A Novel Synthetic Route to Synthesize 2,4,8,10-Tetraoxaspiro[5.5]-Undecane from Formaldehyde under Hydrothermal Conditions

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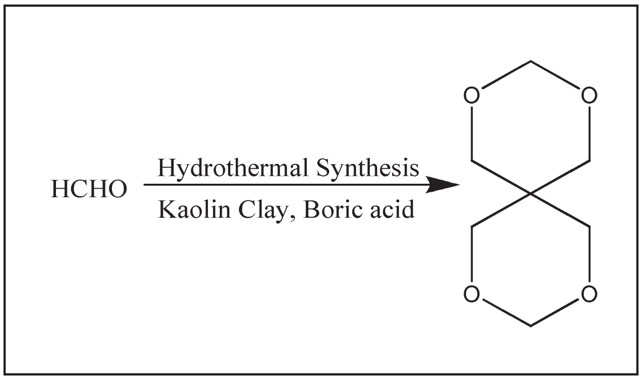

We report here the hydrothermal synthesis of 2,4,8,10-tetraoxaspiro[5.5]-undecane by using formaldehyde, the only precursor, in the presence of kaolin clay and boric acid. The reported method is the simplest one to synthesize the aforementioned product.

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INTRODUCTION

The spectacular nature of the hydrothermal systems provides a great deal of new synthetic routes in innovative, unconventional, as well as safest ways. This is exemplified by a number of novel synthetic discoveries in the realm of hydrothermal synthesis [1,2]. Also, a novel method for the translation of sodium hydrogen carbonate into phenol depicts that hydrothermal reaction routes have diverse applications [2]. Not only this but the hydrothermal synthesis also provides intriguing clues to the origin of life [1,3]. Furthermore, such kind of synthetic routes occupy a special place because of their pollution free nature. Also, the reactions take place safely within closed systems and do not need expensive materials as used in normal organic synthesis. Here, we present a simplest route to synthesize 2,4,8,10-tetraoxaspiro[5.5]-undecane (**1**) under the simplest hydrothermal conditions and demonstrate the versatility of the hydrothermal techniques.

Compound **1** is a very important synthetic precursor of many organic compounds. It has multifarious applications, from simple organic synthesis to medicines. One derivative, like 3,9-bis(2-hydrazidoethyl)-**1**, is used as a curing agent to produce a sufficient amount of cured epoxy resin [4]. Many derivatives of **1** are used as stabilizers for polyolefins and other polymers [5]. Similarly the binary blends of the acrylate rubber and chlorinated polypropylene give dynamic mechanical properties with 3,9-bis[1,1-dimethyl-2{β-(3-*tert*-butyl-4-hydroxy-5-methylphenyl)-propionyloxy}ethyl]-1 [6] and 3,9-di-2-furyl-1 type compounds serve as important intermediates in the synthesis of pesticides [7]. Moreover, its derivatives serve as prominent parts of many patents, *i.e.*, 3,9-bis[2-{3-(3-*tert*-butyl-4-hydroxy-5-methylphenyl) propionyloxy}-1,1-dimethylethyl]-1 is used in the synthesis of high quality antioxidants for many polymers [8,9], 3,9-bis [1,1-dimethyl-2-{β-(3-*tert*-butyl-4-hydroxy-5-methylphenyl)propionyl-oxy}ethyl]-1 serves as an oxidant in the synthesis of molding materials with excellent properties [10], while its many derivatives serve as essential components to bestow excellent chemical makeup for decorating ceramics [11]. Its derivatives enjoy a special place in the field of medicine and surgery, *e.g.*, -1-3,9-dipropamine(11′) is used in the synthesis of anti-inflammatory drug derivatives like pyrimidine and bispyrimidine [12] derivatives, 3,9-diethylidene-1 has potential applications in dental surgery [13], 3,9-dimethylene-1, is used in the synthesis of biodegradable polymers for the controlled release of paracetamol [14]. 1 has been synthesized in many ways, but the most remarkable synthetic routes are achieved by the transacetalization of triols [15]. Here, we report the hydrothermal synthesis of **1** by using formaldehyde as the only starting reagent, by using a mixture of boric acid and kaolin as catalyst, hence it presents the simplest route to synthesize the intended product.

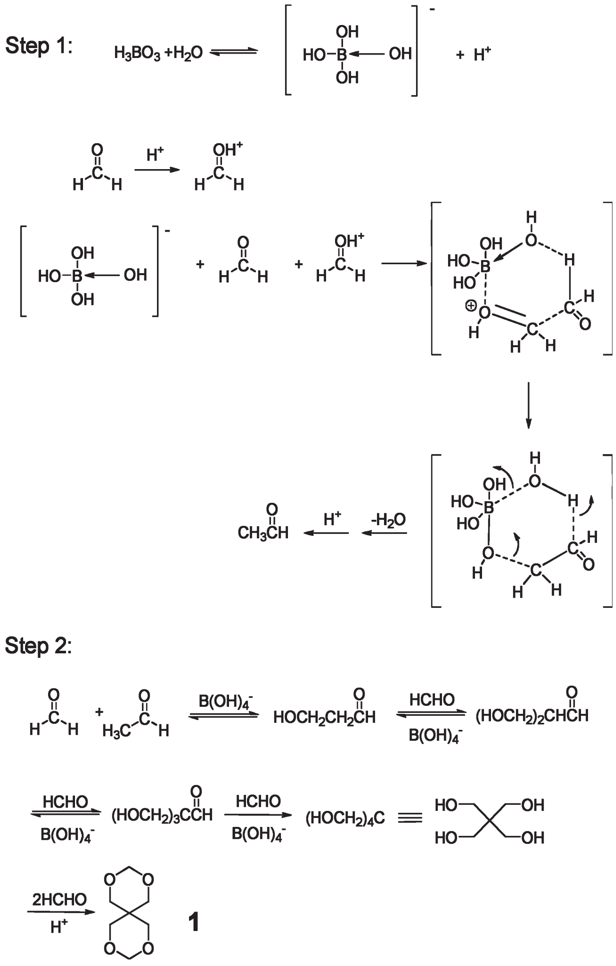
RESULTS AND DISCUSSION

Compound **1** was successfully synthesized. The yield of the reaction was 0.4%. The proposed mechanism for the reaction is described in the Scheme 1.

In the first step (Step 1) of Scheme 1, boric acid hydrolyzes and reacts with formaldehyde which results in the protonation of formaldehyde and another molecule of formaldehyde to form acetaldehyde through a cyclic transition state. In the second step (Step2), this acetaldehyde molecule further undergoes a series of mechanistic steps, to form the product.

Many parameters influence this reaction pathway, *i.e.*, temperature, pH, presence of catalysts. We have found that with any change in anyone of the above described parameters, the reaction fails to occur. Moreover, all of these parameters facilitate the synthesis of **1**. We were interested to know the effect of temperature on our pathway. Hence, we performed the reaction below 100°C. Most interestingly, we found that temperature window of 80–90°C gives a series of small open chained oxygenated products like carbon dioxide, formic acid *etc*. Also, temperature exceeding 100°C, causes degradation and decomposition of the product, implying that the above described method to synthesize **1** is only feasible at 100°C. The presence of catalyst mixture (boric acid and kaolin) is also essential, which is mainly responsible for the condensation, cyclization and stabilization of the formaldehyde units. Similarly, the reaction time and pH are also critical factors for the reaction.

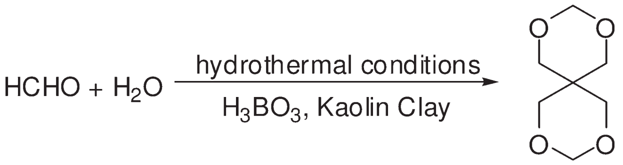
Scheme 1. Mechanism of reaction.



EXPERIMENTAL

In our synthesis, 2 mL formaldehyde and 12 mL doubly distilled water [16] were added into each steel alloy (Fe-Cr-Ni, alloy GB1220-92) autoclaves with a filling capacity of 90% and recrystallized boric acid and kaolin clay (0.1 g each) were also added into the reaction mixture of each of the autoclaves. The final pH of the reaction mixture was nearly 3. The autoclaves were then sealed tightly and placed in the ovens at a temperature range from 100–200°C for 3 days. However, the reaction was successful at 100°C. After 3 days the autoclaves were taken out and analyzed.

The reaction can be written as follows:



CHARACTERIZATION BY GC-MS

The product was identified and characterized by the GC-MS (Thermo Co.). Figure 1 shows the GC-MS of product as well as that of standard.

CONCLUSIONS

As discussed above, in our synthesis, the presence of boric acid and kaolin was essential. Our experiment clearly proves that hydrothermal synthesis provides unique reaction pathways, which in other ways are very difficult to obtain [1,2]. Moreover, in similar ways, many other polymerization reactions can be obtained by utilizing simple precursors [2]. Also, we synthesized our product without using any harmful or expensive reagent.

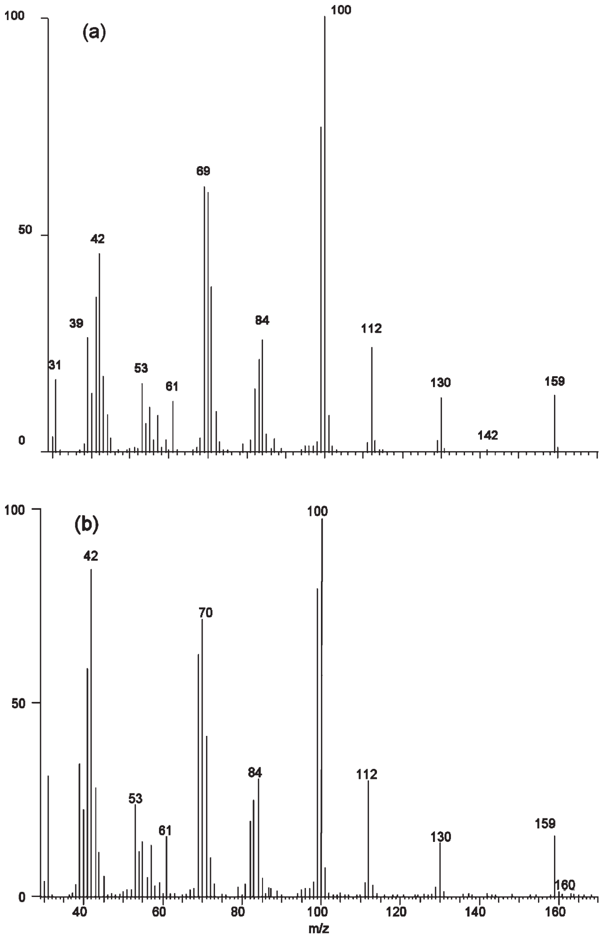


Figure 1. (a) Shows the GCMS of the standard (b) shows the GCMS of the product.

As we know that the progress of today's society depends on the synthesis and development of the advanced materials, which need consumption of energy as well as utilization of very toxic solvents and other chemicals. This all can play havoc with the environment and life. In addition, it is well known that our earth is a closed system with limited resources for use. This provokes an urge of recycling the materials in safest ways, *i.e.*, to ensure maximum recycling at the expense of minimum energy.

Finally, our synthetic route to synthesize 1 clearly proves that hydrothermal routes of synthesis enjoy an important position in the field of synthetic chemistry and a very likely candidate for recycling of waste and conversion of industrial waste (like formaldehyde, carbon monoxide, carbon dioxide, *etc.*) into useful products and the most likely candidate to promote ''Green Chemistry''.

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