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Supercritical Carbon Dioxide as a Reaction Medium and Reaction Partner

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Abstract. The $[\text{Ni}(\text{cod})_2]/\text{Ph}_2\text{P}(\text{CH}_2)_4\text{PPh}_2$ -catalyzed reaction of hex-3-yne with CO_2 under supercritical conditions affords tetraethylpyrone

1. Introduction

Supercritical carbon dioxide (*sc* CO_2) 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* CO_2 is similar to that of CCl_4 , as shown by the *Dimroth-Reichardt* E_T values of 32 [4] and 32.5 [5], respectively. We considered the possibility of utilizing *sc* CO_2 as a solvent and simultaneously as a reaction partner (C_1 -building block). Here, we report the first examples of such a strategy [6].

2. Results

Exploratory experiments were performed using benzene-1,3-diol/ $\text{KHCO}_3/\text{CO}_2$ 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 CO_2 fixation using transition-metal catalysis, specifically the reaction of CO_2 with hex-3-yne (1) to produce tetraethyl-2-pyrone (2) using $[\text{Ni}(\text{cod})_2]/\text{Ph}_2\text{P}(\text{CH}_2)_4\text{PPh}_2$ as the catalyst. This process had previously been carried out at 120° using benzene as the

solvent to produce pyrone 2 and trimers of 1 [7]. In our experiments, we employed *sc* CO_2 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 triisopropylphosphite as a ligand resulted in a slower reaction.

3. Discussion

The outcome of the above non-optimized Ni-induced reaction in *sc* CO_2 is similar to that of the classical reaction in benzene [7]. Thus, the results show that the concept of using *sc* CO_2 as an environmentally safe solvent and as a C_1 -building block is viable. We expect that other catalytic and stoichiometric CO_2 -fixation processes [8] can also be carried out using *sc* CO_2 [6].

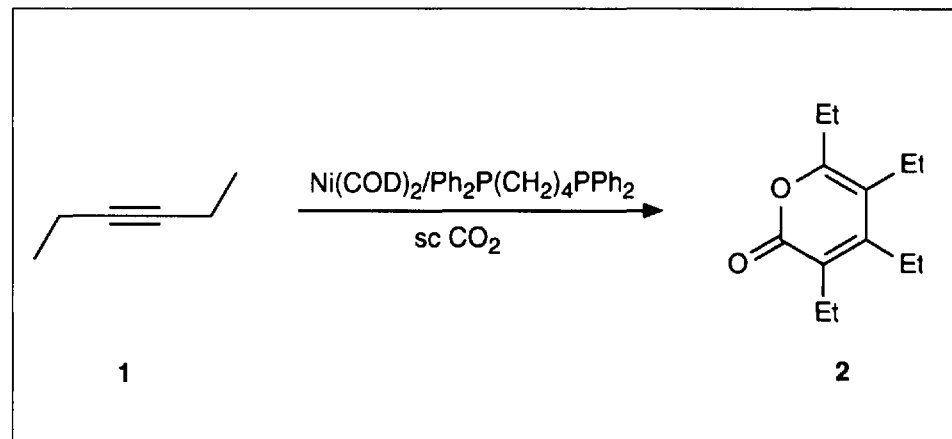
Experimental

In a dry, Ar-flushed 200-ml autoclave were placed 1.5 g (18.2 mmol) of hex-3-yne (1), 240 mg (0.87 mmol) of bis(cycloocta-1,5-diene)nickel ($[\text{Ni}(\text{cod})_2]$), and 800 mg (1.9 mmol) of 1,4-bis(diphenylphosphino)butane. A compressor was then employed to introduce 93 g of CO_2 . The reactor was kept at 102° for 69 h, cooled to 0° , and opened to let excess CO_2 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, 6% trimers of 1 [7], and 35% of tetraethyl-2-pyrone (2).

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- [1] G. Wilke, *Angew. Chem.* **1978**, *90*, 747; *ibid. Int. Ed.* **1978**, *17*, 701; K. Zosel, *Angew. Chem.* **1978**, *90*, 748; *ibid. Int. Ed.* **1978**, *17*, 702.
- [2] See for example: M.E. Paulaitis, G.C. Alexander, *Pure Appl. Chem.* **1978**, *59*, 61; M.E. Sigman, J.T. Barbas, J.E. Leffler, *J. Org. Chem.* **1987**, *52*, 1754; N.S. Isaacs, N. Keating, *J. Chem. Soc. Chem. Commun.* **1992**, 876; Z. Guan, J.R. Combes, Y.Z. Menciloglu, J.M. DeSimone, *Macromolecules* **1993**, *26*, 2663; C.B. Roberts, J. Zhang, J.F. Brenneke, J.E. Chateaufeuf, *J. Phys. Chem.* **1993**, *97*, 5618.
- [3] Polymerization of fluorinated acrylic monomers in *sc* CO_2 : J.M. DeSimone, Z. Guan, C.S. Elsbernd, *Science* **1992**, *257*, 945; biocatalytic reactions in *sc* CO_2 : Y. Ikushima, N. Saito, T. Yokoyama, K. Hatake, S. Ito, M. Arai, H.W. Blanch, *Chem. Lett.* **1993**, 109; and lit. cit. therein.
- [4] Y. Ikushima, N. Saito, M. Arai, K. Arai, *Bull. Chem. Soc. Jpn.* **1991**, *64*, 2224; the E_T -value of *sc* CO_2 is slightly pressure-dependent. J.A. Hyatt, *J. Org. Chem.* **1984**, *49*, 5097; Y. Ikushima, N. Saito, M. Arai, *J. Phys. Chem.* **1992**, *96*, 2293.
- [5] C. Reichardt, 'Solvents and Solvent Effects in Organic Chemistry', 2nd Ed., VCH, Weinheim, 1990.
- [6] T. Strack, Diplomarbeit, Universität Marburg, 1992.
- [7] Y. Inoue, Y. Itoh, H. Kazama, H. Hashimoto, *Bull. Chem. Soc. Jpn.* **1980**, *53*, 3329.
- [8] A. Behr, 'Carbon Dioxide Activation by Metal Complexes', VCH, Weinheim, 1988.

Scheme



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