

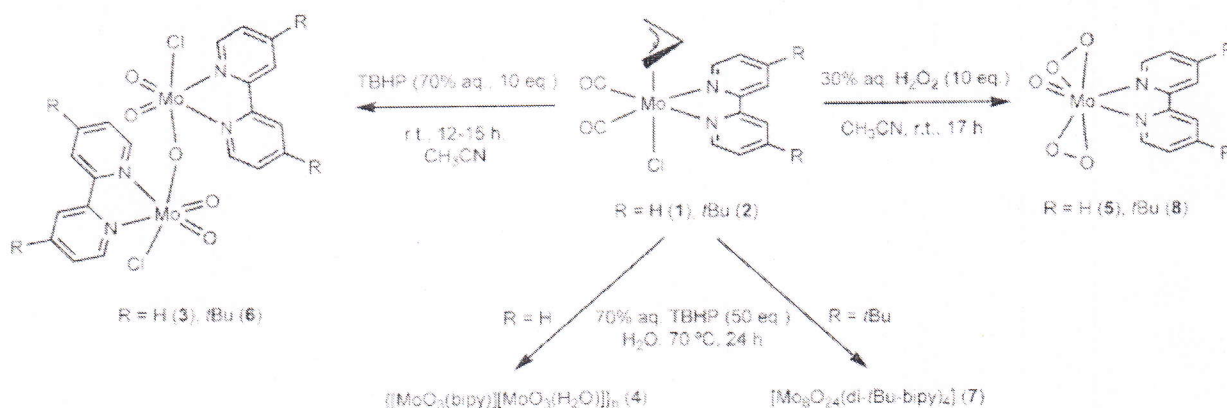
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 MO(VI) CATALYSTS OBTAINED FROM ETA³-ALLYL DICARBONYL PRECURSORS: SYNTHESIS, CHARACTERIZATION AND CATALYTIC PERFORMANCE IN CYCLOOCTENE EPOXIDATION

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ETA³-Allyl complexes [Mo(η^3 -C₃H₅)X(CO)₂(L)_n] (X = halide; L = monodentate or bidentate ligand) have been found to act as catalysts or catalyst precursors in several reactions, such as olefin epoxidation [1]. In the present work, we studied the oxidative decarbonylation of the complexes with X = Cl and L = 2,2'-bipyridine (bipy) (1) or 4,4'-di-*tert*-butyl-2,2'-bipyridine (di-*t*Bu-bipy) (2) by reaction with aqueous *tert*-butylhydroperoxide (TBHP) or H₂O₂ [2]. Depending on the reaction conditions, the following compounds were obtained in good yields: dinuclear oxo-bridged complexes [MoO₂Cl(L)]₂O (L = bipy (3), di-*t*Bu-bipy (6)), the hybrid material {[MoO₃(bipy)][MoO₃(H₂O)]}_n (4), the octanuclear complex [Mo₈O₂₄(di-*t*Bu-bipy)₄] (7), and the oxodiperoxo complexes MoO(O₂)₂(L) (L = bipy (5), di-*t*Bu-bipy (8)).



Compounds 1-8 were used as (pre)catalysts in the epoxidation of *cis*-cyclooctene at 70 °C with aqueous TBHP or H₂O₂ as oxidant. The solvent effect was investigated and the best results were obtained for TBHP/H₂O, where 1,2-epoxy-cyclooctane (CyO) yields were considerably higher for 2 and the derived compounds 6-8 (87-98% CyO yield) than for 1. With H₂O₂ as oxidant, the highest yields were obtained with CH₃CN as solvent (54-81% for 3-8).

References: [1] P.J.C. Alonso, P. Neves, C. Silva, A.A. Valente, P. Brandão, S. Quintal, M.J. Villa de Brito, P. Pinto, V. Félix, M.G.B. Drew, J. Pires, A.P. Carvalho, M.J. Calhorda, P. Ferreira, *Eur. J. Inorg. Chem.* 2008, 1147. [2] C.A. Gamelas, A.C. Gomes, S.M. Bruno, F.A.A. Paz, A.A. Valente, M. Pillinger, C.C. Romão, I.S. Gonçalves, *Dalton Trans.* 2012, 41, 3474.

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