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NOVEL APPLICATIONS OF ZIEGLER-TYPE CATALYSTS, AROMATIZATION OF TETRALIN AND DISPROPORTIONATION OF CYCLIC OLEFINS

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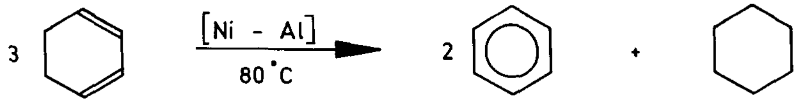
Abstract : Ziegler catalysts based on Co and Ni efficiently promote the aromatization of tetralin as well as the disproportionation of cyclohexadiene and cyclohexene into benzene and cyclohexane.

Ziegler catalysts are well known for their hydrogenation activity [1]; any hydrogenation catalysts should also speed up the rate of the reverse reaction. In fact, the thermodynamics of the process greatly favors the hydrogenation reaction but because the entropy term is negative, there is a temperature at which formation of the unsaturated molecule is favored (i.e. reforming reactions).

We want now to report on what seems to be the first observation of a catalytic dehydrogenation at atmospheric pressure by Ziegler type catalysts, namely the aromatization of tetralin (1,2,3,4-tetrahydronaphthalene) by Ni and Co based catalysts. Typically, when 3 mL of tetralin (neat or in decaline as solvent) are heated at 150-200°C under an inert atmosphere in the presence of a catalytic amount of Co or Ni acetylacetonate (5.10^{-4}mol) and 3 mol equiv. of triisobutylaluminum or of diisobutylaluminum hydride (dibal-H), a rapid evolution of hydrogen takes place and naphthalene is formed in 95-100 % yield, with a typical turnover of 10 h^{-1}. Addition of 1 equiv of a phosphine (PPh_3 or $P(nBu)_3$) completely inhibits the reaction and catalysts based on Fe are inactive. Saturated alkanes (e.g. decaline, cyclohexane) remain unaffected even in the presence of hydrogen acceptors (1-octene, t-butylbenzene, anthracene).

Moreover, these catalytic systems are also very active and much more efficient than the previously reported catalysts [2] for the disproportionation of cyclohexene and 1,3-cyclohexadiene. The latter molecule is instantaneously and quantitatively transformed into benzene and cyclohexene, even at room temperature (eq.1, same catalytic conditions as above), a reaction already


eq.1


eq. 2

observed by Hanson [3] with similar catalytic systems. At higher temperature, cyclohexene itself is cleanly and quantitatively disproportionated into benzene and cyclohexane, (typically, cyclohexene : 2 mL; $Ni(acac)_2$: 5.10^{-4} mol; dibal-H : 3 mol equiv; half reaction time : less than 10 min at 80°C), thus ascertaining the observed overall stoichiometry of eq. 2 for the disproportionation of 1,3-cyclohexadiene at 80°C.

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