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SbCl₃-TEBA complex as a highly efficient catalyst for the Friedel-Crafts acylation reaction

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Abstract: The complex of antimony (Ш) chloride (SbCl₃) and (triethylbenzylammonium chloride (TEBA) called bis (triethylbenzylammonium) pentachloroantimonate (Ш) ($[(C_2H_5)_3C_7H_7)N]_2SbCl_5$) was described as a novel catalyst for Friedel-Crafts acylation reactions of aromatic compounds with acyl chlorides. This catalyst is resistant to atmosphere and moisture with minimal toxicity. Its use is rapid and clean. Furthermore, reusability, easy to perform eco-friendly mild reaction conditions, short reactions time, high yields, and easy work up are some more advantages.

Introduction

The Friedel-Crafts acylation reaction is a useful procedure for the carbon-carbon bonds formation in aryl systems which have been accepted as one of the common transformations in organic synthesis as well as in the chemical industry [1]. The basic operation of the Friedel-Crafts acylation and related reactions requires the addition of a Lewis acid such as metal chlorides (AlCl₃, SbCl₅, BF₃, FeCl₃, BiCl₃, TiCl₄ and SnCl4) as catalyst, which is often strongly oxyphilic [2-5]. Additionally, some other systems containing triflic acid [6] and lithium perchlorate [7] have been reported for such reactions [8-9]. By using transition metal catalyst In [10], Hf [11, 12], Ag [13] and Ga [14] various acylation conditions have recently been reported [15-20]. But these catalysts are generally expensive and require long time to complete transformation, although the yield of product is satisfactory. Furthermore, the acyl derivatives are concerned in some of bimolecular compounds [20].

Since the Friedel-Crafts acylation has unlimited potential for generating novel aryl compounds, alternative catalysts for this type of reactions are desirable. The catalysts which can be served for specific goals in terms of reaction time, yield, substrate scope, catalyst recover, and operation practicality.
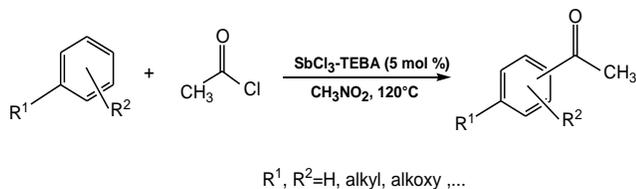
In the present work, we report bis (triethylbenzylammonium) pentachloroantimonate (Ш) complex, abbreviated with SbCl₃-TEBA as a novel Lewis acid and efficient catalytic system for Friedel-Crafts acylation reaction of aromatic compounds (Scheme **1**). There are many advantages to using this catalyst, such as ready access, minimal toxicity, reusability, insensitivity to atmosphere and moisture, rapid acylation with high yield, and ease of operation.

Results and discussion

Initially, optimization of conditions for the acylation of anisole with acetyl chloride was investigated in the presence of various quantities of SbCl₃-TEBA complex at 120°C. Nitromethane was found to be a suitable solvent for this catalytic system [21-22]. Our experiments proved that the catalyst concentration of 5

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mol% was enough to complete conversion of anisole (Table **1**). We found that the increase of the amount of the catalyst did not enhance the yield (entry 2), but the use of lower percent of the catalyst led to lower yield and longer reaction time (entry 3).

Then the optimized conditions for the Friedel-Crafts acylation reaction of benzene and its derivatives (Table **2**) were examined. Consequently, this catalyst is not a good choice for the acetylation of nitrobenzene and boromobenzen (entries 2-3), but it is highly effective for acylation of anisole and other electron-rich derivatives such as toluene, xylene, mesitylene, etc. (entries 4-15). The catalyst affords the corresponding aromatic ketones in high yield.

R^1, R^2 =H, alkyl, alkoxy ,...

Scheme 1: The Friedel-Crafts acylation reaction by bis (triethylbenzylammonium) pentachloroantimonate(Ⅲ).

Table 1: Optimization of the catalyst concentration for the acylation of anisole

Entry	Mol of catalyst (%)	Time (min)	Yield (%)[a]
1	5	30	98
2	10	30	98
3	3	35	91

[a]Isolated yield (4-Methoxyacetophenone).

Table 2: SbCl$_3$-TEBA catalyzed the Friedel-Crafts acylation reactions of benzene and its derivatives

Entry	Substrate	Product	Time (min)	Yield (%)[b]
1	PhH	Acetophenone	135	43
2	PhNO$_2$	3-Nitroacetophenone	180	No reaction
3	PhBr	4-Bromoacetophenone	75	35
4	Cumene	4-Isopropylcetophenone	60	85
5	PhOH	4-Hydroxyacetophenone	30	98
6	PhMe	4-Methylacetophenone	75	85
7	*o*-Xylene	3,4-Dimethylacetophenone	35	93
8	*m*-Xylene	2,4-Dimethylacetophenone	35	92
9	*p*- Xylene	2,5-Dimethylacetophenone	35	93
10	Mesitylene	2,4,6-Ttrimethylacetophenone	30	93

11	PhOMe	4-Methoxyacetophenone	30	98
12	PhOEt	4-Ethoxyacetophenone	30	97
13	Diphenyl ether	4-Phenoxyacetophenone	35	70
14	1,3-Dimethoxybenzene	2,4- Dimethoxyacetophenone	30	94
15	1,4-Dimethoxybenzene	2,5- Dimethoxyacetophenone	30	96

[a]All reactions were carried out in boiling nitromethane with the substrates ratio: ArH/MeCOCl/catalyst = 1/1/0.05.
[b]Isolated yields.

According to Table **2**, using $SbCl_3$-TEBA for the Friedel-Crafts acylation reactions takes a longer time to complete conversion in comparison with $SbCl_5$-TEBA, but it affords the corresponding aromatics ketones in higher yields [1]. One of the most important features of this catalyst is that the complex can be recycled. After reusing for more than four times, the catalyst was recovered quantitatively after each experiment. The activity of the recovered catalyst was also examined. It was found that the catalytic activity decreased gradually, and the obtained 4-methoxyacetophenone reduced from 98% to 83% after four runs (Figure **1**).

An additional feature of the $[BnNEt_3]_2SbCl_5$ catalyst is that the complex is inert to water and oxygen and also easy to handle in the atmosphere without changing the catalytic activity of antimony chloride. Whereas antimony trichloride on contact with water hydrolyzes, it forms antimony oxychloride and releases hydrogen chloride. Thus samples of $SbCl_3$ must be protected from moisture, and it cannot be handled easily in air atmosphere.

$$SbCl_3 \ + \ H_2O \longrightarrow SbOCl \ + \ 2\,HCl$$

Furthermore, the solvation of $SbCl_3$ donor solvents can be greatly compromised by strong complexation, which inhibits further reactivity. Indeed, these complexes known as Mentshutkin complexes are responsible for the inefficiency of $SbCl_3$ in the catalysis of Friedel-Crafts reactions of activated aromatics [23]. Finally, $SbCl_3$ itself is not a good choice for this reaction, and it gives merely <25% isolated yield under the similar conditions.
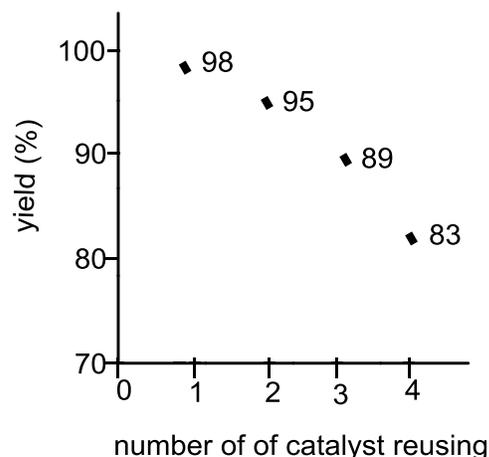

Figure 1: The relationship between run of the catalyst reusing and its yields for the acylation reaction of anisole under the reaction conditions.

Experimental

Materials and methods:

Starting materials were obtained from Merck and Fluka companies. IR spectra were measured on a Brucker Tensor 27 spectrometer. ^{1}HNMR spectra of selected products were recorded on a Varian 400 MH*z* instrument in $CDCl_3$ with TMS as internal standard. The reactions were monitored by thin layer chromatography. Elemental analysis was obtained on a Perkin Elmer Series II analyzer, Cl was determined by Volhard method and Sb was determined by atomic absorption spectroscopy. All products are known compounds and they were identified by comparison of their physical and spectral data with those of authentic samples [24-27]. All yields refer to pure isolated products.

Synthesis of the $[(C_2H_5)_3(C_7H_7)\,N]_2\,SbCl_5$ Complex:

Two freshly prepared solutions of 10 mmol of antimony (Ⅲ) chloride and 100 mmol of

benzyltriethylammonium chloride in a mixture of concentrated hydrochloric acid (36%) with water (HCl: $H_2O = 1 : 1$) was mixed, then the reaction mixture was concentrated in a water bath for several hours. The obtained precipitate was cooled to room temperature, filtered off, washed in succession with isopropanol and diethyl ether. The complex was then recrystallized from ethanol and dried to yielded 5.7gr (83%) of SbCl3-TEBA; white solid, mp 129°C, elemental analysis;. for $C_{26}H_{44}N_2SbCl_5$ (683.67) found: C 45, H 6.4, N 4.1, Cl 26, Sb 17.8.

Acylation of anisole, typical procedure:

To a mixture of anisole (30 mmol) and SbCl$_3$-TEBA catalyst (1.5 mmol, 5 mol %), in nitromethane (25 ml), was added acetyl chloride (30 mmol). The mixture was stirred for 30 minutes at 120°C (oil bath temperature). The progress of the reaction was monitored by TLC (n-heptane/ethyl acetate, 9: 1). After cooling, the mixture was extracted with petroleum ether (50-70°C, 3 × 20 ml), the catalyst remained in the nitromethane, could be either reused in the next reaction directly or recovered by removal of nitromethane under reduced pressure. The petroleum ether layer was washed with water and dried over anhydrous MgSO$_4$. After removal of the solvent under reduced pressure, the crude product was purified by distillation in vacuum.

Typical procedure for catalyst recycling in the acylation of anisole:

When the reaction was complete, the reaction mixture was extracted with petroleum ether several times; the catalyst remained in the nitromethane phase and was reused for the next reaction directly. In each run, the above mentioned procedure was followed for the reaction.

Acetophenone (entry 1): IR (KBr) 3080, 3025, 1696, 1605, 1365, 1268,762 cm^{-1}. ^{1}H NMR δ 2.43 (s, 3H), 7.37-7.80 (5H).

2, 4, 6-Trimethylacetophenone (entry 10): IR (KBr) 1287, 1664, 1685, 3076 cm^{-1}. ^{1}H NMR δ 2.27 (s, 6H), 2.36 (s, 3H), 7.12 (s, 1H), 7.87 (s, 1H).

4-Phenoxyacetophenone (entry 13): IR (KBr) 889, 1312, 1667, 3091 cm^{-1}. ^{1}H NMR δ 2.44 (s, 3H), 6.9-8.11 (m, 9H).

2, 4- Dimethoxyacetophenone (entry 14): IR (KBr) 1311, 1652, 1683, 3079 cm^{-1}. ^{1}H NMR δ 2.49 (s, 3H), 3.66 (s, 3H), 3.84 (s, 3H), 6.69 (d, 1H), 7.78 (d, 1H), 7.10 (s, 1H).

2, 5- Dimethoxyacetophenone (entry 15): IR (KBr) 1251, 1330, 1531, 1652, 3083 cm^{-1}. ^{1}H NMR δ 2.53 (s, 3H), 3.73 (s, 3H), 3.80 (s, 3H), 7. 07 (d, 1H), 7.26 (d, 1H), 7.53 (s, 1H).

Conclusion

In summary, this paper reports the efficient and commercially available catalyst of antimony chloride-TEBA complex for the Friedel-Crafts reactions with high yields. This catalyst can be reused and its activity could be maintained. Therefore, we proposed this catalyst for future studies and using in industrial production and green chemistry as an environmentally friendly procedure.

Acknowledgement

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