 31.13; N, 10.72.

4.1.5. 4-Chlorophenacyl bromide *N*-acetylhydrazone 2e. Yield 5.38 g (93%), mp 146–148 °C. ^{1}H NMR ($CDCl_3$): δ 2.40 (s, 3H), 4.27 (s, 2H,), 7.37 (d, 2H, J=8.7 Hz), 7.68 (d, 2H, J=8.7 Hz), 9.43 (bs, 1H). IR: 3468, 3189, 3081, 1669, 1599, 1378, 1336, 1094, 1009, 834. Anal. Calcd for $C_{10}H_{10}BrClN_2O$: C, 41.48; H, 3.48; Br, 27.60; Cl, 12.24; N, 9.67. Found: C, 41.32; H, 3.55; Br, 27.38; Cl 12.05; N, 9.46.

4.1.6. 4-Methoxyphenacyl bromide *N*-acetylhydrazone 2f. Yield 4.84 g (85%), mp 133–135 °C. ^{1}H NMR ($CDCl_3$): δ 2.40 (s, 3H), 3.82 (s, 3H), 4.27 (s, 2H,), 6.91 (d, 2H, J=8.8 Hz), 7.81 (d, 2H, J=8.8 Hz), 9.38 (bs, 1H). IR: 3467, 3153, 2995, 1640, 1609, 1455, 1249, 1174, 829, 751. Anal. Calcd for $C_{11}H_{13}BrN_2O_2$: C, 46.34; H, 4.60; Br, 28.02; N, 9.82. Found: C, 46.17; H, 4.55; Br, 27.88; N, 9.56.

4.2. General procedure for the electrochemical dimerization of phenacyl bromides *N*-acylhydrazones 3a–f

Anhydrous lithium perchlorate (10 mmol) was dissolved in 40 ml of dry dimethylformamide. 20 ml of this solution was placed in the cathode compartment and the other 20 ml in the anode compartment of the divided (porous glass diaphragm) electrolytic cell. Then the corresponding phenacyl bromide hydrazone (5 mmol) was added to the cathode compartment. For prevention of the accumulation of electrogenerated acid, anhydrous sodium carbonate (3 g) was placed in the anode compartment. The electrolyses were carried out under controlled cathodic potential at −1 V versus SCE. The charge consumed was 1 F/mol in all cases. At the end of the electrolysis, the cathodic solution was poured onto ice water (150 ml). In the case of **3d–f** the cathodic solution was evaporated under reduced pressure up to 10 ml before this operation. After 12 h, the precipitated solid isolated by filtration was washed with chloroform and used for the next reaction without further purification. Analytically pure samples of **3a–f** were obtained by crystallization from dimethylsulphoxide–methanol.

4.2.1. 1,4-Diphenyl-1,4-butanedione di-*N*-(4-methyl-benzoyl)hydrazone 3a. Yield 0.87 g (69%), mp 192–194 °C. ^{1}H NMR (DMSO-d_6): δ 2.38 (s, 6H), 3.12 (s, 4H,), 7.20–7.80 (m, 18H,), 10.82 (bs, 2H). IR: 3336, 3249, 1651, 1524, 1471, 1274, 1116, 918, 829, 744, 692. Anal. Calcd for $C_{32}H_{30}N_4O_2$: C, 76.47; H, 6.02; N, 11.15. Found: C, 76.21; H, 5.92; N, 10.97.

4.2.2. 1,4-Di-(4-chloro)phenyl-1,4-butanedione di-*N*-(4-methylbenzoyl)hydrazone 3b. Yield 0.91 g (64%), mp 219–221 °C. ^{1}H NMR (DMSO-d_6): δ 2.37 (s, 6H), 3.12 (s, 4H,), 7.20–7.85 (m, 16H), 10.72 (bs, 2H). IR: 3466, 3232, 1647, 1521, 1487, 1271, 1091, 833, 744, 669. Anal. Calcd for $C_{32}H_{28}Cl_2N_4O_2$: C, 67.25; H, 4.94; Cl, 12.41; N, 9.80. Found: C, 67.11; H, 4.82; Cl, 12.18; N, 9.67.

4.2.3. 1,4-Di-(4-methoxy)phenyl-1,4-butanedione di-*N*-(4-methylbenzoyl)hydrazone 3c. Yield 0.87 g (62%), mp 215–217 °C. ^{1}H NMR (DMSO-d_6): δ 2.37 (s, 6H), 3.05 (s, 4H,), 3.76 (s, 6H), 6.80–7.80 (m, 16H), 10.61 (bs, 2H). IR: 3473, 3261, 1651, 1608, 1498, 1257, 1176, 1022, 829, 747. Anal. Calcd for $C_{34}H_{34}N_4O_2$: C, 72.58; H, 6.09; N, 9.96. Found: C, 72.31; H, 5.91; N, 9.78.

4.2.4. 1,4-Diphenyl-1,4-butanedione di-*N*-acetylhydrazone 3d. Yield 0.71 g (81%), mp 192–194 °C. ^{1}H NMR (DMSO-d_6): δ 1.99 and 2.15 (s, 6H), 2.89 and 2.92 (s, 4H,), 7.30–7.60 (m, 10H), 10.75 (bs, 2H). IR: 3428, 3227, 1658, 1459, 1383, 1128, 1006, 862, 769, 687. Anal. Calcd for $C_{20}H_{22}N_4O_2$: C, 68.55; H, 6.33; N, 15.99. Found: C, 68.41; H, 6.25; N, 15.78.

4.2.5. 1,4-Di-(4-chloro)phenyl-1,4-butanedione di-*N*-acetylhydrazone 3e. Yield 0.89 g (85%), mp 242–244 °C. ^{1}H NMR (DMSO-d_6): δ 1.97 and 2.13 (s, 6H), 2.89 and 2.91 (s, 4H,), 7.30–7.55 (m, 8H), 10.73 (bs, 2H). IR: 3446, 3235, 1668, 1533, 1490, 1322, 1091, 1011, 845, 668. Anal. Calcd for $C_{20}H_{20}Cl_2N_4O_2$: C, 57.29; H, 4.81; Cl, 16.91; N, 13.36. Found: C, 57.11; H, 4.91; Cl, 16.76; N, 13.15.

4.2.6. 1,4-Di-(4-methoxy)phenyl-1,4-butanedione di-*N*-acetylhydrazone 3f. Yield 0.84 g (82%), mp 210–212 °C. ^{1}H NMR (DMSO-d_6): δ 1.98 and 2.14 (s, 6H), 2.83 and 2.85 (s, 4H,), 3.77 (s, 6H), 6.90–7.80 (m, 8H), 10.67 (bs, 2H). IR: 3447, 3222, 1651, 1513, 1334, 1258, 1102, 1029, 833, 668. Anal. Calcd for $C_{22}H_{26}N_4O_4$: C, 64.38; H, 6.38; N, 13.65. Found: C, 64.17; H, 6.36; N, 13.49.

4.3. General procedure for the cyclization of di-*N*-acylhydrazones 3a–f

Cyclization. Method A. The di-*N*-acylhydrazones **3a–c** (1 mmol) were refluxed 1 h in 4 ml of dry dimethylformamide, then the solvent was evaporated under reduced pressure and the residue was crystallized from ethanol or chloroform–hexane. Isolated yields are presented in Table 1.

Cyclization. Method B. The di-*N*-acylhydrazones **3a–f** (1 mmol) were refluxed 1 h in 4 ml of a mixture of AcOH/EtOH (1:1), then the solvent was evaporated under reduced pressure and the residue was crystallized from ethanol or chloroform–hexane. Isolated yields are presented in Table 1.

4.3.1. 1-*N*-(4-Methylbenzoyl)amino-2,5-diphenylpyrrole 4a. Mp 276–278 °C. ^{1}H NMR ($CDCl_3$): δ 2.33 (s, 3H), 6.41 (s, 2H), 7.20 (d, 2H, J=8.1 Hz,), 7.24 (m, 2H), 7.32 (m, 4H), 7.46 (d, 2H, J=8.1 Hz,), 7.52 (m, 4H), 8.18 (bs, 1H). ^{13}C NMR ($CDCl_3$): δ 21.5, 108.2, 127.1, 127.3, 128.1, 128.4, 129.3, 129.5, 131.8, 134.9, 136.7, 143.0, 167.6. MS *m/z* (relative intensity) EI: 352 (M^+, 26), 233(9), 218(7), 194(3), 130(2), 119(100), 115(5), 102(7), 91(39), 65(12). IR: 3449, 3219, 3015, 1654, 1532, 1304, 1287, 915, 746, 695. Anal. Calcd for $C_{24}H_{20}N_2O$: C, 81.79; H, 5.72; N, 7.95. Found: C, 81.66; H, 5.77; N, 7.82.

4.3.2. 1-*N*-(4-Methylbenzoyl)amino-2,5-di(4-chlorophenyl)pyrrole 4b. Mp 335–337 °C (dec). ^{1}H NMR (DMSO-d_6): δ 2.33 (s, 3H), 6.49 (s, 2H), 7.27 (d, 2H, J=8.3 Hz,), 7.41 (d, 4H, J=8.5 Hz), 7.56 (d, 4H, J=8.5 Hz), 7.63 (d, 2H, J=8.3 Hz), 11.71 (bs, 1H). ^{13}C NMR ($CDCl_3$): δ 20.5, 107.4, 126.6, 127.8, 128.0, 128.4, 128.6, 129.6, 130.9, 133.8, 141.9, 164.9. MS *m/z* (relative intensity) EI: 422 (M^++2, 6), 420 (M^+, 8), 303(1), 301(1), 288(1), 286(1), 267(1), 119(100), 91(25), 65(6). IR: 3481, 3209, 3009, 1648, 1528, 1483, 1285, 1090, 832, 771. Anal. Calcd for $C_{24}H_{18}Cl_2N_2O$: C, 68.42; H, 4.31; Cl, 16.83; N, 6.65. Found: C, 68.51; H, 4.39; Cl, 16.73; N, 6.51.

4.3.3. 1-*N*-(4-Methylbenzoyl)amino-2,5-di(4-methoxyphenyl)pyrrole 4c. Mp 267–269 °C (dec). ^{1}H NMR (DMSO-d_6): δ 2.33 (s, 3H), 3.72 (s, 6H), 6.29 (s, 2H), 6.90 (d, 4H, J=8.8 Hz), 7.27 (d, 2H, J=8.3 Hz), 7.45 (d, 4H, J=8.8 Hz), 7.65 (d, 2H, J=8.3 Hz). 11.53 (bs, 1H). ^{13}C NMR ($CDCl_3$): δ 20.4, 59.7, 105.8, 113.3, 123.9, 126.8, 127.9, 128.3, 128.5, 128.7, 134.0, 141.8, 165.2. MS *m/z* (relative intensity) EI: 412 (M^+, 30), 293(16), 278(23), 235(5), 224(8), 133(9), 119(100), 91(85), 65(32). IR: 3460, 3207, 3003, 1648, 1566, 1464, 1296, 1172, 834, 772. Anal. Calcd for $C_{26}H_{24}N_2O_3$: C, 75.71; H, 5.86; N, 6.79. Found: C, 75.63; H, 5.81; N, 6.85.

4.3.4. 1-*N*-Acetylamino-2,5-diphenylpyrrole 4d. Mp 206–208 °C. ^{1}H NMR ($CDCl_3$) two isomers: δ 1.38 and 1.89 (s, 3H), 6.35 and 6.41 (s 2H), 7.27–7.45 (m, 10H), 7.77 and 8.29 (bs, 1H). ^{13}C NMR ($CDCl_3$): δ 18.7, 20.0, 108.1, 108.2, 127.3, 127.4, 127.7, 128.0, 128.4, 128.7, 128.9, 129.9, 130.8, 131.6, 135.7, 136.3, 169.6, 174.3. MS *m/z* (relative intensity) EI: 276 (M^+, 100), 233(39), 218(26), 204(12), 130(65), 115(17), 102(58), 77(32), 63(18). IR: 3463, 3184, 3028, 1668, 1543, 1449, 1270, 965, 756, 619. Anal. Calcd for $C_{18}H_{16}N_2O$: C, 78.24; H, 5.84; N, 10.14. Found: C, 78.13; H, 5.81; N, 9.95.

4.3.5. 1-*N*-Acetylamino-2,5-di(4-chlorophenyl)pyrrole 4e. Mp 280–282 °C. ^{1}H NMR ($CDCl_3$) two isomers: δ 1.36 and 1.92 (s, 3H), 6.32 and 6.41 (s, 2H), 7.35–7.40 (m, 8H), 7.77 and 8.26 (bs, 1H). ^{13}C NMR ($CDCl_3$): δ 18.5, 20.9, 108.5, 108.7, 128.2, 128.8, 129.0, 129.1, 129.3, 129.4, 133.5, 134.3, 135.7, 136.6, 169.8, 174.5. MS *m/z* (relative intensity) EI: 346 (M^++2, 63), 344 (M^+, 100), 303(23), 301(28), 288(18), 286(25), 164(30), 130(57), 101(14), 75(12). IR: 3445, 3248, 3015, 1674, 1596, 1484, 1096, 1008, 828, 764. Anal. Calcd for $C_{18}H_{14}Cl_2N_2O$: C, 62.62; H, 4.09; Cl, 20.54; N, 8.11. Found: C, 62.53; H, 3.98; Cl, 20.43; N, 7.95.

4.3.6. 1-*N*-Acetylamino-2,5-di(4-methoxyphenyl)pyrrole 4f. Mp 220–222 °C. ^{1}H NMR ($CDCl_3$) two isomers: δ 1.39 and 1.90 (s, 3H), 3.81 (s, 6H), 6.25 and 6.30 (s, 2H), 6.89 (m, 4H), 7.35 (m, 4H), 7.64 and 8.11 (bs, 1H). ^{13}C NMR ($CDCl_3$): δ 18.7, 21.0, 55.3, 107.2, 113.8, 114.2, 123.3, 123.5, 124.4, 128.1, 129.1, 129.4, 134.9, 135.6, 169.7, 174.5. MS *m/z* (relative intensity) EI: 336 (M^+, 63), 321(4), 293(43), 278(57), 160(13), 132(80), 117(24), 102(10), 89(33), 63(14). IR: 3461, 3132, 2931, 1682, 1611, 1503, 1251, 1179, 1034, 836. Anal. Calcd for $C_{20}H_{20}N_2O_3$: C, 71.41; H, 5.99; N, 8.33. Found: C, 71.32; H, 6.04; N, 8.17.

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