three bromine atoms. The precipitate (520 mg) from the $CHCl_3$ extracts and the residue (90 mg) from the methanol eluate were shown, by TLC, to be identical. Mass spectrometric analysis gave a molecular weight of 386 indicating the presence of three bromine atoms. ^1H NMR analysis was not possible because of insufficient solubility of the two compounds in any of the common NMR solvents.

Reaction of 1,5-Naphthyridine 1-Oxide (1) with Acetic Anhydride and Dilute HCl. A solution of 1,5-naphthyridine 1-oxide (1.0 g, 6.85 mmol) and acetic anhydride (1.4 g, 13.7 mmol) in alcohol-free $CHCl_3$ (50 ml) was refluxed for 12 hr and cooled, and dilute HCl (1 ml of a 3.37% solution) was added. The solution was stirred at reflux for an additional 12 hr, cooled, and dried over Na_2CO_3. Removal of the $CHCl_3$ gave only starting material (0.98 g, 98%).

Registry No.—1, 27305-48-2; **2a**, 56247-21-3; **3**, 56247-22-4; **3a**, 56247-23-5; **4**, 10261-82-2; **7**, 56247-24-6; **8a**, 56247-25-7; **9**, 27284-59-9; **10a**, 56247-26-8; **11a**, 56247-27-9; **13**, 56247-28-0; acetic anhydride, 108-24-7; NaBr, 7647-15-6; LiBr, 7550-35-8; HBr, 10035-10-6; KI, 7681-11-0; acetyl bromide, 506-96-7; acetyl chloride, 75-36-5; Br_2, 7726-95-6; HCl, 7647-01-0.

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(7) We have already shown that Eisch bromination of 1,5-naphthyridine 1-oxide affords only, not unexpectedly, 7-bromo-1,5-naphthyridine 1-oxide (D. Pokorny, Ph.D. Thesis, Ohio University, Athens, Ohio, 1972).

The Effect of Ring Size on Hydrogenation of Cyclic Allylic Alcohols

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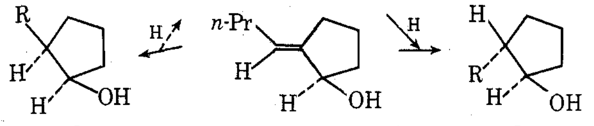
2-Butylidenecyclopentanone, 2-butylidenecyclohexanone, and 2-butylidenecycloheptanone were prepared by the Reformatsky reaction of *n*-butyraldehyde with 2-bromocyclopentanone, 2-bromocyclohexanone enol acetate, and 2-bromocycloheptanone, respectively. Reduction of 2-butylidenecyclanones with lithium aluminum hydride gave the corresponding allylic cyclanols which were characterized by their mass spectra. On catalytic hydrogenation over a variety of catalysts, the products were *cis*- and *trans*-2-butylcyclanols as well as 2-butylcyclanones. The stereochemistry of the epimeric 2-butylcyclanols was assigned by hydroxyl proton splitting in Me_2SO as observed by NMR. Alternatively, 2-butylidenecyclanones could be hydrogenated with Pd/C to 2-butylcyclanones, and reduced by lithium aluminum hydride or Raney Ni hydrogenation to *cis*- and *trans*-2-butylcyclanols.

Although product stereochemistry resulting from catalytic hydrogenation of organic compounds has been attributed to direct transfer of hydrogen,[2] compounds containing polar substituents, notably hydroxyl group, near a reducible double bond are known to exert special directing effects[3–5] in contrast with the well-known case in which the bulk of the nearby substituents is the controlling factor and imposes trans stereochemistry by sterically blocking cis approach to the catalyst surface.[6] In such instances presumably some type of attractive interaction has bound the hydroxyl group to the catalyst surface during reduction so as to enforce addition of hydrogen from the same side in spite of group's hindrance.

From their results Mitsui et al. concluded that in the case of Raney Ni the directive effect of the hydroxyl group was very efficient, but that it was small over Pd.[4d] They suggested that the difference in the affinity of nickel and palladium for the oxygen atom controlled not only the stereochemistry of the hydrogenolysis of benzyl-type alcohols, but also that of the hydrogenation of the double bond of allyl-type alcohols. To clarify the effects of hydroxyl group and also the effect of change in ring size on the stereochemistry of hydrogenation of cyclic allylic alcohols over a number of catalysts, prompted an investigation of five-, six-, and seven-membered 2-alkylidenecyclanols.

Results and Discussion

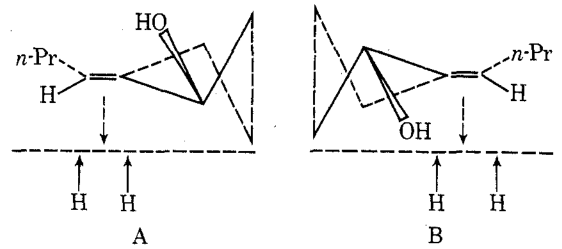
2-Butylidenecyclopentanol (1). Calculations on cyclopentane derivatives containing sp^2 hybridized atoms such as methylenecyclopentane and cyclopentanone suggest that such molecules exist in the half-chair form with the maximum puckering occurring at carbon atoms 3 and 4, i.e., away from the sp^2 hybridized atom.[7] In the hydrogenation of 1 over Raney nickel, a catalyst of low isomerizing ability,[8] 96% 3, is obtained.



2 1 3

R = *n*-Bu

From models of 1 it is found that either side of the double bond can be presented in an equally planar conformation to the catalyst. Thus steric factors cannot be responsible for this overwhelmingly one-sided addition of hydrogen. The two possible adsorption conformations of the unsaturated alcohol (A and B) differ only in that in one the



A B

OH is directed away from the catalyst surface (A), while in the other it is directed toward it (B). It is suggested that the latter is the preferred adsorption conformation, since the molecule may be adsorbed by interaction of the lone

Table I
Hydrogenation of 2-Butylidenecyclopentanol[a]

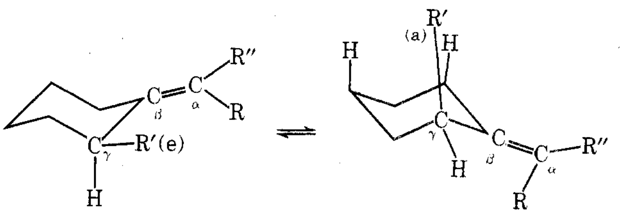
Catalyst	Conditions	2-Butylcyclopentanone[b,d]	trans-2-Butylcyclopentanol[c,d]
BDH[e] Raney nickel	95–70 atm, 16–18°, 6 hr	2	96
W_3 Raney nickel	68–55 atm, 18–24°, 6 hr	1	91
Ni_2B P-1	58–48 atm, 20–28°, 6 hr		73
Ru/C	10 atm, 2 hr	2	69
Pt/C	10 atm, 2 hr	5	55
Rh/C	10 atm, 2 hr	12	64
Pd/alumina	10 atm, 2 hr	50	66
Pd/C	10 atm, 2 hr	60	66
Pd black	10 atm, 2 hr	66	57

[a] 2-Butylidenecyclopentanol was hydrogenated over various catalysts at 10 atm pressure and room temperature for 2 hr (except Raney nickel and nickel boride catalysts, for which higher pressures and longer times were necessary). Product compositions were determined by GLC on a Carbowax column. [b] Percent of total chromatographic area. [c] Percent *trans*-2-butylcyclopentanol formed in various reductions. [d] For relative response of components see relative response of ketones and alcohols (of argon ionization detector).[9] [e] Refers to stabilized Raney nickel purchased from British Drug House.

pairs of the oxygen, as well as π electrons of the double bond with the catalyst. If it is accepted that hydrogen adds cis from the catalyst surface then addition of hydrogen to this adsorption conformation will give the trans alcohol. The alternative adsorption conformation is presumably less favored since adsorption can take place only through the double bond. Results of hydrogenation of **1** over a number of catalysts are presented (Table I).

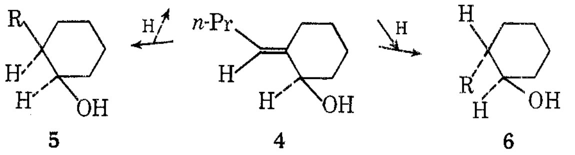
The isomerization of **1** over palladium to **13** as the main product is not surprising since endocyclic systems are almost always of lower energy than the semicyclic systems. Formation of 91% **3** can be attributed to a freshly prepared Raney nickel catalyst, which has not been deactivated by the addition of acetic acid promoting double bond migration in addition to hydrogenation.[10] The results are in good agreement with the isomerizing ability of the catalysts having the sequence Pt > Ru > Ni_2B > Ni rather than a decreasing affinity of the catalysts for adsorption through the hydroxyl group.[4e] In cases of Ni, Ni_2B, Ru/C, and Rh/C the trans isomer predominates indicating preferential adsorption of the allylic alcohol with the hydroxyl group directed toward the catalyst surface.

2-Butylidenecyclohexanol (4). An aspect of steric hindrance associated with substituted allylic groups in conformers (Ia and Ib) of I has been considered.[11]



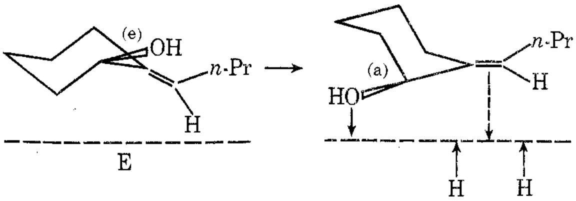
Ia Ib

From models of Ia it is apparent that even when R′ and R are only moderate in size they will interfere with each other drastically, in fact more so than if they were 1,3 diaxially related in a cyclohexane ring. Barring a facile rearrangement of the double bond, relief of this strain can be attained most easily by conformational inversion to Ib. If R and R′ are small, the equilibrium should lie to the left. If R and R′ are medium or large in size it should lie to the right.[12] Thus if R = H and R′ = OH in the conformer Ia the strain present is that due to the interaction of C_γ equatorial OH and C_α H only, whereas in the conformer Ib the strain present is that due to the interaction of OH with two axial hydrogen atoms (two 1,3-diaxial OH–H interactions). To a first approximation it is more likely that I exists predominantly as conformer Ia, with the ring substituent equatorial.[3c] Formation of 61% **6** over Raney nickel implies that the hydroxyl group is predominantly in an axial position and is directed toward the catalyst surface (C) to give the trans product from this adsorption conformation. From models of **4**, with the OH group equatorial, the only conformation in which the double bond is presentable in a planar manner to the catalyst surface is that shown (D). In this conformation the OH is less favorably placed with respect to the surface for interaction to occur through the lone pairs of the oxygen. Since we get only 39% of **5**, it is suggested that as the molecule approaches the catalyst surface, owing to the directing effect of the OH group, a conformational inversion takes place (E); one chair form flips into the other chair form (C). This conformation is preferred since adsorption can take place through the OH group and π electrons of the double bond. Thus, as in the case of **1**, the OH group seems most probably to have a directing effect.



5 **4** **6**

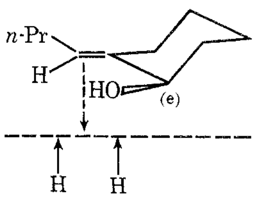
R = *n*-Bu



E

Preferred adsorption conformation

C

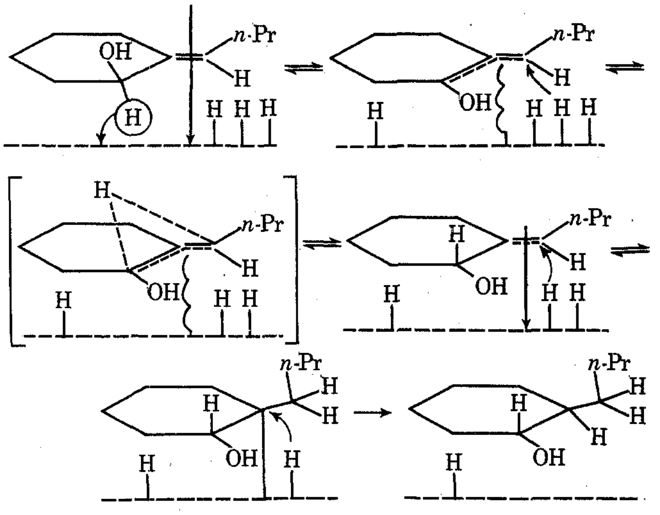


D

Although steric interactions are the most obvious aspects of the mechanism of hydrogenation, another possible explanation could be the existence of a [1,3]-sigmatropic hydrogen shift[13] (Scheme I). The occurrence of such a shift could lead to more trans product than expected from purely steric considerations. Results of hydrogenation of **4** over a number of catalysts are presented (Table II).

Over palladium there is an appreciable amount of isomerization product. Though various catalysts differ little in stereoselectivity, the stereoselectivity of the catalysts follows the sequence W_3 Raney Ni > Rh/C > Pt/C > Ru/C >

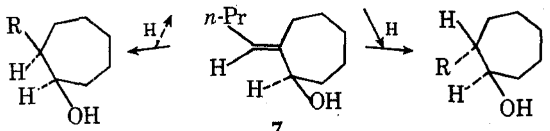
Scheme I



Ni_2B. The sequence is the reverse of that observed in 2-isopropylidene-, 2-cyclopentylidenecyclopentanol,[4e] and **1**, except over Raney nickel.

2-Butylidenecycloheptanol (7). From models the most comfortable location for the carbonyl group in cycloheptanone seemed to be at C-1, C-2, or C-7.[14] The strain appears rather small for any of these possibilities and it seems likely that the compound exists as a conformational mixture. From a study of the cyanohydrin dissociation constants of the methyl-substituted cycloheptanones, it was concluded that the cycloheptanone ring exists in a flexible-chair conformation.[15] There would seem to be little difference in the energies of the twist-chair and regular-chair conformation for cycloheptanone.

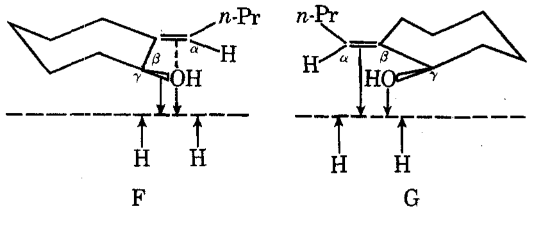
From molecular models of **7** two adsorption conformations (F and G) having minimum nonbonded interactions are possible, in which either side of the double bond can be presented in a planar conformation to the catalyst. In both



8 **7** R = *n*-Bu **9**

conformations the OH can be equally favorably placed with respect to the surface for interaction to occur through the lone pairs of oxygen.

However, the two adsorption conformations in the regular chair form differ only in that in one the OH is quasi-axial (F), and there is a distance of 1.95 Å between the C_α H and C_γ OH, while in the other the OH is quasi-equatorial (G), and there is a distance of 1.45 Å between the C_α H and C_γ OH. However, the C_α–H and C_γ–OH interactions in the two conformations can be modified in the twist-chair conformation. Since 74% **9** is obtained over Raney nickel, this suggests that the adsorption conformation (F) is the more favorable, since by addition of hydrogen cis from the catalyst surface this will give the trans alcohol.



F G

Table II
Hydrogenation of 2-Butylidenecyclohexanol[a]

Catalyst	Conditions	2-Butylcyclohexanone[b,d]	*trans*-2-Butylcyclohexanol[c,d]
W_3 Raney nickel	60–55 atm, 13–21°, 6 hr		61
Rh/C	10 atm, 2 hr	1	57
Pt/C	10 atm, 2 hr		53
Ru/C	10 atm, 2 hr		50
Ni_2B P-1	95–60 atm, 24–27°, 6 hr	1	47
Pd/C	10 atm, 2 hr	12	69
Pd black	10 atm, 2 hr	23	63

[a] 2-Butylidenecyclohexanol was hydrogenated over various catalysts at 10 atm pressure and room temperature for 2 hr (except Raney nickel and nickel boride catalysts, for which higher pressures and longer times were necessary). Product compositions were determined on a polyethylene glycol 400 column. [b] Percent of total chromatographic area. [c] Percent *trans*-2-butylcyclohexanol formed in various reductions. [d] For relative response of components see relative response of ketones and alcohols (of argon ionization detector).[9]

Table III
Hydrogenation of 2-Butylidenecycloheptanol[a]

Catalyst	Conditions	2-Butylcycloheptanone[b,d]	*trans*-2-Butylcycloheptanol[c,d]
W_3 Raney nickel	80–72 atm, 20–28°, 6 hr	2	74
Ni_2B P-1	50–40 atm, 19–21°, 6 hr	2	49
Ru/C	10 atm, 2 hr	4	55
Pt/C	10 atm, 2 hr	4	48
Rh/C	10 atm, 2 hr	16	55
Pd/C	10 atm, 2 hr	55	45
Pd black	10 atm, 2 hr	55	26

[a] 2-Butylidenecycloheptanol was hydrogenated over various catalysts at 10 atm pressure and room temperature for 2 hr (except Raney nickel and nickel boride catalysts, for which higher pressures and longer times were necessary). Product compositions were determined on polyethylene glycol 400 and polyethylene glycol 600 columns. [b] Percent of total chromatographic area. [c] Percent *trans*-2-butylcycloheptanol formed in various reductions. [d] For relative response of components see relative response of ketones and alcohols (of argon ionization detector).[9]

It seems difficult to predict precisely the factors responsible for the adsorption conformation (F) to be more favorable than the alternative adsorption conformation (G). The possibility that in the transition state the course of hydrogenation may be controlled primarily by the relative stability of the epimeric products cannot be ruled out. The occurrence of a [1,3]-sigmatropic hydrogen shift could lead to more trans product as well. Results of hydrogenation of **7** over a number of catalysts are presented (Table III).

Structure of 2-Alkylidenecyclanones. Examination of a number of ethylenic ketones in which the configuration of the conjugated system is fixed revealed that for cisoid conformation ν C=C (cm^{-1}) is considerably smaller than for the transoid conformation.[16] The differences between the ethylenic and carbonyl stretching frequencies are, however, consistently greater for s-cisoid than for s-transoid derivatives.[16] Furthermore, the ratio of the integrated band in-

Table IV
Infrared and Ultraviolet Spectra of 2-Alkylidenecyclanones

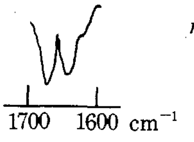
α,β-Unsaturated ketone	λ_{max} (EtOH), nm	ν C=O, cm^{-1}	ν C=C, cm^{-1}	Δ, cm^{-1}
trans-2-Butylidenecyclopentanone	245	1715	1650	65
trans-2-Butylidenecyclohexanone	247	1680	1615	65
trans-2-Butylidenecycloheptanone	242	1675	1610	65

Table V
Percent *cis*-2-Alkylcyclanols Formed in Various Reductions

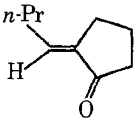
2-Alkylcyclanone	$LiAlH_4$	Raney nickel
2-Butylcyclopentanone	21	60
2-Butylcyclohexanone	37	63
2-Butylcycloheptanone	66	*a*

[a] Unknown, since this reduction was not performed.

tensities of the C=O and C=C stretching vibrations gives the most certain indication of the geometry of the chromophore, being low in cisoid and high in transoid systems.[17]



A



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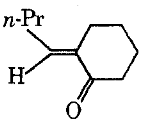

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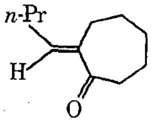

12

Numerical data for uv and ir spectra of 2-butylidenecyclanones are presented (Table IV).

The infrared spectra have characteristic absorption bands attributable to C=O and C=C stretching vibrations which are of nearly equal peak height, proving them to be rigidly cisoid systems (A).

Reduction of 2-Alkylcyclanones. The epimeric 2-alkylcyclanols were also obtained by the Pd/C-catalyzed reduction of 2-alkylidenecyclanones to give the corresponding 2-alkylcyclanones, which in turn were reduced by lithium aluminum hydride or BDH Raney nickel to give the corresponding epimeric 2-alkylcyclanols, and the results are presented (Table V).

The results obtained by the reduction of 2-butylcyclopentanone (**13**), 2-butylcyclohexanone (**14**), and 2-butylcycloheptanone (**15**) have a similar trend as has been observed by the reduction of 2-methylcyclanones by lithium aluminum hydride.[18] The reduction of **13** and **14** by lithium aluminum hydride appears to involve the attack of the reagent from the side of the butyl group, apparently the more hindered direction, to yield predominantly the more stable of the two possible alcohols (trans).[19] However, in the case of **15** (which yields the cis alcohol preferentially), reduction by lithium aluminum hydride is not consistent.[20]

To account for the formation of 60% **2** from the reduction of **13** over Raney nickel, it is suggested that steric interaction between the substituent and the atoms of the cycle combined with the requirements of a precise orientation of the carbonyl group on the catalyst directs the attack of hydrogen on the carbonyl group from the side away from the butyl group. The formation of 63% **5** from the reduction of **14** over Raney nickel is assumed to be a consequence of the ketone being adsorbed onto the catalyst in a conformation which minimizes the nonbonded interactions between the surface and the cycle, while the butyl group tends to be equatorial.[2a]

Experimental Section[21]

2-Bromocyclopentanone (16). Starting with 64 g of cyclopentanone,[22] 50 g (40%) of **16** was obtained, bp 56–58° (1.5 mm), $n^{25.5}D$ 1.5110 [lit.[22] bp 60° (2 mm), $n^{24.5}D$ 1.5114].

2-Butylidenecyclopentanone (10). Starting with 46.18 g (0.28 mol) of **16** and 30.6 g (0.42 mol) of *n*-butyraldehyde,[23] by vacuum distillation were obtained four fractions. GLC of the first three fractions indicated mainly one component present with ca. 8% of low-boiling impurities. Fraction 4 consisted mainly of 2-cyclopentylidenecyclopentanone, by comparison of its retention time with that of an authentic sample. **10** was purified by (1) vacuum fractionation (under N_2) of combined three fractions (14.18 g, 36.6%); (2) decomposing the semicarbazone with pyruvic acid (50%) in acetic acid solution;[24] or (3) preparative GLC on an NGA column (2-cyclopentylidenecyclopentanone was also recovered).

10 has bp 48–50° (0.5 mm), $n^{25.5}D$ 1.4675; darkens slowly on standing; uv λ_{max} (ethanol) 245 nm (lit.[23] 245 nm); ir 1650, 1715 cm^{-1} [lit.[23] 1655 (m), 1670 (m), 1735 cm^{-1} (s)]; NMR (CCl_4) τ 3.4–3.82 (olefinic H), 7.2–9.24 (total of alicyclic and aliphatic protons 13); its semicarbazone (50% alcohol) has mp 191–192° (lit.[23] mp 189–189.5°).

Hydrogenation of **10** over Pd/C in 95% ethanol (10 atm, 0.5 hr) gave **13** as a single component by GLC. Its semicarbazone (50% alcohol) has mp 185–186° (lit.[23] mp 186.5–187°), ir (neat) 1735 cm^{-1}.

2-Butylidenecyclopentanol (1). **10** (25 g, 0.18 mol) in dry ether (250 ml) was stirred vigorously and a suspension of $LiAlH_4$ (1.75 g, 0.046 mol) in dry ether (200 ml) was added gradually at room temperature over a period of 2 hr. The mixture was stirred for 0.5 hr after completion of the addition. The product was decomposed with dilute H_2SO_4 (300 ml, 3 *N*), and the aqueous layer was extracted with ether, washed successively with water and saturated NaCl solution, and dried (K_2CO_3). The solvent was removed after filtration, and the residue (24 g) was vacuum distilled (under N_2) to yield 20 g (78.8%) of a colorless liquid, bp 64–66° (2 mm), $n^{25}D$ 1.4740, and consisted mainly of one component, <1% **10** and traces of low-boiling impurities (GLC on NGA column). On examination, the component which originally showed a single peak on all columns tried, including Carbowax, changed into two major components (believed to be an exo to endo shift of the double bond) during preparative GLC on an NGA column. **1** (0.5 ml) was finally purified on a neutral alumina column (100 g) and eluted (9:1 hexane–methyl acetate). Presence of **1** in the various fractions was spotted by TLC (silica gel), using anisaldehyde–sulfuric acid color reagent.[25] The fractions containing pure **1** were combined and solvent removed under reduced pressure. **1** was obtained free from impurities and characterized: ir 2880, 2960, 3400 cm^{-1}; NMR (CCl_4) τ 4.3–4.8 (olefinic H), 5.6–5.9 (H adjacent to OH), 6.8–7.2 (hydroxyl H), 7.2–9.3 (aliphatic and alicyclic protons); mass spectrum *m/e* 140 (M^+).

Anal. Calcd for $C_9H_{16}O$: C, 77.14; H, 11.43. Found: C, 76.97; H, 11.22.

Its *3,5-dinitrobenzoate (alcohol) had mp 56–57°; mass spectrum m/e* 334 (M^+).

Anal. Calcd for $C_{16}H_{18}N_2O_6$: C, 57.48; H, 5.39; N, 8.38. Found: C, 57.66; H, 5.58; N, 8.48.

Catalytic Hydrogenation of 1. **1** was hydrogenated over various catalysts in 95% ethanol under various conditions (see Table I). Components thus obtained were separated by preparative GLC on Carbowax column.

The first component was shown to be **13** by comparison of its retention time with that of an authentic sample on different columns. The second component was shown to be **2**: ir 2880, 2960, 3420 cm^{-1}; NMR (Me_2SO)[26] τ 5.945 (*J* = 4.2 Hz) (the OH proton is split into a doublet but the peak at τ 5.98 is very intense with respect to the other peak at τ 5.91); mass spectrum *m/e* 125 (M^+ 142, the observed peak corresponds to $M^+ - OH$).

Anal. Calcd for $C_9H_{18}O$: C, 76.05; H, 12.67. Found: C, 75.92; H, 12.82.

Its 3,5-dinitrobenzoate was obtained as colorless needles (ethanol), mp 69–70°, mass spectrum *m/e* 336 (M^+).

Anal. Calcd for $C_{16}H_{20}N_2O_6$: C, 57.14; H, 5.95; N, 8.33. Found: C, 57.27; H, 6.14; N, 8.53.

The third component was shown to be **3**: ir 2880, 2940, 3400 cm^{-1}; NMR (Me_2SO) τ 5.645 (hydroxyl H) (*J* = 5.4 Hz); mass spectrum m/e 125 (M^+ 142, the observed peak corresponds to $M^+ - OH$).

Anal. Calcd for $C_9H_{18}O$: C, 76.05; H, 12.67. Found: C, 76.22; H, 12.59.

Its 3,5-dinitrobenzoate (ethanol) had two melting points of 34–35 and 45–46° (explained as having two distinct crystalline forms).

Anal. Calcd for $C_{16}H_{20}N_2O_6$: C, 57.14; H, 5.95; N, 8.33. Found: C, 57.31; H, 6.01; N, 8.31.

Reduction of 2-Butylcyclopentanone (13). 1. $LiAlH_4$. A suspension of powdered $LiAlH_4$ (25 mg) in dry ether (25 ml) was added to a stirred solution of **13** (0.5 g) in dry ether (5 ml) during ca. 0.5 hr. Stirring was continued for 15 min after completion of the addition. The product was decomposed with dilute H_2SO_4 (50 ml, 3 *N*), washed with water and saturated NaCl solution, and dried (K_2CO_3). The solvent was removed after filtration, and the residue consisted of a mixture of **2** and **3** in the ratio 21:79, respectively (GLC on Carbowax column).

2. Stabilized BDH Raney Nickel. **13** (100 mg) was hydrogenated over Raney Ni (100 mg) in 95% ethanol (25 ml) at a maximum pressure of 137.5 atm and a maximum temperature of 124° for 6 hr. The hydrogenated material was filtered to remove the catalyst and the ethanol was removed on a steam bath under reduced pressure. It consisted of a mixture of **2** and **3** in the ratio 60:40, respectively (GLC on Carbowax column).

1-Cyclohexenyl Acetate. Starting with 100 g (1.02 mol) of cyclohexanone,[27] 1-cyclohexenyl acetate was obtained as a colorless liquid: 100 g (70%); bp 32–34° (1 mm); $n^{25}\mathrm{D}$ 1.4540 [lit.[27] bp 52–55° (4 mm)]; ir 1120 (C–O–C symmetric stretch), 1215 (C–O–C asymmetric stretch), 1740 (C=O stretch), 2920 cm^{-1}.

2-Bromocyclohexanone Enol Acetate (17). By allylic bromination of 1-cyclohexenyl acetate (50 g, 0.34 mol) with *N*-bromosuccinimide[27] in carbon tetrachloride was obtained 30 g (38.3%) of **17** as a colorless liquid, bp 52–55° (0.3–0.5 mm), $n^{25}\mathrm{D}$ 1.5025 [lit.[27] bp 81–82° (3 mm)].

2-Butylidenecyclohexanone (11) was prepared by Reformatsky reaction of **17** and *n*-butyraldehyde by a modification (using benzene as solvent) of the reported method.[23] In a three-necked flask fitted with a mechanical stirrer, dropping funnel with a drying tube, reflux condenser, and tube for introducing nitrogen were placed zinc wool (18.2 g, 0.28 g-atom), mercuric bromide (0.37 g), *n*-butyraldehyde (30 g, 0.41 mol), and several crystals of iodine. Air was blown out by nitrogen and a solution of **17** (61 g, 0.28 mol) in anhydrous benzene (100 ml) was added gradually over a period of 2 hr. Reaction began at a bath temperature of 60°. After the end of the addition, the mixture was boiled for 0.5 hr with intensive stirring, cooled, and decomposed with hydrochloric acid (2% by volume). The water layer was repeatedly extracted with ether (6 × 50 ml). The combined ether extracts were washed with $NaHCO_3$ solution and water and dried (Na_2SO_4). The ether and benzene were distilled under reduced pressure. By vacuum distillation were obtained four fractions. GLC on a number of columns indicated fraction 3, bp 76–80° (0.5 mm), $n^{25}\mathrm{D}$ 1.4842 (19.9 g, 46.8%), to be mainly **11** along with ca. 10% of impurities [lit.[28] bp 95–100° (3 mm), $n^{22}\mathrm{D}$ 1.4800]. Purification of **11** on an NGA column was unsuccessful, for the presence of an unknown component (having OH group) in proximity with the main component, resulting in very poor resolution. Finally, **11** was purified by preparative GLC on a Carbowax column. GLC of the component thus obtained on various columns showed it to be mainly one component along with traces of impurities. **11** has uv λ_{max} (ethanol) 247 nm; ir[29] 1615, 1680 cm^{-1}; its semicarbazone (alcohol) had mp 140–141° (lit.[28] mp 138°).

Hydrogenation of **11** over Pd/C in 95% ethanol (10 atm, 0.5 hr) gave **14** as a major component along with ca. 2% of **5** and **6**. Its retention time was identical with that of an authentic sample on different columns. Its 2,4-DNP was obtained as orange crystals (ethanol), mp 110–111° (lit.[30] mp 110–111°), ir[31] 1700 cm^{-1}.

2-Butylidenecyclohexanol (4). A suspension of powdered $LiAlH_4$ (1.56 g, 0.041 mol) in dry ether (200 ml) was added to a stirred solution of **11** (25 g, 0.16 mol) in dry ether (250 ml) during ca. 2 hr. The reaction mixture was worked up as described for **1**. The solvent was removed after filtration and the residue (24 g), light yellow in color, was vacuum distilled to give a colorless liquid (20 g, 79%), bp 72–80° (5 mm), $n^{25}\mathrm{D}$ 1.4958, and consisted mainly of **4** along with ca. 5% of impurities. On examination, the component which originally gave a single peak on all columns tried, including Carbowax, transformed into two major components (believed to be an exo to endo shift of the double bond) during preparative GLC on an NGA column. **4** was purified on a neutral alumina column and eluted (9:1 hexane–methyl acetate) as in the case of **1**. The sample was confirmed to be a single component (GLC on different columns): ir 2890, 2960, 3420 cm^{-1}; NMR (CCl_4) τ 4.55–4.9 (olefinic H split into a triplet), 5.9–6.25 (H adjacent to OH), 7.94 (hydroxyl H), 7.35–9.35 (aliphatic and alicyclic protons); mass spectrum m/e 154 (M^+).

Catalytic Hydrogenation of 4. **4** was hydrogenated over various catalysts in 95% ethanol under various conditions (see Table II). The first component was shown to be **14** by comparison of its retention time with that of an authentic sample on different columns. A mixture of the second and third components (0.5 ml) was separated by column chromatography on a neutral alumina column (100 g) and eluted (9:1 hexane–methyl acetate). The presence of epimers in the various fractions was spotted by TLC (silica gel), using anisaldehyde–sulfuric acid color reagent.[25] The possible fractions were then monitored by GLC on a polyethylene glycol 600 column. Fractions containing pure **5** and **6** were combined separately and solvent was removed under reduced pressure. Their retention times were identical with those of an authentic sample of 2-butylcyclohexanol. **5** (the component which comes out first on the column): NMR (Me_2SO)[26] τ 5.96 (hydroxyl H) (J = 4.8 Hz). **6** (the later component): NMR (Me_2SO) τ 5.73 (hydroxyl H) (J = 6.0 Hz).

Reduction of 2-Butylcyclohexanone (14). 1, $LiAlH_4$. Reduction of **14** was carried as in the case of **13**. GLC of the components (Carbowax column) resulted in **5** and **6** in the ratio 37:63, respectively.

2. Stabilized BDH Raney Nickel. **14** (200 mg) was hydrogenated over Raney Ni (100 mg) in 95% ethanol (25 ml) at a maximum temperature of 134° and maximum pressure of 112.5 atm for 6 hr. The product was analyzed (GLC on Carbowax column) and consisted of **5** and **6** in the ratio 63:37, respectively.

2-Bromocycloheptanone (18). Starting with 168 g of cycloheptanone[32] and 240 g of bromine, by vacuum distillation were obtained two fractions. Fraction 1 was a mixture of unchanged cycloheptanone and **18** (50 g), bp 50–72° (1 mm), $n^{25.5}\mathrm{D}$ 1.5105. Fraction 2 was **18** (60 g), bp 76–80° (1 mm), $n^{25.5}\mathrm{D}$ 1.5175 [lit.[32] bp 105° (10 mm), $n^{22}\mathrm{D}$ 1.5137].

2-Butylidenecycloheptanone (12) was prepared by the Reformatsky reaction of **18** and *n*-butyraldehyde, by a modification (in one step) of the reported method.[23] In a three-necked flask fitted with a stirrer, reflux condenser, dropping funnel with a drying tube, and tube for introducing nitrogen were placed zinc wool (23.6 g, 0.36 g-atom), mercuric bromide (0.37 g), ethyl acetate (1 ml), *n*-butyraldehyde (32.8 g, 0.46 mol), and several crystals of iodine. Air was blown out by nitrogen, and a solution of **18** (57.04 g, 0.30 mol) in anhydrous benzene (100 ml) was added gradually over a period of 2 hr. Reaction began at a bath temperature of 60°. After the end of the addition, the mixture was boiled for 0.5 hr with intensive stirring and worked up as described in the case of **11**. By vacuum distillation were obtained four fractions. GLC on a number of columns indicated fraction 2, bp 76–80° (0.5–1 mm), $n^{25.5}\mathrm{D}$ 1.4735, and fraction 3, bp 97–99° (1–2 mm), $n^{25.5}\mathrm{D}$ 1.4800, to be mainly **12** (18.6 g, 37.5%) along with ca. 10% of impurities. A crude sample which had been kept for a long time at room temperature was freshly distilled to remove higher boiling components. Two peaks emerged, along with other impurities, during preparative GLC on an NGA column. One component was gradually merging with another component, and finally disappeared. The major component thus obtained was ca. 95% pure (GLC on an NGA column). It was clear that **12** was decomposing on the preparative column. A chromatographically pure sample was not obtained. **12** had uv λ_{max} (ethanol) 242 nm; ir 1610, 1675 cm^{-1}; its semicarbazone (50% alcohol) had mp 121°.

Anal. Calcd for $C_{12}H_{21}N_3O$: C, 64.54; H, 9.48; N, 18.81. Found: C, 64.75; H, 9.31; N, 18.34.

Hydrogenation of **12** over Pd/C in 95% ethanol (10 atm, 0.5 hr) gave mainly **15** with traces of **8** and **9**. Its 2,4-DNP was obtained as golden, irregular plates (alcohol), mp 81–82.5° (lit.[33] mp 80–81.5°), ir 1740 cm^{-1}.

2-Butylidenecycloheptanol (7). A suspension of powdered $LiAlH_4$ (1.425 g, 0.037 mol) in dry ether (200 ml) was added to a stirred solution of **12** (25 g, 0.15 mol) in dry ether (250 ml) during ca. 2 hr. The reaction mixture was worked up as described for **1**. After removal of the solvent under reduced pressure light pink liquid was obtained (24 g, 94.8%). GLC on an NGA column indicated it to be mainly one component along with ca. 5% of impurities. On examination, the component which originally gave a single peak on all columns tried, including Carbowax, transformed into two major components (believed to be an exo to endo shift of the double bond) during preparative GLC on an NGA column. **7** was purified on a neutral alumina column and eluted (9:1 hexane–methyl acetate) as in the case of **1**. The sample was confirmed to be a single component (GLC on various columns): ir 2870, 2940, 3400 cm^{-1}; NMR (CCl_4) τ 4.5–4.9 (olefinic H split into a triplet), 5.8–6.15 (H adjacent to OH, also split into a triplet), 8.15 (hydroxyl H), and 7.7–9.35 (aliphatic and alicyclic protons); mass spectrum *m/e* 168 (M^+).

Catalytic Hydrogenation of 7. 7 was hydrogenated over various catalysts in 95% ethanol under various conditions (see Table III). The first component was shown to be **15** by comparison of its retention time with that of an authentic sample. A mixture of the second and third components was separated by column chromatography as in case of **5** and **6**. **8** (the component which comes out first on the column): ir 2900, 2960, 3460 cm^{-1}; NMR (Me_2SO)[26] τ 5.96 (hydroxyl H) (J = 4.8 Hz); mass spectrum *m/e* 170 (M^+); its 3,5-dinitrobenzoate (alcohol) had mp 53–53.5°.

Anal. Calcd for $C_{18}H_{24}N_2O_6$: C, 59.34; H, 6.59; N, 7.69. Found: C, 59.27; H, 6.72; N, 7.79.

9 (the later component): ir 2950, 3450 cm^{-1}; NMR (Me_2SO) τ 5.81 (hydroxyl H) (J = 4.8 Hz); mass spectrum *m/e* 170 (M^+); its 3,5-dinitrobenzoate (alcohol) had mp 83–84°.

Anal. Calcd for $C_{18}H_{24}N_2O_6$: C, 59.34; H, 6.59; N, 7.69. Found: C, 59.45; H, 6.41; N, 7.54.

Lithium aluminum hydride reduction of 2-butylcycloheptanone (15) was carried as described in the case of **13**. GLC on a polyethylene glycol 400 column resulted in **8** and **9** in the ratio 66:34, respectively.

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Registry No.—**1**, 56292-34-3; **1** 3,5-DNB, 56292-35-4; **2**, 55166-24-0; **2** 3,5-DNB, 56292-36-5; **3**, 55166-25-1; **3** 3,5-DNB, 56292-37-6; **4**, 56292-38-7; **5**, 35242-02-5; **6**, 35242-05-8; **7**, 56292-39-8; **8**, 51113-04-3; **8** 3,5-DNB, 56292-40-1; **9**, 51113-00-9; **9** 3,5-DNB, 56292-41-2; **10**, 56292-42-3; **11**, 56292-43-4; **12**, 56292-44-5; **12** semicarbazone, 56292-45-6; **13**, 934-42-9; **14**, 1126-18-7; **14** 2,4-DNP, 1166-09-2; **15**, 36504-11-7; **15** 2,4-DNP, 56292-46-7; *n*-butyraldehyde, 123-72-8.

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