

Acid catalyzes the synthesis of aromatic *gem*-dihalides from their corresponding aromatic aldehydes

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Abstract

A variety of aromatic *gem*-dihalides were synthesized for the first time from the reaction of their corresponding aldehydes with acid halides in the presence of acid catalysts. Both homogeneous and heterogeneous Lewis and Bronsted acids were successfully employed. AlCl_3 and sulfated zirconia were the most active homogeneous and heterogeneous catalysts respectively. Benzoyl chloride was more reactive than acetyl and propionyl chloride. Replacing the chloride with bromide also resulted in increased activity. Performing the reaction in a polar solvent and in benzaldehyde as a self solvent resulted in a higher product yield. Sulfated zirconia was regenerated and successfully re-used by calcination in static air at 550°C for 0.5 h.

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1. Introduction

α,α -Dihalo aromatic compounds (*gem*-dihalides) are important intermediates in the pharmaceutical, agricultural and dyes industries [1–5]. They can be used as starting materials for several C–C coupling reactions [6–10] and synthesis of imines [11] as well as a parent raw material for synthesis of their corresponding amines, acids and alcohols [12,13]. Generally, α,α -dihalotoluenes can be produced by catalytic or non-catalytic halogenation of toluene or halomethylation of benzene [14], however benzyl chloride is mostly the main product and trichlorobenzene is also formed. Alternatively, benzaldehyde can be reacted with several inorganic chlorinated reagents such as PCl_5 [15], BCl_3 [16] and SOCl_2 [17] to form the corresponding *gem*-dihalides by dihalo-de-oxo-bisubstitution. Yet, when PCl_5 is replaced by PBr_5 it does not give good yields of *gem*-dibromide.

Acid catalysts are widely used in many important chemical transformations such as isomerization, dehydration and

Friedel–Craft acylation and alkylation [18,19]. Traditionally, stoichiometric amounts of homogeneous Lewis and Bronsted acids are employed. However, in recent years there has been intensive research to replace these corrosive and hazardous compounds with heterogeneous acid catalysts [18–25]. Besides the economical and environmental aspects, solid acids offer some practical benefits such as easy catalyst separation and recycling. More than 300 solid acids and bases have been developed, characterized and applied as catalysts in many reactions [26,27], and some of them have already been applied in industry. They can be divided into four main groups: zeolites (Y, Beta, ZSM-5, mordenite) [23], sulfonated resins with surface $-\text{SO}_3\text{H}$ groups (Nafion, Amberlist) [22], sulfated zirconia [24] and Cs-salts of $\text{H}_3\text{PW}_{12}\text{O}_{40}$ heteropolyacid (HPW) [25]. While, sulfonated resins and heteropolyacids as protonic acids contain only Bronsted acid sites, zeolites and sulfated zirconia contain protonic and aprotic (Lewis) acid sites related to defined atomic groups at their surface.

The acylation of benzaldehyde is expected to be unfavorable due to the deactivation of the aromatic ring by the aldehyde group. However, the transformation of aldehydes to α,α -

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diacetates (*gem*-diacetates, acylals) by their reaction with the corresponding anhydride was reported in the presence of various homogeneous Bronsted and Lewis acids [28–33].

In this paper, we report, for the first time, on the synthesis of α,α -dihalo aromatics from the reaction of their corresponding aldehydes with several acid halides in the presence of homogeneous and heterogeneous acid catalysts (Fig. 1). The effect of catalyst type and reaction conditions on catalytic performance was studied. Regeneration and recycling of a selected heterogeneous catalyst were also examined. The products were characterized by GC, GC–MS and ^1H NMR.

2. Results and discussions

2.1. Homogeneous acid catalysts

2.1.1. Effect of catalyst type and reaction conditions

As previously mentioned, the reaction between aromatic aldehydes and anhydrides in the presence of acid catalyst yields α,α -diacetates [28–33]. We believed that replacing the anhydride with acid halide will produce 1-halo,1-benzylacetate and the corresponding α,α -dihalo aromatic compound (Fig. 1). The investigation started with the reaction of benzaldehyde (BA) and propionyl chloride (PC) with AlCl_3 as a catalyst (Table 1). The reaction proceeded in two representative solvents, dichlorobenzene (DCB), which was chosen as a solvent since it does not react in the presence of acid catalyst, and excess of benzaldehyde as a self solvent. Inorganic chlorides such as PCl_5 and BCl_3 react with benzaldehyde to form benzal chloride [15–17] but can also act as Lewis acids. Therefore, the blank reaction of benzaldehyde with AlCl_3 was initially tested to determine if there is any dihalo-de-oxo-bisubstitution between benzaldehyde and AlCl_3 . No product was observed (entry 1). The reaction of benzaldehyde and propionyl chloride in the absence of a catalyst also did not yield any product (entry 2). However, when both acid chloride and an acid catalyst were added to the reaction mixture, it resulted in the production of benzal chloride

(entries 3–11). The product was identified by GC–MS, ^1H NMR and by comparison to commercial standard.

Different homogeneous acid catalysts as well as different reaction conditions were tested and the results are summarized in Table 1. It was found that both homogeneous Lewis and Bronsted acids catalyzed the synthesis of benzal chloride from benzaldehyde and propionyl chloride (Fig. 1a). Propionic anhydride was also observed. The selectivity to benzal chloride was around 60–70% for all reactions in DCB. It was calculated from benzaldehyde conversion and benzal chloride yield that was calculated based on commercial standard. GC–MS analysis of all reaction mixtures showed that 1-chloro,1-benzylpropane is the other major aromatic product. It seems that 1-chloro,1-benzylpropane is an intermediate from the reaction of benzaldehyde with one molecule of propionyl chloride (Fig. 1b) similar to the formation of acylals from the reaction of benzaldehyde and anhydride over acid catalysts (Fig. 1c) [28–33]. This result may imply that benzaldehyde reacts with two molecules of propionyl chloride in two steps whereas 1-chloro,1-benzylpropane is the product of the first step. Traces of benzoylchloride and 1,1-dipropionyloxytoluene from the reaction of benzaldehyde with propionic anhydride (Fig. 1c) were also detected. The low concentration of 1,1-dipropionyloxytoluene might be attributed to the lower concentration of propionic anhydride relatively to propionyl chloride. However, it might be also that 1,1-dipropionyloxytoluene is not stable toward reaction conditions and was converted into benzal chloride. In order to clarify this suggestion propionic anhydride was first added to a reaction mixture of benzaldehyde and AlCl_3 and 1,1-dipropionyloxytoluene was detected. Then excess of propionyl chloride was added and the reaction proceeded for an hour. Analysis of the reaction mixture clearly showed high amount of benzal chloride and negligible amount of 1,1-dipropionyloxytoluene.

For all the catalysts employed, reaction in benzaldehyde as a self solvent resulted in higher product yield and selectivity than the corresponding reaction in DCB. Working in the absence of solvent has also some environmental, economi-

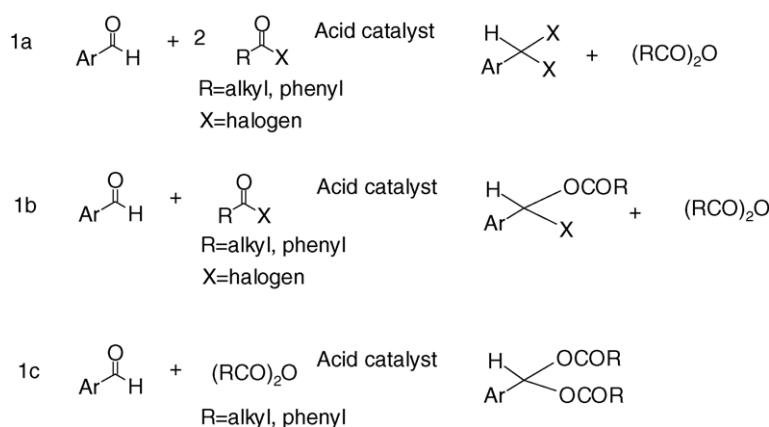


Fig. 1. Acid catalyzes the synthesis of: (a) aromatic *gem*-dihalides from their corresponding aldehydes; (b) aromatic 1-halo,1-ester; (c) aromatic *gem*-diesters.

Table 1
Synthesis of benzal chloride with different homogeneous acid catalysts

Entry	Catalyst type	Catalyst (g)	Product yield (%) in DCB ^a	Product yield (%) in BA ^b
1	AlCl ₃ ^c	1	0	0
2	–	–	0	0
3	SnCl ₄	0.1	4.1 (61)	7.0
4	AlCl ₃	0.1	4.2 (67)	8.2
5	AlCl ₃	0.5	21.8 (58)	22.7
6	AlCl ₃	1	35.2 (58)	25.5
7	AlCl ₃ ^d	1	45.8 (69)	43.9
8	AlCl ₃ ^e	1	52.5 (65)	47.4
9	ZnCl ₂	0.1	1.2 (63)	5.8
10	H ₂ SO ₄	0.1	5.7 (41)	16.1
11	H ₃ PO ₄	0.1	2.9 (67)	13.9

^a Reaction conditions: 12.5 g DCB, 23.6 mmol BA, 47 mmol PC, 110 °C, 1 h (in parenthesis benzaldehyde selectivity).

^b Reaction conditions: 141.5 mmol benzaldehyde, 47 mmol PC, 110 °C, 1 h.

^c No PC.

^d 3 h.

^e 94.5 mmol PC.

cal and practical advantages. Increasing the amount of AlCl₃ from 0.1 to 1 g increased the product yield but did not significantly change the selectivity (entries 4–6). Proceeding the reaction for a longer time (entry 7) or adding an extra amount of propionyl chloride (entry 8) resulted in increased product yield and selectivity.

2.1.2. Effect of reaction components

A variety of acid halides and aromatic aldehydes were examined in optimal conditions to explore the scope of the new synthesis (Table 2). Since some of the reagents are solids, a solvent was necessary. Therefore, for comparison of activities and selectivities, all the reactions were conducted in DCB. In addition, since all products besides benzal chloride are not commercially available, the comparison was based on aldehyde conversions. Yet, only traces of other aromatic

products, mainly the corresponding 1-chloro,1-propionyloxy aromatic compounds were observed by GC–MS analysis, implying high product selectivities. The corresponding anhydrides were also detected in all reactions. Several conclusions may be drawn from the results obtained. All acid chlorides yielded the desired product while benzoyl chloride was the most active and selective (entries 1–3). Substituted benzaldehyde with both electron-withdrawing and electron-donating groups yielded enhanced product yields (entries 5, 7–10). Other aromatics aldehyde such as naphthaldehydes (entries 11 and 12) and indole carboxyaldehydes (entries 13 and 14) were slightly less active than benzaldehyde (entry 2) under similar conditions. 2-Chlorobenzaldehyde (entry 10) was unusual in that, although it yielded high conversion, the selectivity to the desired product based on GC and GC–MS analysis was not high (45% selectivity, based on GC–MS analysis). When *p*-hydroxybenzaldehyde was reacted with propionyl chloride (entry 8) the propionyl cation fully reacted with the hydroxyl group leading to *p*-propionoxybenzaldehyde, which then converted to the corresponding *gem*-dichloride. Replacing acetyl chloride with acetyl bromide and its addition to benzaldehyde (entry 4) and *p*-tolualdehyde (entry 6) yielded only benzal bromide and 4-methylbenzal bromide instead of benzal chloride and 4-methylbenzal chloride. The exclusive formation of the corresponding *gem*-dibromides when acetyl bromide was used in the presence of AlCl₃ indicates that the Lewis acid acts as a catalyst and not as a chlorinating reagent as other inorganic chlorides [15–17], as concluded from the blank reaction with AlCl₃ (entry 1). For both substrates, the detected product yields, which were calculated based on a benzal bromide commercial standard, were higher than the yields obtained with acid chlorides, probably due to the higher activation of acid bromides in the presence of an acid catalyst. When aliphatic aldehydes were used, the corresponding α,α -dichloro compounds were not detected. Finally, conducting the reaction of substituted benzaldehyde without a solvent, whenever possible, also

Table 2
The synthesis of various aromatic *gem*-dihalides

Entry	Aldehyde	Acyl halide	Conversion (%) ^a
1	Benzaldehyde	Acetyl chloride	57.2 (50)
2	Benzaldehyde	Propionyl chloride	60.9 (58)
3	Benzaldehyde	Benzoyl chloride	89.3 (75)
4	Benzaldehyde	Acetyl bromide	98.6 (55)
5	4-CH ₃ C ₆ H ₄ CHO	Propionyl chloride	96.0
6	4-CH ₃ C ₆ H ₄ CHO	Acetyl bromide	100
7	4-(CH ₃) ₂ CHC ₆ H ₄ CHO	Propionyl chloride	66.1
8	4-HOC ₆ H ₄ CHO ^b	Propionyl chloride	48.9
9	4-ClC ₆ H ₄ CHO	Propionyl chloride	74.7
10	2-ClC ₆ H ₄ CHO	Propionyl chloride	93.2
11	1-Naphthaldehyde	Propionyl chloride	41.9
12	2-Naphthaldehyde	Propionyl chloride	34.7
13	Indole-5-carboxyaldehyde	Propionyl chloride	32.5
14	Indole-6-carboxyaldehyde	Propionyl chloride	31.7

^a Reaction conditions: 1 g AlCl₃, 12.5 g DCB, 23.6 mmol aldehyde, 47 mmol acid halide, 110 °C, 1 h (in parenthesis benzaldehyde selectivity).

^b The substrate fully reacted with PC in the presence of acid catalyst to form *p*-propionoxybenzaldehyde.

Table 3
Solid acid catalysts characteristics and performances^a

Catalyst	Manufacturer	Surface area (m ² /g)	Active sites (meqH ⁺ /g) ^b	SiO ₂ /Al ₂ O ₃	Benzal chloride yield (%)
SO ₄ -ZrO ₂	MEL	100	0.4		22.1
HUSY-760 zeolite	PQ	720		60	10.8
H β zeolite	PQ	730		25	1.8
H-Mordenite	PQ	600		20	>0.1
H-ZSM-5 (5020)	PQ	430		50	2.5
Amberlyst [®] -15	Aldrich	0.35	4.74		12.1
SAC-13 ^c	Aldrich	200	0.15		8.3
CS _{2.5} H _{0.5} PW ₁₂ O ₄₀ ^d	–	152 ^e	0.16		3.4

^a Reaction conditions: 12.5 g DCB, 23.6 mmol benzaldehyde, 47 mmol benzoyl chloride, 110 °C, 1 h.

^b For sulfated zirconia and in acid resins, active sites were calculated on the basis of sulfur.

^c Nafion[®] entrapped in silica prepared by the sol–gel method.

^d The catalyst was prepared by precipitation of HPA with Cs₂CO₃ from aqueous solution as written in experimental.

^e BET of freshly prepared catalysts.

showed higher activities when compared with the reaction in DCB.

In conclusion, the synthesis of aromatic *gem*-dihalides from the reaction of their corresponding aldehydes with acid halides in the presence of homogeneous Lewis and Bronsted acids was explored for the first time. The yields to *gem*-dihalides were high and the corresponding mono or tri halogenated products were not detected.

2.2. Solid acids

2.2.1. Effect of catalyst type

First, several representative commercial solid acid catalysts were employed in the dihalo-de-oxo-bisubstitution of benzaldehyde with benzoyl chloride as representative acid chloride under similar conditions. Before being added to the reaction mixture, the catalysts were activated at typical conditions adapted from literature related to acylation reactions [18,19]. The chemical composition and surface areas of all the catalysts as well as their performance in benzal chloride synthesis are summarized in Table 3.

Among all solid acids employed, sulfated zirconia showed the best catalytic performances. It can be attributed to the significant higher acid strength of SO₄-ZrO₂ ($-H_0 < 16$) as determined by the color change method of Hammett indicators when compared with zeolites ($-H_0 = 10$ –14), sulfonated resins with surface -SO₃H groups ($-H_0 = 2$ –12), and Cs-HPW ($-H_0 = 13.5$) [34,35]. Several commercial zeolites with different SiO₂/Al₂O₃ ratios and pore structure were also tested. It is clear that the three-dimensional structured HUSY-zeolites with SiO₂/Al₂O₃ ratios of 40–60 are much more effective catalysts for the synthesis of benzal chloride (Table 3 and Fig. 2), while H β -zeolite and H-ZSM-5 showed very low yields and H-Mordenite was inactive. The huge difference between the different types of zeolites could be attributed to their chemical composition and textural properties. H-Mordenite and H β have a mono-dimensional pore structure and lower pore diameter relative to HUSY [23,36]. H-ZSM-5, which also has a three-dimensional structure, displays the smallest pore size and the lowest surface area among all the

tested zeolites that can lead to mass transfer limitations and enhanced confinement effects [23].

As illustrated in Fig. 2, the benzal chloride yield was also affected by the Al content of the zeolites. While increasing the alumina content up to SiO₂/Al₂O₃ = 60 proportionally increased the product yield with the same magnitude for both HUSY and H-ZSM-5 zeolites, further increasing of the SiO₂/Al₂O₃ ratio resulted in a decrease of product yield. Increasing the alumina content increased the concentration of the acid sites but also decreased their strength. Thus, these two opposing phenomena could be the explanation for the maximum yield of benzal chloride observed around the mole ratio of SiO₂/Al₂O₃ = 60 for both zeolites. At high alumina content the concentration of acid sites is high but their acidity is low, while at low alumina content the concentration of acid sites is low but their acidity is higher.

Sulfonated ion-exchange resins represent an important class of solid acid catalysts [22]. Two main types, styrene-based (Amberlyst[®]) and perfluorinated (Nafion[®]) sulfonic acid resins are usually used. While the perfluorinate resins are much more acidic than the styrene-based resins ($-H_0 = 12$ versus 2.2 respectively), the capacity of the protons of the styrene-based resins is much higher. Both polymers have low surface area and therefore the accessibility of the active sites is limited. Entrapment of Nafion in silica matrix by the sol–gel

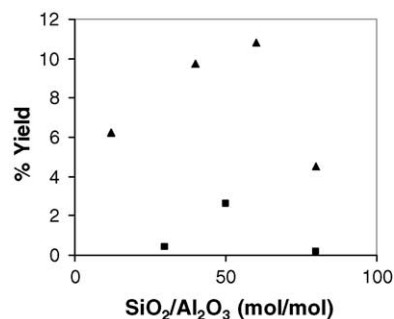


Fig. 2. Effect of alumina content in HUSY and H-ZSM-5 zeolites on product yield. Reaction conditions: 12.5 g DCB, 23.6 mmol benzaldehyde, 47 mmol benzoyl chloride, 0.2 g catalyst, 110 °C, 1 h. (▲) HUSY; (■) H-ZSM-5.

Table 4
Sulfated zirconia catalyst characteristics and performances^a

Calcination temperature (°C)	Sulfur (wt.%)	Tetragonal crystallinity (%)	Particle size (nm)	Surface area (m ² /g)	Benzal chloride yield (%)
350	2.46	–	–	160	4.7
450	2.64	10	–	145	16.7
550	2.15	51	8.5	138	22.1
650	0.54	100	10.5	85	16.1

^a Reaction conditions: 12.5 g DCB, 23.6 mmol benzaldehyde, 47 mmol benzoyl chloride, 0.2 g catalyst, 110 °C, 1 h.

technique resulted in high surface area solid (SAC-13[®]) but the polymer content and the accessibility of the active sites are very limited. As can be seen from Table 3, Amberlyst was slightly more active than SAC-13 for the synthesis of benzal chloride from benzaldehyde.

Heteropolyacid (HPW), particularly the Keggin type 12-tungstophosphoric acid (H₃PW₁₂O₄₀), possesses strong Bronsted type acidity and exhibits superior performance in a wide variety of acid catalyzed reactions [37]. However, they suffer from drawbacks such as very low surface area and high affinity to polar media [37]. Exchanging part of the protons of HPW by Cs⁺ allows its separation and recycling [38], but leads to significant reduction in catalyst acidity. In addition, it forms a microporous solid [39] with diffusion limitations. These are probably the main reasons for the low performance of CS_{2.5}H_{0.5}PW₁₂O₄₀ catalyst, in comparison with other solid acids (Table 3). Consequently, SO₄-ZrO₂ was selected as most efficient heterogeneous catalyst for further experiments.

2.2.2. Effect of catalyst activation temperature

It is well known that the calcination temperature of sulfated zirconium hydroxide has a strong influence on its catalytic performance [40]. It has also been established in different acylations that the ratio of Bronsted to Lewis acidic sites over the catalytic surface, strength of acid sites, surface area, sulfur content as well as the nature of phase composition (e.g. formation of the tetragonal zirconia phase) are important in the formation of appropriate surface acidity [41–43]. All these parameters are influenced by the catalyst calcination temperature.

The characteristic properties of commercial SO₄-ZrO₂ as well as benzal chloride yield as function of catalyst calcination temperature are summarized in Table 4. Increasing the calcination temperature decreased sulfur content and surface area and increased the crystal size and crystallization of ZrO₂ into the tetragonal phase, in agreement with previous reports [41–43]. In addition, it can be seen from Table 4 that benzal chloride yield reached the maximum after activation of the catalyst at 550 °C. It was previously demonstrated that the ratio of Bronsted to Lewis sites at the surface of sulfated zirconia diminishes at high calcination temperatures [44]. However, a combination of a relatively high loading of sulfate species, high surface area and the nature of surface acidity (after 50% crystallization of zirconia phase at a calcination temperature of 823 K) are important. Consequently,

the synthesis of benzal chloride with benzoyl chloride was carried out with a catalyst precalcined at 550 °C.

2.2.3. Effect of solvent

It is well known that the nature of the solvent in catalytic reactions can influence performance [45]. In many cases the effect of the solvent on activity and selectivity is attributed to its polarity. However, this concept of solvent polarity is difficult to define precisely and even more difficult to express quantitatively. The dielectric constant is often used to describe solvent polarity, though this approach does not take into account specific solute/solvent interactions. The reaction was carried out in the presence of different selected solvents that are not reactive toward acylation (Table 5). It was conducted at standard conditions, as well as with benzaldehyde as self solvent. It is clear from Table 5 that the product yield was significantly higher and comparable in the more polar solvents including benzaldehyde. It can be attributed to the enhanced generation and stabilization of carbocation in a polar medium.

2.2.4. Effect of reaction conditions

The progress of reaction in DCB and benzaldehyde with three different acid chlorides, acetyl, propionyl, and benzoyl chloride, is shown in Fig. 3. While the reaction in DCB stopped after 1 h, the reactions in benzaldehyde reached constant product yield after 3 h. It seems that the reaction stopped after a while due to deactivation of the catalysts. As previously detected, when AlCl₃ was employed as catalysts (Table 2), benzoyl chloride was the most reactive acid chloride, probably due to higher dissociation of benzoyl chloride in the presence of acid catalysts. In addition, replacing benzoyl chloride with benzoyl bromide resulted in increased product yield of the corresponding *gem*-dibromide (benzal bromide). Again, it could be attributed to enhanced dissociation of acid bromide in the presence of an acid catalyst.

Table 5
The effect of solvent polarity on catalytic performance^a

Solvent	Dielectric constant	Benzal chloride yield (%)
Nitrobenzene	35.2	22.5
Benzaldehyde	17.8	22.6
Dichlorobenzene	9.9	22.1
Chlorobenzene	5.6	9.39
Decalin	2.2	1.88

^a Reaction conditions: 12.5 g solvent, 23.6 mmol benzaldehyde, 47 mmol benzoyl chloride, 110 °C, 1 h.

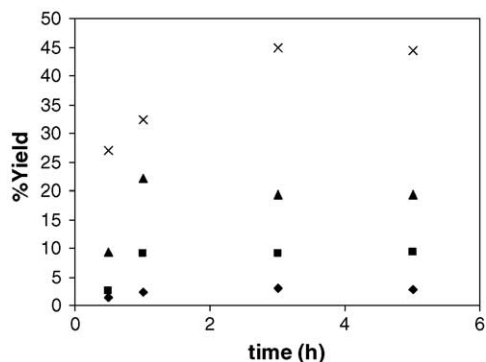


Fig. 3. Effect of reaction time on product yield. Reaction conditions: 12.5 g DCB, 23.6 mmol benzaldehyde, 47 mmol acid chloride, 0.2 g catalyst, 110 °C, 1 h. (◆) Acetyl chloride; (■) propionyl chloride; (▲) benzoyl chloride; (×) 15 g benzaldehyde as self solvent with benzoyl chloride.

The effect of reaction time on product selectivity was also examined using sulfated zirconia as catalyst and propionyl chloride as the acyl halide. The selectivity of benzal chloride was increased from 56% after 0.5 h to 75% after 1 h while the concentration of 1-chloro,1-benzylpropane was correspondingly decreased. The same results were measured when AlCl_3 was employed as catalyst (Table 1, entries 6 and 7). It supports our suggestion that the reaction proceed via two steps with 1-chloro,1-benzylpropane as an intermediate.

The effect of benzoyl chloride concentration in DCB and benzaldehyde was also examined (Table 6). Surprisingly, it did not change the product yield. It might be that at low conversion of benzaldehyde, there is still enough benzoyl chloride to react.

The effect of catalyst loading was studied by varying the amount of catalyst at a fixed total amount of the reaction mixture and with the same content of benzoyl chloride (Fig. 4). For both DCB and benzaldehyde, increasing the catalyst amount at a constant benzoyl chloride concentration and reaction temperature resulted in an increase of benzal chloride yield up to 40%.

As expected, increasing the reaction temperature increased the product yield up to 110 °C for the reactions in DCB and 130 °C for reactions in benzaldehyde (Fig. 5). However further increase of temperature caused a slight decrease in product yield.

Table 6

The effect of benzoyl chloride to benzaldehyde ratio on catalytic performance

Benzoyl chloride (mmol)	Benzal chloride yield (%) ^a	Benzal chloride yield (%) ^b
24	21.1	36.6
47	22.1	32.3
94	21.0	39.6

^a Reaction conditions: 12.5 g DCB, 23.6 mmol benzaldehyde, 110 °C, 1 h.

^b Reaction conditions: 15 g benzaldehyde, 110 °C, 1 h.

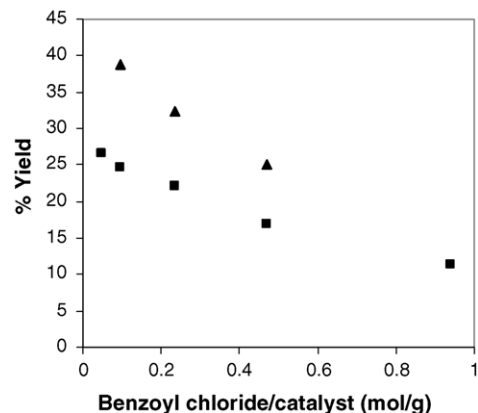


Fig. 4. Effect of catalyst loading on product yield. Reaction conditions: 47 mmol benzoyl chloride, 110 °C, 1 h. (■) 12.5 g DCB; 23.6 mmol benzaldehyde; (▲) 15 g benzaldehyde.

2.2.5. Catalyst regeneration-recycling

Finally, since $\text{SO}_4\text{-ZrO}_2$ undergoes deactivation, its regeneration and recycling were tested. The deactivation of $\text{SO}_4\text{-ZrO}_2$ could be ascribed to various factors acting in parallel, such as inhibition of catalytically active sites due to strong adsorption of product, formation of coke deposits blocking the catalytic surface, loss of sulfur, zirconia phase transition and change in the oxidation state of sulfur. Therefore, in the present study, we tested the oxidative regeneration and recycling of a sulfated zirconia catalyst.

A catalytic run performed with a freshly calcined catalyst for 3 h (entry 1 in Table 7) resulted in 45.1% yield of benzal chloride. Recycling the spent catalyst from first run after 3 h reaction filtration and drying exhibited significantly lower activity (entry 2). Regeneration of the catalyst by calcination of the spent catalyst obtained from run 1 in static air at 550 °C for 1.5 h (entry 3) after prior washing with dichloromethane showed the same benzal chloride yield (45.3%) as the fresh catalytic run (entry 1). The calcination temperature of 550 K was based on a TPO experiment of the spent catalyst that showed a maximum of CO_2 evolution around this temperature. Repeating this procedure yielded good reproducibility (entry 4).

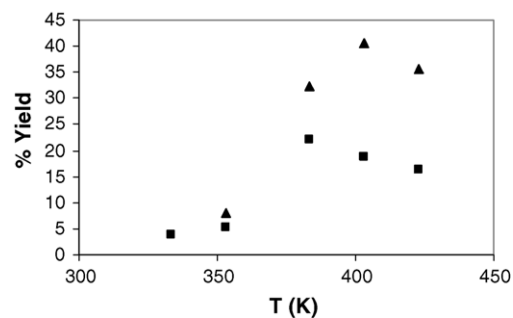


Fig. 5. Effect of reaction temperature on product yield. Reaction conditions: 47 mmol benzoyl chloride, 0.2 g catalyst, 110 °C, 1 h. (■) 12.5 g DCB; 23.6 mmol benzaldehyde; (▲) 15 g benzaldehyde.

Table 7
Regeneration and recycling of sulfated zirconia catalyst in benzal chloride synthesis^a

Entry	Catalyst pretreatment	Benzal chloride yield (%)
1	Fresh, calcined (823 K)	45.1
2	Spent catalyst after entry 1	20.2
3	Washed after entry 1, calcined in air (823 K)	45.3
4	Washed after entry 3, calcined in air (823 K)	44.8

^a Reaction conditions: 15 g benzaldehyde, 47 mmol benzoyl chloride, 0.2 g catalyst, 110 °C, 3 h.

Since the catalyst surface area, its sulfur content, and % crystallinity of the ZrO₂ phase, after oxidative regenerations were not changed, it seems that the main source of deactivation is the strongly adsorbed carbonaceous deposits which blocked the acidic sites. The fact that the oxidative treatment yielded full recovery of catalytic performance for three consecutive catalytic runs demonstrates a good possibility for multiple catalyst recycling.

3. Conclusions

A comprehensive study of the synthesis of *gem*-dihalides from aromatic aldehydes with acid chlorides over several homogeneous and heterogeneous acid catalysts was performed in a batch reactor. AlCl₃ successfully catalyzed the reaction of variety of aromatic aldehydes with acid chlorides and bromides. The reaction with acid halides is probably performed via two steps, whereas the corresponding 1-halo, 1-substituted benzylester is formed as an intermediate. Among all solid acids tested, sulfated zirconia exhibited the highest catalytic performance due to its superior acidity. Conducting the reaction in benzaldehyde as a self solvent resulted in the highest activity. Benzoyl chloride is the most active acid halide. Oxidative regeneration of a spent sulfated zirconia catalyst in air at 550 °C fully recovered its activity and allowed multiple catalyst recycling.

4. Experimental

4.1. Chemicals and catalysts

All chemicals were purchased from Aldrich as well as H₃PW₁₂O₄₀ (HPW), SAC-13[®], and sulfonated ion-exchange catalysts Amberlyst[®] 15. Sulfated zirconium hydroxide catalyst was supplied by MEL[®] Chemicals (MELCat X20999/01) and all zeolites were purchased from PQ Corporation. Sulfated zirconia and zeolites were previously calcined at 350–650 °C for 1.5 h at a heating rate of 13 °/min in an oven. Acid resins (Amberlyst and SAC-13) were dried in a vacuum oven at 100 °C for 4 h. Cs-HPW salt was prepared by precipitation of HPW with Cs₂CO₃ from an aqueous solution followed by filtration and drying of the precipitate. The cata-

lyst was activated at 150 °C in a nitrogen flow. The chemical analysis of sulfated zirconia and Cs-HPW was performed using EDX spectroscopy (JEOL JEM 5600 scanning electron microscope) in order to get sulfur and cesium content after calcination. Surface areas of Cs-HPW salts were obtained from N₂ data using the conventional BET method. The calcinated samples were outgassed under vacuum at 250 °C and nitrogen adsorption was measured at a liquid nitrogen temperature with a NOVA-2000 (Quantachrome, Version 7.01) instrument.

4.2. Experimental procedure

All reagents and solvents were stored in a closed container with a granulated precalcined molecular sieve UOP 3A (Fluka) under moisture-free conditions. A typical benzal chloride synthesis was carried out in a three-necked glass reactor of 50 ml capacity with reflux condenser under magnetic stirring. Reactions in a solvent were carried out by charging benzaldehyde (23.6 mmol), acid chloride (47 mmol) and around 12.5 g of solvent. When acid chloride was used as a catalyst in a homogeneous manner, it was added under water-free nitrogen atmosphere in a glove-box. When solid acids were used, a portion of 0.05–1 g of catalyst, freshly calcined and cooled in a desiccator, was added to the reactor after reagent loading. The reaction mixture was stirred for periods of time (0.5–5 h) and analyzed only once at the end of the run. The samples were withdrawn from the reactor, filtered and analyzed by GC (Hewlett Packard 5890, Series II) using an HP-1 (100% dimethyl poly siloxane) column with the addition of one tenth of octane as an internal standard. Benzaldehyde, benzal chloride, 1-chloro, 1-benzylpropane and propionic anhydride were routinely detected. Identification of the products, *gem*-dihalides and 1-chloro, 1-benzylpropane, was done by GC-MS (Hewlett Packard 6890N, Agilent technology) using HP-5 column. For reactions in DCB, the product yield was determined by calculating the amount of product in the reaction mixture, divided by the amount of substrate in the beginning of the reaction. The selectivity was calculated based on product yield and substrate conversion. For reactions in benzaldehyde as a self solvent, the product yield was determined by calculating the amount of benzal chloride in the reaction mixture, divided by half of the amount of propionyl chloride in the beginning of the reaction.

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