g, 0.0074 mol) and 1.4 g of potassium hydroxide in 20 ml of 50% aqueous methanol was heated at reflux for 3.5 hr. The solution was cooled and acidified to pH 2 with concentrated hydrochloric acid. The solid material was filtered, washed with water, and dried to give 2.0 g of hydroxy acid V, mp 75–76°. A mixture melting point with the acid obtained from the hydrolysis of polyester II was not depressed and the ir spectra were superimposable.

Registry No.—Ia, 34289-54-8; Ib, 34289-55-9; polymer of Ib, 34287-66-6; II, 34268-90-1; III, 34289-56-0; IV, 34289-57-1; V, 34289-58-2; *N*,*N*-dimethyl-3-hydroxy-4-(*n*-hexadecylthio)butyric acid amide, 34289-59-3.

Hydrogenation of Cinnamic Acids with Iridium(I) Catalysts. Effect of Various Ligands

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Recent communications have described olefin hydrogenations using Ir(olefin)$_2$L$_n$ based systems as catalysts.[1-3] Green and coworkers have noted ligand and solvent effects on the rate of hydrogenation of 1,5-cyclooctadiene and 1-hexene with these systems.[2] Van der Ent *et al.*, have studied the rate of hydrogenation of 1-hexene in benzene as a function of the ligand-iridium ratio (R).[3] With L = Ph$_3$P the maximum rate was observed at R = 2 at which point the rate is approximately ten times the rate at R = 1. I now report that *α,β*-unsaturated acids can also be reduced with these iridium catalysts and note some important rate effects based on ligand type, ligand ratio, and the presence or absence of chloride ligand.

Cinnamic acid and *α*-methylcinnamic acid have been hydrogenated to *β*-phenylpropionic acid and *α*-methyl-*β*-phenylpropionic acid, respectively, with [Ir(1,5-cyclooctadiene)Cl]$_2$ and various phosphines in MeOH solvent at 100° and 75 psig of H$_2$. Table I records the per cent reduction after 2 hr under these conditions with a substrate–catalyst ratio of 400. It is found that cinnamic acid is reduced faster than *α*-methylcinnamic acid for all three phosphines (catalyst system A).

The importance of a 2:1 phosphine–iridium ratio as against a 1:1 ratio in the reduction of *α*-methylcinnamic acid (catalyst system A *vs.* B) manifests itself with the less basic phosphines, Ph$_3$P and Ph$_2$PEt, but entirely disappears with PhPEt$_2$. In the latter case the rates of reduction are identical for both systems. Even with Ph$_2$PEt the rate differences are not nearly so pronounced as with Ph$_3$P.[4]

Hydrogenation of *α*-methylcinnamic acid in the absence of chloride ligand (system C) was achieved by use of isolated [Ir(1,5-cyclooctadiene)L$_2$]BF$_4$ as the catalyst. In this case the reduction proceeds much more rapidly with all three phosphines than the same reduction in the presence of chloride (system A).

Table I

Per Cent Reduction at 2 Hr[a]

Catalyst[b]	Cinnamic acid A	*α*-Methylcinnamic Acid A	B	C
Ph$_3$P	82	38	1.5	92
Ph$_2$PEt	55	19	6	39
PhPEt$_2$	64	25	25	78

[a] Reaction cessation at 2 hr was chosen arbitrarily. All catalyst systems were still alive at this point with the possible exception of system B with Ph$_3$P and Ph$_2$PEt. In these cases partial loss of catalyst by iridium plate-out was observed early in the reaction. [b] A = PR$_3$/Ir = 2.0 [Ir(1,5-cyclooctadiene)Cl]$_2$ and PR$_3$ mixed *in situ;* B = PR$_3$/Ir = 1.0 [Ir(1,5-cyclooctadiene)-Cl]$_2$ and PR$_3$ mixed *in situ;* C = Used isolated [Ir(1,5-cyclooctadiene)(PR$_3$)$_2$]BF$_4$: Prepared by previously published general procedures for analogous rhodium and iridium complexes. *Cf.* ref 1 and 2 and R. R. Schrock and J. A. Osborn, *J. Amer. Chem. Soc*, **93**, 2397 (1971).

One further observation of note is that the rate of hydrogenation of cinnamic acid with L = Ph$_3$P was considerably reduced when no effort was made to eliminate the presence of atmospheric oxygen. The inhibitory effect of oxygen with this iridium catalyst is exactly the opposite of the rate-enhancing effect of oxygen in the reduction of maleic acid in DMA catalyzed by IrX(CO)(Ph$_3$P)$_2$ reported by James and Memon.[5] I have repeated the effect reported by these authors in the reduction of cinnamic acid with IrCl(CO)(Ph$_3$P)$_2$ in both DMA and MeOH.

Experimental Section

All hydrogenations were conducted in glass Fischer–Porter aerosol compatibility tubes with 20 mmol of substrate and 0.05 mmol of catalyst dissolved in 25 ml of anhydrous MeOH. For systems A and B, [Ir(1,5-cyclooctadiene)Cl]$_2$[6] and the phosphines were premixed in 5 ml of MeOH under N$_2$ for 15 min prior to the addition of substrate. All reaction mixtures were vigorously sparged with nitrogen prior to being pressured to 75 psig of H$_2$. Reaction timing commenced upon placement of a 100° oil bath under the reaction vessel and activation of a magnetic stirrer.

Analyses were performed by integrating the CDCl$_3$ nmr spectra of solvent-stripped reaction aliquots. The reported integrals for cinnamic acid are actually corrected from observed figures to allow for integral deviations observed from known values in standard mixtures. In the case of *α*-methylcinnamic acid and *α*-methyl-*β*-phenylpropionic acid, standard mixtures integrated correctly.

Registry No.—Cinnamic acid, 621-82-9; *α*-methylcinnamic acid, 1199-77-5.

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[1] J. R. Shapley, R. R. Schrock, and J. A. Osborn, *J. Amer. Chem. Soc.*, **91**, 2816 (1969).

[2] M. Green, T. A. Kuc, and S. N. Taylor, *J. Chem. Soc. D*, 1553 (1970).

[3] H. van Gaal, H. G. A. M. Cuppers, and A. van der Ent, *ibid.*, 1694 (1970).

[4] Van der Ent's work on phosphine–iridium ratios (ref 3) was confined to Ph$_3$P and the hydrogenation of 1-hexene. It is interesting to speculate whether the rate differences would also disappear in this case with use of PhPEt$_2$ instead of Ph$_3$P.

[5] B. R. James and N. A. Memon, *Can. J. Chem.*, **46**, 217 (1968).

[6] Strem Chemicals, Inc.

Reduction of *α*-Substituted Acetoacetate Enolates with Lithium Aluminum Hydride

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In connection with a current synthesis project we had occasion to examine the reduction of *α*-substituted ethyl acetoacetate enolates. A recent report concern-