

HYDROGENATION OF CONJUGATED CARBON-CARBON DOUBLE BONDS USING THE
 $K_3[Co(CN)_5H]$ CATALYST UNDER PHASE TRANSFER REACTION CONDITIONS

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Although the hydrogenation catalyst $K_3[Co(CN)_5H]$ has been known for a long time,¹ it has not proven to be of general synthetic utility. This is surprising in light of the facts that it is easy and inexpensive to prepare, will hydrogenate carbon-carbon double bonds conjugated to virtually any other unsaturated functionality, and will generally not react with isolated double bonds or other functionality. The main problem has been simply that the amount of substrate that can be hydrogenated for each equivalent of the catalyst is low. In fact, the catalyst has been generally used in approximately stoichiometric amounts² or even in considerable excess.³ Other problems that have arisen with this catalyst are that excess substrate frequently inhibit the reaction, only limited control of regiochemistry in the hydrogenation of dienes can be achieved by varying the CN^-/Co ratio used to prepare the catalyst, and the lifetime of the catalyst is relatively short, especially at low CN^-/Co ratios. Also, many of the substrates that have been hydrogenated are insoluble in the water medium of this catalyst.

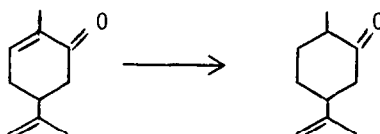
In order to solve these problems, two new approaches have been taken with this catalyst to make it more useful. The first was to use aqueous micellar solutions for these reactions.⁴ The second and more useful approach, which is reported here, is to carry out these reactions under phase transfer reaction conditions.

In a typical reaction, 2.2 mmol of the catalyst (CN^-/Co ratio = 5.2) is prepared under a H_2 atmosphere in 40 ml of H_2O containing 2.2 mmol of NaOH and 2.2 mmol of benzyltriethylammonium chloride as the phase transfer reagent. Benzene (20 ml) is then added followed by 5 ml of 2-methyl-1,3-butadiene (isoprene). The reaction is over in 12 hours and gas chromatographic analysis indicated no starting material and 2-methyl-2-butene as the only product. Distillation gave 87% isolated yield of the product. The phase transfer reagent is critical because if omitted even 2 ml of substrate will not completely hydrogenate under the same conditions after 40 hrs at which time the catalyst has completely decomposed (gas chromatographic analysis yielded 20% starting material, 74% 2-methyl-2-butene, 5% 2-methyl-1-butene and 1% 3-methyl-1-butene). Control experiments demonstrated that the high selectivity under phase transfer reaction conditions is not caused by isomerization of 1-butene products by the catalyst or other possible cobalt species in these solutions. The largest sample of isoprene that could be conveniently hydrogenated using 2.2 mmol of the catalyst is 6 ml. If 6.6 mmol of catalyst is used, 15 ml of substrate is readily regiospecifically hydrogenated in 13 hours. In a similar reaction with 1,3-pentadiene, the only product is trans-2-pentene isolated in 80% yield. The reaction of 2,3-dimethyl-1,3-butadiene yields a mixture containing 80% of 2,3-dimethyl-2-butene and 20% of 2,3-dimethyl-1-butene.

Note that in addition to acting as the phase transfer reagent in these reactions, the large organic cation inhibits decomposition of the catalyst. Thus, in the presence of the large cation, the aqueous phase of these reaction solutions is still yellow (the color of the catalyst) and visually homogeneous even after two days; whereas if it is not present, the catalyst has completely decomposed.

The hydrogenation of α,β -unsaturated ketones under these conditions is also successful. Thus, 3-buten-2-one is hydrogenated to 2-butanone in 60% yield and 3-methyl-3-buten-2-one to 3-methyl-2-butanone in 85% yield. These hydrogenation reactions are not as rapid as with the dienes but are still reasonable for synthetic scale reactions. Using 6.6 mmol of the catalyst, 4 ml of 3-methyl-3-buten-2-one is hydrogenated in one day. These slower rates are presumably caused by the fact that the initial alkyl-cobalt complex which forms upon the addition of the first equivalent of the catalyst is stable (it is visually observed, turning the yellow aqueous layer of the catalyst red), thus tying up the catalyst and making the addition of the second hydrogen more difficult.⁵

The reaction of *l*-carvone proceeds as shown below with only the conjugated carbon-carbon double bond being hydrogenated. The isolated yield was 93%. In this reaction, the trans:cis



ratio is 6:1 as compared to the thermodynamic equilibrium mixture of 9:1.

The α,β -unsaturated aldehyde propenal is also hydrogenated to propanal but only in 20% yield. In this reaction a substantial amount of polymer is formed.

The above reactions demonstrate clearly that the catalyst $K_3[Co(CN)_5H]$ is very useful in the hydrogenation of conjugated carbon-carbon double bonds especially for α,β -unsaturated ketones when used in a two-phase system in the presence of a phase transfer reagent. The full scope of this reaction is being investigated at present.

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