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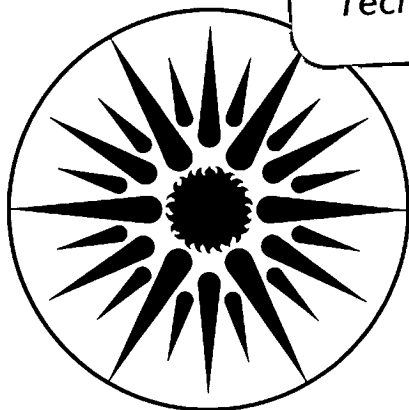
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R.H. Fish, G.A. Cremer, and A.D. Thormodsen

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HOMOGENEOUS CATALYTIC HYDROGENATION: REGIOSPECIFIC REDUCTIONS
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The synthetic fuel products that are derived from coal always require additional hydroprocessing to remove nitrogen and sulfur from compounds that can poison the up-grading catalysts. In this regard, the hydrogenation usually requires substantial reduction of not only the polynuclear heteroaromatic nitrogen and sulfur rings, but other aromatic rings associated with the heterocyclic ring prior to the removal of the nitrogen and sulfur from these compounds.^{1a,b}

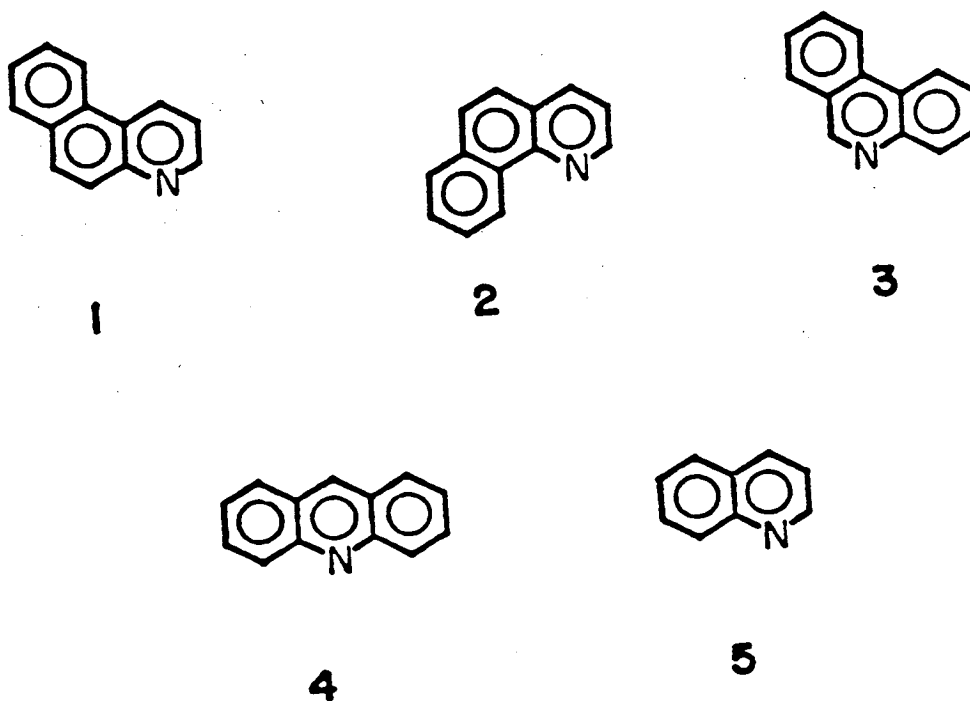
If catalysts, that are used in these processes, could regioselectively reduce the heterocyclic ring without reducing the other aromatic rings, a substantial economic savings would be possible, i.e., less H₂ used.

We have established a research program designed to find transition-metal catalysts that will regioselectively reduce the heterocyclic ring in polynuclear heteroaromatic nitrogen compounds. We have, in fact, recently reported that the nitrogen heterocyclic ring in compounds known to be in coal and coal liquids, e.g., quinoline, acridine, benzoquinolines and phenanthridine can be selectively reduced under a variety of homogeneous hydrogenation conditions, i.e., water gas shift (wgs), synthesis gas (sg) and hydrogen alone (H₂) using transition-metal hydrides as catalysts.^{2a-c}

The model synthetic fuel compounds used in these studies are shown in the Chart. We found that only Fe, Mn and Co carbonyl hydrides generated under wgs (CO, H₂O, base) or sg (CO/H₂, 1:1) conditions were able to hydrogenate compounds, 1-5, while other hydrides of Rh, Ru, Re, Cr, W, Mo and Re were unreactive. Additionally, these results demonstrated the high regioselectivity for the nitrogen heterocyclic ring in compounds 1-5 under both wgs and sg conditions for Fe, Mn and Co carbonyl hydrides.

The fact that Fe, Mn and Co carbonyl hydrides did provide reduced product under wgs or sg conditions, while other mentioned catalysts did

Chart. Model Synthetic Fuel Compounds Used in the Catalytic Hydrogenations with Transition Metal Hydrides



not, may be indicative of the former compounds being poor shift-catalysts.

After examining the various parameters, we found that when we removed carbon monoxide a dramatic increase in reduced product yield occurred when we used both mononuclear and polynuclear ruthenium carbonyl compounds as catalysts e.g., $\text{RuCl}_2(\text{CO})_2(\text{P}_3\text{P})_2$ and $\text{H}_4\text{Ru}_4(\text{CO})_{12}$. Table 1 provides the information for both these catalysts in the selective reductions of compounds 1-5.

We also found that Wilkinson's catalyst, $(\text{P}_3\text{P})_3\text{RhCl}$, could selectively reduce compounds, 1-5, under rather mild conditions (80° , 350 psi H_2 , 2 hr.) in nearly quantitative yields. Furthermore, experiments with the heterogenized form of Wilkinson's catalyst, bonded to divinylbenzene-polystyrene, (2% and 20% crosslinked, ~1.1% loading, ~100:1 substrate to catalyst ratio, 80° , 24 hr.) clearly demonstrated a similar regioselectivity for the nitrogen heterocyclic ring and provides a useful example of the potential applicability of these heterogenized homogeneous catalysts in future synthetic fuel processes.³

Finally, we have also discovered that 9,10-dihydrophenanthridine can act as a hydrogen donor, but only in the presence of rhodium and ruthenium catalysts, and thus transfer its hydrogen to acceptor molecules such as quinoline.⁴ This latter result may have important implications with regards to understanding the role of metal compounds in donor-solvent coal liquefaction processes.⁵

Table 1

Reductions of Compounds 1-5 with $\text{Ru}(\text{Cl})_2(\text{CO})_2(\text{P}_3\text{P})_2$
and $\text{H}_4\text{Ru}_4(\text{CO})_{12}$ as Catalysts

Substrate	Catalyst	Products (%) ^b
<u>1</u>	$\text{Ru}_2(\text{CO})_2(\text{P}_3\text{P})_2^{\text{a}}$	1,2,3,4-tetrahydro-7,8-benzoquinoline (10)
<u>1</u>	" ^c	" (92)
<u>2</u>	" ^a	1,2,3,4-tetrahydro-7,8-benzoquinoline (0)
<u>2</u>	" ^c	" (72)
<u>3</u>	" ^a	9,10-dihydrophenanthridine (5)
<u>3</u>	" ^c	" (15)
<u>4</u>	" ^a	9,10-dihydroacridine (100)
<u>4</u>	" ^c	" (74)
<u>5</u>	" ^a	1,2,3,4-tetrahydroquinoline (42) 5,6,7,8-tetrahydroquinoline (5)
<u>5</u>	" ^c	1,2,3,4-tetrahydroquinoline (100)
<u>1</u>	$\text{H}_4\text{Ru}_4(\text{CO})_{12}^{\text{d}}$	1,2,3,4-tetrahydro-5,6-benzoquinoline (75)
<u>2</u>	" ^d	1,2,3,4-tetrahydro-7,8-benzoquinoline (8)
<u>3</u>	" ^d	9,10-dihydrophenanthridine (15)
<u>4</u>	" ^d	9,10-dihydroacridine (100)
<u>5</u>	" ^d	1,2,3,4-tetrahydroquinoline (100)

- a. Experiments were performed in a 45 ml Parr mini-reactor containing 1 mmole of substrate, 0.1 mmol $\text{Ru}(\text{Cl})_2(\text{CO})_2(\text{P}_3\text{P})_2$ in THF (12 ml), 0.2 M KOH (3 ml), 108°C, 350 psi H_2 for 5 hrs, 1-4, 2 hrs, 5.
- b. Analyzed by gas chromatography on a 12m x 0.1 mm i.d. fused silica capillary column (OV101) using an HP-5880A instrument with flame ionization and digital integration. The % product conversion was obtained by integration of product and any starting material remaining and normalizing to 100%. Products were isolated by column chromatography (Florisil) and identified by GC-MS and nmr spectroscopy (^1H , 250 MHz).
- c. 180°C, THF (12 ml), 0.1 mmole $\text{Ru}(\text{Cl})_2(\text{CO})_2(\text{P}_3\text{P})_2$, 1 mmole substrate, 350 psi H_2 for 2 hr.

- d. Experiments were performed in a 45 ml Parr mini-reactor containing 1 mmole of substrate, 0.1 mmole $H_4Ru_4(CO)_{12}$ (10:1 substrate to catalyst ratio) in 15 ml of cyclohexane with 350 psi H_2 for 2 hr at 150°C.

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