



A Very Useful and Efficient Wacker Oxidation of Higher α -Olefins in the Presence of Per(2,6-di-*O*-methyl)- β -Cyclodextrin

Eric Monflier*, Sébastien Tilloy, Georges Fremy, Yolande Barbaux and André Mortreux

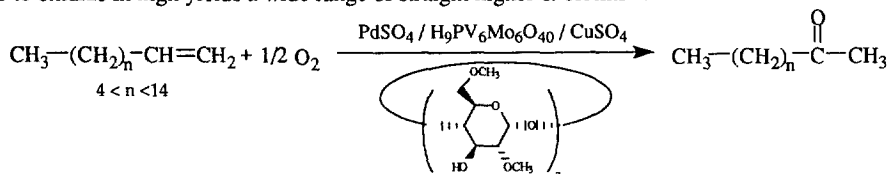
Laboratoire de Catalyse Homogène et Hétérogène associé au CNRS, ENSCL
 Bâtiment C7, B.P. 108 - 59659 Villeneuve d'Ascq, France.

Key words: Wacker oxidation, higher α -olefin, per(2,6-di-*O*-methyl)- β -cyclodextrin

Abstract: Oxidation of higher α -olefins (C_8 - C_{16}) in a two phase system with a multicomponent catalytic system, i.e. $PdSO_4$ / $H_9PV_6Mo_6O_{40}$ / $CuSO_4$ and per(2,6-di-*O*-methyl)- β -cyclodextrin gives the corresponding 2-ketones in high yields (>90 %).

Wacker oxidation of olefins to ketones by palladium / copper or palladium / heteropoly acids systems is a well known process which has been successfully applied to numerous olefins¹. Nevertheless, the oxidation of higher α -olefins (C_8 - C_{16}) proceeded at moderate rates and with poor yields². Consequently, selective oxidation of higher olefins still remains a big challenge.

Recently, we have described an efficient catalytic system, i.e. $PdSO_4$ / $H_9PV_6Mo_6O_{40}$ / $CuSO_4$ and per(2,6-di-*O*-methyl)- β -cyclodextrin (DMCD), to oxidize 1-decene into 2-decanone in high yields in a two phase system³. We would like to report hereby that this multicomponent catalytic system allowed also to oxidize in high yields a wide range of straight higher α -olefins⁴:



Obviously, Table 1 shows that the 2-ketone yields are always higher than 90 % with the DMCD. Oxidation of higher olefins was also carried out with the β -cyclodextrin (CD) and the 2-hydroxypropyl- β -cyclodextrin (HPCD). In order to compare 2-ketone yields and selectivities obtained with these cyclodextrins and the DMCD, the reaction was stopped after 6 hours. Results are presented in figures 1 and 2. These two figures show clearly that the oxidation rate and the ketone selectivity are higher with the DMCD than with the other cyclodextrins whatever the chain length of the olefin.

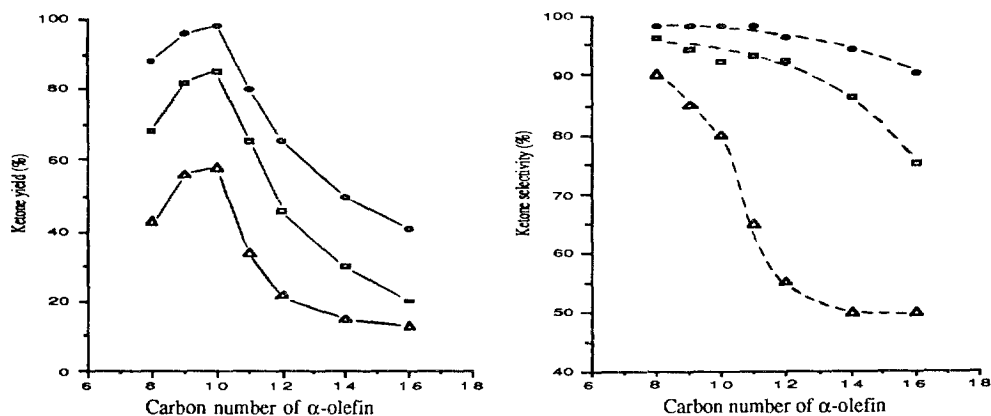
These results may be interpreted from the cyclodextrins solubilities and from the well known molecular recognition between the host cavity of cyclodextrins and organic compounds⁵. Indeed, contrary to the CD, the DMCD is well soluble in water and partly in the organic layer⁶ and can therefore transfer more rapidly the olefin into the aqueous phase. Furthermore, as the stability constant of ketone-DMCD complex is probably weaker than that of ketone-CD complex (decrease of hydrogen bonding forces), we think that the concentration of olefin-DMCD complex in the aqueous phase is higher during the reaction. The unusual high selectivities noticed with DMCD could be due to the deeper hydrophobic host cavity of the DMCD⁷ which would wrap more efficiently the higher olefin than the CD and would avoid therefore the formation of the bulky isomerising palladium complex. The decrease in oxidation rates with the increase in carbon number can be explained by the weaker molecular recognition between the cyclodextrin and the larger olefins. The olefin optimal size and shape are reached with 1-decene.

In conclusion, we have demonstrated that the Wacker oxidation of higher α -olefins in the presence of DMCD is a general and convenient method to synthesize higher 2-ketones. Work is under way in our laboratory to confirm the mechanistic hypothesis mentioned above and to develop this concept in other reactions.

Table 1: Oxidation of higher α -olefins with per(2,6-di-*o*-methyl)- β -cyclodextrin^a

Entry	Olefin	Time required for total conversion (hours)	2-Ketone yield ^b (mol (%))	Isomeric olefins yield (mol (%))
1	C ₆ H ₁₃ CH=CH ₂	10	98	2
2	C ₇ H ₁₅ CH=CH ₂	8	97	3
3	C ₈ H ₁₇ CH=CH ₂	6	98	2
4	C ₉ H ₁₉ CH=CH ₂	24	98	2
5	C ₁₀ H ₂₁ CH=CH ₂	60	96	4
6	C ₁₂ H ₂₅ CH=CH ₂	90	94	6
7	C ₁₄ H ₂₉ CH=CH ₂	120	90	10

a) For quantities used, see *Experimental procedure*; b) 2-ketone gas chromatographic yield.

Figures 1 and 2: Effect of chain length of olefin on 2-ketone yield and selectivity after 6 hours of reaction in the presence of various cyclodextrins^a

a) Δ : CD; \square : HPCD; \circ : DMCD; t = 6 hours, For quantities used, see *Experimental procedure*.

REFERENCES AND NOTES

- Parshall, G.W.; Ittel, S.D. *Homogeneous Catalysis. The Applications and Chemistry of Catalysis by Soluble Transition Metal Complexes*; 2nd ed., Wiley-Interscience: New York, 1992; pp. 138-142.
- a) Bäckvall, J.E.; Bruce, R.E. *Tetrahedron. Lett.* **1988**, 29, 2885-2888. b) Tsuji, J.; Nagashima, H.; Nemoto, H. *Org. Synth.* **1984**, 62, 9-13. c) Zahalka, H.A.; Januszkiewicz, K.; Alper, H. *J. Mol. Catal.* **1986**, 35, 249-253. d) Harada, A.; Hu, Y.; Takahashi, S. *Chem. Lett.* **1986**, 2083-2084.
- Monflier, E.; Blouet, E.; Barbaux, Y.; Morreux, A. *Angew. Chem. Int. Ed. Engl.* **1994**, 33, 2100-2102.
- Experimental procedure*. 0.206 g (0.86 mmol) of PdSO₄·2H₂O, 1.64 g (10 mmol) of CuSO₄, 10 mmol of H₉PV₆Mo₆O₄₀ which was synthesized according to the method reported⁸ and 1.31 g (1 mmol) of DMCD (average molar substitution: 1.8; average molecular weight: 1310 g.) were introduced with 30 mL of water and 40 mmol of 1-alkene in a 150 mL flask. Oxygen was bubbled through the solution which was vigorously stirred at 80 °C until complete reaction. The reaction course was monitored by GLC using an n-alkane as an internal standard. Products were identified by comparison of retention times and spectral properties with authentic samples.
- a) Wenz, G. *Angew. Chem. Int. Ed. Engl.* **1994**, 33, 803-822. b) Saenger, W. *Angew. Chem. Int. Ed. Engl.* **1980**, 19, 344-362.
- a) Duchene, D.; Wouessidjewe D. *J. Coord. Chem.* **1992**, 27, 223-236. b) Ikeda, H.; Kojin, R.; Yoon, C.J.; Ikeda, T. *J. Incl. Phen. & Mol. Reg. Chem.* **1989**, 7, 117-124. c) Spencer, C.M.; Stoddart, J.F.; Zarzycki, R. *J. Chem. Soc. Perkin Trans II* **1987**, 1323-1336. d) Kubota, Y.; Tanimoto, T.; Horiyama, S.; Koizumi, K. *Carbohydr. Res.* **1989**, 192, 159-166.
- a) Czugler, M.; Ecker, E.; Slezowski, J.J. *J. Chem. Soc. Chem. Comm.* **1981**, 1291-1292. b) Tanaka, N.; Yamaguchi, A.; Araki, Y.; Araki, M. *Chem. Lett.* **1987**, 715-718.
- Davison, S.F.; Mann, B.E.; Maitlis, P.M. *J. Chem. Soc. Dalton. Trans.* **1984**, 1223-1228.

(Received in France 14 October 1994; accepted 14 November 1994)