In Situ Anodically Oxidized BMIm-BF₄: A Safe and Recyclable BF₃ Source

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ABSTRACT: The anodic oxidation of 1-butyl-3-methylimidazolium tetrafluoroborate (BMIm-BF₄) efficiently generates BF₃ from BF₄⁻. This Lewis acid, strongly bound to the ionic liquids, can be efficiently used in classical BF₃-catalyzed reactions. We demonstrated the BF₃/BMIm-BF₄ reactivity in four reactions, namely, a domino Friedel–Crafts/lactonization of phenols, the Povarov reaction, the Friedel–Crafts benzylation of anisole, and the multicomponent synthesis of tetrahydro-11H-benzo[a]xanthen-11-ones. In comparison with literature data using BF₃-Et₂O in organic solvents, in all the presented cases, analogous or improved results were obtained. Moreover, the noteworthy advantages of the developed method are the in situ generation of BF₃ (no storing necessity) in the required amount, using only the electron as redox reagent, and the recycling of BMIm-BF₄ for multiple subsequent runs.

Boron trifluoride is a well-known Lewis acid, often used in organic synthesis to carry out many acid-catalyzed transformations.¹ Although this reagent is very common, its use may face problems and small accidents due to its high reactivity and volatility. Additionally, this gas is highly toxic and corrosive and has a suffocating odor.² To make BF₃ easier to handle, liquid etherate complexes, consisting of a 1:1 molar ratio of BF₃ and ether (usually dimethyl or diethyl), are used and dissociated under appropriate temperature and pressure conditions.³ Nonetheless, these compounds show corrosive properties and flammability, so it is necessary to use them under a hood, wearing nitrile gloves and eye protection.⁴ Moreover, they are sensitive to humidity and form acidic fumes in moist air.

The in situ generation of BF₃ in the exact amount needed minimizes these problems.

Organic electrochemistry can help with this scope.⁵ In fact, BF₃ can be easily obtained by anodic oxidation of the BF₄⁻ anion (Scheme 1).⁶ When using electrochemistry, the reagent is the electron (inherently nonpolluting and cheap), very easy to dose simply by closing or opening the electrical circuit.

The conductivity of the solution is normally ensured by a supporting electrolyte in high concentration (up to 0.5 M). The need of such salt in solution (one of the criticisms to organic electrochemistry raised by organic chemists) can be overcome by using an ionic liquid (IL) as both solvent and supporting electrolyte.

Scheme 1. BF₃ Anodic Generation

BF₄⁻ + e⁻ → BF₃ + ½ F₂

ILs are liquid salts formed by a large, nonsymmetrical organic cation and (usually) a noncoordinating anion (organic or inorganic).⁷ Their use as solvents in organic transformations is growing in the past years, due to their ability to solubilize organic and inorganic compounds and, mainly, to their virtually null volatility, allowing for their easy recovery.⁸ In organic electrochemistry, they can be used as supporting electrolytes or also as solvents, permitting carrying out electrolyses and, after workup, to recover the IL.⁹ In this context, the most frequently used class of ILs is the imidazolium one, which are cheap, liquid in a wide range of temperatures, and possess good solvating properties. Nevertheless, imidazolium ILs are in some cases reactive under electrochemical conditions.¹⁰ In fact, the cathodic limit of an imidazolium IL (unsubstituted at the 2-position) is usually the C₂–H bond scission with formation of the corresponding N-heterocyclic carbene (NHC), widely exploited,¹¹ while the anodic limit is the oxidation of the anion. In the case of 1-
butyl-3-methylimidazolium tetrafluoroborate (BMIm-BF$_4$), the oxidation of the anion forms BF$_3$, as previously stated (Scheme 1). The relatively high potential for BF$_3$ generation prevents the presence of electroactive substrates in solution during electrolysis (see cyclic voltammetries in the Supporting Information). We were interested in an alternative, less dangerous source of BF$_3$, generated in situ and thus not stored. The electrochemical oxidation of BF$_4^-$ in IL seemed the good choice, and we carried out some classical BF$_3$-catalyzed reactions in anodically oxidized BMIm-BF$_4$, being this IL really easy to recycle after ethereal extraction. In order to avoid interferences from the cathodically generated NHC, a divided cell was used.

The advantages in this BF$_3$ source can be summarized in

- in situ generation, avoiding the storage (simple galvanostatic electrolysis)
- easy to dose (current on/off)
- no fumes production (strong interaction with IL)
- no particular sensitivity to moisture (IL as moist protector)
- easy IL recovery and multiple recycling after ethereal extraction

The main disadvantage derives from the use of the IL, i.e., the low solubility of apolar molecules.

The examples considered (Scheme 2) are intended to demonstrate the efficiency of this system in classical BF$_3$-catalyzed reactions, and thus no extensive studies for the optimization of yields and reaction scope are reported. It should be underlined that, when more than one reaction was carried out on a particular substrate, the same IL was used in all reactions, recycled after ethereal extraction and submitted to a new anodic oxidation. To the best of our knowledge, anodically generated BF$_3$ in IL was used only in one paper$^{12}$ reporting the BF$_3$ induced Michael addition of a 1,3-dicarbonyl compound to methyl vinyl ketone, without IL recycling.

The reaction between a phenol 1 and diethyl ketomalonate 2, in the presence of a Lewis acid, leads to the formation of a 3-hydroxybenzofuran-2-one 3 and, in the case of incomplete reaction, of the 2-substituted phenol 4 (Table 1).$^{13}$ These products derive from a Friedel–Crafts phenol alkylation in the 2-position, followed by a cyclization with ethanol elimination. The increase of the temperature to 60 °C promoted the lactonization, giving selectively the 3-hydroxybenzofuran-2-one 3.

### Table 1. BF$_3$-Catalyzed Reaction between Phenols and Diethyl Ketomalonate

| entry | R                | BF$_3$ (%)$^a$ | T/time  | $^3$   | $^4$   |
|-------|------------------|---------------|---------|--------|--------|
| 1$^d$ | 4-OCH$_3$ (1a)   | 100           | r.t./15 h | 57% (3a) | 17% (4a) |
| 2$^d$ | 4-OCH$_3$ (1a)   | 100           | 50 °C/4 h | 63% (3a) |        |
| 3$^d$ | 4-OCH$_3$ (1a)   | 30            | r.t./24 h | 56% (3a) | 19% (4a) |
| 4$^d$ | 4-OCH$_3$ (1a)   | 30            | r.t./2 h, 50 °C/2 h | 32% (3a) | 17% (4a) |
| 5$^d$ | 4-OCH$_3$ (1a)   | 30            | 50 °C/4 h | 79% (3a) |        |
| 6     | H (1b)           | 30            | 50 °C/4 h | 88% (3b) |        |
| 7     | fused Ph (2-naphthol, 1c) | 30    | 50 °C/4 h | 86% (3c) |        |
| 8, lit.$^{13}$ | 4-OCH$_3$ (1a) | 30, BF$_3$, Et$_2$O in CH$_2$Cl$_2$ | r.t./24 h | 36% (3a) | traces |
| 9, lit.$^{13}$ | 4-OCH$_3$ (1a) | TiCl$_4$, 10% in CHCl$_3$ | 60 °C/6 h | 84% (3a) | traces |
| 10, lit.$^{13}$ | H (1b) | TiCl$_4$, 10% in CHCl$_3$ | 60 °C/6 h | 87% (3b) |        |
| 11, lit.$^{13}$ | fused Ph (2-naphthol, 1c) | TiCl$_4$, 10% in CHCl$_3$ | r.t./2 h | 95% (3c) |        |

$^a$BMIm-BF$_4$ (divided cell) was electrolyzed (galvanostatic conditions: 10 mA cm$^{-2}$) on platinum electrodes (r.t., N$_2$). At the end of electrolysis, phenol 1 (0.5 mmol) and diethyl ketomalonate 2 (0.5 mmol) were added to the anolyte. The mixture was stirred (T and time in table) and then extracted with diethyl ether.$^b$Amount of electrogenerated BF$_3$ with respect to starting phenol, admitting a 100% current efficiency (96.5 C: 1 mmol of BF$_3$). $^c$Isolated yields after column chromatography. $^d$Entries 1–5: the same recycled IL was used.
Different Lewis acids in catalytic amounts in CH₂Cl₂ at room temperature were used, with good yields.\textsuperscript{13} We tested the anodically generated BF₃ in BMIm-BF₄ in this reaction, and the results are reported in Table 1, along with the corresponding literature data, for a useful comparison.

As reported in Table 1, high yields in products 3a–c (entries 5–7) were obtained using a 30% maximum of catalyst (calculated admitting a 100% current yield), comparable with those obtained in the literature using the best experimental conditions, i.e., TiCl₄ as Lewis acid (entries 9–11). A direct comparison with literature data can be made considering entries 3 and 8, in which the same phenol (1a), amount of BF₃ (30%), reaction time and temperature were used. 3a was obtained in 56% in IL (with a 19% of intermediate 4a) with respect to 36% of 3a obtained in CH₂Cl₂. Also in this case, BMIm-BF₄ demonstrated to be a solvent suitable for reactions involving dipolar intermediates.\textsuperscript{14} Additionally, from the high yield using 30% of BF₃, we can infer that the IL acts as an efficient solvent to bind this volatile reagent and ensures the reiteration of the catalytic cycle. Moreover, the eco-friendly character of this reaction in IL is demonstrated not only by the use of electricity to generate the catalyst but also by the use of the same IL sample in five subsequent runs (entries 1–5), without reactivity loss.

The second reaction considered is the Friedel–Crafts benzylation of anisole 10 with benzyl alcohol 9 (Table 3), in which anisole is monobenzylated in the ortho or para positions (the meta isomer being present only in traces).\textsuperscript{15} Good yields in benzylated anisole 11 were obtained using a stoichiometric (69%, entry 3) or overstoichiometric (80%, entry 5) amount of catalyst. Moreover, milder reaction conditions were used, with respect to the literature (r.t. vs 65–80 °C, Table 3), and more importantly, the efficient recycling of the IL was demonstrated (entries 1–5).

The literature data here reported for comparison (entry 6, Table 3) showed that the thermodynamic favorite product p-11 can be obtained using a very large excess of anisole (10 to 9: 18/1) at 80 °C. The positive effect of an imidazolium IL as solvent in this reaction, involving charged species as intermediates, is confirmed by literature data, besides the results obtained in this work (Table 3, entry 7).\textsuperscript{16} The last example is the multicomponent synthesis of tetrahydro-11H-benzo[a]xanthene-1-one 13 from benzaldehyde 6, 2-naphthol 1c, and dimedone 12 (Table 4).

The literature reaction was carried out in boiling ethanol (80 °C) with 20% of BF₃·Et₂O, obtaining high yields of 9,9-dimethyl-12-aryl-8,9,10,12-tetrahydro-11H-benzo[a]xanthene-11-ones 13 (Table 4, entries 6 and 7). When the reaction was carried out in BMIm-BF₄ using anodically generated BF₃, good yields of product 13 were obtained at room temperature.
The developed methodology was demonstrated by the recycling of literature results. Moreover, the eco-friendly nature of the anodic oxidation of BMIm-BF₄ solutions. By simply using used, the yield was slightly lower (Table 4, entries 4 and 5), but comparable with the literature (entry 7). When 4-cloro benzaldehyde was used, the yield was slightly lower (Table 4, entry 1), while better results were achieved at 60 °C (Table 4, entries 2 and 3). When 4-cloro benzaldehyde was used, the yield was slightly lower (Table 4, entries 2 and 3), but comparable with the literature (entry 7).

In conclusion, we efficiently in situ generated BF₃ via direct anodic oxidation of BMIm-BF₄ solutions. By simply using electrons as redox reagents, precise control of the amount of formed BF₃ could be reached and the anolyte could be used directly to carry out organic reactions. This setup was successfully applied to four classically BF₃-catalyzed transformations, affording similar or improved yields compared with literature results. Moreover, the eco-friendly nature of the developed methodology was demonstrated by the recycling of the IL, which was submitted to up to five subsequent runs without any reactivity loss. We believe that this could be a safer and easier approach to handle this toxic and volatile reagent without storing need and to carry out organic transformations in a sustainable way.

### EXPERIMENTAL SECTION

**General Information.** All chemicals were commercial (Fluorochem, Aldrich) and used without further purification. BMIm-BF₃ (1-butyl-3-methylimidazolium tetrafluoroborate, Iolitec) was kept at 40 °C under vacuum for 3 h before use. ¹H and ¹³C spectra were recorded at ambient temperature on a Bruker Avance spectrometer (400 MHz) or with a Gemini Varian spectrometer (300 MHz), using the solvent as internal standard. The chemical shifts (δ) are given in ppm relative to TMS. GC–MS analyses have been run on an HP 5890 series II GC, equipped with a 5% phenyl silicone 30m × 0.25 mm × 25 mm capillary column and coupled to an HP 5972 MSD instrument operating at 70 eV. Flash column chromatography was carried out using a Merck 60 kieselgel (230–400 mesh) under pressure. Starting compounds 1, 2, 5, 6, 7, 9, 10, and 12 were commercially available (Sigma-Aldrich) and used as received.

**General Procedure for Electrochemical BF₃ Production.** All the experiments were carried out in a homemade divided glass cell separated through a porous glass plug; Pt spirals (apparent area 0.8 cm²) were used as anode and cathode. Electrolyses were performed at constant current (I = 10 mA cm⁻²), at room temperature, under a nitrogen atmosphere, using an Amel Model 552 potentiostat equipped with an Amel Model 731 integrator. 3.0 mL of BMIm-BF₃ was put in the anodic compartment, 1.0 mL of BMImBF₄ in the cathodic one. After a predetermined number of Coulombs (as reported in tables) passed through the electrolysis cell, the current was switched off, the cathodic compartment was removed, and the reagents were added to the anolyte under an inert atmosphere, as specified below. At the end of the reaction, the anolyte was extracted with diethyl ether (3 × 10 mL). The solvent was eliminated from the combined organic phases through the electrolysis cell, the current was switched off, the anodic compartment, 1.0 mL of BMIm-BF₃ in the cathodic one. After a predetermined number of Coulombs (as reported in tables) passed through the electrolysis cell, the current was switched off, the cathodic compartment was removed, and the reagents were added to the anolyte under an inert atmosphere, as specified below. At the end of the reaction, the anolyte was extracted with diethyl ether (3 × 10 mL). The solvent was eliminated from the combined organic phases under reduced pressure, the crude was analyzed by ¹H NMR, and then the products were purified by flash column chromatography.

When the same anolyte was reused in subsequent electrolyses/experiments, prior to its reuse, it was kept under vacuum for 30 min to eliminate diethyl ether residues. All products were known, and their spectral data were in accordance with those reported in the literature.

**Friedel–Crafts/Lactonization Reaction.** The electrolysis was carried out as previously reported, and after the number of Coulombs reported in Table 1, the current was switched off. Then phenol 1 (0.5

### Table 3. BF₃-Catalyzed Friedel–Crafts Benzylation of Anisole

| entry | 9/10⁻ff | BF₃ (%) | III (%) | 11, p/o° |
|-------|---------|---------|---------|----------|
| 1      | 1/2     | 100     | 18      | 53/47    |
| 2      | 1/3     | 100     | 60      | 57/43    |
| 3      | 1/4     | 100     | 69      | 54/46    |
| 4      | 1/4     | 50      | 16      | 58/42    |
| 5      | 1/4     | 150     | 80      | 58/42    |
| 6, lit.17f | 1/18f | 120, BF₃, Et₂O/H₂O, 80 °C | 61 | >99/1 |
| 7, lit.15 | 1/4 | 30, Yb(OTf)₃/BMIm-OTf, 65 °C | 71 | 57/43 |

“Anisole 10 (amount as in table) and benzyl alcohol 9 (0.5 mmol) were added to the anodically generated BF₃/BMIm-BF₄ (footnote a of Table 1). The mixture was stirred at r.t. for 4 h and then extracted with diethyl ether. ⁹Q to 10, molar ratio. ¹Amount of electrogenerated BF₃ with respect to starting 2-naphthol, admitting a 100% current efficiency (96.5 C: 1 mmol of BF₃). ²Isolated yields after column chromatography. ³Determined by the ¹H NMR of the crude. ⁴Entries 1–5: the same recycled IL was used. ⁵²,4-Dichlorobenzyl alcohol was used as benzylating agent.

### Table 4. BF₃-Catalyzed Synthesis of Substituted Tetrahydro-11H-benzo[a]xanthene-11-ones

| entry | R | BF₃ (%) | T (°C), t (h) | 13% |
|-------|---|---------|---------------|-----|
| 1d    | H | 25, r.t., 3 h | 68% (13a) |
| 2d    | H | 25, 60 °C, 1 h | 85% (13a) |
| 3d    | 4-Cl | 25, 60 °C, 2 h | 87% (13a) |
| 4d    | 4-Cl | 25, 60 °C, 1 h | 67% (13b) |
| 5d    | H | 20, BF₃, Et₂O/EtOH, 80 °C, 45 min | 82% (13a) |
| 6, lit.19 | H | 20, BF₃, Et₂O/EtOH, 80 °C, 45 min | 80% (13b) |

“2-Naphthol 1c (0.5 mmol), benzaldehyde 6 (0.5 mmol), and dimedone 12 (0.5 mmol) were added to the anodically generated BF₃/BMIm-BF₄ (footnote a of Table 1). The mixture was stirred (time and temperature as in table) and then extracted with diethyl ether. ⁶Amount of electrogenerated BF₃ with respect to starting 2-naphthol, admitting a 100% current efficiency (96.5 C: 1 mmol of BF₃). ⁷Isolated yields after column chromatography. ⁸Entries 1–3: the same recycled IL was used. ⁹Entries 4 and 5: the same recycled IL was used.

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and diethyl ketomalonate 2 (87 mg, 0.5 mmol, 1 equiv) were added to the anolyte. The mixture was kept at room temperature under stirring at the temperature and for the time reported in Table 1 and then was extracted with diethyl ether (3 × 10 mL).

**Ethyl 3-Hydroxy-2-oxo-2,3-dihydrobenzofuran-3-carboxylate (3a).** The product was isolated after flash chromatography on silica gel (light petroleum ether/EtOAc 7:3) as a yellow oil, 108 mg (88%).

**Ethyl 3-Hydroxy-2-oxo-2,3-dihydrobenzofuran-3-carboxylate (3b).** The product was isolated after flash chromatography on silica gel (light petroleum ether/EtOAc 7:3) as a white solid, 28 mg (19%).

**Ethyl 3-Hydroxy-2-oxo-2,3-dihydrobenzofuran-3-carboxylate (3c).** The product was isolated after flash chromatography on silica gel (light petroleum ether/EtOAc 7:3) as a yellow solid, 117 mg (88%).

**Povarov Reaction. Imine Synthesis.** Amine 5 (0.5 mmol, 1 equiv) and aldehyde 6 (0.5 mmol, 1 equiv) were added to 0.5 mL of BMIM-BF4 and kept under stirring at room temperature for 1 h. Then the mixture was extracted with diethyl ether (3 × 3 mL). The solvent was evaporated by azeotropic distillation to eliminate from the combined organic phases under reduced atmosphere for 4 h, then extracted with diethyl ether.

**5-Methyl-5-phenyl-3,4,4a,5,6,10b-hexahydro-2H-pyra[3,2-c]quinoline (8b).** The cis product was isolated after crystallization from ethanol, the trans product after chromatography on silica gel (light petroleum ether/EtOAc 9:1) of the mother liquor.

**Remarks:**

1. Ethyl 3-Hydroxy-2-oxo-2,3-dihydrobenzofuran-3-carboxylate (3a) 

2. Ethyl 3-Hydroxy-2-oxo-2,3-dihydrobenzofuran-3-carboxylate (3b) 

3. Ethyl 3-Hydroxy-2-oxo-2,3-dihydrobenzofuran-3-carboxylate (3c) 

4. Ethyl 3-Hydroxy-2-oxo-2,3-dihydrobenzofuran-3-carboxylate (3b) 

5. 5-Methyl-5-phenyl-3,4,4a,5,6,10b-hexahydro-2H-pyra[3,2-c]quinoline (8b)
1-Benzyl-4-methoxybenzene (p-11). The product was isolated after flash chromatography on silica gel (light petroleum ether/EtOAc 9:1), deliquescent light yellow solid, 46 mg (46%). 1H NMR (400 MHz, CDCl3) δ 7.32–7.25 (m, 2H), 7.19 (t, J = 7.6 Hz, 3H), 7.11 (d, J = 8.4 Hz, 2H), 6.84 (d, J = 8.4 Hz, 2H), 3.94 (s, 2H), 3.79 (s, 3H), 2.52 (s, 3H) ppm. 13C{1H} NMR (101 MHz, CDCl3) δ 158.0, 141.6, 133.2, 129.9, 128.8, 128.4, 126.0, 113.9, 55.3, 41.0. GC–MS, m/z (%): 199 (M+ +1, 15), 198 (M+, 100), 183 (36) 167 (35), 165 (24), 153 (17), 121 (23), 91 (8).

1-Benzyl-2-methoxybenzene (o-11). The product was isolated after flash chromatography on silica gel (light petroleum ether/EtOAc 9:1), deliquescent light yellow solid, 34 mg (34%). 1H NMR (400 MHz, CDCl3) δ 7.31–7.16 (m, 9H), 7.08 (d, J = 6.2 Hz, 1H), 6.89 (m, 2H), 3.99 (s, 2H), 3.83 (s, 3H). ppm. 13C{1H} NMR (101 MHz, CDCl3) δ 120.5, 110.4, 55.4, 35.9. GC–MS, m/z (%): 254.1 (M+), 245 (16), 198 (M+, 100), 183 (36) 167 (37), 165 (52), 152 (15), 121 (7), 91 (22).

Multicomponent Reaction to Tetrahydro-11H-benz[a]xanthen-11-ones. The electrolysis was carried out as previously reported, and after the number of Coulombs reported in Table 4, the current was switched off. Then benzaldehyde 6 (0.5 mmol, 1 equiv), and dimedone 22, 278.1 (21), 277.1 (100). The product was isolated after flash chromatography on silica gel (light petroleum ether/EtOAc 9:1), deliquescent light yellow solid, 34 mg (34%). 1H NMR (400 MHz, CDCl3) δ 7.31–7.16 (m, 9H), 7.08 (d, J = 6.2 Hz, 1H), 6.89 (m, 2H), 3.99 (s, 2H), 3.83 (s, 3H). ppm. 13C{1H} NMR (101 MHz, CDCl3) δ 120.5, 110.4, 55.4, 35.9. GC–MS, m/z (%): 199 (M+ +1, 16), 198 (M+, 100), 183 (36) 167 (35), 165 (24), 153 (17), 121 (23), 91 (8).

AUTHOR INFORMATION

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.joc.1c00932. Copies of 1H and 13C NMR of products (PDF)

ASSOCIATED CONTENT

Note

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