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Synthesis and characterization of a tetracationic acidic organic salt and its application in the synthesis of bis(indolyl)methanes and protection of carbonyl compounds†

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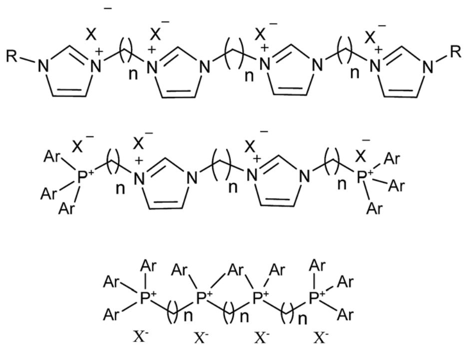
A new tetracationic acidic organic salt (TCAOS) based on DABCO was prepared, characterized and applied as an eco-friendly, powerful and reusable catalyst for the synthesis of bis(indolyl)methanes from indoles and carbonyl compounds in water with high turnover frequency (TOF). Also, this catalyst was successfully applied for acetalization of carbonyl compounds with diols under solvent-free conditions.

Introduction

Solid acids have found wide applications in chemistry due to their important advantages over traditional mineral acids including operational simplicity, environmental compatibility, non-toxicity, reusability, low cost, and ease of isolation. Various solid acids such as silica, montmorillonite, clay, zeolite, Amberlyst-15, acidic polymers, polymer-supported reagents, heteropoly acids, Nafion-H, modified silica-supported acids (silica sulfuric acid, silica phosphoric acid, $NaHSO_4$–SiO_2, SiO_2–Cl and *etc.*), cellulose sulfuric acid and solid organic acids *etc.* have been introduced in various branches of chemistry.[1–14] In recent years, Brönsted acidic organic salts have been designed to replace solid acids and traditional mineral liquid acids in chemical procedures.[15–21] These compounds can potentially be applied as homogenous or heterogeneous catalysts in organic reactions. It is well documented that Brönsted-acidic functional groups such as SO_3H and SO_4H can be simply introduced in the structure of organic compounds, especially as anion in the structure of ionic liquids.[22–24] Among the organic salts, the mono-, di-, and tricationic ammonium salts (ionic liquids) have been extensively applied in analytical chemistry as ion-pairing reagents, as catalyst and solvent in organic transformations and *etc.*[25–33] Recently, Armstrong *et al.* reported a facile procedure for synthesis of novel dicationic and tricationic ionic liquids and investigated their physiochemical properties.[34–36] They have shown that these compounds can be applied in dye-sensitized solar cells, as solvent in high-temperature reactions, and as lubricants. Also, the same group reported the synthesis of series of tetracationic salts applicable (see Scheme 1) as gas-phase ion-pairing agents for the detection of trivalent anions in positive mode electrospray ionization mass spectrometry.[37]

Indole derivatives are prevalent in numerous natural products and are extremely important in medicinal chemistry.[38] Bis(indolyl)methanes, which contain two indole or substituted indole units in a molecule, were found in the structure of many biologically active compounds extracted from various plants.[39] Thus, the development of facile and environmental friendly synthetic methods for the synthesis of bis(indolyl)methanes constitutes an active area of investigation in pharmaceutical and organic synthesis. One of the most applied procedures for synthesis of bis(indolyl)alkanes is based on the electrophilic substitution reaction of indoles with various aldehydes and ketones in the presence of a Bronsted or Lewis acid. Typical protic acids applied for this transformation include silica sulfuric acid (SSA), oxalic acid, zeolites HY, amberlyst, H_2SO_4, HCl, CH_3COOH, sulfamic acid, $NaHSO_4$–SiO_2, $KHSO_4$, $NaHSO_3$, $H_3PW_{12}O_{40}$, $H_3PW_{12}O_{40}$–ZrO_2, $H_3PW_{12}O_{40}$–SiO_2, –TiO_2 or



Scheme 1 Structures of a number of tetracationic ionic compounds prepared by Armstrong *et al.*

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–Al_2O_3, H_3PO_4–SiO_2, PEG-supported sulfonic acid and *etc.* Also, Lewis acids such as lanthanide resins, zeolite (ZnY), montmorillonite clay K-10, cerium ammonium nitrate (CAN), $ZrOCl_2$, $ZrOCl_2 \cdot 8H_2O$–SiO_2, $ZrCl_4$, InF_3, $InCl_3$, $In(OTf)_3$, $SnCl_2 \cdot 2H_2O$, $LiClO_4$, $Bi(OTf)_3$ and *etc.* were successfully developed for this reaction.[39]

The acetals have been introduced as a suitable protection group for carbonyl compounds because of their remarkable stability to neutral and basic conditions.[40,41] Diversities of procedures have been developed for synthesis of acetals from carbonyl compounds in Literature.[42–45]

Results and discussion

Encouraged by the work of Armstrong *et al.*, here we are interested to report for the first time, the synthesis and properties of a new tetracationic acidic organic salt **5** based on DABCO (Scheme 2) and its application as catalyst for the synthesis of bis(indolyl)methanes and acetals from carbonyl compounds.

We began our investigation for the synthesis of compound **5** by the reaction of an excess amount of DABCO **1** with 1,3-dibromopropane **2** in methanol at room temperature to give the dicationic salt **3** in 97% yield. Then, the salt **3** reacted with an excess amount of methyl iodide in neat conditions at room temperature to give the tetracationic salt **4** in quantitative yield. Finally, treatment of salt **4** with sulfuric acid in refluxing dichloromethane afforded the tetracationic acidic organic salt (TCAOS) **5** in 93% yield. This novel TCAOS contains four hydrogen sulfate (HSO_4^-) groups in the structure which caused strong acidic character. The structure of catalyst characterized by IR, ^1H and ^{13}C NMR and CHN analysis. Also, purity of the catalyst (assay more than 98%) was examined by titration with NaOH solution.

Screening the solubility of the TCAOS in polar and nonpolar solvents revealed that it is only miscible with water, MeOH and DMSO, but immiscible in $PhCH_3$, EtOAc, THF, Et_2O, CH_2Cl_2, CCl_4, $CHCl_3$, isopropanol (IPA) and hexane.

The thermal stability of the TCAOS was studied using thermogravimetry analysis (TGA). The TGA curves revealed that the TCAOS is stable until 220 °C and then started to lose only its 10% of weight until 300 °C. At 305–315 °C, it lost more than 60% of its weight. Decomposition finally completed at temperature higher than 315 °C (Fig. 1).

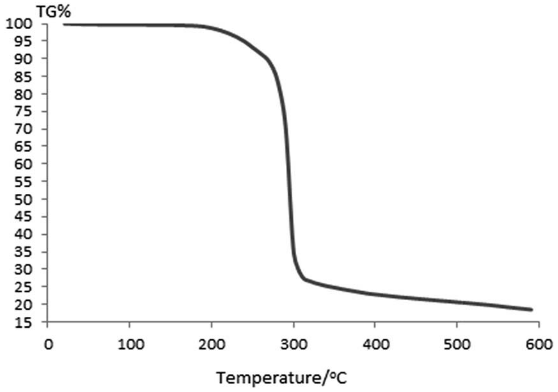
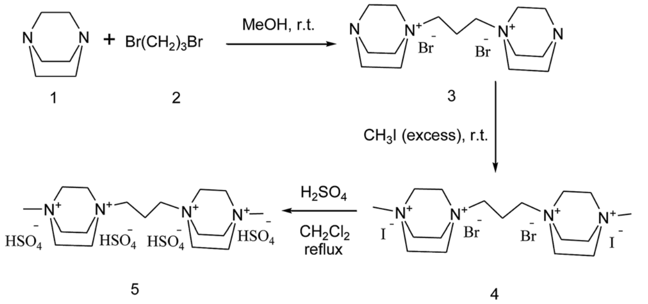


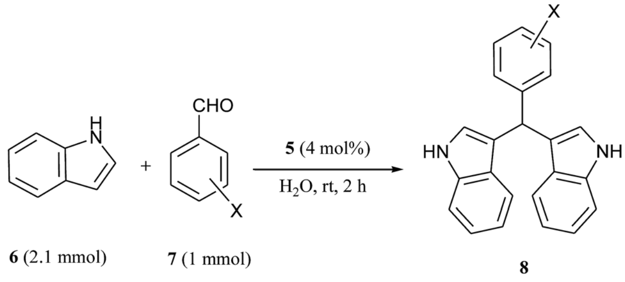
Fig. 1 TGA curve of TCAOS **5**.

To continue, we investigate the catalytic efficiency of the prepared TCAOS for synthesis of bis(indolyl)methanes from indoles and carbonyl compounds (Scheme 3). We have shown that the reactions proceed well in water at room temperature using only 4 mol% of TCAOS. The results of these reactions are summarized in Table 1. As shown in Table 1, indole derivatives such as indole, 2-methyl indole, 1-methyl indole, and 5-bromo indole were applied successfully in this reaction and afforded the corresponding bis(indolyl)methanes in excellent yields. Also, aromatic aldehydes containing both electron-donating and –withdrawing groups on the phenyl ring were found to react equally well in this protocol. Heteroaromatic aldehydes such as furfural and thiophene carbaldehyde are suitable substrates in this protocol (Table 1, entries 6 and 7). Terephthaldehyde was also reacted with indoles to give the corresponding products with four indole groups in the structure (Table 1, entries 14 and 15). Cyclohexanone was successfully applied in this protocol to give the corresponding product in 80% isolated yield (Table 1, entry 17). In addition, aliphatic aldehydes such as formaldehyde and acetaldehyde are suitable starting materials for synthesis of bis(indolyl)alkanes (Table 1, entries 16 and 18). Finally, 3-formylchromone gave high yields with indole, 1-methylindole and 2-methylindole (Table 1, entries 19 to 21).

The reusability of the catalyst in the synthesis of bis(indolyl) methane from benzaldehyde and indole was investigated through separating the product from the reaction mixture by

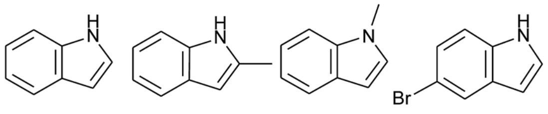


Scheme 2 Synthesis of TCAOS **5**.



Scheme 3 Synthesis of bis(indolyl)methanes catalyzed by TCAOS in water.

Table 1 Diversity in the synthesis of bis(indolyl)methanes in the presence of TCAOS



A B C D

Entry	Indole	Carbonyl compound	Yield[a] (%)	M.p. (°C) (L)
1	A	C_6H_5CHO	93	148–149 (151–152)[46]
2	A	2-ClC_6H_4CHO	Quant.	75–76 (72–74)[47]
3	A	4-ClC_6H_4CHO	Quant.	75–78 (74–77)[47]
4	A	4-$NO_2C_6H_4CHO$	92	216–217 (217–219)[48]
5	A	4-$CH_3C_6H_4CHO$	92	94–95 (95–97)[49]
6	A	Thiophene carbaldehyde	Quant.	183–186 (186–188)[50]
7	A	Furfural	95	114–115 (113–115)[51]
8	B	C_6H_5CHO	96	185–188 (182–185)[52]
9	B	2-ClC_6H_4CHO	Quant.	220–221
10	B	4-ClC_6H_4CHO	Quant.	187–189 (186–188)[53]
11	B	4-$CH_3C_6H_4CHO$	95	175–176 (174–175)[54]
12	C	C_6H_5CHO	90	187–189 (184–187)[54]
13	D	4-$NO_2C_6H_4CHO$	85	294–297 (290–294)[54]
14	A	Terephthaldehyde	80	137–140 (138–140)[55]
15	B	Terephthaldehyde	75	189–191 (188–190)[56]
16	A	Formaldehyde	98	168–170 (150)[57]
17	A	Cyclohexanone	80	116–118 (118–120)[49]
18	A	Acetaldehyde	92	150–153 (148–150)[58]
19	A	3-Formylchromone	78[b]	235–236 (233–234)[59]
20	B	3-Formylchromone	70[b]	311–312 (310–312)[59]
21	C	3-Formylchromone	75[b]	266–267 (265–266)[59]

[a] Isolated yield. [b] The reaction was performed in the presence of 5 mol% of the catalyst at 70 °C.

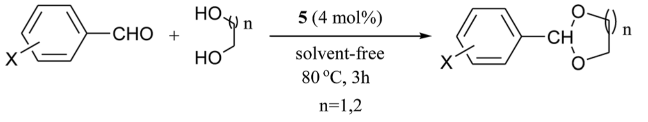
CH_2Cl_2, then reusing the aqueous phase in subsequent reactions. We confirmed that the catalyst can be reused at least five times without significant drop in reaction yield.

The catalytic efficiency of TCAOS in the synthesis of bis(indolyl)methanes from indole and benzaldehyde is compared with those reported in the literatures and summarized in Table 2. As revealed from Table 2, the TOF of the TCAOS (TOF = 23.75) is among the best catalysts reported to date for this transformation.

In addition, we have shown that the TCAOS can be applied as an efficient catalyst for preparation of acetals from aldehydes and diols. The best conditions for this reaction include heating the starting materials at 80 °C in the presence of 4 mol% of the catalyst for 3 h under solvent-free conditions. The results are summarized in Scheme 4.

Table 2 Comparison of the catalytic efficiency of various catalysts reported in the literature for the reaction of indole with benzaldehyde

Catalyst	Solvent	Catalyst amount (mol%)	Time (h)	Yield (%)	TOF (h^{-1})	Ref.
TCAOS	Water	4	1	95	23.75	–
Squaric acid	Water	18	3	90	3.75	54
SiO_2–H_2SO_4	Solvent-free	13	0.75	92	9.43	60
$KHSO_4$	CH_3OH	100	2.5	90	0.36	61
$LiClO_4$	CH_3CN	10	5	90	1.8	49
I_2	Solvent-free	20	0.16	72	22.5	47
Heteropoly acid	Water	14	2	84	2	62
Oxalic acid	Water	100	0.75	96	1.28	63
$ZrCl_4$	CH_3CN	10	0.5	96	19.2	55
$NaHSO_4$–SiO_2	CH_2Cl_2	20	2.5	89	1.78	50
$In(OTf)_3$	[Omim][PF_6]	5	0.25	96	76.8	51
$InCl_3$	[Omim][PF_6]	10	1	71	7.1	51
$BiCl_3$	[Omim][PF_6]	10	1.5	93	6.2	51
TCT	CH_3CN	10	0.25	92	36.8	64
HMTAB	Water	20	2.5	86	1.72	65



X= H, n=1	yield= 80%;	X=H, n=2	yeild= 75%
X= 2-NO_2, n=1	yield= 93%;	X=2-NO_2, n=2	yeild=90%
X=4-NO_2, n=1	yield=99%;	X=4-NO_2, n=2	yeild=95%
X= 2-Cl, n=1	yield=90%;	X=4-Cl, n=1	yeild= 85%
X=2,4-Cl_2, n=1	yield=87%	X=4-F, n=1	yeild=78%

Scheme 4 TCAOS-catalyzed acetalization of aldehydes under solvent-free conditions.

Conclusions

In conclusion, a simple and efficient procedure for synthesis of a new tetracationic acidic organic salt (TCAOS) based on DABCO and its characterization is described in this paper. This compound contains four HSO_4^- groups with strong acidic character. Due to its acidic character, we have shown that it can be applied as an eco-friendly, powerful and reusable catalyst for the synthesis of bis(indolyl)methanes in water with high turnover frequency (TOF) and for acetalization of aldehydes with diols. Also, this compounds may be applicable as electrolyte in metal–acid batteries.

Experimental

General information

All materials were purchased from Merck and Fluka. All NMR spectra's were recorded on a Bruker AMX 300 MHz spectrometer and are referenced to the deuterated solvent used. Elemental analysis performed by a Perkin-Elmer 2004 (II) CHN analyzer. Infrared spectra were recorded in potassium bromide pellets on a Perkin Elmer FT spectrum RX1 over the range 400–4000 cm^{-1} and melting points were determined with a Branstead Electrothermal 9200 apparatus. TGA measurement has been performed by a NETZSCH TG 209 F1 Iris instrument. The measurement has been performed under a flow of nitrogen and the sample (*ca.* 5.90 mg) was scanned between room temperature and 600 °C.

Synthesis of 1,1″-(propane-1,3-diyl)bis(1,4-diazabicyclo[2.2.2]-octan-1-ium) dibromide (compound 3)

A solution of DABCO (4.62 g, 40 mmol) and 1,3-dibromopropane (3.45 g, 15 mmol) in methanol (50 mL) was left stirring for 20 h at rt. The reaction mixture was then evaporated *in vacuo* to give a yellowish residue which was triturated with warm acetone (30 mL, two times) to provide a white precipitate. Finally, the precipitate was collected by filtration and dried under vacuum. White solid; yield: (97%); ^1H NMR (300 MHz, D_2O): δ (ppm) 2.56 (2H, m), 3.13 (12H, t, $J = 7.3$ Hz), 3.27 (4H, t, $J = 8.7$ Hz), 3.37 (12H, t, $J = 7.9$ Hz); ^{13}C NMR (75 MHz, D_2O): 15.2, 44.0, 52.3, 60.3; Anal. Calcd. (%) for $C_{15}H_{30}Br_2N_4$: C, 42.27; H, 7.09; N, 13.14 found: C, 42.07; H, 6.73; N, 12.89.

Synthesis of 4,4′-(propane-1,3-diyl)bis(1-methyl-1,4-diaza bicyclo-[2.2.2]octane-1,4-diium) dibromide diiodide (compound 4)

Compound a (20 mmol) and CH_3I (60 mmol) were mixed and stirred at room temperature for 6 h. Then the reaction mixture was filtered off and washed several times with ethyl acetate to remove any remained CH_3I. The products were collected and dried under vacuum. Colorless solid; yield: (99%); ^1H NMR (300 MHz, D_2O): δ (ppm) 2.48 (2H, m), 3.32 (6H, s), 3.68 (4H, t, J: 8.4 Hz), 4.03 (24H, s); ^{13}C NMR (75 MHz, D_2O): 16.5, 51.7, 52.1, 53.1, 60.5; Anal. Calcd. (%) for $C_{17}H_{36}Br_2I_2N_4$: C, 28.75; H, 5.11; N, 7.89. Found: C, 29.18; H, 5.29; N, 7.89.

Synthesis of 4,4′-(propane-1,3-diyl)bis(1-methyl-1,4-diaza bicyclo-[2.2.2]octane-1,4-diium) tetra hydrogen sulfate (compound 5)

A solution of H_2SO_4 (20 mmol) in CH_2Cl_2 (5 mL) was added dropwise to a suspension of compound 4 (5 mmol) in 5 mL CH_2Cl_2, and the reaction mixture was stirred at 0 °C for 10 min. Then, the resulting reaction mixture was refluxed for 20 h. After completion of the reaction, solvent was removed by evaporation under reduced pressure and the residue was washed several times with ethyl acetate to give the pure tetracationic acidic organic salt 5. Colorless solid; yield: (93%); ^1H NMR (300 MHz, D_2O): δ (ppm) 2.51 (2H, m), 3.37 (6H, s), 3.71 (4H, m), 4.08 (24H, s); ^{13}C NMR (75 MHz, D_2O) δ (ppm) 15.9, 51.4, 52.4, 53.1, 60.5; Anal. Calcd. (%) for $C_{17}H_{40}N_4O_{16}S_4$: C, 29.82; H, 5.89; N, 8.18; found: C, 29.88; H, 5.89; N, 8.12.

General procedure for preparation of bis(indolyl)methanes in water catalyzed by tetra cationic acidic organic salt (TCAOS)

In a 25 mL round bottom flask equipped with magnetic stir bar were added an indole (2.0 mmol), an aldehyde and water (5 mL). To this mixture the catalyst [TCAOS (0.04 mmol, 0.03 g)] was added and the mixture was stirred at room temperature for 2 h. Progress of reaction was monitored by TLC (3 : 7, ethyl acetate–petroleum ether). After completion of the reaction, the product was extracted with diethyl ether (3 × 15) and the combined organic phases were dried with anhydrous Na_2SO_4 and evaporated under reduced pressure to give the crude product which was purified *via* recrystallization in hexane, or ethanol–water mixture. 3-((2-chlorophenyl)(2-methyl-1*H*-indol-3-yl)methyl)-2-methyl-1*H*-indole: m.p. 220–221 °C; ^1H NMR (300 MHz, $CDCl_3$) δ (ppm) 2.04 (6H, s), 6.21 (1H, s), 6.85–7.37 (12H, m), 7.73 (2H, brs); ^{13}C NMR (300 MHz, $CDCl_3$) δ (ppm) 11.8, 36.9, 109.5, 111.5, 118.5, 118.7, 120.2, 126.0, 127.1, 128.5, 129.0, 130.5, 131.5, 134.1, 134.5, 140.9; Anal. Calcd. (%) for $C_{25}H_{21}ClN_2$: C, 78.01; H, 5.50; N, 7.28. Found: C, 78.21; H, 5.30; N, 7.32.

General procedure for acetalization of aldehydes in the presence of TCAOS

In a test tube equipped with a magnetic stir bar, aldehyde (1 mmol), a diol (1.1 mmol) and TCAOS (4 mol%) was added and the mixture was heated at 80 °C for 3 h. progress of reaction was monitored by TLC. After completion, ethyl acetate (10 mL) and water (10 mL) were added to the reaction mixture. The organic phase was separated and dried with Na_2SO_4 and finally evaporated to give the corresponding product.

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