

with time at the expense of the 2-heptenes in the hydrolysate. The disappearance of hydrocarbon corresponding to unrearranged Grignard reagent had a half-life of about 12 hr at 155°, and, from the proportions of heptenes and cyclized materials in the solvent fraction, the half-life for cyclization was estimated as 39 hr, with a half-life of about 17.5 hr for attack on solvent. The Grignard reagent, as originally prepared, contained about 2.5% cyclized material, and no further change was noted after heating for 20 hr at 114°.

**Registry No.**—2-( $\Delta^2$ -Cyclopentenyl)ethyl bromide, 21297-99-4; 2-( $\Delta^2$ -cyclopentenyl)ethyl chloride, 21298-00-0.

### Homogeneous Catalytic Hydrogenation of Unsaturated Organic Compounds<sup>1</sup>

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This paper describes an extensive investigation on the scope and limitations of tris(triphenylphosphine)chlororhodium(I) as a catalyst for homogeneous hydrogenation of unsaturated compounds in organic syntheses.<sup>2</sup> The literature to date deals with the feasibility of this catalyst for the hydrogenation of only simple olefins containing various reducible functional groups.<sup>3-7</sup> We have extended the scope of this catalyst for the reduction of highly substituted internal olefins containing a wide variety of reducible functional groups such as carboxylic acids, esters, aldehydes, ketones, nitriles, etc.

The hydrogenations were carried out in deoxygenated benzene or absolute ethanol at 40–60° and 60–100-psi pressure for 12–18 hr. The reaction products were studied by nmr and ir spectroscopy. In the case of incomplete hydrogenations the product ratio was calculated from the nmr spectra of the reaction mixtures. The results for  $\alpha,\beta$ -unsaturated carboxylic acids and esters are summarized in Table I. The enormous synthetic utility of this catalyst for the reduction of a carbon-carbon double bond in the presence of carboxyl and ester functions is illustrated by the many successful reductions given in Table I.

The failure of 1-menthyl- $\alpha$ -phenylcinnamate to undergo hydrogenation can be attributed to steric hindrance. The results of hydrogenation of a number of  $\alpha,\beta$ -unsaturated nitro compounds, aldehydes, ketones, and nitriles are given in Table II. The  $\alpha,\beta$ -unsaturated nitro compounds underwent olefinic reduction rather smoothly. On the other hand, the reduction of  $\alpha,\beta$ -unsaturated nitriles and ketones apparently depends on the steric influence of the olefinic substit-

TABLE I  
HYDROGENATION OF  $\alpha,\beta$ -UNSATURATED CARBOXYLIC ACIDS AND ESTERS

Reactant	Product	Yield, %	Reduction based on nmr and ir spectral analyses, %
Cinnamic acid	Hydrocinnamic acid	85	100
<i>p</i> -Methylcinnamic acid	<i>p</i> -Methylhydrocinnamic acid	90	100
$\alpha$ -Methylcinnamic acid	$\alpha$ -Methylhydrocinnamic acid	83	100
$\alpha$ -Phenylcinnamic acid	2,3-Diphenylpropionic acid	85	100
Itaconic acid	$\alpha$ -Methylsuccinic acid	92	100
Citraconic acid	$\alpha$ -Methylsuccinic acid	90	80
Ethyl cinnamate	Ethyl hydrocinnamate	93	100
1-Menthyl- $\alpha$ -phenylcinnamate	No reduction		

TABLE II  
HYDROGENATION OF  $\alpha,\beta$ -UNSATURATED NITRO COMPOUNDS, NITRILES, KETONES, AND ALDEHYDES

Reactant	Product	Yield, %	Reduction based on nmr and ir spectral analyses, %
<i>p</i> -Nitro- $\beta$ -nitrostyrene	2-( <i>p</i> -Nitrophenyl)nitroethane	60	100
3,4-Methylenedioxy- $\beta$ -nitrostyrene	2-(3,4-Methylenedioxyphenyl)nitroethane	84	100
3-Methoxy-4-benzyl-oxy- $\beta$ -nitrostyrene	2-(3-Methoxy-4-benzyl-oxyphenyl)nitroethane	90	100
Cinnamonitrile	Hydrocinnamonitrile	86	100
2,3-Diphenylacrylonitrile	No reduction		
Benzal acetone	4-Phenyl-2-butanone	80	100
3,4-Diphenyl-3-buten-2-one	No reduction		
Cinnamaldehyde	60% hydrocinnamaldehyde and 40% ethylbenzene <sup>a</sup>	90	
<i>o</i> -Nitrocinnamaldehyde	60% <i>o</i> -nitrohydrocinnamaldehyde and 40% <i>o</i> -nitroethylbenzene <sup>a</sup>	70	
$\alpha$ -Methylcinnamaldehyde	No reduction		
<i>p</i> -Dimethylaminocinnamaldehyde	No reduction		

<sup>a</sup> Based on nmr spectral analyses.

uents. For instance, both cinnamonitrile and benzal acetone were readily reduced to hydrocinnamonitrile and 4-phenyl-2-butanone, respectively; however, the hydrogenation of more hindered disubstituted olefins such as 2,3-diphenylacrylonitrile and 3,4-diphenyl-3-

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buten-2-one, was unsuccessful. Similar steric effects of substituents on the homogeneous hydrogenation of certain steroids were also observed by Djerassi and Gutzwiller.<sup>5</sup>

The selective hydrogenation of  $\alpha,\beta$ -unsaturated aldehydes by tris(triphenylphosphine)chlororhodium (I) in benzene or benzene-ethanol has been reported by several authors.<sup>3-6</sup> However, the usefulness of this catalyst was hampered because of the undesirable decarbonylation of the aldehydes to the corresponding saturated hydrocarbons.<sup>8</sup> We found that this difficulty can be overcome to a certain extent by carrying out the hydrogenations in absolute ethanol. Thus, the reduction of cinnamaldehyde and *o*-nitrocinnamaldehyde furnished 60% yield of the saturated aldehydes. The reduction of  $\alpha$ -methylcinnamaldehyde and *p*-dimethylaminocinnamaldehyde was, however, unsuccessful.

In summary, the general applicability and usefulness of tris(triphenylphosphine)chlororhodium (I) as a homogeneous hydrogenation catalyst in organic syntheses has been demonstrated by the selective hydrogenation of a wide variety of  $\alpha,\beta$ -unsaturated carboxylic acids, esters, aldehydes, ketones, nitriles, and nitro compounds.

### Experimental Section

The catalyst, tris(triphenylphosphine)chlororhodium(I), was prepared according to Wilkinson's procedure.<sup>3</sup> The solvents were deoxygenated and stored under argon. The solutions were transferred to the reaction vessel under argon and flushed with hydrogen five times. The melting points were taken on a Thomas-Hoover melting point apparatus and are corrected. The elemental analyses were performed by Galbraith Laboratories, Inc., Knoxville, Tenn. The nmr spectra were obtained with a Varian A-60 spectrometer. A Beckman IR-8 spectrophotometer was used to determine the ir spectra. The  $\alpha,\beta$ -unsaturated nitro compounds were prepared according to the procedure of Lange and Hambourger.<sup>9</sup> The procedure of Zimmerman,<sup>10</sup> *et al.*, was used to prepare the  $\alpha,\beta$ -unsaturated ketones. Essentially the same general procedure but different work-up procedures were used to carry out the hydrogenations of various unsaturated compounds.

**General Procedure for Homogeneous Hydrogenation of Unsaturated Compounds.**—The unsaturated compound (0.0123 mol) and tris(triphenylphosphine)chlororhodium(I) (0.435 mmol) were dissolved in 200 ml of the appropriate solvent (mentioned in the work-up procedures) in argon atmosphere. The clear red solutions were transferred to the medium pressure hydrogenation apparatus, and the reductions were conducted at 60° and 60–80-psi pressure for 8–12 hr.

**Work-Up Procedure A. Hydrogenation of  $\alpha,\beta$ -Unsaturated Acids.**—The solvent (benzene) was evaporated and the residual gummy solid treated with 200 ml of 5% sodium hydroxide. The catalyst was removed by filtration through celite and the filtrate acidified with 10% hydrochloric acid to precipitate the saturated acid which was filtered and dried.

**Work-Up Procedure B. Hydrogenation of  $\alpha,\beta$ -Unsaturated Nitro Compounds.**—The solvent (50% benzene-ethanol) was evaporated to afford a dark brown oil which was triturated with 50 ml of ethyl ether. Removal of the catalyst by filtration through celite and evaporation of the filtrate furnished the saturated nitro compounds. The melting points and elemental analyses of the new compounds are given below.

2-(*p*-Nitrophenyl)nitroethane has mp 97–98°. *Anal.* Calcd for  $C_8H_8N_2O_4$ : C, 48.98; H, 4.06; N, 14.28. Found: C, 48.99; H, 4.01; N, 14.09.

2-(3-Methoxy-4-benzyloxyphenyl)nitroethane has mp 63–63.5°. *Anal.* Calcd for  $C_{18}H_{17}NO_4$ : C, 66.88; H, 5.98; N, 4.88. Found: C, 66.78; H, 5.83; N, 4.84.

2-(3,4-Methylenedioxyphenyl)nitroethane has mp 51–54°. *Anal.* Calcd for  $C_9H_9NO_4$ : C, 55.38; H, 4.65; N, 7.18. Found: C, 55.44; H, 4.60; N, 6.99.

**Work-Up Procedure C. Hydrogenation of  $\alpha,\beta$ -Unsaturated Ketones, Nitriles, and Esters.**—The procedure was similar to the work-up procedure B except that petroleum ether (bp 30–60°) was used (instead of ether) to triturate the residual oil.

**Work-Up Procedure D. Hydrogenation of  $\alpha,\beta$ -Unsaturated Aldehydes.**—The hydrogenations were conducted at 80-psi pressure and 60° for 24 hr. First the solvent (absolute ethanol) was evaporated under reduced pressure (5 mm) and then the residual oil was distilled under vacuum (0.1 mm) to furnish the aldehyde mixtures as yellow oils whose composition was determined by nmr and ir spectroscopic analyses.

**Registry No.**—I, 14694-95-2; 2-(*p*-nitrophenyl)nitroethane, 21473-45-0; 2-(3-methoxy-4-benzyloxyphenyl)nitroethane, 21473-46-1; 2-(3,4-methylenedioxyphenyl)nitroethane, 21473-47-2.

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### Benzoylation by a Cocatalyst System of Copper and Magnesium Ions

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During a study of the oxidation of benzoic acid to phenyl benzoate by the thermal reaction of cupric benzoate,<sup>1</sup> *o*- and *p*-hydroxybenzophenone benzoates were produced when benzoic anhydride and magnesium benzoate were introduced into the system. The unusual part of this result was not that benzoylation of phenyl benzoate by benzoic anhydride occurred, but that the presence of both copper and magnesium ions were necessary for observable amounts of ketone formation under a given set of conditions.

Halides of Cu(I), Cu(II), and Mg(II) have been reported previously as Friedel-Crafts catalysts.<sup>2</sup> In this study, the metallic ions were present in the form of benzoates and, therefore, may have catalytic activities differing from those of the halides. Under reflux conditions and without any catalyst present, ketones were reported to be formed by the reaction of acetyl chloride and anisole<sup>3</sup> and benzoyl chloride and anthracene (nitrobenzene solvent).<sup>4</sup> Thus, heat alone could be sufficient for acylation to occur. In this study, temperatures of 250–280° were used, but benzoic anhydride was the acylating agent instead of the acyl halide. Conceivably, phenyl benzoate could also act as an acylating agent as in a Fries reaction. To establish the conditions for benzoylation, a number of experiments were run (see Table I).

When phenyl benzoate was heated with Mg(II), with and without Cu(II) (runs I and A), no detectable ke-

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