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DISPROPORTIONATION OF CYCLOHEXADIENE BY Co(II) AND Ni(II) BASED HOMOGENEOUS ZIEGLER CATALYSTS

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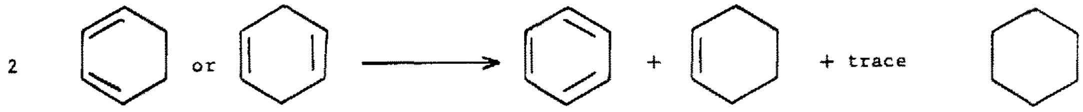
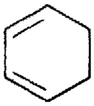
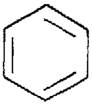
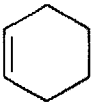
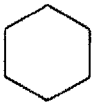
Summary: Homogeneous Ziegler catalysts prepared from Co(II) or Ni(II) alkanoates and aluminium alkyls are highly active for the disproportionation of 1,3- and 1,4-cyclohexadiene to benzene and cyclohexene.

$Zr(H)(\eta^5\text{-}C_6H_7)(dmpe)$ has recently been reported to be an effective homogeneous catalyst for the disproportionation of 1,3-cyclohexadiene to benzene and cyclohexene[1]. Less efficient iridium[2] and rhodium[3,4] based homogeneous catalysts are also known for this reaction. These reports have prompted the disclosure that Co(II) and Ni(II) based homogeneous Ziegler catalysts are even more active for the disproportionation of both 1,3- and 1,4-cyclohexadienes. In addition, these catalysts are particularly convenient because of their ease of preparation. This novel reaction of Ziegler catalysts extends further the utility of these versatile catalyst systems.

Active catalysts are prepared by the addition of AlR_3 (R = ethyl or isobutyl) to MX_2 (M = Co or Ni, X = acetylacetonate, 2-ethylhexanoate or stearate; $Al:M \geq 3:1$) in an aromatic hydrocarbon under argon. Addition of 1,3- or 1,4-cyclohexadiene to the catalyst at ambient temperature results in rapid disproportionation of the cylohexadiene to benzene and cyclohexene together with a trace of cyclohexane.



Typical product from 1,3-cyclohexadiene:

Component				
Mole %	2	49	48	<1

Conditions: Co(2-ethylhexanoate)$_2$ (0.5 mmole), AlEt$_3$ (1.5 mmole) in toluene (10 ml); 1,3-cyclohexadiene (12.5 mmole); reaction time 5 minutes at ambient temperature.

Similar catalysts prepared from FeX$_2$, CuX$_2$ or Ti(Oi-Pr)$_4$ are inactive for disproportionation, even at 100°C, slow polymerisation of the cyclohexadienes being obtained with the Ti based catalyst. This is consistent with the order of hydrogenation activity of these Ziegler catalysts, viz. Ni ≫ Co > Cu ≫ Fe > Ti[5], which together with the detection of cyclohexane indicates a dehydrogenation/hydrogenation mechanism rather than direct H transfer between cyclohexadiene molecules.

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