



Contents lists available at ScienceDirect

Tetrahedron Letters

journal homepage: www.elsevier.com/locate/tetlet

Molybdenum hexacarbonyl: air stable catalyst for microwave assisted intermolecular [2+2+2] co-trimerization involving propargyl halides

Sambasivarao Kotha*, Gaddamedi Sreevani

Department of Chemistry, Indian Institute of Technology-Bombay, Powai, Mumbai 400076, India

ARTICLE INFO

Article history:

Received 10 July 2015

Revised 7 September 2015

Accepted 8 September 2015

Available online xxx

We would like to dedicate this paper to Prof. D. Basavaiah.

Keywords:

[2+2+2] co-trimerization

Propargyl halides

Mo(CO)₆

Microwave irradiation

Benzyl halides

1,6-Diynes

ABSTRACT

Intermolecular [2+2+2] cycloaddition of propargyl halides with 1,6-diynes was achieved with air stable, catalytic amount of Mo(CO)₆ and the benzyl halide derivatives were isolated in good yields. The reaction conditions were optimized and better yields were observed under microwave irradiation conditions using acetonitrile as a solvent.

© 2015 Elsevier Ltd. All rights reserved.

Transition-metal complexes have emerged as indispensable tools in synthetic organic chemistry where a large number of functional groups are tolerated. These compounds enable either difficult or unusual chemical transformations which are not possible by traditional methods. Cycloaddition reactions are powerful tools in synthetic organic chemistry because these reactions allow multiple bond formation exhibiting a high degree of selectivity. In this context, [2+2+2] cycloaddition is found to be an efficient protocol for assembling aromatic compounds which can act as functional materials. This protocol is an atom economic process leading to the formation of unsaturated six-membered, highly substituted carbo- and heterocycles such as benzenes, pyridines, pyridones, and 1,3 cyclohexadienes etc., in a single operation involving catalytic amounts of organometallic complexes of around 15 different transition metals such as Rh,¹ Ir,² Ni,³ Ru,⁴ Co,⁵ Pd,⁶ Nb,⁷ Fe⁸ etc., (Fig. 1).⁹

Reppe pioneered the transition metal-catalyzed trimerization reaction of acetylene in 1948,¹⁰ and later the [2+2+2] cycloaddition reaction has expanded in several directions and found diverse applications in organic synthesis.^{11,12} Now, these protocols reached to a high degree of sophistication where several complex natural prod-

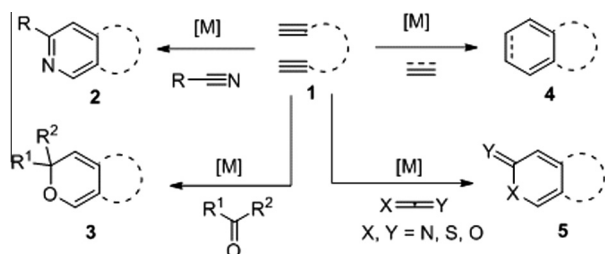
ucts and unnatural compounds have been synthesized easily by utilizing the [2+2+2] cycloaddition reaction as a key step.^{13–16} Although many reports are available related to the [2+2+2] cycloaddition reactions, only a limited number of examples are available where propargyl halides¹⁷ are used as co-trimerization partners.

Synthesis of the dibromo compounds such as **9** from 1,6-diynes has been demonstrated by the [2+2+2] cycloaddition reaction with the diol **7a** in the presence of Wilkinson's catalyst followed by bromination with PBr₃ (Scheme 1).¹⁸ This two step strategy could not be extended to sensitive substrates (e.g., peptides, ether linkage containing compounds) and the starting materials/products decompose during the bromination sequence. Hence, there is a pressing need to develop a new strategy where the halo derivatives such as **9** are assembled directly via a [2+2+2] cycloaddition reaction as a key step without the involvement of the bromination step (Scheme 1).

For this purpose, one of the alkyne partners must be a propargyl halide, however, the products formed will be the benzyl halides, which are good substrates in cross-coupling reactions. Moreover, realization of [2+2+2] sequence without the involvement of the diol intermediate amounts to the 'step economy'.¹⁹ In this context, Kudinov and co-workers attempted a [2+2+2] co-trimerization of 1,6-diynes with various alkyne partners in the presence of naphthalene cyclopentadienyl ruthenium complex and they were unsuccessful

* Corresponding author. Tel.: +91 22 2576 7160; fax: +91 22 2572 7152.

E-mail address: srk@chem.iitb.ac.in (S. Kotha).



[M] = [Co], [Ru], [Rh], [Ni], [Pd], [Ir], [Nb]...

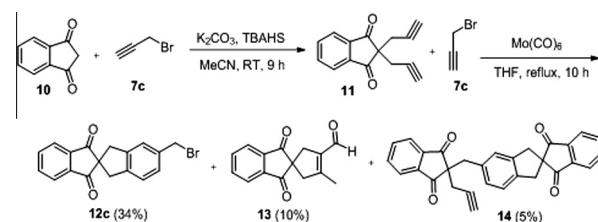
Figure 1. General representation of a [2+2+2] cycloaddition reaction.

when the alkyne partner was propargyl bromide **7c**.^{20a} A perusal of the literature indicated that Fujihara and co-workers have reported the synthesis and the catalytic activity of dinuclear niobium(III) complexes for the regioselective cyclotrimerization of alkynes. Here, they reported the synthesis of hexakis(chloromethyl)benzene by the [2+2+2] cyclotrimerization of 1,4-dichloro-2-butyne **7f** in the presence of a catalytic amount of dinuclear niobium(III) complex. This system tolerates the benzylic halides as the end products.^{17a} However, niobium(V) chloride is air as well as moisture sensitive and hence its handling is not a trivial exercise. Sugihara and co-workers observed that a [2+2+2] co-trimerization is feasible by using $\text{Mo}(\text{CO})_6$ and $\text{Cr}(\text{CO})_6$ complexes than that of the corresponding isonitrile complexes.^{20b} Mori and co-workers have also showed that the alkyne having an *o*-hydroxyphenyl group gave the trimerization product, rather than alkyne metathetic product under Mortreux catalytic conditions.^{20c}

To expand the utility of [2+2+2] cycloaddition strategy in organic synthesis, we examined the catalytic activity of Mo complexes in [2+2+2] cycloaddition reaction²¹ with propargyl halides. In this context we chose dipropargylated 1,3-indane dione **11** as a model substrate. The commercially available 1,3-indane dione **10** was treated with propargyl bromide in the presence of K_2CO_3 as a base under PTC conditions in MeCN at rt to generate the dipropargylated 1,3-indane dione **11**.^{12c,f} Later, the diyne **11** was subjected to a [2+2+2] cycloaddition sequence with propargyl bromide **7c** in the presence of catalytic amount of $\text{Mo}(\text{CO})_6$ under THF refluxing conditions for 10 h. The desired [2+2+2] cycloaddition product **12c** was obtained (34%) along with self dimerized product **14** (5%). We also observed the formation of α , β -unsaturated aldehyde **13** (10%) which was confirmed by ^1H , ^{13}C , DEPT-135 NMR, and mass spectrometric analysis (Scheme 2).

Since $\text{Mo}(\text{CO})_6$ is not a typical catalyst for [2+2+2] cycloaddition reactions as compared to other metal complexes, the mechanism might involve molybdenapentadiene, which would react with the alkyne partner to produce cyclotrimerized product.^{20c,21d}

When the propargyl alcohol or propargyl tosylate was subjected to a [2+2+2] co-trimerization with the diyne **11** in the presence of

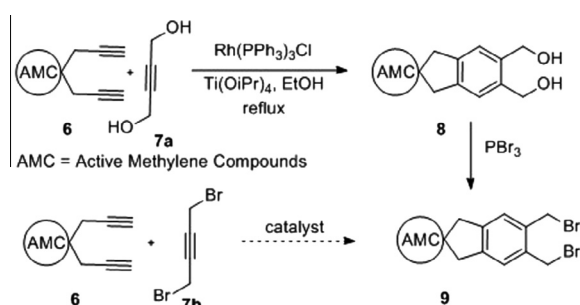


Scheme 2. [2+2+2] co-trimerization with propargyl bromide.

$\text{Mo}(\text{CO})_6$, they were unreactive and the starting material was recovered. However, when we used propargyl halides as co-trimerization partners, the yield was low. To improve the yields of co-trimerization products and to minimize the side products, the reaction was carried out under different conditions (Fig. 2, Table 1).

Based on Sugihara and co-workers report,^{20b} when we used $\text{Cr}(\text{CO})_6$ catalyst for [2+2+2] cyclotrimerization, the reaction did not happen and the starting material was recovered. In view of the literature report,^{20c} later we used the Mortreux catalytic system by adding phenol or *p*-Cl-phenol as an additive, however, no improvement in the yield of the products. We thought changing the ligands may improve the yields, hence, we prepared $\text{Mo}(\text{PPh}_3)_2\text{CO}_4$ and $\text{Mo}(\text{Py})_3(\text{CO})_3$ as reported in the literature²² and carried out the [2+2+2] co-trimerization with propargyl bromide. When the catalyst was $\text{Mo}(\text{Py})_3(\text{CO})_3$, the reaction did not proceed at all and the starting material was recovered. When the catalyst was $\text{Mo}(\text{PPh}_3)_2\text{CO}_4$, the reaction was incomplete even after 10 h of reflux conditions. At this point, we thought changing the solvent system may improve the yields. Hence, we changed the solvent from THF to toluene and later to dioxane, but the results were not encouraging (Table 1).

Recently, Roglans and co-workers reported the Rh catalyzed fully intramolecular [2+2+2] cyclotrimerization of *N*-tosyl-, carbon-, and oxygen-tethered cyanodienes to afford highly functionalized pyridines and bipyridines. They claimed that the solvent and the mode of thermal activation play a dramatic role on the outcome of the reaction. Surprisingly, the self dimerized product was observed under conventional heating conditions; whereas, microwave (MW) irradiation conditions gave the co-trimerized product.^{23a} Hence, we performed the co-trimerization of the diyne **11** with propargyl bromide **7c** under MW conditions in dry THF at 75 °C, but we didn't observe much difference in the yield. However, the reaction was completed within 2.5 h instead of 10 h. Furthermore, when we changed the solvent from THF to 1,4-dioxane under MW conditions at 110 °C, the reaction was completed within 15 min and the yield was also improved to 45%. We felt this may be the suitable conditions, hence the 1,4-dibromo-2-butyne **7b** was reacted with the diyne **11** under similar reaction conditions and found that the dibromo derivative **12b** was formed in 11% yield. As chlorides are less reactive than bromides and we anticipated improved yields. Hence, we performed the [2+2+2] co-trimerization reaction of diyne **11** with propargyl chloride **7e** and 1,4-dichloro-2-butyne **7f** in 1,4-dioxane under MW conditions and the isolated yields of co-trimerized products were found to be 42% (**12e**) and 13% (**12f**), respectively (Scheme 3).



Scheme 1. General strategy for the synthesis of dibromo derivative via [2+2+2] cycloaddition.

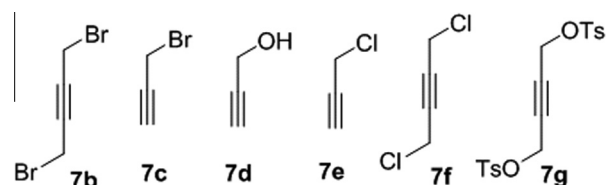


Figure 2. List of alkyne partners studied in [2+2+2] cycloaddition reaction.

Download English Version:

<https://daneshyari.com/en/article/5261569>

Download Persian Version:

<https://daneshyari.com/article/5261569>

[Daneshyari.com](https://daneshyari.com)