The HF/BF$_3$-Catalysed Reaction of Substituted Benzenes with Carbon Monoxide

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Abstract: The HF/BF$_3$-catalysed reactions of phenol and anisole as well as substituted benzenes with CO were investigated as possible routes to commercially important aldehydes.

The results confirmed that HF and BF$_3$ are required in (at least) stoichiometric amounts for effective formylation with CO. With the aim of effecting truly catalytic reaction conditions, the formylation reactions were carried out in ionic liquids. It was shown that phenol is a good substrate for formylation in certain ionic liquids.

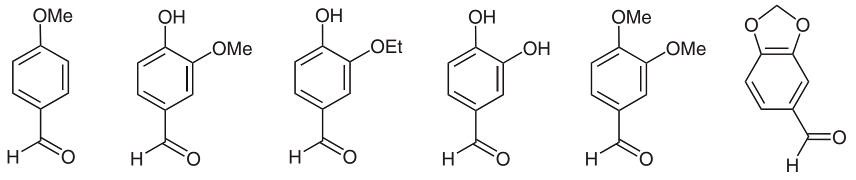
Key words: aldehydes, phenols, electrophilic aromatic substitutions, ionic liquids, Lewis acids

Hydroxy and alkoxy aldehydes such as **1**–**6** are important products that are primarily used in the flavour and fragrance market and as intermediates in the manufacturing of agrochemicals, pharmaceuticals and cosmetics as well as in the electroplating industry.[1]

p-Anisaldehyde (PAA, **1**) in particular is an important precursor in the manufacture of 2-ethylhexyl-*p*-methoxycinnamate [OMC (**7**), a UV adsorber in sunscreens]. It is also used in the synthesis of various pharmaceuticals, including the coronary therapeutic diltiazem (**8**) and chemotherapeutics like trimethoprim (**9**).[2]

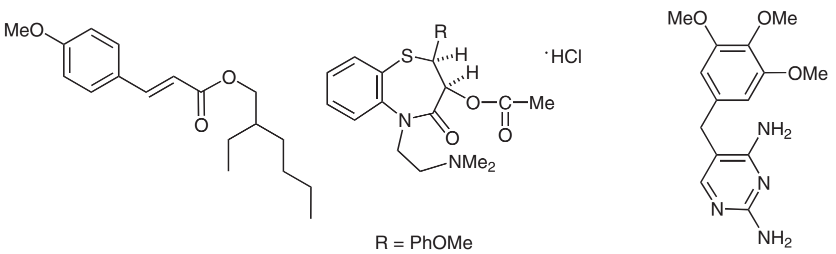
PAA is mainly produced in a two-step process involving O-methylation of *p*-cresol, followed by benzylic oxidation to the corresponding aldehyde using manganese dioxide and sulfuric acid as the catalyst (Scheme 1).[3] Other industrial processes employ liquid-phase oxidation of cresol in the presence of cobalt catalysts[4] and electrochemical oxidation in the presence of lower aliphatic alcohols via the corresponding anisaldehyde dialkyl acetal.[5] These processes suffer from the drawback of either producing large amounts of salt effluent that need to be disposed of and/or making use of expensive starting materials.

Direct aldehyde synthesis using phenol as a cheap feedstock is a viable alternative, but requires the use of a HF/BF$_3$ catalyst system together with HF as solvent (Scheme



1 **2** **3** **4** **5** **6**

Figure 1 Important hydroxy and alkoxy aldehydes



7 **8** **9**

Figure 2 *p*-Anisaldehyde derived synthesis products

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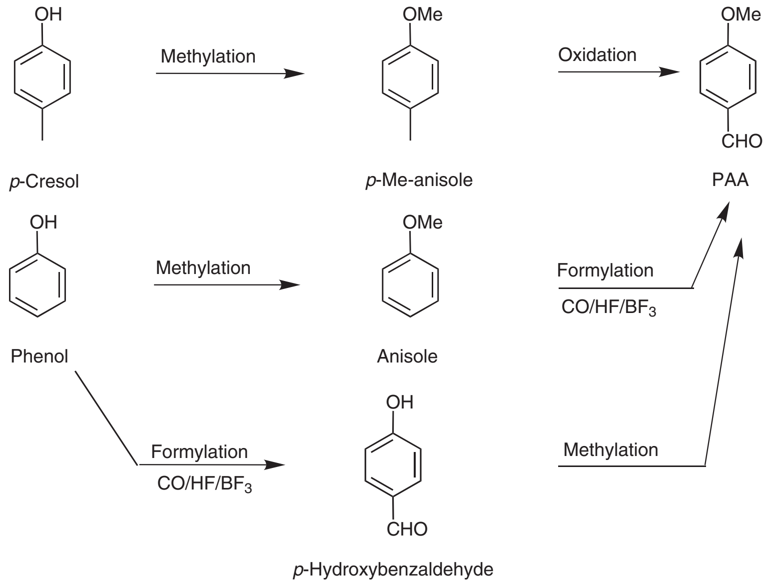


Scheme 1 Alternative routes to PAA

1).[6] Notwithstanding the harmful effects of these volatile compounds, their catalytic usage would be beneficial, with minimal effect on the environment if the use of HF as solvent could be eliminated and the process could be made truly catalytic. With this objective in mind, we now report some new results on the rates and selectivities of the HF/BF_3-catalysed formylation of some substituted benzenes with carbon monoxide.

Superacid catalysts as well as many other catalyst systems are used in the formylation of aromatic hydrocarbons with CO. These reactions generally fail with phenolic substrates.[7] However, two papers by Takezaki[6b,6c] as well as a Hoechst[8] patent, describe the synthesis of phenolic aldehydes by formylation with CO in the presence of a HF/BF_3 catalyst system. Contradicting each other, these publications create doubt around the question of selectivity (*ortho* vs *para*) regarding the formylation reaction in question. It was therefore decided to re-investigate these reactions and to include non-phenolic substrates in this study in the hope of gaining some mechanistic understanding. The reactions were followed by GC analysis of samples taken at regular intervals. All the results showed a definitive preference for *para*-selectivity (Table 1). Surprisingly, the reactivity of phenol proved to be much lower than that of toluene and a reaction time of more than four hours was required to obtain acceptable yields, albeit with reduced *para*-selectivity. When the reaction was extended to anisole, only small differences with respect to conversion were observed within the first hour of the reaction when compared to phenol. With extended reaction times phenol afforded superior conversions. The results indicate that the reaction is sustained for a longer period with phenol than with anisole.

The main aldehyde isomer produced in the HF/BF_3/CO formylations for all the *ortho*/*para*-directing mono-substituted benzenes tested in our laboratories is in accordance with published results.[8,9] We also found that extending the reaction times from one hour to 4.5 hours not only result-

Table 1 Formylation of Aromatic Substrates[a]

Entry	Substrate	Time (h)	Conv. (%)	Yield (%)		
				p-Aldehyde	*o*-Aldehyde	By-products[b]
1	toluene	1	>99	91	5	3
2	phenol	1	49	43	1	5
3	phenol	4.5	99	80	6	13
4	anisole	1	51	38	6	7
5	anisole	4.5	90	50	13	27
6	chlorobenzene	4.5	32	31	1	<1

[a] Conditions: CO (50 bar) in anhyd HF (50 equiv) and BF_3 (2 equiv) at 45 °C.
[b] For by-products, see Figure 3.

ed in increased aldehyde formation, but also in a decrease in the *para*/*ortho* ratio in the case of both phenol and anisole. The increase in *ortho*-products suggests a gradual change from kinetic control to thermodynamic control and the reversibility of the formylation process.

The formation of by-products (Table 1 and Figure 3) in the formylation reaction deserves some comment. Despite the high acidity level in the reaction mixture, by-products generated by these acidic conditions were relatively low (<10%) and anisole dealkylation was almost negligible (<1%). Increasing the reaction time for the anisole reaction from one to 4.5 hours, however, led to a four-fold increase in by-product formation, whilst the aldehyde concentration increased by a factor less than 0.5.

Careful GC-MS analysis confirmed that the majority of the by-products **10**–**14** are diphenylmethane based, thus pointing towards an acid-catalysed reaction between the substrate and formylation products as the most probable origin of these compounds.

The formation of the various secondary products is explained in terms of a two-step mechanism with the undetected unstable (vide infra) alcohol **16** as the key intermediate.

In the first step, acid-catalysed addition of anisole to the aldehyde product leads to alcohol **16** (Scheme 2). If this reaction is followed by an acid-catalysed substitution of the OH group by another anisole molecule, the trimer **17** is formed.

An intermolecular oxidation–reduction reaction between two alcohol molecules can be invoked as one of the possible sources for the formation of **10** and **11**. The occurrence of *p*-methoxyacetophenone (**14**) as a by-product was, however, rather surprising. The same product was reported by Saint-Jalmes et al.[10] during the HCO_2Me formylation of anisole with HF and BF_3. These workers postulated the acid-catalysed decomposition of methyl formate into methanol and CO as a first step in the reaction. This is followed by dehydration of protonated methanol to the methyl cation **18**, which is then carbonylated to produce the acylium ion **19**. Subsequent nucleophilic attack of anisole on **19** produces the observed acetophenone **20**. In a similar way, anisole (**15**) may be dealkylated to phenol and the methyl cation **18**, which in turn is converted into the acylium ion. The latter reacts with anisole to produce **20** (Scheme 3).

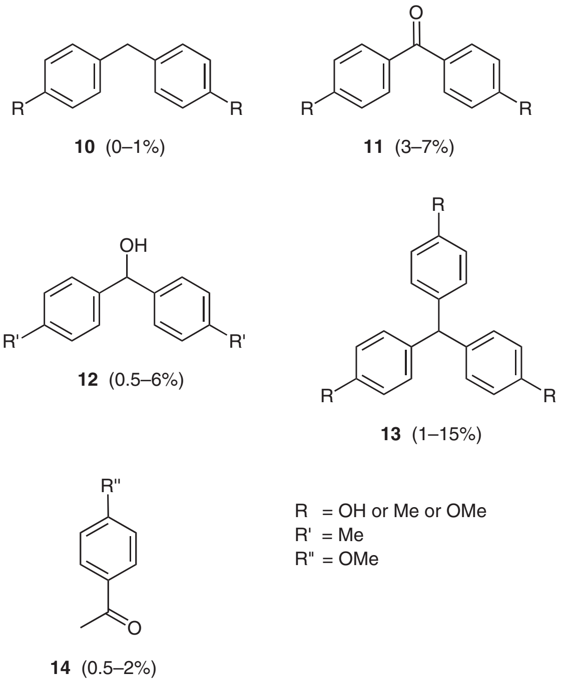
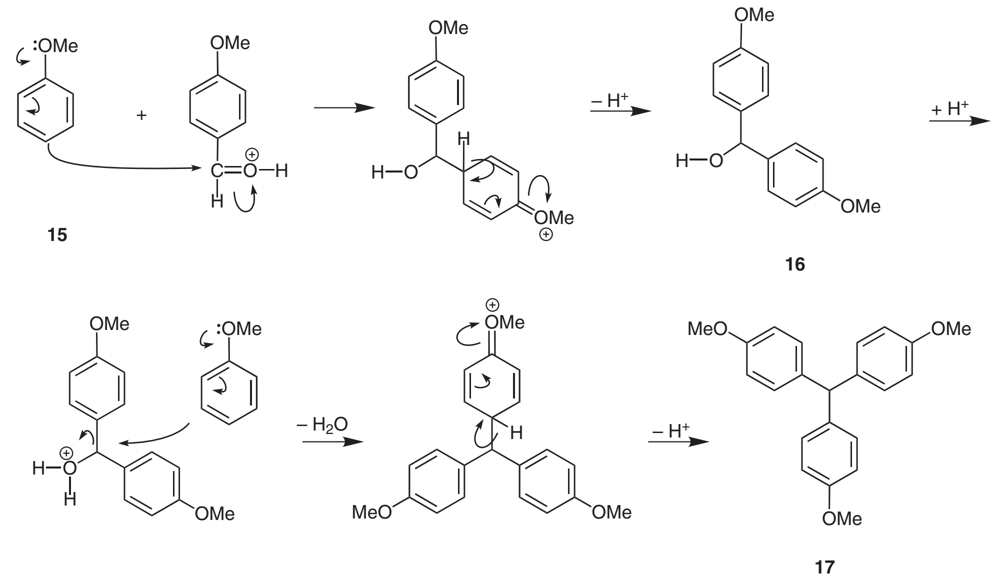
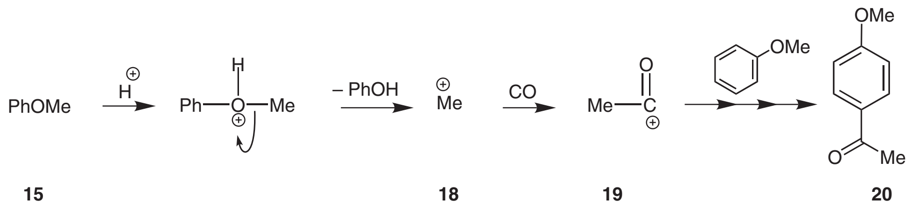


Figure 3 By-products obtained in the formylation of toluene, phenol and anisole (selectivity, %)

In an effort to substantiate the proposed mechanism of by-product formation in the anisole reaction, anisole and



Scheme 2 Nucleophilic addition of anisole to *p*-anisaldehyde



Scheme 3 Acetophenone formation from CO/HF/BF_3 formylation of anisole

PAA were added to HF and BF_3 in the absence of CO under typical reaction conditions. The products **17**, **11** and **10** were obtained in a 7:1:1 ratio, but again none of the alcohol **16** could be detected (Scheme 4). Products **10** and **11** may be formed by disproportionation of the proposed intermediate **16**. To confirm this postulate, the alcohol di(4-methoxyphenyl)methanol (**16**)[11] was prepared and subjected to the reaction conditions in the absence of a nucleophile. The detection of products **10** and **11** suggests that this is a plausible mechanism. The observed reaction is summarized in Scheme 4.

In order to establish relative formylation rates between different substrates, the effect of different substituent groups on *p*-aldehyde formation was compared over time. All reactions [BF_3 (2 equiv) and HF (50 equiv)] were conducted in the presence of *n*-decane as internal standard (20 % with respect to the substrate) under 50 bar CO pressure. From the results presented in Figure 4 it is clear that the formylation rates of toluene and benzene are significantly higher than those of other substrates. Maximum aldehyde yield was achieved after only ten minutes. Thereafter, a gradual drop in aldehyde yield was observed, indicating that the rate of secondary product formation now becomes faster than aldehyde formation. Of the non-alkyl substituted benzenes, fluorobenzene showed the fastest rate of formylation with little evidence of further reaction of the resulting aldehyde. The formylation of chlorobenzene is extremely slow and it appears that the rate of aldehyde formation is soon surpassed by further reactions of the aldehyde. It is clear that anisole has not reached maximum aldehyde yield after one hour and that extended reaction times are necessary to determine the maximum yield of aldehyde. Debromination of bromobenzene occurred under the reaction conditions resulting mainly in benzaldehyde production with little bromobenzaldehyde (<1%). It is further evident that the concentration of aldehyde product from toluene, anisole and chlorobenzene at one hour is somewhat less compared with previous results (cf. Table 1). This may be due to the effect of dilution resulting from the addition of the internal standard and the reduced solubility of CO in *n*-decane. The reaction rates decrease from toluene > benzene > fluorobenzene > anisole > chlorobenzene emphasising the fact that for electrophilic aromatic substitution reactions methyl groups are activating, while halogens are deactivating, relative to benzene as substrate. The decrease in reactivity from fluorobenzene > chlorobenzene > bromobenzene is in accordance with formylation trends observed in HSO_3F/SbF_5[12] and HCO_2CH_3/HF/BF_3[8b] catalyst systems.

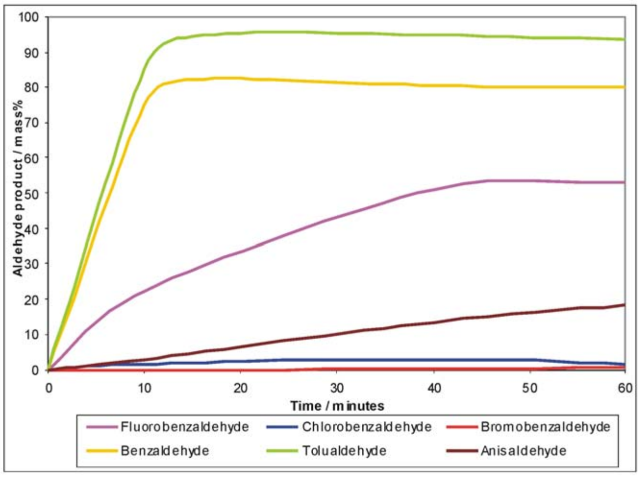
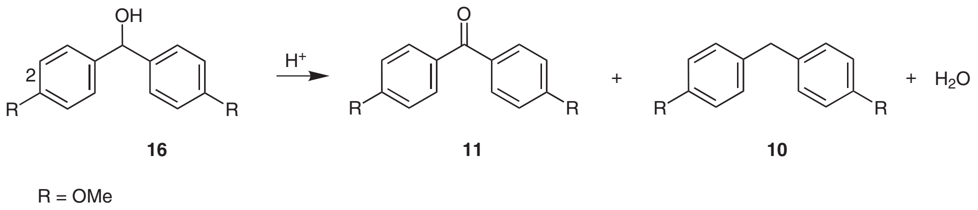


Figure 4 Aromatic aldehyde product distributions during the CO formylation of aromatic hydrocarbons in HF/BF_3 at 45 °C

The present study was also extended to the investigation of ionic liquids as reaction media. The unique properties of ionic liquids in general, allow these compounds to be versatile reagents and solvents for many reactions.[13] The enhanced reactivity and isomer selectivity brought about by ionic liquids in many reactions may also be applicable to phenolic derivatives used in CO formylations, hence the interest in exploring these possibilities. In our hands chloroaluminate ionic liquids promoted the carbonylation



Scheme 4

of alkylated aromatic compounds, but failed in the case of oxygenated aromatics. Toluene, anisole and phenol were successfully formylated in 1-butyl-3-methylimidazolium tetrafluoroborate ([BMIM]BF$_4$) following HF/BF$_3$ acidification (Table 2, entries 1, 2 and 3). In the case of toluene the expected aldehydes were obtained in low yields only, due to facile secondary reactions, while in the case of anisole, demethylation largely preceded formylation. The high selectivity (91%) towards aldehyde with respect to conversion (35%) in the case of phenol is significant, and can be attributed to the suppression of secondary reactions in this mechanism.

While it is known[13a] that the physical properties of ionic liquids can be changed by utilizing different cationic and anionic species, it has also been reported that the solubility of gasses such as CO, O$_2$ and H$_2$ are influenced by the constituents of a particular ionic liquid. In general, it has been found that imidazolium cations with increased chain length favours high CO solubility while this solubility is also enhanced by anions such as BF$_4^-$ and trifluoromethanesulfonimide (Tf$_2$N$^-$).[14] With this in mind the alkyl chain length of the cations was changed from butyl to octyl and the anions from BF$_4^-$ to PF$_6^-$ to Tf$_2$N$^-$. Changing the ionic liquid cation from BMIM to OMIM resulted in a threefold increase in the aldehyde yields for both phenol (Table 2, entries 3 and 4; 32% to 91%) and anisole (Table 2, entries 2 and 5; 8% to 28%). Substituting the BF$_4^-$ counter anion for PF$_6^-$ afforded slightly lower aldehyde yields for anisole (Table 2, entries 6 and 7). When the PF$_6^-$ counter anion was replaced with Tf$_2$N$^-$, however, significantly higher aldehyde yields (45%) were obtained for anisole (Table 2, entry 9); increasing the alkyl chain length resulted in a further improvement in the yield (Table 2, entries 9 and 10). The lower yields of PAA can be attributed to the formation of secondary products. The presence of even small amounts of moisture (0.3%) in the

Table 2 Formylation of Aromatic Substrates in Acidified Neutral Ionic Liquids

Entry	Substrate (mmol)	Ionic liquid (20 g)	Reagents (mmol)	Conditions	Products (%)	Conversion (%)
1	Toluene (11)	[BMIM]BF$_4$	HF (555), BF$_3$ (25)	45 °C, 12 h	p-MeC$_6$H$_4$CHO (5)	44
2	Anisole (11)	[BMIM]BF$_4$	HF (555), BF$_3$ (21)	45 °C, 12 h	p-MeOC$_6$H$_4$CHO (7)	
					o-MeOC$_6$H$_4$CHO (<1)	
					PhOH (21)	40
3	Phenol (11)	[BMIM]BF$_4$	HF (550), BF$_3$ (44)	45 °C, 12 h	p-HOC$_6$H$_4$CHO (31)	
					o-HOC$_6$H$_4$CHO (1)	35
4	Phenol (11)	[OMIM]BF$_4$	HF (550), BF$_3$ (69)	45 °C, 12 h	p-HOC$_6$H$_4$CHO (83)	
					o-HOC$_6$H$_4$CHO (8)	97
5	Anisole (11)	[OMIM]BF$_4$	HF (550), BF$_3$ (59)	45 °C, 12 h	p-MeOC$_6$H$_4$CHO (26)	
					o-MeOC$_6$H$_4$CHO (2)	99
6	Anisole (11)	[OMIM]BF$_4$	HF (550), BF$_3$ (81)	45 °C, 4.5 h	p-MeOC$_6$H$_4$CHO (26)	
					o-MeOC$_6$H$_4$CHO (2)	83
7	Anisole (11)	[OMIM]PF$_6$	HF (550), BF$_3$ (47)	45 °C, 4.5 h	p-MeOC$_6$H$_4$CHO (20)	
					o-MeOC$_6$H$_4$CHO (1)	84
8	Anisole (11)	[HMIM]PF$_6$	HF (550), BF$_3$ (61)	45 °C, 4.5 h	p-MeOC$_6$H$_4$CHO (15)	
					o-MeOC$_6$H$_4$CHO (1)	67
9	Anisole (11)	[OMIM]Tf$_2$N	HF (550), BF$_3$ (69)	45 °C, 4.5 h	p-MeOC$_6$H$_4$CHO (45)	
					o-MeOC$_6$H$_4$CHO (2)	90
10	Anisole (11)	[BMIM]Tf$_2$N	HF (550), BF$_3$ (63)	45 °, 1 h	p-MeOC$_6$H$_4$CHO (8)	
					o-MeOC$_6$H$_4$CHO (1)	
					PhOH (2)	30
11	Anisole (300)	[OMIM]Tf$_2$N	HF (600), BF$_3$ (150)	45 °C, 4.5 h	PhOH and o/p-MeC$_6$H$_4$OMe	76
12	Anisole (11)	[BMIM]Tf$_2$N	HF (550), BF$_3$ (35)	45 °, 4.5 h	–	–

ionic liquid was detrimental to the formylation reaction (Table 2, compare entries 12 and 10).

Anisole was subjected to formylation with reduced amounts of HF (2 equiv) and BF_3 (0.5 equiv) under otherwise similar reaction conditions (Table 2, entry 11). Although high conversions of anisole to phenol and alkylated phenol were observed, no aldehyde products were produced. It is thus clear that this particular type of ionic liquid is unable to facilitate the catalytic use of HF/BF_3 in formylation reactions. However, the effective formylation of phenol in OMIM, coupled with the recycling[6e,15] of HF and BF_3, is a possible commercially viable route to *p*-hydroxybenzaldehyde and these aspects are being investigated.

This study confirms that oxygenated aromatic compounds are less reactive towards acidic CO formylation than other substituted benzenes. This effect can be rationalised in terms of the relative acid/base properties of the substrate and CO. Super stoichiometric amounts of acid are required for acceptable rates and yields. Secondary product formation was shown to result mainly from acid-catalysed reactions between the substrate and the aldehyde product.

Aldehyde yields for formylation in the acidified neutral ionic liquids were generally similar to those of reactions conducted in HF as solvent/catalyst (cf. Table 1). The increase in aldehyde yields with the use of extended cationic alkyl chain lengths may be due to improved CO solubility. HF/BF_3-acidified neutral ionic liquids showed both increases in *para*-selectivity compared to HF as solvent and catalyst. Formylation of anisole and toluene, but not phenol, in neutral ionic liquids resulted in increased secondary product formation in comparison with HF as solvent/catalyst. The results show that phenol is a good substrate for formylation in this medium, particularly with reference to the suppression of by-product formation.

A 100 mL Parr reactor constructed from Hasteloy-C and equipped with a gas entrainment stirrer with variable speeds was used for the formylation reactions. Special PTFE seals were used as the normal acid resistant seals were incompatible with the HF/BF_3 combination. HF was purchased from Pelchem (99.95% purity). BF_3 was purchased from Messer Griesheim (99.98% purity).

GC was performed on a Hewlett-Packard 4890 Series II equipped with a capillary, non-polar PONA column (50 m × 0.25 mm id × 0.25 mm) with a glass liner split injector to quantify the reaction. NMR spectroscopy was conducted on a Bruker Avance 500 instrument. Unless stated otherwise, all NMR spectra were recorded in $CDCl_3$ at 30 °C with TMS as internal standard. A Hewlett-Packard HP5973 mass spectrometer equipped with a photon multiplier was used to determine the accurate mass and to record mass spectra. The molecular ion was generated via EI.

The structure of the formylation products and ionic liquids synthesised, *p*-anisaldehyde,[16] *o*-anisaldehyde,[17] 4,4′-dimethoxybenzophenone,[18] di(4-methoxyphenyl)methane,[19] tri(4-methoxyphenyl)methane,[20] *p*-methoxyacetophenone,[21] di(4-methoxyphenyl)methanol,[22] [BMIM]$AlCl_4$,[23] [EMIM]$AlCl_4$,[24] [BMIM]BF_4,[25] [OMIM]BF_4,[26] [BMIM]PF_6,[27] [OMIM]PF_6,[27] [BMIM]Tf_2N[28] and [OMIM]Tf_2N,[28] was confirmed by comparison of their ^1H NMR spectra and mass spectra with those published.

Formylation Reactions

Pre-cooled (4 °C) anhyd substrate (10–300 mmol) was added to the reactor in an ice-bath under N_2. This was followed by careful addition of HF (0.6–2.5 mol) at 4 °C from a 1-L cylinder.

Stirring was continued, the reactor lid was sealed and the reactor pressurised with BF_3 (20–300 mmol) until the required mass was obtained. The required CO pressure (50–80 bar, 99.99%) was applied and the resulting exotherm (3–10 °C) aided in heating the mixture to the required temperature. On completion of the reaction (10 min–24 h), the reactor was cooled in ice water, and the CO pressure was released as the reaction mixture reached a temperature of 5 °C. The reaction mixture was quenched in ice (500 mL) and extracted with Et_2O (4 × 20 mL). The acid was neutralised (pH 7) with an aq solution of K_2CO_3, the phases were separated and the organic phase was dried over Na_2SO_4. The course of the reaction was followed by GC analysis. Since no *meta*-aldehyde was produced during these formylations, the *meta*-analogue of each aldehyde was used as the internal standard for quantification, unless otherwise stated. Compounds formed in the formylation reaction were initially identified by analysis of the MS fragmentation patterns followed by direct comparison with authentic materials. The products were purified by column chromatography over silica gel.

Preparation of Di(4-methoxyphenyl)methanol

In a round bottom flask, 4,4′-dimethoxybenzophenone (10.0 g, 41.3 mmol) was dissolved in EtOH (200 mL) and THF (200 mL); $NaBH_4$ (1.6 g, 42.3 mmol) was added with stirring at r.t. An additional portion of $NaBH_4$ (2 g, 52.9 mmol) was added and stirring continued overnight. The reaction mixture was quenched with acetone (200 mL) and the solution was concentrated under vacuum (35 °C, 300 mBar). The resultant borate salt was dissolved in H_2O (100 mL) and the alcohol extracted with Et_2O (50 mL). The ethereal solution was concentrated under vacuum (40 °C, 120 mbar) to furnish white alcohol crystals in quantitative yield; water was removed from the crystals by azeotropic distillation with benzene.

Ionic Liquid Preparation

1-Butyl-3-methylimidazolium Chloride [BMIM]Cl, 1-Hexyl-3-methyl-imidazolium Chloride [HMIM]Cl and 1-Octyl-3-methylimidazolium Chloride [OMIM]Cl

1-Methylimidazole (99%) was freshly distilled from CaH_2 and stored under argon over 4 Å MS. A stirred mixture of distilled 1-methylimidazole (246 g, 3 mol) and anhyd alkyl halide (BuCl, 3.6 mol; HexCl, 1.6 mol; OctCl, 1.6 mol; 99.5%] was refluxed for 48 h under argon. Two layers formed, which were separated and the excess alkyl chloride was removed in vacuo at 120 °C overnight.

1-Butyl-3-methylimidazolium Trifluoromethanesulfonimide [BMIM]Tf_2N

To an aq solution of lithium bis(trifluoromethylsulfonyl)imide ($LiTf_2N$, 24.69 g, 0.086 mol, 30 mL) was added an aq solution of [BMIM]Cl (15.02 g, 0.086 mol, 30 mL) and the mixture was stirred for 2 hours at r.t. The [BMIM]Tf_2N produced was separated from the aqueous layer and washed with distilled H_2O (5 × 100 mL) to remove residual LiCl salt. The ionic liquid was subsequently heated at 120 °C under vacuum overnight to remove traces of water.

1-Octyl-3-methylimidazolium Trifluoromethanesulfonimide [OMIM]Tf_2N

To an aq solution of $LiTf_2N$ (24.69 g, 0.086 mol, 30 mL) was added an aq solution of [OMIM]Cl (19.85 g, 0.086 mol, 30 mL) and the mixture was stirred for 2 h at r.t. The [OMIM]Tf_2N produced was separated from the aqueous layer and washed with distilled H_2O (5 × 100 mL) to remove residual LiCl salt. The ionic liquid was subsequently heated in vacuo at 120 °C overnight to remove traces of water.

1-Butyl-3-methylimidazolium Tetrafluoroborate [BMIM]BF_4

BF_4H (48% aq solution; 89.36 g, 0.44 mol) was added dropwise with stirring to an aq solution of [BMIM]Cl (77.31 g, 0.44 mol, 140 mL) at 0 °C. When the addition of the BF_4H was complete, the temperature of the reaction medium was increased to 20 °C and the mixture left overnight. The ionic liquid was extracted with CH_2Cl_2 (5 × 80 mL), traces of unreacted BF_4H were removed by washing the organic phase with distilled H_2O (10 × 100 mL) and the organic phase was concentrated in vacuo overnight (120 °C).

1-Octyl-3-methylimidazolium Tetrafluoroborate [OMIM]BF_4

An aq solution of [OMIM]Cl (101.54 g, 0.44 mol, 140 mL) furnished [OMIM]BF_4 by a similar procedure to the one described above.

1-Butyl-3-methylimidazolium Hexafluorophosphate [BMIM]PF_6

To an aq stirred solution of [BMIM]Cl (118.19 g, 0.6773 mol, 150 mL) at 0 °C was added an aq solution of HPF_6 (60% solution; 200 mL, 1.5 equiv). The resulting bi-phasic system was stirred for 4 h, extracted with CH_2Cl_2 (5 × 80 mL) to remove the ionic liquid, the organic phase was washed with distilled H_2O (10 × 100 mL) to remove unreacted acid and the organic phase was concentrated in vacuo overnight (120 °C).

1-Hexyl-3-methylimidazolium Hexafluorophosphate [HMIM]PF_6

To a stirred solution of [BMIM]Cl (137.31 g, 0.6773 mol) and H_2O (150 mL) at 0 °C was added an aq solution of HPF_6 (60% solution; 200 mL, 1.5 equiv) slowly. The resulting bi-phasic system was stirred for 4 h, extracted with CH_2Cl_2 (5 × 80 mL), the organic phase was washed with distilled H_2O (10 × 100 mL) to remove the unreacted acid and the organic phase was concentrated in vacuo overnight (120 °C).

1-Octyl-3-methylimidazolium Hexafluorophosphate [OMIM[PF_6

An aq solution of [OMIM]Cl (156.30 g, 0.6773 mol) at 0 °C was added to an aq solution of HPF_6 (60% solution; 200 mL, 1.5 equiv), which furnished [OMIM]PF_6 by a similar procedure to the one described above.

1-Butyl-3-methylimidazolium Tetrachloroaluminate [BMIM]$AlCl_4$·0.67($AlCl_3$)

Freshly sublimed $AlCl_3$ (99.9%; 89.34 g, 0.67 mol) was carefully added to [BMIM]Cl (57.64 g, 0.33 mol) with stirring under an argon atmosphere. The resulting ionic liquid was stored under argon.

1-Butyl-3-methylimidazolium Tetrachloroaluminate [BMIM]$AlCl_4$·75($AlCl_3$)

Freshly sublimed $AlCl_3$ (99.9%; 100.0 g, 0.75 mol) was carefully added to [BMIM]Cl (43.67 g, 0.25 mol) with stirring under an argon atmosphere. The resulting ionic liquid was stored under argon.

1-Ethyl-3-methylimidazolium Tetrachloroaluminate [EMIM]$AlCl_4$·0.67($AlCl_3$)

Freshly sublimed $AlCl_3$ (99.9%; 89.34 g, 0.67 mol) was carefully added to [EMIM]Cl (48.38 g, 0.33 mol) with stirring under an argon atmosphere. The resulting ionic liquid was stored under argon.

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