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The Synthesis of Pentaerythrityl Tetraimidazole

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Abstract

A method for the preparation of pentaerythrityl tetraimidazole was reported with pentaerythritol and imidazole as raw material. Pentaerythrityl tetrabromide (PEBr₄) was first prepared starting from pentaerythritol via two steps. Pentaerythrityl tetrabromide was then treated with imidazole, which was converted to pentaerythrityl tetraimidazole. The overall yield was 68.6%. The target product was analyzed and characterized by ¹H-NMR and ¹³C-NMR methods, indicating that our route of synthesis is reasonable and feasible.

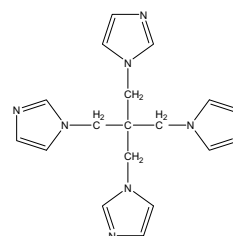
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Keywords: Pentaerythrityl Tetraimidazole; Pentaerythrityl Tet Rabromide; Synthesis

1. Introduction

Pentaerythrityl tetraimidazole, which chemical name is Propane,1,3-diimidazole-2,2-bis(imidazole methyl), is a branched compound with four imidazole groups. The structure formula follows as Scheme 1:

Imidazole ring containing imine N atom can provide the electron doublet. N atoms from four imidazoles as heterocyclic ligands can synthesis complexes, also undergo alkylation and acylation reactions^[1]. Owing to the spatial structure and ring structure, the compounds of poly-imidazole group have promising application in

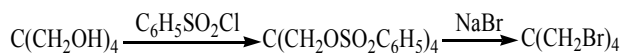


Scheme 1. The structure of pentaerythrityl tetraimidazole

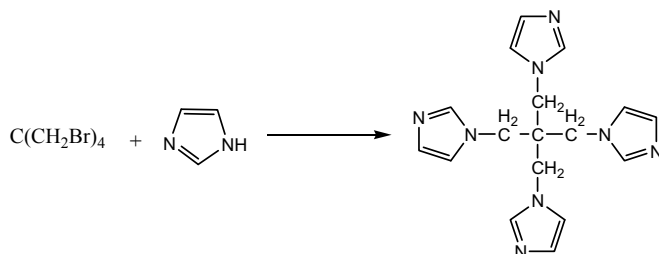
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medicine^[2], polymer material^[3,4], construction of high-porosity materials^[5], oligomeric surfactant^[6] etc. Meanwhile, it will have important theory meaning and realistic application value in host-guest chemistry^[7], molecular recognition^[8] and molecular self-assembly^[9] etc. In this research, we synthesized pentaerythrityl tetraimidazole with cheap pentaerythritol as raw material. The schematic diagram of the synthesis route is presented in Scheme 2:

Step 1



Step 2



Scheme 2. The synthesis route of pentaerythrityl tetraimidazole

2. Experimental Section

2.1. Materials and instrument

Imidazole was purchased from Shanghai Reagent Co.; pentaerythritol, pyridine, hydrochloric acid, methanol, diethylene glycol, sodium bromide, toluene, dimethyl sulfoxide (DMSO), NaOH and acetone are all analytical grade reagents and were purchased from Tianjin Kemiou Reagent Co.

All NMR spectra were taken using a Bruker Avance 400 MHz NMR spectrometer and were analyzed in deuterated chloroform with 99.9% purity. IR spectra were taken using a Bruker-Tensor 27 infrared spectrometer and were analyzed by KBr tableting. The melting temperatures were determined by a micro-binocular loupe melting point apparatus.

2.2. Methods.

2.2.1. The synthesis of pentaerythrityl tetrabromide (PEBr_4)

According to the literature [10], PEBr_4 was synthesized by mixing 0.1 mol pentaerythritol and 60 ml pyridine in a 500 ml three-necked round-bottomed flask equipped with a powerful mechanical stirrer, a thermometer and a dropping funnel. The stirrer is started, and to the resulting suspension is added dropwise 0.44 mole of benzenesulfonyl chloride at such a rate that the temperature of the reaction does not rise above 35°C . The addition requires about 1.5 hours. The resulting slurry is stirred at 40°C for 2.5 hours after the addition is complete. The slurry is then added slowly to a vigorously stirred solution of 80 ml of concentrated hydrochloric acid in 100 ml of water and 200 ml of methanol. The resulting suspension of granular white pentaerythrityl benzenesulfonate is filtered with suction, and washed with 500 ml of water and then with 100 ml of cold methanol in two portions. Drying at 75°C for 24 hours, pentaerythrityl benzenesulfonate was obtained. Melting point $102.4\text{--}103.0^\circ\text{C}$.

The dry 0.05mol pentaerythrityl benzenesulfonate is added to 90ml of diethylene glycol in a 500ml Erlenmeyer flask equipped with a mechanic stirrer. Then 0.45mol of sodium bromide is added, and the mixture is heated in an oil bath at 130–150°C with slow stirring overnight. The resulting orange mixture is allowed to cool to about 60°C, 800ml of ice water is added rapidly with stirring, and finally the mixture is cooled to 10°C by direct addition of ice. The precipitate is filtered with suction, washed three times with water. After recrystallization from cold ethanol, the white solid is obtained in 78%yield, Melting point 158.5-159°C.

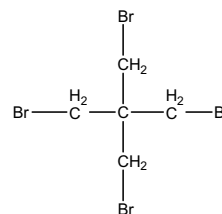
2.2.2. The synthesis of pentaerythrityl tetraimidazole

A 0.2 mol portion of imidazole was dissolved in toluene (24 mL) and DMSO (24 mL). An aqueous solution of NaOH (50% (w/w), 16g NaOHaq) was added and water was removed by azeotropic distillation through a Dean-Stark condenser. Following the removal of water, 0.04 mol of PEBr_4 was added and the mixture was stirred at 120°C for 4 h. The deposit of NaBr was thermally filtered and the solvent was removed under vacuum. The resulting crude product was then dissolved in dichloromethane (40 mL) and the residual NaBr was filtered off. After recrystallization from cold ethanol, the white solid is obtained in 88% yield, Melting point 121.2–121.9°C.

3. Results and discussion

3.1. Characterization of PEBr_4

Scheme 3 shows the structure of PEBr_4 , and its melting point is 158.5°C-159°C (159°C, literature[10]), in the infrared spectra, the $-\text{OH}$ absorption peak around 3300 cm^{-1} disappears, and around 601 cm^{-1} corresponds to the absorption peak of the C-Br, $^1\text{H NMR}$ (CDCl_3): $\delta=3.589\text{ ppm}$ (s, 8H) is the proton peak of $-\text{CH}_2\text{Br}$.



Scheme3. The structure of PEBr_4

3.2. Characterization of pentaerythrityl tetraimidazole

Scheme 1 shows the structure of pentaerythrityl tetraimidazole. Fig.1and Fig.2 are respectively 400 MHz $^1\text{H NMR}$ spectrum and $^{13}\text{C NMR}$ spectrum in CDCl_3 of pentaerythrityl tetraimidazole. In the $^1\text{H NMR}$ spectra, the signals of the protons of the imidazole ring are respectively $\delta=6.957, 6.979, 7.417\text{ ppm}$, which are H3, H2 and H1; the signal at $\delta=4.233\text{ ppm}$ corresponds to the C- CH_2 - protons, which is the H4.

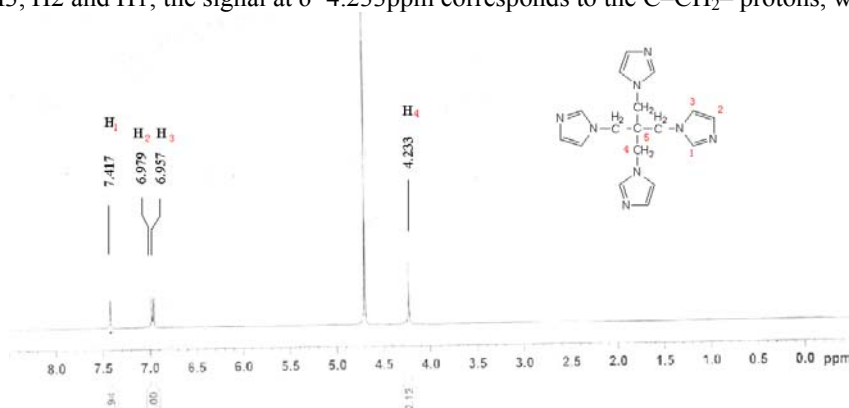


Fig.1. 400 MHz $^1\text{H NMR}$ spectrum in CDCl_3 of pentaerythrityl tetraimidazole

In the ^{13}C NMR spectra, the chemical shifts of the carbon in the imidazole ring are respectively $\delta=121.45, 128.49, 139.24\text{ppm}$, which are C3, C2 and C1; the chemical shift at $\delta=49.58\text{ppm}$ corresponds to the $\text{CH}_2\text{-N}$ carbon linking with imidazole ring, which is the C4; the chemical shift at $\delta=42.33\text{ppm}$ corresponds to the quaternary carbon, which is the C5. so we could confirm that What we synthesised is target product.

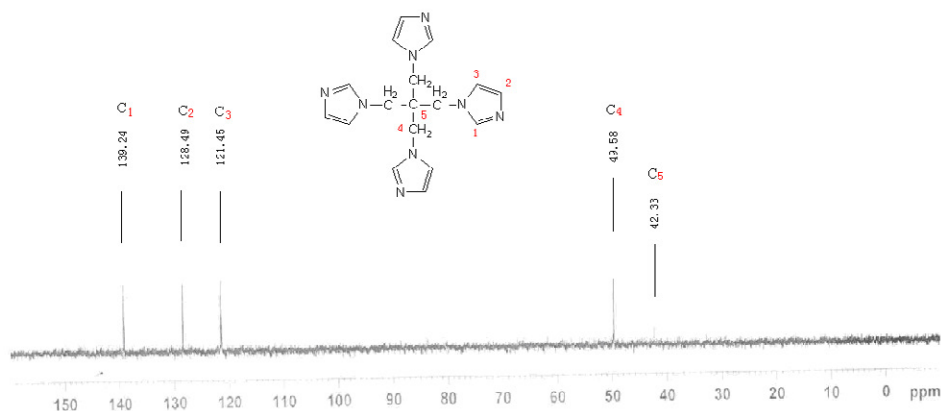


Fig.2. 400 MHz ^{13}C NMR spectrum in CDCl_3 of pentaerythrityl tetraimidazole

4. Conclusion

In summary, we have presented the synthesis method of pentaerythrityl tetraimidazole by two steps. The target product was analyzed and characterized by ^1H -NMR and ^{13}C -NMR methods. The overall yield was 68.6% and the purity of product is higher. This method is suitable for mass production.

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