(polarographic grade, Matheson Coleman and Bell) in dimethylformamide (reagent grade) was used for all measurements. The tetrabromide I exhibited two 2-electron waves at −1.8 and −2.33 V (sce), while compound V exhibited one 2-electron wave at −2.33 V (sce).

Macroscale Electrolysis. Preparation of Compound V.—The electrolysis cell used for controlled potential electrolysis was described in a previous article.[1] Compound I (25 g, 0.06 mol) in 200 ml of 0.05 *N* n-Bu_4NClO_4 in DMF was electrolyzed at a mercury cathode at room temperature. The potential of the cathode varied between −1.2 and −1.4 V (sce). The overall voltage was 80 V and allowed the passage of 0.3 A through the cell.[9] The course of the reaction was followed polarographically (see Figure 1). At the conclusion of electrolysis, as indicated by the near disappearance of the first wave,[10] no product had collected in the trap. Distillation at atmospheric pressure did not afford any low-boiling material. The product was hydrolyzed with 200 ml of water and extracted into 500 ml of pentane. The pentane layer was distilled at atmospheric pressure to give 7.8 g of a slightly yellowish liquid which was distilled at reduced pressure 63° (7 mm) [reported[8] for V, bp 83–87° (22 mm)] to give 6.9 g of V. The identity of V was arrived at from its nmr spectrum (CCl_4) which exhibited two singlets of equal areas at 0.92 and 3.45 ppm (spiropentane and compound I exhibit one singlet each at 0.75 and 3.52 ppm, respectively) and from its elemental analysis. *Anal.* Calcd for $C_5H_8Br_2$: C, 26.34; H, 3.54; Br, 70.17. Found: C, 26.6; H, 3.63; Br, 70.10.

Preparation of Spiropentane from Compound V.—The reduction of the dibromide V (11.0 g) was carried out under the same conditions described for I. The potential of the cathode was kept at −2.2 V (sce). This afforded spiropentane (1.3 g) which was identified from its nmr spectrum (CCl_4) which exhibited a singlet at 0.75 ppm.

Registry No.—I, 3229-00-3; V, 29086-41-7.

(9) Under these conditions enough heat is generated to boil spiropentane and similar products; hence, a Dry Ice–acetone trap was connected to the cathode compartment.

(10) Further electrolysis may cause the formation of spiropentane.

A Facile Reduction of Unsaturated Compounds Containing Oxygen[1]

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During the syntheses of some sesquiterpenoid natural products, we had the necessity of reducing an allylic diol to the corresponding saturated diol. We subsequently found that nickel boride catalyzed the addition of gaseous hydrogen to the π bond quantitatively in 0.5 hr with no accompanying hydrogenolysis of the alcohol functions.

The catalyst, nickel boride, has been described previously.[2] The Browns[3,4] have reported two types of nickel boride catalyst (P-1, prepared in water, and P-2, prepared in ethanol) and the results of hydrogenations of many hydrocarbons over these catalysts in their own hydrogenation apparatus.

(1) Presented in part at the 50th Anniversary Meeting of the Southwestern Rocky Mountain Division of the American Association for the Advancement of Science, Las Vegas, N. M., April 1970.

(2) (a) H. I. Schlesinger and H. C. Brown, U. S. Patent 2,461,661 (1949); (b) R. Paul, P. Buisson, and N. Joseph, *Ind. Eng. Chem.*, **44**, 1006 (1952).

(3) H. C. Brown and C. A. Brown, *J. Amer. Chem. Soc.*, **85**, 1003, 1005 (1963).

(4) (a) C. A. Brown, *Chem. Commun.*, 952 (1969); (b) C. A. Brown, *J. Org. Chem.*, **35**, 1900 (1970).

We have hydrogenated many oxygen-containing compounds employing nickel boride in a Parr hydrogenator. All compounds, with three exceptions, gave quantitative yields of single compounds from reduction of the carbon–carbon π bond(s) only. A representative selection of the olefinic compounds hydrogenated is listed in Table I. Table II lists some acetylenic compounds that were hydrogenated and some olefin derivatives that did not undergo hydrogenation.

TABLE I

TIMES OF HYDROGENATIONS OVER NICKEL BORIDE

Compd	Time[a]
Diallyl ether	20 min[b]
Allyl alcohol	30 min
2-Butene-1,4-diol (cis)	1 hr
Cinnamyl alcohol (trans)	3 hr
2-Cyclopentene-1,4-diol	30 min
1-Phenyl-2-propenol	8 min
Cinnamaldehyde (trans)	24 hr[c]
5-Hexen-2-one	12 min
Mesityl oxide	6.75 hr
Allyl acetate	16 min
Ethyl cinnamate	2 hr
Cinnamic acid (trans)	*d*
Maleic acid	1 hr

[a] Time required for the uptake of 1 equiv of hydrogen. [b] Time required for the uptake of 2 equiv of hydrogen. [c] Half reaction. [d] No hydrogen uptake after 37 hr.

TABLE II

OTHER COMPOUNDS TREATED WITH NICKEL BORIDE

Compd	Reaction time, hr
2-Butyne-1,4-diol	7.25[a]
2-Methyl-3-butyn-2-ol	1[a]
1-Ethynylcyclohexanol	*b*
Propargyl acetate	*b*
1,2-Epoxybutane	20[c]
2-Methyl-1,2-epoxypropane	20[c]

[a] Time required for the uptake of 2 equiv of hydrogen. [b] Not available: data supplied by Dr. C. A. Brown, private communication. [c] No hydrogen uptake.

The reaction products of the compounds listed were isolated by gas chromatographic techniques and identified by spectral methods. No products resulting from either hydrogenation or hydrogenolysis of the functional groups were detected by gas chromatography. Also, no further uptake of hydrogen was observed for any of the compounds listed following the uptake of the calculated amount.

The results of the hydrogenations of the π bonds are similar to results indicated by Polkovnikov, *et al.*,[5] for three other borohydride-reduced metals. They reported times for the uptake of equivalents of hydrogen by cyclopentadiene, cyclohexene, cinnamaldehyde, crotonaldehyde, and dimethyl maleate using platinum, palladium, and rhodium borides. However, they reported no products.

The compounds that did not undergo hydrogenation did not deactivate the catalyst. After attempting to hydrogenate each one, allyl alcohol was added to the

(5) B. D. Polkovnikov, A. A. Balandin, and A. M. Taber, *Dokl. Akad. Nauk SSSR*, **145**, 809 (1962).

hydrogenation flask and the flask was reconnected to the hydrogenator. Propyl alcohol was obtained quantitatively in less than 0.5 hr from each experiment with cinnamic acid and the butylene oxides. Also, the epoxides were not rearranged to carbonyl compounds by the catalyst.

The catalyst is exceedingly simple to prepare and use. It may be prepared in the hydrogenation flask directly or in larger quantities in a centrifuge flask. The catalyst may be isolated by centrifuging the flask, stored indefinitely under nitrogen, either dry or under ethanol, and used as needed.

The results indicate that nickel boride has a great utility in the syntheses of complex organic compounds, not just for the reduction of olefins or acetylenes. While other materials have been reported[6] capable of catalyzing these conversions, nickel boride has not been found to catalyze rearrangements, hydrogenolyses, or carbonyl reductions which can accompany catalytic hydrogenations. We are currently studying the hydrogenation of nitrogen-containing compounds and the use of aprotic solvents to extend the applications of nickel boride.

Experimental Section

Chemicals.—2-Butene-1,4-diol and 2-butyne-1,4-diol were supplied by Antara Chemical Co. 2-Cyclopentene-1,4-diol was prepared by the method of Owen and Smith.[7] 1-Phenyl-2-propenol was prepared by the method of Braude, *et al.*[8] Maleic acid was prepared from the anhydride by the method of Vogel.[9] Cinnamaldehyde was extracted with dilute sodium bicarbonate solution to remove any acid present. Cinnamic acid was converted to the sodium salt which was dissolved in water and extracted with benzene, chloroform, and ether. Addition of gaseous hydrogen chloride precipitated cinnamic acid from the aqueous solution. All other compounds were used from the bottles with no purification.

Catalyst Preparation.—For a single hydrogenation, 1.24 g (5 mmol) of powdered nickel acetate, 50 ml of 95% ethanol, and a short spinbar are placed in the hydrogenation flask. Stirring is begun and the flask flushed with hydrogen. Injection of 5 ml of 1.0 *M* sodium borohydride into the flask produces the black colloidal catalyst.

For the bulk catalyst, the above procedure is followed using larger amounts of nickel acetate and sodium borohydride solutions and a large centrifuge tube. The colloidal catalyst is easily separated from the solution by centrifuging at 3000 rpm for several minutes. The isolated catalyst can be stored under nitrogen indefinitely, either dry or under ethanol.

Hydrogenation Procedure.—To the catalyst and preparatory solutions in the hydrogenation flask is added 10 mmol of the compound to be hydrogenated, neat if liquid or dissolved in a minimum amount of ethanol if solid. If the preprepared catalyst is used, the compound is added to 50 mg of the catalyst in 50 ml of 95% ethanol. The flask is then connected to the Parr hydrogenator and shaken until the theoretical pressure drop for hydrogen is observed. Initial hydrogen pressure was 30 psi in all experiments. The contents of the hydrogenation flask are then centrifuged to separate the catalyst. The decantate was analyzed by gas chromatography. All reaction products were collected and identified by comparison of infrared spectra with those of authentic samples.

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(6) See, *inter alia*, P. N. Rylander, "Catalytic Hydrogenation over Platinum Metals," Academic Press, New York, N. Y., 1967, and references therein.

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Oxidation of *meso*-Tetraphenylchlorins by Dimethyl Sulfoxide to the Corresponding *meso*-Porphyrins[1]

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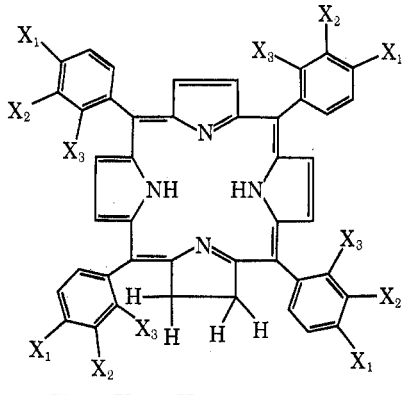
Various meso-tetrasubstituted porphins are prepared by Rothemund synthesis[3–9] but rarely are they obtained chlorin-free.[6] Calvin, *et al.*,[4] separated *meso*-tetraphenylporphin (TTP) from *meso*-tetraphenylchlorin (TPC) by chromatography over talc. This method was later used for purification of similar porphyrins.[8,9] Partial oxidation of chlorins has been achieved with quinones,[10] and selective photooxidative decomposition of zinc chlorins in benzene solution in the presence of quinones followed by chromatography gave pure zinc porphyrins.[9,11] However, these methods of



1, $X_1 = X_2 = X_3 = H$
2, $X_2 = X_3 = H$; $X_1 = CH_3$
3, $X_2 = X_3 = H$; $X_1 = OCH_3$
4, $X_1 = X_3 = H$; $X_2 = OCH_3$
5, $X_1 = X_2 = H$; $X_3 = OCH_3$
6, $X_2 = X_3 = H$; $X_1 = CN$
7, $X_2 = H_3 = H$; $X_1 = NHCOCH_3$

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