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Syntheses of 1-Aryl-2-trifluoromethylbenzimidazoles via Electrochemically Prepared p-Benzoquinone Imines

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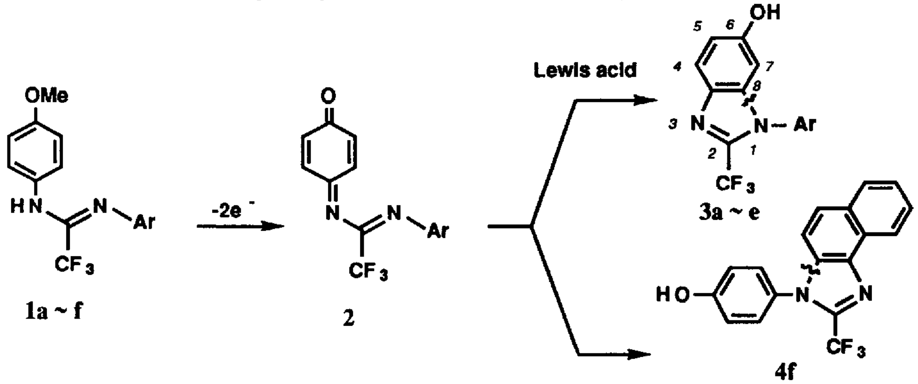
Summary Electrooxidation of N-(4-methoxyphenyl)-N'-aryl-2,2,2-trifluoroethanimidamides **1** in an MeCN-H_2O-$NaClO_4$-(C)-(Pt) system affords p-benzoquinone imines **2** which are converted to 1-aryl-2-trifluoromethylbenzimidazoles **3** by acid catalyzed cyclization.

2-Trifluoromethylbenzimidazoles are potentially insecticidal and herbicidal[1] and have been mostly prepared by the condensation of 2-aminoaniline derivatives with trifluoroacetic acid.[2] However, very few has been known about 1-aryl-2-trifluoromethylbenzimidazoles **3** because of the unavailability of the general preparative method for N-aryl-2-aminoaniline derivatives. Here we describe a novel preparation of **3** from easily available unsymmetrical N,N'-diaryl-2,2,2-trifluoroethanimidamides **1** via a sequence of electrochemical oxidation and acid-catalyzed cyclization which involves N(1) - C(8) bond formation.



Electrolysis[3] of **1** (0.5 mmol)[4] was conducted in MeCN-H_2O (7 ml : 1 ml)-$NaClO_4$ (0.25 mmol) using a glassy carbon anode and a platinum plate cathode in an undivided cell (a constant current of 5 mA/cm^2, 2.2 F/mol, -10 °C). Both current efficiencies and chemical yields were excellent. p-Benzoquinone imines[5] **2a ~ e** (77 ~ 99 % yields) were stable enough to be purified by a silica gel column chromatography in contrast to instability of common N-substituted p-benzoquinone imines.[6] Lower current density and reaction temperature are favorable for the formation of **2a** [87, 64 and 25 % at 5, 10 and 20 mA/cm^2, and 80, 62 and 57 % at -15, 0, and 50 °C, respectively].

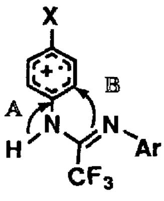
The oxidation occurs exclusively on the methoxy-bearing aromatic ring. The deprotonation and the subsequent one electron oxidation followed by hydrolysis (ECEC mechanism) (path A) from the initially formed cation radical **5** proceed exclusively for 4-methoxyphenylamino compounds **1a ~ f** (X=OMe). On

Table. Electrooxidation of 1 and BF_3 Et_2O-catalyzed cyclization of 2

1	Ar	2 [a](%)	3 [a,c] or	4 [a,e] (%)	React Time (hr)[g]
a	4-MeO-C_6H_4-	87	93	-	0 5
b	4-Me-C_6H_4-	99	100	-	0 5
c	4-Cl-C_6H_4-	85	91	-	1.0
d	3, 4-Cl_2-C_6H_3-	85	91	-	2 0
e	4-NO_2-C_6H_4-	77 [b]	57 [d]	-	1 5
f	1-Naphthyl	not isolated	-	60 [f]	0 5

a isolated yield, b A divided cell was used in order to suppress any cathodic reduction of nitro group, c in refluxed benzene, d in refluxed toluene, e at 35 °C in AcOEt, f over all yield from **1f**, g reaction time for the cyclization of **2**,

the other hands, formation of **6** via intramolecular trapping of electron deficient ring carbon by imino-nitrogen preferentially occurred for **5** (X=Me, Cl, path B) although the yields (ca 30 %) are not satisfactory [7]



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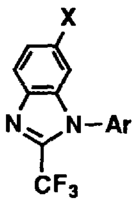

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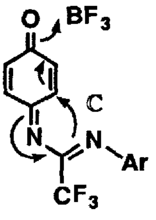

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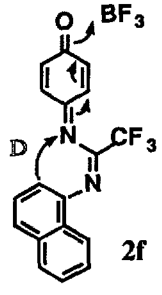

2f

BF_3 Et_2O-catalyzed cyclization of **2a** ~ **f** proceeded smoothly in refluxed benzene to give **3a** ~ **e** or **4f** in 57 ~ 100 % yields (See Table) In contrast to a facile ring closure between the p-benzoquinone ring carbon atom and the aryl-substituted nitrogen atom (path C in **7**), p-benzoquinone imine **2f** (Ar=1-naphthyl) cyclized via path D leading to naphthimidazole **4f**

Although the cyclization mechanism is not clear at this stage, the present sequence of electrochemical and acid-catalyzed reactions (**1**→**2**→**3**) provides a new type of trifluoromethylated benzimidazoles and naphthimidazole of which bioactivities are under investigation

References and Notes

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6 Common p-benzoquinone imines are unstable in either acidic or basic media to be hydrolyzed to amino compounds and p-benzoquinones [5]

7 The detailed electrolysis conditions and results on the formation of **6** will be discussed elsewhere

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