

The effect of substituents and operating conditions on the electrochemical fluorination of alkyl phenylacetates in Et₃N·4HF medium

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Abstract

Selective electrochemical fluorination of alkyl phenylacetates (Ph–CH₂–COOR, where R is methyl, ethyl, *n*-propyl, *n*-butyl, *i*-propyl and *sec*-butyl) under galvanostatic conditions were reported in Et₃N·4HF medium. Preparative electrolysis experiments were carried out both in pre-electrolysed dry Et₃N·4HF and the same electrolyte medium without pre-electrolysis. Very little hydrolysed fluorinated products were obtained in pre-electrolysed medium where as significant quantities of hydrolysed products leading to fluorinated phenylacetic acid were obtained from Et₃N·4HF without pre-electrolysis. Under optimum experimental conditions up to 87% selectivity of monofluoro ester could be achieved. Difluoro alkyl phenylacetate, monofluoro and difluoro phenylacetic acids were the other predominant side products obtained. The hydrolysis appears to be initiated by tautomeric transformation of proton after the initial electro oxidative formation of the cation radical. ¹⁹F as well as ¹H NMR spectroscopy have been employed to identify the minor constituents formed during the electro oxidative process.

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Keywords: Selective electrochemical fluorination; Et₃N·4HF; Alkyl phenylacetates; α-Fluoro phenylacetates

1. Introduction

α-Fluoro carbonyl derivatives themselves are of importance and these can also be used as building blocks to synthesize more complex drug molecules, in which the α-fluorine is able to modify the biological activity [1–4]. Despite the availability of multi-step chemical routes, efforts to synthesize these molecules through single step electrochemical partial fluorination route also continue.

For partial fluorination of aromatic compounds by electrochemical method in fluoride containing solvent-free electrolyte systems has been extensively studied and reviewed [5–8]. These studies indicate high selectivity towards fluorination of active methylene group attached to sulfur atom [5–8]. Relatively few reports on partial fluorination of phenylacetic acid and its derivatives are available in the literature. Selective fluorination at benzylic position and chiral substituents was reported by Laurent and co-workers [9,10]. Ethyl phenylacetate was chemically fluorinated with perchloryl fluoride. Even with

this powerful fluorinating agent, the yield obtained was around 56% [4]. Quite recently Yoneda co-workers have reported 17% yield during the selective electrochemical fluorination of ethyl phenylacetate in dichloromethane using different supporting electrolytes [11]. A brief report by Cao and Fuchigami is also available [12].

Solvent-free electrolytes have been used as the media for compounds, which are relatively more difficult to oxidize [5,7]. Et₃N·3HF [13,14], Et₄NF·*n*HF [15–20] and Et₃N·5HF [21,22] are the most commonly employed solvent-free electrolyte media for partial fluorination. The selective fluorination of benzyl cyanide [23] and cyclic ethers [24] has been achieved in these systems.

In the present work, partial fluorination of methyl, ethyl, *n*-propyl, *n*-butyl, *i*-propyl and *sec*-butyl esters of phenylacetic acid in solvent-free Et₃N·4HF medium is reported. Efforts are made to optimize the galvanostatic experimental condition to achieve higher selectivity of fluorinated products namely α-fluoro esters and α-fluoro phenylacetic acid. In addition to evaluating the effect of pre-electrolysis of solvent-free electrolyte system, the present work also attempts to study the effects of alkyl substituents as well as excessive electric charge on the product selectivity and distribution.

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2. Results and discussion

Selectivity between fluorinated esters and fluorinated free acid was found to be highly dependent on moisture content in the reaction medium. The effects of pre-electrolysis on the voltammetric responses were evaluated. Fig. 1(a) shows the cyclic voltammetric response of $\text{Et}_3\text{N}\cdot 4\text{HF}$ prior to pre-electrolysis. Slightly higher background current is noticed above 0.5 V in this medium. A small anodic wave is also observed around 1.7 V. After pre-electrolysis noticeable background current was observed only above 1.0 V (Fig. 1(b)). The anodic wave also disappears completely after the pre-electrolysis.

Typical cyclic voltammograms for different concentration of ethyl and butyl phenylacetates on platinum electrode in pre-electrolysed $\text{Et}_3\text{N}\cdot 4\text{HF}$ medium are presented in Figs. 2 and 3, respectively, along with the background current. The electro oxidation occurs along with supporting electrolyte oxidation and hence the anodic peaks are found to be merged with background oxidation current. However, the oxidation process for butyl phenylacetate is initiated at around 1.35 V as shown in Fig. 3, whereas the oxidation process for ethyl phenylacetate occurs only beyond 1.45 V as shown in Fig. 2. This suggests that increasing the size of alkyl substituents facilitates the electrochemical oxidation process. Under identical concentration and sweep rate, the anodic peak current for butyl phenylacetate was found to be lower than that of the corresponding ethyl phenylacetate. This may be due to either blocking type of adsorption or decrease in the diffusion coefficient as a result of increase in the molecular size.

Monofluoro alkyl esters (2a–f) were observed to be the predominant products during the electrochemical fluorination in pre-electrolysed $\text{Et}_3\text{N}\cdot 4\text{HF}$ medium (Scheme 1, Table 1).

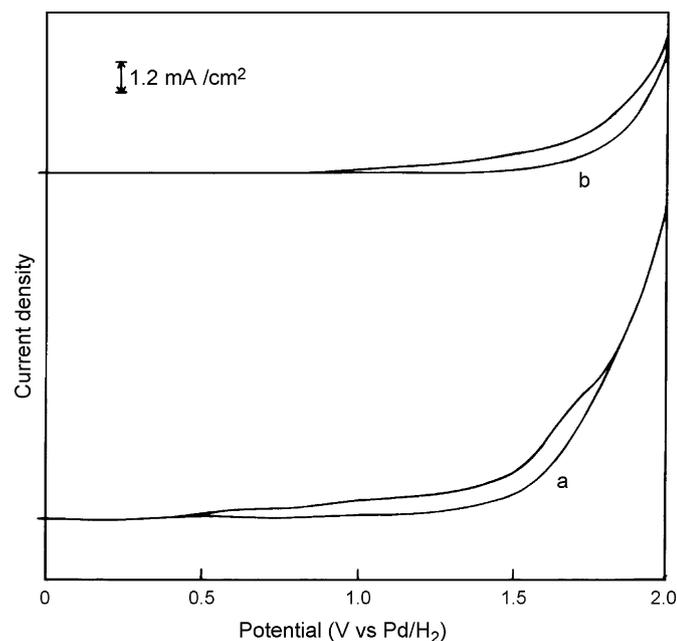


Fig. 1. Typical background cyclic voltammogram of $\text{Et}_3\text{N}\cdot 4\text{HF}$ on Pt electrode with out (a) and with (b) pre-electrolysed electrolyte at a scan rate (ν) of 10 mV/s.

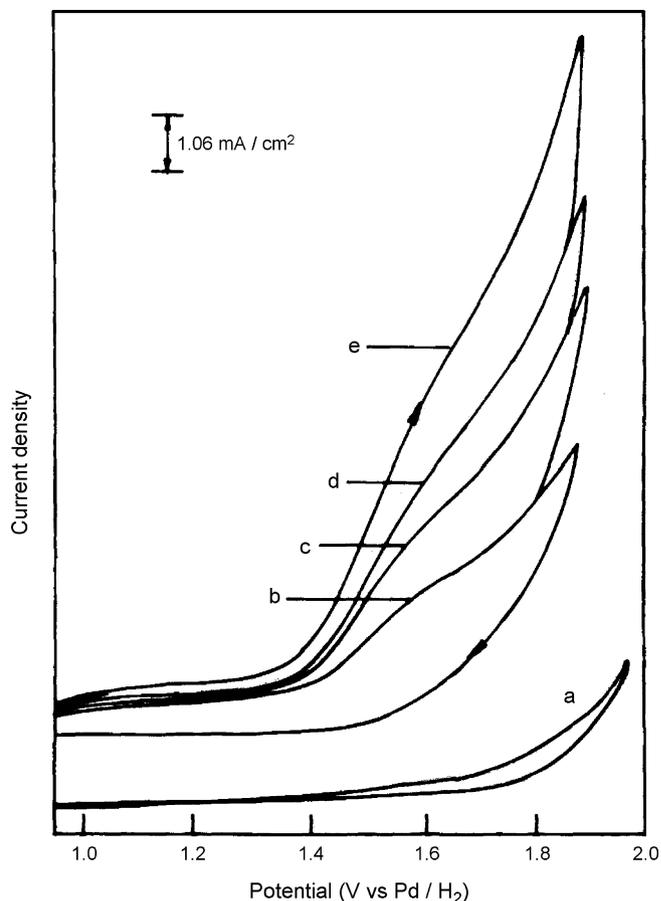


Fig. 2. Typical cyclic voltammogram of 1b in $\text{Et}_3\text{N}\cdot 4\text{HF}$ on Pt electrode at different concentrations b–e = 10, 20, 30, 40 mM, respectively, $\nu = 10$ mV/s. Where (a) is background current.

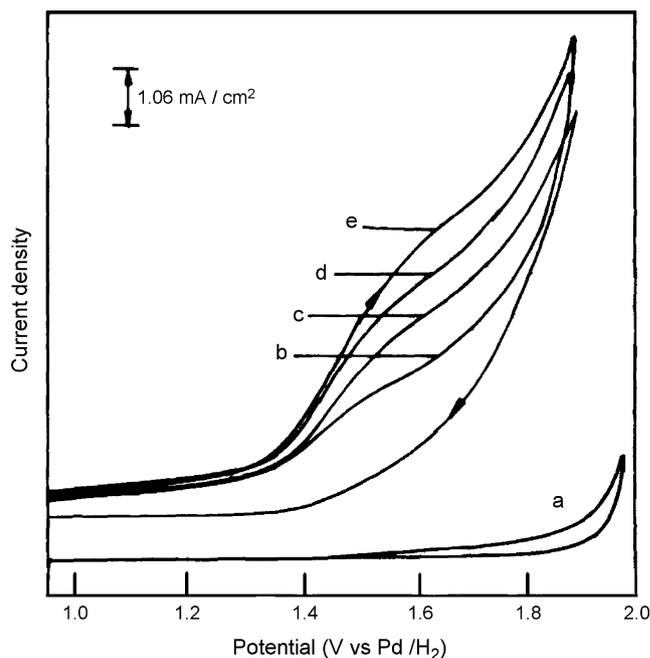
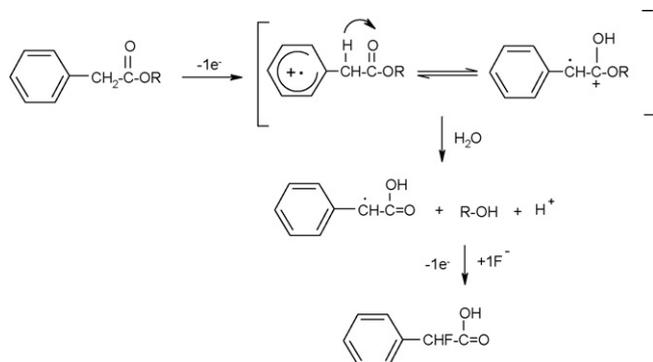


Fig. 3. Typical cyclic voltammogram of 1d in $\text{Et}_3\text{N}\cdot 4\text{HF}$ on Pt electrode at different concentrations b–e = 10, 20, 30, 40 mM, respectively, $\nu = 10$ mV/s. Where (a) is background current.



Scheme 3. Schematic representation of hydrolysis of ester during selective electrochemical fluorination.

Formation of significant quantities of fluorinated acids during the partial fluorination of **1a–f** was an important observation made during this work. The hydrolysis of ester does not occur in blank experiments in the same electrolyte medium, as long as no electric charge was passed. This indicates that the hydrolysis is induced by electron transfer. It appears that the electro-generated cation radical undergoes a tautomerism with adjacent carbonyl group as proposed in Scheme 3, which facilitates hydrolysis with trace level water present in the electrolyte medium.

The intermediate Ph-CH-COOH undergoes further electron transfer followed by fluoride addition leading to the formation

of monofluoro acid. It appears that by controlling the moisture content one can enhance the yield of fluorinated ester rather than the acid.

As indicated in Scheme 1, **1a–f** investigated in this work were found to give measurable quantities of esters **2a–f** and **3a–f** as well as acids **4** and **5**. Typical results obtained during the selective fluorination of **1a–f** after passing 2 F of electric charge at the same current density of 15 mA/cm² are summarized in Table 3. The selectivity for the formation of monofluoro esters was found to increase with increase in alkyl chain length, thus a maximum selectivity of 63% is noted for the monofluoro ester during the electrochemical fluorination of **1d**. In the case of branched alkyl chain with the same number of carbon atoms (**1f**), the selectivity of monofluoro product was found to be lower. Thus the selectivity of monofluoro ester for substrates **1c** and **1d** was found to be significantly higher than that for the corresponding **1e** and **1f**.

The product distributions for **1a–f** after passing the charge of 4 F per mole of reactants are summarized in Table 4. It is noted that the selectivity of monofluoro esters decreases steadily with increasing the chain length for all the four *n*-alkyl esters. In these cases, further passage of electric current lead to significantly higher concentration of hydrolysed monofluoro acids. In the case of branched chain alkyl groups, slightly higher yields of monofluoro ester could still be obtained. From the above experimental results, it is apparent that the actual faraday per mole of the reactant may be different for different

Table 3
Selectivity of products obtained during anodic fluorination of **1a–f**^a

Compound	Conversion ^b (%)	Selectivity of fluorinated products ^c (mole%)				
		Mono fluoro ester	Mono fluoro acid	Difluoro ester	Difluoro acid	Others ^d
1a	80	24.1	26.6	0.8	1.4	47.2
1b	82	49.9	30.3	4.2	2.6	13.0
1c	82	54.5	23.4	5.4	2.3	14.5
1d	85	62.7	16.0	5.7	0.6	15.0
1e	81	33.0	23.4	3.1	1.6	38.9
1f	83	45.6	40.5	5.0	4.3	4.5

^a Charge passed = 2 F/mole.

^b Based on HPLC data.

^c Based on ¹⁹F NMR.

^d Other products include compounds **6–28** depending on the reactants.

Table 4
Selectivity of products obtained during anodic fluorination of **1a–f**^a

Compound	Conversion ^b (%)	Selectivity of fluorinated products ^c (mole%)				
		Mono fluoro ester	Mono fluoro acid	Difluoro ester	Difluoro acid	Others ^d
1a	95	68.2	11.7	2.7	1.5	16.0
1b	96	48.7	21.5	8.8	8.1	13.0
1c	99	18.8	58.4	7.6	6.8	8.4
1d	99	13.5	43.1	5.6	2.5	35.3
1e	96	58.7	12.2	11.0	5.5	12.6
1f	98	39.8	38.2	5.8	5.1	11.1

^a Charge passed = 4 F/mole.

^b Based on HPLC data.

^c Based on ¹⁹F NMR.

^d Other products include compounds **6–28** depending on the reactants.

Table 5
 ^{19}F and ^1H NMR spectral data of fluorinated phenylacetic acid and its derivatives obtained during anodic fluorination of **1a–f** [11,25]

Products	Ph–CHF–COOR	Ph–CF ₂ –COOR
R=H	–180.96 (d, 1F) $^2J_{\text{HF}} = 47.80$ Hz, 5.84 (d, 1H) $^2J_{\text{HF}} = 46.80$ Hz, 10.05 (s, 1H)	–105.45 (s, 2F), 10.05 (s, 1H)
R=CH ₃	–180.33 (d, 1F) $^2J_{\text{HF}} = 47.87$ Hz, 5.83 (d, 1H) $^2J_{\text{HF}} = 47.60$ Hz	–104.27 (s, 2F)
R=C ₂ H ₅	–179.78 (d, 1F) $^2J_{\text{HF}} = 47.44$ Hz, 5.80 (d, 1H) $^2J_{\text{HF}} = 48.00$ Hz	–103.91 (s, 2F)
R=C ₃ H ₇	–179.99 (d, 1F) $^2J_{\text{HF}} = 45.18$ Hz, 5.81 (d, 1H) $^2J_{\text{HF}} = 47.60$ Hz	–104.02 (s, 2F)
R=C ₄ H ₉	–180.02 (d, 1F) $^2J_{\text{HF}} = 45.18$ Hz, 5.80 (d, 1H) $^2J_{\text{HF}} = 47.60$ Hz	–104.05 (s, 2F)
R=CH(CH ₃) ₂	–179.65 (d, 1F) $^2J_{\text{HF}} = 45.18$ Hz, 5.77 (d, 1H) $^2J_{\text{HF}} = 48.00$ Hz	–104.09 (s, 2F)
R=CH(CH ₃)(C ₂ H ₅)	–179.52 (d, 1F) $^2J_{\text{HF}} = 45.18$ Hz, 5.77 (d, 1H) $^2J_{\text{HF}} = 48.00$ Hz	–104.12 (s, 2F)

alkyl groups. However, the selective fluorinated products generally increase with the increase in chain length of the alkyl group and decrease with chain branch. The complete ^1H and ^{19}F NMR data for all the major fluorinated products discussed in Tables 2–4 are summarized in Table 5.

Electrochemical partial fluorination is also commonly termed as selective electrochemical fluorination implying that the process itself is highly selective and yields a single product under ideal experimental conditions. Experimentally, however, high selectivity is observed only in some sulfur linked active methylene groups and lactone-based heterocyclic compounds. Especially in solvent-free Et₄NF·nHF system, Momota et al. have identified a variety of side products during the fluorination of benzene and substituted benzene [15–20]. Similar reports on solvent-free Et₃N·nHF medium have not been reported so far.

In the present work, an attempt was made to identify minor fluorinated products through systematic analysis by ^{19}F NMR data with and without proton decoupling. Wherever possible, supporting literature data are also provided. As indicated by the NMR data, a variety of competitive fluorination processes are possible, of course, with very low selectivity (Table 6). Nuclear fluorination of ortho, meta and para positions (6–8) can occur even before the fluorination of the active methylene group. Even difluoro aromatic derivative **9** without side chain fluorination could be observed. Similar nuclear fluorinated products **10–13** with mono fluorinated active methylene groups were also obtained.

Addition of fluorine to the aromatic nuclei also seems to occur during electrochemical fluorination. Simple **2**, **5** additions to the reactant molecule lead to **16**. 1, 4 additions

Table 6
 ^{19}F NMR data of nuclear substitution and addition products [25–27]

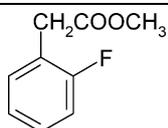
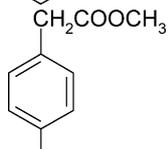
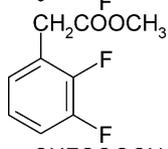
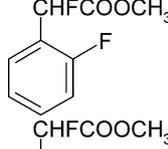
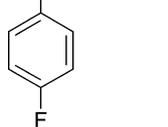
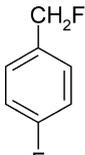
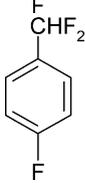
No	Structure	Chemical shifts (δ , ppm)
6		–117.5 (m, 1F)
7		–113.21 (m, 1F)
8		–111.69 (m, 1F)
9		–118.07 (m, 1F), –123.78 (m, 1F)
10		–123.21 (dm, 1F) $^4J_{\text{FF}} = 15.1$, –197.03 (dd, 1F) $^2J_{\text{HF}} = 48.2$, $^4J_{\text{FF}} = 15.1$
11		–111.34 (dm, 1F), –178.92 (dd, 1F) $^2J_{\text{HF}} = 46.7$, $^6J_{\text{FF}} = 3.4$

Table 6 (Continued)

No	Structure	Chemical shifts (δ , ppm)
12		-117.50 (m, 1F), -122.93 (m, 1F), -178.94 (dd, 1F) $^2J_{\text{HF}} = 46.3$, $^6J_{\text{FF}} = 3.76$
13		-117.47 (m, 1F), -123.15 (m, 1F), -196.30 (dd, 1F) $^2J_{\text{HF}} = 48.2$, $^4J_{\text{FF}} = 15.1$
14		-123.51 (m, 1F), -157.70 (m, 1F), -178.33 (dd, 1F) $^2J_{\text{HF}} = 45.2$, $^5J_{\text{FF}} = 3.8$
15		-150.00 (br s, 1F), -88.19 (m, 1F) $J_{\text{AB}} = 320.0$, -89.04 (m, 1F) $J_{\text{AB}} = 320.0$
16		-180.72 (d, 1F) $^2J_{\text{HF}} = 47.1$, -182.87 (d, 1F) $^2J_{\text{HF}} = 46.3$
17		-150.45 (br s, 1F), -178.88 (dd, 1F) $^2J_{\text{HF}} = 46.7$, $^5J_{\text{HF}} = 3.6$, -181.24 (d, 1F) $^2J_{\text{HF}} = 45.2$
18		-130.71 (dd, 2F) $^2J_{\text{HF}} = 52.7$, $^3J_{\text{FF}} = 15.1$, -156.46 (m, 1F), -183.32 (d, 1F) $^2J_{\text{HF}} = 45.2$
19		-129.14 (d, 2F) $^2J_{\text{HF}} = 56.5$, -181.68 (d, 1F) $^2J_{\text{HF}} = 48.9$, -182.16 (d, 1F) $^2J_{\text{HF}} = 58.9$
20		-92.45 (m, 1F) $J_{\text{AB}} = 323.8$, -93.31 (m, 1F) $J_{\text{AB}} = 323.8$, -129.30 (d, 2F) $^2J_{\text{HF}} = 56.5$, -180.70 (d, 1F) $^2J_{\text{HF}} = 48.9$
21		-129.59 (d, 2F) $^2J_{\text{HF}} = 56.5$, -103.45 (s, 2F), -105.05 (s, 2F)
22	Ph-CH ₂ -COO-CH ₂ F	-183.74 (t, 1F) $^2J_{\text{HF}} = 46.3$
23	Ph-CHF-COO-CH ₂ F	-179.53 (d, 1F) $^2J_{\text{HF}} = 46.3$, -181.63 (t, 1F) $^2J_{\text{HF}} = 47.8$
24	Ph-CH ₂ -COO-CF(CH ₃) ₂	-155.97 (br s, 1F)
25	Ph-CHF-COO-CF(CH ₃) ₂	-148.62 (br s, 1F), -180.75 (d, 1F) $^2J_{\text{HF}} = 48.9$
26	Ph-CF ₂ -COO-CF(CH ₃) ₂	-145.71 (br s, 1F), -103.81 (s, 2F)

Table 6 (Continued)

No	Structure	Chemical shifts (δ , ppm)
27		-206.98 (t, 1F) $^2J_{\text{HF}} = 48.1$, -111.64 (m, 1F)
28		-110.54 (d, 2F) $^2J_{\text{HF}} = 56.5$, -109.01 (m, 1F)

and nuclear substitution lead to **14**, **15** and **17**. Fluorination can also occur in the alkyl groups of ester part identified as **22–26**. In the case of *i*-propyl group, the secondary carbon attached to the carbonyl group was preferably fluorinated **24–26**. Cleavage can also occur between the active methylene group and carboxylic acid group. Fluorine substituted toluenes **27**, **28** are formed in these cases. Side chain cleavage, nuclear substitution and addition can also occur. In such processes 1, 4 addition **18** and 3, 4 addition **19–21** are predominant resulting in the formation of *cyclo*-hexadiene derivatives.

Partial fluorination of alkyl phenylacetates thus proceeds at nuclear as well as side chain positions. Selectivity in such cases, however, may be substantially improved by optimizing the experimental conditions including current density, charge passed per mole of the reactant and temperature.

3. Conclusion

Selective electrochemical fluorination of side chain methylene group in alkyl phenylacetates can be conveniently achieved under galvanostatic conditions. The amount of electric charge passed and the nature of the alkyl group are found to substantially influence the product distribution pattern. Hydrolysis through tautomeric transformation of electro-generated cationic radical is an important factor for side product formation. However, in pre-electrolysed $\text{Et}_3\text{N}\cdot 4\text{HF}$ medium, very high yields of mono fluorinated esters may still be obtained under galvanostatic conditions.

4. Experimental

4.1. Preparation of $\text{Et}_3\text{N}\cdot 4\text{HF}$

$\text{Et}_3\text{N}\cdot 3\text{HF}$ is a well-known conventional electrolyte medium for selective electrochemical fluorination. However, during galvanostatic experiments, HF content would decrease during pre-electrolysis as well as selective fluorination process. If the HF content in $\text{Et}_3\text{N}\cdot 3\text{HF}$ goes below this mole ratio, free base Et_3N may be liberated and its redox reaction can complicate the over all process. To ensure that the HF content through out the electrolysis is more than 3 moles, $\text{Et}_3\text{N}\cdot 4\text{HF}$ was selected as the electrolyte medium. Earlier workers also pointed out this advantage of $\text{Et}_3\text{N}\cdot n\text{HF}$ ($n = 4$ and 5) [28].

The following procedure was adopted for the preparation of $\text{Et}_3\text{N}\cdot 4\text{HF}$. A long jar of high-density polypropylene was cooled with ice salt mixture in a well-ventilated fume chamber. Slightly excess quantity of (>4 mole) anhydrous hydrogen fluoride (AHF) was taken to account for possible loss due to volatility of AHF. The reaction vessel was provided with magnetic stirrer and closed with a lid containing a provision for inlet and an outlet tube for the release of AHF vapours during the reaction. One mole of pre-cooled triethylamine was added drop wise using separating funnel. After the addition of each drop, sufficient time was given to ensure cooling of the reactant mixture. The overall addition was completed in 3 h. The HF content was determined by acid–base titration. Excess of AHF if any beyond 1:4 mole ratio of $\text{Et}_3\text{N}:\text{HF}$ in the mixture was appropriately compensated by the addition of triethylamine.

4.2. Preparation of alkyl phenylacetates

Appropriate alcohols (0.05 M) were mixed with 0.5 ml of conc. H_2SO_4 and 0.1 M of phenylacetic acid in a 100 ml round bottom flask fitted with a reflux condenser capped with calcium chloride tube to prevent moisture during the course of reaction. The mixture was refluxed for 4 h. After completion of reaction, the mixture was poured into 25 ml of ice-cold water. The bottom organic layer was removed and then washed with 20 ml of saturated sodium hydrogen carbonate solution and 25 ml of water. Then the crude ester was dried with anhydrous magnesium sulfate, and it was filtered to remove the salt and distilled under vacuum. Alkyl phenylacetates were obtained with a yield of 70–75% and purity of $>99\%$. Purity of the esters was checked using HPLC and NMR. Similar method was adopted for the preparation of all the other esters.

4.3. Electrochemical fluorination

A 5 ml capacity undivided polypropylene tube served as preparative cell for partial fluorination of alkyl phenylacetates. The anode and cathode were a rectangular Platinum foil (3 cm^2). Pre-electrolysis of 5 ml of $\text{Et}_3\text{N}\cdot 4\text{HF}$ solution was carried out at a constant cell voltage of 2.5 V under nitrogen atmosphere. Current at the start of pre-electrolysis was around 1.5 mA/cm^2 and the current dropped to 20% of initial value (0.3 mA/cm^2) within 90 min. Alkyl phenylacetate (300 mmol)

was added subsequently and the electrolysis was continued. In experiments involving without pre-electrolysis, 5 ml of $\text{Et}_3\text{N}\cdot 4\text{HF}$ containing 300 mmol of the substrate was introduced into the cell. Electrolysis was carried out galvanostatically (15 mA/cm^2) at $25 \pm 2 \text{ }^\circ\text{C}$ and pre-determined electric charge was passed. After completion of electrolysis, the electrolyte solution was poured into 50 ml of cold water and extracted with diethyl ether. The extract was washed with brine solution and dried over anhydrous magnesium sulfate. The ether was distilled out to get partially fluorinated alkyl phenylacetates. ^1H and ^{19}F NMR spectra were used to analyse the crude product.

4.4. Analytical instruments for characterization of the products

The purity of the reactant samples as well as the conversions was checked by HPLC (Shimadzu 10VP) with ODS column using UV-vis detector (254 nm). Methanol-water mixture (70:30) was used as eluent. ^1H NMR spectra were recorded with 400 MHz Bruker NMR Spectrometer with CDCl_3 and TMS as solvent and reference, respectively. ^{19}F NMR (376.5 MHz) of the products were taken using CFCl_3 as internal reference. Cyclic voltammograms were recorded using a single compartment polythene beaker as cell. $\text{Et}_3\text{N}\cdot 4\text{HF}$ was used as supporting electrolyte. Platinum wires were used as working (0.0942 cm^2) and counter electrodes. Pd/H_2 reference electrode was polarised cathodically before cyclic voltammetry experiments. Electrolyte was deaerated using Iolar grade nitrogen for about 15 min.

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