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THE PREPARATION OF FLUOROARENES BY THE CATALYTIC DECARBOXYLATION OF ARYL FLUOROFORMATES

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SUMMARY

The catalytic decarboxylation of phenyl fluoroformate to fluorobenzene has been achieved with yields of 70-80% in a flow system using alumina or alumina-based catalysts. The reaction occurs in short space times (<1 s) and with optimal efficiency at ca. 300 °C (some 500 °C lower than the temperature required for the thermal decomposition of the fluoroformate). Impregnation of the alumina with a platinum group metal gave the following order of catalytic activity:

$Pt/Al_2O_3 > Pd/Al_2O_3 > Rh/Al_2O_3 \approx Al_2O_3$.

2,4,6-Trimethylphenyl fluoroformate, a new material, was found to decarboxylate similarly to give 1-fluoro-2,4,6-trimethylbenzene, but 4-chlorophenyl fluoroformate was noted to produce only low yields (~10%) of the corresponding aryl fluoride.

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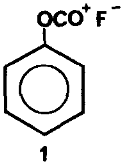
INTRODUCTION

Simple aromatic fluoro-compounds are not easily prepared in a high yield: in contrast with the direct aromatic substitution reactions of elemental chlorine or bromine, direct fluorination cannot be generally employed and halogen exchange chemistry, often applied to the preparation of aliphatic fluorides, cannot be used unless the aromatic material is suitably activated by strongly electron-withdrawing groups [1]. The traditional methods of synthesis employ the Balz-Schiemann reaction [2], involving the decomposition of diazonium tetrafluoroborates [3]:

$$[ArN_2][BF_4] \xrightarrow{\Delta} ArF + BF_3 + N_2$$

or a modification of conventional diazotisation using a large excess of anhydrous hydrogen fluoride [4]. These processes are often employed in large-scale industrial syntheses, but suffer from the disadvantages that the yields are often mediocre and that the reaction mixtures can be excessively corrosive.

Dinitrogen and carbon dioxide are considered to be similar leaving groups [5] and the evolution of CO_2 from a carboxylium ion, such as 1, should provide a large exothermic driving force similar to that obtained by the elimination of N_2 from the diazonium ion 2. Indeed, the catalytic decarboxylation of alkyl fluoroformates to the corresponding alkyl fluorides has been achieved by using pyridine or boron trifluoride etherate as the catalyst [6-8]. Aryl fluoroformates, however, are much more resistant to decarboxylation and the employment of tertiary amines or of BF_3 or $BF_3.Et_2O$ catalysts has been shown to be ineffective [9].



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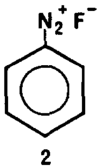

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The thermal decomposition of aryl fluoroformates was examined by Christe and Pavlath [9-11] who found that temperatures typically in the range of 700-800 °C were required in order to produce the most favourable yields of the corresponding fluorides. These temperatures are considered to be beyond the scope of common industrial practice and we now report that the decarboxylation of phenyl fluoroformate can be achieved in a flow system employing alumina catalysts, and that the reaction proceeds at a faster rate and at far lower temperatures than have previously been achieved.

The catalytic decarboxylation of 2,4,6-trimethylphenyl fluoroformate and of 4-chlorophenyl fluoroformate has been examined in order to investigate the influence of the electronic effects imposed by the addition of electron-donating or electron-withdrawing substituents to the aromatic ring.

RESULTS AND DISCUSSION

In their work on the thermal decomposition of aryl fluoroformates, Christe and Pavlath [9-11] used platinum gauze as a filling material. The decarboxylation of phenyl fluoroformate, therefore, was examined as a function of temperature using platinum impregnated upon a γ-alumina material as the catalyst. The results obtained employing a microreactor, operated in the pulse mode, are presented in Table 1. For comparison the reaction was also examined using platinum gauze or platinum black (surface area 24 $m^2\ g^{-1}$) in place of the platinum/alumina.

Only trace quantities of fluorobenzene were produced over the unsupported platinum materials at the temperatures employed in this study and diphenyl carbonate was found to be the major reaction product. By contrast, fluorobenzene was the principal product derived from the passage of phenyl fluoroformate over the supported catalyst. Diphenyl carbonate was the main by-product of the reaction, although the yields of this material were not quantified owing to its tendency to be only slowly desorbed under the pulse-mode conditions of the experiments. Trace amounts of diphenyl ether and 2-hydroxybiphenyl were detected by GC/MS. Diphenyl ether is probably formed as a result of the decarboxylation of the carbonate, and 2-hydroxybiphenyl formed as a rearrangement product of the ether.

On the basis of the results described in Table 1, the activity of the platinum/alumina catalyst (measured at 255 °C) is approximately 1000 times greater than that obtained for the platinum gauze material at the much higher temperature of 800 °C, described by the earlier workers [9].

TABLE 1

Catalytic decarboxylation of phenyl fluoroformate over platinum catalysts: Effect of temperature on fluorobenzene yields (pulse mode experiments)

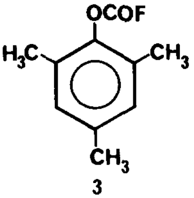
Catalyst	Temp (°C)	Conversion[a](%)	Fluorobenzene Yield [b](%)
4%Pt/Al_2O_3	218	56.9	21.4
	255	99.1	53.9
	287	92.3	55.3
	313	99.8	57.9
	399	99.9	59.8
	464	99.7	59.8
Pt gauze	252	22.6	0.09
	305	23.1	0.15
	411	31.3	0.19
Pt black	250	8.9	0.13
	304	15.9	0.13
	372	34.7	0.11
	427	86.2	0.19
	459	96.4	0.85

[a] Defined as moles of fluoroformate consumed in the reaction/moles of fluoroformate charged to the reactor.

[b] Defined as moles of fluorobenzene produced/moles of fluoroformate charged to the reactor.

Our own study with platinum gauze at 255 °C indicates that this catalyst has an activity of 2.5×10^{-3} g of fluorobenzene per gram of platinum per hour compared to an activity of 1240 g of fluorobenzene per gram of platinum per hour for the Pt/Al_2O_3 catalyst: hence, the production rate of fluorobenzene is improved by six orders of magnitude by using the supported platinum catalyst.

The previously unreported compounds 2,4,6-trimethylphenyl fluoroformate, 3, and 4-chlorophenyl fluoroformate, 4, were prepared in



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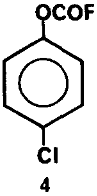

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high yields by the reaction of carbonyl chloride fluoride with 2,4,6-trimethylphenol or 4-chlorophenol, respectively. The reactions were adapted from one described earlier [9]; the products were identified by GC/MS and ^{19}F NMR spectroscopy. The decarboxylation of each of these new fluoroformates was examined over the Pt/Al_2O_3 catalyst; the results are recorded in Table 2.

1-Fluoro-2,4,6-trimethylbenzene is the major product obtained from the reaction of 3 over the whole of the temperature range examined (250-450 °C): at the optimal temperature (350 °C), a yield of 61% was obtained. The small amounts of 1-chloro-2,4,6-trimethylbenzene formed as a by-product (ArCl in Table 2) were generated probably as a result of residual chloride in the dispersed Pt/alumina catalyst (prepared from the hydrogen reduction of impregnated hexachloroplatinic(IV) acid) and are not attributable to the trace amounts of 1-chloro-2,4,6-trimethylbenzene (<0.1%) present in the sample of 3 (formed owing to a small $COCl_2$ impurity in the COClF reagent). Despite the very short space times (ca 0.05 s) employed, the conversion of the fluoroformate was 100% at each temperature examined. It is likely, under the pulse conditions of the experiments, that some carbonate was also produced, but this would be insufficiently volatile, under the experimental conditions, to detect.

In contrast to the examples given for the decarboxylation of phenyl and 2,4,6-trimethylphenyl fluoroformate, only small yields of 1-chloro-4-fluorobenzene were derived from the passage of 4 over the Pt/Al_2O_3 catalyst. 4-Chlorophenol was obtained as the predominant product of this reaction, and this material is probably formed by the exchange of fluoride, from the fluoroformate, for the hydroxyl groups on the alumina surface, followed by the facile decarboxylation of the resulting acid.

TABLE 2

Catalytic decomposition of ArOCOF over Pt/alumina

Ar[a]	Temp (°C)	Yield[b] (%)		
		ArF	ArCl	ArOH
2,4,6-$Me_3C_6H_2$	250	3.7	0.4	-
	300	47.0	3.4	-
	350	61.1	6.5	-
	400	59.7	9.2	-
	450	50.0	10.5	-
	350[c]	57.3	1.7	-
4-Cl-C_6H_4	250	0	-	0
	300	0	-	38.6
	350	1.5	-	14.3
	400	10.6	-	20.9
	450	2.7	-	5.9

[a] Toluene solutions, examined using the pulse method

[b] Defined as moles of product/moles of ArOCOF charged to the reactor

[c] Results obtained after many successive pulses of reactant at 350 °C

This exchange reaction may be expected to be enhanced by the presence of the electron-withdrawing chlorine atom attached to the aromatic nucleus of 4.

Results obtained for the decarboxylation of phenyl fluoroformate using a continuous flow system are illustrated in Figure 1 for both the platinum-impregnated alumina and unimpregnated alumina catalysts. The effect of the platinum impregnation is to slightly enhance the fluorobenzene yield relative to that obtained for the unimpregnated catalyst and to raise the temperature corresponding to optimal performance.

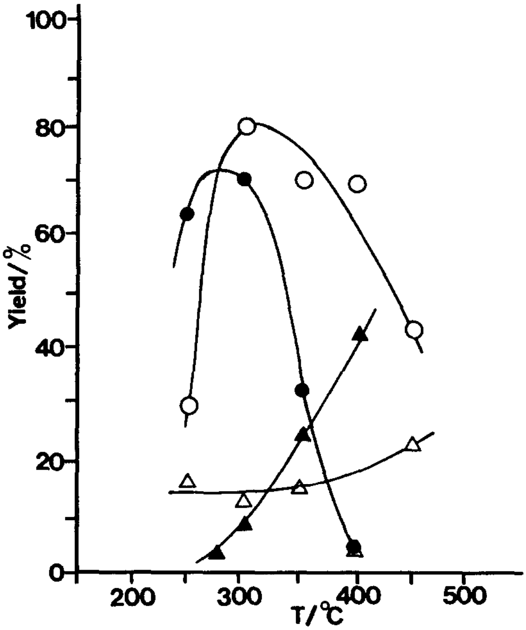

Fig. 1. Catalytic decarboxylation of phenyl fluoroformate. Effect of temperature on product yield during continuous flow operation. Pt/γ-Al_2O_3 catalyst: fluorobenzene (o), diphenyl carbonate (Δ); γ-Al_2O_3 catalyst: fluorobenzene (●), diphenyl carbonate (▲).

Above the optimal temperature (T_o), in each case, the yield of fluorobenzene was noted to fall whilst the CO_2 yield and the yield of by-product carbonate continued to increase. These results are consistent with reactions (1) and (2) being predominant in the system:

$$C_6H_5OCOF \longrightarrow C_6H_5 + CO_2 \; ; \; T < T_o \qquad (1)$$

$$2C_6H_5OCOF + \text{'AlO(OH)'} \longrightarrow (C_6H_5O)_2CO + CO_2 + HF + \text{'AlOF'} ; \; T > T_o \qquad (2)$$

Clearly, treatment at temperatures much in excess of T_o has the effect of deactivating the catalyst. Examination of the spent Pt/Al_2O_3 catalyst by XPES showed the presence of a band at 122.2 eV indicating the presence of fluorine bound to aluminium.

Impregnation of the alumina with palladium or rhodium was also noted to improve the catalyst performance slightly, relative to the untreated material, but not so effectively as the platinum-coated catalyst. The effects of the impregnation upon the conversion of phenyl fluoroformate to fluorobenzene (examined using the microreactor operated in the pulse mode) are compared in Table 3.

TABLE 3

Effect of impregnation of platinum group metals on the decarboxylation of phenyl fluoroformate to fluorobenzene

Catalyst[a]	Temp (°C)	Optimal yield(%)
3.9%Pt/Al_2O_3	250	61
2.1%Pd/Al_2O_3	325	53
2.1%Rh/Al_2O_3	300	49
Al_2O_3	300	48

[a] Impregnated materials equivalent to 0.02 moles of metal per 100g of support

Thus, in conclusion, it has been demonstrated that the use of high surface area alumina catalysts, especially when impregnated with platinum, for the decarboxylation of aryl fluoroformates transforms the reaction from one of no industrial significance to one of great potential importance.

EXPERIMENTAL

Synthesis of starting materials

Phenyl fluoroformate was prepared by exchange fluorination of phenyl chloroformate according to the literature method [12].

2,4,6-Trimethylphenyl fluoroformate was prepared by the slow passage of gaseous COClF into a solution of 2,4,6-trimethylphenol (1 g) in dry toluene (10 cm^3) using a reaction flask fitted with a dry-ice condenser. The temperature of the reactants was maintained at about 60 °C until the reaction, monitored by GLC, was completed. The toluene solution of this fluoroformate was used for the decarboxylation experiments without removal of the solvent. Yield, 96.7 %; m/z: 182 (M^+, 100%), 167 ($M-CH_3$, 7), 135 (M-COF, 31), 134 (M-HCOF, 27), 119 ($M-CO_2F$, 53), 118 ($M-HCO_2F$, 60), 117 ($M-H_2CO_2F$, 54), assignments confirmed by high-resolution mass measurements; ^{19}F NMR ($CDCl_3$): δ = 18.9 (s,OCOF).

4-Chlorophenyl fluoroformate was prepared in a similar way to that described for 2,4,6-trimethylphenyl fluoroformate using 4-chlorophenol (1 g) dissolved in dry toluene (10 cm^3) containing triethylamine (50 µℓ). Yield, 99.8 %; m/z: 174 (M^+, 100%), 130 (28), 127 (50), 99 (67); ^{19}F NMR ($CDCl_3$): δ = 15.8 (s,OCOF).

Carbonyl chloride fluoride was prepared from the reaction of gaseous phosgene (ca 10ℓh^{-1}) with dried calcium fluoride (ca 2 kg) in a flow system at ca 450 °C. The volatile reaction products were passed into a bed of activated charcoal held at ca 200 °C (to recombine the CO and Cl_2 formed as a result of the thermal dissociation of phosgene) and then condensed in a dry-ice trap. The COClF was separated from unreacted phosgene by distillation in a low-temperature fractionating column and collected at ca -45 °C.

Pulse experiments

A stainless steel microreactor (4 mm internal diameter) was used for operation in the pulse mode [13]. The reactor, heated by an aluminium alloy block furnace, was attached directly onto the injection port of a gas chromatograph and capped by a second injection port, constituting the reactor inlet. Separate streams of helium were fed into each port, heated to about 300 °C. Liquid phenyl fluoroformate (1µℓ) or a toluene solution (10µℓ) of mesityl fluoroformate or 4-chlorophenyl fluoroformate (typically 10 % $^w/w$) was injected into the inlet helium stream (10cm^3 min^{-1}) and the vapourized material allowed to flow through the catalyst (ca 0.1 cm^3) held at the required temperature. The product gases were further diluted with the second helium stream (50 cm^3 min^{-1}) to facilitate analysis by gas chromatography.

Continuous flow experiments

For the continuous flow experiments phenyl fluoroformate vapour, at a flow rate of about 0.3 cm^3 min^{-1}, was generated by passing dry dinitrogen into a series of two bubblers containing liquid phenyl fluoroformate held at 41-42 °C. The gases were passed through the catalyst plug (0.4 cm^3) held at the required temperature in an all-glass microreactor and the off-gases were diluted with a heated stream of dinitrogen (71 cm^3 min^{-1}, measured at 20 °C) in order to prevent the condensation of by-product carbonate. The organic products were collected for GLC/MS analysis into a series of two traps held at room temperature and at -78 °C, respectively.

Catalyst preparations

Metal supported catalysts were prepared by impregnation of γ-alumina (Harshaw Al 3912P) with aqueous solutions of $H_2[PtCl_6].xH_2O$, $PdCl_2$ or $RhCl_3.xH_2O$, followed by drying, and reduction in a stream of hydrogen at 450-500 °C. The weights of salts used were such as to give equimolar proportions of supported metal. The alumina sample used as the unimpregnated catalyst was the Harshaw Al 3912P material possessing a BET surface area of 167 m^2 g^{-1}.

Mass spectra

Mass spectra were recorded on a Varian 7070F instrument (electron impact) at an ionising voltage of 70eV.

^{19}F nmr spectra

^{19}F nmr spectra were measured on a Jeol FX100 FT spectrometer operated at 93.65 MHz using CCl_3F as the reference standard.

7 S. Nakanishi, T.C. Myers and E.V. Jensen, J. Am. Chem. Soc., 77 (1955) 5033

8 K.O. Christe and A.E. Pavlath, J. Org. Chem., 30 (1965) 1639

9 K.O. Christe and A.E. Pavlath, J. Org. Chem., 30 (1965) 3170

10 K.O. Christe and A.E. Pavlath, J. Org. Chem., 30 (1965) 4104

11 K.O. Christe and A.E. Pavlath, J. Org. Chem., 31 (1966) 559

12 J. Cuomo and R.A. Olofson, J. Org. Chem., 44 (1979) 1016

13 V.R. Choudhary and L.K. Doraiswamy, Ind. Eng. Chem., Prod. Res. Dev., 10 (1971) 218

Gas chromatography

Chromatographic analyses were performed using a Hewlett Packard 5790A instrument fitted with a flame ionisation detector and employing a glass column, 3 m, 6 mm outside diameter, containing 20 % SP 2100 and 0.1 % Carbowax 1500 on Supelcoport.

XPES

The XPES measurement was obtained on a Kratos ES 200 spectrometer using a Mg(kα) X-ray source (hν = 1253.6 eV). The binding energy is relative to that of hydrocarbon at 285.0 eV.

ACKNOWLEDGEMENTS

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REFERENCES

1 M.M. Boudakion in 'Kirk-Othmer Encylopaedia of Chemical Technology', Wiley, New York, 10, (1980) 902

2 G. Balz and G. Schiemann, Chem. Ber., 60 (1927) 1186

3 H. Suschitzky, Adv. Fluorine Chem., 4 (1965) 1

4 P. Osswald and O. Scherer, G. P. 600706 (1934)

5 P. Beak, R.J. Trancik and D.A. Simpson, J. Am. Chem. Soc., 91 (1969) 5073

6 S. Nakanishi, T.C. Myers and E.V. Jensen, J. Am. Chem. Soc., 77 (1955) 3099