



Synthesis of α -pyrones by catalytic oxidative coupling of terminal alkynes and carbon dioxide



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ABSTRACT

The use of the complex $[(\text{dippe})\text{Ni}(\mu\text{-H})_2]$ (**1**) as a catalyst precursor (10 mol%) in the presence of a variety of terminal alkynes and CO_2 allowed the production of substituted α -pyrones. This reaction occurs using relatively mild conditions (50 °C, 150 psi of CO_2) with good to modest yields, depending on the nature of the substituents in the corresponding alkyne. The produced α -pyrones were characterized by different analytical methods and spectroscopic techniques.

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1. Introduction

The increasing amount of atmospheric CO_2 from anthropogenic sources is a concerning issue of global proportions [1]; therefore, transforming this pollutant gas into useful products, such as fuels [2] and co-polymers [3], among many others, is still a pending task. There are several chemical strategies to use CO_2 as a building block toward more complex materials, e.g., the partial hydrogenation to yield formates [4], the reduction to CO for further use in a variety of processes [5], and the incorporation of CO_2 into alkenes, dienes, allenes, and alkynes [6].

The insertion reaction of CO_2 into M-C bonds has been reported, and Allen and co-workers have documented some relevant examples for Ru [7] and Fe [8]; in these cases, the single or double insertion of CO_2 gives acetates, depending on the pressure of CO_2 used.

The oxidative coupling of alkenes with CO_2 mediated by nickel to yield carboxylic acids, via the formation of nickela-lactone intermediates followed by hydrolysis, was reported by Hoberg and co-workers [9]. A closely related process is the sodium acrylate

synthesis, reported by Limbach and co-workers, using ethylene and CO_2 catalyzed by Ni(0) [10], later improved on by other groups [11]. Similarly, dienes have also been used to produce corresponding α -pyrones with CO_2 catalyzed by palladium [12].

Regarding the coupling of alkynes and CO_2 catalyzed by nickel, reports from 1977 by Inoue et al. indicate the use of $[\text{Ni}(\text{COD})_2]$ and bidentate aromatic phosphines to produce corresponding 2-pyrone or alkyne cyclotrimerization products [13]. Tsuda and co-workers reported on the co-polymerization of diynes with CO_2 catalyzed by $[\text{Ni}(\text{COD})_2]$ using monodentate alkyl phosphines to produce poly-(2-pyrones) [14] and, with a closely related method, bicyclic α -pyrones [15]. Also worthy to mention are the contributions from Walther [16] and Saegusa [17] using low-valent nickel complexes and alkyl-substituted alkynes to yield pyrones with low to moderate yields. Other relevant reports on that field include the use of nickel (0) catalysts and CO_2 along with organo-zinc compounds to produce acrylic acid derivatives [18], recently expanded to the hydrocarboxylation of alkynes using alcohols as proton sources [19] and the production of maleic acid by the double insertion of CO_2 using Zn powder and MgBr_2 [20].

In recent years, our group has been interested in a variety of methods for CO_2 activation and transformations catalyzed by nickel, including the characterization of intermediates in the reduction of CO_2 [21]; these methods includes catalytic

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applications in the hydroesterification of styrenes [22], hydrosilylation to yield formic acid and formates [23], and the production of aliphatic N-methylamines [24].

Here, we want to disclose our findings in the study of the oxidative coupling of a variety of substituted terminal alkynes with CO₂ (99.998%) to produce α -pyrones catalyzed by nickel with good to low yields, depending on the electronic donor/withdrawing characteristic of the substituents at the alkyne moiety.

2. Results and discussion

The optimized reaction conditions were established using phenylacetylene as a model substrate and [(dippe)Ni(μ -H)]₂ (**1**) as a catalyst precursor with variations of reaction time, solvent, catalyst load, temperature, and CO₂ pressure; thus, we found that the use of 69 h, toluene, 10 mol% of **1**, 50 °C, and 150 psi of CO₂ were the best reaction conditions to achieve a 100% conversion of the substrate, with the best selectivity towards the production of the corresponding α -pyrone (4,6-diphenyl-2-pyrone), as represented in Scheme 1.

The produced 4,6-diphenyl-2-pyrone was isolated from the reaction mixture by column chromatography and then fully characterized by a variety of analytical techniques, including ¹H, ¹³C{¹H}, COSY, and HETCOR; see SI section.

Considering that a 100% transformation of phenylacetylene was achieved under the reaction conditions (*vide supra*), the scope of the reaction was extended to closely related alkynes, some of which had electron donor or electron withdrawing substituents or small structural variations; the corresponding results are summarized in Table 1.

As seen in Table 1, the use of terminal phenyl-acetylenes with electron donor substituents in the *para* position (entry 2) of the benzenic ring produce a high conversion and selectivity (91%) towards the production of the corresponding 2-pyrone, compared to the unsubstituted phenyl alkyne (entry 1). A sharp contrast can be seen in entry 3 for the *p*-methoxyphenylalkyne, but this result was due to the low solubility of this alkyne in toluene; efforts to overcome that by using solvent mixtures of toluene/THF did not increase the conversion rate. The use of another electron donor substituent, such as an amino group in the *ortho* position, mostly favored the homocoupling products (96%) and the production of small amounts (2%) of indole as a product of internal cyclization.

Closely related structural variations, like adding a methylene between the triple bond and the phenyl ring, decreased the yield, probably due to increased system flexibility and a lack of conjugation. The use of an internal alkyne yielded a dramatic drop in reactivity (entry 6) to barely produce only 5% hydrogenation; thus, the use of internal alkynes was not further assessed.

The use of mono-fluorinated phenyl alkynes gave a complete conversion (entries 7–9), but with a low selectivity to the corresponding pyrone and an increasing preference for the

cyclotrimerization and homo-coupling products; this was probably due to the high electronegativity of the fluorine atom and the decreasing electronic density in the aromatic ring, compared to simple phenyl acetylene.

To further explore this behavior, we decided to assess the reactivity of trifluoromethyl-substituted phenylacetylenes (entries 10–12); similarly, we observed high conversion of the starting material but with a poor selectivity to the corresponding pyrones, along with an increased preference towards the production of homocoupling and cyclotrimerization products, i.e., products where CO₂ was not incorporated.

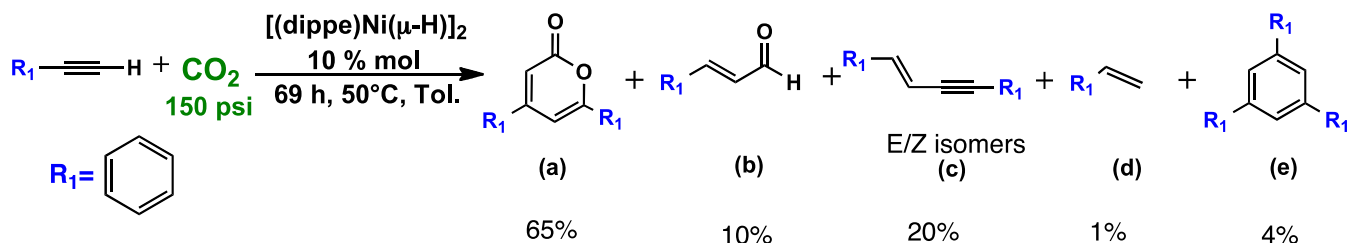
Inspired in the mechanistic reports in the literature [13] [25], and the current observations, a mechanistic proposal for the formation of α -pyrones is depicted in Scheme 2.

As represented in Scheme 2, we envisage the formation of the five-membered nickelacycle (**A**) where the incoming CO₂ can be inserted to yield the corresponding seven-membered metallalactone (**B**), and ultimately giving the corresponding pyrone by having electron-donating substituents at the aromatic ring in the alkyne; this favors a nucleophilic attack at the electrophilic carbon of the incoming CO₂. On the other hand, the cyclo trimerization pathway, which yields the seven-membered metallacycle (**C**) leading to the production of benzenic products, would be favored, with electron-withdrawing substituents at the aromatic ring in the alkyne by insertion of a third alkyne instead of CO₂. A similar scenario might be expected in the case of homo-coupling products; however, this would occur by a different mechanistic proposal, see SI section. Thus, the proposal for the formation of (**A**) as a key intermediate instead of a nickellactone proposed by Hoberg [26] is consistent with the electronic properties of the substituents in the aromatic ring, to produce (**B**) or (**C**) having (**A**) as a common intermediate. However, we do not discard at all the formation of the above-mentioned metallalactone.

The use of 1 mol% of additives, such as BEt₃ and NaBPh₄, did not increase the observed yields; only in the case of NaBPh₄ could the nickel catalyst load be reduced from 10 to 5 mol%, with a very similar product distribution. Last but not least, the cinnamaldehyde formation may be due to a competing reaction of reduction of CO₂ to yield CO, as previously reported by our group [21], along with the hemi-reduction of the corresponding alkyne, followed by CO insertion and reductive elimination.

3. Conclusions

The oxidative coupling of terminal aromatic alkynes with CO₂ catalyzed with nickel to yield α -pyrones (lactones) was achieved in good yields on electron-donating substituents in the aromatic ring. However, the substitution with electron-withdrawing substituents favors the production of cyclotrimerization and homocoupling products instead.



Scheme 1. Optimized reaction conditions with phenylacetylene.

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