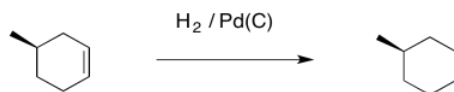


## 5.5: Oxidative Addition in Action- Catalytic Hydrogenation

Catalytic hydrogenation is a tremendously important reaction. It is an essential step in the synthesis of many fine chemicals as well as bulk commodities. In catalytic hydrogenation, a pair of hydrogen atoms are added across a double bond, turning an alkene into an alkane.



In general, the reaction requires a large excess of hydrogen gas, often under high pressure. The reaction can be performed under either homogeneous or heterogeneous conditions. Homogeneous reactions employ a soluble catalyst. Soluble catalysts are those that dissolve under the reaction conditions; they often provide superior control over the reaction. Heterogeneous catalysts do not dissolve; they are solids that sit on the bottom of the reaction, like sand in a lakebed. One of the advantages of heterogeneous catalysts is that they can easily be filtered away from the rest of the reaction, making purification of the product much more straightforward.

### ? Exercise 5.5.1

Indicate whether the following mixtures are homogeneous or heterogeneous.

a) Kool-aid b) a glass of pop with ice c) orange juice d) cranberry juice

**Answer a**

homogeneous

**Answer b**

heterogeneous

**Answer c**

heterogeneous

**Answer d**

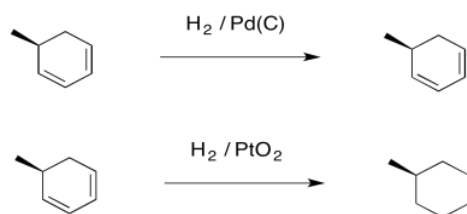
homogeneous

Because of the importance of hydrogenation, a number of catalysts have been developed over the years that are capable of performing the reaction. There are a number of motivations for working on catalyst development. One reason is speed: the faster the catalyst, the more product can be made and the more economical the process. Another reason is selectivity. Suppose there are two double bonds present in a molecule. Maybe you only want to hydrogenate one of these double bonds. By choosing the proper catalyst, you may be able to do that.

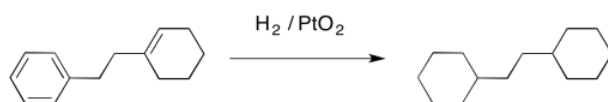
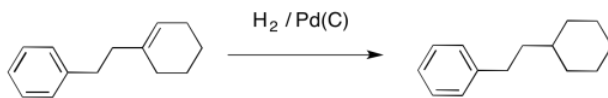
Let's take a look at a few different examples of catalysts with different selectivities.

Perhaps the most commonly used catalyst is palladium metal, a heterogeneous catalyst. Very often, expensive metals like palladium are not used in their pure state. For example, palladium is often dispersed on a "solid support", such as carbon. There are a couple of benefits of doing that. First, the expensive palladium metal is stretched a little further by mixing it with carbon, which is much cheaper. Usually, this mixture is about 5% palladium and 95% carbon, although different compositions can be used. In addition, use of a solid support helps to spread the metal particles out spatially. When the metal isn't all clumped together, it has an increased surface area. That means there are more places available for hydrogen and alkenes to bind and undergo the hydrogenation reaction. Finally, a solid support often tunes the reactivity of the metal that is stuck to it. The solid support might change the rate of the reaction or alter the selectivity because of interactions between the metal and the support.

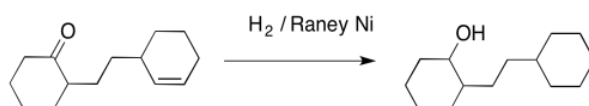
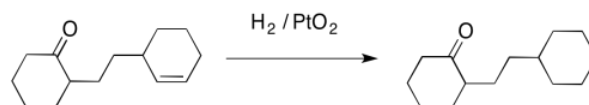
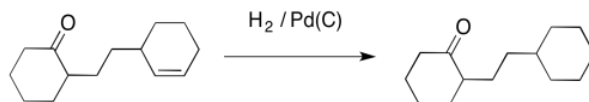
Palladium on carbon, or Pd/C, provides an example of what we mean by selectivity. It is very good at adding hydrogen to alkenes. It can hydrogenate alkynes, too. However, it is not very good at hydrogenating more stable double bonds, such as those in conjugated dienes, or in benzene or other aromatics. In contrast, platinum oxide is much more general, hydrogenating regular alkenes and also conjugated ones.



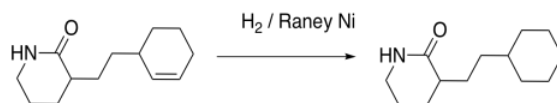
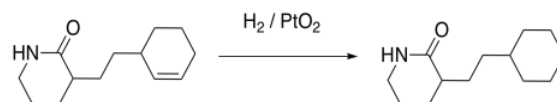
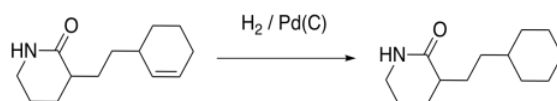
Under the right conditions, platinum oxide can even be used to hydrogenate benzene. That usually means very high pressure of hydrogen gas.



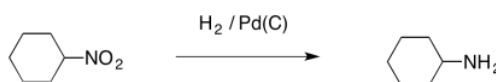
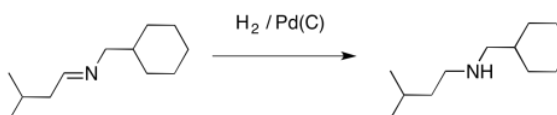
Also, hydrogenation with palladium doesn't work very well with carbonyls. It usually won't reduce aldehydes or ketones. You may remember that other reducing agents (compounds that add hydrogen to carbon atoms) such as  $\text{LiAlH}_4$  can react with carbonyls quite easily, so palladium with hydrogen is very complementary to those reagents. Even  $\text{PtO}_2$  can't induce hydrogen to add across a carbonyl, although another heterogeneous catalyst, a ferocious one called Raney Nickel, can do the job.



However, not even Raney Nickel does very well at hydrogenating more stable carbonyls, such as amides, esters and carboxylic acids. Those are the ones at the bottom of the energetic "ski hill", so they are the least reactive carbonyls. They are difficult to hydrogenate, and are usually left alone.

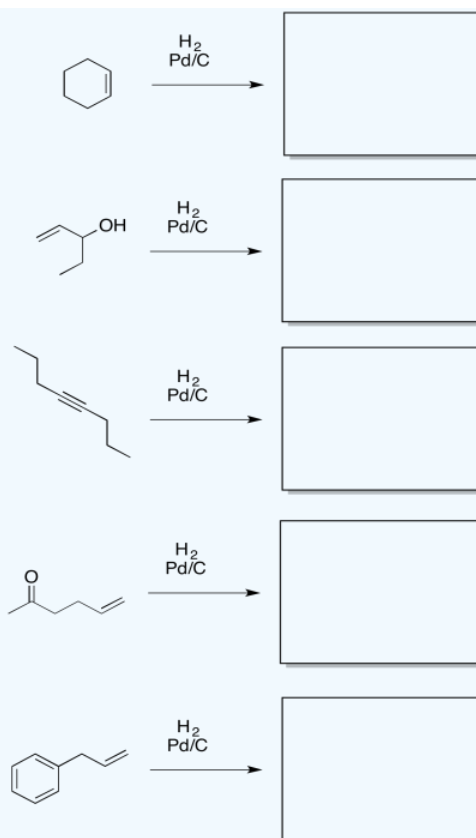


On the other hand, palladium does just fine with some seemingly related compounds, containing imines and nitro groups. Although these groups contain multiple bonds and nitrogen, they do not have the same stability of amides. Imines and nitro groups behave a little more like simple carbonyl compounds when it comes to hydrogenation.

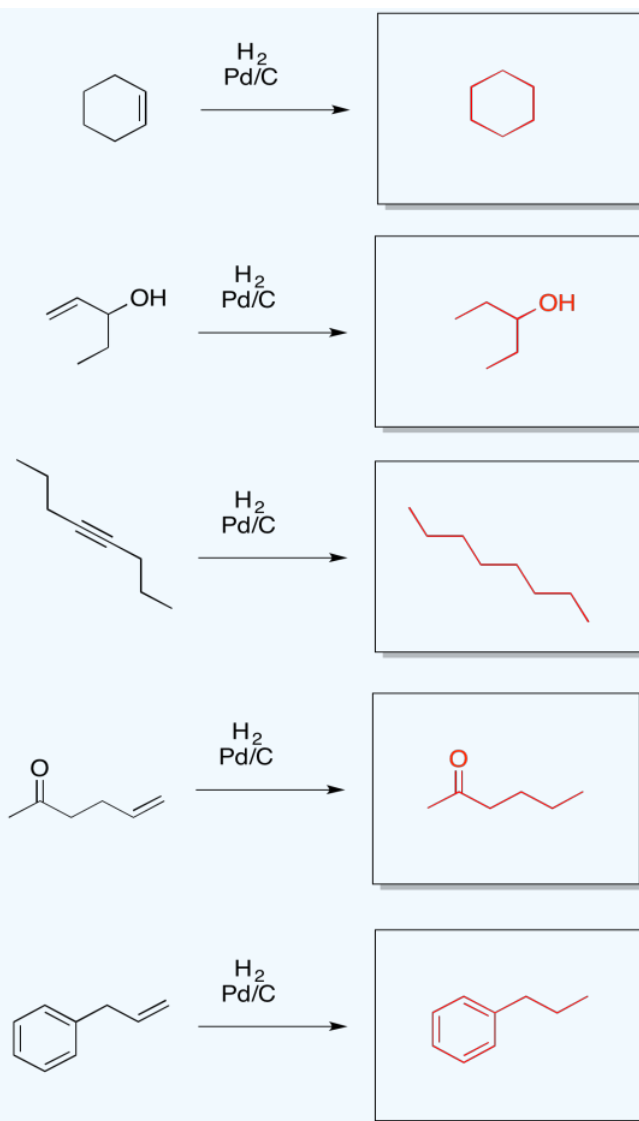


### ? Exercise 5.5.2

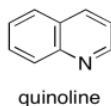
Provide products for the following reactions.



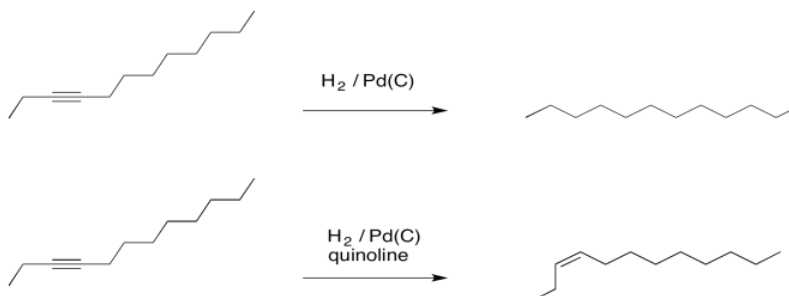
**Answer**



We can make the palladium catalyst even more selective by preparing it in a different way. Lindlar's catalyst is a very dramatic example of how reactivity can be tuned by using different compositions. To make Lindlar's catalyst, palladium is supported on calcium carbonate rather than carbon, together with other components, such as lead acetate and quinoline. That last component turns out to be the key to Lindlar's catalyst. It tunes the reactivity so that the catalyst can react with alkynes but not with alkenes.

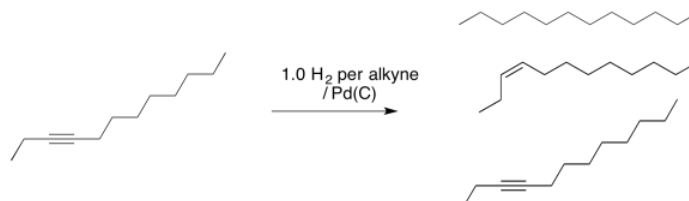


As a result, if a compound is hydrogenated with a palladium catalyst in the presence of quinoline, an alkene is produced. Without the quinoline, you would get an alkane.



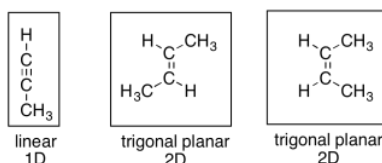
Normally, if a catalyst hydrogenates an alkyne, no alkene is observed. That's because the alkene also reacts under the same conditions and is quickly converted to an alkane.

Not so fast, you say. If we just add one equivalent of hydrogen (that is, one molecule of hydrogen for every molecule of alkyne) then the reaction will stop after forming an alkene. That's very clever of you. However, you've missed a couple of important concepts. First of all, we are never dealing with individual molecules when we run a reaction; instead, we are dealing with vast numbers of molecules at a time. That means we will deal with statistical distributions. Maybe some molecules of hydrogen react with alkyne to produce alkene. Maybe some molecules go ahead and react with that alkene to produce alkane. Now, if we only added enough hydrogen for every alkyne to react with one  $H_2$ , and some of them have already reacted with two, then somebody will be left out. There will be some leftover alkyne, too. That means we have made a mixture of alkyne, alkene and alkane.

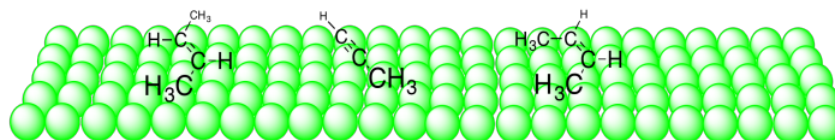


The other missing concept is that hydrogenation reactions usually run under a high pressure of hydrogen gas. That means many equivalents of hydrogen are needed in order to push the reaction forward.

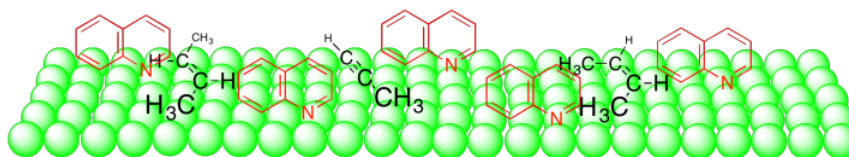
How does the presence of quinoline change the catalyst so dramatically? It seems that the answer is based on steric crowdedness. Although alkenes are flat, and don't seem very crowded, they may be crowded compared to an alkyne, which is linear. That difference makes alkynes even more reactive than alkenes with respect to hydrogenation.



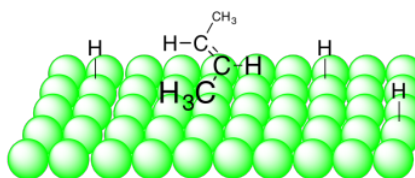
When these compounds bind to the surface of the catalyst, the alkyne takes up less space than the alkenes. It mostly lies along one dimension, whereas the alkenes are spread out into two dimensions.



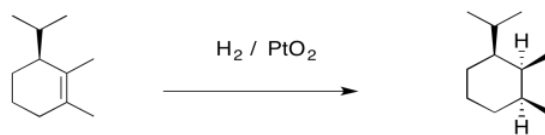
The quinoline seems to simply take up space when it binds to the surface of the catalyst. As a result, the wider alkene can't bind as well as the narrow alkyne.



So it turns out that Lindlar's catalyst is a big deal. It provides a very selective reaction: production of an alkene from an alkyne. Furthermore, it doesn't just make any alkene. It only makes *cis*-alkenes. That's because the hydrogen atoms are both delivered from the surface of the metal. The alkyne binds to the surface of the metal and accepts the hydrogen atoms from that surface. As a result, both hydrogens end up on the same side of the new double bond. The alkene formed is then a *cis*-alkene.

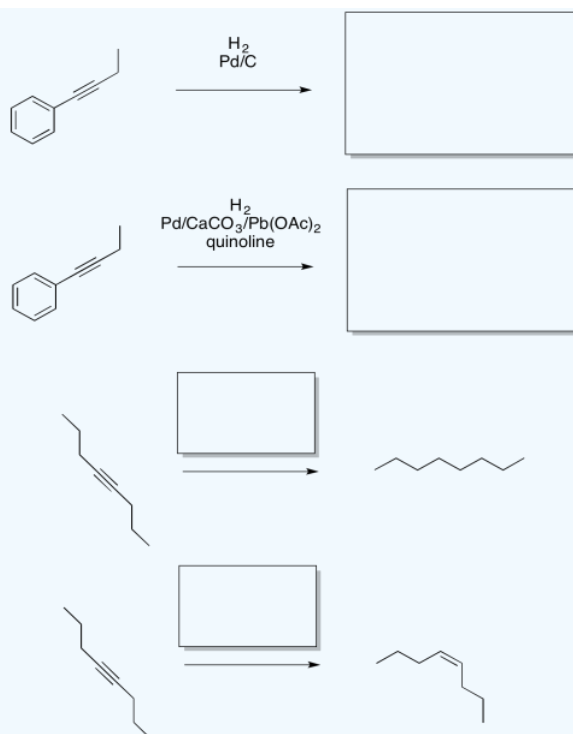


The addition of two hydrogen atoms to the same side of the molecule is not limited to Lindlar's catalyst. It's a general feature of catalytic hydrogenation. As a result, catalytic hydrogenations are often diastereoselective; they result in the formation of one diastereomer, but not the other.

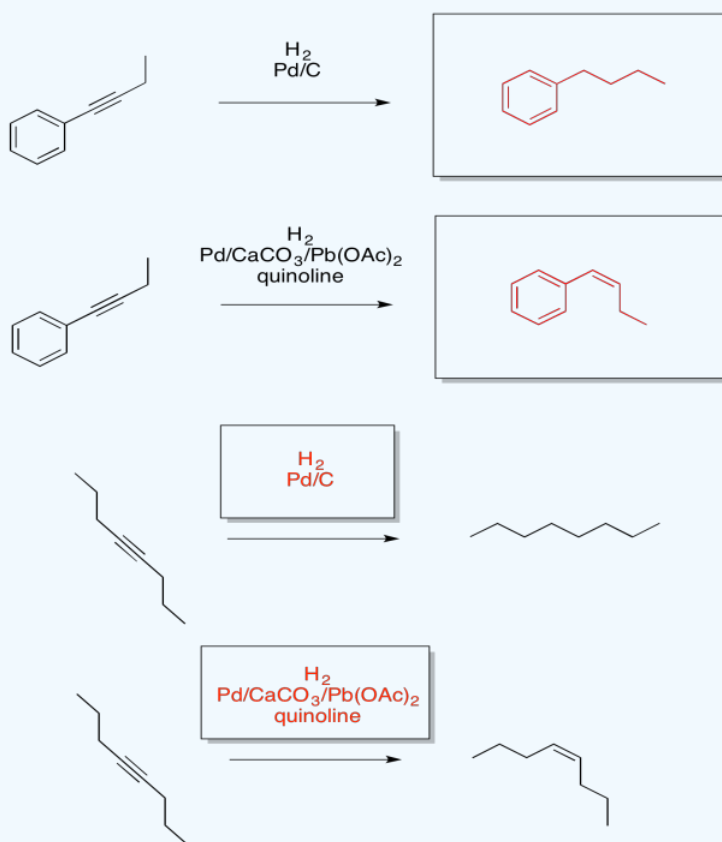


### ? Exercise 5.5.3

Provide the missing reagents or products for the following reactions.



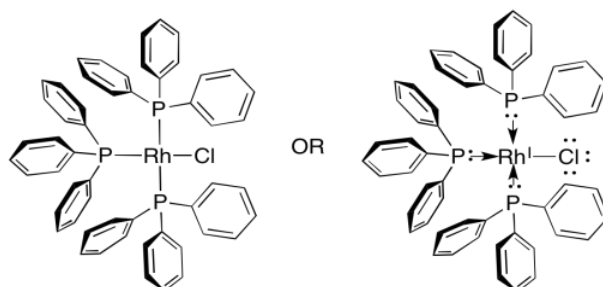
**Answer**



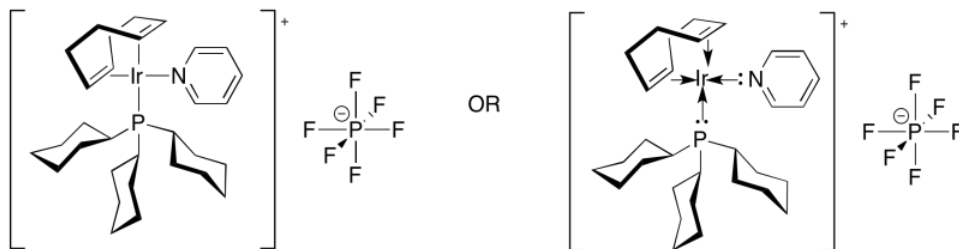
What about homogeneous catalysts? The most common one is Wilkinson's catalyst,  $(\text{Ph}_3\text{P})_3\text{RhCl}$ . Wilkinson's catalyst, like Pd/C, is good at reacting with alkenes but leaving polar bonds alone. It is also highly selective, reacting only with the least sterically



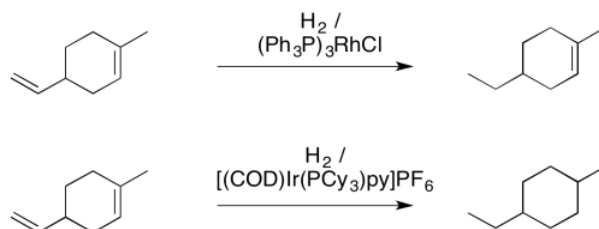
crowded alkenes. It only reacts with monosubstituted and disubstituted alkenes. If an alkene has fewer than two hydrogens attached to the double bond, Wilkinson's catalyst leaves it alone.



In contrast, Crabtree's catalyst,  $[(\text{COD})(\text{PCy}_3)(\text{py})\text{Ir}]\text{PF}_6$  is a much more reactive catalyst. In part, that's because it is a more electrophilic, cationic catalyst; the  $\text{PF}_6$  is a non-reactive counterion. In addition, Crabtree's catalyst contains a sacrificial alkene ligand. COD is cyclooctadiene, a bidentate ligand that contains two double bonds. What happens to that ligand when the catalyst is exposed to hydrogen? It gets hydrogenated, of course. Without double bonds, it can no longer be a ligand. That leaves the catalyst with two open coordination sites, although really these sites are occupied by solvent molecules. Nevertheless, the solvent molecules bind only loosely, and can easily leave to make room for an alkene.

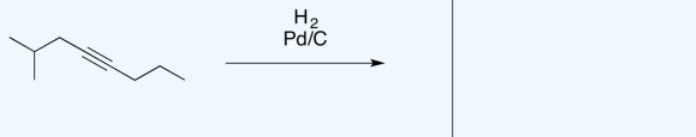
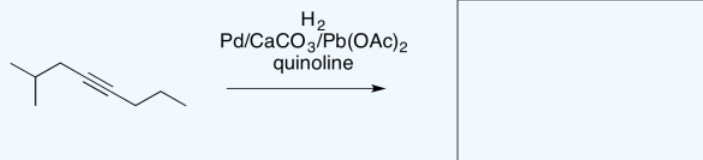
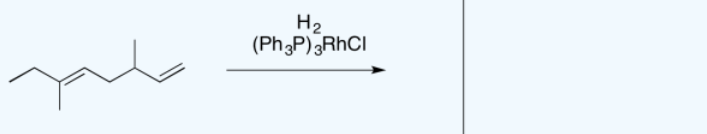
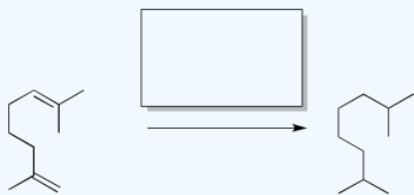
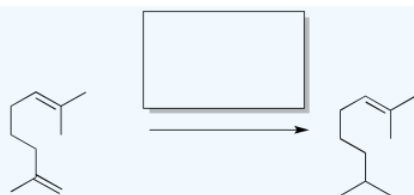


As a result, Crabtree's catalyst is much less sensitive to steric crowding. Unlike Wilkinson's catalyst, it is perfectly capable of hydrogenating trisubstituted or even tetrasubstituted alkenes.

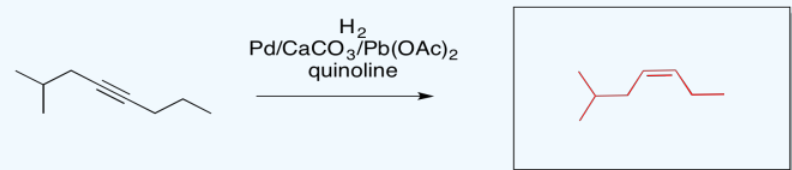
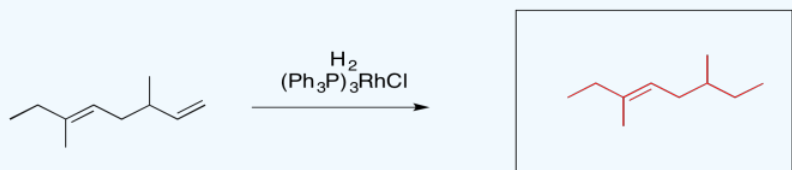
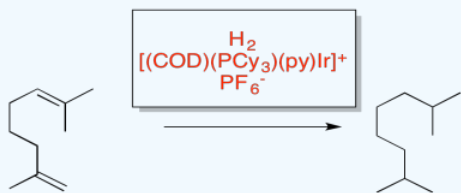
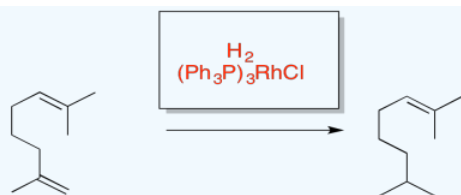


#### ? Exercise 5.5.4

Provide the missing reagents or products in the following reactions.

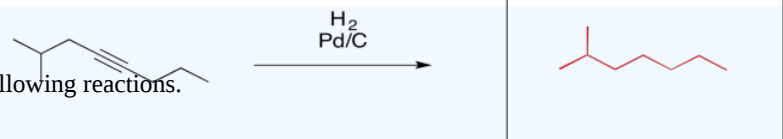


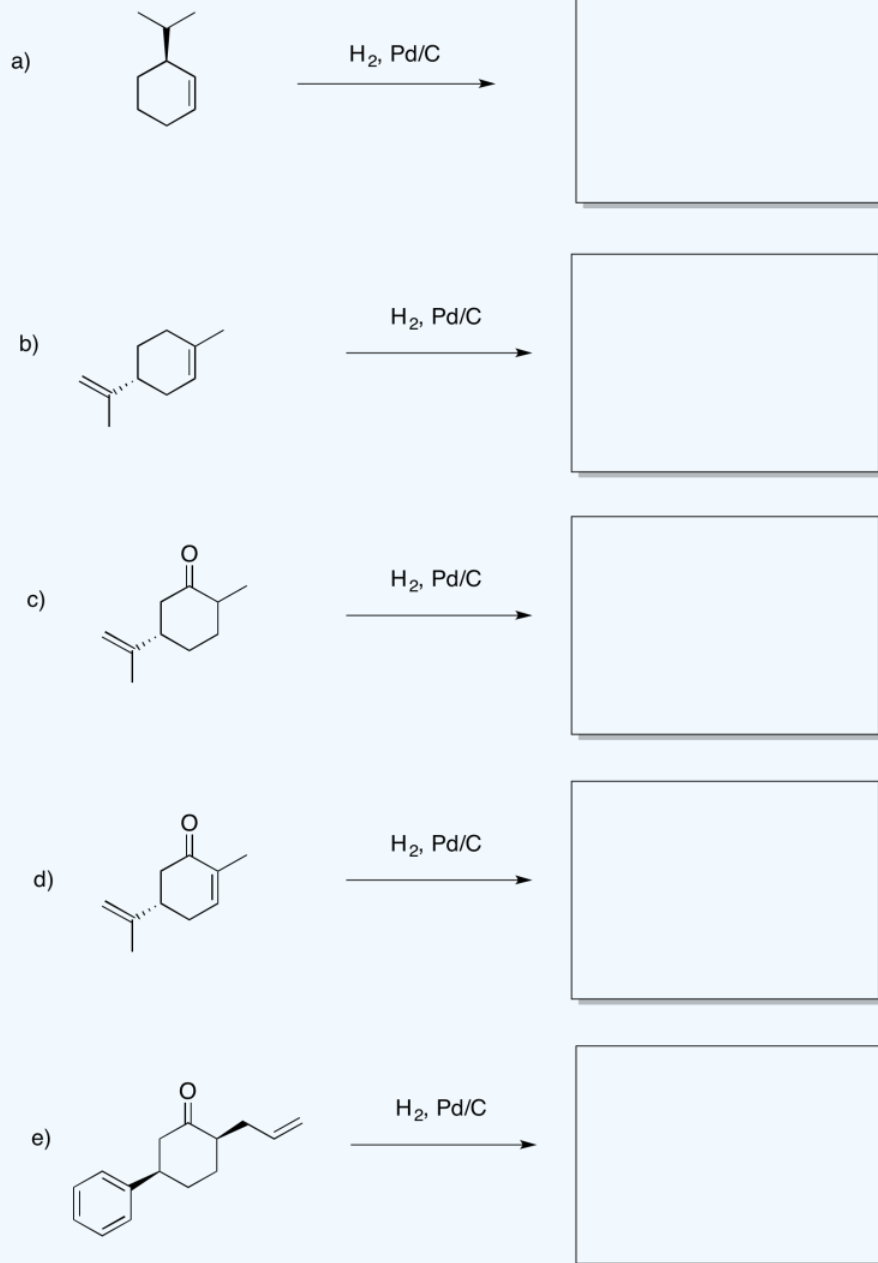
Answer



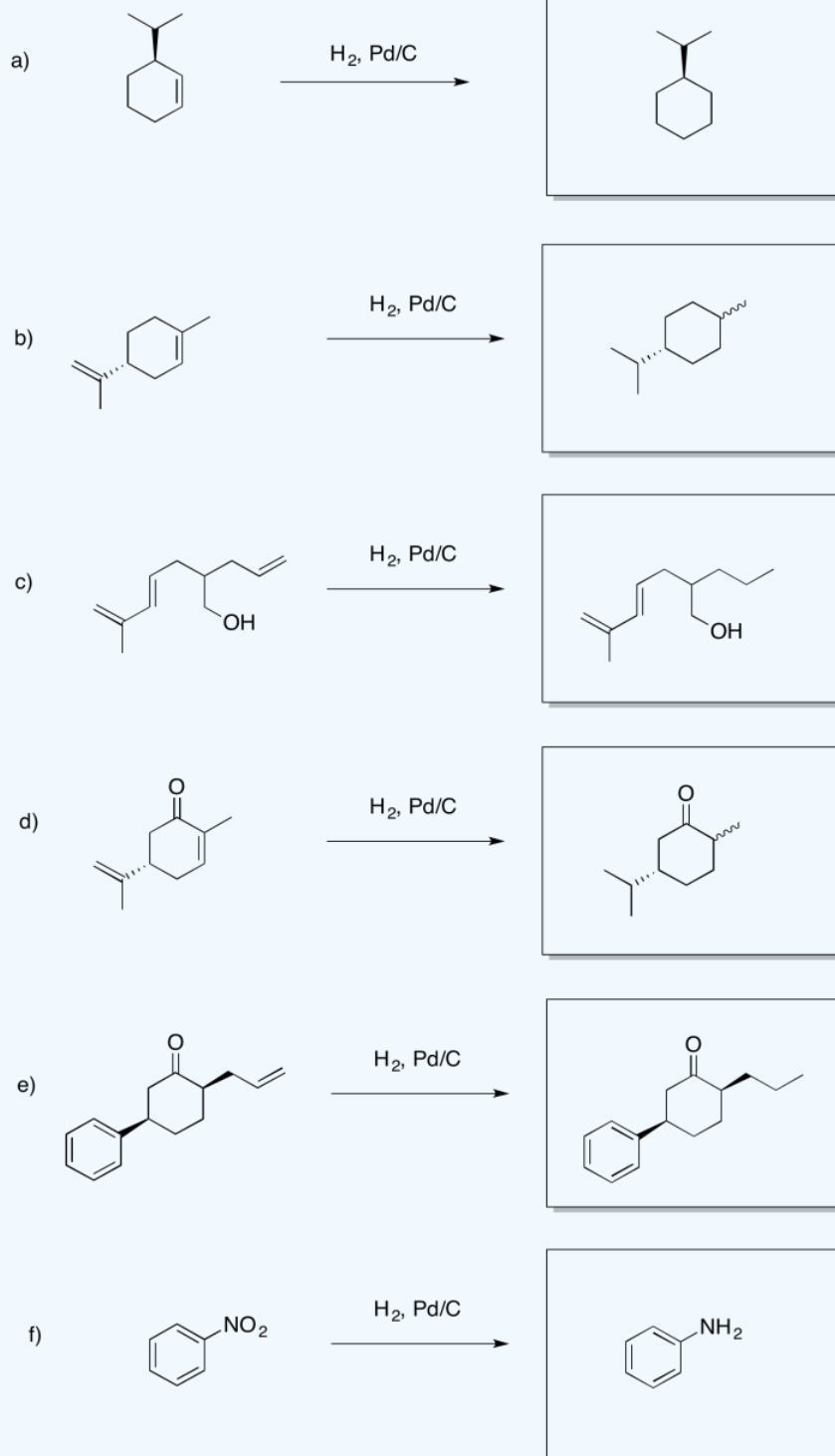
### ? Exercise 5.5.5

Provide products for the following reactions.



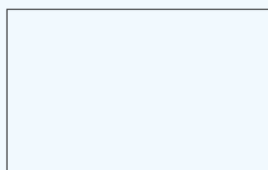
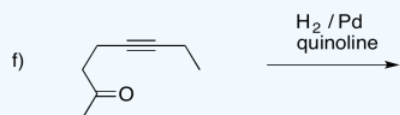
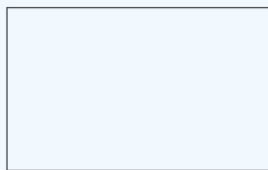
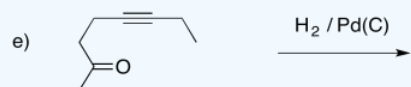
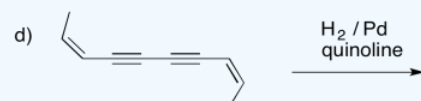
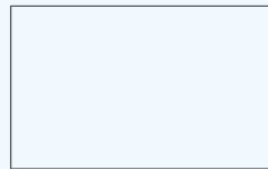
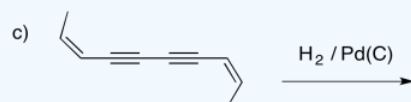
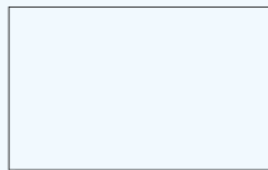
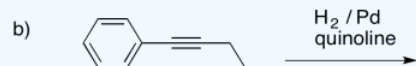
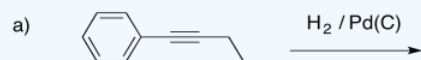


Answer

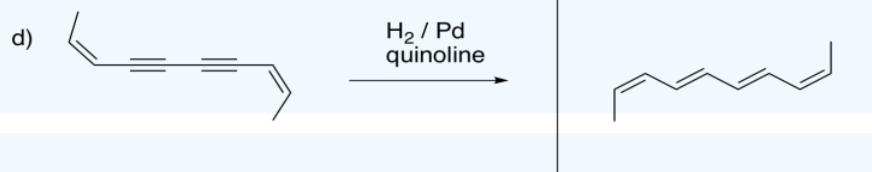
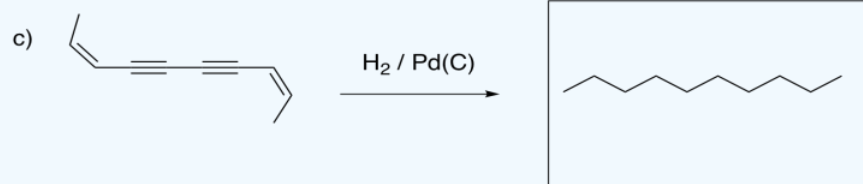
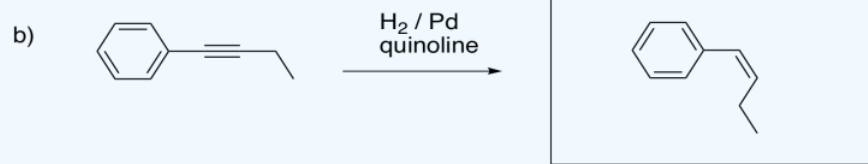
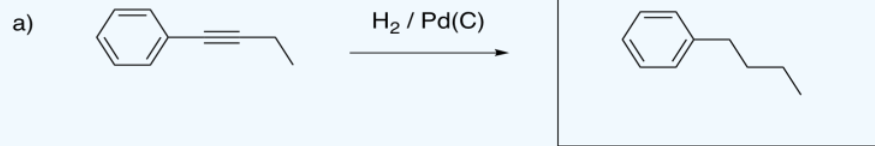


### ? Exercise 5.5.6

Provide products for the following reactions.

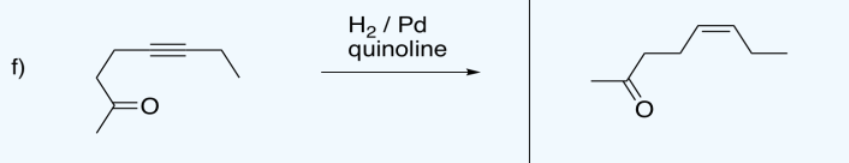
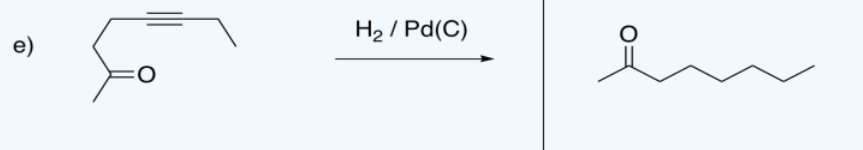


Answer

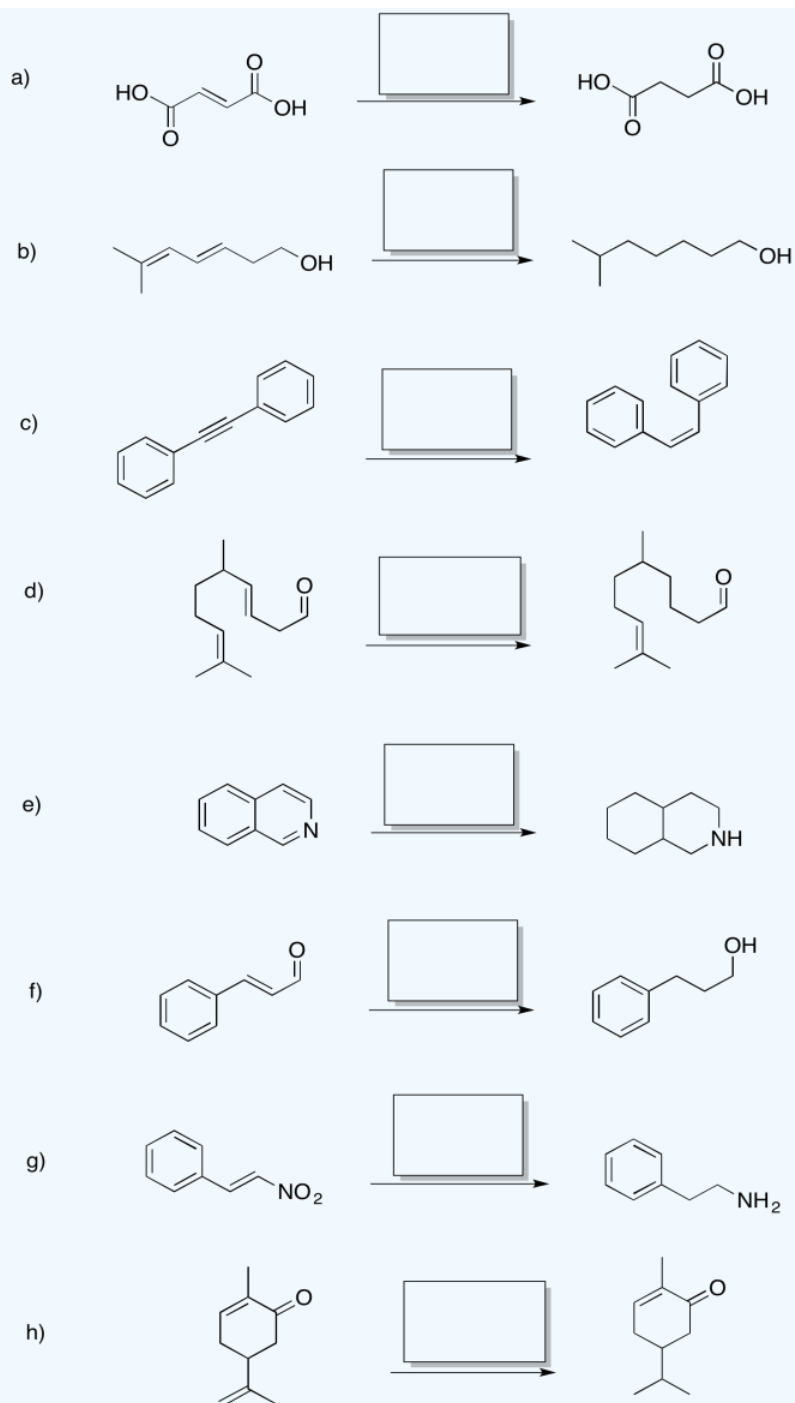


### ? Exercise 5.5.7

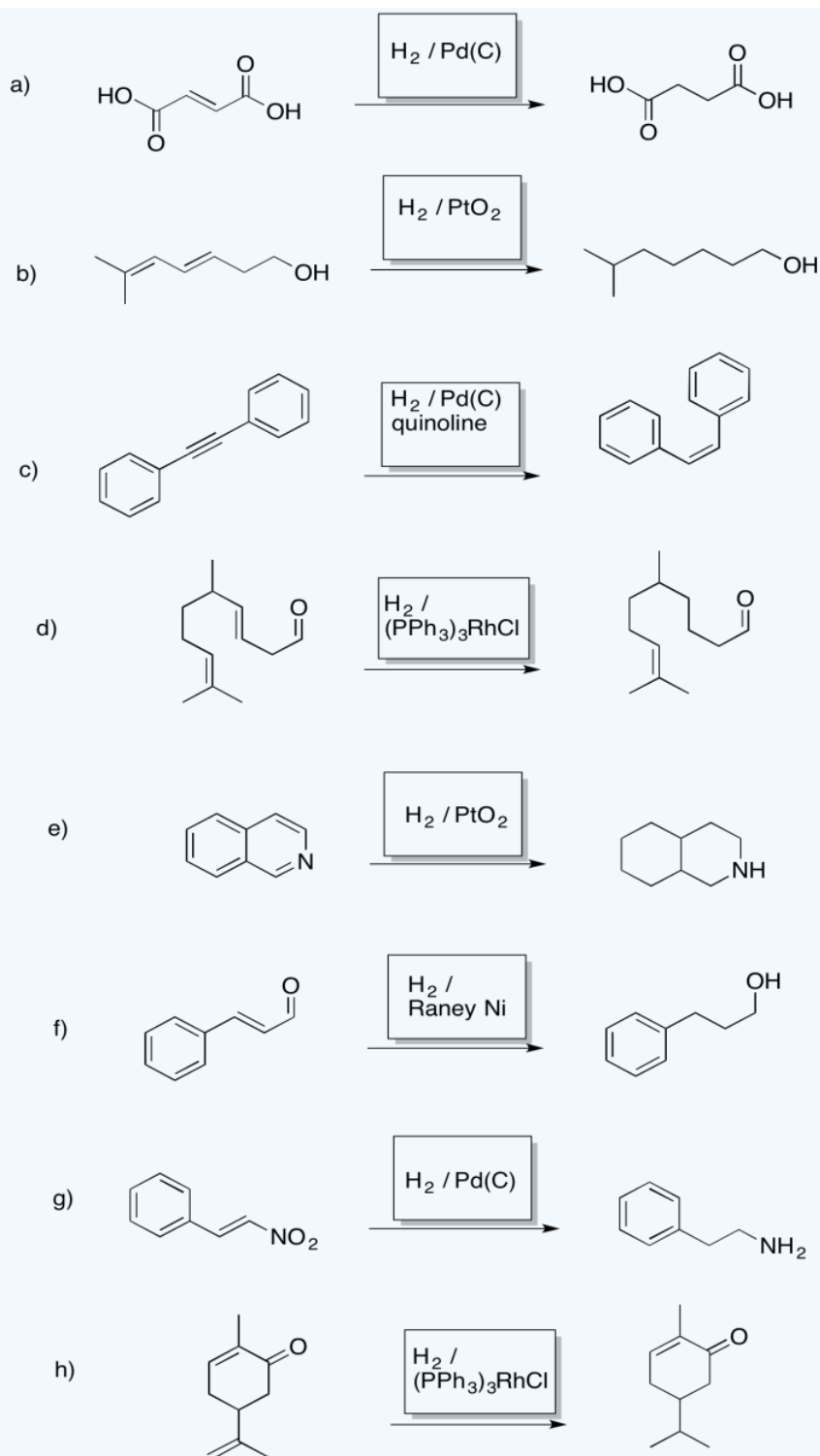
Provide reagents for the following reactions.







Answer



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