

SYNLETT Spotlight 48

Dicobalt Octacarbonyl

Compiled by Stefan Fischer



This feature focuses on a reagent chosen by a postgraduate, highlighting the uses and preparation of the reagent in current research

After receiving his Vordiplom from the University of Konstanz, Germany, Stefan Fischer studied at the University of Oregon, Eugene, where he obtained his MSc in 1997. He then returned to Konstanz where he received his Diplom (1999) and is currently doing research on natural product synthesis for his PhD under the guidance of Prof. Dr. U. Groth. Stefan Fischer is a fellow of the *Cusanuswerk - Bischöfliche Hochbegabtenförderung*.

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Introduction

Applications of transition metal chemistry serve as valuable tools for synthetic chemists. An important example is $\text{Co}_2(\text{CO})_8$, a well known reagent of versatile and still increasing utility since its discovery by L. Mond et al. in 1910.¹

The generation of moderately air stable Co-acetylene complexes is the key property of this reagent. These complexes are formed at ambient temperature by stirring solutions of $\text{Co}_2(\text{CO})_8$ and the alkyne (Figure 1). Purification by silica gel chromatography affords the pure products.

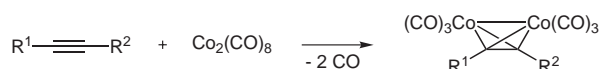
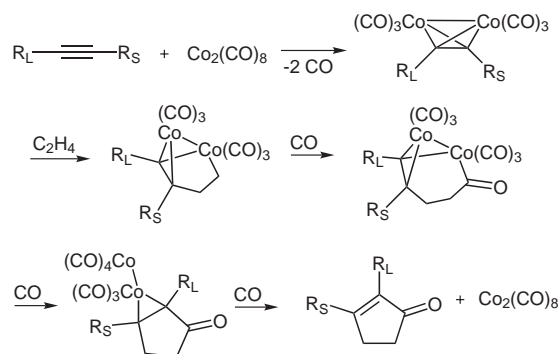


Figure 1

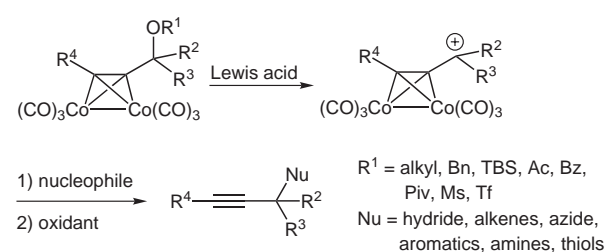
The synthesis of $\text{Co}_2(\text{CO})_8$ usually requires high pressures of CO or CO/H₂ depending on the oxidation state of the starting material.² Moreover $\text{Co}_2(\text{CO})_8$ is commercially available from all major suppliers and often no further purification is necessary.

Abstracts

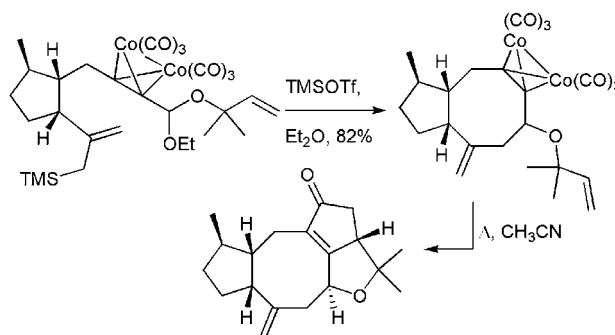
The Pauson–Khand reaction is probably the most widely known process involving $\text{Co}_2(\text{CO})_8$.³ In this reaction cyclopentenones are formed by a cobalt-mediated [2+2+1] cycloaddition of an alkyne, an alkene and CO in a highly convergent manner. The sterically most demanding substituent of the acetylene is incorporated in α -position to the carbonyl group regioselectively. Pauson–Khand reactions were carried out under high pressure and temperature but recent advances allow the use of catalytic amounts of $\text{Co}_2(\text{CO})_8$ under significantly milder reaction conditions.⁴ Thus, in the presence of additives such as N-oxides or primary amines the reaction proceeds at ambient temperature under atmospheric pressure.



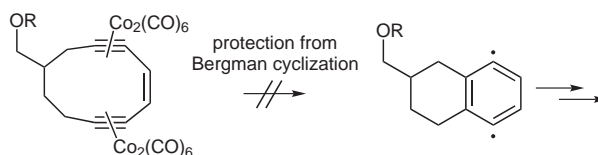
Dicobalt hexacarbonyl-stabilized propargyl cations react with a wide variety of nucleophiles. This process is commonly referred to as the Nicholas reaction.⁵ The cation is formed by treatment of a cobalt-complexed propargyl ether with Lewis acids such as $\text{BF}_3 \cdot \text{Et}_2\text{O}$. The liberation of the free alkyne is accomplished oxidatively by cerium ammonium nitrate or *N*-methylmorpholine-*N*-oxide. Approaches towards an enantioselective variation have also been described.⁶



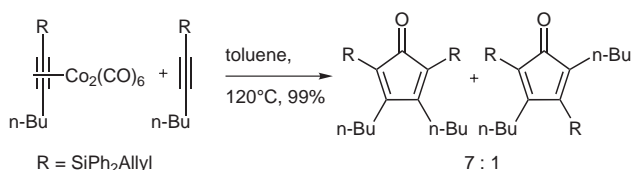
Combinations of Nicholas and Pauson–Khand reactions have been successfully applied in natural product synthesis. A nice example is the synthesis of (+)-epoxydictymene.⁷ The Nicholas reaction served for the closure to the eight-membered ring whereas the two newly formed five-membered rings were formed by a Pauson–Khand reaction.



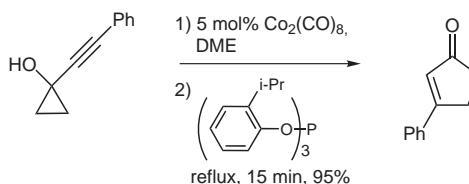
Complexation of alkynes with $\text{Co}_2(\text{CO})_8$ can also be used to decrease the reactivity of a triple bond. The cobalt complex protects the alkyne from addition reactions such as reductions and hydroborations.⁸ Endiynes are prevented from undergoing undesired Bergman cycloaromatization during synthesis, handling and storage of these sensitive compounds.⁹



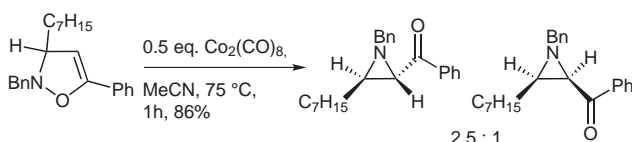
The reagent $\text{Co}_2(\text{CO})_8$ is further known to mediate cyclotrimerization of alkynes to benzene derivatives.¹⁰ Bulky substituents, however, cause the formation of cyclopentadienones exclusively.¹¹



In boiling ethereal solution complexes of 1-(1-alkynyl)cyclopropanols rearrange to 2-cyclopenten-1-ones. A catalytic variation, which uses tri(*o*-isopropylphenyl)phosphite as an additive has also been described.¹²



Promoted by $\text{Co}_2(\text{CO})_8$ in acetonitrile 4-isoxazolines are rearranged to 2-acylaziridines in yields up to 92% with varying selectivities.¹³



References

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