

Efficient acid fluoride synthesis via carbonylation of organic halides

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Abstract

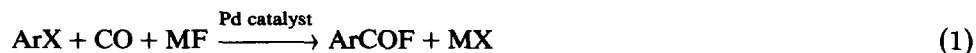
Palladium, platinum, cobalt, and rhodium triphenylphosphine complexes were found to catalyze the formation of acid fluorides via carbonylation of organic halides with fluoride salts. For palladium complex-catalyzed reactions, the use of cesium fluoride in polar solvents such as acetone and acetonitrile exhibited superior performance. The reaction took place even under an atmospheric pressure of carbon monoxide. The success of the acid fluoride synthesis is discussed in terms of the facility of oxidative addition of the starting material and the product.

Introduction

Although a number of halide carbonylations have been devised, successful examples of acid halide synthesis are still rare. Thus, survey of the literature revealed that only allylic chlorides are the exceptional halides which can be efficiently carbonylated. Palladium catalysts seem to be the best for this transformation [1,2]. Though some rhodium complexes also catalyze the reaction of allyl bromide as well as benzyl chloride, the yield is not satisfactory [3]. Since synthesis of acetyl chloride via carbonylation of chloromethane is of great industrial potential, several patents are available [4]. Most of them disclose the use of rhodium catalysts, however, their performance still remains to be improved.

As for the conversion of aryl halides to aroyl halides, nickel [5,6] and palladium [7,8] catalysts are claimed in patents. However, the drastic conditions required for the reaction, typically 600–900 atm and 350 °C, render the process unattractive.

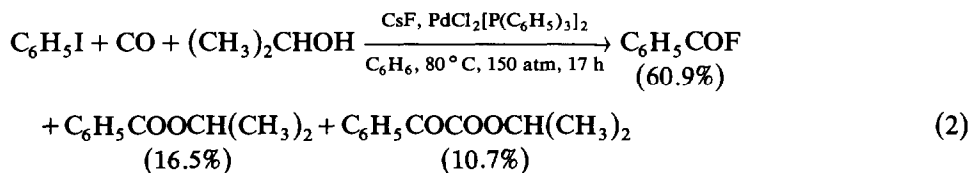
In the course of the investigation on the double carbonylation of aryl halides [9,10], we found that aroyl fluorides were readily formed when aryl halides were treated with carbon monoxide and an alkali metal fluoride in the presence of palladium phosphine complexes (eq. 1).



Aroyl fluorides are a useful class of compounds, especially because their behaviour in acylation reactions is somewhat different from that of aroyl chlorides [11,12]. However, synthetic routes to aroyl fluorides are restricted to the treatment of arenecarboxylic acid derivatives with fluorinating agents [13,14]. Contrary to these, our procedure starts with aromatic halides, and the carbonylation is carried out under exceptionally mild conditions. In this paper, full details of the new procedure are reported.

Results and discussion

While we were searching for an efficient inorganic base for use in the double carbonylation of organic halides, we came across the unexpected formation of benzoyl fluoride. So we examined the performance of cesium fluoride as a base in the carbonylation of iodobenzene with 2-propanol. GLC analysis of the reaction mixture revealed the formation of benzoyl fluoride. As shown in eq. 2, the selectivity



to benzoyl fluoride was higher than those to the expected products, isopropyl benzoate and phenylglyoxylate. The result encouraged us to investigate the reactions carried out without alcohols.

Influence of catalysts

Some transition metal-triphenylphosphine complexes were screened as the catalyst for the reaction of iodobenzene with cesium fluoride. The results are summarized in Table 1. Among these complexes, the palladium complex proved to be the best in terms of activity and selectivity. Complexes of cobalt, rhodium, and platinum were also active, but less effective than the palladium complex. The rhodium-catalyzed reaction was accompanied by formation of benzophenone (7% yield based on the amount of iodobenzene charged). Under the same conditions,

TABLE 1
EFFECT OF CATALYST ON CARBONYLATION OF IODOBENZENE TO BENZOYL FLUORIDE ^a

Catalyst	Conversion (%) ^b	Selectivity (%) ^c
$\text{PdCl}_2[\text{P}(\text{C}_6\text{H}_5)_3]_2$	99.7	91.2 ^d
$[\text{Co}(\text{CO})_3\text{P}(\text{C}_6\text{H}_5)_3]_2$	82.1	81.6
$\text{RhCl}(\text{CO})[\text{P}(\text{C}_6\text{H}_5)_3]_2$	69.1	89.2
$\text{PtCl}_2[\text{P}(\text{C}_6\text{H}_5)_3]_2$	30.5	78.4
$\text{Ru}(\text{CO})_3[\text{P}(\text{C}_6\text{H}_5)_3]_2$	12.2	~ 0
$\text{Ni}(\text{CO})_2[\text{P}(\text{C}_6\text{H}_5)_3]_2$	4.7	~ 0

^a Iodobenzene 4 mmol, CsF 5 mmol, catalyst 0.06 mg-atom, benzene 5 ml, CO 150 atm at room temperature, 150 °C, 16.5 h. ^b Conversion of iodobenzene. ^c (Benzoyl fluoride/consumed iodobenzene) × 100. ^d Isolated yield was 49.4% based on amount of iodobenzene charged (Kugelrohr).

TABLE 2

EFFECT OF FLUORIDE SALT ON CARBONYLATION OF IODOBENZENE TO BENZOYL FLUORIDE ^a

Fluoride	Conversion (%)	Selectivity (%)
LiF	33.4	~ 0
NaF	27.3	60.1
KF	95.5	60.3
RbF	~100	74.7
CsF	99.7	91.2
CaF ₂	43.8	~ 0

^a Fluoride 5 mmol, PdCl₂[P(C₆H₅)₃]₂ 0.06 mmol; for other conditions, see Table 1.

ruthenium and nickel complexes did not catalyze benzoyl fluoride formation, although some iodobenzene was transformed into unidentified entities.

Effect of the nature of fluoride salts

Table 2 shows the effect of the fluoride salt used in conjunction with PdCl₂[P(C₆H₅)₃]₂ as the catalyst. Among the alkali metal fluorides, those with larger cations exhibited higher activities. Since the solubility of these salts is certainly a factor which affects the apparent activity, it may be premature to draw any inclusions from this trend. However, this trend may be due to the enhanced nucleophilicity of the fluoride anion owing to increased ionic radii of the cations. Calcium fluoride did not give benzoyl fluoride at all.

Effect of other factors

The solvent effect on the reactions of iodobenzene with cesium fluoride is summarized in Table 3. In general, polar solvents were favorable for the synthesis of benzoyl fluoride. This is probably due to the solubility of cesium fluoride.

The effect of the pressure of carbon monoxide was negligible; in the range 10–150 atm, the conversion and selectivity obtained after reaction in benzene remained the same at about 10% and 40%, respectively. The results encouraged us to attempt the reaction under an atmospheric pressure. As the time-yield curve in Fig. 1 shows, the reaction occurred at 80 °C in propionitrile solvent to afford benzoyl fluoride nearly quantitatively in 10 h. Catalytically active species must have formed immediately upon heating, since an induction period was not observed.

TABLE 3

EFFECT OF SOLVENT ON CARBONYLATION OF IODOBENZENE TO BENZOYL FLUORIDE ^a

Solvent	ε ^b	Conversion (%)	Selectivity (%)
Acetonitrile	37.5	86.7	88.5
Propionitrile	27.2	72.1	~100
Acetone	20.7	94.0	86.5
Dichloromethane	9.1	46.1	40.1
Benzene	2.3	7.3	49.3
n-Hexane	1.9	9.2	96.7

^a PdCl₂[P(C₆H₅)₃]₂ 0.06 mmol, solvent 5 ml, 80 °C; for other conditions, see Table 1. ^b J.A. Riddick and W.B. Bunger, "Organic Solvents", 3rd ed., Wiley-Interscience, New York (1970).

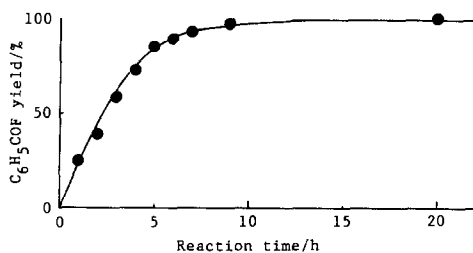


Fig. 1. Atmospheric pressure reaction of iodobenzene with CsF. Catalyst $\text{PdCl}_2[\text{P}(\text{C}_6\text{H}_5)_3]_2$, solvent $\text{CH}_3\text{CH}_2\text{CN}$, CO balloon, 80°C .

Reactions of various halides

Results of acid fluoride synthesis from other organic halides are summarized in Table 4. Yields were determined for the *N,N*-diethylamides formed, by treating a completely degassed reaction solution with dry diethylamine.

Aromatic iodides including iodothiophene were smoothly carbonylated under an atmospheric pressure, and corresponding aroyl fluorides were obtained in good yields. On the other hand, the reactivity of aryl bromides was, as observed in other carbonylations, low under the same conditions. At 150°C , the reaction was faster. The rate sequence of aryl bromides was 1-bromonaphthalene > *p*-chlorobromobenzene > bromobenzene > *p*-methoxybromobenzene. This is presumably due to the facility of these aryl bromides to oxidatively add across low valent palladium species [15]. Products other than the aroyl fluorides have not been investigated. Besides aromatic halides, β -bromostyrene and benzyl chloride reacted similarly, the selectivity of the latter, however, was not as high.

Reaction of $\text{Pd}[\text{P}(\text{C}_6\text{H}_5)_3]_4$ with halides relevant to the catalysis

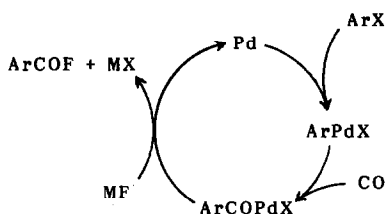
A tentative mechanism for the present reaction is shown in Scheme 1, in which

TABLE 4

CARBONYLATION REACTION OF VARIOUS SUBSTRATES ^a

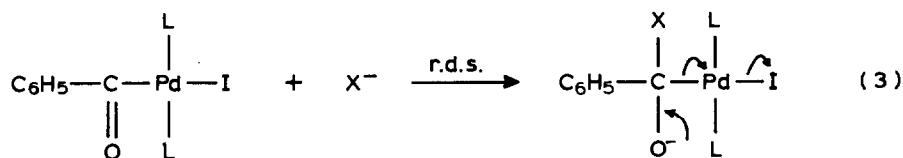
Substrate	Solvent	P_{CO} (atm)	Temperature ($^\circ\text{C}$)	Conversion (%)	Selectivity ^b (%)
<i>p</i> -ClC ₆ H ₄ I	CH ₃ CH ₂ CN	1	80	90.9	79.8
<i>p</i> -CH ₃ OC ₆ H ₄ I	CH ₃ CH ₂ CN	1	80	87.2	81.9
α -IC ₄ H ₃ S ^c	CH ₃ CH ₂ CN	1	80	53.4	~ 100
C ₆ H ₅ Br	CH ₃ CH ₂ CN	1	80	15.0	~ 0
C ₆ H ₅ Br	CH ₃ CN	150	150	63.6	18.9
<i>p</i> -ClC ₆ H ₄ Br	CH ₃ CN	150	150	82.9	48.4
<i>p</i> -CH ₃ OC ₆ H ₄ Br	CH ₃ CN	150	150	1.2	~ 0
α -BrC ₁₀ H ₇ ^d	CH ₃ CN	150	150	99.2	97.7
<i>Trans</i> -C ₆ H ₅ CH=CHBr	CH ₃ CN	150	80	78.8	75.0
C ₆ H ₅ CH ₂ Cl	CH ₃ CH ₂ CN	1	80	62.2	24.4

^a $\text{PdCl}_2[\text{P}(\text{C}_6\text{H}_5)_3]_2$ 0.06 mmol; for other conditions, see Table 1. ^b Yield of acid fluoride was quantified from the amount of *N,N*-diethylamide formed by the diethylamine treatment of the reaction mixture; see the experimental section. ^c 2-Iodothiophene. ^d 1-Bromonaphthalene.



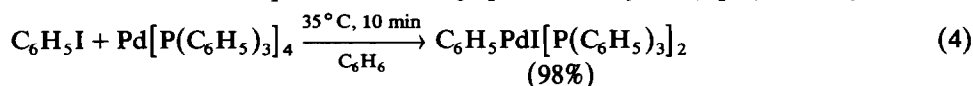
SCHEME 1

fluoride ion is considered to make a nucleophilic attack on a benzoylpalladium intermediate. Although we attempted several reactions of iodobenzene with cesium chloride in place of cesium fluoride, we could not obtain benzoyl chloride. The nucleophilicity of chloride anion in organic nucleophilic substitution reactions is normally higher than fluoride. However, in some cases, including substitution at the carbonyl group in acid halides, the order of reactivity is $F^- > Cl^-$ [16]. In the present reaction, if the structure of the transition state, whatever it may be, resembles the structure of the fluoride-bound product of the rate-determining step, r.d.s., then fluoride ion is more reactive than chloride. One of possibilities is shown in eq. 3. The lack of carbonylation with cesium chloride may be due to the difficulty with which a reaction such as eq. 3 takes place.

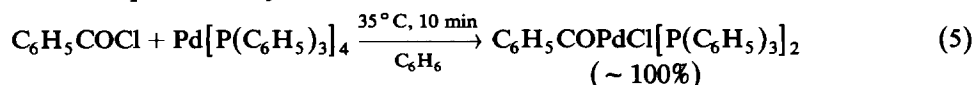


(X = Halogen)

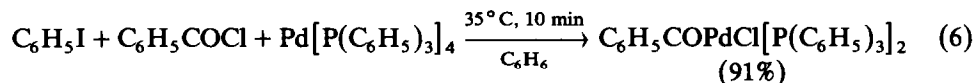
An alternative and more probable reason for the failure of acid chloride synthesis is the lower reactivity of the starting material (iodobenzene) compared with the product (benzoyl chloride). This conclusion was confirmed by following experiments. As is widely known, iodobenzene readily reacts with $\text{Pd}[\text{P}(\text{C}_6\text{H}_5)_3]_4$ to give the oxidative addition product in nearly quantitative yield (eq. 4). Benzoyl chloride



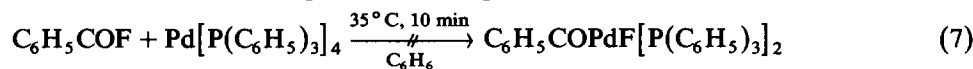
also reacts rapidly with the palladium complex whereby the benzoyl complex is obtained quantitatively. The reaction of 1:1 mixture of iodobenzene and benzo-



yl chloride gave the benzoyl complex in 91% yield. The result indicates that ben-



zoyl chloride is much more reactive than iodobenzene. In addition, benzoyl fluoride did not react with the palladium complex at all. All these observations indi-



cate that benzoyl chloride, even if it can be formed from the reaction with cesium chloride, strongly interacts with the catalyst species to poison it. The success of the present carbonylation is probably due to the low reactivity of acid fluoride as compared with that of the starting materials.

Experimental

Materials

All the organic halides were purchased and distilled before use. Hexacarbonyl-bis(triphenylphosphine)dicobalt(0) was also purchased. *Trans*-dichlorobis(triphenylphosphine)palladium(II) [17], *trans*-chlorocarbonylbis(triphenylphosphine)-rhodium(I) [18], *cis*-dichlorobis(triphenylphosphine)platinum(II) [19], tricarbonylbis(triphenylphosphine)ruthenium(0) [20], dicarbonylbis(triphenylphosphine)-nickel(0) [21], and tetrakis(triphenylphosphine)palladium(0) [22] were prepared by published methods. All solvents were dried and distilled before use.

General reaction procedure

A mixture of catalyst (0.06 mg-atom), fluoride salt (5 mmol), organic halide (4 mmol), and solvent (5 ml) were placed in a reactor (Hasteroy C autoclave or a Schlenk tube) under N₂. Carbon monoxide was pumped into the autoclave to a pressure of 150 atm, or a CO-filled balloon was connected to the degassed (freeze-thaw method) Schlenk tube, and the reactor was heated in a temperature-controlled oil bath for 16.5 h, with stirring. After the reactor had been cooled, carbon monoxide was vented and a small aliquot of the reaction solution was subjected to gas chromatography (OV 17, 100 °C) to quantify benzoyl fluoride. The formation of benzoyl fluoride was also confirmed by IR spectroscopy. The rest of the solution was degassed by the freeze-thaw method and dry diethylamine added to the solution. The resulting mixture was stirred for 2 h and was analyzed for the diethylamide by gas chromatography (OV 17, 150 °C).

Benzoyl fluoride

PdCl₂[P(C₆H₅)₃]₂ (0.06 mmol), CsF (5 mmol), iodobenzene (4 mmol), and benzene (5 ml) were placed in a Hasteroy C autoclave under N₂. Carbon monoxide was pumped in to 150 atm and the autoclave heated in an oil bath controlled at 80 °C for 16.5 h, with stirring. After the autoclave was cooled, CO was vented, and the distillation (Kugelrohr, 50–53 °C/16 mmHg) of the solution gave 230 mg (46.4%) of benzoyl fluoride.

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