

Synthesis of Cyclohexanone Pentaerythritol Ketal Catalyzed by Sulfonated Zeolite

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Abstract. In the previous research, it has been found that cyclohexanone pentaerythritol ketal has some bioactivity in the treatment of hurt in sports. In this work, cyclohexanone pentaerythritol ketal was synthesized from cyclohexanone and pentaerythritol by condensation catalyzed by zeolite and modified zeolite, and the reaction condition was discussed. It was characterized by NMR, MS spectrum and single-crystal X-ray diffraction. It crystallizes in orthorhombic space group, P21, with a unit cell dimensions of $a = 11.1214(9) \text{ \AA}$, $b = 13.9216(6) \text{ \AA}$ and $c = 11.6658(10) \text{ \AA}$. There are two molecules with different conformation in the crystal, varying from bond lengths to angles. The stacking interaction is responsible for the crystal's 1-D supra-molecular structure.

Introduction

In the synthesis chemistry, acetals/ketals are important in synthetic carbohydrate and steroid chemistry [1, 2]. Acetonide formation is the commonly used protection for 1, 2-(cis)- and 1,3-diols, which have extensively been used in carbohydrate chemistry to selectively mask the hydroxyls of different sugars. Besides the interest of acetals/ketals as protecting groups, they are used both as intermediates and as end products, in the phyto pharmaceutical, fragrances and lacquers industries [3,4]. They have found direct applications as solvents in fragrance industries, cosmetics, food and beverage additives, pharmaceuticals, the synthesis of enantiomerically pure compounds, detergent and lacquer industries, and polymer chemistry [5-10]. Acetals have been also used in motor oils, lubricating oils, and hydraulic fluids and as an invert-emulsion for drilling petroleum operations [11].

In the previous research, it has been found that cyclohexanone pentaerythritol ketal has some bioactivity in the treatment of hurt in sports. Besides, pentaerythritol acetals in general are applied as plasticizers and vulcanizers, as physiologically active substance, potential protective groups for aldehydes and ketones, as raw materials for production of valuable resins and lacquers, as physiologically active substances [12]. In this article, we synthesized cyclohexanone pentaerythritol ketal (shown in Scheme 1) and determined its crystal structure by single-crystal X-ray.

Experimental

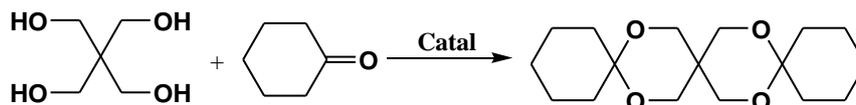
Materials

Chemicals were either prepared in our laboratories or purchased from Merck, Fluka and Aldrich Chemical Companies. All yields refer to isolated products. The products were characterized by comparison of their physical data with those of known samples or by their spectral data. NMR spectrum was recorded in the stated solutions, on a Bruker Drx-400 spectrometer, operating at 400 MHz for ¹H; δ values are reported in ppm and J values in hertz. Mass spectrum were recorded on a Micromass Platform II spectrometer, using the direct-inlet system operating in the electron impact (EI) mode at 75 eV.

All H atoms were positioned geometrically, with C-H = 0.93-0.98 Å, and refined with a riding model, with Uiso(H) = 1.2Ueq(carrier).

Synthesis of Cyclohexanone Pentaerythritol Ketal

The reaction is described in Scheme 1. Cyclohexanone and pentaerythritol were added in a flask with the molar ratio of 2:1, and the toluene was added as the water carrier and the solvent. 5% (wt) solid acid, catalyst was added as catalyst. The mixture was refluxed until no water can be carried out, and the cool to room temperature. The catalyst was filtrated, and the solvent was evaporated to produce the crude product. Colorless crystals of cyclohexanone pentaerythritol ketal were obtained in ethanol by recrystallization. Mp 115.5-116.2 °C; ¹H-NMR (D6-DMSO, 400 MHz), δ: 3.62 (4H, s), 1.76 (4H, t, *J* = 7.2 Hz), 1.55 (4H, td, *J* = 7.6, 1.2 Hz), 1.35 (2H, t, *J* = 7.6 Hz); MS (EI) *m/z*: 296 (M⁺).



Scheme 1 Synthesis of cyclohexanone pentaerythritol ketal

Results and Discussion

Synthesis

In this synthesis, three kinds of zeolite and corresponding sulfonated species were screened, and the results were shown in Fig. 1. From the results, it can be found that the catalytic activity is quite different. For the zeolite, NaY and ZSM-5 are active for this reaction, and ZSM-5 is the most effective one with the yield of 86.3%, compared with 5.9% for 4A. After the sulfonation, all the yields are increased. The yield of cyclohexanone pentaerythritol ketal increases to 98.1%, 96.1% and 37.5% respectively, which may be due to the increased acidity by sulfonation.

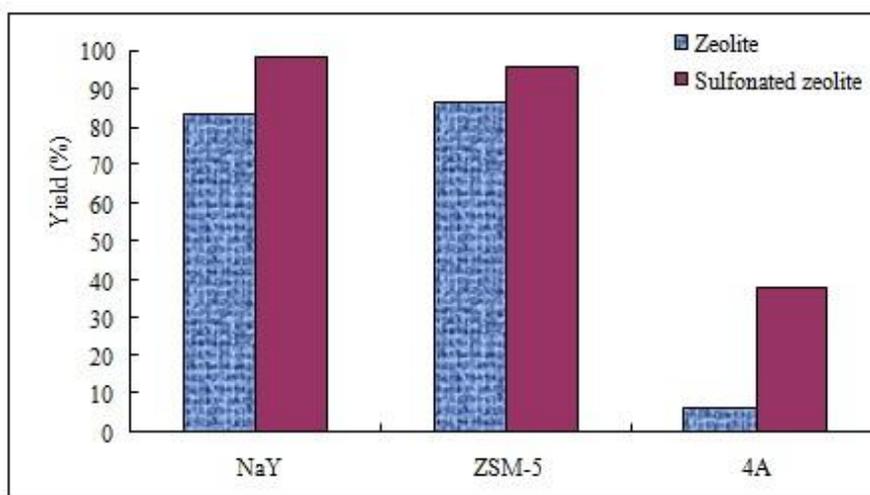


Fig. 1 The yield of cyclohexanone pentaerythritol ketal catalyzed by zeolite

In the following work, the effect of the dosage of ZSM-5 on the yield of cyclohexanone pentaerythritol ketal was investigated by using varying the dosage from 1% to 20%, and the results was shown in Fig. 2. From the results, it can be found that it can be seen that the low amount of catalyst is not efficient to cause the reaction happen. With increasing the amount to 22%, yield of cyclohexanone pentaerythritol ketal increases up to 96.1%. The reason for the increase conversion with an increase in the catalyst weight should be attributed to the increase number of catalytically active sites provided by large amount of ZSM-5. Further increase the amount of catalyst to 20% the yield does not increase further.

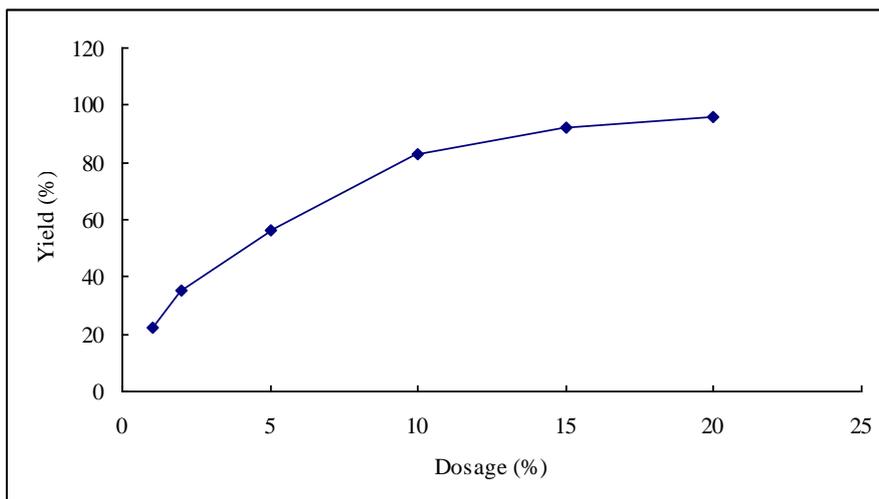


Fig. 2 The effect of the dosage of ZSM-5 on the yield of cyclohexanone pentaerythritol ketal

Structure

The stereo structure of the title compound was corroborated by X-ray diffraction analysis. The molecular structure is shown in Fig. 3, the unit cell is shown in Fig. 4, and the packing of the compounds is depicted in Fig. 5, which were drawn with ORTEP-3. The X-ray structural determination of the title compound confirmed the assignment of its structure from NMR and MS spectra data. Geometric parameters of the title crystal structure are in the usual ranges. There are two independent molecules with different conformation in the crystal, varying in bond lengths and angles. It crystallizes in crystallizes in the triclinic space group, P21, with unit cell dimensions $a = 11.1214(9) \text{ \AA}$, $b = 13.9216(6) \text{ \AA}$ and $c = 11.6658(10) \text{ \AA}$.

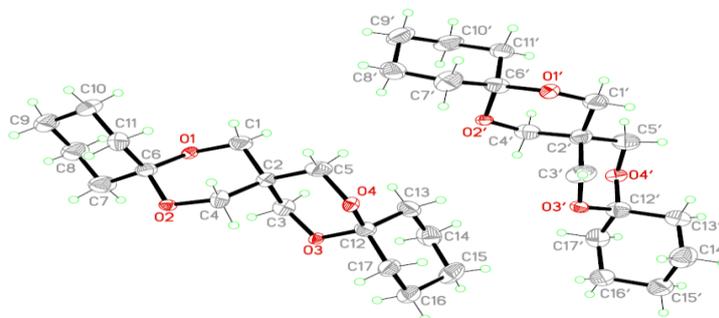


Fig. 3 The molecular structure of cyclohexanone pentaerythritol ketal

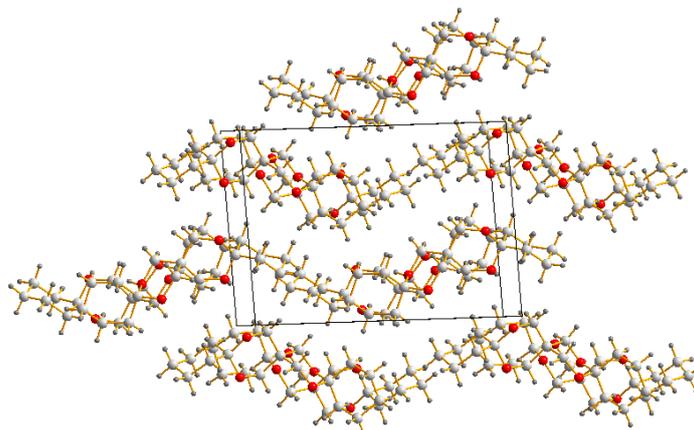


Fig. 4 The unit cell of cyclohexanone pentaerythritol ketal

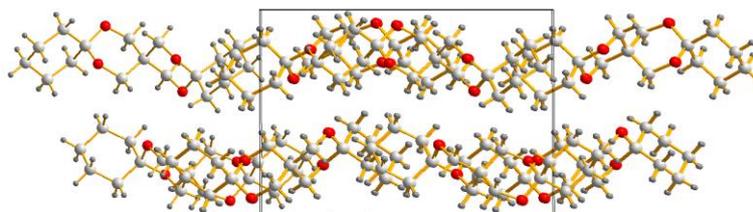


Fig. 5 The 1 D and 2D packing diagram of cyclohexanone pentaerythritol ketal

There are two independent molecules with different conformation in the crystal, varying in bond lengths and angles as shown in Fig. 3. For example, the lengths of the main C-O bonds, C1-O1, C4-O2, C3-O3, and C5-O4 are 1.430, 1.425, 1.429, and 1.421 Å respectively, while, in the other molecular, the lengths of the main C-O bonds, C1'-O1', C4'-O2', C3'-O3', and C5'-O4' are 1.429, 1.417, 1.412, and 1.425 Å respectively. The main angles of C-O-O bonds, \angle C1-O1-C6, \angle C4-O2-C6, \angle C3-O3-C12, and \angle C5-O4-C12, are 114.4, 114.5, 114.2, and 113.4 respectively, while, in the other molecular, the main angles of C'-O'-O' bonds, \angle C1'-O1'-C6', \angle C4'-O2'-C6', \angle C3'-O3'-C12', and \angle C5'-O4'-C12', are 113.4, 114.3, 115.1, and 114.4 ° respectively. There are three quaternary carbons in each molecular. The bonds length related to C2 are very similar in the range from 1.518 Å to 1.532 Å, and the related angles are from 107.0 to 111.0 °, which should be due to the symmetry center role of C2. For other two quaternary carbons, C6 and C12, the related bonds length and the angle are in wider ranges.

Electronic Spectra

Electronic spectra of cyclohexanone pentaerythritol ketal in methanol solution was presented in Fig. 6. In the spectra, the compound exhibits two intra-ligand charge transfer bands at 208 nm (high energy) and at 275 nm (low energy), which is probably due to the electronic transfer from ground state to the excited state.

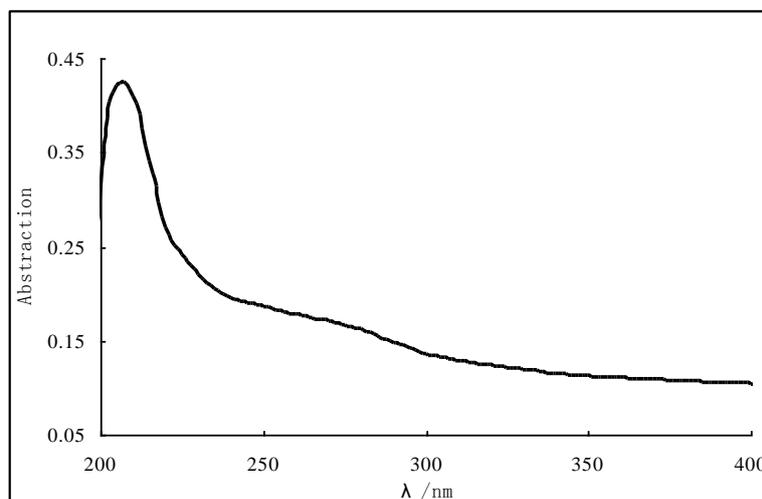


Fig. 6 The electronic spectra of cyclohexanone pentaerythritol ketal

Conclusion

In This work, the synthesis and structure of cyclohexanone pentaerythritol ketal has been studied. The reaction conditions were screened and the structure was determined by d single-crystal X-ray diffraction. It crystallizes in orthorhombic space group, P21, with a unit cell dimensions of $a = 11.1214(9)$ Å, $b = 13.9216(6)$ Å and $c = 11.6658(10)$ Å. There are two molecules with different conformation in the crystal, varying from bond lengths to angles. The stacking interaction is responsible for the crystal's 1-D supra-molecular structure.

Acknowledgement

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