Notes

Catalytic Reduction. 4. Hydrogenation of Aldehydes over Borohydride Reduced Nickel and Palladium[1,2]

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The hydrogenation of unsaturated aldehydes, over any of a myriad of catalysts, gives a wide variety of products depending on the reaction conditions employed. The case of cinnamaldehyde (I) exemplifies well this problem. Using the "same" catalyst, colloidial palladium, to effect hydrogenation of I, Skita in 1915 found only the saturated aldehyde II.[3] However, Straus and Grindel in 1924 found the saturated alcohol III and hydrocarbon IV, and no aldehyde.[4] Bogert and Powell in 1931 obtained only the aldehyde II.[5] Rylander in 1967 was able to obtain either the aldehyde II or the unsaturated alcohol V just by varying the amount of colloidial palladium used.[6]

$$\underset{\mathrm{I}}{\mathrm{PhCH{=}CHCHO}} \rightarrow \underset{\mathrm{II}}{\mathrm{PhCH_2CH_2CHO}}, \underset{\mathrm{III}}{\mathrm{PhCH_2CH_2CH_2OH}},$$

$$\underset{\mathrm{IV}}{\mathrm{PhCH_2CH_2CH_3}}, \underset{\mathrm{V}}{\mathrm{PhCH{=}CHCH_2OH}}$$

In a review of the subject, Rylander lists some of the variables with known effects on the catalytic hydrogenation of aldehydes.[6] These include the method of catalyst preparation, source of metal used, solvents used in catalyst preparation and catalyst use, catalyst support, additives (both known and impurities), and amount of catalyst used. Hence, a desired monoreduction of a di- or polyfunctional compound can make the choice of catalyst a rather lengthy decision.

These uncertainties encountered in the hydrogenations of unsaturated aldehydes over many catalysts are not extant when borohydride-reduced nickel or palladium is the catalyst. And, when combined with previous results,[7] the utility of borohydride-reduced metals as hydrogenation catalysts becomes obvious. Work by this laboratory, the Browns, Strohmeier, and others, has indicated that borohydride-reduced nickel and palladium exhibit an almost perfect selectivity for only one of several potentially reducible groups in a molecule.

Borohydride-reduced palladium does not affect the carbonyl π bond of aldehydes; only carbon–carbon π bonds are reduced. A representative selection of aldehydes studied is listed in Table I. In all cases studied, only the saturated aldehyde was obtained. No other products, such as alcohols or hydrocarbons, were detected.

It is especially noteworthy to point out the failure of borohydride-reduced palladium to effect the hydrogenation of benzaldehyde. One might perceive the rapid formation of the dimethyl acetal of benzaldehyde preventing a carbonyl group from being exposed to hydrogenation. However, this possibility cannot be the reason as the IR spectrum of the final reaction product depicts a strong carbonyl absorption at 5.8 μ. Further, no peaks attributable to compounds other than methanol or the saturated aldehyde were observed in the IR spectra or gas chromatograms of the reaction mixtures.

Table I. Aldehydes Treated with Hydrogen over Borohydride-Reduced Palladium[a]

Reactant	Product	Pd, mmol	Time, h
Crotonaldehyde	Butyraldehyde	2.5	0.25[b]
Butyraldehyde	N.R.	20	27
Cinnamaldehyde	Hydrocinnamaldehyde	2.5	3.5[b]
Benzaldehyde	N.R.	2.5	48

[a] 100 mmol of reactant, 30 psi H_2 initial pressure, ambient temperature, in 40 ml of methanol. [b] Hours for uptake of 100 mmol of H_2, reaction continued for an additional 24 h with no additional uptake of H_2.

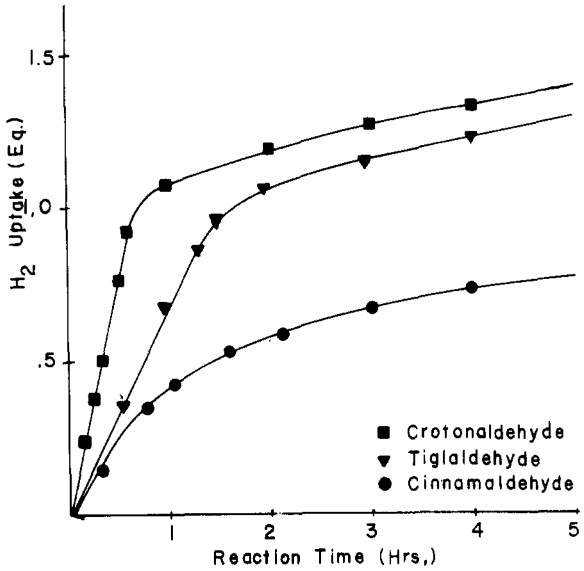

Figure 1. Hydrogenation velocities for 100 mmol of α,β-unsaturated aldehydes over 5 mmol of Ni.

In contrast to the single site affected by palladium, borohydride-reduced nickel does effect hydrogenation of both carbon–oxygen and carbon–carbon π bonds in unsaturated aldehydes. Table II lists a representative selection of the aldehydes studied.

As can be seen from the data in Table II, the carbonyl group is hydrogenated more slowly than the olefinic group over the nickel catalyst. Figure 1 depicts the relative velocities of these two competing reactions for several aldehydes.

The borohydride-reduced palladium effects hydrogenation in a wide variety of solvents. Table III lists hydrogenation times for crotonaldehyde in several solvents. The change in solvent does not change the specificity of the hydrogenation, as no products other than the saturated aldehydes were detected.

The differences between nickel and palladium hydrogenation catalysts produced by borohydride reduction of the metal salts and those "same" metallic catalysts prepared by other reductive methods are clearly apparent. Work is continuing on the elucidation of the properties of these and other borohydride-reduced transition metal catalysts.

Experimental Section

Chemicals. The aldehydes used were extracted with aqueous sodium bicarbonate, dried, and distilled prior to use. Solvents used were

Table II. Aldehydes Treated with Hydrogen over Borohydride-Reduced Nickel[a]

Registry no.	Reactant	Product	Ni, mmol	Time,[b] h
107-02-8	Acrolein	Propionaldehyde	5	0.5
4170-30-3	Crotonaldehyde	Butyraldehyde	5	8
	Crotonaldehyde	Butyraldehyde	20	0.75
104-55-2	Cinnamaldehyde	Hydrocinnamaldehyde	20	1
497-03-0	Tiglaldehyde	α-Methylbutyraldehyde	20	1
123-38-6	Propionaldehyde	Propyl alcohol	50	15
123-72-8	Butyraldehyde	Butyl alcohol	50	21
104-53-0	Hydrocinnamaldehyde	3-Phenylpropanol	20	4
96-17-3	α-Methylbutyraldehyde	2-Methylbutanol	20	7.5
100-52-7	Benzaldehyde	Benzyl alcohol	10	48
98-01-1	Furfural	Furfuryl alcohol	5	12

[a] 100 mmol of reactant, 30 psi initial H_2 pressure, ambient temperature, in 50 ml of 95% ethanol. [b] Hours for uptake of 100 mmol of H_2.

Table III. Hydrogenation Times for Crotonaldehyde in Various Solvents[a]

Solvent	Time,[b] min
Cyclohexane	35
1,2-Dimethoxyethane	20
Dimethylformamide[c]	55
Methanol	15
Toluene	40

[a] 100 mmol of reactant, 2.5 mmol of Pd, 40 ml of solvent, 30 psi H_2 initial pressure, ambient temperature. [b] Minutes for uptake of 100 mmol of H_2. [c] Catalyst prepared in methanol. Black material prepared in DMF did not effect hydrogenation in DMF.

lower grade chemicals and were used directly from the bottles without further purification. Palladium chloride was from Research Organic Chemicals; nickel acetate was from Fisher Scientific. All organic chemicals were analyzed for purity by gas chromatography prior to use. Liquid phases for GC analyses included XF-1150, SE-30, QF-10065, Carbowax 20M, and SF-96.

Catalyst Preparation. Nickel. To a stirred suspension of 1.24 g (5 mmol) of powdered nickel acetate in 50 ml of 95% ethanol was added 5 ml of 1.0 M sodium borohydride in 95% ethanol at room temperature. (Other amounts of catalyst were prepared by using multiples of the amounts of reactants.) Stirring was continued until the evolution of a gas had ceased, usually within 30 min. The black colloidal material was used directly.

Palladium. To a stirred suspension of 0.443 g (2.5 mmol) of powdered palladium chloride in 40 ml of absolute methanol, or other liquid, at room temperature was added 0.19 g (5 mmol) of powdered sodium borohydride over a 5–10-min period. (Other amounts of the catalyst were prepared by using multiples of the amounts of reactants.) Stirring was continued until the evolution of a gas had ceased, usually within 20 min. The black catalyst settled rapidly when stirring was stopped. The solvent is changed readily by decanting and washing two or three times.

Hydrogenation Procedure. To the desired amount of catalyst and solvent in a hydrogenation flask was added 100 mmol of purified aldehyde. The flask was flushed with hydrogen, connected to a Parr low-pressure hydrogenator, and pressurized to 30 psi. Time and pressure were monitored. Reactions were begun at room temperature and conducted under ambient conditions.

The nickel catalyst was removed by centrifugation prior to product analysis. The palladium catalyst settled rapidly upon cessation of shaking.

Product Analysis. Infrared spectra of reaction mixtures were taken prior to gas chromatographic analyses to enable detection of unexpected thermal reactions and incomplete elutions. All reaction mixtures were analyzed directly, after removal of the catalyst, with the exception of those in dimethylformamide. These reaction mixtures were extracted with water and ethyl ether prior to analysis to avoid adverse effects on the GC columns by DMF. The ethereal layer was dried over $CaCl_2$ prior to analysis.

The GC liquid phases used were those aforementioned. Samples of all effluent components were isolated and identified by comparison of IR spectra with those of authentic samples or those in the "Aldrich Library of Infrared Spectra".[8] A comparison was also made of all absorptions of the components of the reaction mixture. No extraneous absorptions were detected.

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Registry No.—Nickel, 7440-02-0; sodium borohydride, 16940-66-2; palladium, 7440-05-3.

References and Notes

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(2) Taken in part from the Masters Thesis of D.M.D. Presented in part at the Second Rocky Mountain Regional Meeting of the American Chemical Society, Albuquerque, N.M., July 1974.
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(6) P. N. Rylander, "Catalytic Hydrogenation over Platinum Metals", Academic Press, New York, N.Y., 1967.
(7) see, inter alia, ref 1; H. C. Brown and C. A. Brown, *Tetrahedron, Suppl. 8, Part 1*, 149 (1966); W. Strohmeier and H. Steigerwald, *Z. Naturforsch. B*, **30**, 643 (1975); R. Paul, P. Buisson, and N. Joseph, *Ind. Eng. Chem.*, **44**, 1006 (1952); and references cited therein.
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Nucleophilic Cleavage Reactions of Cyclic and Acyclic α-Diazo-β-ketophosphoryl Compounds

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Acyl cleavage reactions of diazocarbonyl compounds have only recently achieved a measure of preparative importance, although they have long been known. The reaction has been shown to be useful for the preparation of α-diazocarboxylates,[1] α-diazo ketones,[2] and α-diazo sulfones[3] from the corresponding acyl derivatives which are readily available via the diazo transfer reaction. In the course of our studies on cyclic phosphorus compounds, we became interested in the five-membered cyclic diazoketophosphoryl compound (**2**) which might be converted to the phosphetane system via photochemical ring contraction. Thus, we attempted to prepare 2-diazo-3-phospholanone oxide (**2**) and found that the ring system in **2** was unstable, leading to ring cleavage exclusively at the P–C bond when treated with an alcohol containing amine.