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Journal Name

ARTICLE

Deep eutectic solvent catalyzed Friedel–Crafts alkylation of electron-rich arenes with aldehydes

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Triarylmethanes (TRAMs) and diarylalkanes (DIAAs) are important intermediates in medicinal, materials chemistry and dye precursors. TRAMs and DIAAs are usually obtained from Friedel–Crafts alkylation reaction. However, due to the Friedel–Crafts reaction catalyzed by Bronsted acid or Lewis acid, this brings many problems, such as harsh reaction conditions, large amounts of acidic waste liquid after the reaction, etc. All these defects are bad for the environment. In this study, six deep eutectic solvents (DES) were synthesized for this specific reaction. And the DES act as catalyst and solvent. Research showed that DES can be used for catalyzing Friedel–Crafts alkylation of electron-rich arenes with aldehydes under mild reaction conditions. Among the six synthesized DES, a choline chloride-zinc chloride ([ChCl][ZnCl₂]) based DES was shown to be the best efficient catalyst. Using 2.00 equivalent of [ChCl][ZnCl₂] based on aldehydes for Friedel–Crafts alkylation gave the corresponding TRAMs or DIAAs with the highest yields. The DES was reused directly and without any activation process. After five cycles, the yields remained about 89–94%. Finally, the possible mechanism of this reaction was discussed according to the analysis of IR spectrum and further experiment.

Triarylmethanes (TRAMs) and diarylalkanes (DIAAs) has attracted considerable attention from the scientific community because of the interesting properties in medicinal, materials chemistry and dye precursors.¹ Significant structures of the TRAMs and DIAAs compounds are shown in Figure 1. The synthetic methodologies of TRAMs are different including symmetrical and unsymmetrical approaches. The scaffold of TRAMs was constructed mainly through Electrophilic aromatic substitution (Friedel–Crafts alkylation and hydroxylation reactions of aldehydes catalyzed by Lewis acids, proton acids), cross coupling reactions catalyzed by metal and miscellaneous approaches.^{1a} As an efficient C–C bond-forming processes, Friedel–Crafts alkylation of arenes with aldehydes or benzylic alcohols is a important way to synthesis of TRAMs.² This process has the advantage of high atom efficiency and only produces one molecule of water as a by-product, and usually used Lewis acids, proton acid or solid-supported as catalysts, such as AlCl₃,³ AuCl₃,⁴ SnCl₄,⁵ ZnBr₂/SiO₂,⁶ Yb(OTf)₃,⁷ Sc(OTf)₃,⁸ OBS,⁹ TfOH,¹⁰ ClSiMe₃,¹¹ B(C₆F₅)₃,¹² polystyrene-supported sulfonic acid¹³ and molecular iodine,¹⁴ ionic liquids¹⁵. Although there are many methods can be used in the synthesis of TRAMs, they often encounter with some problems, such as unrecyclability of catalyst, precious metals, high air-sensitivity and toxicity of catalyst, longer reaction time, volatile organic solvents and tedious

workup procedures.¹⁶

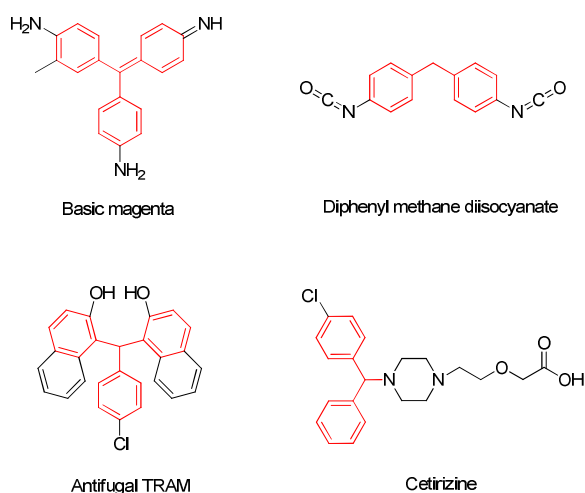


Figure 1. Significant structures of the TRAMs and DIAAs.

Deep eutectic solvent (DES) as a kind of low price and environmentally friendly solvent, has recently attracted increasing interest particularly in the area of green chemistry.¹⁷ Compared with the conventional organic solvent, DES show several advantageous properties including negligible vapor pressure, nonflammability, chemical and thermal stability, and rapid advance in numerous applications.¹⁸ DES are mainly prepared by combining quaternary ammonium salts (such as choline chloride) with different hydrogen bond donors or Lewis acids, such as zinc

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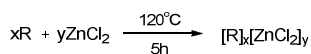
chloride.¹⁹ Choline is a naturally occurring biocompatible compound and choline chloride is commercially produced on a large scale as a chicken feed additive.²⁰ Choline chloride-zinc chloride based DES has been successfully used as Lewis acid catalysts in organic synthesis such as alkylation of alcohol,²¹ Friedel–Crafts alkylation of indoles,²² Diels–Alder reaction,²³ ring opening of epoxides,²⁴ Fischer indole synthesis,²⁵ Kabachnik–Fields reaction²⁶ synthesis of oxazoles²⁷ and synthesis of primary amides.²⁸

In this paper, we will report a deep eutectic solvent [ChCl][ZnCl₂]₂ catalyze Friedel–Crafts alkylation reaction of electron-rich arenes with aldehydes to synthesis either TRAMs or DIAAs, respectively, in high yields under mild conditions.

Experimental

Preparation of DES

Six DES were synthesized according to previous works¹⁹ following the detailed procedure shown below. The choline chloride (ChCl) [or urea, acetamide, ethylene glycol (EG), hexanediol, tetramethylammonium chloride (Me₄NCl)] with ZnCl₂ was put into a round bottom flask at certain molar ratio, and then mixture was stirred at 120 °C. After the reaction was completed, a clear solution could be obtained. The DES can be used directly without any purification, and the synthesis methods for the DES were summarized in Scheme 1.

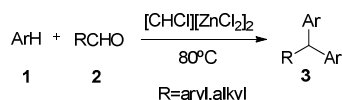


R = Urea, x = 3.5, y = 1
R = Acetamide, x = 4, y = 1
R = EG, x = 4, y = 1
R = Hexanediol, x = 3, y = 1
R = Me₄NCl, x = 1, y = 2
R = ChCl, x = 1, y = 2

Scheme 1. Synthesis of DES.

General procedure for TRAMs and DIAAs synthesis

In a 50 ml round bottom flask, a mixture of electron-rich arenes **1** (2.00 mmol) and aldehydes **2** (1.00 mmol) with [ChCl][ZnCl₂]₂ (2.00 mmol) as catalyst and solvent were added and stirred at 80 °C for the desired time (Scheme 2). The progress of the reaction was monitored by TLC. After the reaction completed, 10ml of water and 10ml ethyl acetate were added into the reaction mixture, the organic layer was separated and evaporated under high vacuum. Then the target compound was obtained. The pure DES was got by evaporating the water and can be reused for another cycle.



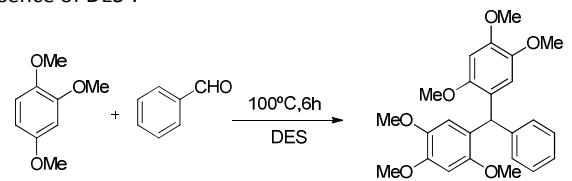
Scheme 2. Synthesis of TRAMs and DIAAs catalyzed by [ChCl][ZnCl₂]₂.

Result and discussion

We chose the 1,2,4-trimethoxybenzene (**1a**) with

benzaldehyde (**2a**) as model reaction to investigate the synthesis of the anticancer TRAM bis(2,4,5-trimethoxyphenyl)phenylmethane (**3a**). The six synthesized DES and ZnCl₂ were added as catalyst and solvent (Table 1). Among these, traditional Lewis acid ZnCl₂ was poorly active (Table 1, entry 1), and there existed some problems such as stirring difficulty during the reaction and workup procedures were cumbersome. When DES was used as catalyst, it was glad to find that [Me₄NCl][ZnCl₂]₂¹⁹ and [ChCl][ZnCl₂]₂¹⁹ were promising (Table 1, entries 6 and 7). Unfortunately, [Urea]_{3.5}[ZnCl₂]₂²⁹, [Acetamide]₄[ZnCl₂]₂²⁹, [EG]₄[ZnCl₂]₂²⁹ and [Hexanediol]₃[ZnCl₂]₂²⁹ were ineffective (Table 1, entries 2-5). We can see that DES made from zinc chloride and quaternary ammonium salts have good catalytic effect, but the effect of DES synthesized by amides or alcohols with zinc chloride were not good. We thought the quaternary ammonium cation is repitious to make aldehydes generate C⁺ and promote the reaction.

Table 1. Friedel–Crafts alkylation reaction of **1a** and **2a** in the presence of DES^a.



Entry	DES	Yield ^b (%)
1	ZnCl ₂	40
2	[Urea] _{3.5} [ZnCl ₂] ₂	0
3	[Acetamide] ₄ [ZnCl ₂] ₂	12
4	[EG] ₄ [ZnCl ₂] ₂	0
5	[Hexanediol] ₃ [ZnCl ₂] ₂	8
6	[Me ₄ NCl][ZnCl ₂] ₂	72
7	[ChCl][ZnCl ₂] ₂	94

^a Reaction conditions: 1,2,4-trimethoxybenzene (2.00 mmol), benzaldehyde (1.00 mmol), DES (0.50 mmol), 100 °C, solvent free, 6h. ^b Isolated yield.

Then we explored some important factors of the reaction, such as system temperature, reaction time and the amount of [ChCl][ZnCl₂]₂. For model studies, we continue to select the benzaldehyde (**2a**) with 1,2,4-trimethoxybenzene (**1a**) for the synthesis of bis(2,4,5-trimethoxyphenyl)phenylmethane (**3a**) (Table 2). Results showed that no desired product could be detected when a mixture of **1a** and **2a** was stirred at 60 °C in the absence of [ChCl][ZnCl₂]₂ (Table 2, entry 1), indicating that [ChCl][ZnCl₂]₂ were absolutely necessary for this procedure. When 0.50 equivalent (**2a** as the standard) [ChCl][ZnCl₂]₂ was added, the reaction proceeded smoothly with a good yield (Table 2, entry 2). Then, the effect of molar ratio of [ChCl][ZnCl₂]₂ on benzaldehyde was studied (Table 2, entries 2-5). It was found that when the molar ratio of [ChCl][ZnCl₂]₂ to benzaldehyde was 2.00, the starting material almost completely transformed (Table 2, entry 5). Raising the temperature to 80 °C, significantly shorten the reaction time (Table 2, entry 6). Increasing the temperature to 100 °C did not

result in shorter reaction times (Table 2, entries 7 and 8).

Table 2. Reaction condition optimization for **3a** synthesis^a.

Entry	DES (mmol)	Temp (°C)	Time (h)	Yield ^b (%)
1	0	60	24	0
2	0.50	60	2	76
3	1.00	60	2	84
4	1.50	60	2	88
5	2.00	60	2	94
6	2.00	80	0.5	94
7	2.00	100	0.5	94
8	2.00	100	0.25	79

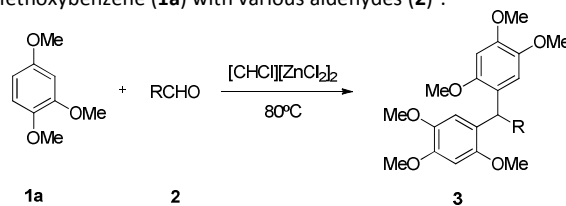
^a Reaction conditions: 1,2,4-Trimethoxybenzene (2.00 mmol), benzaldehyde (1.00 mmol), solvent free. ^b Isolated yield.

To further demonstrate the scope of the Friedel-Crafts alkylation reaction catalyzed by [ChCl][ZnCl₂]₂, 1,2,4-trimethoxybenzene (**1a**) was reacted with aldehydes (**2**) under the optimal conditions (Table 3). In the presence of [ChCl][ZnCl₂]₂ (2.00 mmol), 1,2,4-trimethoxybenzene (2.00 mmol) reacted with a series of electron-poor or electron-rich aromatic aldehydes (1.00 mmol) giving compounds **3a-h** generally in high yields (Table 3, entries 1-8). Furthermore, when aliphatic aldehydes were used, the corresponding DIAAs **3i** and **3j** were also obtained in good yields and with high purity (Table 3, entries 9-10). Due to the low boiling point of butyral and isobutyraldehyde, the reaction temperature was decreased to 60°C. The DIAAs **3k** and **3l** were obtained successfully with favorable yield (Table 3, entries 11-12). From Table 3, we found that, compared with the electron density of aromatic aldehydes and aliphatic aldehyde, the steric hindrance has greater impact on the yield of Friedel-Crafts alkylation reaction.

With the optimized conditions in hand, we then explored the [ChCl][ZnCl₂]₂ catalyzed Friedel-Crafts alkylation reaction of various arenes (**1**) with benzaldehyde (**2a**) for the synthesis of the corresponding TRAMs. The results were shown in Table 4. With the decrease of electron cloud density on the benzene ring (Table 4, entries 1-5), the reaction time gradually prolonged and the yield of

Friedel-Crafts alkylation gradually declined. Other arenes such as 1,4-dimethoxybenzene, anisole, toluene, naphthalene, nitrobenzene, thiophene and furan all failed to provide the Friedel-Crafts product after 12 h.

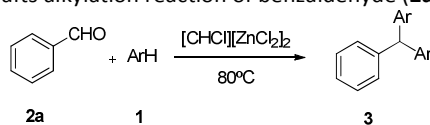
Table 3. Scope of the [ChCl][ZnCl₂]₂ catalyzed reaction of 1,2,4-trimethoxybenzene (**1a**) with various aldehydes (**2**)^a.



Entry	R	Product	Time (h)	Yield ^d (%)
1	H	3a	0.5	94
2	4-NO ₂ H	3b	4	89
3	4-ClH	3c	5	89
4	4-CH ₃ H	3d	5	88
5	4-CH ₂ CH ₃ H	3e	4	86 ^c
6	4-FH	3f	6	86
7	3-CF ₃ H	3g	4	83 ^c
8	2-CH ₃ H	3h	8	65 ^c
9	H ^f	3i	1	93
10	CH(CH ₃) ₂	3j	2	79 ^c
11	CH(CH ₃) ₂	3k	5	81 ^{c,e}
12	(CH ₂) ₂ CH ₃	3l	5	61 ^{c,e}

^a Reaction conditions: 1,2,4-Trimethoxybenzene (2.00 mmol), aldehydes (1.00 mmol), [ChCl][ZnCl₂]₂ (2.00 mmol), 80°C, solvent free. ^b Isolated yield. ^c Isolated from column chromatography. ^d Paraformaldehyde. ^e The reaction was carried out at 60°C.

Table 4. [ChCl][ZnCl₂]₂ catalyzed Friedel-Crafts alkylation reaction of benzaldehyde (**2a**) with nucleophiles (**1**)^a.

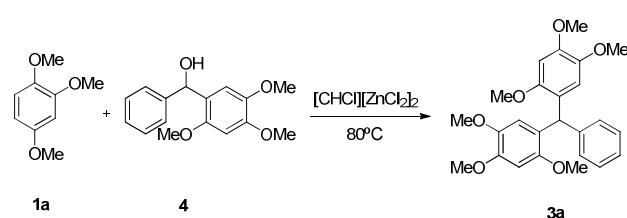


Entry	Ar H	Product	Time (h)	Yield ^d (%)
1			0.5	94

2			2	90
3			4	87
4			6	63 ^c
5			6	41 ^c

^a Reaction conditions: nucleophiles (2.00 mmol), benzaldehyde (1.00 mmol), [ChCl][ZnCl₂]₂ (2.00 mmol), 80^o, solvent free. ^b Isolated yield. ^c Isolated from column chromatography.

The [ChCl][ZnCl₂]₂ catalyzed Friedel-Crafts alkylation reaction was studied by IR. The reaction of **1a** (2.00 mmol) with **2a** (1.00 mmol) was chosen as typical substrates to synthesize the target compound **3a**. When the reaction was carried out for 3 minutes and 10 minutes, samples were removed from the reaction system, respectively. Then water was added to quench the reaction. The corresponding organic layer was determined by IR. From IR spectra, the carbonyl characteristic peak of **2a** is at 1701.6 cm⁻¹, the C-H bond bending vibration peak of **1a** is at 828.3 cm⁻¹ and the C-O bond stretching vibration peak of **1a** is at 1264.1 cm⁻¹. With the processing of reaction (3 min and 10 min), the relative intensity peak of 1701.6 cm⁻¹ and 828.3 cm⁻¹ are decreasing, which indicates that the amount of benzaldehyde (**2a**) and 1,2,4-trimethoxybenzene (**1a**) are decreasing and the reaction is proceeding. But from IR spectrum, the -OH peak of compound **4** was not be found. We believe that this transient state would never be avoided during Friedel-Crafts alkylation reaction. In order to validate our views, another experiment was carried out (Scheme 3). **1a** (1.00 mmol) and **4** (1.00 mmol) were chosen as substrates, and [ChCl][ZnCl₂]₂ (1.00 mmol) acted as the catalyst and solvent. The substrates were converted to **3a** completely within 1 min. That is to say, it is a fast reaction. Compound **4** may be emergent in this specific process. But it was converted into TRAMs quickly. So compound **4** can not be detected through the IR spectrum.



Scheme 3. Reaction of 1,2,4-trimethoxybenzene (**1a**) with phenyl(2,4,5-trimethoxyphenyl)methanol (**4**).

Although the role of [ChCl][ZnCl₂]₂ in the present work is yet to be confirmed, we proposed the following mechanism (Figure 2) for [ChCl][ZnCl₂]₂ as a catalyst in Friedel-Crafts alkylation reaction of electron-rich arenes with aldehydes. Aromatic nucleophilic addition to benzaldehyde took place at the very beginning and after several intermediate steps to generate a diarylmethanol (**4**). However, the reaction did not stop at this step, the compound **4** immediately reacts with a second molecule of the arene-rich compound and TRAMs with an equivalent of water as by-product were got. From the literature,²¹ we believe that the hydrophilic characteristic of [ChCl][ZnCl₂]₂ makes it possible to absorb the water produced in the process of reaction and as the reaction is completed, the target product can be isolated from the reaction system. These different behaviors of the target compound and water can both give an extra driving force for the nucleophilic reaction. The experiment that [ChCl][ZnCl₂]₂ as catalyst yields higher than ZnCl₂ can also prove this point.

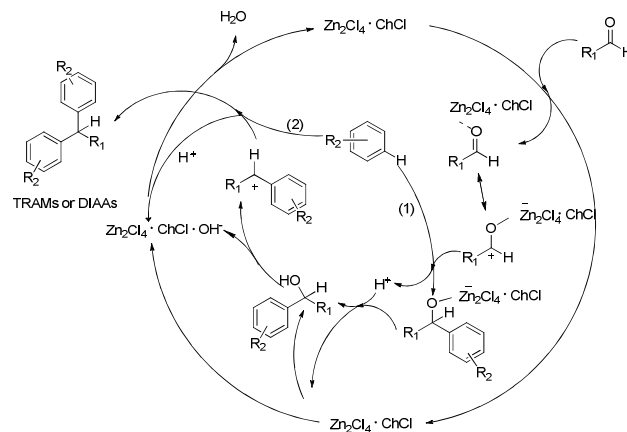


Figure 2. Proposed mechanism of Friedel–Crafts alkylation reaction catalyzed by $[\text{ChCl}][\text{ZnCl}_2]_2$.

Reuse of DES was also carried out by using $[\text{ChCl}][\text{ZnCl}_2]_2$ (2.00 mmol) to catalyze model reaction of substitution **1a** (2.00 mmol) with **2a** (1.00 mmol) at 80 °C. After the reaction, 10 ml of water and 10 ml ethyl acetate were added into the reaction mixture, and $[\text{ChCl}][\text{ZnCl}_2]_2$ was dissolved in water. Then the water layer was separated and evaporated under high vacuum and the pure $[\text{ChCl}][\text{ZnCl}_2]_2$ was obtained. Then the recycled DES can be reused for another cycles directly and it is unnecessary to activate the DES. The results are summarized in Table 5. The yields of 89–94% were obtained during the five recycling cycles.

Table 5. Catalysis properties of the recycled DES.

Cycle Times	1	2	3	4	5
Yield (%)	94	92	92	90	89

Conclusions

In summary, a series of DES were prepared and tested as catalysts for the Friedel–Crafts alkylation reaction of electron-rich arenes with variety of aldehydes. In optimal conditions, the reaction of arenes with aldehydes provided the corresponding TRAMs or DIAAs, regioselectively, in good to excellent yields. After five cycles, the catalytic activity of DES remained very high ranging from 89% to 94%. So, the above study would provide a new green catalyst and solvent for the synthesis of TRAMs and DIAAs.

Acknowledgements

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