

## Exploration on Clean Synthesis of Diphenylmethane Using Ionic Liquid: A Subtle Catalysis

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### ABSTRACT

In present work, Friedal-Craft alkylation of benzene using benzyl alcohol and dibenzyl ether (DBE) has been investigated using Brønsted acidic ionic liquid as a catalyst. It results in 99% conversion of benzyl alcohol, depicting 61% selectivity towards diphenylmethane (DPM) using  $[\text{CSO}_3\text{Hmim}][\text{La}(\text{CF}_3\text{SO}_3)_4]$  as a catalyst within 18 h. Using the same catalyst, 62% selectivity towards DPM has been obtained with DBE as benzylating agent within 16 h. Effect of various reaction conditions on the activity and selectivity was investigated using  $[\text{C}_3\text{SO}_3\text{Hmim}][\text{La}(\text{CF}_3\text{SO}_3)_4]$  as a catalyst with DBE as benzylating agent.

### KEYWORDS

Green chemistry, Acidic ionic liquids, Catalysis.

### INTRODUCTION

Diphenylmethane (DPM) is widely used in the synthesis of luminogens for aggregation-induced emission (AIE), in the preparation of a polymerization initiator, diphenylmethyl potassium (DPMK), as precursors in the synthesis of a dendrimeric polycyclic aromatic hydrocarbon (PAH), *hexakis*-[4-(1,1,2-triphenylethenyl)phenyl]benzene [1].

The literature reviewed hitherto revealed that there are few reports on the use of acidic ionic liquids as catalyst for the alkylation of benzene with benzyl chloride for the synthesis of DPM [2-5]. Ionic liquids used as catalyst include  $(\text{C}_2\text{H}_5)_3\text{NHCl-MCl}_x$  and  $\text{Bmim-MCl}_x$  ( $\text{MCl}_x = \text{AlCl}_3, \text{FeCl}_3, \text{ZnCl}_2$ ). However, in use of benzyl chloride as benzylating agent, HCl is formed as byproduct, which is corrosive and environmentally hazardous. Hence, benzyl alcohol or dibenzyl ether (DBE) is used as a benzylating agent instead of benzyl halides. With these alkylating agents water is produced as a byproduct, which is non-hazardous [6,7]. Ionic liquid supported catalysts like  $\text{BmimBr-ZnCl}_2/\text{SiO}_2$  were used for benzylation using benzyl alcohol as benzylating agent, but very less conversion was obtained [8,9]. Sacra & Laali [10] showed that using  $\text{Yb}(\text{OTf})_3$  as catalyst in ionic liquid  $[\text{Bmim}][\text{OTf}]$ , complete conversion of benzyl alcohol with 83% selectivity to DPM in 20 h is obtained.

Thus, the benzylation of aromatics with benzyl alcohol reaction was studied well, but few reports are available on the

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benzylation of aromatics with DBE. Kamalakar *et al.* [11] studied the role of DBE in benzylation of benzene at a reaction temperature of 90 °C. The time required for 50% conversion of DBE was about 1.67 h. Kumar *et al.* [12] showed that with  $\text{Hf}_{0.5}\text{TPA}$  as catalyst complete conversion to DBE and 47% selectivity to DPM is achieved. Al-Hazmi *et al.* [13] studied the benzylation of benzene with DBE. A 100% conversion of DBE and 95% selectivity of DPM were obtained. However, 100% conversion of DBE was achieved only at high reaction time (24 h) and temperature (180 °C). The Ir/Sn bimetallic catalyst was reported by Podder *et al.* [7] for benzylation of arenes with ethers. The benzylation of anisole reaction was studied at 90 °C and the selectivity of benzylation product was 99% within 0.5 h. But the main disadvantage of this catalyst is limitation to reuse [7].

The goal of this work is to synthesize and use ionic liquid as catalyst for the synthesis of diphenylmethane (DPM), which gave 100% conversion of benzyl alcohol as well as dibenzyl ether (DBE) as alkylating agent with good selectivity to DPM.

## EXPERIMENTAL

1,3-Propanesultone was procured from Sigma-Aldrich, *N*-methyl imidazol was procured from (Spectrochem), while benzene, benzyl alcohol, triflic acid were procured from Avra synthesis. The other reagents were of analytical grade and used without any purification unless and otherwise mentioned.

### Synthesis of ionic liquid $[\text{C}_3\text{SO}_3\text{Hmim}][\text{La}(\text{CF}_3\text{SO}_3)_4]$

**Synthesis of 1-methyl-3-(3-sulfo-propyl)-1*H*-imidazolium trifluoromethane sulphonate  $[\text{C}_3\text{SO}_3\text{Hmim}][\text{CF}_3\text{SO}_3]$ :** The Brønsted acidic ionic liquids were prepared as per the procedure described earlier [13]. *N*-Methyl imidazol (1.252 g, 15.25 mmol) and 1,3-propanesultone (1.862 g, 15.25 mmol) were dissolved in 10 g toluene and refluxed overnight at 110 °C. The desired zwitter ions were formed in quantitative yield and precipitated out as a white solid. The white precipitate formed was isolated by filtration, dried and used for the next step. Conversion to the ionic liquid was accomplished by combining equimolar quantities of trifluoromethane sulphonic acid and the zwitter ions, consequently heating them to 70 °C for 24 h. During this time, solids were completely soluble and reacted, resulting in the formation of ionic liquid 1-methyl-3-(3-sulfo-propyl)-1*H*-imidazolium trifluoromethane sulphonate [14-20].

**Synthesis of lanthanum triflate:**  $\text{La}_2\text{O}_3$  (10 g) was taken in 50 wt.% triflic acid in water (triflic acid, 26.5 g) in ratio of

1:6 and then heated them for 110 °C for 2 h. After heating for 2 h, water was removed under vacuum then the solid product was obtained. This solid product was then heated at 180 °C for 48 h. After heating lanthanum triflate was obtained with 75% yield [(calcd. (found) yield: 37.5 g (28.0 g)].

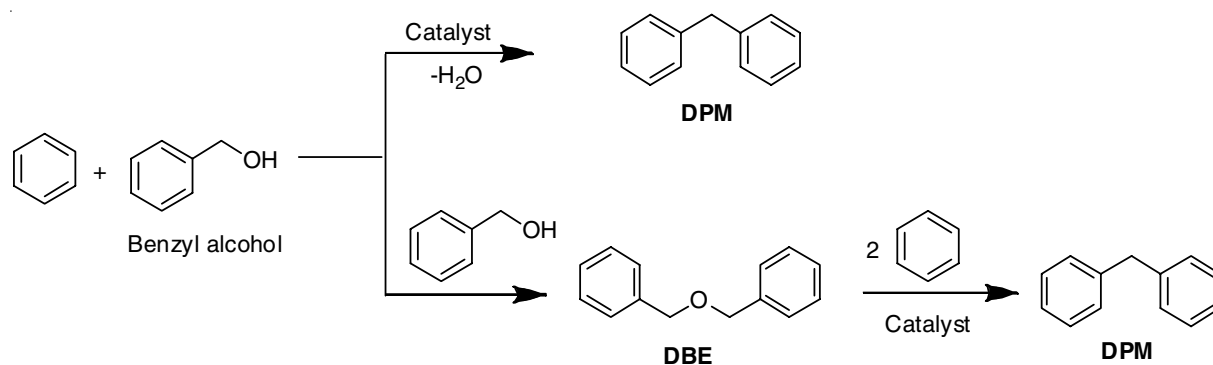
**Synthesis of 1-methyl-3-(3-sulfo-propyl)-1*H*-imidazolium lanthanum trifluoromethane sulphonate,  $[\text{C}_3\text{SO}_3\text{Hmim}][\text{La}(\text{CF}_3\text{SO}_3)_4]$  ionic liquid:** Equimolar (5.64 mmol, 4 g) quantity of ionic liquid  $[\text{C}_3\text{SO}_3\text{Hmim}][\text{CF}_3\text{SO}_3]$  prepared as per above procedure and lanthanum triflate (5.64 mmol, 6.62 g) were taken in 50 mL round bottom flask. About 2 mL of distilled water was added to it to get homogeneous mixture. This mixture was then heated to 100 °C for 2 h. After 2 h, water was removed from reaction mixture using rotary evaporator. The resultant product was used as catalyst for benzylation reaction.  $^1\text{H NMR}$  (300 MHz,  $\text{DMSO}-d_6$ , 25 °C)  $\delta$  ppm: 2.76 (s, 3H,  $-\text{CH}_3$ ), 7.31 (d, 1H,  $=\text{CH}-$ ), 7.38 (d, 1H,  $=\text{CH}-$ ), 8.59 (s, 1H,  $=\text{CH}-$ ), 4.26 (t, 2H,  $-\text{N}-\text{CH}_2-$ ), 2.18 (m, 2H,  $-\text{CH}_2-$ ,  $J = 16$  Hz), 2.14 (t, 2H,  $-\text{CH}_2-$ ,  $J = 16$  Hz) ppm.

**Synthesis of diphenylmethane:** In a typical benzylation, 18.7 g (0.239 mol) of benzene (Bz), 1.3 g (0.012 mol) of benzyl alcohol (BzOH) with mole ratio (BzOH:Bz, 1:20) and 10 mol% ionic liquid were placed in 50 mL round bottom flask. The flask was equipped with reflux condenser and magnetic needle. The desired (100 °C) temperature was maintained using an oil bath. The reaction mixture was stirred at 800 rpm. The sample from reaction mixture was analyzed on gas chromatography (DB-Wax column, FID detector). The quantitative analysis was carried out using external standard method by constructing a calibration curve for reactant and products in the range of concentration studied.

**Scheme-I** shows the schematic presentation of benzylation of benzene using benzyl alcohol as alkylating agent. In this Friedel-Crafts benzylation reaction, diphenylmethane (DPM) is formed as a major product. However, DBE was also formed as a byproduct due to the self-condensation of benzyl alcohol. It was observed that further DBE reacts with benzene to form DPM. Mass analysis:  $[\text{M}+\text{H}]^+$  calculated: 168.23; found: 168.00.

**GC analysis:** The liquid sample were analyzed on a gas chromatograph (Agilent 6850), controlled by chemstation software, using HP-DBWAX column. The standard conditions for gas chromatographic analysis are given in Table-1.

**Quantitative analysis of reaction mixture (by external standard method):** Quantitative analysis of the reaction was carried out by using external standard method. In this method



Scheme-I: Syntheses routes for DPM

TABLE-1  
STANDARD CONDITIONS FOR GC ANALYSIS

Particulars	Parameters		
Injector split temperature	250 °C		
FID temperature	250 °C		
Inlet flow-total (H <sub>2</sub> )	32 mL/min		
Air flow	300 mL/min		
Split ratio for injector	50:1		
Column temperature	Rate	Temp. (°C)	Time
	30	100	4
	30	150	3
	30	180	3
	30	220	2
	30	250	5
Column pressure (Helium)	10 psi		

known quantities of benzyl alcohol, DPM, DBE were diluted to 10 mL with benzene in 10 mL volumetric flask. Five such samples with different concentration of benzyl alcohol, DPM, DBE in benzene were prepared. Analysis of these samples was done on GC and calibration curve (amount/area) was obtained.

**Characterization:** Mass spectra were recorded with Waters, Q-ToF Micromass (LC-MS) spectrometer. The <sup>1</sup>H NMR spectrum of [C<sub>3</sub>SO<sub>3</sub>Hmim][La(CF<sub>3</sub>SO<sub>3</sub>)<sub>4</sub>] was recorded on FT NMR Cryomagnet Bruker Avance-II spectrometer at 300 and 75 MHz, with DMSO-*d*<sub>6</sub> as solvent.

## RESULTS AND DISCUSSION

**Ionic liquid as catalyst for benzylation of benzene using benzyl alcohol as benzylating agent:** Table-2 depicts the results of benzylation of benzene with benzyl alcohol (BzOH) as alkylating agent over the investigated ionic liquids. The reactions were carried out at 100 °C with benzene to benzyl alcohol mole ratio as 1:20. 10 mol% catalyst was used for the reaction.

Under the investigated conditions, it was observed that almost 100% conversion was obtained within 16 h, for the ionic liquid catalysts investigated. About 58% selectivity to DPM was obtained for [C<sub>3</sub>SO<sub>3</sub>Hmim][La(CF<sub>3</sub>SO<sub>3</sub>)<sub>4</sub>] catalyst (Table-2). DBE is also formed as a byproduct due self-condensation of benzyl alcohol ~11-12% DBE product was observed at 16 h reaction time. It was observed that further DBE reacts with benzene to form DPM after 18 h (Table-2). Thus 61% selectivity to DPM was obtained at 18 h. The reaction products DPM and DBE were confirmed by GC analysis. The higher selectivity to DPM was obtained using [C<sub>3</sub>SO<sub>3</sub>Hmim][La(CF<sub>3</sub>SO<sub>3</sub>)<sub>4</sub>] catalyst so further work was carried out using [C<sub>3</sub>SO<sub>3</sub>Hmim][La(CF<sub>3</sub>SO<sub>3</sub>)<sub>4</sub>] ionic liquid as catalyst.

**Effect of water on conversion of benzyl alcohol:** Effect of addition of water was examined to elucidate the role of water on the benzylation of benzyl alcohol using [C<sub>3</sub>SO<sub>3</sub>Hmim][La(CF<sub>3</sub>SO<sub>3</sub>)<sub>4</sub>] as catalyst. The experiments were carried out by varying the mole ratio of water. The results are shown in Table-3. It was observed that the conversion was slightly

decreased by addition of water up to equimolar concentration to benzyl alcohol. However, selectivity to DPM gets sharply decreased from 58% to 19% and 22% with addition of water at 0.4 and 1 mole ratio, respectively. Also, it was observed that, the selectivity to DBE was increased by addition of water from 13% to 53% and 40% at benzyl alcohol to water mole ratio of 0, 0.5 and 1.0. Further increase in addition of water resulted in poor catalytic activity. At mole ratio of 2, conversion dropped to 21% (Table-3).

TABLE-3  
EFFECT OF WATER ON ACTIVITY AND SELECTIVITY

BzOH:H <sub>2</sub> O mole ratio	Water (g)	Conversion (%)	DPM selectivity (%)	DBE selectivity (%)
0	0	98	58	13
0.4	0.1	98	19	53
1.0	0.2	95	22	40
1.9	0.44	21	3	18

Reaction condition: Mole ratio: 1:20 (BzOH:Bz), 10 mol% ionic liquid [C<sub>3</sub>SO<sub>3</sub>Hmim][La(CF<sub>3</sub>SO<sub>3</sub>)<sub>4</sub>], benzene (0.239 mol), BzOH (0.012 mol) Temp.: 100 °C, Time: 16 h.

The mechanism of benzylation of benzene with benzyl alcohol shows that 2 mol of benzyl alcohol reacts to form DBE. Thus DBE formed then reacts with 2 moles of benzene to give DPM (**Scheme-I**). To investigate role of DBE, it was chosen as substrate or benzylating agent. Hence, further study was carried out using DBE as substrate.

**Screening of catalyst for benzylation of benzene using DBE as substrate:** Catalysts presented in Table-4 were screened for benzylation of benzene with DBE as alkylating agent. The reactions were carried out at 100 °C with benzene to DBE mole ratio as 1:20. 10 mol% catalyst was used for the reaction. Under the investigated conditions, it was observed that 100% conversion was observed within 16 h, for ionic liquid [C<sub>3</sub>SO<sub>3</sub>Hmim][La(CF<sub>3</sub>SO<sub>3</sub>)<sub>4</sub>] as catalyst. About 61-62% selectivity to DPM was observed for this reaction. With La(CF<sub>3</sub>SO<sub>3</sub>)<sub>3</sub>, La(NO<sub>3</sub>)<sub>3</sub> as catalyst, no reaction was observed. The best result (100% conversion of DBE and 61% DPM selectivity) was obtained with 1-methyl-3-(3-sulfopropyl)-1*H*-imidazolium lanthanum trifluoro-methane sulphonic acid [C<sub>3</sub>SO<sub>3</sub>Hmim][La(CF<sub>3</sub>SO<sub>3</sub>)<sub>4</sub>] as a catalyst (Table-4). Hence, [C<sub>3</sub>SO<sub>3</sub>Hmim][La(CF<sub>3</sub>SO<sub>3</sub>)<sub>4</sub>] was selected as catalyst for benzylation of benzene using DBE as alkylating agent for further study.

**Quantitative analysis of reaction mixture:** Quantities of benzyl alcohol, DPM, DBE were determined by external standard method using GC. Using Fig. 1, the response factors were calculated.

**Effect of catalyst loading on activity and selectivity:** The effect of catalyst loading on conversion of DBE and selectivity to DPM was carried out using catalyst loading in the range of 2.5 to 20 mol%. The results obtained are shown in Table-5.

TABLE-2  
KEY IONIC LIQUID AS CATALYST FOR BENZYLATION OF Bz\*

Catalyst	Conversion (%)	DPM (selectivity) (%)	DBE (selectivity) (%)	Polyalkylated product	Time (h)
[C <sub>3</sub> SO <sub>3</sub> HMIM][La(CF <sub>3</sub> SO <sub>3</sub> ) <sub>4</sub> ]	98	58	12	18	16
[C <sub>3</sub> SO <sub>3</sub> HMIM][La(CF <sub>3</sub> SO <sub>3</sub> ) <sub>4</sub> ]	99	61	0	10	18

\*Reaction Condition: Mole Ratio: 1:20(BzOH:Bz), Temp: 100 °C, Time: 16 h, Catalyst- 10 mol%, Bz (0.239 moles), BzOH (0.0120 moles)

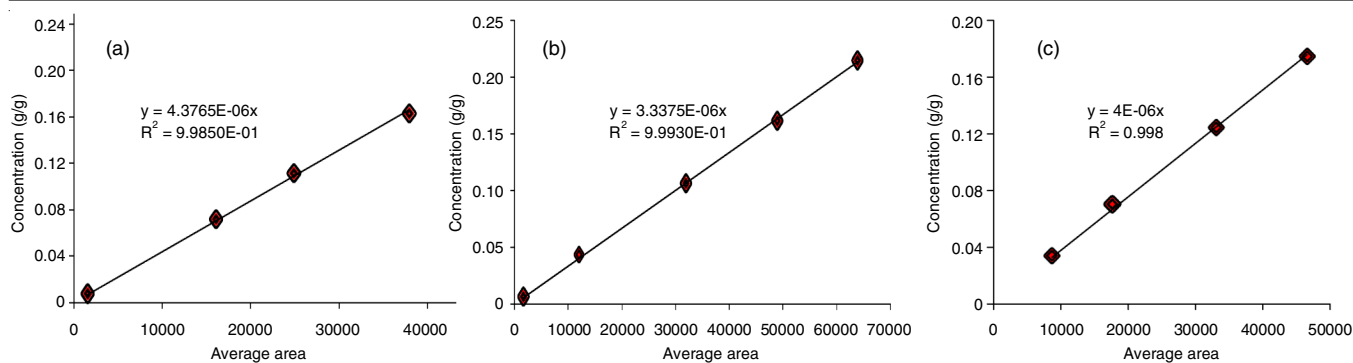


Fig. 1. Calibration curve for quantitative analysis of (a) benzyl alcohol, (b) DPM and (c) DBE (by external standard method using GC)

TABLE-4  
SCREENING OF CATALYST FOR BENZYLATION OF BENZENE

Catalyst	Conversion (%)	DPM selectivity (%)	Polyalkylated product
[C <sub>3</sub> SO <sub>3</sub> Hmim][La(CF <sub>3</sub> SO <sub>3</sub> ) <sub>4</sub> ]	100	62	16
La(CF <sub>3</sub> SO <sub>3</sub> ) <sub>3</sub>	NA	NA	NA
La(NO <sub>3</sub> ) <sub>3</sub>	NA	NA	NA

\*NA = Not applicable as conversion is not seen. Reaction condition: Catalyst 10 mol%, Temp. 100 °C, Time-16 h, DBE: Benzene (1:20), Benzene (0.26 mol), DBE (0.013 mol).

TABLE-5  
EFFECT OF CATALYST LOADING ON ACTIVITY AND SELECTIVITY

Catalyst loading (mol%)	Conversion (%)	DPM selectivity (%)	Polyalkylated product (%)
2.5	66	47	14
5	82	55	19
10	100	62	16
20	98	58	13

Reaction conditions: Mole ratio DBE:benzene (1:20), Temp. 100 °C, Time 16 h, Catalyst: 2.5, 5, 10, 20 mol% [C<sub>3</sub>SO<sub>3</sub>Hmim][La(CF<sub>3</sub>SO<sub>3</sub>)<sub>4</sub>]

**Mole ratio study:** The effect of amount of benzene on benzylation reaction using [C<sub>3</sub>SO<sub>3</sub>Hmim][La(CF<sub>3</sub>SO<sub>3</sub>)<sub>4</sub>] as catalyst is presented in Table-6.

TABLE-6  
MOLE RATIO STUDY (DBE:Bz)

Mole ratio	Conversion (%)	DPM selectivity (%)	Polyalkylated product selectivity (%)
5	82	34	17
10	85	45	20
20	100	62	16
30	85	60	16

Reaction condition: Temp. 100 °C, Time-16 h, Catalyst-10 mol% [C<sub>3</sub>SO<sub>3</sub>Hmim][La(CF<sub>3</sub>SO<sub>3</sub>)<sub>4</sub>]

**Recycle of catalyst [C<sub>3</sub>SO<sub>3</sub>Hmim][La(CF<sub>3</sub>SO<sub>3</sub>)<sub>4</sub>]:** The standard run was carried out for 16 h at 100 °C with DBE: Bz molar ratio of 1:20 and 10 mol% of the catalyst where complete conversion and 62% selectivity to DPM was obtained (Table-7). The catalyst was then separated and washed with benzene and used as it is for further reactions. It was observed that activity of catalyst dropped successively in recycle experiments.

## Conclusion

Lanthanum based Brønsted-Lewis acidic ionic liquid is screened as catalyst for benzylation reaction of benzyl alcohol

TABLE-7  
RECYCLE OF CATALYST

Conversion (%)	DPM selectivity (%)	By product selectivity (%)
100	62	16
86	52	17
71	60	18
56	34	10

Reaction condition: Temp. 100 °C, Time-16 h, DBE:benzene (1:20), Benzene (0.26 mol), DBE (0.013 mol)

and dibenzyl ether (DBE). Lanthanum triflate based ionic liquid [C<sub>3</sub>SO<sub>3</sub>Hmim][La(CF<sub>3</sub>SO<sub>3</sub>)<sub>4</sub>] was found to be highly capable catalyst for the benzylation of benzene with benzyl alcohol as well as DBE. Activity as well as selectivity was found to be dependent on the catalyst loading and DBE:Bz molar ratio. The optimum activity was observed at 100 °C with DBE:Bz molar ratio of 1:20 and catalyst loading of 10 mol%.

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