

Catalytic Hydrogenation. VI.¹ The Reaction of Sodium Borohydride with Nickel Salts in Ethanol Solution. P-2 Nickel, A Highly Convenient, New, Selective Hydrogenation Catalyst with Great Sensitivity to Substrate Structure

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Reduction of nickelous acetate with sodium borohydride in ethanolic solution yields a nearly colloidal black suspension (P-2 nickel) which, used *in situ*, is a hydrogenation catalyst of extraordinary sensitivity to the environment of the double bond. Slight increases in hindrance are strongly reflected in the rate of hydrogenation: 1-octene, 1.00; 3-methyl-1-butene, 0.23; 3,3-dimethyl-1-butene, 0.07. Substitution of the olefinic moiety more markedly affects the reduction rate: 1-octene, 1.0; 2-methyl-1-pentene, 0.004; 2-methyl-2-pentene, <<0.001; 2,3-dimethyl-2-butene, 0. Cyclohexene is peculiarly inert among simple cyclic alkenes: cyclopentene, 1.00; cyclohexene, ~0.010; cycloheptene, 0.60; cyclooctene, 0.20. Strained double bonds are readily reduced: bicyclo[2.2.1]heptene, 1.0; cyclopentene, 0.26; *cis*-2-pentene, <0.01. The presence of an aryl group, even non-conjugated, markedly promotes hydrogenation: 1-octene, 1.0; 3,4-methylenedioxyallylbenzene (safrole), >3.5; allylbenzene, 3.0. Double-bond isomerization and disproportionation of cyclohexadienes are minimal. Benzylic compounds are not hydrogenolyzed significantly in 24 hr, and allylic and propargylic compounds are hydrogenated with no detectable hydrogenolysis. Dienes and acetylenes are partially reduced with high selectivity.

Sodium borohydride reacts with various group VIII B transition metals to yield finely divided black precipitates, some of which are active catalysts for hydrolysis of borohydride.^{3,4} Certain of these materials have been shown to be hydrogenation catalysts with activity equaling or exceeding that of conventionally prepared analogs.⁵⁻⁸

The catalyst prepared by treatment of aqueous nickel salts with an excess of sodium borohydride (designated P-1 nickel) is a granular material with catalytic activity comparable to that of standard commercial Raney nickel catalyst.^{8,9} The P-1 catalyst produces considerably less double bond migration during hydrogenation than does Raney nickel.⁸

Borohydride-reduced noble metal catalysts can be generated and used *in situ* in ethanol.^{7,10} In an extension of this procedure to nickel catalysts, ethanolic nickel acetate was treated with sodium borohydride under nitrogen; a nearly colloidal black suspension formed, in contrast to the granular precipitate resulting from reaction in aqueous solution. This material was nonpyrophoric and nonmagnetic (in contrast to Raney nickel). Hydrogenation of a few model substrates demonstrated major differences between P-1 nickel and the new material, designated P-2 nickel.

Therefore, as part of our systematic studies of the uses of borohydride-reduced transition metals, we undertook a survey of hydrogenations using the P-2 catalyst under model synthetic conditions.

Results¹¹

P-2 nickel is prepared by treating a vigorously stirred solution of nickelous acetate in 95% ethanol (*ca.* 1.25 *M*) with ethanolic sodium borohydride under an inert atmosphere or hydrogen. When hydrogen evolution ceases, the substrate is injected.

Variations in Preparation.—Reduction of nickelous acetate in ethanol was carried out with sodium borohydride in mole ratios of 2:1, 1:1, and 1:2. The 2:1 ratio catalyst was somewhat less active than the others.

The reduction is normally carried out by rapid addition of the borohydride solution to the vigorously stirred nickel acetate solution. Addition of the borohydride in successive smaller increments (mole ratio of Ni(II):NaBH₄ = 1:1 and 1:2) produced no significant change.

In these reductions, some active hydride (from NaBH₄) is utilized in the reduction and does not appear as hydrogen from borohydride ethanolysis. Addition of a 2.5-mmol aliquot of NaBH₄ to 5.0 mmol of Ni(II) yields 6.2 mmol of hydrogen (10.0 mmol theoretical). Subsequent aliquots yield 6.6, 8.8, 9.7, and 10.0 mmol of hydrogen, respectively. A total of 8.7 mmol of hydride is utilized in the reduction of the catalyst.

Metal catalysts have frequently been employed dispersed on inert supports.^{12,13} Preparation of P-2 nickel in the presence of high surface area carbon or silica (23% metal loading by weight) yielded no significant change.

Preparation of the catalyst could be carried out equally satisfactorily under argon, nitrogen, or hydrogen; however, contact with air during the reduction produces a markedly less active catalyst. Once formed, the catalyst appears unaffected by brief exposure (without agitation) to air (as when adding solid substrates).

Catalyst is freshly prepared for each run. Reproducibility is quite high measured by time for an up-

(1) Part V: C. A. Brown, *J. Org. Chem.*, **35**, 1900 (1970).

(2) Uniroyal Summer Research Fellow, 1971.

(3) H. C. Brown, H. I. Schlesinger, A. E. Finholt, J. R. Gilbreath, H. R. Hoekstra, and E. K. Hyde, *J. Amer. Chem. Soc.*, **75**, 215 (1953). This work was carried out during World War II but association with classified research delayed publication for nearly 10 years.

(4) H. C. Brown and C. A. Brown, *J. Amer. Chem. Soc.*, **84**, 1491 (1962).

(5) R. Paul, P. Buisson, and N. Joseph, *C. R. Acad. Sci.*, **232**, 627 (1951).

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

(7) H. C. Brown and C. A. Brown, *Tetrahedron, Suppl. 8, Part I*, 149 (1966).

(8) C. A. Brown, *J. Org. Chem.*, **35**, 1900 (1970).

(9) Samples of preformed Raney nickel were obtained from the Raney Catalyst Co., Inc. Chattanooga, Tenn. This catalyst, essentially the W-2 preparation, is that commonly stocked in organic chemical laboratories.

(10) C. A. Brown and H. C. Brown, *J. Org. Chem.*, **31**, 3989 (1966).

(11) Unless specified otherwise, all hydrogenations were carried out on 40.0 mmol of substrate over P-2 nickel prepared under nitrogen from nickel acetate at 25°, 1 atm of hydrogen, in ethanol solution. These are typical preparative conditions for the automatic borohydride hydrogenator.¹⁰

(12) P. N. Rylander, "Catalytic Hydrogenation over Platinum Metals," Academic Press, New York, N. Y., 1967, p 4.

(13) M. Freifelder, "Practical Catalytic Hydrogenation: Techniques and Applications," Wiley-Interscience, New York, N. Y., 1971, p 75.

take of 0.5 equiv of hydrogen by simple alkenes, generally within $\pm 10\%$ of the average of a series.^{14,15}

Effect of Alkene Structure.—See Tables I and II and Figures 1 and 2. Relative reactivity is reported as ratios of $1/T_{50\%}$.

TABLE I
HYDROGENATION OF REPRESENTATIVE SUBSTRATES
OVER 5.0 MMOL OF P-2 Ni^a

Compd	Initial rate, ^b mmol/min	$T_{50\%}$, ^c min
1-Octene	5.3	4.3
3-Methyl-1-butene	2.0	10
3,3-Dimethyl-1-butene	0.53	48
2-Methyl-1-pentene	0.13	720
2-Methyl-2-pentene	0.01*	>24 hr
2,3-Dimethyl-2-butene	0	∞
<i>cis</i> -2-Pentene	0.31	120
<i>trans</i> -2-Pentene	0.03*	>8 hr
Cyclopentene	0.6	8.0
Cyclohexene	0.08*	>8 hr
Cycloheptene	2.1	13
Cyclooctene	0.67	40
Norbornene	5.6	3.4 ^e
α -Methylstyrene ^d	0.25	120
Benzene	0	∞

^a 40.0 mmol of substrate, 0.8 min, 95% ethanol at 25°, 730-mm pressure. ^b Average from 0.0 to 0.2 H₂. * denotes values measured between 0.0 and 0.05 or 0.1 H₂. ^c Time for uptake of 20.0 mmol of H₂. ^d No reduction of aromatic ring. ^e May reflect slight amount of diffusion limitation.

TABLE II
HYDROGENATION OF REPRESENTATIVE
SUBSTRATES OVER 1.25 MMOL OF P-2 Ni^a

Compd	Initial rate, ^{b,f} mmol/min	$T_{50\%}$, ^c min
1-Octene	2.7	7.8
1-Octene + cyclohexane ^e	2.7	7.9
1-Octene + benzene ^{d,e}	2.3	9.5
Norbornene	5.0	4.0
Safrole ^d	8.0	2.5
Allylbenzene ^d	4.0	4.1
Styrene ^d	3.3	5.5

^{a-d} See Table I. ^e 40.0 mmol of each compound. ^f Because of lower concentration of salts from *in situ* preparation of 1.25 (vs. 5.0) mmol of catalyst, rates are not always proportional to the amount of metal; rates are independent of stirring rate, however.

Substitution of the α position of a 1-alkene markedly interferes with hydrogenation, presumably by increasing hindrance to substrate adsorption: 1-octene, 1.0; 3-methyl-1-butene, 0.23; 3,3-dimethyl-1-butene, 0.07. Direct substitution of the double bond produces even more dramatic effects: 1-octene, 1.0; *cis*-2-pentene, 0.03; 2-methyl-1-pentene, 0.004; *trans*-2-pentene, 0.003; 2-methyl-2-pentene, <0.001; 2,3-dimethyl-2-butene, 0. This extreme sensitivity to substitution is in marked contrast to Pt, Pt/C, and P-1 Ni, which reduce even the tetrasubstituted alkenes without difficulty.

Although most medium-ring alkenes are reduced smoothly, cyclohexene is unexpectedly inert, even less

(14) Hydrogen uptake often slows as hydrogenation proceeds; thus comparison of half-hydrogenation times is preferable to 100% reaction times. The reactions appear to be first order in olefin; a detailed kinetic study of borohydride-reduced catalysts has been initiated.

(15) Reactions are carried out in a magnetically stirred reactor under conditions where hydrogenation rate is independent of agitation rate. Stirrer speeds in excess of 10,000 rpm are available (see Experimental Section).

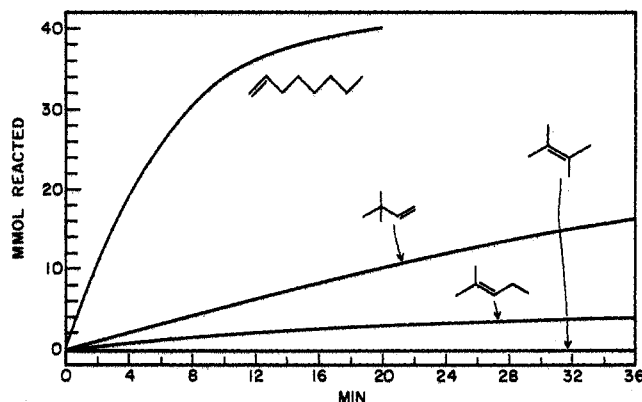


Figure 1.—Hydrogenation of substituted ethylenes over P-2 nickel at 25°: 40.0 mmol of substrate + 5.0 mmol of catalyst.

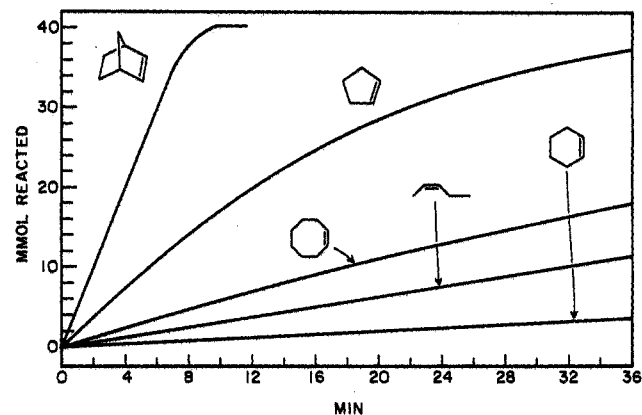


Figure 2.—Hydrogenation of disubstituted alkenes over P-2 nickel at 25°: 40.0 mmol of substrate + 5.0 mmol of catalyst (1.25 mmol for norbornene and cyclopentene).

reactive than *cis*-2-pentene: cyclopentene, 1.0; cycloheptene, 0.60; cyclooctene, 0.20; *cis*-2-pentene, 0.07; cyclohexene, 0.010. This order of reactivity parallels that of P-1 Ni (but is much more pronounced over P-2 Ni), yet differs from that of borohydride-reduced platinum catalysts, which are most active toward cyclohexene.¹⁶

Benzene was not hydrogenated detectably in 24 hr. Compounds containing both olefinic and aromatic unsaturation (*e.g.*, styrene) absorb only 1.0 equiv of hydrogen. However, hydrogenation is markedly faster than in structurally similar aliphatic olefins: 3,4-methylenedioxyallylbenzene (safrole), >3.5; allylbenzene, 3.0; styrene, 1.6; 1-octene, 1.0. The effect is also felt for hindered bonds: α -methylstyrene, 1.0; 2-methyl-1-pentene, 0.17. The presence of benzene slightly retards hydrogenation of 1-octene.

Double-bond strain promotes hydrogenation markedly (norbornene is even more reactive than 1-octene): norbornene, 1.0; cyclopentene, 0.26; *cis*-2-pentene, <0.01.

Migration of double bonds appears minimal over P-2 nickel. After absorption of 0.5 H₂, 1-pentene yields only 2 mol % 2-pentene (largely *trans*). Both P-1 nickel and Raney nickel¹⁰ yield substantially more 2-pentene (10 and 23 mol %, respectively).¹⁷

The initial rates and half-hydrogenation times are

(16) C. A. Brown and V. Ahuja, unpublished observations.

(17) Although hydrogenation predominates over isomerization with nickel, with certain other metals, most notably Pd, isomerization predominates. See ref 7.

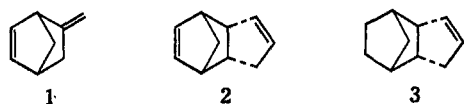
listed in Table I. In a few cases hydrogenations could not be rendered independent of stirring rate with 5.0 mmol of P-2 nickel even at stirring rates of 10,000 rpm. Hydrogenations independent of stirring rate could be obtained over 1.25 mmol of catalyst (Table II).

Selective Hydrogenation of Alkenes.—As the high structural sensitivity suggests, P-2 nickel is highly selective for hydrogenations of one double bond in the presence of another. Hydrogenations proceed smoothly to the equivalence point and then slow sharply. Thus an equimolar mixture of 1-octene and 2-methyl-1-pentene yields (uptake of 1.00 H₂) the respective alkanes in the ratio 16:1. Similarly, 1-octene is reduced in the presence of cyclohexene with a preference of 32:1.

Even in cases where both substrates are readily reduced, addition of 1.0 H₂ yields high selectivity: a mixture of bicyclo[2.2.1]heptene and cyclopentene yields a >13:1 ratio of the respective hydrocarbons. Selectivity, as in the above case, frequently exceeds that predicted from independent initial rates or half-hydrogenation times.

Dienes are hydrogenated with selectivity equal to or greater than that of structurally similar olefin mixtures. Half-hydrogenation of 2-methyl-1,5-hexadiene required 20 min for absorption of 1.04 H₂, 2-methyl-1-hexene accounting for 98% of the olefinic products (49:1 selectivity). Similarly, 4-vinylcyclohexene (1.02 H₂) yielded 4-ethylcyclohexene as 99% of the monounsaturated products.

Methylenenorbornene (**1**) was readily hydrogenated to 2-methylenenorbornene and **2** was reduced to **3** over



P-2 nickel; in both cases only 1–2% of isomeric alkenes and of tetrahydro derivatives were formed.

Reduction of **2** has been carried out on a 3-mol (400 g) scale without difficulty to yield 98.5% pure **3** in 90% distilled yield.

Selective Hydrogenation of Alkynes.—P-2 nickel is an excellent catalyst for selective partial hydrogenation of dialkylacetylenes to *cis* olefins. Hydrogen uptake is smooth and rapid until 1.00–1.02 H₂ is absorbed. For example, 3-hexyne is hydrogenated over P-2 nickel (mole ratio 8:1) to yield 3-hexene (*cis:trans* >30:1) quantitatively. Selectivity on a large scale run (200 mmol, substrate:catalyst 20:1) was higher, with *cis:trans* ≥ 50:1. P-2 nickel has recently been useful for selective hydrogenations of various long-chain acetylenic alcohols in the synthesis of insect sex attractants.¹⁸

Hydrogenation of 1-hexyne is not so selective as that of disubstituted alkynes; at half-hydrogenation a 1:4:1 ratio of *n*-hexane:1-hexene:1-hexyne is found by glpc (no isomeric hexenes are formed). During hydrogenation, the hexane:hexene ratio is constant at 0.27 as long as 1-hexyne is present.¹⁹

Conjugated Dienes.—Isoprene is selectively reduced to a mixture of all three methylbutenes. Hydrogen uptake continued after the equivalence point until 3-

methyl-1-butene was removed, as expected from the structural sensitivity of P-2 nickel discussed above. Hydrogenation of 1,3-cyclohexadiene nearly ceases after uptake of 0.85 H₂. The product consists mainly of cyclohexene and benzene (formed *via* disproportionation²⁰ of the diene) in a 10:1 ratio.

Hydrogenolysis.—Benzylic derivatives such as the alcohol and methyl ether are not subject to hydrogenolysis over P-2 nickel for at least 24 hr. Allylic alcohols such as 1-penten-3-ol and 1-vinylcyclohexanol are hydrogenated to the corresponding saturated derivatives without scission of the C–O bond, as is allyl acetate. Similarly, ethynylcarbinols absorb exactly 2.0 H₂ without hydrogenolysis.

Selective hydrogenation data are listed in Table III.

Discussion

Reduction of nickel salts with sodium borohydride represents a convenient direct method to active catalysts. It is surprising, and currently unexplained, that the alteration of preparation solvent from water to ethanol should result in such a pronounced change in properties.

P-2 nickel is probably an amorphous mixture of nickel and boron.²¹ Such mixtures usually contain nickel and boron in a mole ratio of 2.0–2.5:1.²¹ Reduction of nickel(II) to nickel(0) with borohydride results in utilization of 1.0 equiv of H[–], or 5.0 mmol of H[–] for 5.0 mmol of nickelous acetate. The formation of B(0) would utilize 1.5 equiv of H[–], or 3.0–3.75 mmol of H[–] for the usual alloy mole ratios. Thus preparation of P-2 nickel requires 8.0–8.75 mmol of H[–], in excellent agreement with the 8.7 mmol actually found to be utilized.

The lack of effect of supports such as high surface area carbon upon P-2 nickel was at first surprising, since a considerable effect is obtained with borohydride-reduced platinum metals.⁷ The effect of supports is most probably to increase the available metal surface area; thus the extremely high state of dispersion of P-2 nickel may be unimproved by support. Similar phenomena have been observed for silane-reduced²² and borane-reduced²³ catalysts.

Hydrogenations over P-2 nickel proceed at a steadily decreasing rate, unlike the zero-order hydrogenations observed over borohydride-reduced platinum catalysts. Studies in progress suggest that hydrogenations over P-2 nickel proceed by kinetics first order in substrate, indicating a weak adsorption of the double bonds for the P-2 nickel surface. Refinements in technique are in progress to allow analysis of the effects of substrate structure.

The study reports a preliminary survey of a novel catalyst system, P-2 nickel. This scan reveals a readily prepared, simple catalyst with considerable selectivity: reduction of one double bond in the presence of others; selective half-hydrogenation of conjugated dienes; reduction of alkynes to pure *cis* olefins; and hydrogenation

(20) Such disproportionation occurs with both 1,3- and 1,4-cyclohexadienes over a variety of catalysts, predominating over hydrogenations with Pd/C. Low-temperature aromatization utilizing this effect is under investigation.

(21) See the discussion in ref 8 and the references therein.

(22) C. Eaborn, B. C. Pant, E. R. A. Peeling, and S. C. Taylor, *J. Chem. Soc. C*, 2823 (1969).

(23) C. A. Brown, research in progress.

(18) K. W. Greenlee, private communication.

(19) Hexane and 1-hexene are formed *via* a common chemisorbed intermediate; little or no hexane is formed *via* reduction of 1-hexene in competition with 1-hexyne. C. A. Brown, *Chem. Commun.*, 139 (1970).

TABLE III
SELECTIVE HYDROGENATIONS OVER P-2 NICKEL

Compd ^a	Product (%)
1-Hexyne	<i>n</i> -Hexane (16) 1-Hexene (68) 1-Hexyne (16)
3-Hexyne	<i>n</i> -Hexane (1) <i>c</i> -3-Hexene (96) <i>tert</i> -3-Hexene (3) 3-Hexyne (0)
1-Octene + 2-methyl-1-pentene	<i>n</i> -Octane (48) 1-Octene (2) 2-Methylpentane (3) 2-Methyl-1-pentene (47)
1-Octene + cyclohexene	<i>n</i> -Octane (49) 1-Octene (1) Cyclohexane (2) Cyclohexene (48)
Norbornene + cyclopentene	Norbornane (47) Norbornene (3) Cyclopentane (2) Cyclopentene (48)
2-Methyl-1,5-hexadiene	2-Methylhexane (2) 2-Methyl-1-hexene (96) Other methylhexenes (2) 2-Methyl-1,5-hexadiene (0)
4-Vinylcyclohexene	Ethylcyclohexane (2) 4-Ethylcyclohexene (97) Vinylcyclohexane (1) 4-Vinylcyclohexene (0)
Isoprene	2-Methylbutene (4) Methylbutenes (91) Isoprene (5)
1,3-Cyclohexadiene ^b	Cyclohexane (2) Cyclohexene (89) 1,3-Cyclohexadiene (0) Benzene (9)
5-Methylenenorbornene	Methylnorbornanes (1) Methylnorbornenes (2) 2-Methylenenorbornane (96) 5-Methylenenorbornene (1)
<i>endo</i> -Dicyclopentadiene (2)	Tricyclodecane (2) Dihydro (3) (>97) Other dihydro (<1) Dicyclopentadiene (0)
1-Penten-3-ol ^c	<i>n</i> -Pentane (0) 3-Pentanol (100%)
1-Vinylcyclohexanol ^c	Ethylcyclohexane (0) 1-Ethylcyclohexanol (100)
3-Methyl-1-pentyn-3-ol ^d	3-Methylpentane (0) 3-Methyl-3-pentanol (100)
1-Ethynylcyclohexanol ^d	Ethylcyclohexane (0) 1-Ethylcyclohexanol (100)

^a Hydrogenation of 40.0 mmol of substrate (40.0 mmol of each in mixtures) over 5.0 mmol of P-2 nickel in 95% ethanol at 25°, 1 atm; 40 ± 0.8 mmol of hydrogen used. ^b 32.0 mmol of hydrogen. ^c Hydrogen uptake 40.0 mmol. ^d Hydrogen uptake 80.0 mmol.

tion without hydrogenolysis. Future studies will examine these uses individually in detail. The ease of preparation, high selectivity, nonpyrophoric nature, and reproducibility of P-2 nickel make it a potentially powerful new synthetic tool.

Experimental Section

Apparatus.—The all-glass automatic borohydride hydrogenator described in early studies⁸ was employed throughout this work.²⁴ The reactor flask was agitated with a 1.5 × 0.375 in. TFE-

covered magnetic stirring bar; the drive magnet was powered by a motor supplied with a 0–145-V continuously variable power source. Under reaction load speeds of at least 11,000 rpm were obtained, as monitored with a stroboscopic tachometer. Speed variations during runs were less than 500 rpm. The reactor was generally a 125-ml modified erlenmeyer flask but special cylindrical flasks of 150-ml capacity with antivortex indentations were employed for faster runs. The reactor was immersed in a water bath maintained at 25 ± 1°. Reaction rates were shown to be independent of stirring rate at the speeds employed.

Reagents.—Nickelous acetate [Ni(C₂H₃O₂)₂·4H₂O] was obtained from J. T. Baker (Baker A. R. grade).

Sodium borohydride, 98% dry solid, was produced and supplied by Ventron Corp. A stabilized solution suitable for catalyst reduction is prepared by dissolving 4.0 g of sodium borohydride powder in a mixture of 95 ml of absolute ethanol and 5 ml of 2 *N* sodium hydroxide and filtering the resulting solution. This solution is best prepared freshly the day of use for maximum catalyst reproducibility but may be utilized satisfactorily for up to 5 days if kept refrigerated. Formation of small amounts of sediment under refrigeration is not harmful.

Organic substrates were obtained from Phillips Petroleum Co. or Chemical Samples Co. and were distilled under nitrogen before use. If a substrate was colored or had a refractive index significantly varied from published values (American Petroleum Institute), it was fractionally distilled from LiAlH₄ or NaBH₄. Purified samples were stored at 0° under nitrogen.

Catalyst Preparation and Use.—Nickel acetate tetrahydrate (1.24 g, 5.0 mmol) was dissolved in (50 - *n*) ml (*n* = volume of substrate to be added) of 95% ethanol in a 125-ml erlenmeyer flask (modified for high-speed magnetic stirring). This flask was attached to a borohydride hydrogenator, which was then flushed with nitrogen. With vigorous stirring, 5.0 ml of 1.0 *M* sodium borohydride solution in ethanol (see above) was injected over 15 sec. When gas evolution from the mixture ceased, the catalyst was ready for use. The hydrogenator was purged with hydrogen, and reaction was initiated by injecting substrate. Addition of solid substrates was accomplished with the stirrer stopped just before purging with hydrogen. When two compounds were run, they were either injected as a mixture or else stirring was stopped momentarily while the two were added in rapid succession.

Catalyst for 1.25-mmol runs was prepared *in situ* on 1/4 scale; alcohol was then added to maintain a total volume of 50 ml.

Samples were withdrawn from the reactor with a syringe and stainless steel needle. Sampling did not affect reaction reproducibility.

Analysis.—Samples were analyzed by glpc and compared with known materials. In general, total hydrogen uptake was within ±2% of theoretical; certain runs were also checked with internal standards, confirming quantitative yields (*i.e.*, no substrate polymerization).

Columns made from the following materials proved exceptionally useful in analyzing various olefin and hydrocarbon mixtures: adiponitrile, triethylene glycol-silver nitrate, tris(cyanoethoxy)propane, UCON 50 HB 2000, and squalene.

5,6-Dihydro-*endo*-dicyclopentadiene (3).—Dicyclopentadiene (Matheson Coleman and Bell) was chilled until the major portion had solidified. The material was filtered and the solid was pressed on a Buchner funnel with dental dam to remove as much liquid as possible. The solid was warmed just to melt, and the process was repeated. The resulting solid had mp 28–30° (lit.²⁵ mp 27–28°).

In a 2-l. flask, 37.5 g (150 mmol) of nickel acetate tetrahydrate was dissolved in 200 ml of 95% ethanol. The flask was attached to a Brown[□] hydrogenator and flushed with hydrogen. With rapid stirring 150 ml of 1.0 *M* sodium borohydride solution in ethanol was added to reduce the nickel acetate to P-2 nickel. The purified *endo*-dicyclopentadiene (407 g, 3.08 mol) was melted with 200 ml of ethanol and the mixture was injected into the hydrogenator. With vigorous stirring, the reaction proceeded smoothly; hydrogen uptake ceased when 3.08 mol of hydrogen had been absorbed.

Five grams of activated carbon was added to the reaction mixture to aid in catalyst removal and the warm (40°) mixture was filtered through a thin (0.125 in.) pad of carbon on a Buchner funnel. The filter pad was washed with 2 × 100 ml of warm

(25) H. Staudinger and A. Rheiver, *Helv. Chim. Acta*, **7**, 23 (1924).

(26) C. E. Waring, E. E. Kern, and W. A. Blann, *J. Amer. Chem. Soc.*, **63**, 1787 (1941).

(24) A commercial model was obtained from Delmar Scientific Laboratories, Maywood, Ill.

acetone. The combined organic layers were distilled to remove solvent. The residue was distilled through a short Vigreux column to give 370 g, 2.76 mol (90%), of 5,6-dihydro-*endo*-dicyclopentadiene (3), bp 178–180°, mp 48–50°. Recrystallization from methanol gave mp 50° (lit.²⁷ mp 48.5–50°); nmr (CCl₄, TMS) δ 1.25 (s, 3.8 H), 1.45 (s, 2.2 H), 2.0–3.2 (m, broad, 6.2 H), 5.70 (s, broad, 2.0 H). Product was free from starting material by glpc.

(27) K. Alder and G. Stein, *Justus Liebigs Ann., Chem.*, **485**, 241 (1931).

Registry No.—Nickelous acetate, 373-02-4; sodium borohydride, 16940-66-2.

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Studies on Heterocage Compounds. V.¹ Reaction of 5-Hydroxymethyl-2-norbornene with Dihalocarbene. Novel Synthesis of Some Oxa-Modified Adamantane Analogs

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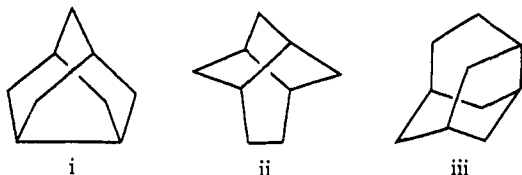
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Reaction of *endo*-5-hydroxymethyl-2-norbornene (1) with dichloro- and dibromocarbene afforded oxahomobrendene derivatives, 3-chloro- (2) and 3-bromo-5-oxatricyclo[5.2.1.0^{4,8}]dec-2-ene (10), in good yields. Catalytic hydrogenation of 2 and 10 gave 5-oxahomobrendane (6). The Birch reduction of 2 afforded *endo*-6-hydroxymethylbicyclo[3.2.1]oct-2-ene (7), which was shown to be an excellent precursor to 5-oxaprotadamantane (12) and its 10-acetoxy derivative (13). The mechanism for the reaction of 1 with dihalocarbene was discussed from the product distributions under various conditions.

Much attention has been paid recently to adamantane and its related cage compounds since the discovery of an efficient synthetic route to the adamantyl ring system by Schleyer and Donaldson, and the subsequent findings of the biological activities of a number of compounds with these ring systems.² However, studies on the heteroanalogs of the related cage compounds seem to be not extensively investigated compared to the carbocyclic analogs; this might be due to the lack of a very efficient synthetic route to heteroanalogs such as carbonium ion rearrangements.³ In a continuation of our studies on heterocage compounds,⁴ this paper describes a novel and facile synthetic route to 5-oxahomobrendane and 5-oxaprotadamantane.

endo-6-Substituted bicyclo[3.2.1]octane is involved as the characteristic skeletal moiety in some of the representative modified adamantane skeletons such as noradamantane (i), twistane (ii), and protadamantane (iii).



On the other hand, dihalocarbene addition to norbornene is known to afford bicyclo[3.2.1]octane derivatives.⁵ Furthermore, dihalocarbene in a surfactant-

catalyzed emulsion has been found recently to react with substrates very effectively.^{6–8} Taking into consideration these facts, we employed readily accessible *endo*-5-hydroxymethyl-2-norbornene (1) as one of the most promising starting materials for synthesis of some oxa-modified adamantane analogs and examined the reactions of 1 with dihalocarbene.

Results and Discussion

Reaction of *endo*-5-Hydroxymethyl-2-norbornene (1) with Dichlorocarbene.—Dichlorocarbene addition to 1⁹ in 50% aqueous sodium hydroxide–benzene emulsion catalyzed with benzyltriethylammonium chloride at 20° afforded a mixture of 3-chloro-5-oxatricyclo[5.2.1.0^{4,8}]dec-2-ene (2), 3,3,6-trichlorotricyclo[3.3.1.0^{2,4}]nonane (3), 3,4,6-trichlorobicyclo[3.3.1]non-2-ene (4), and 3,3,7,8-tetrachlorotricyclo[4.3.1.0^{2,4}]dec-8-ene (5) (Table I, Scheme I). Both 3 and 5 were isolated by chromatography on basic alumina in 8.4 and 3.2% yields, respectively. Oily products 2 and 4 were purified on preparative glpc. Structural assignment of these products was based on the analytical and physical data, and some chemical conversions. The major product 2 had a formula C₉H₁₁OCl from analysis and characteristic mass spectrum, *m/e* 170 (M⁺) and 172 (M + 2) in 3:1 ratio. In the nmr (CDCl₃) spectrum, 2 had signals at τ 3.87 (d, 1, *J*_{1,2} = 7.5 Hz, H₂), 5.58 (d, 1, *J*_{4,8} = 6.5 Hz, H₄), 5.89 (t, 1, *J*_{6,8} = *J*_{6,7} = 8.8 Hz,

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(3) For a recent review on heteroadamantane, see G. Gelbard, *Ann. Chim. (Paris)*, 331 (1969).

(4) For example, see (a) T. Sasaki, S. Eguchi, and T. Kiriya, *J. Amer. Chem. Soc.*, **91**, 212 (1969); (b) T. Sasaki, S. Eguchi, and T. Kiriya, *Tetrahedron*, **27**, 893 (1971).

(5) C. W. Jefford, S. Mahajan, J. Weslyn, and B. Waegell, *J. Amer. Chem. Soc.*, **87**, 2183 (1965), and references cited therein.

(6) For addition reactions of carbene to olefin, see (a) M. Makosza and M. Warzyniez, *Tetrahedron Lett.*, 4659 (1969); (b) M. Makosza and E. Biacka, *ibid.*, 4517 (1971).

(7) (a) For insertion reaction of dihalocarbene, see I. Tabushi, Z. Yoshida, and N. Takahashi, *J. Amer. Chem. Soc.*, **92**, 6670 (1970); (b) for reaction of alcohol with dichlorocarbene, see I. Tabushi, Z. Yoshida, and N. Takahashi, *ibid.*, **93**, 1820 (1971).

(8) For the reaction site and the reaction mechanism, see (a) C. M. Starks, *J. Amer. Chem. Soc.*, **93**, 195 (1971); (b) G. C. Joshi, N. Singh, and L. M. Pande, *Tetrahedron Lett.*, 1461 (1972); (c) A. W. Herriott and D. Picker, *ibid.*, 4521 (1972).

(9) An *exo*-*endo* mixture (1:4) was used as a practical starting material because a 1:19 mixture gave a similar result (see Table I).