The experiments described below are representative reactions for each of the 1-alkenes that were reactive toward lithium dispersion.

Reactions of 1-Alkenes with Lithium Dispersion. Derivatization with Chlorotrimethylsilane. Hexene-1.—The products resulting from the reaction of 1.75 g (0.25 g-atom) of lithium dispersion and 70 ml (47 g, 0.56 mole) of purified 1-hexene (distilled from lithium aluminum hydride) after 1.5 hr at reflux were treated with 15 ml of tetrahydrofuran and 8.5 g (0.08 mole) of chlorotrimethylsilane. Distillation under vacuum gave the following fractions: (1) 0.25 g of material, bp 62–64° (18 mm), and (2) 6.6 g of material, bp 64–70° (18 mm). Fraction 2 was shown to consist of three compounds by gc; 2.7% of an unknown compound, 6.3% *trans*-1-hexenyltrimethylsilane, and 91% 1-hexynyltrimethylsilane.

The residue remaining in the Grignard flask was washed thoroughly with hexane, and dispersed in *ca.* 50 ml of octane. Water was then slowly and carefully introduced into the system resulting in the evolution of hydrogen. The volume of gas collected corresponded to 0.20 mole at STP [theory = (0.75) (0.25 g-atom of lithium used) = 0.19 mole].

Pentene-1.—The products resulting from the reaction of 1.4 g (0.2 g-atom) of lithium dispersion and 60 ml (38.4 g, 0.55 mole) of 1-pentene, refluxed for 1.5 hr, and subsequently treated with 5 ml of tetrahydrofuran and 8.5 g (0.08 mole) of chlorotrimethylsilane, were distilled to give 3.7 g of material, bp 62–64° (40 mm). A gas phase capillary chromatographic analysis demonstrated that the distillate consisted of 2% of an unknown compound, 26% *trans*-1-pentenyltrimethylsilane, and 72% 1-pentynyltrimethylsilane.

Heptene-1.—The products resulting from the reaction of 1.75 g (0.25 g-atom) of lithium dispersion and 53 ml (37 g, 0.38 mole) of 1-heptene, refluxed for a 1.25-hr period, and subsequently treated with 10 ml of THF and 8.5 g (0.08 mole) of chlorotrimethylsilane, were distilled to give 4.1 g (*ca.* 40%) of 1-heptynyltrimethylsilane, bp 72–82° (12 mm).

Octene-1 (Promoted with Water).—To a mixture of 1.75 g (0.25 g-atom) of lithium dispersion and 70 ml (50 g, 0.45 mole) of 1-octene at *ca.* 100°, 0.4 g (0.022 mole) of water was added over a 1-hr period. After an additional 1.5 hr of stirring, the reaction mixture was allowed to cool to room temperature and 15 ml of THF and 8.5 g (0.08 mole) of chlorotrimethylsilane (dropwise) were added successively. The products obtained on work-up were distilled to give 5.2 g (45.7%) of 1-octynyltrimethylsilane, bp 98–108° (26 mm).

Decene-1 (Promoted with Water).—To a mixture of 1.75 g (0.25 g-atom) of lithium dispersion and 50 ml (37 g, 0.26 mole) of 1-decene at *ca.* 100°, 0.35 g (0.02 mole) of water was added over a 1-hr period. After a 3.5-hr total reaction time, the mixture was allowed to cool, and 15 ml of THF and 8.5 g (0.08 mole) of chlorotrimethylsilane were then added successively. The usual work-up and distillation afforded the following fractions: (1) 0.55 g, bp 86–116° (15 mm), and (2) 2.0 g, bp 116–120° (15 mm). Fraction 1 was shown by gc to consist of a mixture of 81% 1-decene and 19% 1-decynyltrimethylsilane. Fraction 2 consisted of 10% 1-decene and 90% of the alkynyltrimethylsilane. The total yield of 1-decynyltrimethylsilane was 15%.

Butene-1.—A mixture of 3.5 g (0.5 g-atom) of lithium dispersion and an excess of 1-butene was heated at 50° for 16 hr in a rocking autoclave. After exhausting the excess 1-butene, the bomb liner was removed and cooled, and the contents were treated with 50 ml of THF and 17 g (0.16 mole) of chlorotrimethylsilane. After the usual work-up, distillation afforded the following fractions: (1) 0.3 g of a mixture, bp 49–59° (100 mm); (2) 0.21 g of a mixture, bp 55–60° (100 mm); and (3) 0.03 g, bp 61° (100 mm). Fraction 1 was shown to contain *ca.* 36% *trans*-1-butenyltrimethylsilane, 37% 1-butynyltrimethylsilane, and 23% of two unknown compounds by gc. An infrared spectrum of the distillation residue (0.77 g) revealed strong absorption bands at 4.61, 5.23, and 8.0 μ, characteristic of acetylenic, allenic, and trimethylsilyl groups, respectively.

Propene.—A mixture of 3.5 g (0.5 g-atom) of lithium dispersion and an excess of propene was agitated in a stirred autoclave at 60° for 24 hr without evidence of any reaction.

Reaction of 1-Hexene, Lithium, and Trimethylchlorosilane. In the Absence of THF.—A mixture of 40 g (0.48 mole) of 1-hexene, 3.5 g (0.25 g-atom) of lithium dispersion, and 8.5 g (0.08 mole) of trimethylchlorosilane was heated at reflux for 1 hr. Subsequently, the reaction mixture was cooled and 10 ml of THF was added to insure complete coupling of any organolithium compounds with the chlorosilane. Work-up in the usual manner afforded 4.04 g of a mixture comprised of 6% *trans*-1-hexenyltrimethylsilane and 94% 1-hexynyltrimethylsilane, as evidenced by gas phase chromatography.

In the Presence of THF.—A mixture of 67 g (0.8 mole) of 1-hexene, 2.8 g (0.4 g-atom) of lithium dispersion, 13.5 g (0.13 mole) of trimethylchlorosilane, and 20 ml of THF was heated at reflux for 12 hr. After standing overnight, the reaction mixture was filtered into chilled, aqueous ammonium chloride and worked up in the usual manner. Distillation afforded a 1.33-g fraction, bp 90–96° (90 mm), comprised of 5% of 1-hexynyltrimethylsilane and 93% 1-hexenyltrimethylsilane.

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Metal Hydrides. Hydrogenation and Isomerization Catalysts

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Several metal hydrides are catalysts for the selective hydrogenation of 1,3-pentadiene and 2-pentyne to *n*-pentenes. The initial rates vary with the particular catalyst in the order: potassium hydride ≫ sodium hydride > magnesium hydride > lithium hydride > zirconium hydride > titanium hydride. The rates of hydrogenation are solvent dependent. In the presence of sodium hydride, 1,3-pentadiene is selectively hydrogenated to pentenes without affecting 1,5-hexadiene present in the same solution. On the other hand, potassium hydride promotes the hydrogenation of nonconjugated dienes to monoolefins. The hydrogenation of 1,3- or 1,5-cyclooctadiene and bicyclo[2.2.1]heptadiene produced, in addition to the expected monoolefins, *cis*-bicyclo[3.3.0]oct-2-ene and nortricyclene, respectively. Potassium hydride is a very effective catalyst in the absence of hydrogen for the isomerization of cyclooctadienes to *cis*-bicyclo[3.3.0]oct-2-ene. Stereochemical and deuterium tracer studies indicate that at least some of the alkali metal hydrides function as heterogeneous catalysts.

Lithium aluminum hydride ($LiAlH_4$) is a homogeneous catalyst for the selective hydrogenation of 2-pentyne and conjugated dienes to monoolefins.[1] The hydride promotes hydrogenation by adding to the unsaturated system to form an intermediate metal alkyl which subsequently undergoes hydrogenolysis (eq 1 and 2).

$$CH_2{=}CHCH{=}CHCH_3 + LiAlH_4 \longrightarrow Li(n\text{-}C_5H_9)AlH_3 \quad (1)$$

$$Li(n\text{-}C_5H_9)AlH_3 + H_2 \longrightarrow n\text{-}C_5H_{10} + LiAlH_4 \quad (2)$$

It has been claimed that group I and II metal hydrides also will add to double bonds to form metal

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[1] L. H. Slaugh, *Tetrahedron*, **22**, 1741 (1966).

TABLE I

HYDROGENATION OF 1,3-PENTADIENE[a]

Expt	Metal hydride[b]	Temp, °C	Max rate, mmoles of H_2/hr	Time, hr	Product compn, % of starting diene[c]			
					1,3-C_5H_8	n-C_5H_{12}	n-C_5H_{10}	Dimer
1	NaH	185	224	0.8	4.9	1.4	79.1	14.9
2	NaH	150	12	7.5	5.6	0.6	62.4	20.2
3	LiH	190	11	6	0	0.8	61.7	14
4	KH	100	782	0.5	0	0	46.5	32.5
5	KH	20	8	15	25.7	0	9.9	26.0
6	TiH_2	225	<1[d]	1	56.8	0	<1	32.7
7	ZrH_2	225	...	0.3	67.3	0.3	10.5	16.3
8	MgH_2	186	35	1.5	24.3	3.1	63.8	9.7
9	NaH t-BuOK[e]	135	2700	0.1	0	0	56.5	25.7
10	t-BuOK[e]	190	0	1	88	0	0	15
11	$C_5H_{11}Na$, 7 mmoles in n-heptane	100	121	1.5	0	<4[f]	96	4
12	...	190	0	2	83.2	0	0	16.8

[a] Solvent, THF (40 ml); metal hydride or metal salt, 20 mmoles (except where noted); 1,3-pentadiene, 90 mmoles; pressure, 900–1500 psi. The solvent used in expt 12 was n-heptane. [b] All metal hydrides, obtained from Metal Hydrides, Inc., were powdered before they were used. [c] Determined by gas–liquid partition chromatography. The reproducibility of these analyses usually was ±7%. Low material balances may be due in part to polymer formation. [d] Too slow to measure accurately. [e] Twenty mmoles. [f] Corrected for estimated n-C_5H_{12} formed by the hydrogenolysis of n-$C_5H_{11}Na$. This value could be as low as 0.5 to 1.0%.

alkyls.[2] Therefore, one might reasonably expect these materials to function as hydrogenation catalysts *via* an addition–hydrogenolysis mechanism. Previous use of alkali and alkaline earth metal hydrides has been limited mainly to the gas phase hydrogenation of ethylene.[2-8] Therefore, it seemed of interest to investigate the catalytic properties of these hydrides in solvents and to determine their selectivity, stereochemistry, and mechanism of hydrogenation. As a consequence of this study, the catalyzed isomerization of cyclooctadienes to *cis*-bicyclo[3.3.0]oct-2-ene also has been investigated.

Results and Discussion

The reactions were accomplished simply by contacting hydrogen and the substrate with the powdered metal hydride (or precursor) in an autoclave. The rates of hydrogenation were estimated from the initial rates of pressure decline.

In 40 ml of anhydrous tetrahydrofuran (THF) at 190°, sodium hydride (20 mmoles) failed to catalyze the hydrogenation of 1-pentene. In 1 hr, only 2% double-bond isomerization occurred to produce 2-pentene. With potassium hydride, a 10% yield of n-pentane resulted, and the unreacted olefin consisted of a mixture of isomers whose relative concentrations approximated those calculated for a thermodynamic equilibrium distribution.[9] Although these metal hydrides are poor hydrogenation catalysts for monoolefins, potassium hydride, but not sodium hydride, is an effective double-bond isomerization catalyst.

Sodium hydride promoted the selective hydrogenation of 1,3-pentadiene mainly to a nonequilibrium mixture of pentenes (expt 1 and 2, Table I). Only a low yield of n-pentane was produced. The initial rates of hydrogenation in several solvents varied in the following order: THF > 1,4-dioxane, 1,2-dimethoxyethane, triethylamine > diethyl ether, trimethylamine > n-heptane. The rate was at least 300 times greater in THF than in n-heptane.

Several other metal hydrides also were found to be catalysts for the selective hydrogenation of 1,3-pentadiene (Table I). The rates varied considerably with the particular metal hydride employed. In THF the observed order of activity was potassium hydride ≫ sodium hydride > magnesium hydride > lithium hydride > zirconium hydride > titanium hydride. Potassium hydride appears to be several thousand times as active as titanium hydride and several hundred times as active as sodium hydride. In fact, the initial rate of hydrogenation with potassium hydride at room temperature (expt 5) was nearly as great as that observed for sodium hydride (expt 2) at 150°. Their intrinsic activity may not be represented by the above relative order since the mode of preparation could have an effect on the catalyst activity. For example, sodium hydride generated *in situ via* the hydrogenolysis of amylsodium (eq 3) was an active catalyst in

$$n\text{-}C_5H_{11}Na + H_2 \longrightarrow n\text{-}C_5H_{12} + NaH \qquad (3)$$

n-heptane at 100° (expt 11), whereas powdered, commercial sodium hydride had little activity at 190° in this solvent.

Although potassium *t*-butoxide does not promote the hydrogenation of 1,3-pentadiene, it enhances considerably the catalytic activity of sodium hydride (compare expt 2, 9, and 10). Perhaps, potassium *t*-butoxide and sodium hydride reacted to form potassium hydride, a more active catalyst.

In addition to pentenes, varying amounts (4–33%) of dimeric products also were formed during the hydrogenations of 1,3-pentadiene. Part of this material likely resulted from the Diels–Alder dimerization of the diene. Thermal dimerization was shown to occur at 190° in the absence of a catalyst (expt 12). However, this is not the sole path to C_{10} hydrocarbons since dimeric compounds were formed during the potas-

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(2) S. M. Blitzer and T. H. Pearson, U. S. Patent 2,987,558 (1961).

(3) R. N. Pease and L. Stewart, *J. Am. Chem. Soc.*, **47**, 2763 (1925).

(4) D. G. Hill and G. B. Kistiakowsky, *ibid.*, **52**, 892 (1930).

(5) O. Schmidt, *Chem. Rev.*, **12**, 363 (1933).

(6) L. Wright and S. Weller, *J. Am. Chem. Soc.*, **76**, 5305 (1954).

(7) S. Weller and L. Wright, *ibid.*, **76**, 5302 (1954).

(8) S. E. Voltz, *J. Phys. Chem.*, **61**, 756 (1957).

(9) The thermodynamic data were taken from "Selected Values of Properties of Hydrocarbons and Related Compounds," API Research Project 44, Carnegie Institute of Technology, Pittsburgh, Pa., Dec 31, 1962.

TABLE II

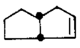
HYDROGENATION OF LINEAR DIENES[a]

Expt	Olefin, mmoles	Catalyst, mmoles	Temp, °C	Time, hr	Product compn, % of original olefins[b] n-C_6H_{14}	n-C_6H_{12}	1,5-C_6H_{10}	n-C_5H_{12}	n-C_5H_{10}	Dimers
13	1,5-C_5H_{10},[c] 98	NaH, 20 t-BuOK, 20	160	0.1	1.5	103	0	...	...	0
14	1,5-C_6H_{10},[c] 107	KH, 20	150	0.8	...	101	...	...	...	5.6
15	1,4-C_5H_8,[d] 97	KH, 20	150	0.3	...	...	...	0.3	44.3	31.8
16	1,5-C_6H_{10},[c] 92 1,3-C_5H_8,[e] 97	NaH, 20	190	1.3	0	0	92.3[c]	3.2	76.6	?

[a] Solvent, THF (40 ml); maximum pressure, 1400–1600 psi. [b] Based upon glpc analyses. [c] 1,5-Hexadiene [d] 1,4-Pentadiene. [e] 1,3-Pentadiene.

TABLE III

HYDROGENATION AND ISOMERIZATION OF CYCLOOCTADIENE[a]

Expt	Diolefin,[b] mmoles	Catalyst	H_2, psig[c]	Temp, °C	Time, hr	Product compn, % of original diene[d] Cyclo-octene		1,3-COD	1,4-COD	1,5-COD
17	1,3-COD, 98	NaH	1780	195	6	23.4	16.8	58	0	1.8
18	1,3-COD, 104	KH	1630	100	4	18.8	16.7	63.1	0	1.4
19	1,5-COD, 100	NaH	740	190–240	1.5	3.5	8.1	8.0	0	80.4
20	1,5-COD, 86	KH	1360	150	5	34.8	65.2	0	0	0
21	1,5-COD, 98	None	0	190	6	0	0.6	0.6	0.6	98.2
22	1,5-COD, 98	KH	0	190	4	5.8	72.4	4.2	0.6	17.0
23[a]	1,5-COD, 472	KH	0	190	4	3.3	84.4	0.7	0.5	11.1
24	1,5-COD, 96	NaH	0	190	6	3.6	5.8	3.2	0.2	87.2
25	1,3-COD, 96	KH	0	190	4	5.6	93.7	0.7	0	0
26	1,3-COD, 96	t-BuOK	0	190	4	0.6	0	98.9	0	0.6
27	1,5-COD, 96	t-BuOK	0	190	4	0	0	94.8	0	5.2

[a] Solvent, THF (40 ml), catalyst, 20 mmoles. Tetrahydrofuran solvent was not employed in expt 23. The 1,5-COD was neat. [b] COD is cyclooctadiene. [c] No H_2 was present in expt 21–27. The other values include the vapor pressure of the solvent. [d] Based upon glpc analyses. The material balances were always >94% and in most instances were ~98%.

sium hydride catalyzed hydrogenation of 1,3-pentadiene at room temperature (expt 5).[10]

Of the catalysts tested sodium hydride in n-heptane, produced by the hydrogenolysis of amylsodium, is best for the selective hydrogenation of 1,3-pentadiene, or, presumably, any conjugated diene, because the yield of dimers was low. The low material balances obtained with several of the other catalysts listed in Table I indicate that product of molecular weight greater than that of the dimer also must have been formed.

Potassium hydride and sodium hydride with potassium t-butoxide present are effective catalysts for the hydrogenation of nonconjugated dienes to monoolefins. For example, 1,5-hexadiene and 1,4-pentadiene were converted to n-hexenes and n-pentenes, respectively (see Table II). Since little hydrogenation of monoolefins occurs under these conditions, it seems likely that double-bond isomerization to form conjugated dienes precedes the hydrogenation.

Sodium hydride, being a poor double-bond isomerization catalyst, promotes the selective hydrogenation of conjugated dienes in the presence of nonconjugated dienes without affecting the latter. The hydrogenation of a mixture of 1,3-pentadiene and 1,5-hexadiene produced mainly n-pentenes (expt 16).

Although 1,5-cyclooctadiene was inert, 1,3-cyclooctadiene was hydrogenated to cyclooctene in high yield with $LiAlH_4$ as catalyst.[1] The sodium hydride and potassium hydride catalyzed hydrogenations of cyclooctadienes have given an unexpected result (Table III; expt 17–20). In addition to cyclooctene, significant amounts of *cis*-bicyclo[3.3.0]oct-2-ene were formed by a transannular ring-closure reaction. Little thermal rearrangement of 1,5-cyclooctadiene occurred at 190° (expt 21). Subsequently, we tested potassium hydride in the absence of hydrogen and found it to be an excellent catalyst for the isomerization of either neat or THF solutions of cyclooctadiene to the bicyclic olefin (expt 22, 23, and 25). Recently, Stapp and Kleinschmidt reported that small amounts of phenylpotassium, phenylsodium, or potassium metal promotes the isomerization of cyclooctadienes to *cis*-bicyclo-[3.3.0]oct-2-ene in 50–65% yield.[11] Potassium hydride apparently is a superior catalyst since a yield >90% of the bicyclic olefin has been obtained (expt 25). The amount of high-boiling by-product is less with potassium hydride than it is with phenylpotassium, phenylsodium, or potassium metal. With the latter catalysts, 10–27% high-boiling residue remained after distillation of the C_8 products.[11] However, in each of the examples listed in Table III, the amount of residue was <5%. In one experiment (see the Experimental Section), where 1900 g of neat 1,5-cyclooctadiene was isomerized by potassium hydride, the residue (mainly dimers) was 6%. The C_8 product composition was roughly the same as that of expt 23.

The isomerization of 1,5-cyclooctadiene to the bicyclic olefin can be accomplished at atmospheric pressure in conventional glass equipment. For example, 1 mole of 1,5-cyclooctadiene containing 40

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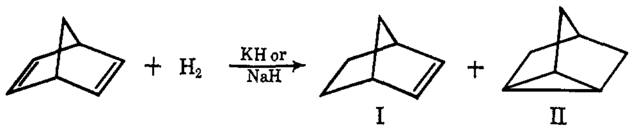
[10] The dimeric product, consisting of several components (glpc analysis), produced during the sodium hydride catalyzed hydrogenation of the neat diene at 190° had the empirical formula $C_{10}H_{16}$ and was converted by hydrogenation into a compound with empirical formula $C_{10}H_{20}$. This dictates a monocyclic structure. The thermal dimers formed in the absence of a metal hydride probably are monocyclic also; however, neither these compounds nor the dimers formed at room temperature were analyzed to determine their structure.

[11] P. R. Stapp and R. F. Kleinschmidt, *J. Org. Chem.*, **30**, 3006 (1965).

mmoles of potassium hydride was refluxed for 4 hr. Twenty-three per cent of the diene was converted into a mixture of 93% *cis*-bicyclo[3.3.0]oct-2-ene and 7% cyclooctene.

Transannular ring closure also occurred during the hydrogenation of bicyclo[2.2.1]heptadiene in THF (eq 4). With potassium hydride or sodium hydride at



(4)

190°, 50% bicyclo[2.2.1]heptene (I), 43% nortricyclene (II), and 7% dimers were obtained. At 150° with the former hydride, 76% I, 23.2% II, and only 0.8% dimer were formed. The isomerization of I to II is relatively slow at 190° in the presence of the metal hydrides; thus the latter must have formed directly during the hydrogenation and not *via* a subsequent isomerization of I.

Earlier, $LiAlH_4$ was found to be a catalyst for the selective hydrogenation of 2-pentyne to 2-pentenes.[1] Lithium hydride and sodium hydride also are quite selective; however, potassium hydride produces considerable *n*-pentane (~12–20%) and 1-pentene. It is rather strange that in the latter case the amount of the thermodynamically less favored 1-pentene is approximately three times that of 2-pentene. C_5 allenes were found in the product when only partial hydrogenation of the 2-pentyne was allowed. The 2-pentene products consisted largely of the *cis* isomer. The *cis*-2-pentene/*trans*-2-pentene product ratios were 91:9 for sodium hydride, 92:8 for lithium hydride, and 77:23 for potassium hydride (see the Experimental Section for further details).

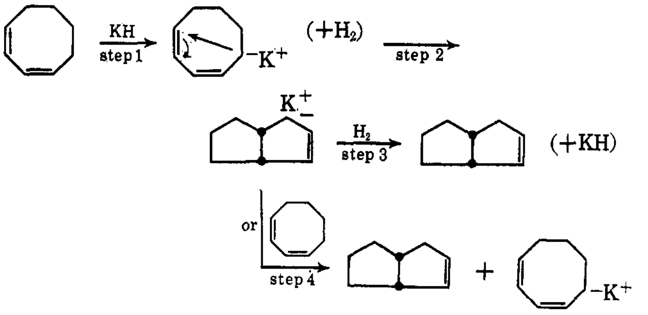
These stereochemical results differ from those obtained with $LiAlH_4$, which produced predominantly *trans*-2-pentene from 2-pentyne. The latter functions in solution as a homogeneous catalyst by adding to the acetylene or diene system to form an adduct that subsequently undergoes hydrogenolysis (eq 1 and 2). The alkali metal hydrides appear to be insoluble, heterogeneous catalysts, although some material may be dissolved at the elevated reaction temperatures. The high proportion of the *cis* isomer obtained is consistent with heterogeneous catalysis. Catalysts of the latter type are known to promote the hydrogenation of acetylenes to *cis* olefins.[12]

Since the alkali metal hydrides could add *cis* to triple bonds, the stereochemistry of hydrogenation *per se* is insufficient grounds for excluding homogeneous catalysis. However, deuterium tracer studies show that, at least, lithium hydride functions as a heterogeneous catalyst. 1,3-Pentadiene (50 mmoles) in 40 ml of THF was hydrogenated (200 mmoles or 1000 psi of H_2) over a relatively large amount of lithium deuteride catalyst (225 mmoles) for 20 min at 170–190°. The pentene product consisted of 94% pentene-d_0 and 6% pentene-d_1. The preponderance of undeuterated pentene shows that the lithium deuteride promoted the reaction of H_2 and 1,3-pentadiene without significant donation of its deuterium atoms.[13] A similar experiment with lithium aluminum deuteride produced pentene containing 94% pentene-d_1 which is predicted by the proposed addition–hydrogenolysis mechanism (eq 1 and 2).[1] If a similar mechanism were operative for lithium hydride, pentene-d_1 rather than the pentene-d_0 would have been produced.

In the presence of lithium hydride or sodium hydride, the rate of reduction of 1,3-pentadiene was considerably lower with D_2 than it was with H_2. Consequently, exchange reactions were competitive with hydrogenation and pentene-d_1, -d_2, -d_3, -d_4, -d_5, and -d_6 species were produced (see the Experimental Section for quantitative analyses). The rate of hydrogenation increased during the course of the hydrogenations (90–150 min), presumably owing to an increase of H_2 or HD concentrations from exchange reactions. With potassium hydride and D_2, the exchange rate was very fast and polydeuterated pentenes were produced in ~10 min.

The metal hydride surfaces must consist of contiguous positive (M^+) and negative (H^-) sites. Therefore, a polarized transition state for the combination of hydrogen and the substrate would be expected. Although the reactants likely are bound to the catalyst surface, solvation from the backside should be possible. This may be the reason that the sodium hydride promoted hydrogenation of 1,3-pentadiene was faster in THF than in *n*-heptane (*vide supra*). The latter is the poorer solvent for charged species.

The mechanism by which the formation of bicyclo[3.3.0[oct-2-ene occurs is not clear. One possibility for the isomerization of 1,3-cyclooctadiene is shown in eq 5. The transannular ring closure would occur



(5)

via the allylic carbanion generated by either step 1 or step 4 of eq 5. Potassium *t*-butoxide in THF does not promote the isomerization although carbanions are generated, as evidenced by the isomerization of 1,5-cyclooctadiene to 1,3-cyclooctadiene (expt 26 and 27, Table III). If the above mechanism is correct, the carbanions formed by the hydride are much more prone to rearrange. Perhaps this is a consequence of being developed on the surface of the metal hydride.

A second possibility is that the 1,3-diene first is converted to 1,5-cyclooctadiene, for which a different mechanism of isomerization may be operative. A double bond of the latter may interact with the hydride to form an incipient carbanion which ring closes and decomposes to bicyclo[3.3.0]oct-2-ene. A hydride shift is involved in the over-all process which might be de-

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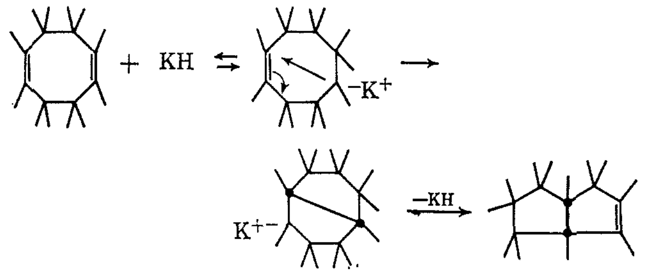
(12) D. J. Cram and N. L. Allinger, *J. Am. Chem. Soc.*, **78**, 2518 (1956); E. F. Meyer and R. L. Burwell, *ibid.*, **85**, 2877 (1963); G. Webb and P. B. Wells, *Trans. Faraday Soc.*, **61**, 1232 (1965).

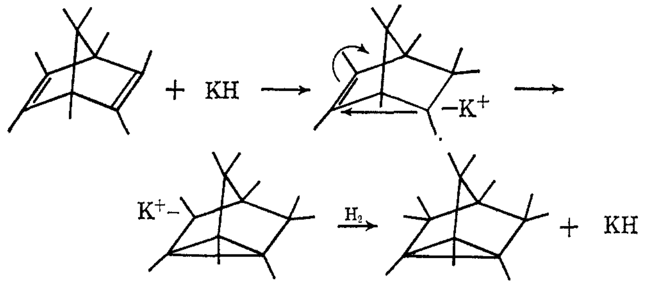
(13) The low yield of pentene-d_1 may have resulted from competitive exchange reactions.

picted by eq 6. Like 1,3-cyclooctadiene (eq 5), 1,5-cyclooctadiene also may form an allylic carbanion which could further react to give the bicyclic product.



(6)

This type of double bond–metal hydride interaction shown by eq 6 must be operative for the hydroisomerization of bicyclo[2.2.1[heptadiene to nortricyclene (eq 7). In this instance, intermediate carbanions cannot be formed by proton abstraction from the bicyclic diene. Proton abstraction from the intermediate bicyclo[2.2.1]heptene followed by transannular ring closure is a possibility; however, it was shown independently that this compound isomerizes to nortricyclene very slowly in the presence of potassium hydride.



(7)

Experimental Section

Reagents.—The metal hydrides, purchased from Metal Hydrides, Inc., were powdered in an inert atmosphere. Emission spectrographic analyses showed that they were free of transition metal contaminants. Purified potassium *t*-butoxide, from MSA Research Corp., was sublimed in an inert atmosphere. 1,3-Pentadiene (Phillips Petroleum Co.) contained ~10% cyclopentene which was inert under the present experimental conditions. All solvents, high purity 2-pentyne and 1,4-pentadiene (Aldrich Chem. Co.) and 1,3- and 1,5-cyclooctadiene (Cities Service Research and Development Co.) were distilled from calcium hydride.

General Procedure.—An 80-ml, stainless steel autoclave was used for all of the hydrogenation experiments. Stirring was provided by a bar magnet (sheathed with stainless steel) placed inside the autoclave. The magnet was set in motion by an external magnetic stirrer. The autoclave was loaded in a nitrogen-filled drybox with the solvent, metal hydride or metal deuteride, and substrate to be hydrogenated. Hydrogen or D_2 was introduced into the assembled autoclave and the system was heated to the desired temperature. The progress of the hydrogenation was followed by the decrease in the pressure as measured by a suitable transducer and a Daystrom–Weston recorder. The initial rates of reaction were not affected by changes in the rate of stirring. With the exception of the details given below, the reaction conditions, quantities of reagents, and yields of products for each experiment are listed in the tables or the text. Several metal hydride catalyzed isomerizations of cyclooctadienes were carried out as above in the absence of hydrogen.

The product compositions were determined quantitatively by glpc. Frequently, the organic products were extracted from the THF (diluted with water) into decane before they were analyzed. To do this, the THF solutions were placed in a separatory funnel along with decane. Water and finally 5% HCl were added slowly to decompose the excess hydride reagent. The combined hydrocarbon extracts were washed several times with ice water and dried over potassium carbonate.

The individual components of the various products were identified by the coincidence of their glpc emergence times with those of authentic materials. Also each compound was individually trapped by glpc techniques and further analyzed by comparing its infrared spectrum and/or mass spectrometric fragmentation pattern with those of an authentic sample.

Hydrogenation of 1-Pentene.—One-hundred mmoles of 1-pentene in 40 ml of THF was hydrogenated at 190° with 1600 psi of hydrogen for 1.0 hr in the presence of 20 mmoles of a hydride catalyst. With sodium hydride, the product composition was 98.2% 1-pentene and 1.8% 2-pentene (mixture of *cis* and *trans* isomers). With potassium hydride, the product composition was 9.5% *n*-pentane, 11.2% pentene-1, 43.1% *trans*-2-pentene, and 36.2% *cis*-2-pentene.

Hydrogenation of 1,3-Pentadiene.—In 40 ml of a solvent at 190° under 1600 psi of hydrogen, 100 mmoles of 1,3-pentadiene was hydrogenated mainly to pentenes in the presence of 20mmoles of powdered, commercial sodium hydride. The relative rates of hydrogenation, up to 10% conversion of the diene, in the various solvents were *n*-heptane, 1; trimethylamine, 11; diethyl ether, 11; 1,2-dimethoxyethane, 54; triethylamine, 59; 1,4-dioxane, 76; and THF, 320.

To identify the dimeric products formed during the sodium hydride catalyzed hydrogenation of neat 1,3-pentadiene at 190°, the product was washed several times with water, dried with Drierite, and then hydrogenated over palladium on charcoal at 25–65° and 450 psig of hydrogen. A negative Baeyer permanganate test and a trivial bromine number indicated that the olefins in the product had been completely hydrogenated. Before the hydrogenation, the dimeric product, consisting of several compounds, was analyzed by a mass spectrometer and found to be mainly $C_{10}H_{16}$ and a little $C_{10}H_{14}$. After complete saturation, the material was mainly $C_{10}H_{20}$ accompanied by a little $C_{10}H_{18}$ and a C_4-substituted benzene. The empirical formula of the major component dictates a monocyclic structure. The easy loss of a C_3H_7 fragment in the mass spectrometer might indicate that the $C_{10}H_{20}$ compound was a methylpropylcyclohexane. Similar information indicates that the C_4-substituted benzene probably was a methylpropylbenzene.

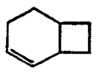
Isomerization of Cyclooctadienes to *cis*-Bicyclo[3.3.0]oct-2-ene.—In addition to the experiments listed in Table III, the following were performed.

In a large-scale experiment, 507 g (4.7 moles) of 1,5-cyclooctadiene and 8 g (0.02 mole) of potassium hydride were agitated and heated at 190° in a suitable autoclave for 10–11 hr. The autoclave was cooled and the organic product was decanted from the potassium hydride and washed with water. The liquid from four experiments was combined and dried. Distillation of 1900 g of material gave 1786 g of a C_8 fraction (bp ~130–152°) whose composition was roughly the same as the product composition listed for expt 23 (Table III). The residue from the distillation was 114 g or 6% of the total material. The residue consisted mainly of dimeric compounds which were not characterized. Pure bicyclooctene, bp 132–133.5°, was obtained by distilling the above C_8 fraction.

Potassium hydride (40 mmoles) and 1,5-cyclooctadiene (1.0 mole) were placed in a three-necked flask and the mixture was refluxed (140–150°) and stirred under nitrogen for 4 hr. During this time, the color of the solution changed from pale blue to yellow to a light brown. A glpc analysis indicated that ~23% of the diene had reacted. The C_8 compounds formed were *cis*-bicyclo[3.3.0]oct-2-ene (93%) and cyclooctene (7%).

cis-Bicyclo[3.3.0]oct-2-ene was isolated from a typical product by preparative glpc (Wilkins Autoprep instrument) and analyzed. The mass spectrum of the compound was consistent with the proposed structure. A 100-Mcps nmr spectrum indicated two *nonequivalent* vinylic (olefinic) hydrogens, three allylic hydrogens (two of one type and one of another), and seven hydrogens bonded to saturated carbon atoms. Of all the possible C_8 bicyclic structures, only III and IV are consistent with the

III



IV

nmr data. Infrared analysis showed conclusively that III rather than IV is the correct structure. The infrared spectrum of the compound in question was identical in every detail with the spectrum of *cis*-bicyclo[3.3.0]oct-2-ene published by Germain and Blanchard.[14]

Corroboration of structure III was obtained from the hydrogenation of the compound over palladium on charcoal (1.01 mole of hydrogen per mole of III was consumed). The resulting product was *cis*-bicyclo[3.3.0]octane whose infrared spectrum was identical with that published by Roberts and Gorham for the authentic material.[15] It should be noted that the infrared spectrum for *trans*-bicyclo[3.3.0]octane differs considerably from that of the *cis* compound.[15]

Hydrogenation of 2-Pentyne.—One-hundred mmoles of 2-pentyne in 40 ml of THF was hydrogenated at 190° under 1600 psi of hydrogen in the presence of 20 mmoles of a metal hydride catalyst. With sodium hydride catalyst and a 1.0-hr reaction time, the product composition was 1,2- and 2,3-pentadiene, 4.4%; *n*-pentane, 0.7%; 1-pentene, 2.3%; *cis*-2-pentene, 19.0%; *trans*-2-pentene, 1.9%; and 2-pentyne, 71.7%. With potassium hydride catalyst and a 0.7-hr reaction time, the product composition was 1,2- and 2,3-pentadienes, 13.2%; *n*-pentane, 9.0%; 1-pentene, 16.8%; *cis*-2-pentene, 3.6%; *trans*-2-pentene, 1.0%; 2-pentyne, 56.4%; and dimer, trace. With lithium hydride catalyst and a 0.5-hr reaction time, the product composition was *n*-pentane, 3.0%; 1-pentene, 0.4%; *cis*-2-pentene, 23.5%; *trans*-2-pentene, 2.0%; and 2-pentyne, 71.1%.

Hydrogenation of 1,3-Pentadiene. Tracer Studies.—The hydrogenation of the substrate over lithium deuteride is described in the text. The relative amounts of the deuterated pentenes were determined by mass spectrometry. A 96.5% conversion of the diene into 20% *n*-pentane and 80% pentenes was obtained in 0.3 hr. The *n*-pentane was composed of 85% C_5H_{12}, 14% $C_5H_{11}D$, and 1% $C_5H_{10}D_2$. See text for the pentene analysis.

Fifty mmoles of the diene in 40 ml of THF was treated with deuterium gas (685 psi) at 190° in the presence of 224 mmoles of lithium hydride. After 1.3 hr, 43.5% of the diene had been converted into a mixture of pentenes. The deuterium content of the latter was C_5H_{10}, 7.1%; C_5H_9D, 34%; $C_5H_8D_2$, 49%; $C_5H_7D_3$, 7.3%; $C_5H_6D_4$, 1.6%; $C_5H_5D_5$, 0.5%; and $C_5H_4D_6$, 0.1%.

With similar quantities of reagents, 1,3-pentadiene was 100% converted mainly into pentenes in 2.6 hr at 190–225° in the presence of deuterium gas and sodium hydride. The pentene consisted of 1.9% C_5H_{10}, 17% C_5H_9D, 65% $C_5H_8D_2$, 13.5% $C_5H_7D_3$, 2.1% $C_5H_6D_4$, and 0.6% $C_5H_5D_5$.

The product from a similar experiment with potassium hydride (0.2 hr) gave a pentene product which consisted of 4.3% C_5H_{10}, 27% C_5H_9D, 49.5% $C_5H_8D_2$, 16% $C_5H_7D_3$, 2.8% $C_5H_6D_4$, 0.4% $C_5H_5D_5$, and 0.1% $C_5H_4D_6$.

Hydrogenation of Bicyclo[2.2.1]heptadiene.—Twenty mmoles of a metal hydride catalyst was used for the hydrogenation of 100 mmoles of the topic diene in 40 ml of THF. With sodium hydride at 190°, the diene was 90% converted in 5.5 hr into a product consisting of 50.1% bicyclo[2.2.1]heptene, 42.9% nortricyclene, and 7.0% unidentified dimers. With potassium hydride at 190°, the diene was 91% converted in 0.3 hr into a product having a similar composition as above. With potassium hydride at 150° for 2.3 hr, a 100% conversion was obtained; the product consisted of 76% bicyclo[2.2.1]heptene, 23% nortricyclene, and 0.8% dimer.

The isomerization of bicyclo[2.2.1]heptene to nortricyclene also was examined. One-hundred mmoles of the olefin and 20 mmoles of potassium hydride in 40 ml of THF were heated at 190° for 1.3 hr. Only 4.8% of the olefin was converted into nortricyclene.

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The Reduction of Malonic Enolates with Lithium Aluminum Hydride

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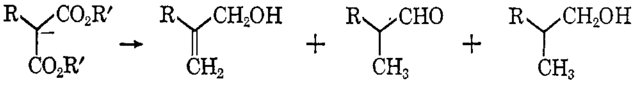
Diethyl cyclohexylmalonate (**1**) and the corresponding sodio derivative **3** were reduced with lithium aluminum hydride. The free ester afforded 2-cyclohexylpropane-1,3-diol in 95% yield, whereas the derived enolate **3** gave a mixture of 2-cyclohexylpropanal (**4**), 2-cyclohexyl-2-propen-1-ol (**5**), and 2-cyclohexylpropan-1-ol (**7**). The relative amounts of these products varied with the method of work-up. A reaction scheme which accommodates these findings is presented and critically examined.

Enolizable 1,3-dicarbonyl compounds frequently afford products of reduction and elimination upon treatment with lithium aluminum hydride. This reaction, first recognized for *β*-keto esters and *β*-keto aldehydes by Dreiding and Hartman,[3] also takes place with *β*-diketones[4] and, less readily, with malonic esters.[5] Dreiding and Hartman[3] correctly surmised that the reduction–elimination reaction depended upon the initial formation of an enolate. Subsequently, Eschenmoser and his co-workers showed that the enolate prepared from a *β*-keto ester with sodium hydride underwent reduction with nearly exclusive formation of the elimination product.[6] We applied this modified reduction–elimination procedure to monosubstituted malonic esters and thereby were able to prepare allylic alcohols possessing key structural features of certain natural products.[7] However, the yields of desired materials usually suffered owing to the formation of aldehydes and saturated alcohols as significant byproducts in these reductions. Similarly, we also noted



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