pound **4a** was refluxed in 4 *N* HCl for 4 hr, and the solution was then evaporated and the resulting oil distilled under reduced pressure: bp 133–134° (0.25 mm); ir (CHCl$_3$) 1712, 1740 (C=O), and 2700–3600 cm^{-1} (OH); nmr (CDCl$_3$) δ 1.11 (d, $^3J \cong$ 7.0 Hz, 3, 3-CH$_3$), 1.70–3.00 (m, 8, cyclopentane protons and –CH$_2$COOH), and 8.58 ppm (s, 1, –OH).

Anal. Calcd for C$_8$H$_{12}$O$_3$: C, 61.52; H, 7.75. Found: C, 61.45; H, 7.68.

B. A suspension of **6** (4.0 g) in 48% HBr (40 ml) was refluxed for 5 hr. Ammonium chloride was added and the solution was extracted with chloroform to yield 1.5 g of an oil with the same characteristics as that obtained with method A.

2-Methyl-4-oxo-1-cyclopentaneacetic Acid (5b). This compound was obtained from the corresponding ester **5a** using the procedure described for **4b**. The resulting oil was distilled under reduced pressure: bp 135–139° (0.3 mm); ir (CHCl$_3$) 1710, 1740 (C=O), and 2500–3600 cm^{-1} (OH); nmr (CDCl$_3$) δ 0.95 and 1.13 (2 d, $^3J \cong$ 6.5 Hz, 3, 2-CH$_3$, trans and cis forms), 1.50–3.00 (m, 8, cyclopentane protons and –CH$_2$COOH), and 7.75 ppm (s, 1, –OH).

Anal. Calcd for C$_8$H$_{12}$O$_3$: C, 61.52; H, 7.75. Found: C, 61.62; H, 7.80.

Diethyl 3-Carbethoxy-3-methyl-4-oxo-1-cyclopentanemalonate (6). Diethyl malonate (6.4 g, 0.04 mol) and then ethyl 1-methyl-2-oxo-3-cyclopentene-1-carboxylate[8] (6.8 g, 0.04 mol) were added to a solution of Na (0.23 g, 0.01 mol) in anhydrous ethanol (12 ml) with cooling in a water bath. The reaction mixture was left for 2 hr at room temperature, and then decomposed with water and acidified with acetic acid. Extraction with ether and washing with saturated NaHCO$_3$ solution yielded an oil that was distilled under reduced pressure: bp 142–144° (0.04 mm); yield 9.7 g; ir (neat) 1730, 1740, and 1755 cm^{-1} (C=O).

Anal. Calcd for C$_{16}$H$_{24}$O$_7$: C, 58.52; H, 7.37. Found: C, 58.61; H, 7.49.

Registry No.—**1a**, 51965-77-6; **1b**, 51965-78-7; **2a**, 51965-79-8; **2b**, 51965-80-1; **3a**, 51965-81-2; **3b**, 51965-82-3; **4a**, 51965-83-4; **4b**, 51965-84-5; *cis*-**5a**, 51965-85-6; *trans*-**5a**, 51965-86-7; *cis*-**5b**, 51965-87-8; *trans*-**5b**, 51965-88-9; **6**, 51965-89-0; 4-methyl-4-cyclopentene-1,3-dione, 30268-57-6; triphenylcarbethoxymethylenephosphorane, 1099-45-2; diethyl malonate, 105-53-3; ethyl 1-methyl-2-oxo-3-cyclopentene-1-carboxylate, 51965-90-3.

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highly selective manner. A partial investigation reveals significant differences in the catalytic activities of this material from other palladium catalysts. In 1962, Polkovnikov, *et al.*,[3] reported that the rates of hydrogen uptake by a series of multifunctional olefins over borohydride reduced palladium were twice those over alkaline-formalin reduced palladium. Brown and Brown[4] in 1966 briefly described the activity of borohydride reduced palladium on some olefinic hydrocarbons.

Borohydride reduced palladium is a very versatile hydrogenation catalyst, as evidenced by the data in Table I. The material effectively and rapidly catalyzes the hydrogenation of carbon–carbon π bonds in a variety of solvents. Neither hydrogenation nor hydrogenolysis of nitrogen or oxygen functions σ bonded to carbon have been observed, with the exception of a slow ring opening of epoxides. Nitrogen–nitrogen and nitrogen–oxygen π bonds were reduced, whereas carbon–nitrogen and carbon–oxygen π bonds were not in the compounds studied. Presumably, the nitrogen–oxygen σ bond does undergo hydrogenolysis.

Experimental Section

Chemicals. All chemicals hydrogenated were reagent grade and were used directly from the bottles without further purification. Hydrogenation media were lower grade solvents. The palladium chloride was from Research Organic Chemicals. All organic chemicals, except the acids, amides, and azobenzene, were analyzed for purity by gas chromatography prior to use.

Catalyst Preparation. To a stirred solution of 0.443 g (2.5 mmol) of palladium chloride in 40 ml of absolute methanol, or other liquid at room temperature, was added 0.19 g (5.0 mmol) of powdered sodium borohydride over a 5–10-min period. Stirring was continued for 20 min, or until the evolution of a gas had ceased. The black reaction product settled rapidly when stirring was stopped.

The catalyst was used directly or stored under a liquid in a stoppered flask. The solvent was changed by decanting and washing twice.

Hydrogenation Procedure. To 2.5 mmol of catalyst and 40 ml of solvent in a Parr hydrogenation flask was added 100 mmol of the material to be hydrogenated. The flask was flushed with hydrogen, connected to a Parr low-pressure hydrogenator, and pressurized to 30 psi. Time and pressure were monitored. The conditions were maintained until no further uptake of hydrogen was observed. Reactions were begun at room temperature and conducted under ambient conditions.

The catalyst settled rapidly upon removing the reaction flask from the hydrogenator. The liquid was decanted for subsequent analysis. Following two washings, the catalyst was ready for reuse.

Product Analysis. All hydrogenation reaction mixtures were analyzed by gas chromatography. Only one product was detected in all cases. It was isolated and its infrared spectrum was taken on a Beckman IR-8. All spectra obtained were compared with those of authentic samples or those in the "Aldrich Library of Infrared Spectra."[5]

Results and Discussion

Applications. The versatility of borohydride reduced palladium as a hydrogenation catalyst can best be seen by a comparison of its activity with those of other catalysts.

No hydrogenolyses of nitrogen and oxygen groups σ bonded to carbon has been detected in alcohols, amides, amines, esters, ethers, or lactones studied. These results are in contrast with many findings that many palladium catalysts do effect hydrogenolysis of allylic and benzylic functions as well as reduction of a wide variety of other functions.[6]

Epoxides are very slowly opened, yielding monoalcohols at the sole products; however, since carbon–carbon π bonds are hydrogenated rapidly, the epoxide group should be unaffected in such a reaction over borohydride reduced palladium. It is of interest to note that the nickel analog did not open epoxides.[7]

Catalytic Reduction. III. Hydrogenation of Unsaturated Compounds over Borohydride Reduced Palladium[1,2]

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Partial reduction of multifunctional unsaturated compounds, using a variety of reagents or catalysts, is of considerable synthetic utility. In all preparatively useful conversions, it is of utmost importance that the reduction be highly selective as to site.

The product from the reaction between sodium borohydride and palladium(II) chloride catalyzes the partial hydrogenation of difunctional unsaturated compounds in a

Table I
Times of Hydrogenation over Borohydride Reduced Palladium[a]

Reactant[b]	Registry no.	Methanol	Dimethyl-formamide	Solvent[c] Cyclohexane	1,2,-Dime-thoxyethane	Toluene
Allyl alcohol	107-18-6	13	23	51	18	19
Cinnamyl alcohol	104-54-1	27	40	38		
1,4-Butynediol[d]	110-65-6	67				
2-Methyl-3-butyn-2-ol[d]	115-19-5	72	63	46	42	40
Butyl vinyl ether	111-34-2	17	40	20	22	34
Allyl phenyl ether	1746-13-0	16	24	21		
Diallyl ether[d]	557-40-4	44	120	72		
1,2-Epoxybutane[e]	106-88-7	24[f]				
Epoxyethane	75-21-8	26[f]				
α-Methylstyrene	98-83-9	24	40	31	24	34
5-Hexen-2-one	109-49-9	21	35	21	20	32
Mesityl oxide	141-79-7	28	68	38		
Crotonaldehyde	4170-30-3	18	55	36	22	40
Butyraldehyde	123-72-8	g	g	g	g	g
Cinnamaldehyde	104-55-2	208				
Cinnamic acid	621-82-9	25	58	75	37	67
Crotonic acid	3724-65-0	25				
Maleic anhydride	108-31-6					270
Ethyl cinnamate	103-36-6	27	70	62		
Vinyl acetate	108-05-4	12	30	20	21	28
Acrylamide	79-06-1	20	51			
Methacrylamide	79-39-0	17	52	73		
Allylamine	107-11-9	15	33	22	23	25
Diallylamine[d]	124-02-7	45	55	60		
2-Butenenitrile	4786-20-3	35	28	46		
3-Butenenitrile	109-75-1	10	17	12	9	12
Cinnamonitrile	4360-47-8	80				
2-Acetylbutyrolactone	517-23-7	g				
Azobenzene	103-33-3	152	34[h]			
Nitrobenzene[i]	98-95-3	55	147	77	77	104

[a] Time in minutes. [b] 100 mmol, 2.5 mmol of catalyst, 30 psi H₂ initial pressure, ambient temperature. [c] 40 ml. [d] Uptake of 2 equiv of hydrogen. [e] 20 mmol of catalyst. [f] Hours. [g] No hydrogen uptake after 18 hr. [h] 50 mmol of reactant. [i] Uptake of 3 equiv of hydrogen.

Table II
Hydrogenation Times for 5-Hexen-2-one in Various Solvents

Solvent	Time,[a] min Catalyst prepared and run in	Catalyst prepared in methanol and run in
Methanol	21	21
Dimethylformamide	b	35
Cyclohexane	14	21
1,2-Dimethoxyethane	13	20
Toluene	16	32

[a] 100 mmol of reactant, 2.5 mmol of catalyst, 40 ml of solvent. [b] Black material prepared but did not effect reduction in 24 hr.

Rylander[8] has summarized the reduction of carbon–carbon and carbon–nitrogen π bonds over a variety of catalysts. No reduction of the carbonyl function in acids, aldehydes, amides, esters, and lactones was observed over borohydride reduced palladium. The nitrile function was unaffected under normal conditions, by using 20 mmol of catalyst, or by adding Ti(II) to the reaction mixture as suggested by van Tamelen, *et al.*[9] Nitriles[1] and aldehydes[7] yielded primary amines and alcohols, respectively, over borohydride reduced nickel.

Azo compounds undergo hydrogenation and hydrogenolysis simultaneously over Pd/C, yielding amines and anilines.[10] Borohydride reduced palladium catalyst was selective in that it catalyzed only the reduction of the nitrogen–nitrogen π bond in azobenzene. No aniline was detected.

Hydrogenolysis was observed in the reduction of nitrobenzene. Aniline was the only product detected.

Solvents. A wide variety of solvents are available for use with borohydride reduced palladium. Table I lists four aprotic solvents used with the catalyst prepared in methanol—dimethylformamide (DMF), cyclohexane, 1,2-dimethoxyethane (glyme), and toluene. Some differences in reduction times are observed but no differences in products.

Table II lists reduction times of 5-hexen-2-one over borohydride reduced palladium prepared in each of the five solvents. It is interesting to note that DMF was not suitable for use as a catalyst preparation medium but was suitable as a hydrogenation solvent when the catalyst had been prepared in methanol.

Deactivation. As the catalytic material is coarse and settles rapidly upon cessation of agitation, recovery and reuse is a simple matter. In a series of successive reductions of 5-hexen-2-one in methanol, reduction time increased less than 50% after 30 consecutive reactions, from 20 to 29 min. As no effort was made to exclude air from the catalyst (see below), the deactivation may have been due to handling and not catalyst "fatigue."

General. Two other facets of the borohydride reduced palladium catalyst enhance its utility. The material is not pyrophoric as are some hydrogenation catalysts. Apparently, it does not ignite hydrogen in the presence of air, thus eliminating a dangerous element inherent in some other catalysts.

The material was not observed to be sensitive to air under routine handling. In this study, no special effort was made to exclude air from the glassware containing the catalyst. The operations of catalyst preparation, solvent change, product separation from catalyst, and catalyst washing for reuse were done under ambient atmosphere. A purge of air from vessels containing the catalyst was found

to be necessary only when connecting a hydrogenation flask to the Parr apparatus.

Work extending the application of borohydride reduced palladium to heterocyclic and homocyclic rings, halides, and sulfides is currently underway.

Registry No.—Palladium chloride, 7647-10-1; sodium borohydride, 16940-66-2.

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Organic Synthesis Using Borane-Methyl Sulfide. II.[1] Reduction of Aromatic Carboxylic Acids in the Presence of Trimethyl Borate

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Borane–methyl sulfide (BMS) is a concentrated and stable source of BH_3 and we have reported its utility in the hydroboration of alkenes.[1] The stability, commercial availability in pure form, and solubility in a wide variety of solvents makes BMS an attractive alternative to borane-tetrahydrofuran (BH_3-THF).

The approximate rates and stoichiometry for the reaction of BH_3-THF with various organic functional groups has been reported by Brown and coworkers.[2] The reduction of carboxylic acids with BH_3-THF was found to yield the corresponding alcohols rapidly and quantitatively under remarkably mild conditions. The obvious potential of this reaction for selective reductions in multifunctional molecules resulted in a detailed study of the scope of this reduction.[3]

As part of our continuing study on the full potential of BMS as a reagent in organic synthesis, we have investigated the use of this reagent for the reduction of carboxylic acids. Initially, the approximate rates of reduction were determined using *n*-hexanoic and benzoic acid as representative carboxylic acids. When *n*-hexanoic acid was added to a solution of BMS in THF, a quantitative yield of 1-hexanol was observed after 4 hr at 20–25°. Reversing the order of addition resulted in an apparent increase in the rate of reduction; *i.e.*, when BMS was added to a solution of *n*-hexanoic acid in THF, a quantitative yield of 1-hexanol was ob-
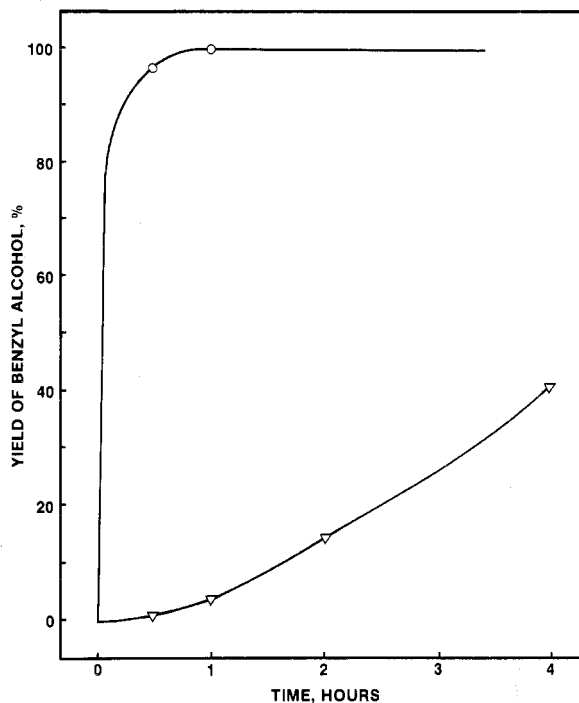

Figure 1. The effect of trimethyl borate on the reduction of benzoic acid (30 mmol) with BMS (33 mmol) at 20–25°: ▽, THF (30 ml) alone; ○, THF (20 ml) plus trimethyl borate (10 ml).
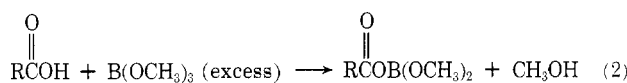
served after only 30 min at 20–25°. Surprisingly, the reduction of benzoic acid was appreciably slower and gave only a 40–50% yield of benzyl alcohol after 4 hr at 20–25°, irrespective of the order of addition. The use of either ethyl ether or hexane as the solvent in place of THF had essentially no effect upon the rate of reduction of benzoic acid. In all cases, instantaneous hydrogen evolution was observed due to the initial reaction of BH_3 with the acidic hydrogen of the carboxylic acid. The complete results of this preliminary investigation on the BMS reduction of *n*-hexanoic and benzoic acid are summarized in Table I.

The reduction of both *n*-hexanoic and benzoic acid with BH_3-THF at 25° has been reported to give the corresponding alcohols rapidly and nearly quantitatively.[3] We have duplicated these results.

Although many questions exist concerning the mechanism of the reduction of carboxylic acids with BH_3-THF,[3,4] the first step probably involves the formation of an acyloxyborane (eq 1). The carbonyl group of this acyloxyborane

$$RCOOH + BH_3 \xrightarrow{\text{fast}} RC\overset{\displaystyle O}{\underset{\displaystyle \|}{}}OB\diagdown + H_2 \qquad (1)$$
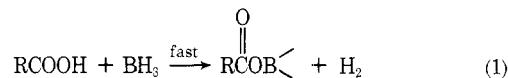
has been postulated to be "activated" toward attack by borane because of possible resonance interaction of the electron pairs on the acyloxy oxygen with the electron-deficient boron atom.[3] We reasoned that a similar activation might be possible in the presence of excess trimethyl borate as a result of a disproportionation reaction (eq 2).

$$R\overset{\displaystyle O}{\underset{\displaystyle \|}{C}}OH + B(OCH_3)_3 \text{ (excess)} \longrightarrow R\overset{\displaystyle O}{\underset{\displaystyle \|}{C}}OB(OCH_3)_2 + CH_3OH \quad (2)$$

Irrespective of the precise reasons, a pronounced increase in the rate of reduction of benzoic acid with BMS was observed when the reaction was conducted in the presence of excess trimethyl borate, as illustrated in Figure 1.

Triacyloxyboranes are unstable and are known to undergo a dismutation to acid anhydride and an oxybisdiacyloxyborane (eq 3).[4] Pelter has shown that for both *n*-hexanoic