Supercritical Carbon Dioxide as a Reaction Medium and Reaction Partner

Manfred T. Reetz*, Werner Könen, and Thomas Strack

Abstract. The [Ni(cod)]2/Ph2P(CH2)4PPh2-catalyzed reaction of hex-3-yne with CO2 under supercritical conditions affords tetraethyl-2-pyrone

1. Introduction

Supercritical carbon dioxide (sc CO2) has not only been used for extraction purposes as in the production of caffeine-free coffee [1], but occasionally also as a solvent for organic reactions [2]. In the latter case, pronounced effects on the outcome of reactions are rare [3]. Nevertheless, due to environmental reasons this reaction medium may become important in the future. The solvent polarity of sc CO2 is similar to that of CCl4, as shown by the Dimroth-Reichardt E2 values of 32 [4] and 32.5 [5], respectively. We considered the possibility of utilizing sc CO2 as a solvent and simultaneously as a reaction partner (C1-building block). Here, we report the first examples of such a strategy [6].

2. Results

Exploratory experiments were performed using benzene-1,3-diol/KHCO3/CO2 in a Kolbe-Schmitt reaction under supercritical conditions without additional solvents [6]. Conversion to 2,4-dihydroxybenzoic acid turned out to be ca. 40%, but several side products were also formed. We then turned to CO2 fixation using transition-metal catalysis, specifically the reaction of CO2 with hex-3-yne (1) to produce tetraethyl-2-pyrene (2) using [Ni(cod)]2/Ph2P(CH2)4PPh2 as the catalyst. This process had previously been carried out at 120° using benzene as the solvent to produce pyrrole 2 and trimers of 1 [7]. In our experiments, we employed sc CO2 as the reaction medium at 102°. Gas chromatographic (GLC) analysis of the crude product mixture, after a reaction time of 69 h, showed the presence of 2 (35%) as well as small amounts of trimers of 1 (6%). Non-reacted 1 amounted to ca. 59%. Reproducible results were obtained in several runs. The use of trisopropylphosphite as a ligand resulted in a slower reaction.

3. Discussion

The outcome of the above non-optimized Ni-induced reaction in sc CO2 is similar to that of the classical reaction in benzene [7]. Thus, the results show that the concept of using sc CO2 as an environmentally safe solvent and as a C1-building block is viable. We expect that other catalytic and stoichiometric CO2-fixation processes [8] can also be carried out using sc CO2 [6].

Experimental

In a dry, Ar-flushed 200-ml autoclave were placed 1.5 g (18.2 mmol) of hex-3-yne (1), 340 mg (0.87 mmol) of bis(cycloocta-1,5-diene)nickel ([Ni(cod)]2), and 800 mg (1.9 mmol) of 1,4-bis(diphenylphosphino)butane. A compressor was then employed to introduce 93 g of CO2. The reactor was kept at 102° for 69 h, cooled to 0°, and opened to let excess CO2 escape. The crude product was dissolved in 4 ml of toluene and then examined by GLC using cod as the internal standard. The analysis showed 59% of non-reacted 1, 5% trimers of 1 [7], and 35% of tetraethyl-2-pyrene (2).

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Scheme

[Correspondence: Prof. Dr. M.T. Reetz
Max-Planck-Institut für Kohlenforschung
Kaiser-Wilhelm-Platz 1
D-45470 Mülheim/Ruhr, Germany]