

# Uranium<sup>IV</sup> and uranyle salts, efficient and reusable catalysts for acylation of aromatic compounds

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## Abstract

Uranium tetrachloride, uranyle chloride, fluoride and also nitrate or acetate are very efficient homogeneous catalysts for the Friedel–Crafts acylation of aromatic compounds. With uranyle salts, the reaction, carried under dry air, is highly specific and the mono- or bisacylation products are obtained in high yield. Uranyle catalyst can be quantitatively recovered and reused and the organic products are obtained free of uranium. © 2000 Elsevier Science B.V. All rights reserved.

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## 1. Introduction

In spite of numerous works, obtaining efficient, reusable and cheap catalysts for the Friedel–Crafts acylation of aromatic compounds remains a challenge. For this purpose, a great number of metal salts have been tested, especially hard Lewis acids, non-hydrolysable lanthanides derivatives. Soluble lanthanides trifluoromethane-sulfonates [1–7] and bis(trifluoromethylsulfonyl)amides [8,9] act as homogeneous catalysts. In another way, supported lanthanides halides act as heterogeneous catalysts [10–12] whereas unsupported salts or their ethers adducts act also as homogeneous catalysts [13]. The catalytic activity of the salts of 4f elements has fo-

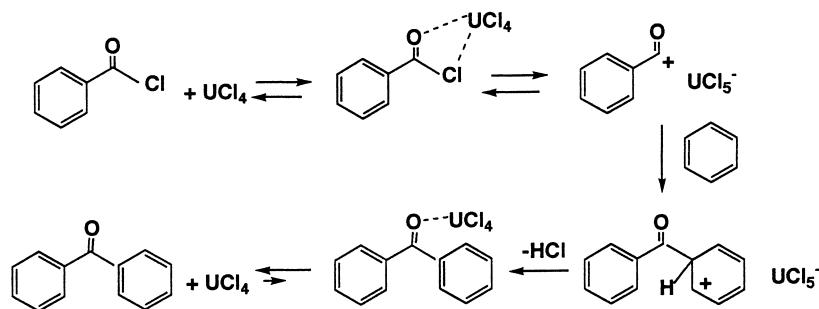
cused our attention on the homologous 5f elements: the actinides. Among natural actinides, only uranium complexes are commercially available or easily synthesized. Like rare earth, uranium salts are non-hydrolysable and very strong Lewis acids and, therefore, appear as reusable catalysts for these reactions.

We report here on the performances of uranium<sup>IV</sup> and uranium<sup>VI</sup> salts as catalysts for Friedel–Crafts acylations reactions.

## 2. Results and discussion

It has been clearly established that the ability of a Lewis acid to catalyse a Friedel–Crafts reaction is strongly related to the formation of the acylium ion and essentially to the stability of the complex formed with the reaction product. In a catalytic process, this

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Scheme 1.

complex must be easily dissociated, obtaining a stable complex preventing catalysis [14]. Preliminary experiments have shown that  $U^{IV}$  and  $U^{VI}$  complexes gave deep colored (red to deep purple) charge transfer complexes with acid chlorides indicating an easy formation of the acylium ion. At the opposite, not any stable complexes with the ketones obtained in acylation reactions (benzophenone, benzonaphthone, etc.) were formed; in solution, no significant change of the position of the  $C=O$  band has been observed. Aromatic ethers (anisole, veratrole, etc.) were also unable to give adducts with these salts. Then, uranium and uranyle salts must act as good catalysts for the Friedel–Crafts acylation. A possible mechanism is reported in Scheme 1.

### 3. Uranium salts

All commercially available uranium salts are obtained from depleted uranium provided by nuclear industry. Depleted uranium contains weakly radioactives  $^{238}U$ , ca. 99.8% ( $T_{1/2}$   $4.51 \times 10^9$  years) and  $^{235}U$ , ca. 0.2% ( $T_{1/2}$   $7.00 \times 10^8$  years) and a variable amount, 10–80 ppm of much more active  $^{234}U$  ( $T_{1/2}$   $2.47 \times 10^5$  years). All are essentially  $\alpha$  emitters (4.2–4.7 MeV).  $^{238}U$  is poisonous for kidney and both  $^{234}U$  and  $^{235}U$  are poisonous for bones. Of course, the storage and the handling of their derivatives require some elementary precautions: the glass wall of the vessel is sufficient to stop the  $\alpha$  beam and oral intake or inhalation must be carefully prevented. Schlenk-type vessels are used for storage and the reactions were performed in a closed hood. Uranium salts are very soluble in water and can be easily removed from the organic crude ma-

terial or from the reactors by washing with neutral or acidic water. As they are non-hydrolysable, they can be recovered from aqueous solutions.

#### 3.1. Uranium<sup>IV</sup>

$UCl_4$  is the most common  $U^{IV}$  salt. It is commercially available, but a high quality product can be rapidly synthesized on a large scale from uranyle nitrate or uranium oxide [15]. This compound is obtained anhydrous and free of solvent. It forms stable adducts with ethers and is well soluble in these solvents.  $UCl_4$  is hygroscopic but not easily oxidised, it can be dissolved without change of oxidation state in degassed water. It is stored and handled under dry nitrogen.

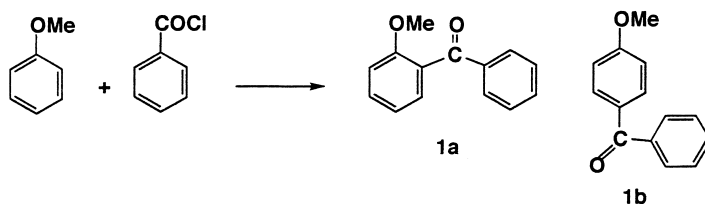
#### 3.2. Uranium<sup>VI</sup>

Commercially available uranyle salts are: hexahydrated nitrate:  $UO_2(NO_3)_2 \cdot 6H_2O$ , dihydrated acetate:  $UO_2(CH_3CO_2)_2 \cdot 2H_2O$  and uranium oxide  $U_3O_8$ . Uranyle chloride:  $UO_2Cl_2HCl \cdot 2H_2O$ , is very easily prepared from uranium oxide  $U_3O_8$ . Uranium fluoride:  $UO_2F_2$ , is the most common salt providing from nuclear industry and has been purchased by COGEMA. These two last compounds are very hygroscopic and must be kept and handled in a dry box.

## 4. Acylation reactions

#### 4.1. $U^{IV}$ as catalyst

The standard test is the benzoylation of anisole with benzoyl chloride (Scheme 2):



Scheme 2.

This reaction was performed under nitrogen with an excess of anisole (0.05 mol) and benzoyl chloride (0.01 mol) without additional solvent, the temperature was limited by reflux of anisole: 154°C. At this temperature,  $\text{UCl}_4$  was completely dissolved in the liquid and the colour turned immediately intense red-orange. At 84°C, the dissolution of  $\text{UCl}_4$  was much slower and the colour turned orange-brown. In all cases, the mixture became homogeneous and no precipitate was obtained after cooling. The reaction was highly regioselective, affording ca. 95% of 4-methoxybenzophenone **1b** and ca. 5% of 2-methoxybenzophenone **1a**. Yields corresponding to the total amount of methoxybenzophenone were estimated by gas phase chromatography (GC). The experimental results are given in Table 1.

$\text{UCl}_4$  was recovered after removal of the solvents under vacuum or after concentration and precipitation by addition of pentane.

Under dry nitrogen, no significant oxidation occurred, the UV–VIS spectrum of pure and recovered  $\text{UCl}_4$  were identical (peaks at 625 and 630 nm;  $\text{U}^{\text{VI}}$  salts give a peak at 420 nm [16]).

Good yields are obtained in a short time, with 1% of  $\text{UCl}_4$  as catalyst. Further experiments will be performed with 1% or less of uranium salts.

Table 1  
Benzoylation of anisole, no solvent

$\text{UCl}_4$ % <sup>a</sup>	Time (h)	Temperature (°C)	TR% <sup>b</sup>	Yield %
5	1	154	100	92
1	1	154	100	72
0.1	5	154	80	53
0.1	5	84	5	2

<sup>a</sup> The amount of  $\text{UCl}_4$  is given in moles of uranium per moles of benzoyl chloride.

<sup>b</sup> TR% corresponds to the transformation rate of  $\text{PhCOCl}$  estimated by GC.

Table 2

Comparison between uranium and lanthanide chlorides in anisole benzoylation (anisole/ $\text{PhCOCl}$  = 5, 154°C)

Catalyst	Amount %	Time (h)	Yield %
$\text{NdCl}_3$ anhydrous	5	5	27
$\text{NdCl}_3$ , 3THF	5	5	84
$\text{GdCl}_3$ anhydrous	5	5	70
$\text{UCl}_4$	5	0.2	92
$\text{UCl}_4$	1	1	72

A comparison between these results and those obtained with lanthanides salts [17] in anisole benzoylation is reported in Table 2. In the same conditions, uranium tetrachloride is more efficient than analogous trichlorolanthanide salts. The same regioselectivity was observed (**1b/1a** = 95/5) with lanthanides or uranium salts.

## 5. $\text{U}^{\text{VI}}$ as catalyst

### 5.1. Standard experiments

Uranyl salts are stronger Lewis acids than partially covalent  $\text{UCl}_4$ , then they must be more active catalysts. Uranyl chloride:  $\text{UO}_2\text{Cl}_2$ , fluoride:  $\text{UO}_2\text{F}_2$ , nitrate:  $\text{UO}_2\text{N}_2$  and acetate:  $\text{UO}_2\text{Ac}_2$ , have been tested for anisole benzoylation (vide supra). All these salts being very stable, the reactions were performed under dry air. In all cases, the mixture turned very rapidly red-orange and became homogeneous. After complete consumption of benzoyl chloride and cooling at room temperature,  $\text{UO}_2\text{Cl}_2$  and  $\text{UO}_2\text{F}_2$  precipitated and were recovered by filtration whereas more soluble  $\text{UO}_2\text{N}_2$  and  $\text{UO}_2\text{Ac}_2$  remained in solution. In all reactions, a mixture of 4-methoxy (**1b**) (96%) and 2-methoxybenzophenone (**1a**) (4%) was obtained. Experimental results are summarised in Table 3.

Table 3  
Benzoylation of anisole, uranyl salts as catalysts, 154°C

Entry	Catalyst	Yield %			
		1 h	4 h	8 h	24 h
1	UCl <sub>4</sub> 1%	72	–	–	–
2	UO <sub>2</sub> Cl <sub>2</sub> 1%	93 <sup>a</sup>	–	–	–
3	UO <sub>2</sub> Cl <sub>2</sub> 0.1%	32	63	71	–
4	UO <sub>2</sub> F <sub>2</sub> 1%	92	–	–	–
5	UO <sub>2</sub> F <sub>2</sub> 0.1%	40	59	–	–
6	UO <sub>2</sub> N <sub>2</sub> 1%	77	88	–	–
7	UO <sub>2</sub> N <sub>2</sub> 0.1%	27	30	41	74
8	UO <sub>2</sub> Ac <sub>2</sub> 1%	52	–	–	–
9	U <sub>3</sub> O <sub>8</sub> 1%	29	55	–	95

<sup>a</sup> After 30 min 88%.

From these results, it appears that

1. For short reaction times, the best yields are obtained with UO<sub>2</sub>Cl<sub>2</sub>, entries 2, 3 and UO<sub>2</sub>F<sub>2</sub>, entries 4, 5. Both uranyl fluoride and chloride show very similar performances.
2. A total of 1% molar of catalyst gives high yields within 1 h. When 0.1% of chloride or nitrate are used (entries 3, 5, 7), reaction times are much longer. Further reactions will be carried with 1% of catalyst.
3. The small amount of crystallisation water contained in the catalysts or water in anisole, used without

purification, is insufficient to prevent the reaction. However, additional water decreases significantly the reaction rate. After addition of 2% of water, no reaction occurred.

4. With U<sub>3</sub>O<sub>8</sub>, the reaction is slow (entry 9). In fact, the catalyst is UO<sub>2</sub>Cl<sub>2</sub> formed by reaction of the oxide with HCl generated in situ. After workup, a mixture of U<sub>3</sub>O<sub>8</sub> and UO<sub>2</sub>Cl<sub>2</sub> is isolated by filtration. Fig. 1 compares the catalytic activities of uranium and uranyl salts to the best result obtained in lanthanides series for anisole benzoylation [12] (1% catalyst, 1 h).

## 6. Scope of the activity of UCl<sub>4</sub> and UO<sub>2</sub>Cl<sub>2</sub>

To establish the limits of activity of the catalysts, benzoylation of various activated or deactivated aromatic compounds are investigated. In all cases, the reaction temperature was the boiling point of the reagents. Using UCl<sub>4</sub> (Table 4), fluoro (or chloro)benzene or benzene or toluene cannot be acylated. Good yields were obtained with mesitylene (1,3,5 trimethylbenzene) and 2-methoxynaphthalene.

In the same manner, with UO<sub>2</sub>Cl<sub>2</sub> as catalyst (Table 5, Fig. 2), no reaction occurred from fluoro-

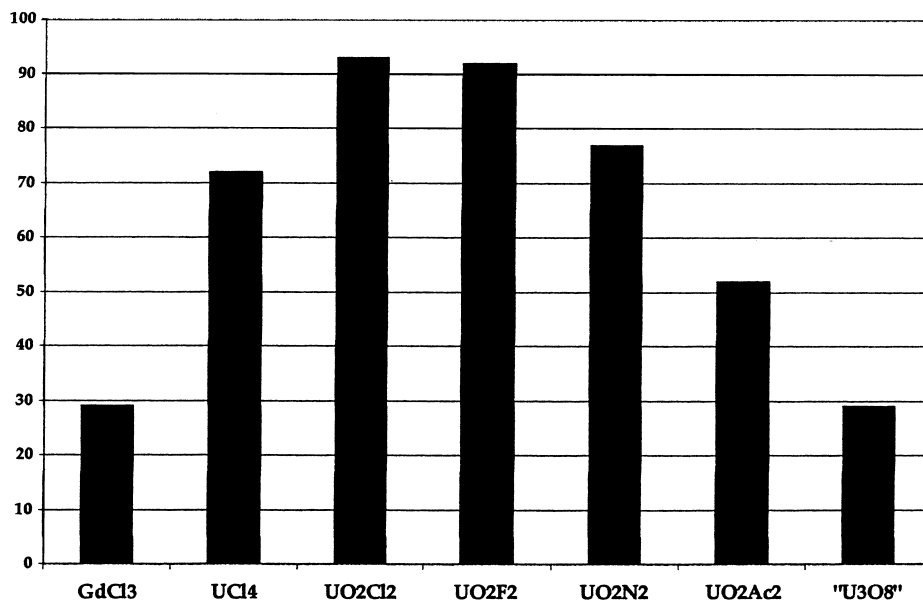


Fig. 1. Catalytic activity of uranium<sup>IV</sup>, uranium<sup>VI</sup> and lanthanide<sup>III</sup> derivatives.

Table 4  
Benzoylation of aromatic substrates  $\text{UCl}_4$  1%, no solvent, reflux

Substrate	Aspect	Time (h)	Yield %
Fluorobenzene	Heterogeneous	5	0
Benzene	Heterogeneous	5	0
Mesitylene	Homogeneous	5	87
Anisole	Heterogeneous	1	72
2-Methoxy-naphtalene	Heterogeneous	30 <sup>b</sup>	88 <sup>a</sup>

<sup>a</sup> Three isomers, see below.

<sup>b</sup> The unit is expressed in minutes.

(or chloro-) benzene or benzene. From toluene, a slow reaction afforded a mixture of *meta*, *ortho* and *para* isomeres in the ratio 1/4/6, an excess of benzoyl chloride was necessary to obtain a good yield. Cumene (isopropylbenzene) deactivated by hyperconjugation, did not react whereas paraxylene reacted rapidly and, with an excess of benzoyl chloride, led to the formation of a small amount of bisbenzoylation product. The more substituted, but more activated mesitylene was very reactive. After 1 h, the monoalkylation compound **2** was formed in high yield and, with an excess

Table 5  
Benzoylation of aromatic substrates, 1%  $\text{UO}_2\text{Cl}_2$  as catalyst, no solvent, reflux

Substrate	Ratio ArH/PhCOCl	Yield (GC) after			
		1 h	4 h	8 h	24 h
Fluorobenzene	5/1				0
Fluorobenzene	1/5				0
Benzene	5/1				0
Benzene	1/5				0
Toluene	5/1	12	20	22	22
Toluene	1/5	44	70	83	
Cumene	5/1	0	0	0	Traces
<i>p</i> -Xylene	5/1	36	44	47	63
<i>p</i> -Xylene	1/5	76	86	93	95 + 5 <sup>a</sup>
Mesitylene	5/1	99			
Mesitylene	1/5	8 + 92 <sup>a</sup>	99 <sup>a</sup>		
Mesitylene <sup>b</sup>	1/5	17 + 83 <sup>a</sup>	99 <sup>a</sup>		

<sup>a</sup> Bisbenzoylation products.

<sup>b</sup>  $\text{UO}_2\text{F}_2$  as catalyst.

of acyl chloride, the bisbenzoylation compound **3** was obtained nearly quantitatively (Scheme 3). Similar yields were obtained with  $\text{UO}_2\text{F}_2$  as catalyst.

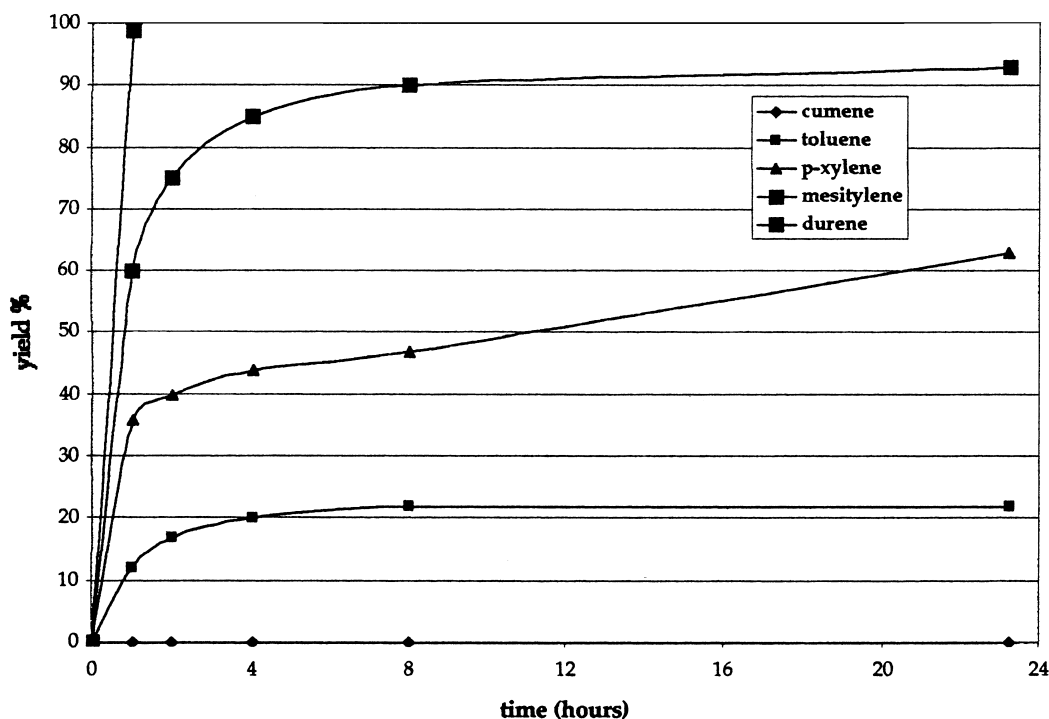
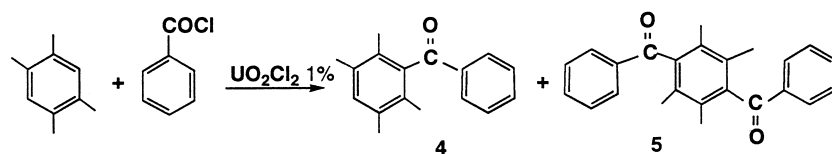
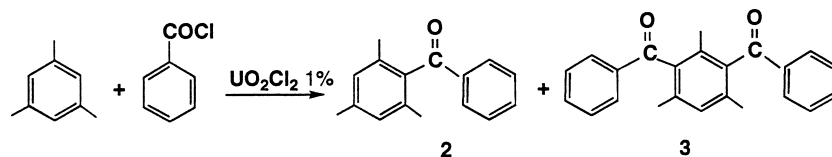


Fig. 2. Benzoylation rate of substituted benzenes (ratio ArH/ArCOCl = 5/1, reflux, 1%  $\text{UO}_2\text{Cl}_2$  as catalyst).



In the same conditions, sterically hindered durene (1,2,4,5-tetramethylbenzene) reacted slowly (Scheme 4) in the presence of a stoichiometric amount of benzoyl chloride. The monobenzoylation compound **4** was obtained after 8 h nearby ca. 10% of the bisbenzoylation compound **5**. With an excess of benzoylchloride, a large amount of **5** was obtained. Nevertheless, the reaction was not complete, even after 24 h heating (Table 6, Fig. 2).

Activated aromatic ethers reacted rapidly whatever the catalyst (Table 7). From anisole or phenetole (ethoxybenzene), the *para* isomers **1a** and **6** were obtained in 95–96% yield. From thioanisole, the reaction was significantly slower giving **7** and a small amount (ca. 3%) of disubstituted products. Addition of pen-

Table 6  
Benzoylation of durene, no solvent,  $T = 198^\circ\text{C}^a$

Ratio of ArH/ArCOCl	TR (GC) and rate 4/5 after			
	2 h	4 h	8 h	24 h
1/1	60 (100/0)		90 (88/12)	93 (85/15)
1/2	98 (67/33)	99 (37/63)	100 (23/77)	
1/5	100 (64/36)	(38/62)	(24/76)	(13/87)

<sup>a</sup> The values in the parenthesis denote the rate of **4/5**.

tane after cooling afforded directly greenish-white crystals in high yield (85%).

Veratrole (1,2-dimethoxybenzene) gave exclusively **8** (Scheme 5). 2-methoxynaphtalene reacted very rapidly with benzoyl chloride. After 10 min, benzoyl

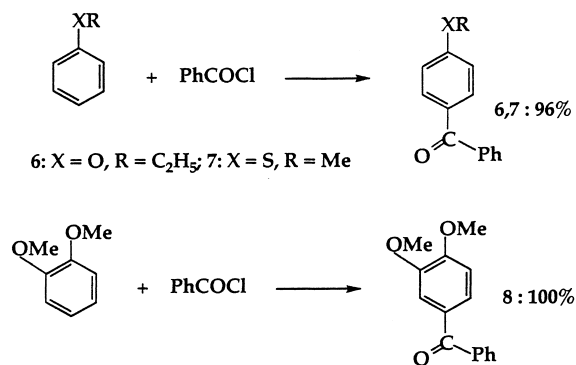
Table 7  
Acylation of aromatic ethers, 1% catalyst

Substrate	Reagent	Ratio <sup>a</sup>	Catalyst	Time (h)	$T$ ( $^\circ\text{C}$ )	TR%	Yield% (GC)
Anisole	PhCOCl	1.1/1	$\text{UO}_2\text{Cl}_2$	1	154	100	90
Anisole	(PhCO) <sub>2</sub> O	1/1	$\text{UO}_2\text{Cl}_2$	5	154	25	Traces
Anisole	MeCOCl	1/10	$\text{UO}_2\text{Cl}_2$	5	52	20	0
Thioanisole	PhCOCl	1/1	$\text{UO}_2\text{Cl}_2$	4	154	100	85 <sup>*</sup>
Phenetole	PhCOCl	1.1/1	$\text{UO}_2\text{Cl}_2$	1	154	100	74
Phenetole	4-ClPhCOCl	1.1/1	$\text{UO}_2\text{Cl}_2$	1	169	100	74
Veratrole	4-ClPhCOCl	1.1/1	$\text{UO}_2\text{Cl}_2$	1	206	100	67
2-MeONp	PhCOCl	1/1	$\text{UO}_2\text{Cl}_2$	10 <sup>c</sup>	198	100	92
2-MeONp	PhCOCl	1/1	$\text{UO}_2\text{F}_2$	15 <sup>c</sup>	198	100	90
2-MeONp	MeCOCl	1/10	$\text{UCl}_4$	1	52	100	84 <sup>b</sup>
2-MeONp	MeCOCl	1/10	$\text{UO}_2\text{Ac}_2$	1	52	100	90

<sup>a</sup> ArOR/RCOCl.

<sup>b</sup> Isolated crude crystals.

<sup>c</sup> Units are expressed in minutes.



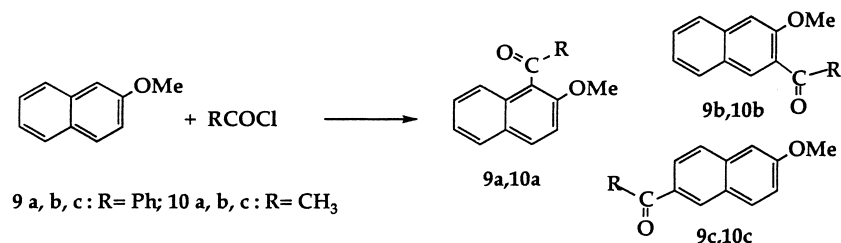
Scheme 5.

chloride was completely consumed to give a mixture of three isomers. The major isomer (80%) was identified by NMR as 2-methoxy,1-benzonaphthone (**9a**). The same reaction performed with UO<sub>2</sub>F<sub>2</sub> as catalyst afforded exclusively **9a** (Scheme 6).

Acetylation of 2-methoxynaphthalene has been carried with a large excess of acetyl chloride at 50°C. The crude product was isolated (84% yield) and recrystallised to give 55% of pure 2-methoxy,1-acetonaphthone (**10a**). In the same conditions, no reaction occurred from naphthalene, even after 24 h.

It was of great interest to try to reduce the amount of catalyst. Table 8 reports the results obtained with only 0.25% of UO<sub>2</sub>Cl<sub>2</sub>. Consumption of the reagents needed 1 h or less, then 0.25% of catalyst allows obtaining of acylated ethers, with high yields in a short time.

Bisbenzoylation compounds are possible precursors to synthesise polyketones. Such complexes of general formula ArCOAr'COAr are available using a diacid chloride. Terephthaloyl chloride reacted readily with one equivalent of mesitylene (Scheme 7). After 1 h the



Scheme 6.

Table 8  
Acylation of aromatic ethers, ArOR/RCOCl = 1.1/1, 0.25% UO<sub>2</sub>Cl<sub>2</sub>

Substrate	Reagent	Time (h)	T (°C)	TR/ArCOCl
Anisole	PhCOCl	30 <sup>a</sup>	154	98
Phenetole	PhCOCl	1	154	90
Phenetole	4-ClPhCOCl	1	169	100
Veratrole	4-ClPhCOCl	1	206	100

<sup>a</sup> Unit is expressed in minutes.

crude product was a mixture containing ca. 25% of the monoacylation product **11** and ca. 75% of the bisacylation compound **12** nearby unreacted acid chloride.

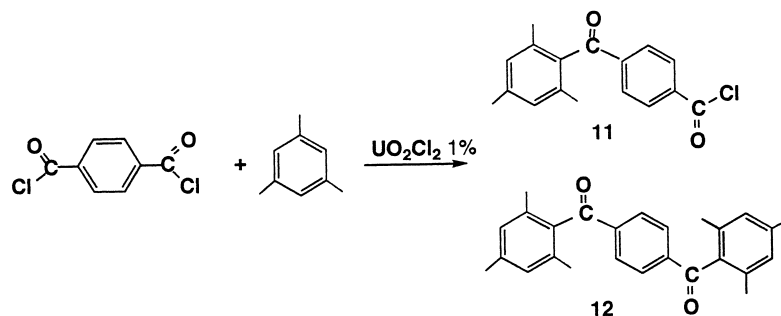
With 2 equivalents of mesitylene, only **12** was obtained within 1 h. After cooling, dissolution of the crude solid in toluene and usual workup, analytically pure **12** was isolated in 66% yield as a white crystalline powder.

The same reaction has been performed from durene (Scheme 8). The reaction was very slow at 266°C and only the monosubstituted product **13** was obtained. Sublimation of durene cannot be avoided and was an obstacle to the achievement of the reaction.

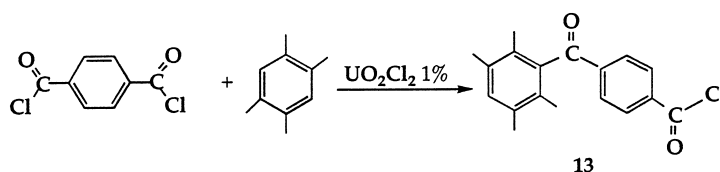
## 7. Recovery and reuse of the catalyst

In all reported reactions, the catalyst is recoverable after workup, it can be reused. To verify this point, the following experiments have been performed from mesitylene and terephthaloyl chloride (see Scheme 7).

Mesitylene, terephthaloyl chloride (2/1) and UO<sub>2</sub>Cl<sub>2</sub> 1% were refluxed. After 45 min, the consumption of the acid chloride was complete. After cooling, the bisbenzoylation compound **12** was extracted with toluene, the remaining insoluble UO<sub>2</sub>Cl<sub>2</sub> was used for a second run; after 1 h, the consumption of the chloride was complete, the solution contained 93.5%



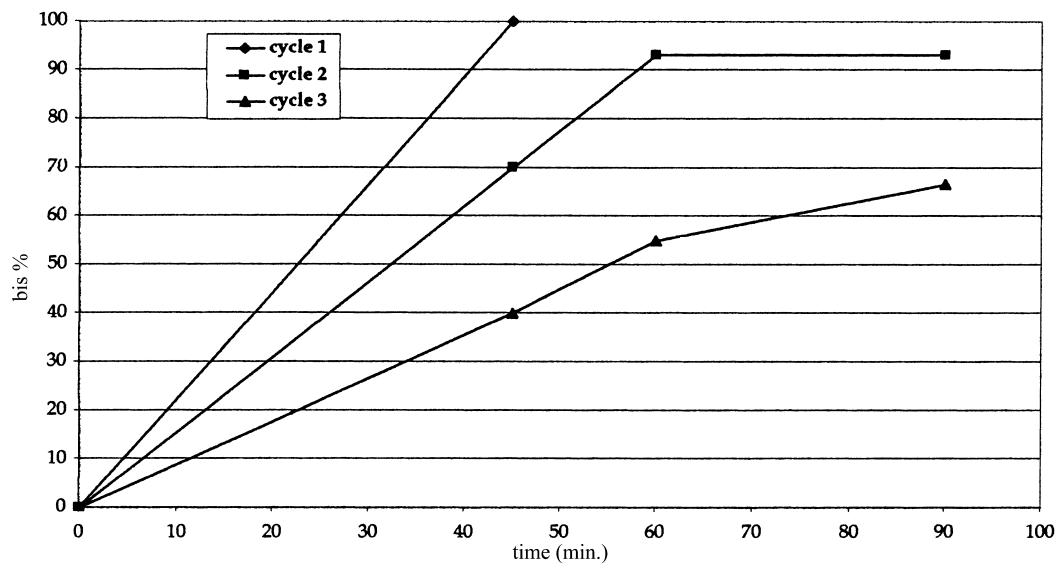
Scheme 7.



Scheme 8.

of **12** and 6.5% of monoacylation compound **11**. A third reaction was performed with the recovered catalyst. Consumption of the chloride needed 1.5 h and the solution contained 66.5% of **12** and 33.5% of **11**. In fact, after each synthesis, the catalyst is not quantitatively recovered, a part of  $\text{UO}_2\text{Cl}_2$  is entrained with

the organic compounds during the toluene extraction. The decreasing of the rate catalyst/reagents explains the progressive decreasing of activity. A more efficient recovering needed water treatment of the crude material to extract  $\text{UO}_2\text{Cl}_2$  (see Section 9). Experimental results are reported in Fig. 3.

Fig. 3. Recycling of  $\text{UO}_2\text{Cl}_2$  for benzoylation of mesitylene.



## 8. Purification of the organic product

The organic product must be obtained pure and free of catalyst. In an attempt to evaluate the amount of catalyst contained in the organic product, the benzylation of anisole was carried out with 1% of  $\text{UO}_2\text{Cl}_2$ , the crude mixture was diluted with toluene and treated in the following two ways: *A* and *B*.

Way *A*. After removal of toluene, a crystallisation in hexane afforded **1a** (sample **A**) in 74% yield.

Way *B*. The toluene solution was washed one time with water, the solution was dried and treated as pre-viously described. **1a** (sample **B**) was obtained in 72% yield. The amount of residual uranium in both sam- ples **A** and **B** was measured (ICP AES) at the labora- tory of analytical chemistry of Valduc (CEA DAM). Sample **A**, contained 35 ppm of uranium. Sample **B**, contained 3 ppm of uranium.

Then, it appears that after only one washing with water the amount of uranium is drastically decreased, the complete removal of this element from the acyla- tion products would be easily performed.

## 9. Experimental

### 9.1. Materials

Commercial organic reagents and solvents (analyt- ical grade) are used without further purification.

Uranium tetrachloride is synthesized on a 100 g scale from uranyle nitrate following the described procedure [14] (oxidation with  $\text{H}_2\text{O}_2$  to obtain  $\text{UO}_4$ , which is heated at  $400^\circ\text{C}$  to give orange  $\text{UO}_3$  and chlo- rination of  $\text{UO}_3$  with refluxing hexachloropropene. This reaction is very exothermic and must not be moderated to obtain a good yield. Then, the volume of the flask must be adapted to preclude overflowing).

Uranyle fluoride:  $\text{UO}_2\text{F}_2$ , is purchased by CO- GEMA (Pierrelatte). Uranyle chloride:  $\text{UO}_2\text{Cl}_2\text{HCl}\cdot 2\text{H}_2\text{O}$ , is synthesized from uranium oxide  $\text{U}_3\text{O}_8$ . The oxide: 8.42 g (10 mmol) is stirred at room tem- perature with 100 ml of 12 M aqueous HCl and  $\text{H}_2\text{O}_2$  is added until complete dissolution. The yel- low solution is evaporated to dryness and the solid is dried under vacuum. A yellow crystalline powder is obtained (11.55 g, 93% yield). Uranyle nitrate:  $\text{UO}_2(\text{NO}_3)_2\cdot 6\text{H}_2\text{O}$ , acetate:  $\text{UO}_2(\text{CH}_3\text{CO}_2)_2\cdot 2\text{H}_2\text{O}$  and uranium oxide  $\text{U}_3\text{O}_8$  are purchased by Prolabo.

All the salts are very hygroscopic and are stored in Schlenk vessels and handled in a Jacomex glove box. Oxides are stored in glass flasks and handled in a glove bag.

### 9.2. Analytical techniques

Composition and yields of the organic reaction products are determined with a GC 8000 Series gas chromatograph equipped with a flame ionisation de- tector, a data jet integrator (Thermo Separation Prod- uct) and a  $25\text{ m} \times 0.32\text{ mm}$  OV 1 capillary column.

$^1\text{H}$  NMR spectra are recorded on a Bruker AC 200 in  $\text{CDCl}_3$ .

The amount of remaining uranium in organic products is measured with a inductive coupling plasma-atomic emission spectroscopy (ICP-AES) ap- paratus at the CEA-DAM Research Center of Valduc.

UV-VIS and IR spectra are recorded on a Varian CARY 1 E and a Bruker IFS 28, respectively.

### 9.3. Acylation reaction with $\text{UCl}_4$ , typical experiment

In the glove box, 38 mg (0.1 mmol) of uranium tetra- chloride are weighed in a 100 ml vessel. The vessel is transferred on a vacuum line and filled with argon. Benzoyl chloride: 1.40 g (0.01 mol) and anisole: 5.4 g (0.05 mol) are added with a syringe and the mixture is vigorously stirred and heated until reflux of anisole ( $154^\circ\text{C}$ ). Green  $\text{UCl}_4$  is dissolved and the mixture turned immediately red orange. After 1 h refluxing, the mixture is cooled and analyzed by gas chromato- graphy. Transformation rate of benzoylchloride: TR = 100%, yield 72% (2-methoxybenzophenone (**1a**): 3%, 4 methoxybenzophenone (**1b**): 69%).

### 9.4. Acylation reaction with uranyle salts and recovering of the catalyst, typical experiment

In the glove box, 413 mg (1 mmol) of uranyle chlo- ride are weighed in a 100 ml vessel. The vessel is equipped with a condenser and a drying tube. Ben- zoyl chloride: 14.7 g (0.105 mol) and anisole 10.8 g (0.1 mol) are added and the orange mixture is vigor- ously refluxed for 1 h then cooled at  $0^\circ\text{C}$ . After 2 h warm toluene (50 ml,  $50^\circ\text{C}$ ) is added and the solu- tion filtered, leaving a greenish-yellow precipitate. The precipitate is washed with  $3 \times 5\text{ ml}$  toluene which

are collected and added to the toluenic solution, then dried for further use. Toluene is removed under reduced pressure and the creamy crude product containing 96% of *para* **1b** and 4% of *ortho* **1a** isomers (18.5 g, 87% yield) is extracted with 2 × 100 ml hexane. The solution is concentrated until the beginning of the crystallisation and stored for one night at –25°. After filtration and drying 15.7 g (74% yield) of white crystals of **1b** containing traces of **1a** are isolated.

Another reaction is conducted as described above, but the toluene solution is washed once with 50 ml of water, dried over magnesium sulfate and treated as precedently, affording 15.3 g (72% yield) of **1b**. The precipitate is dried to remove toluene and dissolved in the water used for washing. After filtration, evaporation of water and drying under reduced pressure, 400 mg (96.5%) of pure UO<sub>2</sub>Cl<sub>2</sub> are recovered.

### 9.5. Recycling of the catalyst

In the glove box, 413 mg (1 mmol) of uranyle chloride are weighed in a 100 ml vessel. The vessel is equipped with a condenser and a drying tube. Mesitylene: 12 g (0.1 mol) and terephthaloyl chloride 10.15 g (0.05 mol) are added and the mixture is refluxed under dry air. After 45 min, the consumption of the acid chloride is complete. The mixture is cooled, the organic solid is extracted with 50 ml toluene, at 40–50°C, the solution is filtered, the solid is washed once with 10 ml toluene and dried under vacuum before the next use. The toluene solutions contained only the bisbenzoylation product **12**.

A second synthesis is performed in the same conditions with the recovered catalyst. After 1 h, consumption of the acid chloride is complete. The crude solution contained 93.5% of **12** and 6.5% of monoacylation compound **11**. The catalyst is recovered and used for a third synthesis. Consumption of the acid chloride needed 1.5 h and the toluene solution contained 66.5% of **12** and 33.5% of **11**.

## 10. Conclusion

The U<sup>IV</sup> and U<sup>VI</sup> salts are very efficient catalysts for Friedel–Crafts acylations. The best results are

obtained with the strongest Lewis acids: uranyle salts. Those are stable towards oxidation and hydrolysis, the reaction can be carried out under dry air. After reaction, these salts can be recovered by filtration and reused without loss of activity. Uranyle salts are highly soluble in water; after usual workup, solvent extraction and washing of the organic solution with water until neutral, organic products can be obtained free of uranium.

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## References

- [1] K. Ishihara, M. Kubota, H. Kurihara, H. Yamamoto, J. Am. Chem. Soc. 117 (1995) 4413.
- [2] L. Hachiya, M. Morivaki, S. Kobayashi, Tetrahedron Lett. 36 (1995) 409.
- [3] K. Ishihara, M. Kubota, H. Yamamoto, Synlett (1996) 265.
- [4] A. Kawada, S. Mitamura, S. Kobayashi, Chem. Commun. (1996) 183.
- [5] T. Tsuchimoto, K. Tobita, T. Hiyama, S.I. Fukuzawa, Synlett (1996) 557.
- [6] S. Kobayashi, S. Nagayama, J. Am. Chem. Soc. 120 (1998) 2985.
- [7] S. Kobayashi, Eur. J. Org. Chem. (1999) 15.
- [8] K. Mikami, O. Kotera, Y. Motoyama, H. Sakaguchi, M. Maruta, Synlett (1996) 171.
- [9] J. Nie, J. Xu, G. Zhou, J. Chem. Res. 8 (1999) 446.
- [10] D. Baudry, A. Dormond, F. Montagne, New J. Chem. 18 (1994) 871.
- [11] D. Barbier-Baudry, A. Dormond, F. Duriau-Montagne, C.R. Acad. Sci.-Serie IIc (1998) 41.
- [12] D. Barbier-Baudry, A. Dormond, F. Duriau-Montagne, J. Mol. Catal. A 149 (1999) 215.
- [13] S. Richard, Thesis, Dijon, France, 1999.
- [14] R. Ashford, J.R. Desmurs, in: J.R. Desmurs, J.P. Ratton (Eds.), The Roots of Organic Development, Ind. Chem. Lib., Vol. 3, 1996, Elsevier, Amsterdam.
- [15] J.A. Hermann, J.F. Suttle, Inorg. Synth. 5 (1957) 143.
- [16] L. Arnaudet, G. Folcher, H. Marquet-Ellis, E. Klähne, K. Yünlü, R.D. Fischer, Organometallics 2 (1983) 344.
- [17] D. Barbier-Baudry, J.R. Desmurs, A. Dormond, S. Richard, J. Mol. Catal. A 161 (2000) 23.