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New approach to the generation of aryldifluoroboranes – prospective acid catalysts of organic reactions

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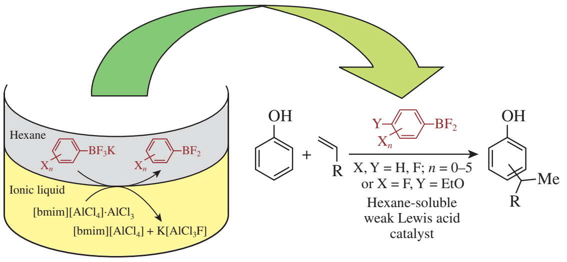
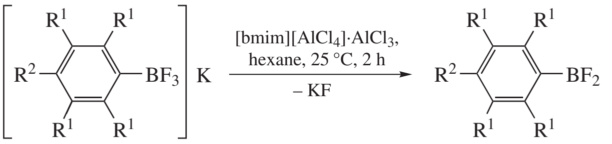
A new approach for preparation of aromatic and fluoroaromatic difluoroboranes *via* the interaction between corresponding aryltrifluoroborates and ionic liquids containing tetrachloroaluminate-anion and aluminum chloride has been developed. Catalytic properties of obtained aryldifluoroboranes have been investigated in model reactions of phenols alkylation. The dependence of catalytic properties on both the nature of solvent used and the type of substituents in the aromatic ring of difluoroborane has been established.



Despite a large number of studies on the reactions catalyzed by Lewis acids and significant progress achieved in this field, a lot of issues involving the production of soluble and stable in organic solvents Lewis acids with the controlled acidity remain relevant.[1,2] Such Lewis acids are of importance as catalysts for transformations of highly active substrates and compounds containing several reaction centers with different reactivity. Among the whole variety of known Lewis acids, of special interest are fluorinated aryldihalogenoboranes, formal derivatives of boron trifluoride, which are used for different processes in fine organic synthesis.[3] Fluorinated aryldihalogenboranes are relatively stable and variation of the nature of substituents at the boron atom allows one to control the Lewis acidity and catalytic activity. However, complicated generation of these compounds is an obstacle to their widespread use. For example, fluorinated aryldihalogenoboranes obtained by reaction between corresponding organotin compounds and boron halides are contaminated with hardly separable tin-containing by-products.[4,5] The synthesis of fluorinated aryldifluoroboranes (Ar_FBF_2), which is based on potassium fluoride detachment from the corresponding potassium organotrifluoroborate under the action of BF_3, requires special installation for handling gaseous boron trifluoride.[6,7]

Here, we propose a convenient method for the preparation of various aryldifluoroboranes *via* the interaction between the corresponding potassium organotrifluoroborates and an ionic liquid containing free aluminum chloride and investigate their catalytic properties.



1 $R^1 = R^2 = F$
2 $R^1 = H, R^2 = F$
3 $R^1 = F, R^2 = OEt$
4 $R^1 = R^2 = H$

Scheme 1

Aryldifluoroboranes ($ArBF_2$) **1**–**4** were generated *via* the elimination of KF from $[ArBF_3]K$ by the action of aluminum chloride dissolved in ionic liquid 1-butyl-3-methylimidazolium chloride [bmim]Cl (Scheme 1).[†] Reactant $[bmim][AlCl_4]\cdot AlCl_3$ was obtained as a low-viscosity transparent liquid by mixing anhydrous $AlCl_3$ and [bmim]Cl in a molar ratio of 1.5 : 1. The content of

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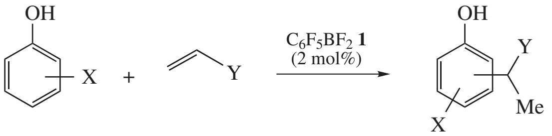
[†] *General procedure for preparation of organofluoroboranes* **1**–**4**. $[bmim][AlCl_4]\cdot AlCl_3$ (224 mg, 0.3 mmol) and corresponding potassium organotrifluoroborate (0.3 mmol) were placed in flame-dried flask upon dry atmosphere, then the flask was closed by septum. Using a syringe, hexane (3 ml) was added and the mixture was stirred at 25 °C under argon atmosphere for 2 h. After that a sample was analyzed by ^{19}F NMR spectroscopy using benzotrifluoride (3 μl, 24.6 μmol) as a quantitative internal standard. Organofluoroboranes were used in catalytic experiments as a solution in hexane.

Difluoro(pentafluorophenyl)borane **1**. ^{19}F NMR (hexane) δ: –73.02 (br. s, 2F, BF_2), –128.65 (br. s, 2F, 2-F, 6-F), –144.45 (tt, 1F, 4-F, $^3J_{FF}$ 19.6 Hz, $^5J_{FF}$ 7.3 Hz), –161.69 (m, 2F, 3-F, 5-F). ^{11}B NMR (hexane) δ: 23.21 (br. s, 1B, BF_2).

Difluoro(4-fluorophenyl)borane **2**: ^{19}F NMR (hexane) δ: –93.56 (q, 2F, BF_2, $^1J_{BF}$ 64.7 Hz), –104.12 (br. s, 1F, 4-F). ^{11}B NMR (hexane) δ: 24.50 (t, 1B, BF_2, $^1J_{BF}$ 64.6 Hz).

Difluoro(4-ethoxy-2,3,5,6-tetrafluorophenyl)borane **3**. ^{19}F NMR (hexane) δ: –75.74 (br. s, 2F, BF_2), –131.31 (br. s, 2F, 2-F, 6-F), –158.66 (dd, 2F, 3-F, 5-F, $^3J_{FF}$ 18.0 Hz, $^5J_{FF}$ 8.2 Hz). ^{11}B NMR (hexane) δ: 22.91 (br. s, 1B, BF_2). ^1H NMR (benzene-d_6) δ: 3.91 (q, 2H, OCH_2Me, $^3J_{HH}$ 7.1 Hz), 1.01 (t, 3H, OCH_2Me, $^3J_{HH}$ 7.0 Hz). ^{13}C NMR (benzene-d_6) δ: 151.42 (dddd, 2-C, 6-C, $^1J_{CF}$ 254.4 Hz, $^2J_{CF}$ 11.9 Hz, $^3J_{CF}$ 10.3 Hz, $^4J_{CF}$ 1.9 Hz), 140.66 (ddd, 3-C, 5-C, $^1J_{CF}$ 245.9 Hz, $^2J_{CF}$ 13.4 Hz, $^3J_{CF}$ 2.5 Hz), 137.98 (tt, 4-C, $^2J_{CF}$ 13.0 Hz, $^3J_{CF}$ 3.8 Hz), 70.33 (s, OCH_2Me), 14.95 (s, OCH_2Me), the signal of 1-C atom, a weak broad multiplet at about 110–120 ppm, was not identified.

Difluoro(phenyl)borane **4**. ^{19}F NMR (hexane) δ: –92.89 (q, 2F, BF_2, $^1J_{BF}$ 65.9 Hz). ^{11}B NMR (hexane) δ: 25.34 (t, 1B, BF_2, $^1J_{BF}$ 66.2 Hz).



X = H, 4-Br, 4-NH_2, 2-Ph
Y = Bu, CH_2Br, Ph

Scheme 2

Table 1 Catalytic activity of borane **1** in the alkylation reactions of phenols.

Entry	X	Y	Solvent	*T*/°C	*t*/min	Conversion (%)
1	H	Bu	Hexane	65	30	0
2	H	CH_2Br	Hexane	65	30	0
3	H	Ph	Hexane	65	180	90
4	H	Ph	CH_2Cl_2	25	30	100
5	4-Br	Ph	CH_2Cl_2	25	30	100
6	4-NH_2	Ph	CH_2Cl_2	25	180	0
7	2-Ph	Ph	CH_2Cl_2	25	30	78

‘active’ aluminum chloride was 1.335 mmol g^{-1}. The reagent is immiscible with non-polar solvents such as hydrocarbons, benzene and CCl_4 and stable under dry atmosphere conditions, these properties being very useful for our purpose.

The generation of aryldifluoroboranes was carried out in two-phase ionic liquid–hexane system. The product has a non-ionic structure and moves to a hexane phase. The aryldifluoroborane concentration in solution was determined using ^{19}F NMR spectroscopy and internal standard. We developed a new alternative rapid method for determination of the aryldifluoroborane concentration in solution. It is based on the chromatographic determination of the residual amount of 2-methylpyridine after the quantitative formation of corresponding borane adduct insoluble in non-polar solvents.[4,5,‡] The results obtained by this method are in good agreement with NMR spectroscopy data, which confirms its suitability for the rapid determination of the organofluoroboranes concentration.

The catalytic properties of the difluoro(pentafluorophenyl)-borane **1** obtained were investigated in phenol alkylation reactions (Scheme 2, Table 1). Compound **1** did not exhibit catalytic properties in the alkylation of phenol with hex-1-ene and allyl bromide (Table 1, entries 1, 2). However, the acidity of **1** is sufficient to promote the phenol reaction with styrene (entries 3, 4). Exhaustive alkylation of 4-bromophenol proceeded in dichloromethane (entry 5). At the same time, the attempt to alkylate 4-aminophenol failed. It may be caused by catalyst deactivation due to the formation of the adduct of borane and 4-aminophenol (entry 6). It was of interest to study catalytic alkylation of substrates containing several reaction centers. Thus, as result of interaction between 2-phenylphenol and styrene in the presence of catalyst **1**, *ortho*- and *para*-products of alkylation of the phenolic ring were obtained (entry 7). Meantime, no products of alkylation of the unactivated ring were observed.

The examples are known when halogenated solvents are inappropriate reaction media in the presence of classical Lewis acids (for example, $AlCl_3$) due to their participation in reactions.[9] In our case, dichloromethane does not act as alkylation reagent in the presence of compound **1** (Table 1, entries 4–7). Note that benzene and toluene may also be used as solvents for alkylation reactions in the presence of catalyst **1**. This fact allows one to considerably extend the range of solvents for the processes catalyzed by Lewis acids. To determine the effect of the solvent nature on organofluoroborane catalytic properties, we performed a series of phenol alkylation experiments with various solvents (Table 2).

Table 2 Effect of the solvent nature on the phenol alkylation with styrene catalyzed by compound **1**.

Entry	Solvent	AN	*t*/min	Conversion (%)	*ortho*-product (%)	*para*-product (%)
1	CH_2Cl_2	20.4	30	100	57	43
2	Benzene	8.2	30	79	67	33
3	Hexane	0	30	65	46	54
4	CCl_4	8.6	30	56	65	35

It was shown that the alkylation proceeds quantitatively in dichloromethane within 30 min (see Table 2, entry 1). It may be explained by high solvent polarity affecting the carbocation stabilization and, as a consequence, lower activation energy of the process. For the alkylation reaction in benzene medium (entry 2), higher catalytic activity of borane **1** was demonstrated as compared to that in hexane and tetrachloromethane. Apparently, it is caused by partial carbocation stabilization due to π-stacking interactions. A lower catalytic activity of compound **1** in tetrachloromethane (entry 4) compared to that in hexane (entry 3) can be explained by Hutman’s acceptor numbers (AN) scale, where different solvents are located on a relative scale from 0 to 100.[10] The larger the acceptor number, the more effective the involved substance is in the donor–acceptor interactions with Lewis acids. It may be assumed that the use of CCl_4 as a solvent results in partial organofluoroborane deactivation due to its strong interaction with the latter. Negative influence of this factor seems to be balanced by positive effect of transition state stabilization at the limiting stage of the alkylation process.

Thus, organofluoroborane catalyst activity depends on a number of solvent characteristics, the main of which is the solvent ability to stabilize reaction intermediates. Donor–acceptor interactions with Lewis acids have a lower effect, but they become noticeable in the absence of carbocation stabilizing factors.

To study the influence of aromatic substituents in organofluoroboranes on their catalytic activity, a series of phenol alkylation experiments in the presence of organofluoroboranes **1**–**4** was carried out.[‡] Hexane was chosen as a solvent, since its solvating effect is minimized, thus the key factors affecting the organofluoroborane catalyst activity are the electronic properties of the aromatic substituents on the boron atom. We established a well-traced dependence of catalytic properties of the considered organofluoroboranes on the aromatic substituent electronic effects (Table 3). According to published data, the presence of fluorine substituents in the aromatic ring increases Lewis acidity of the boron atom due to the electron density displacement by the aromatic ring action and the absence of positive mesomeric effects.[11] This fact determines the maximal catalytic activity of borane **1** (Table 3, entry 1). Compound **2** containing one strong-accepting substituent in the aromatic ring has analogous properties

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[‡] To determine the organofluoroborane concentration, the reaction mixture (1 ml) was added to 0.54 M solution of 2-methylpyridine in *n*-decane (300 μl). The precipitate was separated, excess amount of 2-methylpyridine was determined by gas chromatography using absolute calibration.

Catalytic experiments (general procedure). The substrate (20 mmol), *viz.* phenol, 4-bromophenol, 4-aminophenol or 2-phenylphenol, 0.05 M aryldifluoroborane solution in hexane (1 ml, 0.05 mmol) and the solvent (20 ml), *viz.* hexane, benzene, dichloromethane, were placed in flame-dry flask filled with argon. The mixture was thermostatted at the desired temperature for 15 min. Then an alkylating agent (2 mmol), *viz.* 1-hexene, allyl bromide or styrene, was added. The conversion of the starting compound and the mixture quantitative composition were determined by gas chromatography. The qualitative composition of the mixture was determined by GC-MS. The products were identified by comparison of retention times and mass spectra with those of previously described compounds.[8]

Table 3 Catalytic activity of aryldifluoroboranes **1**–**4** in alkylation of phenol with styrene.

Entry	Catalyst	Conversion of styrene (%)	*ortho*-product (%)	*para*-product (%)
1	**1**	90	58	42
2	**2**	22	44	56
3	**3**	20	53	47
4	**4**	0	0	0
5	$BF_3 \cdot Et_2O$	27	54	46

(entry 2). Appending the electron-donor substituents such as ethoxy group leads to increase in the electron density in the perfluoroaryl ring and, as a consequence, a decrease in the boron atom Lewis acidity and catalytic activity of borane **3** (entry 3). In addition, the coordination between the oxygen atom of the ethoxy group and the boron atom is possible, which may reduce Lewis acidity. Apparently, a similar situation is observed for the alkylation reaction in the presence of $BF_3 \cdot Et_2O$ (entry 5), whose catalytic activity is much lower as compared to that of compound **1**. The phenyl substituent in borane **4** does not have negative electronic effects. Therefore, the effective charge on the boron atom is diminished. Also, Lewis acidity and catalytic activity in this case are the lowest due to the presence of a combined π-system associated with the boron atom, which leads to an additional displacement of the electron density in the active center (entry 4).

In conclusion, an efficient and convenient method for preparing aryldifluoroboranes containing various substituents in the aromatic ring was developed. It was found that obtained compounds are soft Lewis acids and their catalytic activity in the reactions of phenol alkylation with styrene was demonstrated. It was established that the catalytic properties of aryldifluoroboranes are affected by both the nature of the solvent used and the electronic properties of substituents in the aromatic ring of borane. These results open new approaches to obtaining soft Lewis acids with controlled acidity and catalytic activity, which are promising for the use in selective transformations of activated and polyfunctional substrates.

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