Synthesis of 1,2-Bis(4'-Oxa-3',5'-Dioxotricyclo-[4.3.0.1^{2,5}]Decane-8'-Yloxy)Ethane Involving a Flexible Bridging Moiety by Combination of Heteropolyacids as Solid Acid Catalysts and 1,4-Dioxane as a Bridging Reagent

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1,2-Bis(4'-oxa-3',5'-dioxotricyclo-[4.3.0.1^{2,5}]decane-8'-yloxy)ethane (BNA), which is a candidate for a monomeric starting material of the soluble polyimide, has been synthesized from 5-norbornene-2,3-dicarboxylic anhydride (NA) and 1,4-dioxane (1,4-DO) via solid acid catalysis over the heteropolyacids such as H₃PW₁₂O₄₀•30H₂O and H₄SiW₁₂O₄₀•30H₂O. In all the conditions without 1,4-DO, no reaction occurs. Thus, it seems that this novel reaction contains an acid-catalyzed cleavage step of 1,4-DO by the very strong acidity of the heteropolyacids. The target compound (BNA) can be obtained in satisfactory yields (~90%).

Key Word : 1,2-bis(4'-oxa-3',5'-dioxotricyclo-[4.3.0.1^{2,5}]decane-8'-yloxy)ethane, heteropolyacid, solid acid, 1,4-dioxane, acid-catalyzed cleavage

1. Introduction

From the industrial point of view, a new class of intermediates such as aliphatic carbonyl derivatives has been noticed as a candidate for the versatile building blocks of polyimide resins. We have already reported several new derivatives such as cyclobutane-1,2,3,4-tetracarboxylic dianhydride (CBDA)¹⁾, norbornene-2,3,5,6-tetracarboxylic dianhydride (NDA)²⁾, tricyclo[5.2.1.0^{2,6}]dec-3-ene-8,9-diester (TCDE), and tricyclo[5.2.1.0^{2,6}]dec-3-ene-8,9-dicarboxylic anhydride (TCDA).³⁾ Recently, the one-step synthesis of bis(tricyclo[4.3.0.1^{2,5}]dec-7-ene-3-yl)ether (BTDE)⁴⁾ from dicyclopentadiene (DCPD) with heteropolyacid as a catalyst was also reported.⁵⁾ Unfortunately this coupling reaction is specific only for DCPD and the related compounds such as 5-norbornene-2,3-dicarboxylic anhydride (NA) hardly afford the similar coupling products.

In the process of this research, we found a quite novel coupling reaction promoted by 1,4-DO. We report here that 1,2-bis(4'-oxa-3',5'-dioxotricyclo-[4.3.0.1^{2,5}]decane-8'-yloxy)ethane (BNA), which is NA dimer linked with 1,2-ethylene diether, can be obtained from NA and 1,4-DO via solid acid catalysis over the heteropolyacids⁶⁻¹⁰⁾ in the yield of ~90%.

2. Experimental

¹H-NMR spectra were measured at 25°C with a Varian Unity Inova 400 spectrometer at 400 MHz. Each sample was dissolved in deuterated solvents such as CDCl₃. TMS was used as an internal standard. The product analysis were performed by a gas chromatography with a Shimadzu GC-17A instrument equipped with a flame ionization detector through a capillary column CBP1-W25-100 (25 m x 0.53 mm ϕ x 1- μ m). The conditions are as follows : injector temperature, detector temperature, initial column temperature, first retention time, programming rate, final column temperature, and second retention time were 290°C, 290°C, 100°C, 2 min, 8°C/min, 290°C, and 10 min, respectively. Helium was used as a carrier gas.

2.1 General procedure of preparation of BNA

A mixed solution of 5-norbornene-2,3-dicarboxylic anhydride (NA) (16.4 g, 0.1 mol), dodecatungstophosphoric acid (H₃PW₁₂O₄₀•30H₂O, 7.94 g), and 1,4-dioxane (1,4-DO, 65 g) was refluxed with stirring for 20 h at 100°C. After cooling the reaction mixture to room temperature, the solid matter adhered to the bottom of flask. This solid material was decanted off and the resulting solution was concentrated by evaporation. The purification of 2 times with a chromatography of the residue on a column of silica gel

using AcOEt-heptane (1 : 1~1 : 0 v/v, followed by addition of C H₃CN) as eluent affords oily compound BNA (8.9 g, 97% purity checked by GC). ¹H-NMR (CDCl₃): δ = 1.58 (t, J = 11.0 Hz, 4H), 1.78 (d, J = 10.8 Hz, 2H), 1.86-1.91 (m, 2H), 2.77 (s, 4H), 3.04 (s, 2H), 3.25 (s, 2H), 4.29-4.38 (m, 4H), 4.82 (t, J = 6.5 Hz, 2H). ¹³C-NMR (CDCl₃) δ = 35.6, 35.7, 38.0, 40.8, 42.5, 42.6, 45.9, 50.1, 62.8, 62.9, 80.2, 171.9, 178.9, 179.0. MS : m/z (%) : 280 (M⁺, 100), 264 (35), 260 (20).

3. Results and discussion

In the process of the research for the synthesis of bis(tricyclo [4.3.0.1^{2,5}]dec-7-ene-3-yl)ether (BTDE) from dicyclopentadiene (DCPD) over heteropolyacid (Scheme 1), we found that a novel aliphatic carbonyl compound, i.e., 1,2-bis(4'-oxa-3',5'-dioxotricyclo-[4.3.0.12,5]decane-8'-yloxy)ethane (BNA), which is NA dimer linked with 12-ethylene diether, can be obtained from 5-norbornene-2,3-dicarboxylic anhydride (NA) and 1,4-dioxane (1,4-DO) via solid acid catalysis over the heteropolyacids in the yield of ~90% (Scheme 2). The product BNA was identified on the basis of ¹H-NMR, ¹³C-NMR and the mass spectrometry (FAB). A BNA's gas chromatogram consisting of two large peaks which are further slightly separated into two peaks respectively indicates that there are four stereoisomers in the product. The former mixture of two isomers having a shorter retention time is liquid at room temperature, while the latter is solid (mp. 162-163°C). In this study, BNA refers to a mixture of four stereoisomers.

The results of reactions with a large excess of 1,4-DO at high temperature, i.e., 130°C are summarized in Table 1. In all cases, BNA was obtained in the yield of 78-92 %. In the comparison

Table 1 Results of reactions with a large excess of 1,4-DO at 130°C

Run	Catalyst	Catalyst Weight g (wt%)	1,4-Dioxane Weight g (eq.)	Time h	GC area% BNA
1	H ₃ PW ₁₂ O ₄₀ ·30H ₂ O	0.66 (20)	7.0 (4)	24	85.7
2	H ₃ PW ₁₂ O ₄₀ ·30H ₂ O	0.66 (20)	17.6 (10)	24	88.1
3	H ₄ SiW ₁₂ O ₄₀ ·30H ₂ O	0.66 (20)	17.6 (10)	7	78.1
4	H ₄ SiW ₁₂ O ₄₀ ·30H ₂ O	0.66 (20)	17.6 (10)	24	91.9

between run 1 and 2, both conditions afford BNA in almost same yield inspite of the large difference in the amount of 1,4-DO used. In contrast, the reaction time has significant influence to the yields of product from the comparison of run 3 and 4.

In Table 2 the results of reactions with a small excess of 1,4-DO at various conditions are summarized. Both run 5 (with very small amount of catalyst) and run 6 (at lower temperature) give the product in dissatisfied yields (26-40%). Even in the condition with only 1.8 eq. of 1,4-DO for NA (run 9), the yield of BNA is almost same in comparison with that of condition with 4.5 eq. of 1,4-DO (run 7). Therefore, in this reaction 1,4-DO can react with NA efficiently. Here again, the reaction time has significant influence to the yields of BNA (run 7 and 8 ; run 13 and 14). From these results, it seems that the optimal reaction time, temperature and the amount of catalyst are > 20 h, ~110°C and the ~20 wt %, respectively.

In Table 3, the results of reactions without 1,4-DO at various

Scheme 1 Synthesis of BTDE

Scheme 2 Synthesis of BNA

Table 2 Results of reactions with a small excess of 1,4-DO

Run	Catalyst Weight g (wt%)	1,4-Dioxane Weight g (eq.)	Bath Temp. °C	Time h	GC area% BNA
5	0.5 (5)	8 (1.8)	120	24	26.2
6	1 (10)	20 (4.5)	80	24	39.8
7	2 (20)	20 (4.5)	110	8	71.0
8	2 (20)	20 (4.5)	110	16	82.1
9	2 (20)	8 (1.8)	120	7	71.6
10	2 (20)	8 (1.8)	110	8	73.6
11	4 (40)	8 (1.8)	110	7	63.1
12	4 (40)	8 (1.8)	110	24	74.2

Reaction conditions : Catalyst : $\text{H}_3\text{PW}_{12}\text{O}_{40} \cdot 30\text{H}_2\text{O}$.

Table 3 Results of reaction without 1,4-DO

Run	Catalyst	Catalyst Weight g (wt%)	Solvent	Solvent Weight g	Bath Temp. °C	Time h	GC area% Main-product
13	$\text{H}_3\text{PW}_{12}\text{O}_{40} \cdot 30\text{H}_2\text{O}$	0.6 (40)	$\text{CH}_3\text{OC}_2\text{H}_4\text{OCH}_3$	4.5	100	24	0
14	$\text{H}_3\text{PW}_{12}\text{O}_{40} \cdot 30\text{H}_2\text{O}$	0.6 (40)	CH_3CN	4.5	100	24	0
15	$\text{H}_3\text{PW}_{12}\text{O}_{40} \cdot 30\text{H}_2\text{O}$	0.6 (40)	$\text{CH}_3\text{CO}_2\text{C}_2\text{H}_5$	4.5	100	24	0
16	95% H_2SO_4	4 (240)	H_2O	11	120	7	0
17	H_2WO_4	0.3 (20)	1,3-dioxane	17	100	15	0
18	$\text{H}_3\text{PW}_{12}\text{O}_{40} \cdot 30\text{H}_2\text{O}$	0.3 (20)	1,3-dioxane	6	100	24	0
19	$\text{CH}_3\text{C}_6\text{H}_4\text{SO}_3\text{H} \cdot \text{H}_2\text{O}$	0.8 (50)	1,3-dioxane	6	100	24	0

conditions are summarized. All the reactions without 1,4-DO hardly afford product BNA. Interestingly, even with 1,3-dioxane no products detected and NA as a starting material was completely recovered. Thus, it seems that this novel reaction contains an acid-catalysed cleavage step of 1,4-DO by so called "super strong acidity" of the heteropolyacids.

In summary, the present work demonstrates that 1,2-bis(4'-oxa-3',5'-dioxatricyclo[4.3.0.1^{2,5}]decane-8'-yloxy)ethane (BNA), which has a flexible dioxy ethane bridging moiety of NA dimer and is a candidate for a monomeric starting material of the soluble polyimide, can be easily obtained from 5-norbornene-2,3-dicarboxylic anhydride (NA) and 1,4-dioxane (1,4-DO) via a solid acid catalysis of the heteropolyacids such as $\text{H}_3\text{PW}_{12}\text{O}_{40} \cdot 30\text{H}_2\text{O}$ and $\text{H}_4\text{SiW}_{12}\text{O}_{40} \cdot 30\text{H}_2\text{O}$. This reaction would contain an acid-catalyzed cleavage step of 1,4-DO, but details of the reaction mechanism and the reason of inactivity of 1,3-DO are not clear at present.

4. Conclusion

A novel aliphatic carbonyl compound 1,2-bis(4'-oxa-3',5'-dioxatricyclo[4.3.0.1^{2,5}]decane-8'-yloxy)ethane (BNA) can be easily obtained in satisfactory yields (~90%). The activity of $\text{H}_3\text{PW}_{12}\text{O}_{40} \cdot 30\text{H}_2\text{O}$ is almost same to that of $\text{H}_4\text{SiW}_{12}\text{O}_{40} \cdot 30\text{H}_2\text{O}$. Therefore, other heteropolyacids such as $\text{H}_3\text{PMo}_{12}\text{O}_{40} \cdot 30\text{H}_2\text{O}$ seem to show the similar activity.

Further work is now under way to separate and characterize the four stereoisomers of BNA as well as to construct the novel

soluble polyimide resins having unique flexible aliphatic moieties.

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