

Friedel–Crafts synthesis of triarylmethanes over 3-methyl-1-sulfonic acid imidazolium tetrachloroaluminate under green conditions

Saeid Azimi^{a,*}, Mohammad Ali Zolfigol^{b,*}, Ahmad Reza Moosavi-zare^c

^aDepartment of Chemistry, Payame Noor University, PO BOX 19395-4697 Tehran, Iran.

^bFaculty of Chemistry, Bu-Ali Sina University, Hamedan 6517838683, Iran.

^cDepartment of Chemistry, University of Syyed Jamaledin Asadabadi, Asadabad, 6541835583, Iran.

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ABSTRACT

In this work, Friedel–Crafts (FC) alkylation of various arenes with aromatic aldehydes catalyzed by 3-methyl-1-sulfonic acid imidazoliumtetrachloroaluminate {[Msim]AlCl₄}, to prepare triarylmethanes (TAMs) has been carried out. Some aromatic aldehydes were reacted with arenes containing electron-donor substitutions such as anisole, veratrole, phenols, indole and 2-naphthole under solvent-free conditions. The catalyst was recovered and reused successfully for four times. Simple methodology, easy work up, solvent-free condition and excellent yields are some advantages of this work.

Keywords: Triarylmethane, Sulfonic acid functionalized Imidazolium salt (SAFIS), 3-Methyl-1-sulfonic acid imidazoliumtetrachloroaluminate {[Msim]AlCl₄}, Solvent-free.

1. Introduction

Triarylmethanes are significant compounds and recently have been considered because of their activities as antitumor reagents [1] and their role in scaffold constituents, textile industry and their properties like convenient dyes and also due to their applications in the ionic-conductivity switching of composite films [2].

Some of synthetic methods have been reported for the synthesis of triarylmethanes such as Friedel-Crafts reaction of arenes with aldehydes using various catalysts including InCl₃, SnCl₄, AuCl₃, AgOTf [3] or alkylation of arenes catalyzed by HCl, [3] ZnBr₂/SiO₂ and Yb(OTf)₃ or Suzuki-Miyaura coupling of diarylmethyl carbonate with aryl boronic acids in the presence of [Pd(η³-C₃H₅)Cl]₂-DPPPEnt (1,5-bis(diphenylphosphine) pentane) catalyst [4]. Moreover, silica sulfuric acid has been also reported as a reusable catalyst for this transformation [5].

Although, some of these methods suffer harsh conditions such as long reaction time, use of toxic solvents, use of corrosive and non-reusable catalyst, formation of by-products and high temperature. Recently sulfonic acid functionalized imidazolium salts (SAFIS) have been introduced as a new category of acidic ionic liquids and considered as eco-friendly solvents, catalysts and reagents in green chemistry. S–N bond formation between imidazole derivatives, as five member heterocyclic ring compound and SO₃H, as acidic functional group, was reported for the first time by employing such acidic ILs as catalyst [6-16].

In continuation of previous works on the synthesis and application of SAFIS in organic transformations, herein, we report a new method for the synthesis of triarylmethanes (TRAMs) by the condensation of aromatic aldehyde with various nucleophiles such as anisole, veratrole, phenols, indole and 2-naphthole in the presence of 1-methyl-3-sulfonic acid imidazolium tetrachloro aluminate {[Msim]AlCl₄} Fig. 1. as sulfonic acid functionalized imidazolium salts (SAFIS) under solvent-free conditions. The promising points for the presented method are high yield, easier work up and simplicity which make it a useful process for the preparation of various triarylmethanes (Scheme 1).

*Corresponding authors email: s_azimi@pnu.ac.ir

Tel: +98 81 3622 5541, Fax: +98 81 3622 3951

mzolfigol@yahoo.com

Tel.: +98 81 3828 2807; Fax: +98 81 3825 7407

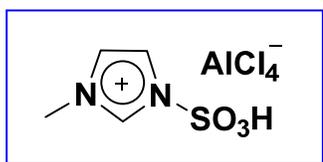


Fig. 1. The structure of 3-methyl-1-sulfonic acid imidazolium tetrachloroaluminate {[Msim]AlCl₄}.

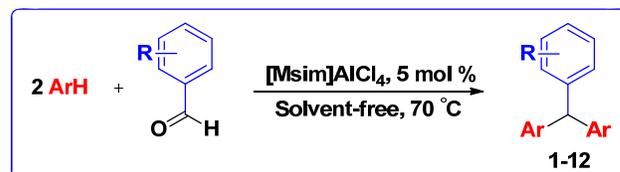
2. Experimental

2.1. General

All chemicals were purchased from Merck or Fluka Chemical Companies. The known products were identified by comparison of their melting points and spectral data with those in the authentic samples. The ¹HNMR (400 or 90 MHz) and ¹³CNMR (100 Hz or 22.5 MHz) were run on a Bruker AVANCE- DRX. FT-NMR spectrometer (δ in ppm). Melting points were recorded on a Büchi B-545 apparatus in open capillary tubes. IR spectra were run on a Perkin Elmer PE-1600-FTIR. Mass spectra were recorded on Agilent Technology (HP) Network Mass Selective Detector 5973 (70eV) apparatus.

2.2. General procedures for the synthesis of Triarylmethanes (TRAMs)

To a mixture of aldehyde (1mmol) and [Msim]AlCl₄ (0.0164 g, 5 mol%) in a 10 mL round bottomed flask connected to a reflux condenser, 2 mmol of nucleophile (anisole, veratrole, 2-naphtole or indole) was added and the resulting mixture was stirred in an oil-bath at 70 °C in appropriate time (Table 3). After completion of the reaction, as monitored by TLC

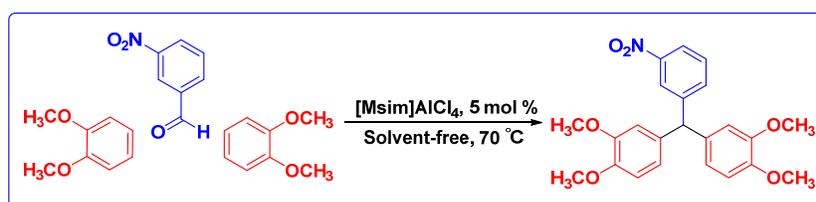


Scheme 1. The preparation of triarylmethanes (TRAMs) catalyzed by [Msim]AlCl₄.

(n-hexan/ ethylacetate 10:4 as eluent), the reaction mixture was cooled to room temperature, extracted with CH₂Cl₂ (5 mL) to separate the catalyst (the crude product is soluble in warm CH₂Cl₂; however, the catalyst is not soluble in this solvent). After the filtration and separation of [Msim]AlCl₄, CH₂Cl₂ was evaporated and the solid residue (crude product) was purified by plate chromatography on silica gel with n-hexan/ethylacetate (10:4) as an eluent to give the desired triarylmethanes. The recovered catalyst was washed with CH₂Cl₂ (2× 10 mL), dried at 90°C under vacuum condition, and reused for the preparation of triarylmethanes according to the mentioned procedure. The catalyst was recovered and reused for four times without any significant changes in the yield and the reaction time.

3. Results and discussion

In the first step the reaction of 3-nitrobenzaldehyde (1mmol) with veratrol (2 mmol) in the presence of [Msim]AlCl₄ (0.0164 g, 5 mol%) was selected as a model reaction (Scheme 2) and different conditions such as kind of solvent, the amount of catalyst and temperature were optimized. The results were summarized in Table1 and Table 2.



Scheme 2. The reaction of 3-nitrobenzaldehyde with veratrol using [Msim]AlCl₄ as catalyst.

Table 1. Optimization of condition of reaction of 3-nitrobenzaldehyde with veratrole in presence of [Msim]AlCl₄ under solvent-free conditions.

Entry	Catalyst (mol %)	Temp. (°C)	Time (min)	Yield ^a (%)
1	5	60	60	61
2	5	60	100	67
3	5	70	90	96
4	7	75	120	96
5	10	70	100	96

^aIsolated yield.

Table 2. Reaction of 3-nitrobenzaldehyde with veratrole using [Msim]AlCl₄ (5mol%) in different solvents under reflux condition.

Entry	Solvent	Time (min)	Yield ^a (%)
1	EtOH	60	50
2	MeOH	70	45
3	CH ₃ CN	60	85
4	MeCOOEt	60	51
5	CH ₂ Cl ₂	120	82
6	--	90	96

^aIsolated yield.

As Table 1 and Table 2 indicates, the best result was obtained in the presence of 5 mol% of [Msim]AlCl₄ at 70°C under solvent-free condition to afford the desired product in high yield (Table 1 entry 3). Because of the model reaction is one of the multi component reactions, and in this category of reactions with the increasing of temperature, effective knocking between the starting materials will increase to the optimum temperature, we observed that in the presence of 5 mol% of catalyst, by increasing temperature of reaction, the yield of product was increased.

The catalyst was hydrolyzed in the presence of aqueous ethanol or methanol and transformed to sulfuric acid and methyl imidazolium cation. Therefore, solvent-free was the best condition in this reaction.

Therefore, we studied the reaction of aromatic compounds such as anisole, veratrole, 2-naphtole or indole with various aldehydes in the optimized conditions. The results were depicted in Table 3.

As shown in Table 3, indicates that, when aromatic compounds containing electron donor substitutions and aldehydes with electron withdrawing substitutions were employed in this reaction condition, the yields of the products were increased (Table 2 entries 9, 11, 12).

In the previous methods [5] the best results were obtained by 3:1 molar ratio of aromatic compound and aromatic aldehyde. But in our method, using the presented catalyst, the best yield was obtained when 2:1 molar ratio of the starting materials (aromatic compound and aldehyde) were used.

When we used 2-naphtol in the reaction with benzaldehyde, by the elimination of one molecule of H₂O, the first product was converted to 14-aryl-14H-dibenzo[a,j]xanthene as main product (Table 3 entry 5) and this point was confirmed by IR and ¹HNMR spectra.

In another investigation, we used terphthaldehyde as a bis-aldehyde, with two functional groups, in this reaction condition. The reaction was completed just

when 4.5 mmol of anisole or veratrole reacted with 1 mmole of terphthaldehyde in presence of 5 mol% of [Msim]AlCl₄ (Table 3 entries 6, 7).

In another study, reusability of the catalyst was investigated upon the reaction of 3-nitrobenzaldehyde (1mmol) and veratrol (2 mmol) in the presence of [Msim]AlCl₄ at 70°C under solvent-free condition. The reaction mixture was extracted by CH₂Cl₂ to separate from the [Msim]AlCl₄. Afterward, the reused catalyst was employed for another reaction. We observed that catalytic activity of [Msim]AlCl₄ was restored within the limits of experimental errors for four successive runs respectively (Fig. 2).

4. Conclusions

In conclusion, we have introduced [Msim]AlCl₄ as a reusable catalyst for the synthesis of triarylmethanes (TRAMs) at 70°C under solvent-free conditions.

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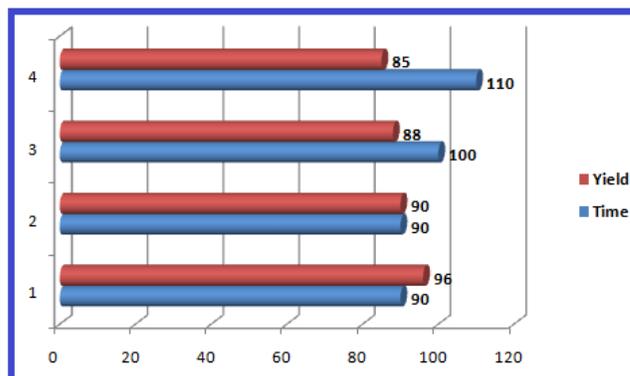


Fig. 2. The synthesis of triarylmethanes in the presence of reused [Msim]AlCl₄ under solvent-free conditions at 70°C.

Table 3. The synthesis of triarylmethanes (TRAMs) in presence of [Msim]AlCl₄ (5mol%) at 70°C under solvent-free conditions.

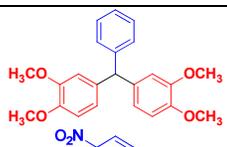
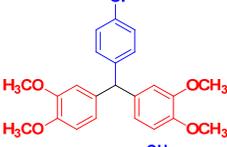
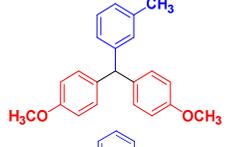
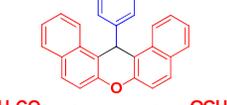
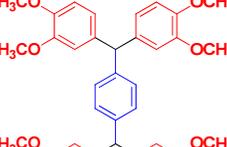
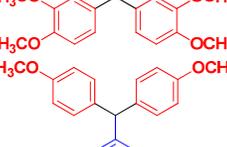
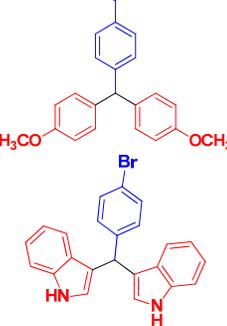
Entry	Product	Time (min)	Yield ^a (%)	m.p. (°C)		Ref.
				Found	Reported	
1		100	89	120-122	122-124	[5]
2		90	96	150-152	154-155	[5]
3		90	95	189-191	193-194	[5]
4		110	82	Oil	-	-
5		120	91	189-190	186-188	[8]
6 ^b		80	93	175-177	173-176	[5]
7 ^b		100	89	111-112	114-116	[5]
8		80	92	Oil		[5]
9		35	98	111-112	113-115	[17]

Table 3. (Continued).

10		100	87	Oil	-	[5]
11		80	93	154-156	159-161	[5]
12		90	84	166-167	164-165	[5]

^aIsolated yield.^bIn these entries the molar ratio of nucleophile to aldehyde was 4:1.

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