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Some Synthetic Applications of 2,3-Dichloro-*N*-phenylmaleimide : A Novel Synthesis of 2-Phenylpyrrolo[3,4-*b*]quinoxaline-1,3-diones. I

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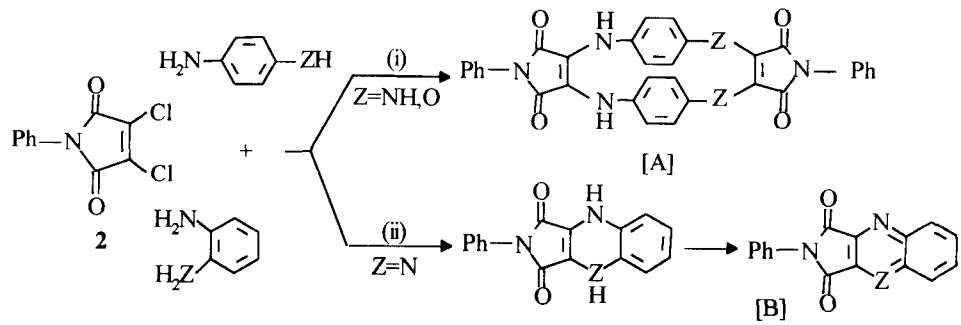
Abstract. 2,3-Dichloro-*N*-phenylmaleimide **2** undergoes nucleophilic substitution reactions by a variety of nucleophiles giving either monosubstituted **5** or disubstituted **3** products. Treatment of **5** with sodium azide at room temperature results in cyclization to the corresponding 2-phenylpyrrolo[3,4-*b*]quinoxaline-1,3-diones **6**, while at higher temperatures **5** is reduced to the 2-amino-3-amino-*N*-phenyl-maleimides **7**.

Many nucleophilic substitution reactions at vinylic carbon have been studied, using the six-membered ring systems of 2,3-dichloro-1,4-naphthoquinone,[1-6] chloranil[5] and 2,3-dichloronaphthazarin.[7] The products, monosubstituted, disubstituted or cyclized, depended on the nucleophile and the solvent. Since no nucleophilic substitution reactions in the five-membered ring system of 2,3-dichloro-*N*-phenylmaleimide have been reported, we decided to explore the synthetic potential of this compound as a route to more complex heterocycles of the type [A] and [B].



Scheme 1

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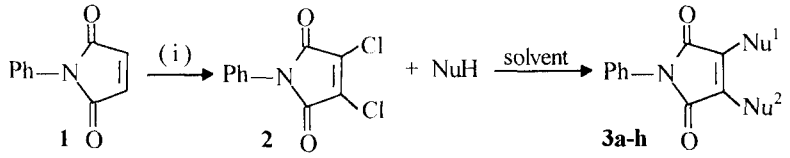
Type [B] compounds (Z=N) are of particular interest, as a new series of 2-arylpyrrolo[3,4-*b*]quinoxaline-1,3-diones. There is the added possibility of hydrolyzing the imide link to give quinoxaline dicarboxylic acids which in turn can be converted to other derivatives. Biological activity has been claimed for a large number of synthetic quinoxalines and their derivatives.[8]

RESULTS AND DISCUSSION

N-phenylmaleimide **1** was converted by a new route to 2,3-dichloro-*N*-phenylmaleimide **2** by refluxing in $SOCl_2$ / CH_2Cl_2 with pyridine as base. Reaction of **2** with pyrazole, imidazole, phenylhydrazine, and phenols gave the disubstituted products **3a-h** in relatively poor yields.



(i) $SOCl_2$ / CH_2Cl_2 + pyridine; reflux 8 h

Scheme 2

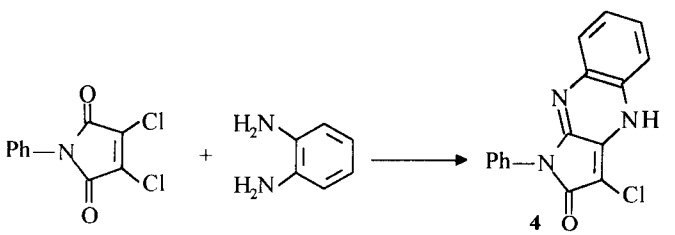
When **2** reacted with imidazole, the nature of the disubstituted product depended on the nucleophilicity of the solvent. In CH_3CN, 2,3-di-(1-imidazolyl)-*N*-phenylmaleimide **3d** was obtained. In the more nucleophilic EtOH, one of the imidazolyl groups was apparently exchanged by a solvent molecule to give 2-ethoxy-3-(1-imidazolyl)-*N*-phenylmaleimide **3c** (Table 1). 2,3-Di-(1-pyrazolyl)-*N*-phenylmaleimide **3a** did not show such an exchange reaction. Similar results were reported[5] for 2,3-dichloro-1,4-naphthoquinone and chloranil with imidazole, 1,2,4-triazole and pyrazole in Me_2SO and EtOH as solvents.

Reaction of **2** with phenols gave varied results. Phenol and *p*-chlorophenol in CH_2Cl_2 / K_2CO_3 gave **3f** and **3g** respectively, while catechol and *p*-hydroquinone failed to react. Physical, analytical and spectral data supporting the structures of **3a-h**, are presented in the Experimental. IR spectra showed one C=O absorption for all compounds, except **3c** where two such absorptions were observed, NH stretching modes for **3e** and **3h**, and an OH band for **3h**. ^{1}H NMR spectra exhibited a signal around δ 7.4 (5H,m) for the aromatic protons of the *N*-phenylmaleimide moiety, while other signals were due to substituents Nu^1 and Nu^2. ^{13}C NMR spectra gave the characteristic C=O signals in the range δ155.8-166.2.

Table 1. 2,3-Disubstituted compounds **3a-h**

Product	Yield (%)	Nu^1	Nu^2	Solvent
3a	16	1-pyrazolyl	1-pyrazolyl	abs. EtOH
3b	15	1-pyrazolyl	1-pyrazolyl	dry CH_3CN
3c	40	1-imidazolyl	OC_2H_5	abs. EtOH
3d	12	1-imidazolyl	1-imidazolyl	dry CH_3CN
3e	57	$NHNHC_6H_5$	$NHNHC_6H_5$	abs. EtOH
3f	34	OC_6H_5	OC_6H_5	CH_2Cl_2/anh. K_2CO_3
3g	37	OC_6H_4Cl (*p*)	OC_6H_4Cl (*p*)	CH_2Cl_2/anh. K_2CO_3
3h	38	NHC_6H_4OH(*p*)	NHC_6H_4OH(*p*)	abs. EtOH

In an attempt to prepare heterocycles of type [A] and [B] (Scheme 1), the behavior of **2** with bifunctional nucleophiles was examined. 4-Aminophenol, 2-aminophenol and *o*-phenylenediamine gave three different products **3h, 5a and 4**, respectively, but none of type [A] or [B] heterocycles. 4-Aminophenol, in absolute EtOH, gave the 2,3-disubstituted **3h** (Table 1), while 2-aminophenol, in the same solvent, gave the monosubstituted product **5a** (Table 2). Attempts to induce the OH group in **3h** and **5a** to cyclize intra- or intermolecularly failed. With *o*-phenylenediamine, the initial monosubstituted product condensed with the carbonyl group at C2 to give 3-chloro-1-phenyl-1H,4H-pyrrolo[2,3-*b*]-quinoxaline-2-one **4**. The structure of **4** was confirmed by elemental analysis and spectral data. A similar result was reported by Matsuoka and co-workers[7] for 2,3-dichloro-naphthazarin with 1,2-diamines.

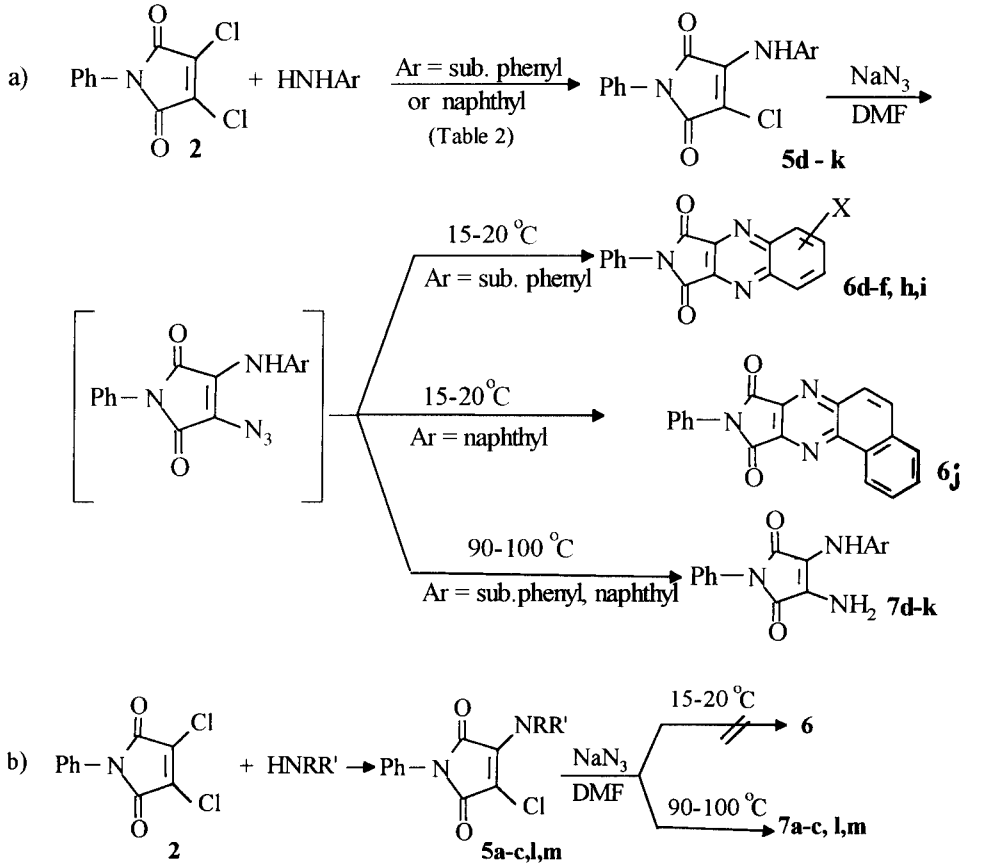


Scheme 3

With most aryl- and cycloalkyl-amines as nucleophiles, **2** gave monosubstituted products **5a-m** (Table 2 and Scheme 4). Formation of **5** (Scheme 4), *via* a Michael addition, appeared to be somewhat influenced by the nature and location of the substituent (X) in the arylamine. *p*-Nitroaniline, for example, failed to react with **2**, presumably due to its low nucleophilicity, a finding also reported by VanAllan for 2,3-dichloronaphthoquinone.[3] *o*-Substituted arylamines gave only monosubstituted products (**5a, 5b** and **4**), while the other nucleophiles varied, some giving monosubstituted products (Table 2), others disubstituted ones (Table 1). The lower yield of the *o*-isomer **5b** (66%) relative to the *p*-isomer **5h** (81%) may also be due to the ortho effect.

Table 2. 2-Amino-3-chloro-*N*-phenylmaleimides **5a-m**

Product	Yield (%)	Substituent	Product	Yield (%)	Substituent
5a	75	HNC_6H_4OH (*o*)	**5h**	81	$HNC_6H_4CH_3$ (*p*)
5b	66	$HNC_6H_4CH_3$ (*o*)	**5i**	81	$HNC_6H_4OCH_3$ (*p*)
5c	85	$N(CH_3)C_6H_5$	**5j**	73	HN-1-naphthyl
5d	86	HNC_6H_5	**5k**	76	HN-2-naphthyl
5e	79	HNC_6H_4Br (*p*)	**5l**	78	$N(CH_2CH_2)_2$ O
5f	84	HNC_6H_4Cl (*m*)	**5m**	75	NC_5H_{10}
5g	77	HNC_6H_4Cl (*p*)			



R=H, R'= *o*-sub. phenyl **(5a, b)**; R = CH_3, R' = phenyl **(5c)**; R=R'= alkyl **(5l,m)**

Scheme 4

The structures of **5** were confirmed by analytical and spectral data. When the 2-arylamino-3-chloro-*N*-phenylmaleimides **5d-k** were treated with NaN_3 in DMF, the presumed azide intermediates were found to undergo either cyclization to the 2-phenyl-

pyrrolo[3,4-*b*]quinoxaline-1,3-diones **6**, or reduction to the 2-arylamino-3-amino-*N*-phenyl-maleimides **7**, depending on experimental conditions. Compounds **6** were obtained in optimum yields at room temperature, whereas conducting the reaction at 90-100 °C gave the reduction products **7**. At room temperature, the arylamines **5a-c** and the alkylamines **5l** and **5m** (Scheme 4b) gave the corresponding amines **7**, but no cyclised products. The isomeric *m*- and *p*-chloro derivatives **5f** and **5g** and the 1- and 2-naphthylamines **5j** and **5k** cyclized to the same corresponding quinoxalines **6f** and **6j** respectively, suggesting that in the latter case ring closure occurred at C2 in the naphthyl ring of **5j** and at C1 in **5k**.

Characterization data for compounds **6** and **7** are shown in Table 3 and in the Experimental.

Table 3. Products **6d-f, h-j** and **7a-m**

Substituent	2-Phenylpyrrolo[3,4-*b*] quinoxaline-1,3-diones **6**		2-Amino-3-amino-*N*-phenylmaleimides **7**	
NHAr	Product	Yield (%)	Product	Yield (%)
HNC_6H_4OH (*o*)	**6a**	-	**7a**	26
$HNC_6H_4CH_3$ (*o*)	**6b**	-	**7b**	23
$N(CH_3)C_6H_5$	**6c**	-	**7c**	46
HNC_6H_5	**6d**	20	**7d**	33
HNC_6H_4Br (*p*)	**6e**	21	**7e**	26
HNC_6H_4Cl (*m*)	} **6f**	15	**7f**	21
HNC_6H_4Cl (*p*)		24	**7g**	28
$HNC_6H_4CH_3$ (*p*)	**6h**	29	**7h**	26
$HNC_6H_4OCH_3$ (*p*)	**6i**	20	**7i**	20
HN-1-naphthyl	} **6j**	39	**7j**	55
HN-2-naphthyl		39	**7k**	47
$N(CH_2CH_2)_2O$	**6l**	-	**7l**	32
NC_5H_{10}	**6m**	-	**7m**	36

A mechanism described by Messer and Farge[10] and involving an intermediate azide decomposing to a nitrene, which electrophilically attacks the aromatic rings of the aryl- or naphthylamine, seems likely here. This would explain the failure of the alkylamine derivatives **5l** and **5m** to cyclize, while the failure of the *o*-substituted **5a** and **5b** may be attributed to steric hindrance. In **5c**, dehydrogenation cannot occur, which would explain its failure to give **6** while undergoing reduction to **7**. This mechanism better explains our results than the alternative one presented by VanAllan *et al*,[3] investigating 1,4-naphtho-quinones, suggesting nitrene insertion into the CH bonds of alkyl- and aryl-amines.

EXPERIMENTAL

Melting points are uncorrected. IR spectra ($CHBr_3$ films on NaCl discs) were recorded on Perkin Elmer 577 Spectrophotometer. ^1H NMR spectra were measured in $CDCl_3$, except where otherwise stated, on a Varian T-60 and on a Bruker Spectrospin-80 with TMS as an internal standard. ^{13}C NMR spectra were recorded on a Bruker Spectrospin (20 MHz) with the same solvents as for ^1H NMR. A Varian MAT 112 Mass Spectrometer was used to obtain electron impact (EI) mass spectra. Microanalyses were performed by M. H. W. Laboratories, Arizona, U. S. A.

2,3-Dichloro-N-phenylmaleimide 2 : A solution of recrystallized *N*-phenylmaleimide[9] (3.0 g, 17.3 mmol) in dry CH_2Cl_2 (120 ml) was refluxed with $SOCl_2$ (10.3 g, 87.0 mmol) in the presence of pyridine (3.1 g, 39.2 mmol) for 8 h. After evaporation of the solvent, H_2O (50 ml) was added and the precipitate collected, washed with H_2O, and air dried (3.0 g, 16.1 mmol, 93.2%). The colorless plates had m.p. 202-3°C (EtOH-C_6H_6) (Lit.[11] m.p. 204-6 °C). ν_{max} 1730-1700 (br) cm^{-1}; EI-MS : *m/z* 241 ($M^{+\cdot}$, 100%); ^1H NMR : δ 7.4 (m, 5H)

2,3-Disubstituted-N-phenylmaleimides 3 and monosubstituted 2-amino-3-chloro-N-phenylmaleimides 5 : 2,3-Dichloro-*N*-phenylmaleimide **2** (1.0 g, 4.13 mmol) in absolute EtOH (80 ml) was refluxed with the desired amine (16.5 mmol) for periods ranging from 5-48 h depending on the nucleophile. The reaction was monitored by TLC. The solution was then concentrated, cooled and the resulting yellow to orange precipitates, washed, air-dried and recrystallized from suitable solvents. For **3b** and **3d**, dry CH_3CN (60 ml) was used instead. The phenolic nucleophiles **3f** and **3g** required a modification since no reaction occurred as above: **2** (0.5 g, 2.1 mmol) and the phenol (8.3 mmol) in dry CH_2Cl_2 (30 ml) was stirred with anhyd. K_2CO_3 (1.42 g, 10.3 mmol) at 35-40°C for 48 and 96 h, respectively. The K_2CO_3 (excess) was decomposed by cautious addition to a mixture of $CHCl_3$ and 1M HCl (100 ml each). The organic layer was separated, washed, dried over anhyd. $MgSO_4$, and the solvent concentrated then cooled. The product that precipitated was collected and recrystallized from EtOH. Attempts, under different experimental conditions, to react **2** with catechol or *p*-hydroquinone failed, and the starting material was recovered unchanged. To induce the phenolic OH in **3h** and **5a** to react further, the compounds were heated under reflux at 40°C for 48 h in CH_2Cl_2 and anhyd. K_2CO_3. Absolute EtOH / Et_3N and 1.0 M NaOH were also tried but all attempts failed.

2,3-Disubstituted-N-phenylmaleimides 3a-h :

3a : yellow needles (EtOH), m.p. 165-6°C. ν_{max} 1720 (C=O) cm^{-1}; EI-MS : *m/z* 305 ($M^{+\cdot}$, 100%); ^1H NMR : δ 8.3 (2H, d, *J* 4 Hz), 7.8 (2H, d, *J* 4 Hz), 7.4 (5H, m, ArH), 6.5 (2H,

dd, *J* 4 Hz); ^{13}C NMR : δ 164.1 (C=O); *Anal.* for $C_{16}H_{11}N_5O_2$, Calc. C 62.95 H 3.63 N 22.94%, Found C 62.72 H 3.86 N 22.61%.

3b : identical to **3a** in m.p., IR, El-MS, ^{1}H NMR and ^{13}C NMR.

3c : yellow rod-like crystals (C_6H_{12} / C_6H_6), m.p. 104-5 °C. ν_{max} 1710, 1685 (C=O) cm^{-1}; El-MS : *m/z* 283 ($M^{+\cdot}$, 100%); ^{1}H NMR : δ 8.4 (1H, s), 7.8 (1H, d, *J* 2 Hz), 7.4 (5H, m, ArH), 7.2 (1H, d, *J* 2 Hz), 4.8 (2H, q), 1.5 (3H, t); ^{13}C NMR : δ 164.2 (C=O); *Anal.* for $C_{15}H_{13}N_3O_3$, Calc. C 63.53 H 4.62 N 14.82%, Found C 63.47 H 4.58 N 14.80%.

3d : yellow needles (C_6H_{12} / $CHCl_3$), m.p. 154-5 °C. ν_{max} 1725 (C=O) cm^{-1}; El-MS : *m/z* 305 ($M^{+\cdot}$, 70%); ^{1}H NMR : δ 8.1 (2H, s), 7.5 (5H, m, ArH), 7.3 (2H, d, *J* 3 Hz), 7.1 (2H, d, *J* 3 Hz); ^{13}C NMR : δ 164.1 (C=O); *Anal.* for $C_{16}H_{11}N_5O_2$, Calc. C 62.95 H 3.63 N 22.94%, Found C 62.88 H 3.77 N 22.82%.

3e : orange needles (EtOH), m.p. 253 °C (dec.). ν_{max} 3270 (NH), 1750 (C=O) cm^{-1}; El-MS : *m/z* 383 ($M^{+\cdot}$, 100%); ^{1}H NMR (DMSO-d_6) : δ 12.0 (2H, s, NH), 11.6 (2H, s, NH), 7.3-7.7 (15H, m, ArH); ^{13}C NMR : δ 161.8 (C=O); *Anal.* for $C_{22}H_{19}N_5O_2$, Calc. C 68.54 H 4.97 N 18.18%, Found C 68.78 H 4.64 N 18.45%.

3f : yellow needles (EtOH), m.p 155-6 °C. ν_{max} 1720 (C=O) cm^{-1}; El-MS : *m/z* 357 ($M^{+\cdot}$, 66%); ^{1}H NMR : δ 7.4 (5H, m, ArH), 6.8-7.3 (10H, m, ArH); ^{13}C NMR : δ 155.9 (C=O); *Anal.* for $C_{22}H_{15}NO_4$, Calc. C 73.92 H 4.23 N 3.92%, Found C 73.32 H 4.41 N 4.05%.

3g : yellow needles (EtOH), m.p. 206-7 °C. ν_{max} 1720 (C=O) cm^{-1}; El-MS : *m/z* 425 ($M^{+\cdot}$, 100%); ^{1}H NMR : δ 7.4 (5H, m, ArH), 7.2 (4H, d, *J* 9 Hz), 6.9 (4H, d, *J* 9 Hz); ^{13}C NMR : δ 163.4 (C=O); *Anal.* for $C_{22}H_{13}Cl_2NO_4$, Calc. C 61.96 H 3.08 N 3.29%, Found C 61.76 H 3.31 N 3.32%.

3h : yellow plates (EtOH), m.p. 262-3 °C. ν_{max} 3260-3220 br (OH), 3150 (NH), 1695 (C=O) cm^{-1}; El-MS : *m/z* 387 ($M^{+\cdot}$, 1%); ^{1}H NMR (DMSO-d_6) : δ 9.7 (2H, s, OH), 9.5 (2H, s, NH), 7.3 (7H, d, *J* 9 Hz), 6.8 (6H, d, *J* 9 Hz); ^{13}C NMR : δ 166.2 (C=O); *Anal.* for $C_{22}H_{17}N_3O_4$, Calc. C 68.21 H 4.43 N 10.85%, Found C 68.39 H 4.43 N 10.99%.

2-Amino-3-chloro-N-phenylmaleimides 5a-m : The yellow to orange precipitates were recrystallized from EtOH.

5a : m.p. 200-1 °C. ν_{max} 3460-3400 br (OH), 3360 (NH), 1710, 1665 (C=O) cm^{-1}; El-MS : *m/z* 314 ($M^{+\cdot}$, 47%); ^{1}H NMR (DMSO-d_6) : δ 9.7 (1H, s, OH), 9.3 (1H. s, NH), 7.4 (5H, m, ArH), 6.8-7.3 (4H, m, ArH); ^{13}C NMR : δ 163.9, 165.9 (C=O); *Anal.* for $C_{16}H_{11}ClN_2O_3$, Calc. C 61.03 H 3.52 N 8.90%, Found C 60.94 H 3.52 N 9.20%.

5b : m.p. 136-7 °C. ν_{max} 3350 (NH), 1710, 1660 (C=O) cm^{-1}; El-MS : *m/z* 312 ($M^{+\cdot}$, 60%; ^{1}H NMR : δ 7.4-7.5 (6H, m, ArH+NH), 7.0-7.4 (4H, m, ArH), 2.4 (3H, s, CH_3); ^{13}C NMR :

δ 17.89 (CH_3), 165.1, 166.2 (C=O); *Anal.* for $C_{17}H_{13}ClN_2O_2$, Calc. C 65.29 H 4.19 N 8.96%, Found C 65.09 H 4.40 N 9.10%.

5c : m.p. 191-2 °C. ν_{max} 1710, 1620 (C=O) cm^{-1}; El-MS : *m/z* 312 ($M^{+\cdot}$, 100%); ^1H NMR : δ 7.1-7.5 (10H, m, ArH), 3.8 (3H, s, CH_3); ^{13}C NMR : δ 164.5, 165.1 (C=O); *Anal.* for $C_{17}H_{13}ClN_2O_2$, Calc. C 65.29 H 4.19 N 8.96%, Found C 65.04 H 4.16 N 8.91%.

5d : m.p. 184-5 °C. ν_{max} 3320 (NH), 1710, 1660 (C=O) cm^{-1}; El-MS : *m/z* 298 ($M^{+\cdot}$, 100%); ^1H NMR : δ 7.4-7.5 (6H, m, ArH+NH), 7.1-7.4 (5H, m, ArH); ^{13}C NMR : δ 165.2, 175.1 (C=O); *Anal.* for $C_{16}H_{11}ClN_2O_2$, Calc. C 64.27 H 3.71 N 9.42%, Found C 63.99 H 3.61 N 9.25%.

5e : m.p. 180-1 °C. ν_{max} 3300 (NH), 1730, 1675 (C=O) cm^{-1}; El-MS : *m/z* 380 (M (^{81}Br, ^{37}Cl),70%), 378 (M (^{81}Br,^{35}Cl/^{79}Br,^{37}Cl), 95%) 376 ($M^{+\cdot}$, 100%); ^1H NMR : δ 7.3-7.5 (6H, m,ArH+NH), 7.5 (2H,d, *J* 9 Hz), 7.1 (2H, d, *J* 9 Hz); ^{13}C NMR : δ 165.1, 166.4 (C=O); *Anal.* for $C_{16}H_{10}BrClN_2O_2$, Calc. C 50.86 H 2.67 N 7.42%, Found C 51.05 H 2.58 N 7.43%.

5f : m.p. 165-6 °C. ν_{max} 3300 (NH), 1710, 1665 (C=O) cm^{-1}; El-MS : *m/z* (334 (M (^{37}Cl, ^{35}Cl), 60%), 332 ($M^{+\cdot}$, 100%); ^1H NMR : δ 7.0-7.4 (10H, m, ArH+NH); ^{13}C NMR : δ 165.1, 166.0 (C=O); *Anal.* for $C_{16}H_{10}Cl_2N_2O_2$, Calc. C 57.64 H 3.03 N 8.41%, Found C 58.00 H 3.50 N 8.20%.

5g : m.p. 189-90 °C. ν_{max} 3280 (NH), 1710, 1655 (C=O) cm^{-1}; El-MS : *m/z* (334 (M (^{37}Cl, ^{35}Cl), 66%), 332 ($M^{+\cdot}$, 100%); ^1H NMR : δ 7.4-7.5 (6H, m, ArH+NH), 7.4 (2H, d, *J* 9 Hz), 7.1 (2H, d, *J* 9 Hz); ^{13}C NMR : δ 165.1, 166.0 (C=O); *Anal.* for $C_{16}H_{10}Cl_2N_2O_2$, Calc. C 57.64 H 3.03 N 8.41%, Found C 57.36 H 3.05 N 8.37%.

5h : m.p. 163-4 °C. ν_{max} 3340 (NH), 1710, 1655 (C=O) cm^{-1}; El-MS : *m/z* 312 ($M^{+\cdot}$, 100%); ^1H NMR : δ 7.4-7.5 (6H, m, ArH+NH), 7.2 (4H, d, *J* 3 Hz), 2.4 (3H, s, CH_3); ^{13}C NMR : δ 165.2, 166.3 (C=O); *Anal.* for $C_{17}H_{13}ClN_2O_2$, Calc. C 65.29 H 4.19 N 8.96%, Found C 65.06 H 4.28 N 8.91%.

5i : m.p. 161-2 °C. ν_{max} 3350 (NH), 1710, 1660 (C=O) cm^{-1}; El-MS : *m/z* 328 ($M^{+\cdot}$, 100%); ^1H NMR : δ 7.3-7.5 (6H, m, ArH+NH), 7.2 (2H, d, *J* 10 Hz), 6.9 (2H, d, *J* 10 Hz), 3.9 (3H, s, CH_3); ^{13}C NMR : δ 158.7, 165.3 (C=O); *Anal.* for $C_{17}H_{13}ClN_2O_3$, Calc. C 62.10 H 3.98 N 8.52%, Found C 62.21 H 3.94 N 8.52%.

5j : m.p. 163-4 °C. ν_{max} 3320 (NH), 1710, 1650 (C=O) cm^{-1}; El-MS : *m/z* 348 ($M^{+\cdot}$, 100%); ^1H NMR : δ 7.5-8.1 (7H, m, naphthyl-H), 7.4-7.5 (6H, m, ArH+NH); ^{13}C NMR : δ 168.1, 177.9 (C=O); *Anal.* for $C_{20}H_{13}ClN_2O_2$, Calc. C 68.86 H 3.76 N 8.03%, Found C 68.87 H 3.70 N 8.07%.

5k : m.p. 187-8 °C. ν_{max} 3340 (NH), 1710, 1650 (C=O) cm^{-1}; El-MS : *m/z* 348 ($M^{+\cdot}$, 100%); ^1H NMR : δ 7.5-9.6 (7H, m, naphthyl-H), 7.4-7.5 (6H, m, ArH+NH); ^{13}C NMR : δ 165.3, 166.2 (C=O); *Anal.* for $C_{20}H_{13}ClN_2O_2$, Calc. C 68.86 H 3.76 N 8.03%, Found C 68.50 H 3.73 N 8.03%.

5l : m.p. 160-1 °C. ν_{max} 1710, 1620 (C=O) cm^{-1}; El-MS : *m/z* 292 ($M^{+\cdot}$, 100%); ^1H NMR : δ 7.3-7.5 (5H, m, ArH), 4.0-4.1 (4H, m, CH_2), 3.7-3.9 (4H, m, CH_2); ^{13}C NMR : δ 164.5, 164.9 (C=O); *Anal.* for $C_{14}H_{13}ClN_2O_3$, Calc. C 57.45 H 4.48 N 9.57%, Found C 57.67 H 4.59 N 9.63%.

5m : m.p. 122-3 °C. ν_{max} 1710, 1625 (C=O) cm^{-1}; El-MS : *m/z* 290 ($M^{+\cdot}$, 100%); ^1H NMR : δ 7.3-7.5 (5H, m, ArH), 3.8-4.1 (4H, m, CH_2), 1.5-1.9 (6H, m, CH_2); ^{13}C NMR : δ 165.4, 169.1 (C=O); *Anal.* for $C_{15}H_{15}ClN_2O_2$, Calc. C 61.97 H 5.20 N 9.64%, Found C 61.86 H 5.08 N 9.89%.

3-Chloro-1-phenyl-1H,4H-pyrrolo[2,3,b]quinoxaline-2-one 4 : The same procedure, as above, in absolute EtOH and with freshly crystallized 2-phenylenediamine, precipitated compound **4** (82%) in a few minutes. It recrystallized in yellow needles (CH_3CN), m.p. 245°C (dec.). ν_{max} 3220, (NH), 1690 (C=O) cm^{-1}; EI-MS : *m/z* 295 ($M^{+\cdot}$, 51%); ^1H NMR (DMSO-d_6) : δ 12.9 (1H, s, NH), 7.2-7.7 (9H, m, ArH); ^{13}C NMR: δ 165.3 (C=O); *Anal.* for $C_{16}H_{10}ClN_3O$, Calc.C 64.98 H 3.41 N 14.21 % , Found C 64.84 H 3.63 N 14.52 % .

2-Phenylpyrrolo[3,4-b]quinoxaline-1,3-diones 6d-f,h-j : To a solution of the 2-arylamino-3-chloro-*N*-phenylmaleimide **5** (0.75 g) in DMF (10-15 ml) was added NaN_3 (3 molar equivalents) dissolved in H_2O (3 ml). The reaction mixture was left stirring overnight at 15-20°C. The creamy product that precipitated was washed with EtOH, dried and recrystallized from *o*-dichlorobenzene.

6d : pale yellow needles, m.p. 255 °C (dec.). ν_{max} 1710 (C=O) cm^{-1}; El-MS : *m/z* 275 ($M^{+\cdot}$, 100%); ^1H NMR (DMSO-d_6) : δ 8.4 (2H, m, quinoxaline-H), 8.2 (2H, m, quinoxaline-H), 7.5 (5H, m, ArH); *Anal.* for $C_{16}H_9N_3O_2$, Calc. C 69.81 H 3.29 N 15.27%, Found C 69.81 H 3.06 N 15.17%.

6e : white plates m.p. 276 °C (dec.). ν_{max} 1730 cm^{-1}; El-MS : *m/z* 355 (M(^{81}Br), 100%), 353 (M (^{79}Br), 100%); ^1H NMR (DMSO-d_6) : δ 8.7 (1H, s, quinoxaline-H), 8.5 (1H, d, *J* 9 Hz, quinoxaline-H), 8.2 (1H, m, quinoxaline-H), 7.5 (5H, m, ArH); *Anal.* for $C_{16}H_8BrN_3O_2$, Calc. C 54.26 H 2.28 N 11.86%, Found C 53.91 H 2.47 N 11.84%.

6f : white plates m.p. 285 °C (dec.). ν_{max} 1720 (C=O) cm^{-1}; El-MS : *m/z* 311 (M(^{37}Cl), 40%), 309 (M (^{35}Cl), 100%); ^1H NMR (DMSO-d_6) : δ 8.6 (2H, m, quinoxaline-H), 8.2 (1H,

m, quinoxaline-H), 7.5 (5H, m, ArH); *Anal.* for $C_{16}H_8ClN_3O_2$, Calc. C 62.05 H 2.60 N 13.57%, Found C 61.91 H 2.47 N 13.33%.

Compound **5g** gave product **6g** identical to **6f**

6h : white needles m.p. 305 °C (dec.). ν_{max} 1710 (C=O) cm^{-1}; El-MS : *m/z* 289 ($M^{+\cdot}$, 100%); ^1H NMR : δ 8.3 (2H, m, quinoxaline-H), 8.0 (1H, d, *J* 9 Hz, quinoxaline-H), 7.3 (5H, m, ArH), 2.6 (3H, s, CH_3); *Anal.* for $C_{17}H_{11}N_3O_2$, Calc. C 70.58 H 3.83 N 14.53%, Found C 69.37 H 3.85 N 14.80%.

6i : pale yellow needles m.p. 249 °C (dec.). ν_{max} 1720 (C=O) cm^{-1}; El-MS : *m/z* 305 ($M^{+\cdot}$, 100%); ^1H NMR (DMSO-d_6) : δ 8.3 (1H, d, *J* 9 Hz, quinoxaline-H), 7.7 (2H, m, quinoxaline-H), 7.5 (5H, m, ArH), 4.1 (3H, s, OCH_3); *Anal.* for $C_{17}H_{11}N_3O_3$, Calc. C 66.88 H 3.64 N 13.77%, Found C 66.39 H 3.51 N 13.70%.

6j : creamy needles m.p. 340 °C (dec.). ν_{max} 1720-1710 br (C=O) cm^{-1}; El-MS : *m/z* 325 ($M^{+\cdot}$, 100%); ^1H NMR (DMSO-d_6) : δ 9.3 (1H, d, C5-H, *J* 9 Hz), 8.5 (1H, d, C6-H, *J* 9 Hz), 8.3 (2H, m, naphthyl-H), 8.0 (2H, m, naphthyl-H), 7.5 (5H, m, ArH); *Anal.* for $C_{20}H_{11}N_3O_2$, Calc. C 73.84 H 3.41 N 12.92%, Found C 73.70 H 3.44 N 12.78%.

Compound **5k** gave product **6k** identical to **6j**.

2-Amino-3-amino-N-phenylmaleimides 7a-m : Compound **7** was isolated when the above reaction was conducted at 90-100°C. The precipitate that resulted on the addition of H_2O, was washed, dried and recrystallized from EtOH or EtOH-H_2O to give dark red needles or rod shaped crystals.

7a : m.p. 192-3 °C. ν_{max} 3460-3400 br (OH), 3360 (NH), 1690-1665 br (C=O) cm^{-1}; El-MS : *m/z* 295 ($M^{+\cdot}$, 51%); ^1H NMR (DMSO-d_6) : δ 9.7 (1H, s, OH), 9.3 (1H, s, NH), 7.4 (5H, m, ArH), 6.8-7.3 (4H, m, ArH), 6.3 (2H, br s, NH_2); *Anal.* for $C_{16}H_{13}N_3O_3$, Calc. C 65.08 H 4.41 N 14.23%, Found C 65.32 H 4.08 N 14.37%; λ_{max} 402 nm (ε 4550).

7b : m.p. 105-6 °C. ν_{max} 3460, 3360 (NH), 1700-1670 br (C=O) cm^{-1}; El-MS : *m/z* 293 ($M^{+\cdot}$, 100%); ^1H NMR (DMSO-d_6) : δ 7.4 (5H, m, ArH), 7.2 (1H, s, NH), 6.7 (4H, m, ArH), 6.3 (2H, br s, NH_2), 2.3 (3H, s, CH_3); ^{13}C NMR : δ 166.0, 168.1 (C=O); *Anal.* for $C_{17}H_{15}N_3O_2$, Calc. C 69.61 H 5.15 N 14.33%, Found C 69.57 H 5.26 N 14.13%; λ_{max} 430 nm (ε 4067).

7c : m.p. 187-8 °C. ν_{max} 3320 (NH), 1690-1660 br (C=O) cm^{-1}; El-MS : *m/z* 291 ($M^{+\cdot}$, 100%); ^1H NMR (DMSO-d_6) : δ 6.4-7.5 (10H, m, ArH), 6.2 (2H, br s, NH_2), 3.3 (3H, s, CH_3); ^{13}C NMR : δ 166.0, 168.8 (C=O); *Anal.* for $C_{17}H_{15}N_3O_2$, Calc. C 69.61 H 5.15 N 14.33%, Found C 69.52 H 4.95 N14.52%; λ_{max} 452 nm (ε 2600).

7d : m.p. 172-3 °C. ν_{max} 3460, 3340 (NH), 1690-1660 (C=O) cm^{-1}; El-MS : *m/z* 279 ($M^{+\cdot}$, 100%); ^1H NMR (DMSO-d_6) : δ 7.3-7.5 (6H, m, ArH+NH), 6.6-7.2 (5H, m, ArH), 6.5 (2H, br s, NH_2); ^{13}C NMR : δ 166.0, 168.3 (C=O); *Anal.* for $C_{16}H_{13}N_3O_2$, Calc. C 68.82 H 4.69 N 15.05%, Found C 68.52 H 4.39 N 14.93%; λ_{max} 420 nm (ε 3700).

7e : m.p. 189-90 °C. ν_{max} 3470, 3350 (NH), 1700-1670 br (C=O) cm^{-1}; El-MS : *m/z* 361 (M(^{81}Br),100%), 359 (M(^{79}Br),100%); ^1H NMR (DMSO-d_6) : δ 7.2-7.7 (10H, m, ArH+NH), 6.7 (2H, br s, NH_2); ^{13}C NMR : δ 165.8, 168.1 (C=O); *Anal.* for $C_{16}H_{12}BrN_3O_2$, Calc. C 53.63 H 3.38 N 11.73%, Found C 53.65 H 3.31 N 11.80%; λ_{max} 425 nm (ε 4225).

7f : m.p. 184-5 °C. ν_{max} 3420, 3360 (NH), 1690-1660 br (C=O) cm^{-1}; El-MS : *m/z* 313 (M (^{37}Cl), 35%), 311 (M (^{35}Cl), 100%); ^1H NMR (DMSO-d_6) : δ 7.4 (6H, m, ArH+NH), 7.2 (2H, d, *J* 9 Hz), 6.8 (2H, d, *J* 9 Hz), 5.7 (2H, br s, NH_2); ^{13}C NMR : δ 165.7, 168.3 (C=O); *Anal.* for $C_{16}H_{12}ClN_3O_2$, Calc. C 61.25 H 3.86 N 13.36%, Found C 61.24 H 4.00 N 13.35%; λ_{max} 428 nm (ε 3400).

7g : m.p. 175-6 °C. ν_{max} 3460, 3340 (NH), 1690-1660 br (C=O) cm^{-1}; El-MS : *m/z* 313 (M (^{37}Cl), 35%), 311 (M (^{35}Cl), 100%); ^1H NMR (DMSO-d_6) : δ 7.3 (6H, m, ArH+NH), 7.1 (2H, d, *J* 9 Hz), 6.7 (2H, d, *J* 9 Hz), 5.2 (2H, br s, NH_2); ^{13}C NMR : δ 165.8, 168.2 (C=O); *Anal.* for $C_{16}H_{12}ClN_3O_2$, Calc. C 61.25 H 3.86 N 13.36%, Found C 61.19 H 4.10 N 12.96%; λ_{max} 430 nm (ε 2889).

7h : m.p. 179-80 °C. ν_{max} 3460, 3360 (NH), 1710-1690 br (C=O) cm^{-1}; El-MS : *m/z* 293 ($M^{+\cdot}$, 100%); ^1H NMR (DMSO-d_6) : δ 7.3-7.4 (6H, m, ArH+NH), 6.6-7.2 (4H, m, ArH), 5.6 (2H, br s, NH_2), 2.3 (3H, s, CH_3); ^{13} C NMR : δ 166.2, 168.2 (C=O); *Anal.* for $C_{17}H_{15}N_3O_2$, Calc. C 69.61 H 5.15 N 14.33%, Found C 69.68 H 5.35 N 14.36%; λ_{max} 442 nm (ε 2500).

7i : m.p. 170-1 °C. ν_{max} 3480, 3380 (NH), 1710-1690 br (C=O) cm^{-1}; El-MS : *m/z* 309 ($M^{+\cdot}$, 100%); ^1H NMR (DMSO-d_6) : δ 7.4 (6H, m, ArH+NH), 6.9 (2H, d, *J* 10 Hz), 6.6 (2H, d, *J* 10 Hz), 6.1 (2H, br s, NH_2), 3.7 (3H, s, OCH_3); ^{13}C NMR : δ 166.4, 168.1 (C=O); *Anal.* for $C_{17}H_{15}N_3O_3$, Calc. C 66.02 H 4.89 N13.59%, Found C 65.83 H 4.92 N 13.70%; λ_{max} 446 nm (ε 3265).

7j : m.p. 107-8 °C. ν_{max} 3460, 3340 (NH), 1690-1660 br (C=O) cm^{-1}; El-MS : *m/z* 329 ($M^{+\cdot}$, 60%); ^1H NMR (DMSO-d_6) : δ 7.2-8.5 (13H, m, ArH+NH), 6.7 (2H, br s, NH_2); ^{13}C NMR : δ 165.8,168.0 (C=O); λ_{max} 442 nm (ε 3630).

7k : m.p. 225-6 °C. ν_{max} 3460, 3360 (NH), 1665-1630 br (C=O) cm^{-1}; El-MS : *m/z* 329 ($M^{+\cdot}$, 100%); ^1H NMR (DMSO-d_6) : δ 7.0-7.9 (13H, m, ArH+NH), 6.2 (2H, br s, NH_2); ^{13}C NMR : δ 166.0, 168.3 (C=O); *Anal.* for $C_{20}H_{15}N_3O_2$, Calc. C 72.93 H 4.59 N 12.77%, Found C 72.70 H 4.67 N 12.72%; λ_{max} 444 nm (ε 4900).

7l : m.p. 172-3 °C. ν_{max} 3460, 3340 (NH), 1710-1690 br (C=O) cm^{-1}; El-MS : *m/z* 273 ($M^{+\cdot}$, 100%); ^1H NMR : δ 7.3-7.5 (5H, m, ArH), 6.2 (2H, br s, NH_2), 4.0-4.1 (4H, m, CH_2), 3.7-3.9 (4H, m, CH_2); ^{13}C NMR : δ 164.5, 164-9 (C=O); *Anal.* for $C_{14}H_{15}N_3O_3$, Calc. C 61.54 H 5.49 N 15.38%, Found C 61.86 H 5.61 N 15.21%; λ_{max} 396 nm (ε 3730).

7m : m.p. 113-4 °C. ν_{max} 3420, 3360 (NH), 1710-1690 br (C=O) cm^{-1}; El-MS : *m/z* 271 ($M^{+\cdot}$, 100%); ^1H NMR : δ 7.3-7.5 (5H, m, ArH), 6.3 (2H, br s, NH_2), 3.8-4.1 (4H, m, CH_2), 1.5-1.9 (6H, m, CH_2); ^{13}C NMR : δ 165.3, 167.9 (C=O); *Anal.* for $C_{15}H_{17}N_3O_2$, Calc. C 66.42 H 6.27 N 15.50%, Found C 66.13 H 6.59 N 15.23%; λ_{max} 436 nm (ε 5550).

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