P-2 Nickel Boride, a Catalyst with a Remarkable Affinity for Norbornene Double Bonds. A Highly Convenient Method for the Selective Hydrogenation of Strained Bicyclic Double Bonds

By CHARLES ALLAN BROWN†

(*Departments of Chemistry, University of California, Berkeley, California* 94720, *and Stanford University, Stanford, California* 94305‡)

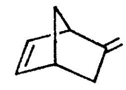
Summary The new nickel boride hydrogenation catalyst allows a simple, convenient selective hydrogenation of norbornene double bonds in the presence of other double bonds.

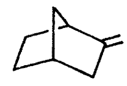
DURING a study of the new nickel boride catalyst,[1] we observed that norbornene is hydrogenated over this material smoothly and rapidly, much more rapidly than other *sym*-disubstituted ethylenes.[2] For example, the half-hydrogenation (25°, 1 atm.) of 40·0 mmoles of norbornene over 5·0 mmoles of P-2 nickel boride requires 6 min. In contrast, *cis*-pent-2-ene needs 2 hr. for half-hydrogenation, cyclohexene over 4 hr., and even the very reactive cyclopentene takes 10 min. Furthermore, the hydrogenation of norbornene proceeds linearly to completion, whereas that of most other olefins become progressively slower as the reaction proceeds.

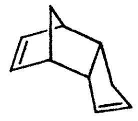
A mixture of 20·0 mmoles each of norbornene and cyclopentene was hydrogenated over 5·0 mmoles of P-2 nickel boride. After consumption of 20·0 mmoles of hydrogen, g.l.p.c. analysis revealed that the norbornene had been reduced preferentially—92% of the norbornene had undergone hydrogenation but only 8% of the cyclopentene, despite the fact that cyclopentene is one of the most reactive olefins studied with P-2 catalyst.[2]

The utility of this high selectivity for the strained norbornene double bond was tested with two readily available dienes: 5-methylenenorbornene (I), and *endo*-dicyclopentadiene (III). In both cases the hydrogenation (40·0 mmoles of diene, 5·0 mmoles of catalyst) proceeded smoothly. After 1 equiv. of hydrogen had been absorbed, the rates decreased substantially; in fact, the hydrogenation of (III) virtually stopped at this point. Analysis by g.l.p.c. and n.m.r. indicated essentially quantitative yields of mono-olefin, *ca.* 95% pure dihydro-derivatives (II) and (IV).

2-Methylenenorbornane (II) is readily isomerized to 2-methylnorbornene.[3] Consequently, the formation of 2-methylenenorbornane in this hydrogenation further confirms the remarkably low isomerization characteristics of the P-2 nickel boride catalyst,[1] and emphasizes the great promise of this catalyst for the selective hydrogenation of dienes where it is desirable to retain the structural identity of the unhydrogenated double bond.


(I)


(II)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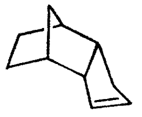
(IV)

The practicality of such selective hydrogenation on a large preparative scale was demonstrated. Thus 396 g. (3·0 moles) of (III) was reduced over 150 mmoles of P-2 nickel boride in 7 hr. After work-up, a yield of 361 g. (90%) was isolated, b.p. 178—180°, m.p. 48·5—50° (lit.[4] 50—51°), 98·5% (IV) (capillary g.l.p.c.).§

P-2 nickel boride is a highly convenient and safe material to use. It is prepared and used *in situ* from two common reagents, nickel(II) acetate and sodium borohydride, and is completely non-pyrophoric.¶

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† National Science Foundation Fellow, 1964—67, and Mobil Oil Company Summer Fellow, 1967 at U.C., Berkeley.

‡ Current address.

§ This preparation was carried out in co-operation with Dr. I. Rothberg.

¶ Selective reductions with P-2 nickel boride are greatly facilitated by the automatic borohydride hydrogenator.[5] This device is well suited to the generation of catalysts *in situ* and allows the hydrogen uptake of a selective hydrogenation to be followed to ±1% even on a large preparative scale.

[1] H. C. Brown and C. A. Brown, *J. Amer. Chem. Soc.*, 1963, **85**, 1004.

[2] C. A. Brown, unpublished observations.

[3] S. Bank, C. A. Rowe, jun., A. Schriesheim, and L. A. Naslund, *J. Amer. Chem. Soc.*, 1967, **89**, 6897.

[4] J. Pirsch, *Ber.*, 1934, **67**, 1115.

[5] C. A. Brown and H. C. Brown, *J. Org. Chem.*, 1966, **31**, 3989.