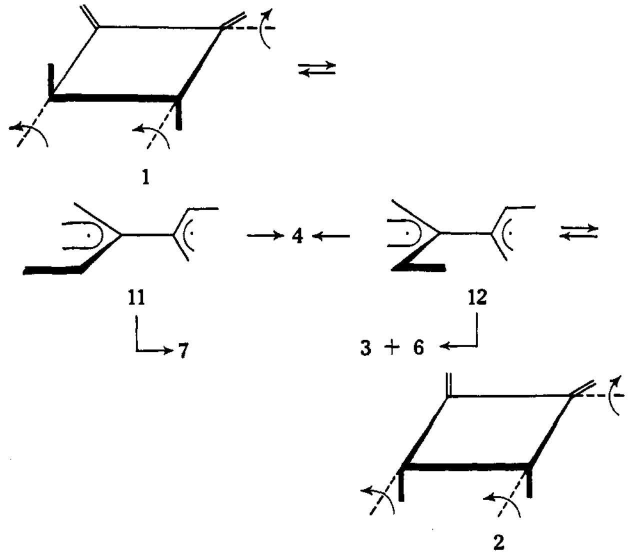
tion to the double-inversion products, **5**, **6**, and **7**. More striking, however, are the facts that (a) interconversion of **1** and **2** occurs relatively slowly in short-term thermolyses; (b) **1** gives almost exclusively **4** and **7**; (c) **2** gives almost exclusively **3**, **4**, and **6** and the subsequent rearrangement product of **3**, namely **8**.

If the reasonable assumption that rotation about bonds occurs slowly relative to ring closure in the nearly, or completely, developed allylic radicals at the higher reaches of the energy surface for the rearrangement, then the relative ratios of the double-inversion products, **5**, **6**, and **7**, indicate that conrotatory over disrotatory opening of the cyclobutane ring is favored by a factor of at least 100 from **1** and at least 10 from **2**. Further, if it is assumed that the intermediate responsible for the double-inversion product is also responsible for the single-inversion product, then orthogonal, or effectively so, Me_2TME species must be involved, and the one which must be produced from **1** is **11**, and the one which is produced from **2** is **12** by the conrotatory motions indicated above.[5–7]



By virtue of the bidentate nature of the allyl radical, **11** can give **7**, **4** (two ways), and **1** (by the microscopic reverse of its formation), and **12** can give **6**, **3**, **4**, and **2**. Thus, the conrotatory mode of ring opening deduced from the double-inversion product distribution is qualitatively in accord with the distribution of single-inversion products since little **3** is found in the *trans*-**1** thermolysis.[8,9] It is interesting that **12** must give 5 to 6 times as much **3** as **4** if it is the sole intermediate in the thermolysis of **2**.

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(5) (a) It is possible that the double inversion product results from initial closure to a $\Delta^{1,4}$-bicyclo[2.2.0]hexene which reopens in the opposite direction. The single inversion product then must result from 1,3-sigmatropic rearrangements[5b] proceeding *via* species which would not have D_{2d} symmetry as would the TME species envisioned here, *sans* methyl groups. It is difficult to imagine such species, however, since they would differ from the D_{2d} species by only a stretching vibrational motion. (b) J. A. Berson, *Accounts Chem. Res.*, **1**, 152 (1968).

(6) A third Me_2TME species can be formed by conrotatory opening of **1**, namely one in which the two methyl groups are directed to the interior of the system. However, **3** and **5** are the expected products from this species, and these are formed only to a limited extent, if at all, from **1**.

(7) (a) SCF π-electron calculations with extensive configuration interaction[7b] suggest that the orthogonal and planar TME species are nearly equivalent in energy; thus, steric interactions may control the relative energies, and EHT calculations suggest that the D_{2d} geometry is favored over the D_{2h} geometry by 4 kcal/mol.[7b] (b) R. Hoffman, private communication.

(8) If **11** is solely responsible for product from **1**, there are two possible rotations about the C-1–C-2 bond with respect to the other bond rotations. At the point of intersection of the rotation axes in the above figure, the relative rotations are as meshed bevel gears. However, an "antibevel" pathway is also possible which gives exactly the same stereochemical results.

(9) Disrotatory ring opening to form **3** and **4** cannot be ruled out by these experiments, as has been implied above and stated by a referee; however, conrotatory ring opening is sufficient to explain all the observations with a minimum number of assumptions and apparent contradictions.

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Low-Temperature Hydrogenation over Borohydride-Reduced Catalysts. A New Convenient Procedure for Improving the Selectivity of Reduction

Sir:

In the course of a systematic study of the uses of the new borohydride-reduced metal catalysts,[1] we found that the observed rates of hydrogenation of a representative olefin, 1-octene, were remarkably insensitive to temperature decreases.[2] This unexpected insensitivity of the reaction (run under preparatively useful conditions) suggested a convenient technique for affecting the course of hydrogenations merely by lowering the temperature. This communication reports that such reductions at low temperature are eminently feasible and, in fact, examples chosen at random show considerable improvements in the selectivity of hydrogenation.

The feasibility of the technique was demonstrated with the hydrogenation of a series of increasingly substituted ethylenes over $Pt(BH_4^-)$-C[3] at 25, 0, and −25°, using a low (0.005:1) metal:olefin ratio. The times for total hydrogenation increased appreciably from 1-hexene, to 2-methyl-1-pentene, to 2-methyl-2-pentene, to 2,3-dimethyl-2-butene. However, even the tetrasubstituted olefin was completely reduced in 4 hr at −25° with the low amount of catalyst. It is clear that, if desired, reaction times could be considerably shortened

Table I. Effect of Temperature upon Hydrogenation of Four Representative Olefins[a]

Substrate	25°	0° $T_{100\%}$, min[b]	−25°
1-Hexene	10	14	24
2-Methyl-1-pentene	10.5	13.5	46
2-Methyl-2-pentene	12	29	152
2,3-Dimethyl-2-butene	14	52	240

[a] Hydrogenation of 40.0 mmoles of distilled substrate over 0.20 mmole of Pt on 1.0 g of Darco G-60 carbon at 1 atm. [b] Time for complete reduction. The time for 50% reduction was 40–50% of this. Temperatures were held to ±1° except −25° (±3°).

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

(2) C. A. Brown, unpublished observations.

(3) The borohydride-reduced carbon-supported catalyst,

Table II. Effect of Temperature on Hydrogenation Selectivity[a]

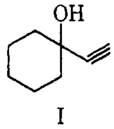
Substrate	Catalyst	Temp, °C	Products	Product ratio
Cyclopentene[b] +	$Pt(BH_4^-)$-C	25	Cyclopentane[d]	$C_5/C_6 = 3.4$
cyclohexene[b]		−25	Cyclohexane	$C_5/C_6 = 7.8$
				$\Delta^1/\Delta^2 = 5.8$
1-Pentene[c]	$Pt(BH_4^-)$-C	25	1-Pentene[d]	$\Delta^1/\Delta^2 = 9.0$
		0	2-Pentenes	$\Delta^1/\Delta^2 = 17$
1-Ethynylcyclo-	$Pd(BH_4^-)$-C	−25	1-Ethylcyclohexanol (II)[e]	III/II = 0.25
hexanol[c]		25	Ethylcyclohexane (III)	III/II = 0.05
		0		III/II = 0.01
β-Pinene[c]	$Pt(BH_4^-)$-C	−25	*cis*- and *trans*-[f]	*c*/*t* = 6.1
		25	pinane	*c*/*t* = 16
		0		
1,2-Dimethylcyclo-	$Pt(BH_4^-)$-C	25	*cis*- *and trans*-1,2-	*c*/*t* = 2.5
hexene[d]		0	dimethylcyclohexane[d]	*c*/*t* = 5.2

[a] Hydrogenation in 40 ml of ethanol at 1 atm in the presence of 0.1 *N* hydrochloric acid (0.1 *N* acetic acid for *β*-pinene), using 0.20 mmole of $M(BH_4^-)$-C catalyst. [b] 20.0 mmoles of substrate used. [c] 40.0 mmoles. [d] 20.0 mmoles of hydrogen used. [e] 80+ mmoles, *i.e.*, total saturation. [f] 40.0 mmoles.

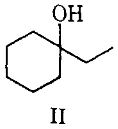
by increasing the relative amount of catalyst employed.[4]

These results are summarized in Table I. The use of the technique for improved selectivity is demonstrated by the following examples.

Hydrogenolysis. Ethynylcyclohexanol (I) has been reported to undergo extensive hydrogenolysis of the hydroxyl function during complete hydrogenation over palladium catalysts;[5] a number of additives were reported of varying efficiency in suppressing this undesirable side reaction.[5] However, hydrogenation at 0° is much more specific for formation of II than at 25° and, in fact, at −25°, 40.0 mmoles of I underwent smooth hydrogenation over 0.20 mmole of $Pd(BH_4^-)$-C^3 with *no detectable loss of the hydroxyl group.* Similarly, hydrogenolysis (ring opening) of the cyclopropyl moiety in sabinene (IV) and thujene (V) (25 and 14% at 25°) was completely suppressed during hydrogenation at −20° over $Pt(BH_4^-)$-C^3 or PtO_2.[6]



I



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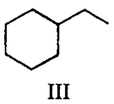

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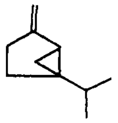
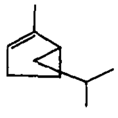
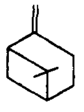


IV



V



VI

Stereochemistry. Even though the temperature drop was only 25° in the hydrogenations of 40.0 mmoles of *β*-pinene (VI) and 20.0 mmoles of 1,2-dimethylcyclohexene over 0.20 mmole of $Pt(BH_4^-)$-C,[3] both showed a marked increase in the yield of *cis*-dihydro material. Thus *cis*-pinane of 94% isomeric purity may be realized *via* such low-temperature hydrogenation.

Bond Migration. The isomerization of a double bond during hydrogenation is a considerable problem in systems where product stereochemistry is altered by a change in double bond position. Such isomerization was substantially reduced in the reduction of 40.0 mmoles of 1-pentene over 0.20 mmole of $Pt(BH_4^-)$-C^3 at lower temperatures.

Double Bond Mixtures. Hydrogenation of 20.0 mmoles each of cyclopentene and cyclohexene over 0.20 mmole of $Pt(BH_4^-)$-C^3 with 20.0 mmoles of hydrogen yielded a C_5:C_6 cyclane ratio more than twice as large at −25° as at 25°.

These results are summarized in Table II.

The reaction procedure is extremely simple. The catalyst is prepared *in situ* in the borohydride hydrogenator[7,8] reactor flask according to the procedures of ref 1 and 7. Then a cooling bath is placed around the reactor, the hydrogen generator is packed in ice, the system is allowed to come to equilibrium, and substrate is injected.

Low-temperature hydrogenations are greatly facilitated by the borohydride hydrogenator. The stationary, thin-walled reactor and generation of hydrogen within the cooled area markedly contribute to the convenience of the procedure.

Further applications of this technique in organic synthesis are currently under study.

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(4) Surprisingly, although the effects of temperature on hydrogenation have been examined for numerous systems, virtually none of these studies has included subambient temperatures. In general, temperature increases were utilized, primarily to increase rate. For a detailed review of the literature see P. N. Rylander, "Catalytic Hydrogenation over Platinum Metals," Academic Press, New York, N. Y., 1967.

(5) R. J. Tedeschi and G. Clark, Jr., *J. Org. Chem.*, 27, 4232 (1962).

(6) S. P. Acharya and H. C. Brown, private communication.

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

(8) A commercial model of the hydrogenator was obtained from Delmar Scientific Laboratories, Maywood, Ill. 60154.

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