



Preparation of *meso*-substituted *trans*-A₂B-corroles in ionic liquids

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ABSTRACT

A new and simple method for the preparation of *meso*-substituted *trans*-A₂B-corroles was developed by using ionic liquid as reaction medium. The reaction can be performed to offer the desired corroles with reasonable to satisfied yields.

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Corroles, the analogues of porphyrins bearing a direct pyrrole–pyrrole linkage,¹ have been received much attention in recent years because of their wide-ranging applications to coordination chemistry,² photophysics,³ synthesis,⁴ chemical transformations,⁵ electrochemistry,⁶ and others.⁷ On the other hand the rapid development of corrole chemistry was ascribed to the improvement of synthetic method. In 1999, Gross reported a solvent-free method for the preparation of 5,10,15-tris-(pentafluorophenyl)corrole,⁸ which makes the triaryl corrole soon available by one-pot reaction. Nearly at the same time, Paolesse⁹ and Gryko¹⁰ developed more general method, the so-called Rothmund synthetic method, for the preparation of corroles. Nowadays, Rothmund method has been widely used for the synthesis of corrole derivatives.¹¹ Although the preparation of corrole is now as nearly convenient as that of porphyrin, there are still some challenges to develop more convenient synthetic methods in the corrole chemistry. For examples, the yield of corrole is rather low, and it is sensitive to the electronic and/or steric structure of aldehyde used.¹² Gross' solvent-free method is limited to the synthesis of tris-(pentafluorophenyl)corrole in alumina unless the reaction proceeds under microwave irradiation.¹³ Thus, any new attempt to explore reaction conditions is of fundamental interests and may be meaningful in extending the library of corrole synthesis.

During the past decade, room-temperature ionic liquids (RTILs) have been emerging as promising green solvents for various reactions,¹⁴ including olefin oligomerisation,¹⁵ Heck reaction,¹⁶ hydrogenation,¹⁷ condensation reactions¹⁸ and cyclization reaction.¹⁹ As compared to traditional organic solvents, the nonvolatile nature of RTILs gives them significant advantage in minimizing solvent consumption. Furthermore, the polarity of RTILs renders them good solvents for various organic, inorganic and polymeric compounds. In an effort to extend the scope of corrole synthesis, we herein wish to report the first try to apply a series of RTILs to Gryko's reaction

that generate *meso*-substituted *trans*-A₂B-corroles with reasonable to satisfied yields.

The reaction of 5-(pentafluorophenyl)dipyrromethane (**1a**) with benzaldehyde (**2a**) was chosen as a model system in four common different anionic RTILs²⁰ (Fig. 1) with the same cation, 1-butyl-3-methylimidazolium [Bmim]⁺. The results are collected in Table 1. Among these RTILs, [Bmim][BF₄] gives the highest yield. With the decrease of RTILs viscosity, the yield of corrole increased significantly. Nevertheless, traces of corrole **3aa** were found by replacing RTILs with DMF and DMSO. Hence, [Bmim][BF₄] was exclusively used as the solvent for further investigation.

After determining of the proper ionic liquid, we employed different types of acids as catalysts for this model reaction. Results are summarized in Table 2. In the reactions catalyzed by HPF₆, HBF₄ or HCO₂H, yields of corrole **3aa** were almost as low as that in the non-catalyzed reaction (Table 2, entries 1, 7–9). However, TFA, HCl, CH₃SO₃H, CF₃SO₃H or C₂H₅CO₂H catalyst led to a substantial increase in yields of **3aa** (entries 2, 3, 5, 6 and 10). It is noteworthy that the yield of corrole doubled as compared with that of TFA (trifluoroacetic acid) when Lewis acids BF₃·Et₂O, ZnCl₂ and AlCl₃ were used as catalysts except AgBF₄ (entries 4, 11–13).

Performing the reaction at different concentrations of BF₃·Et₂O led to a profound effect on the yield of corrole **3aa** (Table 3, entries 1–3). The best yield (34%) was obtained when the concentration of BF₃·Et₂O was 20 mM. Raising the concentration of substrates from 5 mM to 15 mM, the yield of product also increased (entries 3–5). Further increases of the concentration of substrates led to a substantial decrease in yield (entry 6). Again, 2 equiv DDQ (vs aldehyde **2a**) gave no further increase in the yield of corrole **3aa**

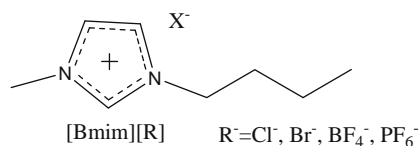
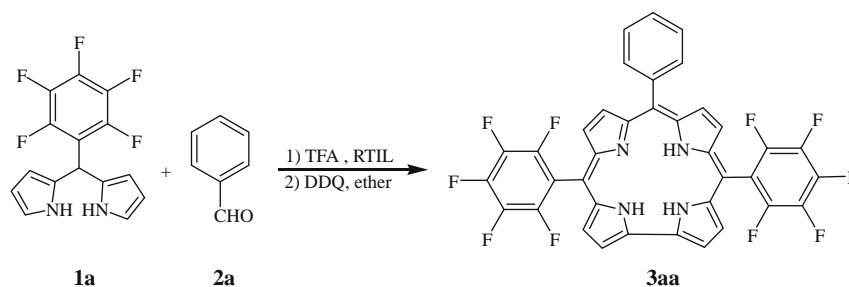


Figure 1.

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Table 1
RTILs used for corrole **3aa** preparation^a

Entry	Solvent	Viscosity of IL/cP ^c	Isolated yield (%)
1 ^b	[Bmim]Cl	–	Trace
2 ^b	[Bmim]Br	1462	Trace
3	[Bmim][PF ₆]	289	9
4	[Bmim][BF ₄]	92.2	14

^a Reaction conditions: first step, ratio **1a:2a** = 2:1, [**2a**] = 10 mM, [TFA] = 10 mM, rt, 5 h in ionic liquid; second step, extraction with ether absolute, DDQ (1 equiv vs aldehyde **2a**), rt, 2 h.

^b Temperature was 60 °C.

^c Ref. 21.

Table 2
Results of an acid survey in the reaction of DPM **1a** with aldehyde **2a** in [Bmim][BF₄]^a

Entry	Acid	Isolated yield (%)
1	None	4
2	TFA	14
3	HCl	10
4	BF ₃ ·Et ₂ O	30
5	CH ₃ SO ₃ H	12
6	CF ₃ SO ₃ H	15
7	H ₂ PO ₄	8
8	HBF ₄	7
9	HCO ₂ H	5
10	C ₂ H ₅ CO ₂ H	13
11	ZnCl ₂	27
12	AlCl ₃	29
13	AgBF ₄	0

^a All reactions were performed under the following constant conditions: first step, ratio **1a:2a** = 2:1, [**2a**] = 10 mM, [acid] = 10 mM, reaction time for 5 h in [Bmim][BF₄], rt; second step, extraction with ether absolute, DDQ (1 equiv vs aldehyde **2a**), rt, 2 h.

(entry 7). When changing the reaction time for 2 h or 12 h, the yield decreased sharply (entries 8 and 9). Use of a large excess of dipyrromethane or aldehyde did not give any improvement (entries 10 and 11). When oxidation was performed under milder conditions (room temperature, overnight) with *p*-chloranil, the yield increased slightly to 52% (entry 12). Although the yields for the corrole-forming reaction were high with DDQ or *p*-chloranil oxidants, other oxidizing agents were also investigated. But traces of corrole **3aa** were found when DDQ was replaced with H₂O₂, *p*-benzoquinone or anthraquinone (room temperature, overnight) (entries 13–15). When 0.1% (v/v) water was intentionally added to the [Bmim][BF₄], the isolated yield of corrole **3aa** decreased to 48%, which revealed that the contained water may disturb the condensation reaction. The recycling performance of [Bmim][BF₄] was very good. It had consistent activity after reusing for five times (Fig. 2).

Different substrates were subjected to the reaction under the optimized conditions. Representative examples are tabulated in Table 4. All the products were well characterized by UV–vis, NMR and MS spectrometry.²² DDQ was chosen as oxidant in our study, although Gryko and co-workers^{11c} have shown that DDQ resulted in a slightly lower yield of corrole than *p*-chloranil except

Table 3
Optimization of conditions for the reaction of benzaldehyde **2a** with 5-(pentafluorophenyl)dipyrromethane (dpm) **1a**^a

Entry	Time (h)	BF ₃ ·Et ₂ O (mM)	Ratio 1a:2a	Aldehyde (mM)	Isolated yield (%)
1	5	10	2:1	10	28
2	5	20	2:1	10	34
3	5	30	2:1	10	30
4	5	10	2:1	5	12
5	5	30	2:1	15	51
6	5	40	2:1	20	42
7 ^b	5	30	2:1	15	49
8	12	30	2:1	15	10
9	2	30	2:1	15	5
10	5	30	3:1	15	50
11	5	30	1:1	15	22
12 ^c	5	30	2:1	15	52
13 ^d	5	30	2:1	15	Trace
14 ^e	5	30	2:1	15	Trace
15 ^f	5	30	2:1	15	Trace

^a All reactions were performed under the following constant conditions: first step, 5 h in [Bmim][BF₄], BF₃·Et₂O, rt; second step, extraction with ether absolute, DDQ (1 equiv vs aldehyde **2a**), rt, 2 h.

^b Added 2 equiv DDQ (vs aldehyde **2a**).

^c DDQ was replaced with *p*-chloranil.

^d DDQ was replaced with H₂O₂.

^e DDQ was replaced with *p*-benzoquinone.

^f DDQ was replaced with anthraquinone.

aldehydes with strong electron-withdrawing groups. Both aromatic and alkyl substrates were used in conjunction with 5-(pentafluorophenyl)dipyrromethane **1a**, phenyl-dipyrromethane **1b** and 4-pyridyldipyrromethane **1c**. In general, for *n*-butyraldehyde **2i** and aldehydes similar to benzaldehyde **2a–c**, **2g**, **2k**, the reactions worked very well (yield 39–53%) (entries 1–3, 7, 9 and 11). Interestingly, the reaction with terephthalaldehyde **2f** did not result in the corresponding corrole dimer but corrole **3af** (entry 6), even if changed the ratio of substrates from 1:1 to 4:1 (ratio **1a:2f**). Corroles **3ad** and **3ck** with pyridyl were obtained in less than 1% yield. Furthermore, acrylaldehyde **2j** and sterically hindered aldehyde **2e**, **2h** did not afford corresponding corroles (entries 5, 8 and 10).

In summary, we have presented a new and simple method for the preparation of *meso*-substituted *trans*-A₂B-corroles in ionic liquids. [Bmim][BF₄] was found a suitable reaction medium, and the

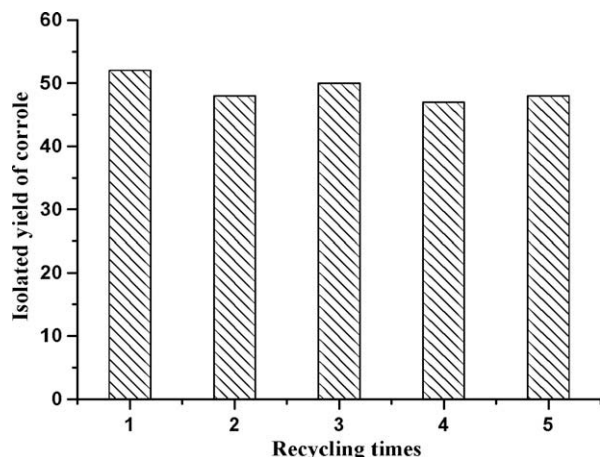


Figure 2. Reuse of [Bmim][BF₄] for the synthesis of corrole **3aa**. Reaction was performed under the optimized reaction conditions.

Table 4
Isolated yield of corroles formed from various dipyrromethanes (DPMs) and aldehydes^a

Entry	DPM	Aldehyde	Corrole	Yield (%)
1			3aa	51
2	1a		3ab	45
3	1a		3ac	42
4	1a		3ad	<1
5	1a		3ae	0
6	1a		3af	20
7	1a		3ag	39

Table 4 (continued)

Entry	DPM	Aldehyde	Corrole	Yield (%)
8	1a		3ah	0
9	1a		3ai	53
10	1a		3aj	0
11			3bk	45
12		2k	3ck	<1

^a All reactions were performed under the following constant conditions: first step, ratio dipyrromethane (dpm): aldehyde = 2:1, [aldehyde] = 15 mM, [BF₃·Et₂O] = 30 mM, reaction time for 5 h in [Bmim][BF₄], room temperature; second step, extraction with ether absolute, DDQ (1 equiv vs aldehyde), room temperature, 2 h.

reaction can be performed to offer electron deficient corrole with a yield up to 53%. Besides, a significant advantage of this protocol is to reduce the use of the organic solvents in response to the demand of green chemistry.

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22. (a) Typical procedure for the synthesis of corrole in ionic liquid: Into 6 mL IL solution of dipyrromethane and aldehyde at room temperature, acid was added. After stirred for 5 h, the reaction was worked up by extraction with ether absolute. DDQ was added followed by the addition of 2 equiv of TEA to the acid. The reaction mixture was purified by the chromatographic separation with n-hexane/CH₂Cl₂ (3/1 to 1/1) to yield the products. (a) 10-Phenyl-5,15-dis(pentafluorophenyl)corrole (**3aa**). FAB-MS: *m/z* (%): 706 (100) [M⁺] (calcd for C₃₇H₁₆N₄F₁₀: 706.58); UV-vis (CH₂Cl₂): λ_{max} (relative intensity) = 410 (1.09), 563 nm (0.18), 612.8 nm (0.11); ¹H NMR (400 MHz, CDCl₃) δ 7.735–7.755 (m, 3H), 8.145–8.164 (m, 2H), 8.545–8.562 (m, 2H), 8.678–8.695 (m, 4H), 9.011–9.106 (m, 2H); ¹⁹F NMR (376.498 MHz, CDCl₃, 25 °C): δ -138.24 to -138.32 (m, 4F), -153.15 to -153.30 (m, 2F), -162.04 to -162.22 (m, 4F). (b) 10-(4-Bromophenyl)-5,15-dis(pentafluorophenyl)corrole (**3ab**). ESI-MS: *m/z* (%): 785.1(100) [M⁺] (calcd for C₃₇H₁₅N₄F₁₀Br: 785.43); UV-vis (toluene): λ_{max} (relative intensity) = 419 (0.41), 562 (0.07), 615 nm (0.05); ¹H NMR (400 MHz, CDCl₃) δ 7.887–7.909 (m, 2H), 8.015–8.033 (m, 2H), 8.535–8.551 (m, 2H), 8.674–8.715 (m, 4H), 9.063–9.084 (m, 2H); ¹⁹F NMR (376.498 MHz, CDCl₃, 25 °C): δ -137.83 to -138.10 (m, 4F), -152.54 to -152.85 (m, 2F), -161.44 to -161.71 (m, 4F). (c) 10-(4-Iodophenyl)-5,15-dis(pentafluorophenyl)corrole (**3ac**). FAB-MS: *m/z* (%): 832 (100) [M⁺] (calcd for C₃₇H₁₅N₄F₁₀I: 832.43); UV-vis (toluene): λ_{max} (relative intensity) = 420 (0.94), 564.0 (0.15), 615 (0.09), 639 nm (0.06); ¹H NMR (400 MHz, CDCl₃) δ 7.888–7.907 (m, 2H), 8.083–8.102 (m, 2H), 8.554–8.560 (m, 2H), 8.663–8.712 (m, 4H), 9.097–9.106 (m, 2H); ¹⁹F NMR (376.498 MHz, CDCl₃, 25 °C): δ -137.74 to -137.92 (m, 4F), -152.55 to -152.73 (m, 2F), -161.63 to -161.81 (m, 4F). (d) 10-(4-pyridylphenyl)-5,15-dis(pentafluorophenyl)corrole (**3ad**). ESI-MS: *m/z* (%): 705.7 (100) [M⁺] (calcd for C₃₆H₁₅N₅F₁₀: 707.52). Other analytical data are consistent with literature values.²³ (e) 10-(4-Formylaryl)-5,15-dis(pentafluorophenyl)corrole (**3af**). ESI-MS: *m/z* (%): 735.2 (100) [M⁺] (calcd for C₃₈H₁₆N₄F₁₀O: 734.54); UV-vis (toluene): λ_{max} (relative intensity) = 424 (0.25), 566.0 (0.04), 614 nm (0.03); ¹H NMR (400 MHz, CDCl₃) δ 8.26–8.28 (m, 2H), 8.34–8.36 (m, 2H), 8.56–8.57 (m, 2H), 8.63–8.64 (m, 2H), 8.71–8.72 (m, 2H), 9.11–9.12 (m, 2H), 10.33 (s, 1H); ¹⁹F NMR (376.498 MHz, CDCl₃, 25 °C): δ -137.82 to -137.88 (m, 4F), -152.44 to -152.55 (m, 2F), -161.53 to -161.62 (m, 4F). (f) 10-(2-Hydroxyl-3,5-diiodophenyl)-5,15-dis(pentafluoro-phenyl)corrole (**3ag**). FAB-MS: *m/z* (%): 974.3 (100) [M⁺] (calcd for C₃₇H₁₄ON₄F₁₀I₂: 974.33); UV-vis (toluene): λ_{max} (relative intensity) = 414 (0.81), 562 (0.12), 608 nm (0.08); ¹H NMR (400 MHz, CDCl₃) δ 8.20 (s, 1H), 8.39 (s, 1H), 8.54–8.55 (m, 2H), 8.61–8.62 (m, 2H), 8.71–8.72 (m, 2H), 9.07–9.08 (m, 2H); ¹⁹F NMR (376.498 MHz, CDCl₃, 25 °C): δ -138.21 to -138.44 (m, 4F), -152.54 to -152.68 (m, 2F), -161.73 to -161.75 (m, 4F). (g) 10-Butyl-5,15-dis(pentafluorophenyl)corrole (**3ai**). ESI-MS: *m/z* (%): 673.3 (100) [M⁺] (calcd for C₃₄H₁₈N₄F₁₀O: 672.52); UV-vis (toluene): λ_{max} (relative intensity) = 418 (0.33), 564.0 (0.05), 621 nm (0.04); ¹H NMR (400 MHz, CDCl₃) δ 1.284–1.320 (t, J = 3.2 Hz, 3H), 2.468–2.524 (m, 2H), 4.748–4.834 (m, 2H), 8.468–8.530 (m, 2H), 8.732–8.794 (m, 2H), 9.019–9.081 (m, 2H), 9.264–9.275 (m, 2H); ¹⁹F NMR (376.498 MHz, CDCl₃, 25 °C): δ -137.76 to -137.81 (m, 4F), -152.95 to -153.05 (m, 2F), -161.79 to -161.89 (m, 4F). (h) 10-Pentafluorophenyl-5,15-dis(phenyl)corrole (**3bk**). FAB-MS: *m/z* (%): 616 (100) [M⁺] (calcd for C₃₇H₂₁N₄F₅: 616.58); UV-vis (toluene): λ_{max} (relative intensity) = 413 (0.96), 574 nm (0.16); ¹H NMR (400 MHz, CDCl₃) δ 7.75–7.80 (m, 6H), 8.07–8.23 (m, 2H), 8.32–8.40 (m, 4H), 8.65–8.72 (m, 4H), 8.82–8.90 (m, 2H); ¹⁹F NMR (376.498 MHz, CDCl₃, 25 °C): δ -137.92 to -138.23 (m, 2F), -154.04 to -154.31 (m, 1F), -162.56 to -162.85 (m, 2F). (i) 10-Pentafluorophenyl-5,15-dis(4-pyridylphenyl)corrole (**3ck**). ESI-MS: *m/z* (%): 616.8 (100) [M⁺] (calcd for C₃₅H₁₉N₆F₅: 618.56). Other analytical data are consistent with literature values.²³
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