

Hydrocyanation

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This literature discussion was inspired by a talk given by Dr. Nora Radu, recipient of the 2025 ACS Award for Distinguished Service in the Advancement of Inorganic Chemistry. Although the primary focus of this will be on hydrocyanation, it is important to understand why this process is important. To do so, you should first read the brief article in C&EN (<https://cen.acs.org/materials/polymers/chemical-industry-bracing-nylon-66/96/i40>). Although slightly dated, it does provide useful background information.

- 1) Two important terms throughout this discussion will be monomer and polymer. Define these two terms.
- 2) Although it is presented in a condensed structure in this article, draw the expanded structure of Nylon-6,6.
- 3) How is Nylon-6,6 prepared? Your answer can be fairly vague and it does not require exact experimental details but should identify the monomers.
- 4) What does the term polycondensation mean?
- 5) In preparing this condensation polymer, what small molecule is generated when two monomer units come together?
- 6) Nylon-6,6 can be described as a co-polymer. What do you think is meant by this term?
- 7) What do you think is the source of the 6,6? Hint, the monomers provide a clue.
- 8) What are some of the properties and uses of Nylon-6,6 that make this polymer important?
- 9) Now that we know a little more about Nylon-6,6, how significant is this product in terms of economics? It is expected you will need to find a source for this information which you will of course, properly cite.
- 10) What does Nylon-6,6 look like?
- 11) As a reminder, this literature discussion is about hydrocyanation. Hydrocyanation is important in the production of one of the monomers. Which monomer do you think requires hydrocyanation? Why?

At this point, you will want to look at parts of the International Patent WO2001021579 which is included as a link in the LO. This patent was awarded to E. I. Du Pont de Nemours & Co. which is the parent company of Invista.

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- 12) Start by reading the Field of the Invention and Technical Background of the Invention sections which span the first two and one-half pages. What sentence from these sections that serves as the take home message.
- 13) Now read the Summary of the Invention section. In your own words, what are the significant points of this work?
- 14) You can now move on to the Hydrocyanation of Monoolefinic compounds section (page 9). What sorts of organic compounds are useful reagents in this process?
- 15) What is the importance of the last paragraph on page 11?
- 16) What important points are raised in the first three paragraphs on page 12? Why are these significant? You may wish to turn to an additional source for consideration of the third paragraph.

Finally, we turn our attention to portions of a paper detailing the hydrocyanation of butadiene (*J. Chem. Educ.* **1986**, 63, 199). Read the selected parts of this paper included with this handout before answering the following questions.

- 17) In this paper, we are provided with a little insight into the conversion of adiponitrile to hexamethylenediamine. How does this reaction occur?
- 18) Figure 1 presents the catalytic cycle proposed from the hydrocyanation of butadiene (BD) when $L = P(OEt_3)_3$. There are 10 steps in the mechanism. Classify each of the nickel compounds depicted and determine the valence and electron count for each. Provide a name or description for the reaction that is occurring in each step.
- 19) Draw structures of the two products, 3PN and 2M3BN.
- 20) The author describes the 2M3BN as undesirable. Why is that the case? As part of your answer, you should comment on the k_5/k_6 value given in the figure.
- 21) The author mentions the next step (Step II) in making hexamethylenediamine from 3PN first requires double-bond migration to give 4PN. What would 4PN look like and why is this important?
- 22) Figure 1 lists two ν_{CN} values for compounds that were observed during the catalytic process. What do these values suggest about the electron richness at the nickel center in these two compounds?

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- 23) The following table lists equilibrium constants for reaction 3 in figure 1, the ν_{CO} values for the corresponding $\text{NiL}_3(\text{CO})$ compounds and cone angles for the various L groups. Rationalize the data presented in this table.

| L | K | $\nu_{\text{CO}} (\text{cm}^{-1})$ | Cone angle |
|--|---------|------------------------------------|------------|
| $\text{PPh}(\text{OEt})_2$ | 0.03 | 2074.2 | 116 |
| $\text{P}(\text{OEt})_3$ | 0.005 | 2076.3 | 109 |
| $\text{P}(\text{OCH}_2\text{CH}_2\text{Cl})_3$ | 0.0001 | 2084.0 | 110 |
| $\text{P}(\text{O-}o\text{-tolyl})_3$ | $>10^4$ | 2084.1 | 141 |

- 24) Figure 2 presents the catalytic cycle proposed from the hydrocyanation of ethylene when $\text{L} = \text{P}(\text{O-}o\text{-tolyl})_3$. This combination allowed for more of the intermediate species to be detected and also provided some insight into the formation of side products. Classify each of the nickel compounds depicted and determine the valence and electron count for each. Provide a name or description for the reaction that is occurring in each step. The mechanism can be thought of as starting in the lower left corner.
- 25) The $\text{P}(\text{O-}o\text{-tolyl})_3$ ligand allowed the author to study the coordination of various alkenes to $\text{Ni}(\text{P}(\text{O-}o\text{-tolyl})_3)_3$. Some of these results are shown in the table below. What can you conclude from these results, in particular, why is it important in relation to the statement about step II the author made in the Background section?

| Entry | Olefin | K |
|-------|---|----------------------|
| 1 | $\text{H}_2\text{C}=\text{CHCN}$ | 4.0×10^4 |
| 2 | $\text{H}_2\text{C}=\text{CH}_2$ | 2.5×10^2 |
| 3 | 2M3BN | 6.0 |
| 4 | 4PN | 3.6 |
| 5 | $\text{H}_2\text{C}=\text{CHCH}_2\text{CH}_2\text{CH}_2\text{CH}_3$ | 0.5 |
| 6 | <i>trans</i> - $\text{CH}_3\text{CH}=\text{CHCH}_2\text{CN}$ | 1.7×10^{-2} |

- 26) Finally, the author mentions that the addition of a Lewis acid to the hydrocyanation process and this can increase both the catalyst turnover (moles of product/moles of catalyst) and the selectivity in terms of the product formed (unbranched/branched). For example, for the reaction depicted in Figure 3, the addition of BPh_3 to the system results in 98% formation of the linear product whereas without the BPh_3 the linear product accounts for 78% of the product. The BPh_3 is proposed to act as a Lewis acid and coordination with the nitrogen atom of the cyanide ligand. How might this account for the difference in product selectivity?