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Studies on the SYNTHETIC Method of 2,5-Dihydroxyterephthalaldehyde

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Abstract: 2,5-Dihydroxyterephthalendehyde (Dha) can be used as an intermediate in organic chemistry and synthetic materials, which can participate in a variety of chemical reactions. Through these reactions, a variety of valuable compounds can be synthesized. However, the existing synthesis methods are cumbersome, difficult to operate, and have low yields. Referring to the reported Dha synthesis process, we successfully synthesized Dha using inexpensive 1,4-dimethoxybenzene with simple steps. The correct structure was proved by Fourier transform infrared (FT-IR) spectroscopy, nuclear magnetic resonance (^{1}H-NMR) hydrogen spectroscopy, and nuclear magnetic resonance (^{13}C CP-MAS NMR) carbon spectroscopy, which provides a valuable reference for the synthesis of Dha.

1. Introduction

2,5-Dihydroxyterephthalendehyde (Dha) is an organic compound with important chemical properties and application value. Depending on its chemical structure and properties, it has many applications. Dha can be used as an intermediate in organic chemistry and synthetic materials [1, 2], involved in a variety of chemical reactions. Using these reactions, a variety of valuable chemical structures can be synthesized. Dha in the field of chemical testing [3] and materials chemistry is widely used [4, 5]. For example, Yan and collaborators used Dha to design and synthesize Por-COFs with highly photosensitizing activity for photodynamic inactivation of bacteria through a coupling regulation strategy [6]. He and his collaborators chose Dha with the -OH group and 2,5-dimethoxyterephthalate (DMTP) with -OCH_3 was condensed with 1,3,5-tris (4-aminophenyl) benzene (TAP) respectively to construct loaded COF film [7]. Liao and collaborators synthesized a europium (Eu)-containing covalent organic framework (DhaTab-COF-EuIL) by Schiff base reaction, as a novel luminescence sensor, which shows high sensitivity and selectivity for the detection of volatile acetone, with a detection limit of up to 1% [2]. Kubiak and his collaborators used 5, 10, 15, 20-Tetras (4-aminophenyl) porphyrin iron(III) chloride (FeTAPPCl) and Dha to synthesize a covalent organic framework due to the integration of CO_2 revert to CO [8]. Zhao and his co-workers constructed a highly crystalline three-dimensional hydroxylated covalent organic framework (COF-301) with tetrakis(4-phenyl)methane (TAM) and Dha as the building blocks and used it as an adsorbent for glucocorticoid solid-phase extraction (SPE), and carried out theoretical investigations on the potential adsorption mechanism of glucocorticoids onto COF-301 [9]. Han and his co-workers utilized Dha first modified by nucleophilic substitution reaction to form the superhydrophobic monomer Dha-octyl. Then poly-octyl was condensed with 1,3,5-(1,3,5-triazine-2,4,6-triyl)triphenylamine (Tz) to synthesize the superhydrophobic covalent organic framework TzDa-octyl.TzDa-octyl can be used in complex environments due to its high thermal and chemical stability.TzDa-octyl can be grown in-situ on melamine foams for oil/water separation. The prepared foams have high adsorption capacity and good reusability for oil/water separation. This work not only provides a strategy for the construction of functional COFs, but also opens a way for the growth of COFs on different substrates for oil/water separation [10].

The potential application of Dha is very considerable, but the existing synthesis methods are cumbersome and the operation of the frameworks is not easy. synthesis methods are cumbersome, difficult to operate and have low yields. In this experiment we successfully synthesized 2,5-dihydroxyterephthalaldehyde using inexpensive 1,4-dimethoxybenzene in a simple procedure.

2. Material and Instrument

2.1. Material

1,4-dimethoxybenzene and paraformaldehyde were purchased from Shanghai McLean Biochemical Technology Co., Ltd., 1,4-dioxane was purchased from Tianjin Fuyu Fine Chemical Co., Ltd., formaldehyde, acetone, dichloromethane, boron tribromide (BBr_3), petroleum ether, ethyl acetate, n-hexane were purchased from Anhui Zesheng Technology Co., Ltd., concentrated hydrochloric acid, Chloroform, hexamethylenetetramine and acetic acid were purchased from Sinopharm Chemical Reagent Co., Ltd.

2.2. Instrument

Nuclear magnetic resonance hydrogen spectroscopy (^{1}H-NMR) and nuclear magnetic resonance carbon spectroscopy (^{13}C CP-MAS NMR) data were measured by Bruker AVANCE-400 HD and AVANCE II 400 NMR spectrometers. Fourier transform infrared spectroscopy (FT-IR) data were measured by the Bruker ALPHA Fourier Variation Infrared Spectrometer.

3. Experimental results and Analysis

3.1. Synthetic method

This is shown in Figure 1

a: 1,4-dimethoxybenzene (10 g, 72.3 mmol) was dissolved in 1,4-dioxane (60 mL) and formaldehyde (37 wt%, 5 mL) was added) and paraformaldehyde (3.0 g, 100 mmol). After heating the system to 90°C, concentrated hydrochloric acid (10 mL) was added dropwise, and heated at 90°C for 1 h, followed by hydrochloric acid (37 wt%, 30 ml of hydrochloric acid) was introduced into the reaction system After cooling to

room temperature, the filtered collected precipitate is washed with water and vacuum-dried. After drying, acetone is used to recrystallize to obtain product A.

B: The above products A (5 g, 21.3 mmol) and hexamethylenetetramine (6 g, 42.5 mmol) were added to chloroform (50 mL), keep it at 90°C and stir for 24 h, cool to room temperature after heating, and wash the filtered collected pellet with chloroform and vacuum dry. The dried product was dissolved in H_2O, acetic acid (10 mL) was added to it for acidification, heated at 90°C and stirred for 24 h, and then cooled to room temperature. The above system is extracted by dichloromethane, the organic phase is dried with anhydrous magnesium sulfate, and the solvent is evaporated under reduced pressure to obtain product B. Purification was performed using column chromatography (dichloromethane: petroleum ether = 2:1).

Dha: dissolve the above product b (1.0 g) in dichloromethane (100 mL), add BBr_3 (4.0 mL) dropwise at 0°C, N_2 atmosphere, heat up the reaction system to room temperature and stir overnight. After the end of the reaction, H_2O was added dropwise at 0°C to stop the reaction, the residue in the reaction system was extracted by dichloromethane, the organic phase was dried with anhydrous magnesium sulfate, and the product Dha was obtained by evaporating the solvent under reduced pressure. Purification was performed using column chromatography (n-hexane: ethyl acetate = 4:1).

3.2. Interpretation of result

As shown in Figure 1, we use 1,4-dimethoxybenzene as raw material to synthesize 2,5-dihydroxyterephthalene. As shown in the FT-IR spectrum (Figure 2), the presence of peaks A, B, and C demonstrates the successful synthesis of Dha. The characteristic peak of -OH appeared at 3276 cm^{-1}, the characteristic peak of HC=O at 1661 cm^{-1}, and the characteristic peak of Ar at 1480 cm-1. The correctness of the structure of the synthesized 2,5-dihydroxyterephthalenide was demonstrated. In order to further verify the correctness of the Dha structure, the obtained products were tested by ^{1}H-NMR and ^{13}C-NMR. As shown in Figure 3, the peaks at 7.2 ppm and 10.3 ppm fully demonstrate the successful synthesis of 2,5-dihydroxyterephthalenaldehyde. As shown in Figure 4, the characteristic peaks at 115.7 ppm, 128.1 ppm, 153.3 ppm, and 190.7 ppm further demonstrate the correctness of the structure of 2,5-dihydroxyterephthalendehyde.

4. Conclusion

We successfully synthesized 2,5-dihydroxy-p-phenylenedicarboxaldehyde with reference to the synthetic process of Dha. The correct structure was proved by FT-IR, ^{1}H-NMR and ^{13}C-NMR. The existing synthesis method is cumbersome with difficult steps and low yield. The improved process successfully synthesized Dha using inexpensive 1,4-dimethoxybenzene via a facile procedure.

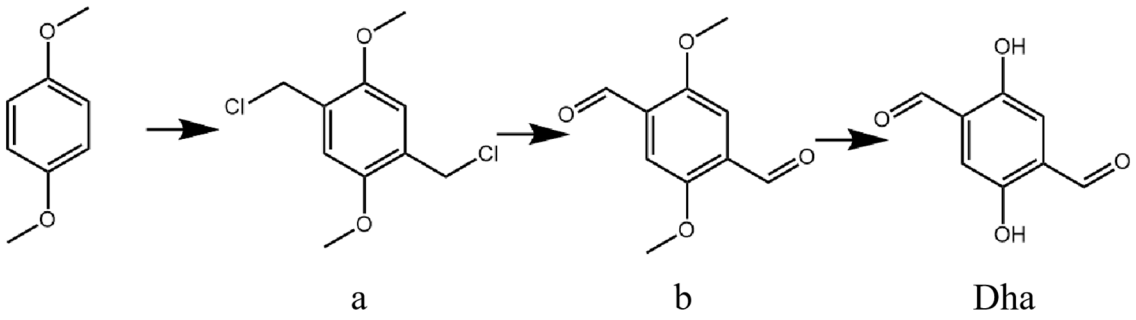

Figure 1. Dha synthesis roadmap

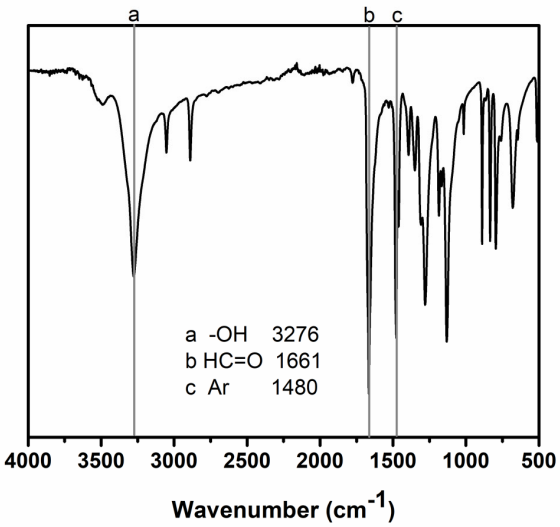

Figure 2. FT-IR（KBr，cm^{-1}）of Dha :3276(s), 3042(w), 2889(m), 1661(s), 1480(s), 1396(w), 1354(w), 1271(s),1201(w), 1138(s), 1020(w), 894(m), 831(m), 804(m), 678(m).

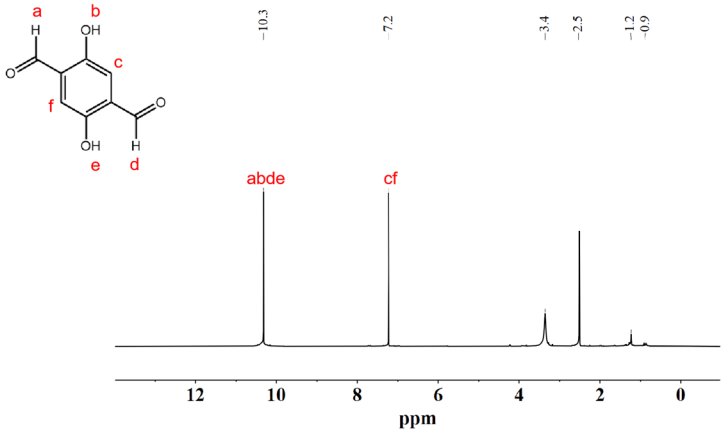

Figure 3. ^{1}H-NMR（400 MHz，DMSO-d_6，ppm）of Dha： δ 7.2 (2H, m), 10.3 (4H, s).

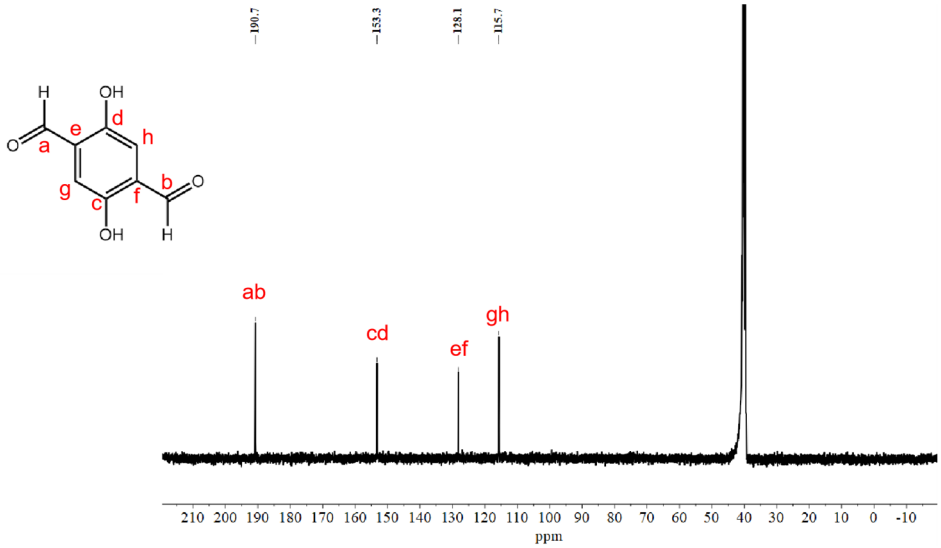

Figure 4. ^{13}C-NMR (101 MHz, DMSO-d_6, ppm) of Dha: δ 190.7, 153.3, 128.1, 115.7.

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