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

The selective hydrogenation of α,β-unsaturated aldehydes by tris(triphenylphosphine)chlororhodium (I) in benzene or benzene–ethanol has been reported by several authors.[3-6] However, the usefulness of this catalyst was hampered because of the undesirable decarbonylation of the aldehydes to the corresponding saturated hydrocarbons.[8] 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 α-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 α,β-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.[3] 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 α,β-unsaturated nitro compounds were prepared according to the procedure of Lange and Hambourger.[9] The procedure of Zimmerman,[10] *et al.*, was used to prepare the α,β-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 α,β-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 α,β-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 $C_{16}H_{17}NO_4$: 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 α,β-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 α,β-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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(8) F. H. Jardine and G. Wilkinson, *J. Chem. Soc.*, *C*, 270 (1967).

(9) N. A. Lange and W. E. Hambourger, *J. Amer. Chem. Soc.*, **53**, 3865 (1931).

(10) H. E. Zimmerman, L. Singer, and B. S. Thyagarajan, *ibid.*, **81**, 108 (1959).

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,[1] *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.[2] 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[3] and benzoyl chloride and anthracene (nitrobenzene solvent).[4] 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-

(1) W. W. Kaeding, *J. Org. Chem.*, **26**, 3144 (1961).

(2) G. A. Olah, Ed., "Friedel–Crafts and Related Reactions," Vol. I, Interscience Publishers, New York, N. Y., 1963, pp 216, 220, and 221.

(3) O. C. Dermer, D. M. Wilson, F. M. Johnson, and V. H. Dermer, *J. Amer. Chem. Soc.*, **63**, 2881 (1941).

(4) P. Rona and U. Feldman, *J. Chem. Soc.*, 1737 (1958).

TABLE I
BENZOYLATION EXPERIMENTS
(Conditions: air flow,[a] 46 cc/min; 270°; 4 hr)

	Reagents						Products	
Run	Cu^{2+}, mmol	Cocatalyst, mmol	$PhCO_2H$, mmol	$PhCO_2H$, mmol	$(PhC{=}O)_2O$, mmol	$PhCO_2Ph$, mmol	$PhCO_2Ph$-(C=O)Ph, mmol[b]	$PhCO_2Ph$, mmol[c]
A[d]	...	Mg^{2+}	24.5	...	...	119	None	...
B[d]	...	Mg^{2+}	24.5	...	55	55	None	...
C	...	Mg^{2+}	65.6	...	100	50	None	...
D[e]	8.2	...	...	...	100	50	~2	...
E	16.4	...	...	...	100	50	None	...
F	16.4	Mg^{2+}	65.6	...	100	50	26.2	108
G	8.2	Mg^{2+}	16.5	...	100	50	12.6	105
H	4.1	Mg^{2+}	65.6	...	100	...	3.1	23.3
I[f]	8.2	Mg^{2+}	65.6	...	...	100	None	...
J[g]	8.2	Mg^{2+}	16.6	33.8	100	50	8.2	93.2
K	8.2	Li^{+}	32.1	35.2	127	...	Trace	24.8
L	8.2	Fe^{3+}	39.2	...	100	...	3.9	23.4
M	8.2	Zn^{2+}	32.0	64.0	132	...	10.7	43.1
N	8.2	Ni^{2+}	32.0	64.0	132	...	None	48.5
O	8.2	$Co^{2+,3+}$[h]	33.2	85.6	143	...	8.8	65.6

[a] Air was introduced in all experiments involving copper, since the thermal reaction of cupric benzoate can reduce the ion to the free metal.[1] Air was not used in runs A and B. [b] The ketonic products were analyzed as a mixture. [c] Where analyzed, the total phenyl benzoate found is reported. [d] 280° and 5 hr. [e] 7 hr. [f] 2 hr. [g] 250°. [h] Co_2O_3, was used to form the benzoate salts.

tone formation occurred. Therefore, phenyl benzoate was not the acylating agent. Two experiments (runs B and C) with benzoic anhydride, phenyl benzoate, and Mg(II) yielded no ketone. These experiments established that neither Mg(II) nor the thermal conditions used in this study brought about benzoylation of phenyl benzoate by benzoic anhydride. Two experiments (runs D and E) with benzoic anhydride, phenyl benzoate, and Cu(II) yielded small amounts of hydroxybenzophenone benzoates in the 7-hr run. When both Cu(II) and Mg(II) were present (runs F, G, H, and J), significant amounts of ketones were made. Thus, a cocatalyst system of copper and magnesium benzoates appears to be involved in the benzoylation of phenyl benzoate by benzoic anhydride. Ketone formation also occurred when Cu(II) and Fe(III), Zn(II), or Co(II, III) were present. Inactive were Li(I) and Ni(II) in the presence of Cu(II).

The effect of benzoic acid, a proton donor, on the reaction was not evident from these qualitative experiments. Two experiments were designed so that different levels of benzoic acid would be maintained throughout the reaction. When the benzoic acid concentration was maintained at 10–30%, no hydroxybenzophenone benzoate formed in a 9-hr run. When the benzoic acid concentration was maintained at 1–5%, the concentration of ketones increased linearly to 35% during a 10-hr period. Thus, benzoic acid, at concentrations above 10%, inhibits the acylation reaction.

Experimental Section

The small-scale reactions were carried out in a 50-ml, round-bottomed flask which was heated at the desired temperature by a stirred, thermostated oil bath (DC-710 silicone oil). The reagents were premixed in the flask. Magnesium and copper were added as the benzoate salts. The other metallic ions were added as the oxides, which reacted with benzoic acid to form benzoate salts. At the end of the reaction period, samples were analyzed at the carbonyl stretching frequencies by infrared spectrophotometry. By glpc analysis of run F, *o*- and *p*-hydroxybenzophenone benzoates were present in approximately equal amounts.

The large runs were carried out in a cylindrical reactor (internal d = 5 cm, l = 60 cm). The reactor had a widened section (internal d = 10 cm, l = 12 cm) at the top. Air and nitrogen flows were measured by flowmeters and introduced at the bottom of the reaction mixture. A mixture of benzoic acid and benzoic anhydride was added at a rate which maintained a reactant volume of 1 l. A feed composition of 60% benzoic acid and 40% benzoic anhydride maintained benzoic acid concentrations above 10% and a feed composition of 20% benzoic acid and 80% benzoic anhydride maintained a benzoic acid level below 5%. The vapors which escaped from the reactor were condensed and collected.

The copper benzoate level in both runs was 1% by weight based on the copper ion, while the magnesium benzoate concentration was 1.5%. The air flow for the first run was 164 l./hr, while air at 68 l./hr and nitrogen at 142 l./hr were used in the second experiment. The temperature was controlled at 260° by an electrically heated nichrome ribbon which was wrapped around the reactor. Measurement of the temperature was by an IC thermocouple inserted in a thermocouple well within the solution. Samples of the reaction were taken periodically and analyzed by infrared spectrophotometry for benzoic acid, benzoic anhydride, phenyl benzoate, and *o*- and *p*-hydroxybenzophenone benzoates. The run which gave the ketones was demetallized by the washing of its solution in perchloroethylene with hydrochloric acid and water. The organic residue obtained from removal of the perchloroethylene was distilled under reduced pressure. A fraction which distilled at 235° and 2 Torr was recrystallized twice from ethanol. White crystals of *p*-hydroxybenzophenone benzoate were obtained: mp 111.5–113° (lit. mp 111–113°,[5] 113–114°[6]); calcd, mol wt 302.3; found, mass spectrometric parent ion *m/e* 302. The nmr and ir spectra were consistent for *p*-hydroxybenzophenone benzoate.

Anal. Calcd for $C_{20}H_{14}O_3$: C, 79.45; H, 4.68. Found: C, 79.6; H, 4.67.

A sample of the ester was hydrolyzed by a sodium hydroxide–water–ethanol solution. The structure of the *p*-hydroxybenzophenone isolated was confirmed by comparing its infrared spectrum and mass spectrometric cracking pattern with those of an authentic sample. The melting point was 132.5–133.5° (lit.[6] mp 132.0–133.5°).

Registry No.—*p*-Hydroxybenzophenone benzoate, 16513-74-9.

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(5) P. Gardner, *J. Amer. Chem. Soc.*, **77**, 4674 (1955).
(6) C. Houser and E. Man, *J. Org. Chem.*, **17**, 390 (1952).