New and Efficient Synthesis of Pyrrolo[3,2-*b*]pyrrole-2,5-diones by Double-Anion-Capture Reactions of Ester Carbanions with Bis(imidoyl)chlorides of Oxalic Acid†

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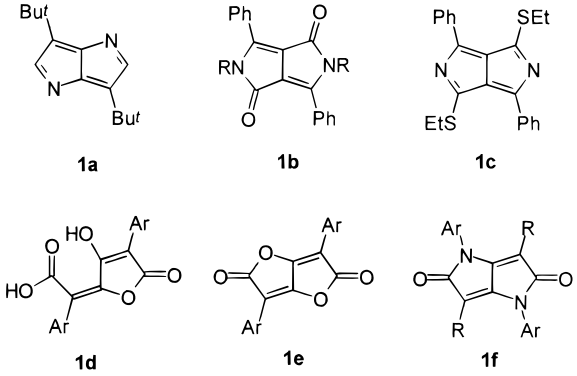
A variety of pyrrolo[3,2-*b*]pyrrole-2,5-diones were efficiently prepared by a new domino-reaction of ester carbanions with oxalic acid−bis(imidoyl)chlorides. This reaction proceeded by condensation of 2 equiv of the ester with the bis(imidoyl)chloride and subsequent intramolecular attack of the nitrogen atoms of the bis-enamine intermediate onto the ester groups. The products, which can be regarded as dilactams of pentalene, represent useful synthetic pigments due to their optical features, their stability, and low solubility. The UV−vis properties of the pyrrolo[3,2-*b*]pyrrole-2,5-diones could be efficiently controlled by the substituents attached to the heterocyclic core. The scope and the limitations of the new cyclization reaction were investigated.

Heterocyclic pentalene derivatives are of great current interest both in the field of material sciences and theoretical chemistry due to their unusual electronic features and physical properties. For example, 1,4-diazapentalene **1a** has been prepared in order to study the influence of the nitrogen atoms on the antiaromaticity of the pentalene unit.[1] 2,5-Diazapentalene (pyrrolo[3,4-*c*]pyrrole) **1c** has been prepared via the corresponding nonaromatic dilactam **1b** (R = H). Dilactams **1b** were obtained by reaction of succindiamides with *N*,*N*-dimethylarylamide diethyl acetals.[2] Besides their unusual electronic situation, diazapentalene-1,4(2*H*,5*H*)-diones **1b** exhibit interesting pigment properties.[3] The related pyrrolo[3,2-*b*]pyrrole-2,5-diones **1f** also represent useful synthetic pigments.[4] Similar to heterocycles **1b**, these nonaromatic compounds can be regarded as dilactams of pentalene and as unsaturated cyclic *β*-dipeptides. They also represent azaanalogues of dilactones **1e** which are derived from pulvinic acids **1d**, natural pigments found in lichens.[5,6]



1a **1b** **1c**

1d **1e** **1f**

Previously, selected pyrrolo[3,2-*b*]pyrrole-2,5-diones have been prepared in three steps starting with (*N*-phenylacetyl)acetic acid amino ester[7] or in one step from pulvinic acid using relatively harsh reaction conditions (autoclave reaction, 140−180 °C).[8] Due to the genuine interest in pyrrolo[3,2-*b*]pyrrole-2,5-diones, we have sought for a more general and convenient synthesis of this type of compound. In the course of our interest in the development of new domino-cyclization reactions of carbanions with oxalic acid derivatives,[9,10] we envisaged that pyrrolo-[3,2-*b*]pyrrole-2,5-diones could be prepared by condensation of 2 equiv of ester carbanions **2** with 1 equiv of oxalic acid−bis(imidoyl)chlorides **3**[11] and subsequent 2-fold intramolecular attack of the nitrogen atoms of the

† Dedicated to Professor Dr. Dr. h. c. mult. Dietmar Seyferth on the occasion of his 70th birthday.

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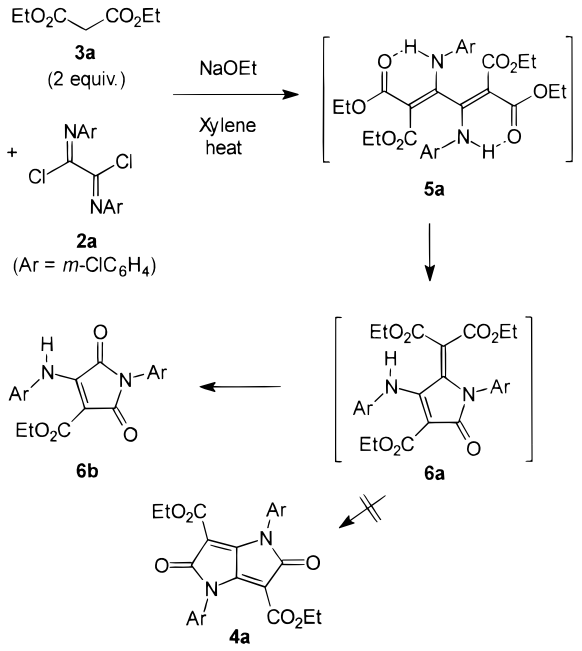
Scheme 1. Condensation of Diethyl Malonate with Bis(imidoyl)chloride 2a



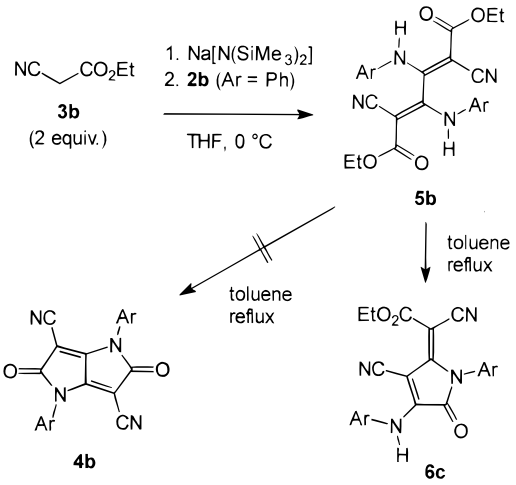
initially formed bis-enamine intermediate onto the ester groups.[12] We have now developed a double-anion-capture reaction which indeed provides a convenient synthesis of a variety of pyrrolo[3,2-*b*]pyrrole-2,5-diones. Herein, we wish to report full details and studies related to the scope and the limitations of our new cyclization reaction. The physical data of all products, which exhibit excellent pigment properties, are also reported.

Results and Discussion

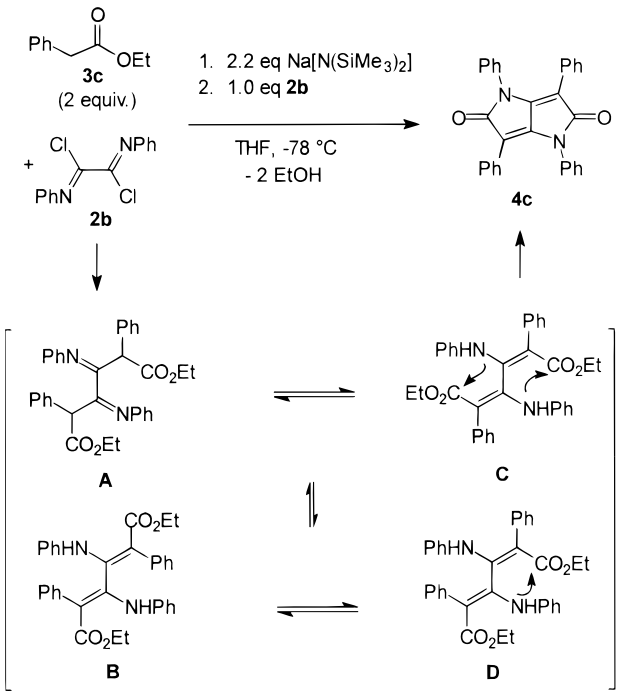
The condensation of sodium diethyl malonate (**3a**) with bis(*m*-chlorophenylimidoyl)chloride **2a** was reported to give a mixture of the maleic imide **6b** (main product) and of the bis-enamine **5a** (side product) (Scheme 1).[13] Imide **6b** was presumably formed by cyclization of the open-chained condensation product **5a** to give intermediate **6a** and subsequent cleavage of the semicyclic double bond of the latter. Although the desired pyrrolo[3,2-*b*]pyrrole-2,5-dione **4a** could not be isolated, this reaction suggested that formation of a bis-enamine intermediate and subsequent cyclization should be a feasible process.

Our first attempts to induce a cyclization reaction in order to prepare pyrrolo[3,2-*b*]pyrrole-2,5-diones were unsuccessful: reaction of ethyl cyanoacetate (**3b**) with bis(phenylimidoyl)chloride **2b** afforded the bis-enamine **5b** in good yield (Scheme 2). Unfortunately, all attempts to induce a base-mediated cyclization (Na[N(SiMe$_3$)$_2$], NaOEt) failed. When bis-enamine **5b** was refluxed in toluene for 2 days a complex reaction mixture was obtained from which the 5-ylidenepyrrol-2(5*H*)-one **6c** rather than the desired pyrrolo[3,2-*b*]pyrrole-2,5-dione **4b** was isolated in low yield. Compound **6c** was formed by cyclization *via* the carbon rather than the nitrogen atom and two subsequent rearrangement reactions.[9e] The intramolecular attack of the nitrogen atoms onto the ester groups of **5b** was presumably disfavored by the

Scheme 2. Condensation of Ethyl Cyanoacetate with Bis(imidoyl)chloride 2b



Scheme 3. Reaction of Ethyl Phenylacetate 3c with Bis(imidoyl)chloride 2b



Z-configuration of the latter. In addition, the presence of the electron-withdrawing cyano groups accounted for a reduced nucleophilicity of the nitrogen atoms.

On the basis of these results, the reaction of bis(imidoyl)chlorides with ethyl phenylacetate **3c** was next studied. Much to our satisfaction, reaction of 1 equiv of bis(imidoyl)chloride **2b** with 2 equiv of sodium ethyl phenylacetate (generated by NaN(SiMe$_3$)$_2$ in THF) resulted in formation of the pyrrolo[3,2-*b*]pyrrole-2,5-dione **4c** in 75% yield (Scheme 3). The isolation of **4c** was surprisingly simple: after addition of a THF solution of the bis(imidoyl)chloride to a solution of the ester carbanion at −78 °C, the temperature was allowed to rise to ambient. The mixture was poured into a saturated aqueous solution of NH_4Cl to give an orange precipitate which was isolated by filtration and purified by recrystallization from DMF.

The formation of pyrrolo[3,2-*b*]pyrrole-2,5-dione **4c** can be explained by attack of 2 equiv of the ester carbanion

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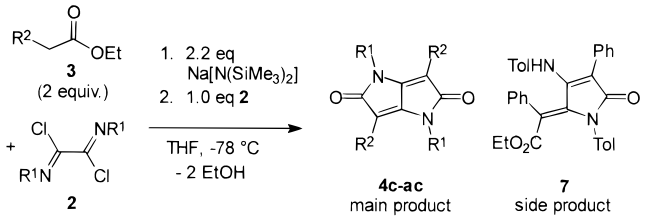
(14) For a review on NIR dyes, see: Fabian, J.; Nakazumi, H.; Matsuoka, M. *Chem. Rev.* **1992**, *92*, 1197.

Scheme 4. Preparation of Pyrrolo[3,2-*b*]pyrrole-2,5-diones 4c−ac



onto the bis(imidoyl)chloride to give the open-chained intermediate **A**, which rapidly equilibrates with the enamine tautomers **B**, **C**, and **D**. The dilactam **4c** is formed by 2-fold attack of the nitrogen atoms onto the ester groups in tautomer **C**. It is noteworthy, that the configuration of intermediate **C** is different from that of bis-enamine **5b** (Scheme 2), which adopts the configuration as present in isomer **B**. The equilibration between the tautomers is presumably catalyzed by the excess of base present in the reaction mixture. The pyrrolo[3,2-*b*]-pyrrole-2,5-dione **4** is withdrawn from the equilibrium by precipitation due to its low solubility in THF. In fact, this cyclization reaction represents a new type of double-anion-capture process which has not been previously reported.

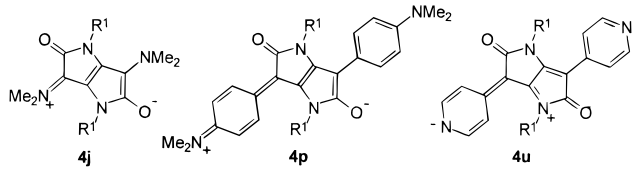
In order to investigate the scope and the limitations of the new cyclization reaction for the preparation of pyrrolo[3,2-*b*]pyrrole-2,5-diones, the substituents of the esters and of the bis(imidoyl)chlorides were systematically varied (Scheme 4, Table 1). Reaction of bis(phenylimidoyl)chloride **2b** with ethyl *p*-tolylacetate and ethyl *p*-methoxyphenylacetate afforded the pyrrolo[3,2-*b*]pyrrole-2,5-diones **4d** and **4e**, respectively. Treatment of bis(*p*-tolylimidoyl)chloride **2c** with ethyl acetate, ethyl propionate, and ethyl 3,3-dimethylbutanoate gave the corresponding alkyl-substituted pyrrolo[3,2-*b*]pyrrole-2,5-diones **4f**, **4g**, and **4h**, respectively. Reaction of **2c** with ethyl 3-phenylpropionate afforded the benzyl-substituted dilactam **4i**. Employment of ethyl *N*,*N*-dimethylaminoacetate and of ethyl diphenylmethyliminoacetate provided the nitrogen-substituted pyrrolo[3,2-*b*]pyrrole-2,5-diones **4j** and **4k**, respectively. Treatment of bis(imidoyl)-chloride **2c** with various ethyl arylacetates afforded the aryl-substituted dilactams **4l**−**q** in moderate to good yields. In the case of the preparation of **4l**, pyrrolidenone **7** (derived from tautomer **D**) was isolated as a side product in 15% yield. Reaction of bis(imidoyl)chloride **2c** with ethyl 2-thienylacetate, ethyl (*N*-methyl-2-pyrrolyl)-acetate, ethyl 3-pyridylacetate, and ethyl 4-pyridylacetate afforded the pyrrolo[3,2-*b*]pyrrole-2,5-diones **4r**−**u** containing heterocyclic substituents in good yields.

Variation of the substituents of the bis(imidoyl)chloride was next studied: treatment of bis(*p*-methoxyphenylimidoyl)chloride **2d** with ethyl phenylacetate gave the dilactam **4v** in 68% yield. The methoxy groups of **4v** could be cleaved by treatment with $AlCl_3$ to give the pyrrolo-[3,2-*b*]pyrrole-2,5-dione **4w**. Reaction of bis(*p*-nitrophenylimidoyl)chloride **2e** with ethyl phenylacetate and ethyl (*N*-methyl-2-pyrrolyl)acetate afforded the heterocycles **4x** and **4y**. Employment of bis(*p*-*tert*-butylphenylimidoyl)-chloride **2f** provided the pyrrolo[3,2-*b*]pyrrole-2,5-dione **4z** in 55% yield. Reaction of bis(3-trifluoromethylphenylimidoyl)chloride **2g** with ethyl 3,3-dimethylbutanoate, ethyl phenylacetate, and ethyl (N-methyl-2-pyrrolyl)-acetate afforded the pyrrolo[3,2-*b*]pyrrole-2,5-diones **4aa**−**ac**.

The pyrrolo[3,2-*b*]pyrrole-2,5-diones **4** were the main products in all reactions carried out, and a variety of different substrates including aryl-, hetaryl-, and alkyl-substituted ethyl acetates could be used. The best yields were obtained in those reactions where the carbanions of ethyl phenylacetate, ethyl 1-naphthylacetate, and ethyl 2-thienylacetate were employed. The yields dropped when the bis(*p*-nitrophenylimidoyl)chloride **2e** or alkyl-substituted ethyl acetates were used.

Vibrational absorptions (IR) of the lactam carbonyls appear in the range of 1741 (**4ac**) to 1695 cm^{-1} (**4j**) and are shifted to low energies relative to the carbonyl band of 2-oxopyrrolidene **7**. This result can be explained by the lack of amide resonance within the lactam groups.

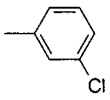
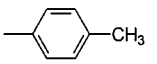
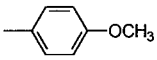
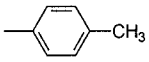
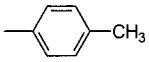
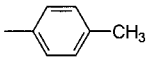
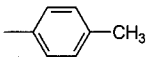
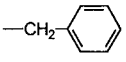
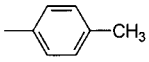
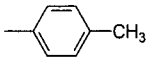
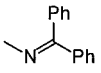
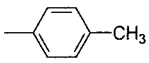
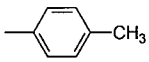
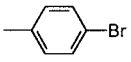
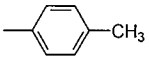
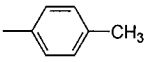
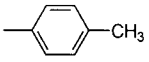
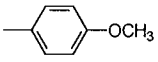
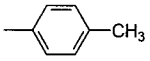
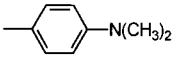
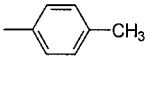
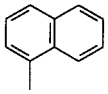
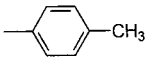
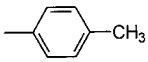
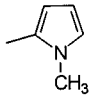
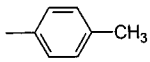
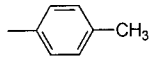
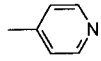
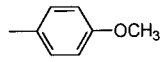
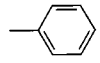
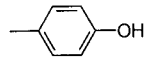
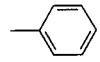
As shown in Table 1, the n→π* transitions λ_1 in the UV−vis spectra of the pyrrolo[3,2-*b*]pyrrole-2,5-diones **4** are not significantly influenced by the substituents R^1 and R^2. In contrast, the π→π* transitions λ_2 and λ_3 are strongly influenced: depending on the type of substituent R^2, different colors are observed for the diones **4**. The colors vary from light yellow for the (1-naphthyl)-substituted dilactam **4q** (λ_3 = 363) to deep red for the (2-thienyl)-substituted dilactam **4r** (λ_3 = 536) or the (*N*-methyl-2-pyrrolyl)-substituted dilactam **4s** (λ_3 = 423). It is interesting to compare the UV−vis absorptions of the *p*-tolyl-substituted pyrrolo[3,2-*b*]pyrrole-2,5-diones (R^1 = Tol) containing different substituents R^2: relative to the phenyl-substituted compound **4l**, strong bathochromic shifts are observed for **4j**, **4p**, **4s**, and **4r**. Bathochromic shifts are also observed for the acceptor-substituted pyrrolo[3,2-*b*]pyrrole-2,5-diones **4t** and **4u**. As expected, only weak effects can be detected in the case of **4n** and **4o**. These effects can be explained by the increased influence of zwitterionic mesomeric structures when donor- or acceptor-substituents R^2 are attached to the heterocyclic core. In general, the UV−vis properties of the pyrrolo[3,2-*b*]pyrrole-2,5-diones **4** are more influenced by the substituents R^2 than by R^1.



Pyrrolo[3,2-*b*]pyrrole-2,5-diones **4** are insoluble in a variety of organic solvents which is, in fact, an important feature of synthetic pigments. However, the identity and the purity of the products could be unambigiously proven by an X-ray structure of **4h**,[12] by the ^1H and ^{13}C NMR spectra of **4i**, **4s**, and **4ac**, and by correct elemental analyses and mass spectra of all the pyrrolo[3,2-*b*]pyrrole-2,5-diones prepared. All products are thermally very stable, which is also an important feature of pigment dyes. The melting points range from 216 to 430 °C.

In summary, we have described a new double-anion-capture reaction of ester carbanions with oxalic acid−bis(imidoyl)chlorides. This cyclization allowed a convenient and general synthesis of a variety of *N*-aryl substituted pyrrolo[3,2-*b*]pyrrole-2,5-diones **4**. Heterocycles **4** represent stable and largely insoluble synthetic pigments which are of interest in the field of material sciences. The UV−vis properties of the pyrrolo[3,2-*b*]-

Table 1. Preparation and UV−Vis Data of Pyrrolo[3,2-*b*]pyrrole-2,5-diones 4

4	R^1	R^2	λ_1[a], λ_2, λ_3	yield (%)[b]
a		$-CO_2Et$		0
b		$-CN$		0
c			246 (4.42) 344 (4.35)	75
d			265 (4.40) 363 (4.43)	36
e			266 (4.39) 384 (4.38)	34
f		$-H$	247 (4.51) 294 (4.53) 387 (2.72)	32
g		$-CH_3$		17
h		$-C(CH_3)_3$	241 (4.46) 296 (4.64) 385 (2.68)	25
i			247 (4.50) 300 (4.51) 397 (2.60)	35
j		$-N(CH_3)_2$	254 (4.62) 414 (4.46)	21
k				23
l			267 (4.60) 366 (4.07)	60
m			246 (4.51) 340 (4.26)	36
n			247 (4.60) 359 (4.39)	42
o			249 (4.82) 378 (4.53)	72
p			272 (3.92) 457 (3.67)	67
q			246 (4.47) 295 (4.42) 363 (4.09)	63
r			261 (4.32) 302 (4.34) 536 (4.38)	76
s			246 (4.49) 302 (4.21) 423 (4.28)	37
t			245 (4.38) 336 (4.27) 446 (2.80)	62
u			266 (4.41) 336 (4.59) 430 (3.03)	56
v			244 (4.61) 341 (4.36)	68
w				42[c]
x			236 (3.93) 337 (4.05)	35
y			294 (4.50) 344 (4.36) 441 (4.18)	26
z			255 (4.34) 349 (4.36) 435 (3.03)	55
aa		$-C(CH_3)_3$	299 (4.48) 372 (2.74)	26
ab			243 (4.35) 345 (4.22)	64
ac			257 (4.38) 409 (4.11) 518 (4.08)	21

[a] UV−vis, λ_{max} (log ϵ) (acetonitrile/nm). [b] Isolated yield. [c] Prepared from **4v**.

pyrrole-2,5-diones could be efficiently controlled by the substituents R^2 attached to the heterocyclic moiety, and high absorption coefficients were observed for all products. Current work is in progress in our laboratories

toward the synthesis of unsymmetrical, push−pull substituted pyrrolo[3,2-*b*]pyrrole-2,5-diones for the development of new pigment dyes which exhibit absorptions in the NIR range.[14,15]

Experimental Section

General Procedure for the Preparation of Pyrrolo[3,2-*b*]pyrrol-2,5-diones (4). To a THF solution (50 mL) of the ester **3** (10 mmol) was added a THF solution of $NaN(SiMe_3)_2$ (1 M, 11 mmol). After stirring for 1 h the reaction mixture was cooled to −78 °C and a THF solution (30 mL) of the bis(imidoyl)chloride **2** (5 mmol) was slowly added by syringe (30 min). The temperature was allowed to rise to ambient and the mixture was stirred for 2 h. The mixture was transferred to an aqueous solution of NH_4Cl (5 M, 250 mL). Addition of a mixture of ether and THF (1:1) resulted in precipitation of the product which was isolated by filtration, washed with ether, dried in vacuo, and recrystallized from DMF or DMSO. Due to the low solubility of the pigment dyes obtained, NMR data could be obtained only for selected products. However, correct elemental analyses were obtained in all cases. The products can be prepared in similar yields using LDA rather than $NaN(SiMe_3)_2$.

1,4-Bis(phenyl)-3,6-bisphenylpyrrolo[3,2-*b*]pyrrol-2,5-dione (4c). IR (Nujol, cm^{-1}): $\tilde{\nu}$ = 1728 (s, ν_{CO}), 1640 (s, $\nu_{C=C}$). MS [CI (H_2O), *m*/*z* (%)]: 441 ($M^+ + 1$, 100), 74 (68). Anal. Calcd for $C_{30}H_{20}N_2O_2$ (440.50): C, 81.80; H, 4.58; N, 6.36. Found: C, 81.66; H, 4.59; N, 6.56.

1,4-Bis(phenyl)-3,6-bis(4-tolyl)pyrrolo[3,2-*b*]pyrrol-2,5-dione (4d). IR (Nujol, cm^{-1}): $\tilde{\nu}$ = 1723 (s, ν_{CO}), 1639 (s, $\nu_{C=C}$). MS [CI (H_2O), *m*/*z* (%)]: 468 ($M^+ + 1$, 82), 103 (10), 77 (44). Anal. Calcd for $C_{32}H_{24}N_2O_2$ (468.55): C, 82.03; H, 5.16; N, 5.98. Found: C, 81.76; H, 5.18; N, 6.08.

1,4-Bis(phenyl)-3,6-bis(4-methoxyphenyl)pyrrolo[3,2-*b*]pyrrol-2,5-dione (4e). IR (Nujol, cm^{-1}): $\tilde{\nu}$ = 1728 (s, ν_{CO}), 1654 (s, $\nu_{C=C}$). MS [CI (H_2O), *m*/*z* (%)]: 501 ($M^+ + 1$, 44), 481 (25), 241 (100). Anal. Calcd for $C_{32}H_{24}N_2O_4$ (500.55): C, 76.79; H, 4.83; N, 5.60. Found: C, 76.11; H, 4.72; N, 5.67.

1,4-Bis(4-tolyl)pyrrolo[3,2-*b*]pyrrol-2,5-dione (4f). IR (Nujol, cm^{-1}): $\tilde{\nu}$ = 1726 (s, ν_{CO}), 1647 (s, $\nu_{C=C}$). MS [CI (H_2O), *m*/*z* (%)]: 317 ($M^+ + 1$, 100), 158 (76), 130 (88). Anal. Calcd for $C_{20}H_{16}N_2O_2$ (316.36): C, 75.93; H, 5.10; N, 8.85. Found: C, 75.46; H, 5.37; N, 8.81.

1,4-Bis(4-tolyl)-3,6-bismethylpyrrolo[3,2-*b*]pyrrol-2,5-dione (4g). IR (Nujol, cm^{-1}): $\tilde{\nu}$ = 1738 (s, ν_{CO}), 1663 (s, $\nu_{C=C}$). MS [CI (H_2O), *m*/*z* (%)]: 345 ($M^+ + 1$, 100), 330 (18), 91 (38). Anal. Calcd for $C_{22}H_{20}N_2O_2$ (344.41): C, 76.71; H, 5.85; N, 8.13. Found: C, 75.95; H, 5.50; N, 8.88.

1,4-Bis(4-tolylyl)-3,6-bis-*tert*-butylpyrrolo[3,2-*b*]pyrrol-2,5-dione (4h). IR (Nujol, cm^{-1}): $\tilde{\nu}$ = 1728 (s, ν_{CO}), 1632 (s, $\nu_{C=C}$). MS [CI (H_2O), *m*/*z* (%)]: 431 ($M^+ + 1$, 42), 413 (100), 385 (18). Anal. Calcd for $C_{28}H_{34}N_2O_2$ (430.59): C, 78.10; H, 7.96; N, 6.51. Found: C, 78.09; H, 7.44; N, 6.81.

1,4-Bis(4-tolyl)-3,6-bisbenzylpyrrolo[3,2-*b*]pyrrol-2,5-dione (4i). H NMR (200 MHz, DMF-d_7, 90 °C): δ = 2.39 (s, 6 H, Tol-CH_3), 3.50 (s, 4 H, Benzyl-CH_2), 6.89 (m, 4 H, Ar), 7.11 (m, 6 H, Ar), 7.28 (m, 8 H, Ar). ^{13}C NMR (50 MHz,): δ = 20.7 (Tol-CH_3), 28.6 (benzyl-CH_2), 104.42, 126.6, 127.5, 128.7, 130.2, 132.7, 138.5, 139.1, 147.8, 172.3 (CO). IR (Nujol, cm^{-1}): $\tilde{\nu}$ = 1731 (s, ν_{CO}), 1658 (s, $\nu_{C=C}$). MS [CI (H_2O), *m*/*z* (%)]: 497 ($M^+ + 1$, 100), 91 (46). Anal. Calcd for $C_{34}H_{28}N_2O_2$ (496.61): C, 82.23; H, 5.68; N, 5.64. Found: C, 82.16; H, 5.74; N, 5.86.

1,4-Bis(4-tolyl)-3,6-bis(dimethylamino)pyrrolo[3,2-*b*]pyrrol-2,5-dione (4j). IR (Nujol, cm^{-1}): $\tilde{\nu}$ = 1695 (s, ν_{CO}), 1663 (s, $\nu_{C=C}$). MS [CI (H_2O), *m*/*z* (%)]: 403 ($M^+ + 1$, 100). Anal. Calcd for $C_{24}H_{26}N_4O_2$ (402.50): C, 71.62; H, 6.51; N, 13.92. Found: C, 72.59; H, 6.40; N, 13.86.

1,4-Bis(4-tolyl)-3,6-bis(diphenylimino)pyrrolo[3,2-*b*]pyrrol-2,5-dione (4k). IR (Nujol, cm^{-1}): $\tilde{\nu}$ = 1717 (s, ν_{CO}), 1675 (s, $\nu_{C=C}$). MS [CI (H_2O), *m*/*z* (%)]: 675 ($M^+ + 1$, 100). Anal. Calcd for $C_{46}H_{34}N_{4O2}$ (674.80): C, 81.88; H, 5.08; N, 8.30. Found: C, 81.24; H, 5.49; N, 8.21.

1,4-Bis(4-tolyl)-3,6-bisphenylpyrrolo[3,2-*b*]pyrrol-2,5-dione (4l). IR (Nujol, cm^{-1}): $\tilde{\nu}$ = 1726 (s, ν_{CO}), 1645 (s, $\nu_{C=C}$). MS [CI (H_2O), *m*/*z* (%)]: 469 ($M^+ + 1$, 100), 234 (14). Anal. Calcd for $C_{32}H_{24}N_2O_2$ (468.55): C, 82.03; H, 5.16; N, 5.98. Found: C, 82.14; H, 5.12; N, 5.71.

1,4-Bis(4-tolyl)-3,6-bis(4-bromophenyl)pyrrolo[3,2-*b*]pyrrol-2,5-dione (4m). IR (Nujol, cm^{-1}): $\tilde{\nu}$ = 1733 (s, VCO), 1651 (s, $\nu_{C=C}$). MS [CI (H_2O), *m*/*z* (%)]: 627 ($M^+ + 1$, 100), 149 (21). Anal. Calcd for $C_{32}H_{22}N_2O_2Br_2$ (626.35): C, 61.36; H, 3.54; N, 4.47. Found: C, 60.46; H, 3.49; N, 4.52.

1,4-Bis(4-tolyl)-3,6-bis(4-tolyl)pyrrolo[3,2-*b*]pyrrol-2,5-dione (4n). IR (Nujol, cm^{-1}): $\tilde{\nu}$ = 1728 (s, ν_{CO}), 1644 (s, $\nu_{C=C}$). MS [CI (H_2O), *m*/*z* (%)]: 497 ($M^+ + 1$, 46), 108 (14), 74 (100). Anal. Calcd for $C_{34}H_{28}N_2O_2$ (496.61): C, 82.23; H, 5.68; N, 5.64. Found: C, 81.33; H, 5.69; N, 5.82.

1,4-Bis(4-tolyl)-3,6-bis(4-methoxyphenyl)pyrrolo[3,2-*b*]pyrrol-2,5-dione (4o). IR (Nujol, cm^{-1}): $\tilde{\nu}$ = 1729 (s, ν_{CO}), 1653 (s, $\nu_{C=C}$). MS [CI (H_2O), *m*/*z* (%)]: 529 ($M^+ + 1$, 100), 119 (35). Anal. Calcd for $C_{34}H_{28}N_2O_4$ (528.61): C, 77.25; H, 5.34; N, 5.30. Found: C, 76.84; H, 5.29; N, 5.55.

1,4-Bis(4-tolyl)-3,6-bis[(4-dimethylamino)phenyl]pyrrolo[3,2-*b*]pyrrol-2,5-dione (4p). IR (Nujol, cm^{-1}): $\tilde{\nu}$ = 1728 (s, ν_{CO}), 1651 (s, $\nu_{C=C}$). MS [CI (H_2O), *m*/*z* (%)]: 555 ($M^+ + 1$, 100), 277 (32), 134 (19). Anal. Calcd for $C_{36}H_{34}N_4O_2$ (554.69): C, 77.95; H, 6.18; N, 10.10. Found: C, 77.43; H, 5.99; N, 10.27.

1,4-Bis(4-tolyl)-3,6-bis(1-naphthyl)pyrrolo[3,2-*b*]pyrrol-2,5-dione (4q). IR (Nujol, cm^{-1}): $\tilde{\nu}$ = 1739 (s, ν_{CO}), 1655 (s, $\nu_{C=C}$). MS [CI (H_2O), *m*/*z* (%)]: 569 ($M^+ + 1$, 54), 284 (100), 241 (66). Anal. Calcd for $C_{40}H_{28}N_2O_2$ (568.67): C, 84.48; H, 4.96; N, 4.93. Found: C, 84.14; H, 4.97; N, 5.09.

1,4-Bis(4-tolyl)-3,6-bis(2-thienyl)pyrrolo[3,2-*b*]pyrrol-2,5-dione (4r). IR (Nujol, cm^{-1}): $\tilde{\nu}$ = 1723 (s, VCO), 1644 (s, $\nu_{C=C}$). MS [CI (H_2O), *m*/*z* (%)]: 481 ($M^+ + 1$, 100), 212 (17), 91 (13). Anal. Calcd for $C_{28}H_{20}N_2O_2S_2$ (480.60): C, 69.98; H, 4.19; N, 5.83. Found: C, 69.19; H, 4.38; N, 5.95.

1,4-Bis(4-tolyl)-3,6-bis(*N*-methylpyrrol-2-yl)pyrrolo-[3,2-*b*]pyrrol-2,5-dione (4s). ^{1}H NMR (200 MHz, CD_2Cl_2): δ = 2.31 (s, 6 H, Tol-CH_3), 3.16 (s, 6 H, N-CH_3), 6.00 (m, 4 H, Hetar), 6.52 (t, 2 H, J = 2.1, Hetar), 6.95−7.06 (m, 8 H, Ar). ^{13}C NMR (50 MHz, CD_2Cl_2): δ = 21.0 (tolyl-CH_3), 34.6 (N-CH_3), 98.3, 108.7, 113.6, 120.1, 121.1, 124.6, 124.8, 129.3, 130.0, 131.4, 137.3, 145.5, 170.6 (CO). IR (Nujol, cm^{-1}): $\tilde{\nu}$ = 1737 (s, ν_{CO}), 1657 (s, $\nu_{C=C}$). MS [CI (H_2O), *m*/*z* (%)]: 475 ($M+ + 1$, 76), 241 (42), 154 (86). Anal. Calcd for $C_{30}H_{26}N_4O_2$ (474.56): C, 75.93; H, 5.52; N, 11.81. Found: C, 76.01; H, 5.56; N, 11.93.

1,4-Bis(4-tolyl)-3,6-bis(3-pyridyl)pyrrolo[3,2-*b*]pyrrol-2,5-dione (4t). IR (Nujol, cm^{-1}): $\tilde{\nu}$ = 1732 (s, ν_{CO}), 1663 (s, $\nu_{C=C}$). MS [CI (H_2O), *m*/*z* (%)]: 471 ($M^+ + 1$, 100), 364 (81), 207 (34). Anal. Calcd for $C_{30}H_{22}N_4O_2$ (470.53): C, 76.58; H, 4.71; N, 11.91. Found: C, 76.36; H, 4.59; N, 12.04.

1,4-Bis(4-tolyl)-3,6-bis(4-pyridyl)pyrrolo[3,2-*b*]pyrrol-2,5-dione (4u). IR (Nujol, cm^{-1}): $\tilde{\nu}$ = 1732 (s, ν_{CO}), 1663 (s, $\nu_{C=C}$). MS [CI (H_2O), *m*/*z* (%)]: 471 ($M^+ + 1$, 100), 135 (19), 91 (17). Anal. Calcd for $C_{30}H_{22}N_4O_2$ (470.53): C, 76.58; H, 4.71; N, 11.91. Found: C, 76.36; H, 4.59; N, 12.04.

1,4-Bis(4-methoxyphenyl)-3,6-bis(4-phenyl)pyrrolo[3,2-*b*]pyrrol-2,5-dione (4v). IR (Nujol, cm^{-1}): $\tilde{\nu}$ = 1728 (s, ν_{CO}), 1655 (s, $\nu_{C=C}$). MS [CI (H_2O), *m*/*z* (%)]: 501 ($M^+ + 1$, 100), 222 (61), 89 (73). Anal. Calcd for $C_{32}H_{24}N_2O_4$ (500.55): C, 76.79; H, 4.83; N, 5.60. Found: C, 76.11; H, 4.88; N, 5.88.

1,4-Bis(4-nitrophenyl)-3,6-bis(4-phenyl)pyrrolo[3,2-*b*]pyrrol-2,5-dione (4x). IR (Nujol, cm^{-1}): $\tilde{\nu}$ = 1728 (s, ν_{CO}), 1639 (s, $\nu_{C=C}$). MS [CI (H_2O), *m*/*z* (%)]: 531 ($M^+ + 1$, 17), 329 (26), 139 (100). Anal. Calcd for $C_{30}H_{18}N_4O_6$ (530.50): C, 67.92; H, 3.42; N, 10.56. Found: C, 67.83; H, 3.54; N, 10.92.

1,4-Bis(4-nitrophenyl)-3,6-bis(*N*-methylpyrrol-2-yl)pyrrolo[3,2-*b*]pyrrol-2,5-dione (4y). IR (Nujol, cm^{-1}): $\tilde{\nu}$ = 1738 (s, ν_{CO}), 1666 (s, $\nu_{C=C}$). MS [CI (H_2O), *m*/*z* (%)]: 537 ($M^+ + 1$,

(15) Push−pull substituted heterocycles are of both theoretical and practical interest: (a) Gompper, R.; Wagner, H.-U. *Angew. Chem.* **1988**, *100*, 1492; *Angew. Chem. Int. Ed. Engl.* **1988**, *27*, 1437. (b) Effenberger, F.; Schlosser, H.; Bäuerle, P.; Maier, S.; Port, H.; Wolf, H. C. *Angew. Chem.* **1988**, *100*, 274; *Angew. Chem., Int. Ed. Engl.* **1988**, *27*, 281.

75), 147 (100). Anal. Calcd for $C_{28}H_{20}N_6O_6$ (536.50): C, 62.69; H, 3.76; N, 15.66. Found: C, 61.12; H, 3.96; N, 15.50.

1,4-Bis(4-*tert*-butylphenyl)-3,6-bisphenylpyrrolo[3,2-*b*]-pyrrol-2,5-dione (4z). IR (Nujol, cm^{-1}): $\tilde{\nu}$ = 1735 (s, ν_{CO}), 1653 (s, $\nu_{C=C}$). MS [CI (H_2O), *m*/*z* (%)]: 553 ($M^+ + 1$, 100), 497 (10), 261 (11). Anal. Calcd for $C_{38}H_{36}N_2O_2$ (552.72): C, 82.58; H, 6.57; N, 5.07. Found: C, 82.42; H, 6.62; N, 5.33.

1,4-Bis(3-trifluoromethylphenyl)-3,6-bis-*tert*-butylpyrrolo[3,2-*b*]pyrrol-2,5-dione (4aa). IR (Nujol, cm^{-1}): $\tilde{\nu}$ = 1722 (s, ν_{CO}), 1636 (s, $\nu_{C=C}$). MS [CI (H_2O), *m*/*z* (%)]: 537 ($M^+ + 1$, 46), 521 (100), 145 (65). Anal. Calcd for $C_{28}H_{26}N_2O_2F_6$ (536.52): C, 62.68; H, 4.88; N, 5.22. Found: C, 62.36; H, 5.16; N, 5.35.

1,4-Bis(3-trifluoromethylphenyl)-3,6-bisphenylpyrrolo-[3,2-*b*]pyrrol-2,5-dione (4ab). IR (Nujol, cm^{-1}): $\tilde{\nu}$ = 1733 (s, ν_{CO}), 1649 (s, $\nu_{C=C}$). MS [CI (H_2O), *m*/*z* (%)]: 577 ($M^+ + 1$, 100), 557 (8), 260 (6). Anal. Calcd for $C_{32}H_{18}N_2O_2F_6$ (576.50): C, 66.67; H, 3.15; N, 4.86. Found: C, 66.22; H, 3.31; N, 4.99.

1,4-Bis(3-trifluoromethylphenyl)-3,6-bis(*N*-methylpyrrol-2-yl)pyrrolo[3,2-*b*]pyrrol-2,5-dione (4ac). ^{1}H NMR (200 MHz, CD_2Cl_2): δ = 3.30 (s, 6 H, N-CH_3), 5.95−6.05 (m, 4 H, Hetar), 6.61 (t, 2 H, J = 2.2, Hetar), 7.34−7.53 (m, 8 H, Ar). ^{13}C NMR (50 MHz, CD_2Cl_2): δ = 34.8 (N-CH_3), 99.4, 109.1, 114.6, 120.2, 121.6 (q, ^3J = 3.8 Hz), 123.8 (q, ^3J = 3.8), 125.5, 128.2, 130.9 (q, ^2J = 32.5), 134.3, 144.6, 169.8 (CO). IR (Nujol, cm^{-1}): $\tilde{\nu}$ = 1741 (s, ν_{CO}), 1659 (s, $\nu_{C=C}$). MS [CI (H_2O), *m*/*z* (%)]: 583 ($M^+ + 1$, 100), 563 (18). Anal. Calcd for $C_{30}H_2ON_4O_2F_6$ (582.50): C, 61.86; H, 3.46; N, 9.62. Found: C, 61.50; H, 3.66; N, 9.35.

Preparation of 1,4-Bis(4-hydroxyphenyl)-3,6-bisphenylpyrrolo[3,2-*b*]pyrrol-2,5-dione (4w). Heterocycle **4v** (0.18 g, 0.36 mmol) was melted in the presence of 1.38 g of $AlCl_3$ (10.5 mmol). After cooling to ambient, the mixture was hydrolyzed and the orange precipitate was washed with MeOH and dried in vacuo. Recrystallization from DMF yielded orange crystals (71 mg, 42%) which readily dissolved in an aqueous NaOH solution to give a red solution. IR (Nujol, cm^{-1}): $\tilde{\nu}$ = 1718 (s, ν_{CO}), 1654 (s, $\nu_{C=C}$). MS [CI (H_2O), *m*/*z* (%)]: 473 ($M^+ + 1$, 100). Anal. Calcd for $C_{30}H_2ON_2O_4$ (472.50): C, 76.26; H, 4.27; N, 5.93. Found: C, 75.88; H, 4.35; N, 6.13.

Isolation of [3-(4-Tolyl)amino-5-oxo-4-phenyl-1-(4-tolyl)-1,5-dihydropyrrol-2-yliden]phenylacetic Acid Ethyl Ester (7). The solvent of the filtrate, which was obtained during the workup procedure of compound **4l**, was removed in vacuo and to the residue was added 3 mL of MeOH. A colorless solid precipitated which was recrystallized from DMF to give compound **7** as colorless crystals (116 mg, 15%) of mp 328−330 °C. ^{1}H NMR (200 MHz, DMF-d_7): δ = 0.69 (t, 3 H, J = 6.9, ester-CH_3), 2.22, 2.35 (2 × s, 2 × 3 H, Tol-CH_3), 3.35 (q, 3 H, J = 6.9, ester-CH_2), 6.93−7.73 (m, 18 H, Ar), 10.40 (s, 1 H, NH). ^{13}C NMR (50 MHz, CD_2Cl_2): δ = 15.2 (ester-CH_3), 20.9, 21.5 (Tol-CH_3), 69.8 (ester-CH_2), 121.6, 125.7, 126.5, 128.2, 128.4, 128.6, 128.7, 129.4, 129.6, 130.0, 131.2, 133.3, 135.6, 135.9, 139.7, 143.2, 160.0, 163.2, 164.7. IR (Nujol): $\tilde{\nu}$ = 3240 (m, ν_{NH}), 1651 (s, ν_{CO}), 1603 (m), 1544 (m), 1523 (m), 1516 (m), 1495 (m) cm^{-1}. MS [CI (H_2O), *m*/*z* (%)]: 515 [$M^+ + 1$] (14), 201 (12), 173 (21), 108 (13), 93 (100). Anal. Calcd for $C_{34}H_{30}N_2O_3$ (514.62): C, 79.35; H, 5.88; N, 5.44. Found: C, 79.50; H, 6.05; N, 5.14.

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