Hydroboration of Enol Acetates[1]

Alfred Hassner, Ronald E. Barnett, P. Catsoulacos, and S. H. Wilen[1b]

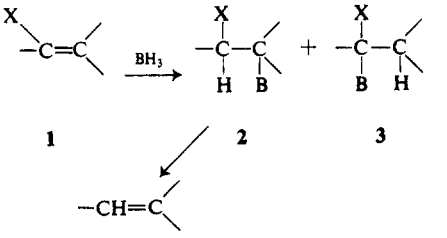
Contribution from the Department of Chemistry, University of Colorado, Boulder, Colorado 80302. *Received November 27, 1968*

Abstract: The directive effect of an acetoxy substituent in the hydroboration of olefins was examined. Cyclohexenyl acetate and 2-cholesten-3-ol acetate (7) yielded the expected diols, but in addition a considerable amount of monols was obtained. Cyclopentenyl acetate and 2-cholesten-3-ol benzoate gave only monols and none of the expected diol products. Δ^{16}-17-Acetoxy steroid **6** gave a *trans* diol on hydroboration. The yield of monol from cyclohexenyl acetate was raised with increasing temperature and increasing amount of diborane. Pyridine borane–aluminum chloride gave solely cyclohexanol. It was shown that the monol derived from **7** did not result from an elimination–rehydroboration reaction. Deuterium-labeling experiments were performed and the reaction mechanism is discussed.

The discovery by Brown and coworkers[2] that diborane and similar alkyl boranes add *cis* and regioselectively[3] to olefins has led to many useful applications and syntheses.[2,4] This reaction has a marked degree of selectivity, with the boron portion of diborane adding to the less substituted carbon of the double bond without skeleton rearrangement, and represents a regiospecific[3] and stereospecific method of introduction of alcohol functions by sterically controlled and *cis* hydration of olefins.

In alkenes containing a functional group close to the double bond hydroboration is not always completely regiospecific. Even the electronic effects of a phenyl group influence the direction of addition of diborane, with styrene leading to a 20:80 mixture of 1-phenyl-:2-phenylethanol.[5] Substituents on the phenyl ring of styrenes further control the direction of hydroboration.[5c] The influence of substituents other than carbon on a double bond has recently received some attention. Vinyl and allyl chlorides on hydroboration gave products that can undergo a facile elimination to olefins and cyclopropanes respectively.[6] On the other hand, B–halogen regioselective additions of diborane to vinyl halides leading largely to **3** (X = halogen) have been reported.[7] Diborane additions to boron-substituted olefins (X = BR_2, as in the dihydroboration of acetylenes), led to products derived mainly from **3** but also from **2** (X = BR_2).[8]

Enol ethers (**1**, X = OR) and thioethers (**1**, X = SR),[9] as well as enamines (**1**, X = NR_2)[10,11] have been hydroborated.



In general the **2**:**3** product ratio formed in the hydroboration of heterosubstituted organoboranes varies quite widely, *i.e.*, for vinyl halides from 2:98 to 80:20, for vinyl sulfides from 10:90 to 90:10.

While enol acetates of cyclic ketones have been hydroborated in two instances to produce *trans* diols,[12,13] cyclohexenyl acetate has been found[14] to give nearly equal amounts of *trans*-1,2-cyclohexanediol and cyclohexanol.[15] The monoalcohol could have been produced by elimination of boron acetate from **2** (X = OAc) to yield cyclohexene which would be hydroborated to cyclohexanol. On the other hand addition of diborane could have proceeded to **3** (X = OAc) which could either undergo acetoxy transfer to boron or conversion to cyclohexanone both of which would lead to the monoalcohol.

To shed light on the effect of a polar acetoxy substituent on the reacting double bond in diborane addition, we chose to study this reaction with cyclohexenyl acetate (**4**), cyclopentenyl acetate (**5**), 16-androsten-3β,17-diol diacetate (**6**), and 2-cholesten-3-ol acetate (**7**). It was hoped that the well-defined and conformational aspects of substituents on steroids would make a study of **7** particularly fruitful.

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(4) (a) H. C. Brown, H. R. Ayyangar, and G. Zweifel, *J. Am. Chem. Soc.*, **86**, 397 (1964); (b) H. C. Brown, W. R. Heydkamp, E. Brener, and W. S. Murphy, *ibid.*, **86**, 3565 (1964); H. C. Brown and N. V. Bhatt, *ibid.*, **88**, 1440 (1966); H. C. Brown, G. W. Kabalka, and M. W. Rathke, *ibid.*, **89**, 4530 (1967); H. C. Brown and E. Negiski, *ibid.*, **89**, 5477 (1967); H. C. Brown, M. Rogić, M. W. Rathke, and G. W. Kabalka, *ibid.*, **89**, 5709 (1967), and references cited therein.

(5) (a) H. C. Brown and G. Zweifel, *J. Am. Chem. Soc.*, **82**, 4708 (1960); (b) E. L. Allred, J. Sonnenberg, and S. Winstein, *J. Org. Chem.*, **25**, 26 (1960); (c) H. C. Brown and R. L. Sharp, *J. Am. Chem. Soc.*, **88**, 5851 (1965).

(6) (a) M. F. Hawthorne and J. A. Dupont, *ibid.*, **82**, 1886 (1960); (b) H. C. Brown and O. J. Cope, *ibid.*, **86**, 1801 (1964); (c) S. J. Cristol, F. P. Parimgo and E. E. Plorde, *ibid.*, **87**, 2870 (1965).

(7) (a) D. J. Pasto and R. Snyder, *J. Org. Chem.*, **31**, 2773 (1966); (b) D. J. Pasto and J. Hickman, *J. Am. Chem. Soc.*, **89**, 5608 (1967).

(8) (a) A. Hassner and B. H. Braun, *J. Org. Chem.*, **28**, 261 (1963); (b) D. S. Matteson and J. G. Shdo, *ibid.*, **85**, 2684 (1963); (c) D. J. Pasto, *ibid.*, **86**, 3039 (1964); (d) G. Zweifel and H. Arzoumanian, *ibid.*, **88**, 291 (1967).

(9) (a) D. J. Pasto and C. C. Cumbo, *ibid.*, **86**, 4343 (1964); (b) D. J. Pasto and R. Snyder, *J. Org. Chem.*, **31**, 2777 (1966).

(10) J. W. Lewis and A. A. Pearce, *Tetrahedron Letters*, 2039 (1964).

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(12) F. S. Alvarez and M. Arrequin, *Chem. Ind.* (London), 720 (1960).

(13) (a) L. Caglioti, G. Cainelli, G. Maina, and A. Selva, *Gazz. Chim. Ital.*, **92**, 309 (1962).

(14) For a preliminary report, see A. Hassner and B. H. Braun, *Univ. Color. Studies, Ser. Chem. Pharm.*, **4**, 48 (1962).

(15) After this paper had been submitted, a detailed account of hydroboration of vinyl halides, enol ethers, and enol acetates was published: H. C. Brown and R. L. Sharp, *J. Am. Chem. Soc.*, **90**, 2915 (1968). Their results on cyclohexenyl acetate **4** generally agree well with ours but the results on cyclopentenyl acetate **5** differ, presumably because of the different ratio of BH_3/enol ester used in the two investigations.

Results

Hydroboration of Cyclohexenyl Acetate (4). Hydroboration of **4** was carried out either *in situ*, by addition of sodium or lithium borohydride in diglyme to a solution of the olefin and of boron trifluoride etherate in tetrahydrofuran or by adding a tetrahydrofuran solution of diborane to an ether solution of the olefin. In both cases using a 2:1 molar ratio of borane to olefin at 0° the distribution of products was approximately 60% *trans*-1,2-cyclohexanediol (**8**) and 20% cyclohexanol (**9**). It was established the cyclohexenyl acetate was stable to boron trifluoride etherate as well as to sodium borohydride under reaction conditions.

The ratio of monol to diol formed in the hydroboration of **4** was temperature dependent and increased as the reaction temperature was raised from 0 to 25°. Furthermore, the yield of monol increased at the expense of diol as the ratio of diborane to enol acetate was raised from 2 to 10 (see Table I). Cyclohexanol was the only reaction product isolated (80%), when the hydroboration of **4** is carried out with pyridine borane and aluminum chloride. The enol acetate **4** was not hydrolyzed to a ketone in the presence of pyridine or aluminum chloride under reaction conditions.

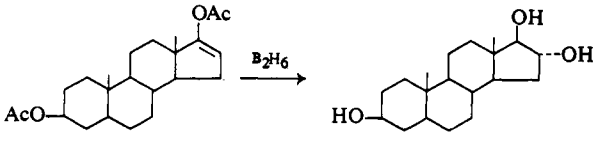
When cyclohexenyl acetate (**4**) was allowed to react with half a molar equivalent of borane as required by the following equation and the reaction was monitored by gas chromatography for unreacted **4** it was found that only

$$2\underset{\text{OAc}}{\underset{|}{\text{C}}}\!=\!\text{C} + \text{BH}_3 \rightarrow (\underset{\text{OAc}}{\underset{|}{\text{CC}}})_2\text{BH}$$

half of the enol acetate had been consumed. A ratio of at least 1.5:1 of borane to enol acetate (see Table I) is required for complete consumption of the olefin. In keeping with these results ethanol was isolated, as the 3,5-dinitrobenzoate, among the hydroboration products of **4**.

Hydroboration of Cyclopentenyl Acetate (5). This enol acetate yielded only cyclopentanol (75–80%) under all reaction conditions attempted and no diol could be isolated. The stoichiometry of the reaction, like for enol acetate **4**, required 1.5–2 mol of borane/mol of **5** (see Table II). Ethanol was found as a reaction product.

Hydroboration of 16-Androsten-3β,17-diol Diacetate (6). Diborane reduction of the steroidal 16-ene-17-acetate **6** in tetrahydrofuran gave the *trans*-16α,17β-diol **10** in over 80% yield as the only isolable material. The product was identical with **10** prepared by another route.



6 **10**

Hydroboration of 2-Cholesten-3-ol Acetate (7). Enol acetate **7** led to both monol and diol on hydroboration. The products were separated by chromatography on alumina. The monols, formed consisted mainly of cholestan-3β-ol (**11**) and a small percentage (less than 10%) of cholestan-3α-ol (**12**). No cholestan-2-ols could be detected. The diol isolated was cholestane-2α,3β-diol (**13**). The ratio of monol to diol formed in the hydroboration of **7** depended on whether diborane was added or generated *in situ* (Table III). Whereas *in situ* hydroboration of enol acetate **7** gave 80% monols and 15% diol, reaction with diborane solution changed the yields to 44 and 51%, respectively. *In situ* hydroboration of 2-cholesten-3-ol benzoate (**14**) yielded only monol.

Finally, 2-cholesten-3-ol acetate (**7**) was treated with deuteriodiborane generated *in situ* from sodium borodeuteride and boron trifluoride. The product was chromatographed and cholestan-3β-ol (**11**) was isolated. Its infrared spectrum indicated the presence of C–D stretching at 2125 cm^{-1}. The nmr spectrum of this product showed absence of a hydrogen at C-3 and the mass spectrum indicated that two deuterium atoms had been incorporated—parent ion at *m/e* 390 compared to nondeuterated cholestan-3β-ol (**9**) with *m/e* at 388. Careful oxidation of deuterated **9** with chromic acid in acetone yielded cholestan-3-one which still contained one deuterium atom as evidenced by infrared absorption near 2100 cm^{-1} and by its mass spectrum—parent ion *m/e* 387 compared to 386 for nondeuterated cholestan-3-one.

Table I. *In Situ* Hydroboration of Cyclohexenyl Acetate (**4**) at 25°[a]

Moles of BH_3/mol of **4**	% reaction[b]	% monol **9**	% diol **8**
0.25	28	12	14
0.50	45	18	23
1.00	76	37	35
1.50	95	40	45
2.0	100, 100	44	40
4.0	100	48	31
10.0	100	56	12

[a] With BF_3 and $LiBH_4$ in tetrahydrofuran: reaction time 1 hr. [b] ±5%. Consumption of **4** followed by glpc with xylene as an internal standard.

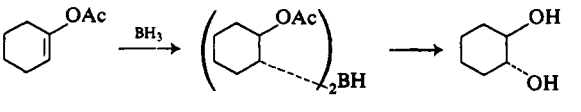
Table II. Consumption of Enol Acetates **4** or **5** in Hydroboration at 25°[a]

Moles of BH_3/mol of **4** or **5**	% reaction
0.25	30
0.50	50
1.0	80
2.0	100

[a] Using a tetrahydrofuran solution of diborane. Reaction time 30 min. Consumption followed by glpc, with xylene as an internal standard.

Discussion

If polar effects are disregarded, the usual sterically influenced regiospecific process of addition of diborane to the enol acetates under study is expected to lead upon work-up to *trans*-1,2-diols. The stoichiometry expected for addition of diborane to cyclohexenyl acetate (**4**) leading to *trans* diol **8** *via* **15** would require 1 mol of BH_3 for every 2 mol of enol acetate, based on the fact that 1-



4 **15** **8**

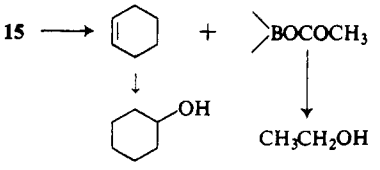
Table III. Effect of Reaction Conditions on the Hydroboration of 4 and 7 at 0°

	Moles of BH_3/mol of acetate	% monol	% diol	Reactn cond
Cyclohexenyl (4)	2.00	17	58	*In situ*
	2.00	20	61	Borane–THF
Cholestenyl (7)	Large	80	15	*In situ*
	Large	44	51	Borane–THF

methylcyclohexene yields largely a dialkyl borane adduct analogous to **15**.[2]

Our findings that at least 1.5 mol of BH_3/mol of enol acetate (see Table I) were required for complete consumption of the latter indicate that a slow rate-determining first step (*e.g.*, addition of diborane to the double bond) is followed by faster steps in which borane is being consumed.

It was at first thought that the monol (**9**) may have been produced by an elimination of an acetoxyboron moiety to give cyclohexene which would be rehydroborated to give **9**.



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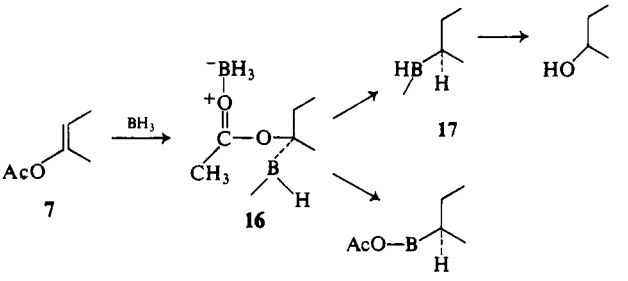
Analogous eliminations from β-chloro alkyl boranes are well documented[6] and acyloxyboron moieties are known to be involved in the hydroboration of carboxylic acids and are reduced fast to alcohols.[2] This would be consistent with the isolation of ethanol from the hydroboration of **4** as well as with the high ratio of diborane/olefin required.

The results with 2-cholesten-3-ol acetate (**7**), however, preclude the above elimination–rehydroboration mechanism, at least for this enol acetate. Hassner and Pillar[16] have shown that hydroboration of 2-cholestene yields 50% cholestan-3α-ol, 25% cholestan-2α-ol, and 20% cholestan-3β-ol. On the other hand, hydroboration of **7** under similar conditions in THF yielded 37% cholestan-3β-ol and 7% cholestan-3α-ol in addition to diol **13**. Hence the mono alcohols could not have resulted from hydroboration of 2-cholestene.

The formation of monols can be accounted for by a B–OAc regioselective addition of diborane to the enol acetate leading mainly to **16**.[17] Intermediate **16** could undergo an inter- or intramolecular displacement by H^- leading to **17** or **18**, respectively, and thence to a monol.[18] Assuming complete inversion of stereochemistry in the intermolecular displacement or the intramolecular transfer reaction,[7b] the ratio of 3β:3α cholestanols formed in the hydroboration of **7** requires an 87:13 ratio of α:β attack on cholestene. This is not inconsistent with known effects in these systems (77:23 ratio).[16]



7 **16** **17** **18**

If simple HMO calculations are made on the system **19** with $\alpha_{C_2} = \alpha_O + 0.3\beta_O$, one obtains $\gamma_1 = -0.136$ and

19

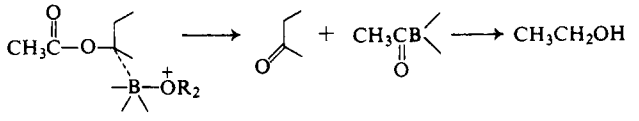
$\gamma_2 = +0.136$. We have assumed that the acetate group acted solely by induction hence increasing the effective electronegativity of C-1. This is a reasonable approximation since electron donation by resonance from oxygen into the double bond is probably not very effective due to cross-conjugation with the carbonyl group. These calculations indicate qualitatively that in enol esters the π-electron density has been shifted toward C-1 making it the kinetically favored center of attack by diborane. With the electronic effect counterbalancing steric factors, one would predict that more mono alcohol should be formed at higher temperature. This is borne out qualitatively by the results in Tables I and III. Furthermore, since phenyl is more electron withdrawing than methyl one would expect less electrophilic attack by diborane on C-2 in enol benzoates. Accordingly, if diborane were generated *in situ*, 2-cholesten-3-ol acetate (**7**) gave the diol **13** in 15% yield whereas no diol was formed from 2-cholesten-3-ol benzoate (**14**).

However, resonance should become important for enol ethers **19** (X = R). Indeed, HMO calculations on this more complex system using $\alpha_{OR} = \alpha_O + \beta_O$, $\alpha_{C_1} = \alpha_O + 0.1\beta_O$, $\alpha_{C_2} = \alpha_O$, $\beta_{OR-C_1} = 0.8\beta_O$, and $\beta_{12} = 1.1\beta_O$ leads to $\gamma_{OR} = 0.15$, $\gamma_1 = 0.04$, and $\gamma_2 = -0.19$.

Hence for enol ethers the greatest electron density is predicted at C-2, consistent with the finding that enol ethers lead predominantly to diol products.[9] In general HMO calculations predict that electronegative substituents will enhance attack at C-1 if resonance effects are not important. If electron donation by resonance be-

(16) A. Hassner and C. Pillar, *J. Org. Chem.*, **27**, 2914 (1962).

(17) Alternatively, the reaction may involve the intermediacy of a ketone (see below). In fact, the α:β ratio of alcohols is similar to that found in the hydroboration of cholestan-3-one.



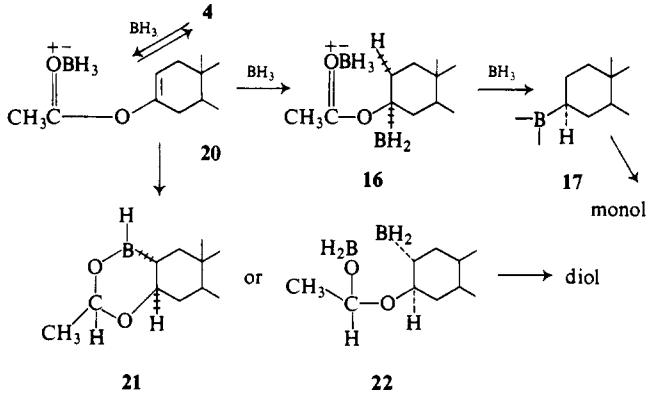
(18) Independent evidence for an intermolecular displacement of type **16** → **17** has just been presented by A. Suzuki, K. Ohmori, H. Takenada, and M. Itoh, *Tetrahedron Letters*, 4937 (1968). On the other hand, kinetic evidence was found for an intramolecular displacement of type **16** → **18** by D. J. Pasto, J. Hickman, and T. C. Cheng, *J. Am. Chem. Soc.*, **90**, 6259 (1968).

comes important, then attack at C-2 will be favored both by charge density and on steric grounds. These predictions are in agreement with recent experimental findings.[15]

The results of deuterioboration of enol acetate **7** clearly indicates the incorporation of deuterium at the 2 position of cholestanol. Regioselective addition leading to **16** followed by displacement of acetoxy by hydride with inversion is consistent with these data.

Although, following normal addition to cyclopentenyl acetate **5** there may be a greater propensity for elimination of acetoxyboron than in **6**, the contrasting formation of monol from **5** and diol from **6** can be explained by a B–OAc regiospecific addition of borane to **5** which is reversed for steric reasons (neopentyl-type system) in **6**.

Considerable changes in the ratio of monol to diol product were observed depending on the hydroboration conditions. Thus a large ratio of diborane to enol acetate **4** favored monol formation as did *in situ* hydroboration (in the presence of BF_3)[19] of enol acetate **7**. Both **4** and **7** have been shown to be stable to BF_3 under reaction conditions. Similarly *in situ* hydroboration of 2-cholesten-3-ol benzoate (**14**) gave 88% of monols but not diol, whereas Caglioti[13] reported a 30% yield of cholestane-2α,3β-diol by bubbling diborane into a diglyme solution of **14**. These results can be accounted for by a scheme such as shown below.



The first step, complexation of the enol acetate with the electrophilic BH_3 or BF_3, can be followed by a slow intermolecular addition of borane favored by an excess of borane. Displacement of $CH_3CO_2BH_2$ by hydride would lead to monol *via* **17**. Alternatively, **20** may react in an even slower and possibly intramolecular step (*i.e.*, *via* **21**) leading to diol. The exclusive formation of cyclohexanol from treatment of **4** with pyridine borane and aluminum chloride is compatible with this scheme. Further work to substantiate this mechanism is under way.

Experimental Section[20]

Cyclohexenyl acetate (4) was prepared by the method of Leonard and Owens[21] in 80% yield, bp 82–83° (23 mm). The material was pure by glpc.

Cyclopentenyl acetate (5) was prepared in 69% yield as described for **4**, bp 61–63° (22 mm), pure by glpc, corresponding by ir to known **5**.[22]

16-Androstene-3,17-diol diacetate (6), mp 169–170°, was obtained as described by Leeds, *et al.*[23]

2-Cholesten-3-ol acetate (7), mp 93–95°, was synthesized according to Caglioti, *et al.*[13]

2-Cholesten-3-ol benzoate (8), mp 125–126°, was prepared by the method of Ruzicka.[24]

Pyridine borane, mp 9–11°, was prepared according to Brown.[25]

Borane in THF was synthesized by bubbling diborane generated by the method of Brown and Turney[26] into dry THF at 0°. The solution was standardized by taking aliquots and decomposing them with water, adding mannitol, and titrating to a phenolphthalein endpoint.

Stoichiometric Procedures. Two milliliters of 0.987 *M* BH_3 in THF was added to a solution of 1.10 g of enol acetate **4** in 0.13 ml of xylene at 25°. After 30 min the extent of consumption of **4** was determined by glpc using a Perkin-Elmer column K at 100°. The reaction was nearly 30% complete. Similar experiments using different proportions of **4** or **5**, respectively, gave the results shown in Table II.

***In Situ* Hydroboration of Cyclohexenyl Acetate (4).** In a 125-m erlenmeyer flask equipped with a pressure equalized dropping funnel was placed 2.0 g of **4** and 0.451 g of $LiBH_4$ in 20 ml of anhydrous ether at 25°. Boron trifluoride etherate (12.3 g of freshly distilled) in 10 ml of anhydrous ether was added with stirring through the dropping funnel over a 20-min period. The reaction mixture was left to stand 40 min and was then poured into 25 ml of water. After bubbling ceased, 25 ml of 10% potassium hydroxide in methanol was added, followed by 10 ml of 30% hydrogen peroxide. After 1 hr at room temperature the mixture was acidified and the white precipitate was removed by filtration. The precipitate was added to a 0.1 *M* hydrochloric acid solution and extracted eight times with 50-ml portions of chloroform. The mother liquor was also extracted eight times. The chloroform was removed *in vacuo* and the resulting oily solid was washed with Skellysolve F. The remaining solid material was identical by ir with authentic[27] *trans*-1,2-cyclohexanediol (**8**). The Skellysolve F solution was washed with water. The water was then extracted eight times with chloroform and the chloroform removed *in vacuo*. A small amount of diol was obtained. The Skellysolve F layer was analyzed by glpc using cyclohexyl propionate as an internal standard to quantitatively determine cyclohexanol on a column of 1.9% SE-30 on acid washed Chromosorb W. The total yield of *trans*-1,2-cyclohexanediol (**8**) was 40%; the yield of cyclohexanol (**9**), 44%. Glpc analysis of the reaction mixture before oxidation and hydrolysis showed it to be 100% complete (based on destruction of enol acetate).

In a similar manner, using different proportions of $LiBH_4$–BF_3 to enol acetate at 25° the results shown in Table I were obtained. The hydroboration of **4** *in situ* at 0° and with BH_3–THF at 0° (maintained at 0° for 3 days) and work-up as above gave the results shown in Table III.

Hydroboration of 4 with Pyridine–Borane and Aluminum Chloride. To 1.75 g of cyclohexenyl acetate **4** and 2.3 g of pyridine borane in a constant-temperature bath was added 3.0 g of anhydrous aluminum chloride in 50 ml of dry THF over a period of 15 min at 25°. Gas continued to be evolved for 5 hr. After the evolution of gas had ceased, the reaction mixture was poured into 20 ml of cold water and stirred thoroughly. Then 40 ml of 10% potassium hydroxide in methanol was added and a precipitate of aluminum hydroxide was produced. Then 20 ml of 30% hydrogen peroxide was added and the reaction mixture was left to stand for 3 hr. The aluminum hydroxide was filtered off and extracted overnight with 200 ml of chloroform. The reaction mixture was extracted 16 times with chloroform and combined with the other chloroform extract. The chloroform was removed *in vacuo*. The ir of the remaining oil indicated the presence of cyclohexanol, cyclohexanone, and pyridine borane. The oil was washed with 100 ml of Skellysolve F. The remaining oil contained pyridine borane and cyclohexanone. The Skellysolve F layer was washed with water and

(19) Similar effects have been reported for enol ethers, see ref 9.

(20) All melting points were taken on a Fisher-Johns melting point block and are uncorrected. Infrared spectra were obtained in KBr disks on a Beckman IR-5 spectrometer, whereas nmr spectra were run in 10% solutions of chloroform on a Varian A-60 spectrometer using tetramethylsilane as an internal standard.

(21) N. J. Leonard and F. H. Owens, *J. Am. Chem. Soc.*, **80**, 6044 (1958).

(22) L. Goodman, A. Benitz, C. D. Anderson, and B. R. Baker, *ibid.*, **80**, 6587 (1958).

(23) N. S. Leeds, D. K. Fukushima, and T. F. Gallagher, *ibid.*, **76**, 2943 (1954).

(24) L. Ruzicka and W. H. Fischer, *Helv. Chim. Acta*, **19**, 1371 (1936).

(25) H. C. Brown, *J. Am. Chem. Soc.*, **64**, 325 (1942).

(26) H. C. Brown and P. A. Tierney, *ibid.*, **80**, 1552 (1958).

(27) Obtained from Aldrich Chemical Co.

Table IV

Moles of BH_3/moles of **4**	% cyclohexanol (**9**)
2.0	80
1.0	37
0.5	21

the water was extracted 16 times with chloroform. The chloroform was evaporated to yield pure cyclohexanol. The Skellysolve F also yielded cyclohexanol. The total yield of cyclohexanol (**9**) was 80%. There was no evidence of diol.

Using different molar ratios of BH_3 to **4** the results can be summarized as shown in Table IV. There was no evidence for diol **8** formation in any of these experiments.

Isolation of Ethanol. Hydroboration of 5.0 g of cyclohexenyl acetate (**4**) in THF was carried out with an excess of diborane gas bubbled through the solution at 30–50° and worked up with $NaOH–H_2O_2$ (1 hr). Fractional distillation of the organic phase gave a low-boiling fraction, bp 48–84°, which consisted mainly of THF but which on treatment with 3,5-dinitrobenzoyl chloride and pyridine yielded ethyl 3,5-dinitrobenzoate (25%), mp 88–93°, recrystallized from Skellysolve B and identical by ir with authentic material, prepared from ethanol.

From the other fractions of the distillate 53% of cyclohexanol (**9**) and 14% of *trans*-1,2-cyclohexendiol (**8**) were obtained.

In a similar manner 20% of ethyl 3,5-dinitrobenzoate was isolated from hydroboration of cyclopentenyl acetate (**5**).

Hydroboration of Cyclopentenyl Acetate (5). To 0.63 g of **5** was added 80 ml of 0.126 *M* of BH_3 in THF cooled to −20°. The temperature rapidly rose to 25°, and the reaction mixture was allowed to stand for 12 hr, then treated with $NaOH–H_2O_2$. The resulting solution was extracted 16 times with 50 ml of $CHCl_3$. From the $CHCl_3$ extract on evaporation an oil was obtained which was extracted into Skellysolve F (bp 40–60°). Partitioning between water and Skellysolve F and extraction of the water layer with chloroform yielded only cyclopentanol from both the $CHCl_3$ and Skellysolve F. The total yield of cyclopentanol was 76%, converted to its 3,5-dinitrobenzoate, mp 114–115°, identical by ir with authentic material, prepared from commercial cyclopentanol.

When the hydroboration was carried out with $NaBH_4–ZnCl_2–BF_3$ or pyridine borane–aluminum chloride the same results were obtained, the yield of cyclopentanol varying between 74 and 80%.

Hydroboration of 6 was carried out with 400 mg of 16-androstene-3β,17-diol diacetate in 30 ml of THF and 3 ml of 1 *M* BH_3 in THF for 90 min. Usual work-up and extraction with ether yielded 280 mg of triol **10**, mp 245–248°, identical by ir with authentic material.[23]

Hydroboration of 2-Cholesten-3-ol Acetate (7). Into 319 mg of **7** in 50 ml of THF swept with N_2 was bubbled a large excess of diborane. After 1 hr at 25° 20 ml of 10% methanolic KOH was added followed by 3 ml of 30% H_2O_2. The mixture stood overnight and was then diluted with 50 ml of water and extracted with 150 ml of ether. The ether layer was washed and dried and yielded 295 mg of crude product. This was dissolved in Skellysolve F–benzene (1:1) and chromatographed on a column of 5 g of Woelm alumina (activity I). Elution with benzene–Skellysolve F (95:5) gave 2 mg (0.3%) of cholestan-3-one identified by ir. With ether–benzene (1:9) there was obtained 22 mg (14%) of 3α-cholestanol (**12**) identified by ir and melting point comparison with authentic sample.[16] Ether–benzene (15:88) eluted 107 mg (37%) of 3β-cholestanol (**11**), mp 139–140°, identical with authentic material.[16] Elution with ether gave 162 mg (51%) of cholestane-2α,3β-diol (**13**) identified by melting point and ir.

When 293 mg of **7** was hydroborated with boron trifluoride etherate (2 ml) and 0.2 g of $LiBH_4$ in THF and the product was chromatographed on magnesium silicate there was obtained 227 mg (80%) of monols and 15% of diol **13**.

Enol acetate **7** was recovered unchanged on standing at 25° for 20 min in THF in the presence of $NaBH_4$ or BF_3 etherate.

Hydroboration of 2-Cholesten-3-ol Benzoate (14). To 85 mg of (**14**) in 25 ml of THF and 2 ml of BF_3 etherate was added 0.2 g of $LiBH_4$ in 25 ml to THF over a period of 15 min. Work-up as above gave 72 mg of product which was chromatographed on 5 g of alumina to yield 7 mg (10%) of 3α-cholestanol, and 54 mg (78%) of 3β-cholestanol (**11**).

Deuterioboration of 7. To 500 mg of 2-cholesten-3-ol acetate (**7**) in 30 ml of THF was added 3 ml of BF_3 etherate and then over a period of 20 min a solution of 350 mg of $NaBD_4$ in 40 ml of THF. After 2 hr at 25° $KOH–H_2O_2$ was added and within 15 min the mixture was diluted with water and extracted with ether. The product, 450 mg, was chromatographed on silica gel. Elution with ether–benzene (1:4) gave 3β-cholestanol-d_2, mp 140–141°, ir 2125 cm^{-1} (C–D), *m/e* 390, identical by ir with 3β-cholestanol which showed *m/e* 388.

Oxidation of 3β-Cholestanol-d_2. To a solution of 50 mg of the above alcohol in 10 ml of acetone was added dropwise a solution of 2.67 g of CrO_3 in 2.3 ml of H_2SO_4 and 10 ml of water at 0–5°. Dilution with water and extraction with $CHCl_3$ gave 3-cholestanone-d_1, mp 128°, *m/e* 387, identical by ir with authentic 3-cholestanone which showed *m/e* 386.

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