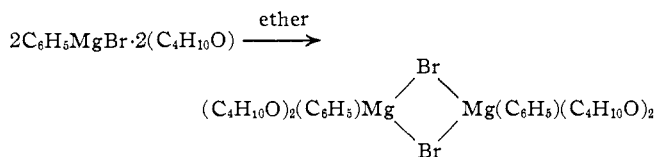


causes polymerization and precipitation tends to confirm that polymerization involves loss of ethers of solvation.

(2) Alternatives which require dimerization without loss of ether, but with higher coordination numbers in solution, such as



are contrary to entropy and thermodynamic data below, and seem unlikely.

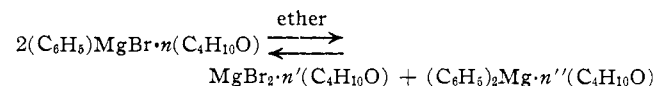
(3) The Mg-O bond to ether in this Grignard is among the strongest Mg-O bonds known (2.06 Å. vs. 2.10 in MgO, 2.09 in Mg(OH)₂⁶ and 2.14 in Mg(H₂O)₆(ClO₄)₂⁷). The bond energies of Mg-O bonds are expected to be greater than those of Mg-Br bonds, and this is supported by thermodynamic data, including $\Delta H_{25}^0 = -44.5$ kcal./mole for solution of crystalline MgBr₂ in water.⁸ The high Madelung energy of MgBr₂ along with the relative low heat of hydration of the bromide ion, and octahedral coordination of magnesium in both crystal and solution, all are factors consistent with increased bond energies in the hydrated solution. Also, for MgBr₂(s) + 6H₂O(l) = Mg(OH)₂·6Br₂(s) $\Delta H_{25}^0 = -104.9$ kcal./mole.⁹ In this reaction bromide ions are displaced by water in the coordination polyhedron about magnesium, and again competing effects do not seem to be large enough to alter the conclusion that increased bond energy in the product is a key factor in the heat of reaction.

(4) C₆H₅MgBr·2(C₄H₁₀O) forms molecular crystals with normal van der Waals packing and nothing to suggest an unusual lattice energy.

These points make it very unlikely that dimagnesium species such as (I) predominate in ether solution. Higher complexes are even less likely.

The crystal structure does not exclude the possibility that in solution the Grignard consists of (C₆H₅)₂Mg·n(C₄H₁₀O) plus Br₂Mg·n'(C₄H₁₀O). This possibility is, however, eliminated by n.m.r. examination of diphenylmagnesium in ether solution and phenylmagnesium bromide in ether solution. In both solutions there is evidence for only one type of phenyl group. In both cases resonances of *ortho*-hydrogens of the phenyl group are well separated from the combined *meta-para* resonances, both are found at low fields. But the separation of *ortho* and *meta-para* resonances for diphenylmagnesium is about 0.1 p.p.m. greater than for phenylmagnesium bromide. This difference in internal chemical shifts persists unchanged over a considerable concentration range.

These n.m.r. data do not eliminate an equilibrium



with a rapid phenyl exchange. (Rapid phenyl exchange is to be expected.^{10,11}) In any case our results strongly imply that C₆H₅MgBr·2(C₄H₁₀O), or possibly

(6) W. G. Wyckoff, "Crystal Structures," Interscience Publishers, Inc., New York, N. Y., 1948.

(7) C. D. West, *Z. Krist.*, **91**, 480 (1935).

(8) Data from W. M. Latimer, "Oxidation Potentials," 2nd Ed., Prentice-Hall, Inc., New York, N. Y., 1952.

(9) Selected Values of Chemical Thermodynamic Properties, National Bureau of Standards Circular 500, U. S. Government Printing Office, Washington, D. C., 1952.

(10) A. L. Allred and C. R. McCoy, *Tetrahedron Letters*, **27**, 25 (1960).

(11) E. N. Sinotova, Y. Vobetski, Y. N. Lognirov and V. N. Evikhev, *Radiochemia*, **1**, 687 (1959).

a higher etherate of the monomer, is a significant feature of this Grignard reagent prepared in the traditional way.

At this time there seems to be no certain evidence that mixing diphenylmagnesium and magnesium bromides in ether leads rapidly to the traditional Grignard

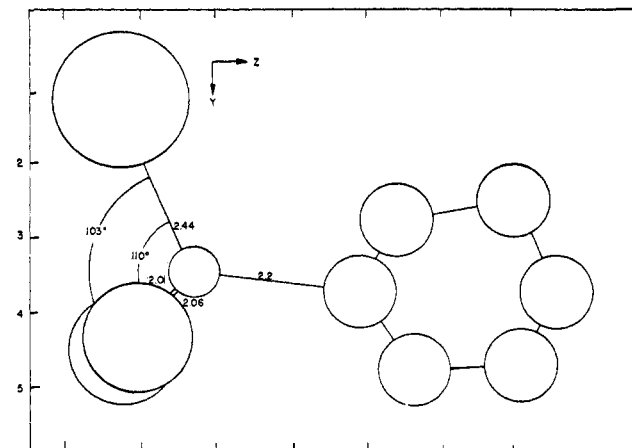


Fig. 1.—Molecular structure of (C₆H₅)MgBr·2C₄H₁₀O in the crystal. Ether carbons are omitted for clarity.

reagent, though this is frequently assumed. It is possible that phenyl-bromine exchange is very slow, although phenyl-phenyl exchange is rapid, since quite different mechanisms may be involved. Until there is evidence to the contrary slow phenyl-bromine exchange offers the simplest explanation of the lack of exchange of magnesium between diphenylmagnesium and magnesium bromides when the two are dissolved together in ether.³

The literature on Grignard reagents is confusing and often inconsistent. Generalizations to other groups and to other ethers are not yet justified.

The full report of the structure of phenylmagnesium bromide dietherate and other studies of Grignard reagents now underway will be published in due course.

The authors are indebted to Dr. R. W. King for the n.m.r. spectra, and to Dr. King and to Profs. H. Gilman and O. Chapman for helpful discussions.

(12) Cont. No. 1264. Work was performed in the Ames Laboratory of the U. S. Atomic Energy Commission.

INSTITUTE FOR ATOMIC RESEARCH AND GALEN D. STUCKY
DEPARTMENT OF CHEMISTRY R. E. RUNDLE
IOWA STATE UNIVERSITY, AMES, IOWA¹²

RECEIVED JANUARY 14, 1963

THE REACTION OF SODIUM BOROHYDRIDE WITH NICKEL ACETATE IN AQUEOUS SOLUTION—A CONVENIENT SYNTHESIS OF AN ACTIVE NICKEL HYDROGENATION CATALYST OF LOW ISOMERIZING TENDENCY

Sir:

The reaction of sodium borohydride with nickel salts in aqueous solution produces a granular black material which is an active catalyst for the hydrolysis of borohydride ion.^{1,2} This material, which has been considered to be a nickel boride, Ni₂B,^{1,3} is a hydrogenation catalyst which has been reported to approach Raney nickel in activity.³

In the course of investigating the effect of olefin structure upon the rate of hydrogenation over various

(1) J. I. Schlesinger, H. C. Brown, A. E. Finholt, J. R. Gilbreath, H. R. Hoekstra and E. K. Hyde, *J. Am. Chem. Soc.*, **75**, 215 (1953).

(2) H. C. Brown and C. A. Brown, *ibid.*, **84**, 1493 (1962).

(3) R. Paul, P. Buisson and N. Joseph, *Ind. Eng. Chem.*, **44**, 1006 (1952).

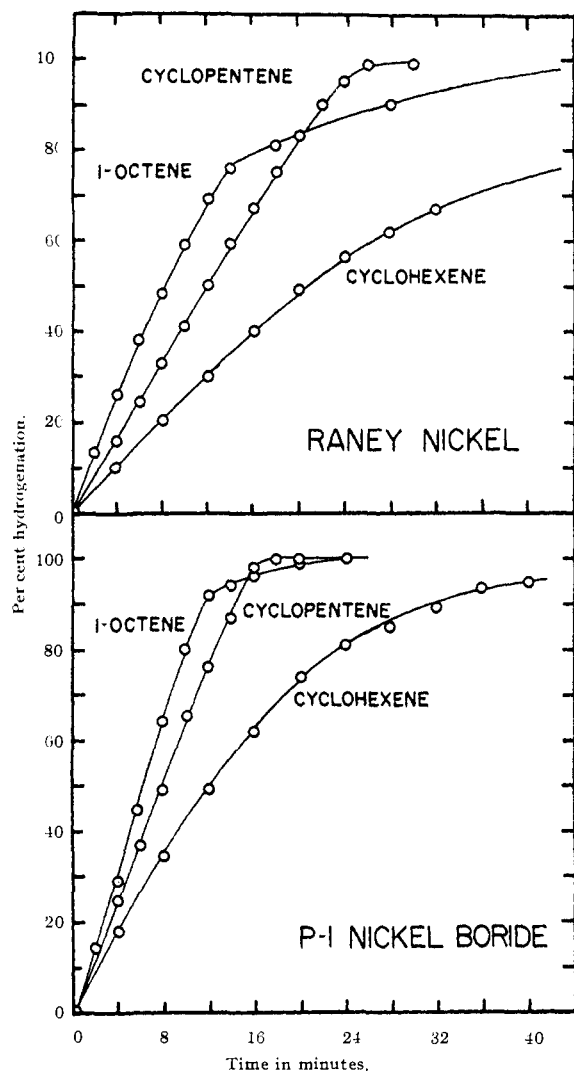


Fig. 1.—Rates of hydrogenation at one atmosphere pressure and 25° of 40 mmoles of 1-octene, cyclopentene and cyclohexene over 5.0 mmoles of Raney nickel (commercial) and P-1 nickel boride.

catalysts, we observed that this nickel boride catalyst⁴ is considerably more active than commercial Raney nickel⁵ toward the less active olefins⁶ (Table I, Fig. 1).

TABLE I
RATES OF HYDROGENATION^a OF REPRESENTATIVE OLEFINS OVER
RANEY NICKEL AND NICKEL BORIDE (P-1)

Olefin	Time (min.) for 50% hydrogenation—	
	Raney nickel	P-1 nickel boride
Safrole	6	6
1-Octene	8	6
Cyclopentene	12	8
Cyclohexene	21	12
Cyclooctene	32	12

^a Hydrogenation of 40 mmoles of olefin at 25°, 1 atm. pressure, in ethanol, over 5.0 mmoles of nickel in the catalyst.

(4) It is convenient to refer to this material as nickel boride for the present, although we have some evidence that its composition is more complex than that represented by the literature formula, Ni₂B. The symbol P-1 is used to distinguish this active catalyst from the more selective one, P-2, described in the following Communication: H. C. Brown and C. A. Brown, *J. Am. Chem. Soc.*, **85**, 1005 (1963).

(5) We utilized a commercial sample of preformed Raney nickel obtained from the Raney Catalyst Co., Inc., Chattanooga, Tenn. Although many different procedures have been described for generating Raney nickel catalysts, it has been reported that these differ little in activity, as measured by the rate of hydrogenation of limonene: H. A. Smith, W. C. Bedoit, Jr., and J. R. Fuzek, *J. Am. Chem. Soc.*, **71**, 3769 (1948).

(6) Paul, Buisson and Joseph (ref. 3) used safrole to compare the activity of Raney nickel and nickel boride catalysts. In the case of this reactive

Even more unexpected was the observation that the nickel boride catalyst exhibits a markedly lower tendency to isomerize olefins in the course of the hydrogenation.

This is indicated by the hydrogenation data for 1-octene (Fig. 1). The rate of hydrogenation over Raney nickel proceeds almost linearly up to approximately 70% completion, but then decreases sharply. Gas chromatographic examination of the reaction mixture at this point reveals the complete absence of 1-octene. On the other hand, the reaction over the nickel boride catalyst proceeds linearly considerably beyond the 70% point (Fig. 1).

In order to test this question more quantitatively, the hydrogenation of 1-pentene over commercial Raney nickel and over P-1 nickel boride was followed by removing samples at intervals and analyzing them by vapor phase chromatography. The results are summarized in Table II.

TABLE II
ISOMERIZATION OF 1-PENTENE IN THE COURSE OF HYDROGENATION^a AT 25° IN ETHANOL OVER RANEY NICKEL AND P-1 NICKEL BORIDE

Hydrogenation, %	Product, mmoles—			
	1-Pentene	<i>cis</i> -2-Pentene	<i>trans</i> -2-Pentene	<i>n</i> -Pentane
A. Raney nickel				
0	40	0	0	0
25	24.8	4.0	1.6	9.2
50	10.4	8.0	1.2	20.4
75	0	7.2	2.4	30.4
100	0	0	0	40
B. P-1 nickel boride				
0	40	0	0	0
25	28.7	1.2	0.4	9.7
50	16.6	2.0	0.8	20.6
75	4.4	3.3	1.7	30.6
100	0	0	0	40

^a Hydrogenation of 40 mmoles of olefin at 1 atm. pressure over 5.0 mmoles of nickel in catalyst.

The preparation of the nickel boride catalyst is exceedingly simple—in marked contrast to the elaborate procedures described for the preparation of Raney nickel catalysts from the alloy.⁷

Five mmoles of nickel acetate in 50 ml. of distilled water was placed in a 125-ml. erlenmeyer flask connected to a mercury bubbler and flushed with nitrogen. To the magnetically stirred solution, 10 ml. of a 1.0 *M* solution of sodium borohydride in water was added over 30 sec. with a syringe. When gas evolution had ceased, a second portion of 5.0 ml. of the borohydride solution was added. The aqueous phase was decanted from the granular black solid and the latter washed twice with 50 ml. of ethanol, decanting the wash liquid each time. The catalyst was then ready for the hydrogenation.

The hydrogenations were carried out with a commercial model⁸ of the hydrogenation apparatus described earlier.⁹ To the above flask containing the catalyst was added (50 - *m*) ml. of ethanol (*m* being the volume of the olefin to be hydrogenated). The flask was attached to the hydrogenator and then flushed with 1 l. of hydrogen, generated in the generator flask. Stirring was initiated, the olefin was injected and the hydrogenation proceeded automatically.

olefin, the rates are almost identical (Table I). These authors concluded that the activity of nickel boride was equal to or slightly less than Raney nickel, but that the activity could be improved by adding certain promoters.

(7) R. Mazingo, *Org. Syn.*, **III**, 181 (1955); H. R. Billica and H. Adkins, *ibid.*, 176 (1955).

(8) Available from the Delmar Scientific Laboratories, Inc., 317 Madison Street, Maywood, Illinois.

(9) C. A. Brown and H. C. Brown, *J. Am. Chem. Soc.*, **84**, 2829 (1962).

This very simple preparation of an active nickel catalyst, together with its low isomerizing tendency, promise to make this catalyst a very useful one for laboratory hydrogenations.

This study was assisted in part by a Research Award (585C) from the Petroleum Research Fund of the American Chemical Society.

RICHARD B. WETHERILL LABORATORY
PURDUE UNIVERSITY
LAFAYETTE, INDIANA

CHARLES A. BROWN
HERBERT C. BROWN

RECEIVED JANUARY 11, 1963

THE REACTION OF SODIUM BOROHYDRIDE WITH NICKEL ACETATE IN ETHANOL SOLUTION—A HIGHLY SELECTIVE NICKEL HYDROGENATION CATALYST

Sir:

We wish to report that the reaction of sodium borohydride with nickel acetate in ethanol solution produces a colloidal black material, presumably nickel boride,^{1,2} which exhibits remarkable selectivity in the hydrogenation of olefins of different structural types. Moreover, it exhibits an unusually low tendency to isomerize olefins during the hydrogenation. Consequently, this catalyst promises to be exceedingly useful for the selective hydrogenation of one olefin in the presence of another, for the selective hydrogenation of the more reactive double bond of a diene and for the conversion of internal acetylenes into *cis* olefins of high purity.³

TABLE I
RATES OF HYDROGENATION^a OF REPRESENTATIVE OLEFINS OVER NICKEL BORIDE (P-2)

Olefin	Time (min.) for hydrogenation ^b	
	10%	50%
1-Octene	1	7
1-Pentene	1	9
3-Methyl-1-butene	2	15
3,3-Dimethyl-1-butene	8	56
2-Methyl-1-butene	35	(400)
<i>cis</i> -2-Pentene	10	120
<i>trans</i> -2-Pentene	40	(360)
Cyclopentene	2	10
Cyclohexene	30	(200)
Cyclooctene	4	28
Styrene	2	9
Safrole	1	3.5

^a Hydrogenation of 40 mmoles of olefin at 25°, 1 atm. pressure, in ethanol, over catalyst prepared from 5.0 mmoles of nickel acetate. ^b Values in parentheses are estimated by extrapolating the experimental data.

The experimental procedure is exceedingly simple. The nickel acetate, 5.0 mmoles, was dissolved in approximately 40 ml. of 95% ethanol contained in the usual hydrogenation flask. The flask was connected to the hydrogenation apparatus⁴ and flushed with 1 l. of hydrogen by introducing the required quantity of sodium borohydride solution into the generator flask. The catalyst was produced by injecting 5.0 ml. of a 1.0 M solution of sodium borohydride in ethanol to the rapidly stirred solution of nickel acetate. Hydrogenation was then initiated by introducing 40 mmoles of the olefin with a hypodermic syringe.

It was observed that safrole underwent hydrogenation with a half-life of 3.5 min., approximately twice the

(1) H. I. Schlesinger, H. C. Brown, A. E. Finholt, J. R. Gilbreath, H. R. Hoekstra and E. K. Hyde, *J. Am. Chem. Soc.*, **75**, 215 (1953).

(2) R. Paul, P. Buisson and N. Joseph, *Ind. Eng. Chem.*, **44**, 1006 (1952).

(3) The designation P-2 is proposed to differentiate this selective nickel boride catalyst from the highly active catalyst (P-1) prepared in aqueous solution: C. A. Brown and H. C. Brown, *J. Am. Chem. Soc.*, **85**, 1003 (1963).

(4) C. A. Brown and H. C. Brown, *ibid.*, **84**, 2829 (1962). This apparatus is now available from the Delmar Scientific Laboratories, Inc., 317 Madison Street, Maywood, Illinois.

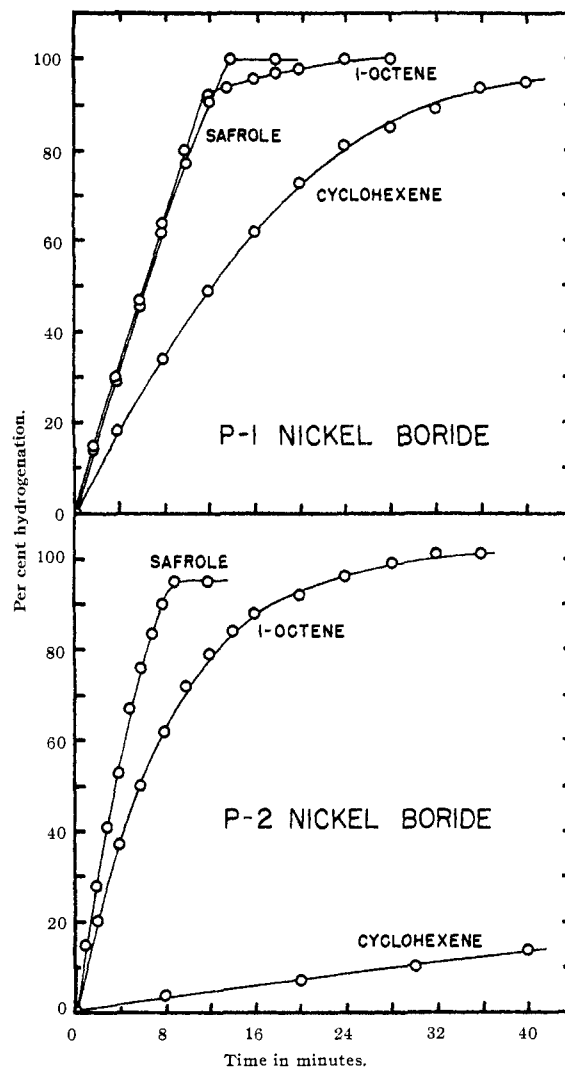


Fig. 1.—Rates of hydrogenation at one atmosphere pressure and 25° of 40 mmoles of safrole, 1-octene and cyclohexene over 5.0 mmoles of P-1 and P-2 nickel boride.

rate observed with the P-1 catalyst. The half-life for 1-octene was 7 min., very similar to that realized with the P-1 catalyst. Finally, the rate with cyclohexene was exceedingly slow, with a half-life of approximately 200 min., in contrast to the 12-min. half-life observed with the P-1 catalyst (Fig. 1). Consequently, this catalyst, prepared in ethanol, achieves a major spread in rates, as compared to that observed with platinum,⁵ Raney nickel³ or the P-1 nickel boride.³

A detailed study revealed that the catalyst is indeed highly sensitive to the structure of the olefin (Table I).

Moreover, this catalyst is remarkably free from isomerization tendencies (Table II).

TABLE II
ISOMERIZATION OF 1-PENTENE IN THE COURSE OF HYDROGENATION^a AT 25° IN ETHANOL OVER P-2 NICKEL BORIDE

Hydrogenation, %	Product, mmoles			
	1-Pentene	<i>cis</i> -2-Pentene	<i>trans</i> -2-Pentene	<i>n</i> -Pentane
(0)	40	0	0	0
26	28.9	0.6	0.1	10.4
52	18.5	.7	.1	20.7
79	7.2	.9	.2	31.7
100	0	0	0	40

^a Hydrogenation of 40 mmoles of olefin at 1 atm. pressure over catalyst prepared from 5.0 mmoles of nickel acetate.

(5) H. C. Brown and C. A. Brown, *ibid.*, **84**, 2827 (1962).