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Selective fluorination of substituted trichloromethyl benzenes by HF in liquid phase: Preparation of fluorinated building blocks

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ABSTRACT

The selective fluorination by successive Cl/F exchanges of α,α,α-trichlorotoluene, substituted or not by a chlorine atom, was studied in the presence of HF as the fluorinating agent. The influence of the presence of a catalyst or a basic solvent (such as dioxane, pyridine, tributylphosphate) in order to control the fluorination was also investigated. In mild conditions (50 °C and after 1 h of reaction), HF in excess was required in order to obtained the trifluoromethylation by Cl/F exchanges. The presence of $SbCl_5$ in small amount activated the Cl/F exchanges and only a stoichiometric amount of HF was required whatever the chlorinated molecules. Selective mono and difluorination could be obtained by using basic solvents.

1. Introduction

The incorporation of fluorine, especially the $-CF_3$ group, into organic compound results in changes in the physical, chemical and biological properties [1–3]. These changes make them suitable for diverse applications in the areas of material science, agrochemistry and pharmaceuticals [4–6]. While a wide variety of methods have been developed for introducing trifluoromethyl groups into organic molecules [7–11], the fluorine–chlorine exchange is the most widely used technology in industrial scale especially for the selective synthesis of fluorinated building blocks. This reaction can be carried out using two different sources of fluorine: alkali metal fluorides, such as potassium fluoride (KF) [12], or anhydrous hydrogen fluoride (HF). Although KF is more safe and cheap to use, some organic compounds need more vigorous conditions to be fluorinated and in this case HF is required. The reaction between hydrofluoric acid and an organic halide can be carried out either in vapour phase or in liquid phase. Moreover in both cases, the use of Lewis acid as catalyst can improve the reaction. The most commonly used in liquid phase fluorination reactions are antimony pentachloride ($SbCl_5$) or antimony mixed halides [13]. Even if antimony chlorides suffer from the fact that they are very corrosive and they can be reduced from Sb^V to Sb^{III}, to lead to a deactivation of the catalytic system (Sb^{III} halides are inert) [14], antimony chlorides are very powerful catalysts for fluorination reactions. That is why they are used in industrial scale reactions [15–17]. The catalytic processes offer a lot of advantages from classical chemistry. Indeed, the catalytic fluorination with HF as the fluorinating agent and a catalyst such as $SbCl_5$ for the fluorination of chlorinated molecules such as chlorinated hydrocarbon (to produce hydrofluorocarbon) and chlorinated aromatics (to produce building blocks) which involved only Cl/F exchanges lead to high degree of fluorinated molecules and only to HCl as the by-product. Only a few examples of catalytic fluorination reactions have been reported in the academic literature.

Previous works [17] have been carried out on the fluorination of trichloromethoxy-benzene by liquid HF with various Lewis acids as catalysts. Only Lewis acids with an oxidation state of +V are efficient and $SbCl_5$ is the most powerful. The efficiency of these Lewis acids is due to there abilities to form nucleophilic complexes in the presence of HF. Indeed, the presence of few amount of the catalyst favoured the last Cl/F exchange to produce fluoromethoxy-benzene only in stoichiometric amount of HF and at a temperature of 50 °C. Moreover, few works in the literature reported selective fluorination in the presence of a solvent [18–22]. HF–pyridine is well known to be a good fluorinating agent.

This paper deals with the operating conditions for the fluorination of chlorinated compounds and more particularly of trichloromethyl benzene substituted or not by a chlorine atom. Indeed the presence of chlorine atom which is an attractive atom

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Table 1
Effect of the amount of HF in the transformation of various trichloromethyl benzenes (P_i = 10 bar, time = 1 h, T = 50 °C, substrate = 0.2 mol).

Substrate	HF/substrate molar ratio	Conversion (mol%)[a]	Yield (mol%)[b]	Selectivity[c] (%)		
				R-CCl_2F	R-$CClF_2$	R-CF_3
TCT[d]	1	79	79	66	33	1
	2	99	95	3	84	13
	3	100	99	0	19	81
	4	100	89	0	4	96
4CTCT[e]	1	87	68	70	29	2
	2	100	85	2	86	12
	3	100	87	1	71	28
	4	100	82	2	2	96
2CTCT[f]	1	71	66	74	24	2
	2	100	100	3	96	1
	3	100	84	1	41	58
	4	100	82	2	2	96
TCMB[g]	3	100	93	0	98	2

[a] Amount of substrate transformed.
[b] Molar amount of fluorinated products (by-products excepted).
[c] Amount of mono, di and trifluorinated compounds.
[d] α,α,α-Trichlorotoluene, R = Ph.
[e] 4-Chloro-α,α,α-trichlorotoluene, R = *p*-Cl-Ph.
[f] 2-Chloro-α,α,α-trichlorotoluene, R = *o*-Cl-Ph.
[g] Trichloromethoxy-benzene.

(in position ortho or para) in the aromatic ring could modify the reactivity of the $-CCl_3$ group. Consequently, the influence of the substitution on the aromatic ring, the amount of HF used as fluorine source and $SbCl_5$ used as the catalyst on the reaction has been studied. Selective fluorinations (mono and di) were also studied by using various HF-base systems with dioxane, tributylphosphate or pyridine as base.

2. Results and discussion

2.1. Fluorination of trichloromethyl benzenes

The fluorination of different chlorinated molecules (α,α,α-trichlorotoluene, TCT; 4-chloro-α,α,α-trichlorotoluene, 4CTCT; 2-chloro-α,α,α-trichlorotoluene, 2CTCT) was carried out for 1 h at 50 °C with different amounts (from 1 to 4 equiv. from chlorine atoms) of HF (Table 1). The conversion corresponds to the amount of the substrate which is transformed into fluorinated products and the yield to the sum of molar percentages of mono, di and trifluorinated products. In all reactions, yields were good.

When 1 equiv. of HF was added to the reaction medium, the conversion of chlorinated substrates was not total and only traces of trifluorinated products were obtained. Whatever the trichlorinated compounds, the monofluorinated compound was the major product (66–74%) but the difluorinated compound was also present (24–33%). While the amount of HF increased to 2 equiv., the amount of difluorination reaction product increased from 84% to 96% and conversions became complete. The product of trifluorination was isolated (from 1% to 13%). The different molecules tested had similar reactivities with 1 or 2 equiv. of HF. The presence of the chlorine atom in 2 or 4 position on the aromatic ring or the monofluorination of the $-CCl_3$ group did not change the reactivity of the substrate for the last two Cl/F exchanges. Theses experiments confirmed that the two first Cl/F exchanges were very fast.

With 3 equiv. of hydrogen fluoride (corresponding to the stoichiometric amount for the total Cl/F exchanges for the $-CCl_3$ group), the trichlorotoluene (TCT) appeared to be the most reactive and 81% of trifluorotoluene (TFT) was isolated. However, for the 2-chloro-trichlorotoluene (2CTCT), 58% of trifluorination product was obtained and only 28% of the para compound (4CTCT). Only small amount of trifluoromethoxy-benzene (2%) was isolated from trichloromethoxy-benzene (TCMB) under theses conditions.

When 4 equiv. of HF were added, the trifluorination was almost total in all cases.

The results showed that the first two Cl/F exchanges were rather fast and that the last one was the slowest. This is in accordance with other studies on the fluorination of aliphatic chlorinated compounds [23]. In fact, the presence of two fluorine atoms on carbon atom makes the rupture of the last C–Cl bond more difficult due to the high electronegativity of the fluorine atom.

The trichloromethoxy-benzene (TCMB) is less reactive than the other chlorinated compounds. Indeed, the presence of the methoxy group and mainly the presence of the oxygen modified the electronegativity and consequently the C–Cl bond rupture. In this case, the last Cl/F exchange was inhibited with 3 equiv. of HF (Table 1). The presence of chlorine atom on benzene ring modified the reactivity of the –C–Cl bond of the $-CCl_3$ group and disfavoured also the third Cl/F exchange. Indeed, the presence of the chlorine atom on benzene ring modified the selectivity towards the trifluoromethylation of the $-CCl_3$ group. Morevover, the 2-chloro-α,α,α-trichlorotoluene was more reactive than the 4-chloro-α,α,α-trichlorotoluene. These results show that the para position is more deactivated than ortho position. These observations are in accordance with the other work performing on acidity of aromatic compounds [24,25]. It has been shown that acidities of chloro benzoic acid and chloro phenol are more significant when the chlorine atom is in para position than in ortho position. Therefore the electron-withdrawing power of chlorine is increased for the para position.

2.2. Effect of the presence of $SbCl_5$

The effect of the presence of antimony pentachloride as catalyst (2 mol%) was studied in the same conditions (Table 2). Whatever the chlorinated compounds, the reaction of trifluorination was almost complete. All yields were goods (77–92%) with three equivalents.

With 1 equiv. of HF, the conversion was not total in all cases (54–60%). The product obtained was the product of trifluoromethylation (78–82%). Small amount of mono or difluorinated product were also isolated. The increase of the amount of HF to 2

Table 2
Effect of the amount of HF in the transformation of various trichloromethyl benzenes in the presence of $SbCl_5$ (P_i = 10 bar, time = 1 h, T = 50 °C, substrate = 0.2 mol, $SbCl_5$ = 0.004 mol: 2 mol%).

Substrate	HF/substrate molar ratio	Conversion. (mol%)[a]	Yield (mol%)[b]	Selectivity[c] (%)		
				R-CCl_2F	R-$CClF_2$	R-CF_3
TCT[d]	1	54	40	8	10	82
	2	87	74	3	5	92
	3	98	77	0	3	100
4CTCT[e]	1	60	45	9	12	79
	2	83	63	3	8	89
	3	100	84	0	0	100
2CTCT[f]	1	58	41	10	12	78
	2	81	63	4	8	88
	3	100	92	0	0	100
TCMB[g]	3	100	86	0	0	100

[a] Amount of substrate transformed.
[b] Molar amount of fluorinated products (by-products excepted).
[c] Amount of mono, di and trifluorinated compounds.
[d] α,α,α-Trichlorotoluene, R = Ph.
[e] 4-Chloro-α,α,α-trichlorotoluene, R = *p*-Cl-Ph.
[f] 2-Chloro-α,α,α-trichlorotoluene, R = *o*-Cl-Ph.
[g] Trichloromethoxy-benzene, R = Ph-O.

and 3 equiv. led to an increase to the conversion whatever the substrate with selectivity towards the trifluoromethylation product of 100%. No significant selectivity was observed by the increase of the amount of HF.

For all molecules studied, the catalyst enabled the selective formation of trifluoromethylated compound even if a sub-stoichiometric amount of HF was used. With only 2% of $SbCl_5$ and a stoichiometric amount of HF, α,α,α-trichlorotoluene and trichloromethoxy-benzene had the same reactivity. The conversion was complete for both molecules. Trifluorotoluene and trifluoromethoxy-benzene were isolated with good selectivity (100%). Moreover, the presence of the catalyst inhibited effects of substitution. Whatever the substituent position on the aromatic ring, all molecules tested showed the same reactivity to the trifluorination reaction. The trifluoromethylated product was always the major product. With $SbCl_5$, a stoichiometric amount of HF was enough to obtain a selectivity of 100% of trifluorinated products with good to excellent yields (77–92%).

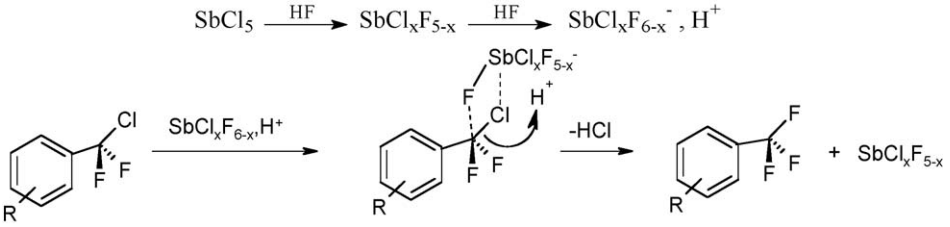
For each substrate, no secondary product corresponding to the Friedel–Craft products was observed. Moreover, there was no product of substitution of the chlorine atom on aromatic ring by a fluorine atom. Only chlorine atoms on the methyl group were exchanged by fluorine atom, even if $SbCl_5$ was used.

These results confirm that $SbCl_5$ is effective to activate the last Cl/F exchange. This is in accordance with other works performed on fluorination of trichloromethoxy-benzene [19] or other substrates [28–32]. The activity of antimony pentachloride is related to its ability to form mixed halides and to its strong Lewis acidity. In the presence of HF, $SbCl_5$ can form species such as $SbCl_xF_{5-x}$ which could give protons and very reactive nucleophilic species (Scheme 1). A SN_2 concerted mechanism can be proposed to explain the last Cl/F exchange as reported for fluorination of aliphatic chlorinated molecules [26–30].

2.3. Fluorination by HF-base system

It could be possible to produce selectively the mono or difluorinated compounds in the presence of HF and a basic solvent such as dioxane, tributylphosphate (TBP) or pyridine. As reported in the literature, pyridine was more basic than dioxane and tributylphosphate [31]. The presence of a basic solvent in the reaction, allowed the selective fluorination of the different substrates and the production with good selectivity of the mono or difluorinated products. All reactions were carried out in the same conditions as described before (50 °C, 1 h, P = 10 bar of N_2).

The change of the conversion, the yield in fluorinated products and the selectivity towards mono and difluorination are respectively reported in Table 3 with the introduction of dioxane, in Table 4 with pyridine, and in Table 5 with tributylphosphate. The introduction of dioxane allows the control of the fluorination whatever the chlorinated starting materials. Whatever the amount of HF used, no more trifluorinated products were produced. With a HF/dioxane ratio of 3.5, the conversion of α,α,α-trichlorotoluene was around 57% and the monofluorinated products was isolated with a selectivity of 94%. For the 4-chloro-α,α,α-trichlorotoluene and the 4-chloro-α,α,α-trichlorotoluene, the monofluorinated product could be isolated with a selectivity of 82% and 94% with respectively an HF/dioxane ratio of 4 or 6 (Table 3). Increasing the HF/dioxane ratio to 5 for the α,α,α-trichlorotoluene and 6 for the 4-chloro-α,α,α-trichlorotoluene, the conversion of the substrate increased respectively to 95% and 97%. Moreover the difluorinated product was isolated with a selectivity of 84% for the α,α,α-



Scheme 1. Formation of mixed halides of antimony and mechanism of Cl/F exchange by nucleophilic substitution.

Table 3
Effect of the amount of HF/dioxane in the transformation of various trichloromethyl benzenes (P_i = 10 bar, time = 1 h, T = 50 °C, substrate = 0.2 mol).

Substrate	HF/diox	HF/substrate	Conversion (mol%)[a]	Yield (mol%)[b]	Selectivity[c] (%)		
					R-CCl_2F (%)	R-$CClF_2$ (%)	R-CF_3 (%)
TCT[d]	–	4	100	89	–	4	96
	3.5	6	57	51	94	6	–
	5	9	95	87	12	84	4
4CTCT[e]	–	4	100	82	2	2	96
	4	7	56	50	82	18	–
	6	11	97	76	18	78	4
2CTCT[f]	–	4	100	82	2	2	96
	6	11	62	35	94	6	–

[a] Amount of substrate transformed.
[b] Molar amount of fluorinated products (by-products excepted).
[c] Amount of mono, di and trifluorinated compounds.
[d] α,α,α-Trichlorotoluene, R = Ph.
[e] 4-Chloro-α,α,α-trichlorotoluene, R = *p*-Cl-Ph.
[f] 2-Chloro-α,α,α-trichlorotoluene, R = *o*-Cl-Ph.

Table 4
Effect of the amount of HF/pyridine in the fluorination of various trichloromethyl benzenes in the presence of $SbCl_5$ (P_i = 10 bar, time = 1 h, T = 50 °C, substrate = 0.2 mol).

Substrate	HF/pyridine	HF/substrate	Conversion (mol%)[a]	Yield (mol%)[b]	Selectivity[c] (%)		
					R-CCl_2F (%)	R-$CClF_2$ (%)	R-CF_3 (%)
TCT[d]	–	4	100	89	–	4	96
	5	10	43	33	80	20	–
	7	14	97	83	13	78	9
4CTCT[e]	–	4	100	82	2	2	96
	7	14	41	35	88	12	–
2CTCT[f]	–	4	100	82	2	2	96
	7	14	10	10	100	–	–

[a] Amount of substrate transformed.
[b] Molar amount of fluorinated products (by-products excepted).
[c] Amount of mono, di and trifluorinated compounds.
[d] α,α,α-Trichlorotoluene, R = Ph.
[e] 4-Chloro-α,α,α-trichlorotoluene, R = *p*-Cl-Ph.
[f] 2-Chloro-α,α,α-trichlorotoluene, R = *o*-Cl-Ph.

Table 5
Effect of the amount of HF/tributylphosphate (TBP) in the transformation of various trichloromethyl benzenes (P_i = 10 bar, time = 1 h, T = 50 °C, substrate = 0.2 mol).

Substrate	HF/TBP	HF/substrate	Conversion (mol%)[a]	Yield (mol%)[b]	Selectivity[c] (%)		
					R-CCl_2F (%)	R-$CClF_2$ (%)	R-CF_3 (%)
TCT[d]	–	3	100	99	–	19	81
	5	3	58	51	90	10	–
	7	4	92	75	47	52	1
4CTCT[e]	–	3	100	87	1	71	28
	6	3.5	83	74	77	23	–
2CTCT[f]	–	3	100	84	1	41	58
	6	3.5	51	41	99	1	–

[a] Amount of substrate transformed.
[b] Molar amount of fluorinated products (by-products excepted).
[c] Amount of mono, di and trifluorinated compounds.
[d] α,α,α-Trichlorotoluene, R = Ph.
[e] 4-Chloro-α,α,α-trichlorotoluene, R = *p*-Cl-Ph.
[f] 2-Chloro-α,α,α-trichlorotoluene, R = *o*-Cl-Ph.

trichlorotoluene and 78% for the 4-chloro-α,α,α-trichlorotoluene. For the 2-chloro-α,α,α-trichlorotoluene, no difluorinated product could be isolated with good selectivity even increasing the amount of HF.

As with dioxane, the presence of pyridine slowed down the reaction and no trifluorinated product was formed whatever the amount of HF introduced (Table 4). For the α,α,α-trichlorotoluene, an increase of the amount of HF, from a HF/pyridine ratio from 5 to 7, led to an increase of the conversion from 43% to 97%. The selectivity depends on the amount of HF used. With HF/pyridine = 5, monofluorinated was formed with a selectivity of 80%. The increase of the HF/pyridine ratio to 7 allowed the formation of the difluorinated product with 78% of selectivity. In the case of the 4-chloro-α,α,α-trichlorotoluene, the conversion was 41% with a HF/pyridine ratio of 7 and only the monofluorinated product could be isolated with a good selectivity (88%). The

Table 6
Effect of the presence of $SbCl_5$ in the transfomation of α,α,α-trichlorotoluene (TCT) (P_i = 10 bar, time = 1 h, T = 50 °C, substrate = 0.2 mol, $SbCl_5$ = 0.004 mol: 2 mol%).

Solvent	Catalyst	HF/TCT[a]	Conversion. (mol%)[b]	Yield (mol%)[c]	Selectivity[d] (%)		
					R-CCl_2F (%)	R-$CClF_2$ (%)	R-CF_3(%)
Dioxane (HF/diox = 2)	–	3.5	5	5	100	0	0
	$SbCl_5$	3.5	44	33	90	10	0
Pyridine (HF/py = 4)	–	8	23	20	99	1	0
	$SbCl_5$	8	34	17	77	17	6
TBP[e] (HF/TBP = 7)	–	4	92	75	47	52	<1
	$SbCl_5$	4	97	79	15	82	3

[a] α,α,α-Trichlorotoluene, R = Ph.
[b] Amount of substrate transformed.
[c] Molar amount of fluorinated products (by-products excepted).
[d] Amount of mono, di and trifluorinated compounds.
[e] Tributylphosphate.

2-chloro-α,α,α-trichlorotoluene was the less reactive substrate and in the same conditions as for the 4-chloro-α,α,α-trichlorotoluene, the conversion was only 10%.

The introduction of tributylphosphate (TBP) during the reaction was less selective than dioxane or pyridine (Table 5). For the α,α,α-trichlorotoluene, without tributylphosphate and with 3 equiv. of HF with respect of the substrate, the conversion was 100% and the major product was the trifluorinated compound (81% of selectivity). The introduction of tributylphospate (HF/tributylphosphate = 5) led to a decrease of the conversion to 58% and under these conditions the monofluorinated product was formed with a selectivity of 90%. The selectivity of the difluorinated product increased to 52% when the ratio HF/tributylphosphate raised to 7. In the case of a substituted molecules (4-chloro-α,α,α-trichlorotoluene and 2-chloro-α,α,α-trichlorotoluene), the introduction of tributylphosphate (HF/tributylphosphate = 6) in the reaction medium led to the formation of the monofluorinated products with a selectivity of 77% for the 4-chloro-α,α,α-trichlorotoluene and 99% for the 2-chloro-α,α,α-trichlorotoluene.

These results show that the introduction of a basic solvent slows down the reaction of halogen exchange which allows the selective formation of mono or difluorinated products. On the other hand, as reported previously, the presence of a chlorine atom, on the aromatic ring, deactivated the Cl/F exchanges. A higher amount of HF was required to obtain good conversions of substrates. Moreover, it is well known that HF molecules form polymers and decrease the nucleophilicity in anhydrous conditions [32]. The basic solvent could complex a part of this polymer and decreases the acidity of the medium and the nucleophilic of the fluoride atom as reported in the literature for pyridine [20]. Two sources of nucleophilic fluoride could be present, one from free HF and the other from the complex HF-base. The formation of the mono and difluorinated products depends on the amount of these two fluorine sources. If all HF was complexed with the heteroatom of the basic solvent (oxygen or nitrogen atoms), mainly the mono fluorination was observed whatever the chlorinated substrates. If the amount of HF was too high, the fluorination of the chlorinated molecules involved two sources of nucleophilic fluoride and the reaction was less selective. Indeed, a mixture of mono and difluorinated products was observed as reported for the transformation of α,α,α-trichlorotoluene. These results show that it could be possible to adapt the amount of HF and the basic solvent to the reactivity of the chlorinated starting molecule in order to produce selectively the mono or difluorinated compound.

The impact of the presence of $SbCl_5$ (2 mol%) as the catalyst was studied on the fluorination reaction of α,α,α-trichlorotoluene by HF-base system (Table 6) in order to enhance the conversion and/or the selectivity of mono and difluorinated products. The ratio between HF and the basic compound was chosen in order to show the influence on the conversion and the selectivities. Consequently, the different ratios were 2 for HF/dioxane, 4 for HF/pyridine and 7 for HF/tributylphosphate. With HF–dioxane system (HF/dioxane = 2), the presence of 2% of $SbCl_5$ allowed an increase of the conversion from 5% to 44% and in the same time, the selectivity waited in favour of the monofluorinated product (90%). In the case of the HF–pyridine system (HF/pyridine = 4), the increase of conversion was quite low (from 23% to 34%) and the addition of catalyst led to decrease the selectivity of monofluorinated product (from 99% to 77%) and the formation of the difluorinated and trifluorinated products appeared. The transformation in the presence of tributylphosphate (HF/tributylphosphate = 7) and $SbCl_5$ (2%) led to the selective formation of the difluorinated product with a selectivity of 82%. In this case, the presence of the catalyst allowed the increase of the selectivity from 52% to 82%. The conversion in both cases was around 100%.

These results show that with the HF–dioxane system, the presence of $SbCl_5$ could activate the C–Cl bond and favour the Cl/F exchange without modification of the selectivity. This could also correspond to the formation of a complex between HF and the Lewis acid as reported previously in different works [19,28–32]. This system could have an increased nucleophilicity compared to HF-base alone (Scheme 1). With dioxane, in conditions which disfavour the fluorination reaction, the formation of a mixed halide allows the transformation of the α,α,α-trichlorotoluene and the formation of the monofluorinated product. In the case of tributylphosphate which is less basic than dioxane, the formation of a mixed halide promotes the halogen exchange and the selective formation of the difluorinated product. The effect of the catalyst is very low in the presence of pyridine as the basic solvent due to the high basicity of pyridine.

3. Conclusion

Based on our finding, we can conclude that the selective trifluoromethylation of the corresponding chlorinated compounds was obtained by successive Cl/F exchanges under mild conditions with antimony pentachloride as catalyst and HF in stoichiometric amount as fluoride source. At 50 °C with 2% of $SbCl_5$ and a stoichiometric amount of HF the conversion of trichlorinated substrates is complete and the selectivity towards the trifluoromethylation is close to 100%. Moreover the presence of the catalyst inhibits the effects of substituents on benzene ring. On the other hand, the introduction of basic solvent (dioxane, pyridine or tributylphosphate) allows the selective formation of the mono or difluorinated products depending on the HF-base amount that modulates the nucleophilicity of the fluoride source. Finally, the introduction of a catalyst with the HF-base system can increase

either the conversion or selectivity of mono or difluorinated products. Depending of the fluorinating system, it could be possible to adapt the operating conditions in order to prepare selectively the mono, di or trichlorinated compound with a good conversion of the starting materials.

4. Experimental

4.1. Chemical products

All commercially available reagents were used without further purification. Hydrogen fluoride was purchased from Air Liquid; $SbCl_5$ from VWR; α,α,α-trichlorotoluene, 2-chloro-α,α,α-trichlorotoluene, 4-chloro-α,α,α-trichlorotoluene, dioxane, pyridine and tributylphosphate from Aldrich and $C_6H_5OCCl_3$ was kindly provided by Rhodia.

4.2. General experimental procedure

All reactions were performed in a 100 mL stainless steel autoclave under an initial pressure of 10 bar. The temperature was regulated and controlled by means of a thermocouple placed in a thermometric well in the furnace wall. At the early stage of the experiment, the substrate (0.125 mol) depending on the experiment, the basic solvent (19 ml) and the catalyst (2.5 mmol) were introduced in the autoclave. The difference in temperature between an HF cylinder warmed by means of a heating cord and the autoclave cooled in liquid nitrogen enabled the required amount of HF to be transferred to the reaction medium. The reaction then took place with continuous stirring, at the desired temperature (50 °C) and under autogene pressure. At the end of the reaction, the autoclave was cooled down and vented with dry dinitrogen in order to eliminate the HCl and the unreacted HF. The contents were quenched with 30 mL of water/dichloromethane mixture (50/50), using a 316 L stainless steel tank. After extraction with CH_2Cl_2, the organic phase was dried with $MgSO_4$ and analysed by GC. The fluorinated products and the chlorinated reactant were quantified by gas chromatography using bromobenzene as internal standard. The yield corresponds to the mol% of the various chlorinated compounds transformed into the corresponding fluorinated compounds. The difference between conversion and yield corresponds to non-identified by-products and the discrepancy of the experiment.

The chromatograph was a Varian 3380 equipped with 30 m VF-5ms (Varian) capillary column (inside diameter: 0.25 mm; film thickness: 1 μm) with a temperature program from 80 °C to 200 °C (5 °C/min) and then from 200 °C to 300 °C (10 °C/min).

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