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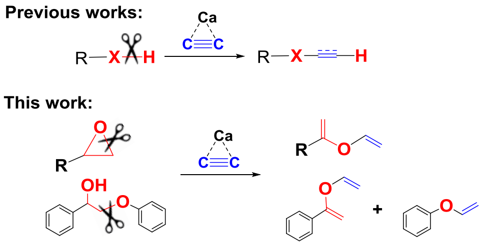
Vinylation of Aryl Ether (Lignin β-O-4 Linkage) and Epoxides with Calcium Carbide *via* C-O Bond Cleavage **

*Siew Ping Teong, Jenny Lim and Yugen Zhang**

Abstract: *Calcium carbide has been increasingly used as a sustainable, easy-to-handle, and low-cost feedstock in organic synthesis. Currently, methodologies of using calcium carbide as "solid acetylene" in synthesis are strictly limited to activation and reaction with X-H (X = C, N, O, S) bonds. Herein, a mild and transition metal-free protocol was developed for the vinylation of epoxides and aryl ether linkage (β-O-4 lignin model compound) with calcium carbide via C-O bond cleavage, forming valuable vinyl ether products. CaC_2 plays a vital role in the C-O bond activation and cleavage, and in providing acetylide source for the formation of vinylated products. These exciting results may provide new methodologies for organic synthesis and new insights towards lignin or biomass-related degradation to useful products.*

Lignin is the world's second most abundant renewable polymer besides cellulose. Due to its aromatic-rich units, depolymerization of the renewable lignin to high value-added aromatic monomers is particularly attractive in sustainable chemistry.[1] However, the complexity of the lignin structure also makes selective depolymerization into small aromatic fragments challenging.[1-4] Therefore, most of the efforts have been devoted to using model compounds to mimic the representative linkages in lignin which will help to further understand the bond cleavage mechanism.[5] β-O-4 linkage with aryl ether unit is the most abundant and stable substructure in lignin. Various methodologies have been developed for the cleavage of β-O-4 linkage which include base[6] or acid[7] mediated cleavage, oxidative cleavage[8] and reductive cleavage[9] and others.[10] These methods either require harsh conditions and expensive reagents or suffer from low selectivity.

In recent years, the attractive calcium carbide has been increasingly used as a sustainable, easy-to-handle, and low-cost feedstock in organic synthesis.[11-12] Although many excellent synthetic methodologies have been developed by using calcium carbide as the acetylene/acetylide source, the substrate scopes are still strictly limited to activation and reaction with X-H (X = C, N, O, S) bonds. As part of our group's effort[12] in exploring calcium carbide utilization in organic synthesis, we then questioned if it can be used as the acetylide source to activate the much stable C-O bond (Scheme 1). Therefore, CaC_2-mediated ring opening of strained epoxides for further chemical transformation was investigated. Herein, a mild and transition-metal free system with calcium carbide was demonstrated to yield highly value-added vinyl ethers[13-14] from epoxides and lignin β-O-4 linkage model compounds via C-O bond cleavage.



Scheme 1. Methodologies for using calcium carbide as acetylid source in organic synthesis.

We previously reported the formation of vinyl ethers fro alcohols with calcium carbide under the Cs_2CO_3/DMSO system.[1 While employing this superbasic system on the styrene oxide 100 °C for 16 h, vinylated product **3a** was isolated via ring openin under this mild condition (Scheme 2). Various conditions wer screened using styrene oxide as the model substrate (Table S1-2 Additives such as KBr, TBAB and 18-crown-6 were added in a attempt to improve the efficiency but to no avail (Table S2, entry 3 5). Similar to alcohol vinylation,[15] small amount of water additiv is important to this ring opening and vinylation reaction (Figure S1 Optimized product yield and selectivity of 85% was obtained wit calcium carbide (2.5 equiv.) in DMSO in the presence of Cs_2C (0.5 equiv.) at 100 °C for 16 h when 6 vol% of water was added int the reaction system. A control reaction was carried out unde anhydrous conditions where no desired product was observed afte the reaction.

Interesting phenomena were observed from these results, albei the limited success of expanding the substrate scope (Scheme 2 The majority of the substrates (**1a – 1e, 1h**) gave a similar vinylox product whereas substrate **1f** formed a di-vinyloxy product. Initiall a diol intermediate reaction pathway was proposed (Scheme 3b(I) This mechanism is supported by a control reaction where 72% of **3** was obtained when 1-phenyl-1,2-ethanediol (**1i**) was used as th substrate under similar conditions (Scheme 2, Table S3). It wa hypothesized that the small amount of water in the system may hav led to ring opening of epoxide to diol, followed by rapid vinylatio of the *in-situ* generated diol and β-elimination to form the en product (Scheme 3b(I)). However, efforts to track the di intermediate from the reaction of **1a** were not successful. Whe substrate **1a** was carried out at a shorter time, no diol intermediat was observed. In fact, the control reaction of **1a** without calciu carbide gave only trace amount of diol product (**1i**), leaving most the starting material unreacted. In addition, 1-phenyl-1,2-ethanedi (**1i**) is inert under the above conditions (without CaC_2) (Scheme 3a). These results indicate that the superbasic system may be not favourable for the hydrolysis reaction of **1a** and β-elimination of **1i**. Calcium carbide plays an important part in facilitating epoxide ring-opening. With that, a plausible mechanism was proposed as shown in Scheme 3b(II). Firstly, acetylide interacts with epoxide and activates the C-O bond.[11c] Ring opening then occurs along with the new C-O bond formation to give vinyloxyl intermediate (**A**). Following with this, transferring of α-carbon proton to vinyl anion and subsequent vinylation gave the final product α-vinyloxy styrene. For cyclohexene oxide **1f**, however, diol intermediate was observed in the absence of CaC_2, suggesting that it could undergo the diol pathway shown in Scheme S1.

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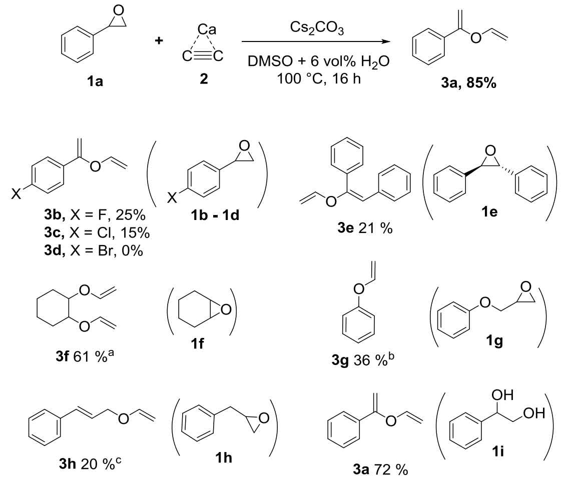
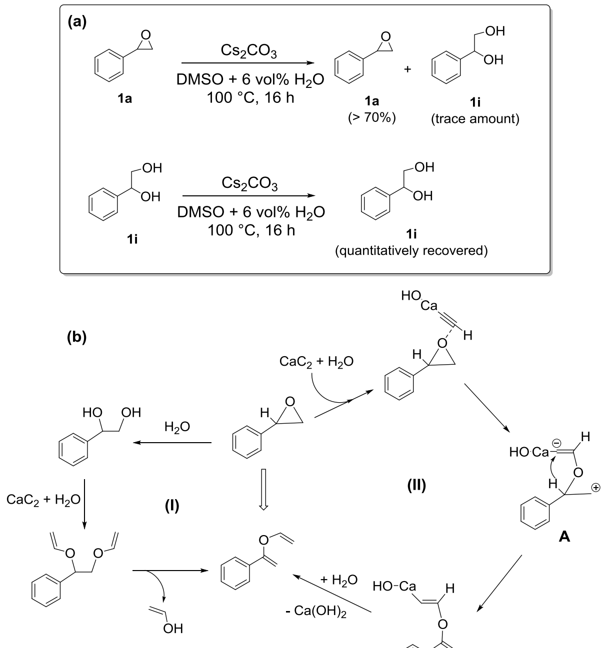


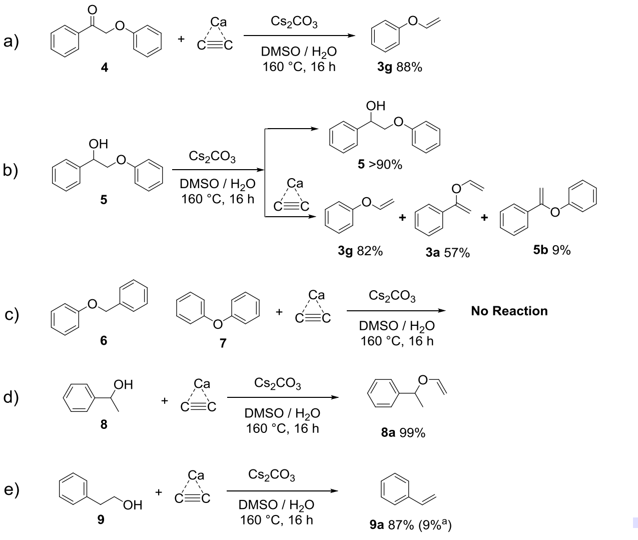
Epoxide (1 mmol), CaC_2 (2.5 mmol), DMSO + 6 vol% H_2O (5 mL), Cs_2CO_3 (0.5 mmol), 100 °C, 16 h. NMR yield. [a] CaC_2 (5 mmol), 5 vol% H_2O, 140 °C. [b] CaC_2 (4 mmol), 4 vol% H_2O, 140 °C. [c] CaC_2 (4 mmol), 6 vol% H_2O.

Scheme 2. Vinylation of epoxides using calcium carbide



Scheme 3. (a) Control reactions in the system without CaC_2. (b) Proposed mechanism for vinylation of epoxides.

Unexpectedly, (vinyloxy)benzene was obtained from substrate **1g,** which may be due to cleavage of aryl-ether C-O bond. This led us to further explore the possibility of this methodology for lignin which consists of abundant *β*-O-4 aryl-ether linkages for cleavage. Promising results were shown in Scheme 4. Initial screenings with lignin model compound **4** representing the oxidized *β*-O-4 linkage showed that C-O bond cleavage occurred with 88% of (vinyloxy)benzene **(3g)** after optimization (Scheme 4a). It was noted that the other half of the cleavage product from **4** could be acetophenone which is not stable under the given conditions. This was confirmed by a control reaction using acetophenone as the starting material where full conversion of acetophenone was observed, but attempts to characterize these unknowns were unsuccessful. Addition of metal catalysts was not compatible with the CaC_2 superbase system (Table S4, entries 4 - 7). The cleavage of *β*-O-4 linkages in lignin often suggests a radical pathway,[16] however, the addition of radical initiator did not help to further improve the yield (Table S4, entries 9 - 12). For lignin model compound **5**, 82% of **3g** was obtained. (1-(vinyloxy)vinyl)benzene **(3a)** was characterized to be the second half of the cleavage product in 57% yield under the optimized condition (Scheme 4b). In addition to the product **3a** and **3g**, about 9% of by-product **5b** was also isolated. When different linkages of lignin model compounds **6** (*α*-O-4) and **7** (*α*-O-5) were tested in this system, starting materials were quantitatively recovered, even after extending the reaction time to a week (Scheme 4c). Simple alcohols were used as substrates under similar conditions that represent the *α*-O and *β*-O linkages (Scheme 4d – e). It was found that generally, *α*-O alcohols underwent *O*-vinylation instead of elimination and vice versa. Similar to the epoxide reactions, addition of CaC_2 is vital. In the absence of CaC_2, no reaction happened and more than 90% of mode compound **5** or **9** was recovered from the reaction system whic exclude the posibility of base catalyzed cleavage of *β*-O-4 ethe bond via an epoxide intermediate.[17]



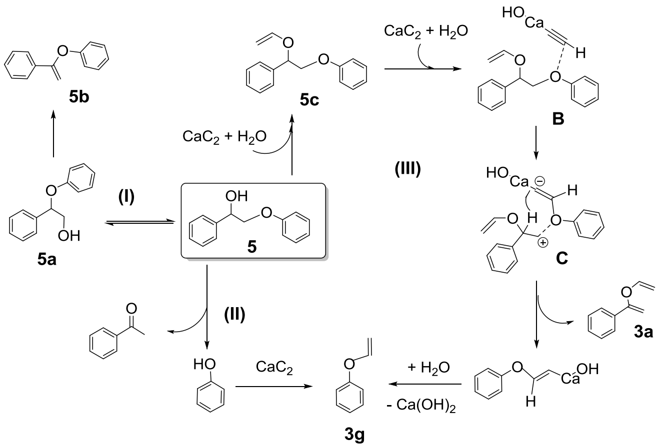
Conditions: Substrate (1 mmol), CaC_2 (4 mmol), DMSO + 9 vol% H_2O (5 mL), Cs_2CO_3 (0.5 mmol), 160 °C, 16 h. NMR yield. [a] without CaC_2, **9** was recovered in 90%.

Scheme 4. Reaction of lignin model compounds with/withou calcium carbide.

Delighted by this mild, selective and transition metal-free direc vinylation method to cleave the aryl-ether linkages and convert t valuable vinyl ethers in a simple process, we then went on t conduct kinetic studies with model compound **5**. According t Figure S2, all 3 products increased sharply in first 2 h and the remained relatively constant as time continued to extend to 24 h Maximum yields for **3g** and **3a** are of 88% and 57%, respectively At the beginning of the reaction, trace amount of acetophenone an phenol was detected. When the reaction was carried out in th absence of CaC_2, approximately 90% of the starting material wa found, alongside with trace amount of **5b** and the isomerizatio product **5a** (Scheme 5). Based on these results, a proposed reactio pathway is shown in Scheme 5.

It was postulated that isomerization of lignin model compound **5** could have taken place to form **5a**, followed by elimination which gave product **5b**. This side reaction (pathway (**I**) in scheme 5) is slow as only small amount of intermediate **5a** and by-product **5b** (< 10%) was observed in the systems with or without calcium carbide. The initial detection of acetophenone and phenol in GCMS analysis could have occurred from direct *β*-elimination of **5**, followed by vinylation to form **3g** (pathway (**II**)).[11c, 15] *O*-vinylation of **5** could have taken place as a fast and dominant reaction in the system to give **5c** intermediate which was experimentally observed in GCMS during the reaction process.

Similar to the epoxide reactions, it was assumed that **5c** was then activated by acetylide and went through intermediate **C** (C-O cleavage and hydrogen transfer) to give **3a** and **3g**. It is clear that pathway (III) is the fast and dominant reaction, while pathway (**I**) and (**II**) coexist in the system as complimentary reaction paths.



Scheme 5. Proposed pathway for the cleavage and vinylation of lignin model compound.

In summary, we have developed a mild and transition metal-free protocol for the vinylation of epoxides and aryl-ether linkage (*β*-O-4 lignin model compound) via C-O bond cleavage, forming valuable vinyl ether products. CaC_2 plays a vital role in the C-O bond activation and cleavage, and in providing acetylide source for the formation of vinylated products. These thrilling results may provide new methodology for organic synthesis and new insights towards lignin or biomass-related degradation to useful products.

Experimental Section

General procedure for vinylation of epoxides: In a 8 mL pressure vial, Cs_2CO_3 (0.5 mmol) and CaC_2 (2.5 mmol) were added. The vial was then purged and refilled with argon thrice before DMSO + 6 vol% H_2O (5 mL) and epoxide (1 mmol) were added to the vial using a syringe. The reaction was stirred at 100 °C for 16 h, cooled to room temperature before it was diluted with H_2O (10 mL) and extracted with diethyl ether (3 x 10 mL). The combined organic layer was dried over anhydrous Na_2SO_4 and concentrated *in vacuo*. The residue was further purified by column chromatography on silica gel to afford the corresponding vinyl ethers.

General procedure for vinylation of lignin model compounds: In a 8 mL pressure vial, substrate (1 mmol), Cs_2CO_3 (0.5 mmol) and CaC_2 (4.0 mmol) were added. The vial was then purged and refilled with argon thrice before DMSO + 9 vol% H_2O (5 mL) was added to the vial using a syringe. The reaction was stirred at 160 °C for 16 h, cooled to room temperature before it was diluted with H_2O (10 mL) and extracted with diethyl ether (3 x 10 mL). The combined layer was dried over anhydrous Na_2SO_4 and concentrated *in vacuo*. The residue was further purified by column chromatography on silica gel to afford the corresponding vinyl ethers.

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Siew Ping Teong, Jenny Lim and Yugen Zhang*

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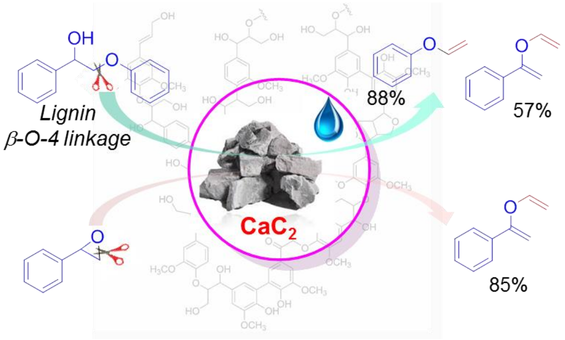
Vinylation of Aryl Ether (Lignin β-O-4 Linkage) and Epoxides with Calcium Carbide *via* C-O Bond Cleavage



A mild and transition metal-free protocol for the vinylation of epoxides and aryl ether linkage (β-O-4 lignin model compound) with calcium carbide via C-O bond cleavage, forming valuable vinyl ether products.

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