

Supporting Information

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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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 20h 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%); \(^1\)H NMR (300 MHz, D\(_2\)O): \(\delta\) (ppm) 2.56 (2H, m), 3.13 (12H, t, \(J=7.3Hz\)), 3.27 (4H, t, \(J=8.7Hz\)), 3.37 (12H, t, \(J=7.9Hz\)); \(^1^3\)C NMR (75 MHz, D\(_2\)O): 15.2, 44.0, 52.3, 60.3; Anal. Calcd. (%) for C\(_{15}\)H\(_{30}\)Br\(_2\)N\(_4\): 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\(_3\)I (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\(_3\)I. The products were collected and dried under vacuum. Colorless solid; yield: (99%); \(^1\)H NMR (300 MHz, D\(_2\)O): \(\delta\) (ppm) 2.48 (2H, m), 3.32 (6H, s), 3.68 (4H, t, \(J=8.4Hz\)), 4.03 (24H, s); \(^1^3\)C NMR (75 MHz, D\(_2\)O): 16.5, 51.7, 52.1, 53.1, 60.5; Anal. Calcd. (%) for C\(_{17}\)H\(_{36}\)Br\(_2\)I\(_2\)N\(_4\): 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\(_2\)SO\(_4\) (20 mmol) in CH\(_2\)Cl\(_2\) (5 mL) was added dropwise to a suspension of compound 4 (5 mmol) in 5 mL CH\(_2\)Cl\(_2\), 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%); $^1$H NMR (300 MHz,
D$_2$O): $\delta$ (ppm) 2.51 (2H, m), 3.37 (6H, s), 3.71 (4H, m), 4.08 (24H, s); $^{13}$C NMR (75 MHz,
D$_2$O) $\delta$ (ppm) 15.9, 51.4, 52.4, 53.1, 60.5; Anal. Calcd. (%) for C$_{17}$H$_{40}$N$_4$O$_{16}$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 2h. 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$_2$SO$_4$ 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-1H-
indol-3-yl)methyl)-2-methyl-1H-indole:** m.p. 220-221 °C; $^1$H NMR (300 MHz, CDCl$_3$) $\delta$
(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$_3$) $\delta$ (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 3h. 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$_2$SO$_4$ and
finally evaporated to give the corresponding product.