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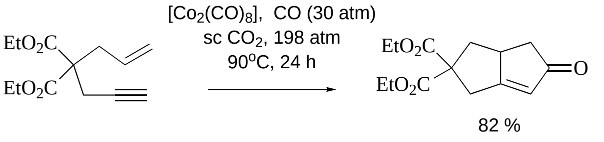
Catalytic Intermolecular Pauson – Khand Reactions in Supercritical Ethylene[**]

Nakcheol Jeong[*] and Sung Hee Hwang

Supercritical fluids are rapidly becoming alternative reaction media for conventional organic reactions.[1] The advantages of reactions in supercritical fluids include the high solubility of gaseous reactants, rapid diffusion of solutes, and weakening of the solvation around the reacting species. In addition, these fluids are easily recycled and allow the separation of the dissolved compounds by selective precipitation, which implicates possibilities in the development of environmentally benign processes. Sequential precipitation of the product and catalyst is possible by a gradual release of pressure.[2]

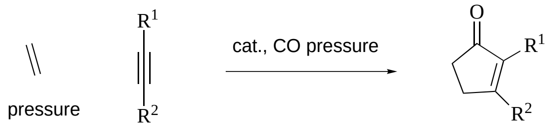
Recent progress has shown that supercritical fluids can substitute conventional organic solvents in various transition metal catalyzed transformations.[3] We demonstrated that catalytic intra- and intermolecular Pauson – Khand reactions could be carried out in supercritical CO_2 with high efficiency (Scheme 1).[4] We report here a new dimension of this application, that is, an intermolecular Pauson – Khand reaction in supercritical ethylene. Ethylene is one of the most abundant raw materials in the petrochemical industry. Direct coupling of ethylene with the proper acetylenes under Pauson – Khand conditions provides an efficient and economical method for preparing synthetically useful cyclopentenones.[5]



Scheme 1. Example for a Pauson – Khand reaction in supercritical (sc) CO_2.

Pauson – Khand reactions of ethylene with stoichiometric amounts of hexacarbonyldicobalt – alkyne complexes have been reported.[6, 7] Rautenstrauch et al. described the first catalytic Pauson – Khand reaction between heptyne and ethylene in toluene in 1990.[8] This catalytic reaction showed a high turnover number (220), but it suffered from the harsh reaction conditions and had a low chemical yield (< 50 %). This might be attributed to the low effective concentration of ethylene in the solvent and the ill-defined, catalytic cobalt – carbonyl species formed under the reaction conditions employed.

Encouraged by our success with CO_2 as a supercritical fluid, we first tried to apply the previously employed conditions for the reaction with ethylene. We ran a series of reactions (48 h at 80 °C) in supercritical CO_2 ($p_{\text{final}} = 200$ atm) with phenylacetylene (**1a**) and ethylene (10 – 45 atm at 34 °C) with various pressures of CO (1 – 30 atm) and in the presence of a catalytic amount of $[Co_2(CO)_8]$ (**I**). The result was disappointing and the chemical yield of 2-phenylcyclopentenone (**1b**) never exceeded 10 %. Therefore, we decided to seek the possibility of a direct coupling reaction in supercritical ethylene (Scheme 2).



Scheme 2. Intermolecular Pauson – Khand reactions between ethylene and alkynes (see Table 1).

Supercritical ethylene can be obtained easily ($T_c = 9$ °C, $p_c = 34$ atm) and has been used for the preparation of the complex $[Cr(CO)_5(CH_2CH_2)]$ and its polymer.[9, 10] We envisioned that it can also be used for the Pauson – Khand reaction. Under these conditions, a high effective concentration of the rather less reactive ethylene as well as of carbon monoxide would be expected.

The catalysts examined with substrate **1a**, which are all soluble in supercritical ethylene—for example, $[Co_2(CO)_8]$ (**I**), $[Co_4(CO)_{11}\{P(OPh)_3\}]$ (**II**), or $[Co_4(CO)_{12}]$ (**III**), worked well although the efficiency of each catalyst varied from case to case. On the other hand, $[Co_2(CO)_6\{P(OPh)_3\}_2]$ (**IV**), which is a reliable catalyst in organic solvents,[5d] did not work because of its low solubility in supercritical ethylene.

We optimized the reaction conditions with catalysts **II** and **III** in most cases.[11] Ethylene (110 atm at 34 °C) and CO (5 atm at 34 °C) were charged into a mixture of phenylacetylene (3 mmol) and catalyst **II** (0.09 mmol) in a stainless-steel reactor (80 mL). The reaction mixture was gradually warmed to 85 °C over 6 h, where the pressure in the reactor usually reached 200 – 210 atm. The reaction mixture was allowed to react at that temperature for 46 h. 2-Phenylcyclopentenone (**1b**) was obtained in 80 % yield (Table 1, entry 1). Only 2-substituted cyclopentenone was obtained.

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Table 1. Results of intermolecular catalytic Pauson – Khand reactions in supercritical ethylene (Scheme 2).[a]

Entry	Substrate	R^1	R^2	Catalyst [mol%]	t[h]	Conversion [%]	Products	Yield [%]
1	**1a**	Ph	H	**II** (3)	46	100	**1b**	80
2	**1a**	Ph	H	**III** (3)	24	100	**1b**	77
3	**2a**	C_5H_{11}	H	**II** (3)	42	100	**2b**	70
4	**3a**	$HO(CH_2)_3$	H	**II** (3)	46	100	**3b**	46
5	**4a**	$Me_3SiO(CH_2)_3$	H	**II** (3)	64	100	**3b**	82[b]
6	**4a**	$Me_3SiO(CH_2)_3$	H	**I** (3)	30	50	**3b**	40[b]
7	**5a**	$CH_3CH(OSiMe_3)CH_2$	H	**II** (5)	44	100	**5b**	74[b]
8	**6a**	Me_3SiOCH_2	H	**II** (5)	24	100	**6b**	30[b]
9	**6a**	Me_3SiOCH_2	H	**III** (5)	48	100	**6b**	23[b]
10	**7a**	tBuMe$_2$SiOCH$_2$	H	**II** (5)	24	100	**6b**	41[b]
11	**8a**	$MeO_2C(CH_2)_2$	H	**II** (5)	30	100	**8b**	75
12	**8a**	$MeO_2C(CH_2)_2$	H	**III** (5)	40	100	**8b**	87

[a] The optimum conditions for each substrate are given. The reactions were carried out in a bomb equipped with a sapphire window at 85 °C for the specified reaction time. The initial pressure of CO was 5 atm and of ethylene was 110 atm at 34 °C. The liquid phase was observed at that temperature. At 85 °C the reaction mixture became one red, homogeneous supercritical phase. It remained as a single phase even after completion of the reaction. [b] Yield of free alcohol isolated after treatment with concentrated HCl.

Complications by alkyne trimerization leading to triphenylbenzenes (1,3,5- or 1,3,4-substituted) were not observed under these reaction conditions. For **1a**, catalyst **III** worked equally well to provide **1b** in 77% yield. It is noteworthy that catalyst **III** was once considered as thermally inactive for the Pauson – Khand reaction.[12]

The reaction with aliphatic terminal alkyne **2a** proceeded uneventfully to provide **2b** in 70% yield (Table 1, entry 3). When alcohols were used as substrate the hydroxyl groups needed to be protected for clean reaction and high chemical yield. For example, alkynol **3a** reacted without protection to give the desired product **3b** (entry 4) together with many unidentified side products in only 46% yield after column chromatography. Use of the trimethylsilyl-protected substrate **4a** improved the reaction significantly to generate **3b** in 82% yield after treatment of the resulting Pauson – Khand product with acid (entry 5).

The trimethylsilyl-protected homopropargyl alcohol **5a** underwent the reaction very nicely to give **5b** in 74% yield (entry 7). However, propargyl alcohol derivatives **6a** and **7a** were inferior to the previous substrates under these conditions (entries 8 to 10). Regardless of the protecting groups and reaction conditions employed, only modest chemical yields were obtained (41% at best).

ω-Alkynoate **8a** provided the corresponding cyclopentenone **8b** in high yield (up to 87% with catalyst **III**; entries 11 and 12). $[Co_4(CO)_{12}]$ (**III**) turned out to be the best catalyst for this substrate. However, the limitation of the reaction in supercritical ethylene was also evident. For example, a disubstituted alkyne such as 2-butyne did not react under these reaction conditions. A similar observation is also reported in the literature.[13] $[CpCo(CO)_2]$-catalyzed trimerization of alkyne in supercritical H_2O is limited to terminal alkynes. α,ω-Bisalkyne (e.g. 1,7-octadiyne), which is a good substrate in the intermolecular reaction with norbornadiene in supercritical CO_2, was reluctant to undergo the Pauson – Khand reaction.[4]

In summary we have demonstrated an efficient catalytic Pauson – Khand reaction in supercritical ethylene. Supercritical ethylene can be used not only as a substrate but also as a solvent. Under these conditions, even a low pressure of CO (5 atm) is sufficient for the reaction to take place.[14]

Experimental Section

To **1a** (306 mg, 3.0 mmol) in a pressure bomb was added $[Co_4(CO)_{12}]$ (**III**, 54.5 mg, 0.091 mmol), and the bomb (80 mL) was flushed three times with CO and then charged with CO (5 atm, 99.9%) at 34 °C. Subsequently ethylene (99.5%) was added and then compressed to 110 atm. The reaction mixture was warmed to 85 °C and allowed to react for 24 h. After that it was cooled to room temperature, and the CO and excess ethylene were released carefully in a well-vented hood. The reaction residue was dissolved in acetone, concentrated in vacuo, and purified by chromatography (SiO_2, *n*-hexane/ethyl acetate 9/1) to give the product **2a** as a colorless oil (366 mg, 2.3 mmol, 77%).[14]

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[11] **Caution!** Although no incident occurred during this study, we observed that highly purified [Co$_2$(CO)$_8$] and [Co$_4$(CO)$_{12}$] ignited spontaneously at times upon contact with air. Special precaution should be paid. Therefore, we prefer to use stable [Co$_4$(CO)$_{11}$-{P(OPh)$_3$}] to avoid any potential danger.

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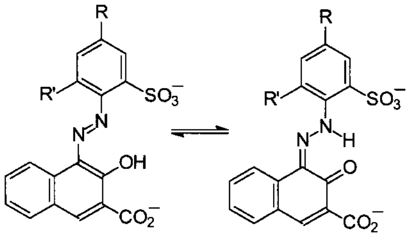
The First Red Azo Lake Pigment whose Structure is Characterized by Single Crystal Diffraction[**]

Alan R. Kennedy,* Craig McNair, W. Ewen Smith, Greig Chisholm, and Simon J. Teat

As organic pigments are used in the form of crystals dispersed throughout the media to be colored, their color characteristics depend not only on their molecular structure but also crucially upon their crystal structure. Furthermore, the crystal structure influences the stability of the pigment to solvent, heat, and light and also determines the crystal morphology which is in turn related to color strength, hiding power, stability, flow, and dispersion properties.[1] As a good pigment is, by design, highly insoluble, it is difficult to grow the large, high-quality crystals needed for conventional diffraction methods and thus little detailed structural information is available. These generalizations are true of the red azo pigments as exemplified by Ca4B toner (the calcium salt of 4-(4-methyl-2-sulfophenyl)azo-3-hydroxy-2-naphthalic acid; also known as CIPR57:1) which is considered the worldwide standard process red for printing and its continuing industrial importance is attested to by the patent literature.[2]

Previous work on the structure of Ca4B[3] showed that the classification "azo pigment" is actually a misnomer, as in the solid state the pigment exists largely as the keto-hydrazone tautomer (Scheme 1). Further, dideprotonation occurs at the sulfonate and carboxy groups but not at the hydroxy/hydrazo group, and there is only one type of calcium binding site. Harris et al.[3a] suggested from solid-state NMR measurements that the calcium atom is complexed by sulfonate and carboxylate groups from different molecules and thus proposed a simple polymeric structure with azo molecules bridged by Ca^{2+} ions, whereas Fryer and coworkers[3c] showed evidence from electron microscopy that Ca4B exists as head-to-tail dimers.



Scheme 1. Tautomerism in red azo pigments.

We have now succeeded in growing, by slow evaporation of a DMF solution, small crystals of a dichloro analogue of Ca4B (**1**) suitable for characterization by synchrotron radiation.[4] Compound **1** displays a complex, supramolecular structure of a type not previously suspected for red azo pigments but which we believe to be consistent with the experimental evidence in the published work on Ca4B, and which we propose to be a suitable model structure to relate to the structure of many other red azo pigments.

The structural analysis confirms that the azo dianion is deprotonated at the sulfonate and carboxylate groups. The Ca atoms are eight coordinate through bonding to three sites (carboxylate, keto, and sulfonate) on one azo anion, to two terminal water molecules, and to three oxygen atoms supplied by bridging interactions to the carboxylate groups of neighboring azo anions (Figure 1). That the azo anion acts in such a

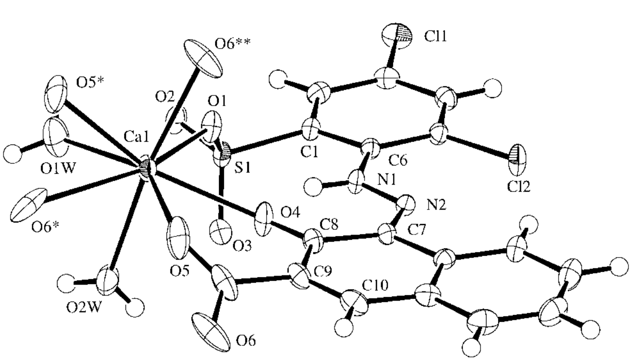


Figure 1. Molecular structure of **1** showing the coordination geometry about Ca1. Selected distances [Å]: Ca1-O1 2.542(2), Ca1-O4 2.394(2), Ca1-O5 2.385(2), Ca1-O1W 2.449(2), Ca1-O2W 2.352(2), Ca1-O5* 2.440(2), Ca1-O6* 2.881(2), Ca1-O6** 2.374(2), N1-N2 1.304(2), N1-C6 1.395(2), N2-C7 1.333(2), C8-O4 1.257(2), C7-C8 1.458(3), C8-C9 1.451(3), C9-C10 1.349(3). Symbols: * = $-x+1, y+0.5, -z+0.5$; ** = $x, y+1, z$.

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