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One-step construction of saturated six-membered rings directly using calcium carbide as an acetylene source: synthesis of 1,3,5-triaroylcyclohexanes

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ABSTRACT

Saturated six-membered rings were constructed directly using calcium carbide as an acetylene source by one-step procedure, and functionalized cyclohexanes, 1,3,5-triaroylcyclohexanes, were efficiently synthesized by reactions of calcium carbide with aromatic or heteroaromatic aldehydes in high yield. This protocol has the advantages of using inexpensive and renewable resource, no flammable and explosive gas and no transition-metal catalysts.

1. Introduction

Calcium carbide as an important industrial raw material has been used for a long time. The general method for the use of calcium carbide in chemical industry is to convert it into acetylene gas first by reaction with water. Then acetylene gas is used to further produce various organic chemicals. However, acetylene as a flammable and explosive gas is not easily handled in a standard laboratory setup for corresponding reactions. The risk of explosion and technical difficulties drastically complicate the equipment and greatly increase the cost. Therefore, the exploration of the reactions directly using calcium carbide is very necessary. Recently, Liu and co-workers reported that calcium carbide could be prepared by fine biochars as feed using autothermal process at a temperature about 500 °C lower than that of the current electric arc process. And furthermore, the corresponding reaction time was also reduced from 1 to 2 h to less than 5 min. The low production costs of this new method have put calcium carbide in a better position to serve as a sustainable resource for the chemical industry.[1] In fact, calcium carbide as a solid has low solubility in organic solvents and poor reactivity with other substances except water. Therefore, only a few examples on the use of calcium carbide for synthetic purposes, such as bis-stannylacetylenes,[2] diarylethynes,[3] 1-aryl-1,2,3-triazoles,[4] propargyl alcohols,[5] enaminones,[6] vinyl thioethers,[7] aryl pyrroles,[8] and poly(*p*-phenyleneethynylene)s,[9] have been described.

In addition, saturated six-membered ring compounds, such as the simplest cyclohexane, are of importance in chemical industry. The traditional synthetic route to cyclohexane includes the hydrolysis of calcium carbide to acetylene gas, cyclotrimerization of acetylene to benzene,[10] and hydrogenation of benzene to cyclohexane (Scheme 1).[11] However, some drawbacks exist for this pathway, such as multiple steps, high temperature, high pressure, use of transition-metal catalysts, and use of flammable and explosive gas (acetylene and hydrogen).

Functionalized saturated six-membered rings, for example, tribenzoylcyclohexane, are important intermediates for organic synthesis, which only synthesized by Möhrle and co-workers through the reactions of 1-phenyl-2-propyne-1-ol or vinylketone derivatives with pyrrolidin-2-one using sodium hydride as a base in dimethylsulfoxide media.[12] However, these methods using commercially unavailable substrates, which have to synthesize by multiple steps under rigorous conditions prior to use.

Here, we report a novel route for the one-step construction of functionalized saturated six-membered rings, 1,3,5-triaroylcyclo hexanes, directly using calcium carbide as an acetylene source under gas-free, transition metal-free, low temperature, low pressure and open air conditions (Scheme 2).

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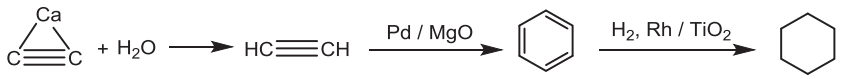
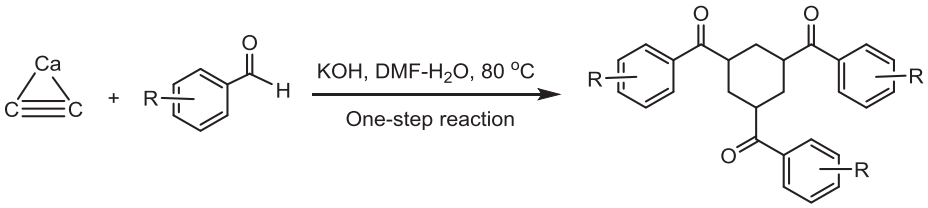


Scheme 1. Traditional route to prepare saturated six-membered ring.



Scheme 2. The one-step route to prepare functionalized saturated six-membered rings.

2. Results and discussion

In order to investigate the applications of directly using calcium carbide as a starting material in organic synthesis, the reaction between calcium carbide and benzaldehyde was selected as a model reaction. In previous literature, Seidel and co-workers reported that the reaction between calcium carbide and benzaldehyde assisted by tetrabutylammonium fluoride could give propargyl alcohol in very low yield (32%).[5a] Zhang et al. also reported that no propargyl alcohol was observed by the reaction of calcium carbide and benzaldehyde in the presence of cesium carbonate as a base.[5b] Our work still focused on the reaction of calcium carbide and benzaldehyde and expected to prepare propargyl alcohol in high yield. Surprisingly, an unexpected product, 1,3,5-tribenzoylcyclohexane (**2a**), was isolated during the reaction of calcium carbide and benzaldehyde at 80 °C using potassium hydroxide as a base in *N,N*-dimethylformamide and trace water media (Scheme 2, R=H). This result indicated that a tandem reaction undergoing an addition, tautomerization, and cyclotrimerization process was taken place (see the rear mechanism). The structure of **2a** was confirmed by ^{1}H NMR, ^{13}C NMR, and MS (see the Supplementary data). The further structure confirmation of **2a** was also conducted by single crystal X-ray diffraction (Fig. 1, see the Supplementary data). Fig. 1 shows that the stereochemistry of **2a** is the six-membered ring of cyclohexane in a chair conformation, and three substituents, benzoyls, in a *cis* structure on the ring. The conformational structure of **2a** is also expressed in Fig. 2.

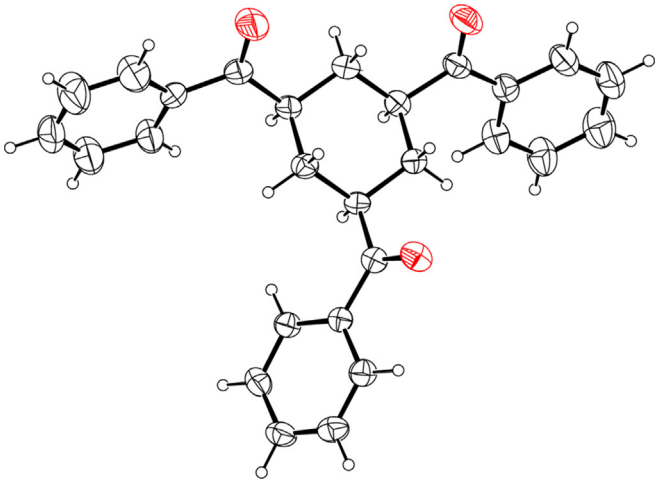


Fig. 1. X-ray crystal structure of **2a**.

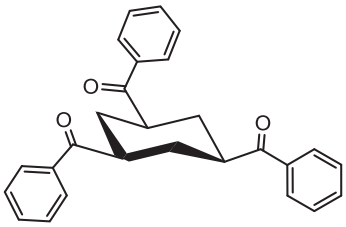


Fig. 2. Conformational structure of **2a**.

In order to optimize the reaction conditions, the model reaction was conducted under various conditions. It is noteworthy to mention that sometimes another coproduct, 1,2,4-tribenzoylcyclohxane (**3a**), was also isolated from the reaction system in addition to **2a**. Among the various conditions, the selection for the solvents was quite important. No any products were observed in dimethylsulfoxide, 1,4-dioxane, chloroform, ethanol and isopropanol. Meanwhile the reaction in acetonitrile, toluene and *tert*-butanol gave **2a** in trace amount (Table 1, entries 1–3). However, *N,N*-dimethylformamide was found to be an efficient solvent for the reaction to give **2a** as a major product and **3a** as a minor product (Table 1, entries 4–15). The bases were indispensable for the reaction. Some organic bases, such as 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU), 4-dimethylaminopyridine (DMAP) and triethylamine (Et_3N), and some inorganic bases, such as sodium carbonate and potassium carbonate, were found to be no effect on the reaction. The reaction using cesium fluoride and cesium carbonate as bases could give **2a** and **3a** in low yield (Table 1, entries 5–6). However, potassium hydroxide, sodium hydroxide and potassium *tert*-butoxide were efficient bases for the reaction (Table 1, entries 4, 7–8). Among them, potassium hydroxide was the best base for the reaction (Table 1, entry 4). In addition, the reaction was completed at the optimal temperature of 80 °C (Table 1, entry 4). The increase of temperature had no obvious improvement of the yield (Table 1, entries 9–10). In contrast, the drop of temperature resulted in the decrease of yield (Table 1, entries 11–13). The amount of base had a certain effect on the yield. The use of more than 1.5 equiv of potassium hydroxide exhibited no significant increase of the yield (Table 1, entry 14), but the use of less amount of potassium hydroxide could lead to reduce of the yield (Table 1, entry 15).

With the optimized reaction conditions in hand, the scope and limitation of the reaction were examined (Table 2). It was found that the reactions of calcium carbide with various aromatic aldehydes could afford the corresponding products, 1,3,5-triaroylcyclohexanes (**2a**–**p**), in high yield at 80 °C using potassium hydroxide as a base in *N,N*-dimethylformamide and trace water media. Due to the quite low yield, the minor coproducts,