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THE STEREOCHEMISTRY OF HYDROBORATION OF CONJUGATED KETONES[1]

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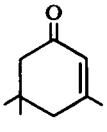
Abstract—The hydroboration of isophorone (I) and 3-methylcyclohexenone (II) yielded single diols, which were shown to be the diequatorial isomers (X and XIII) by chemical and physical methods. The same reaction with piperitone (III) yielded two diols (XV and XVI) both with hydroxyls in diequatorial positions. A small fraction of monoalcohols was also obtained. The mechanism of these reactions is discussed. The open chain analog IV did not show stereospecificity during hydroboration.

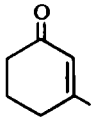
BROWN[3] has established the relative reactivity of diborane with various functional. groups. This difference in the rates of hydroboration and reduction was utilized[4] for selective reaction of double bonds in the presence of other isolated functional groups. Very little is known however about the relative reactivities of two functional groups, conjugated one to another. In the reaction of cholestenone with diborane, the ketone was reduced first,[5] and the double bond hydroborated subsequently. This reaction was also found to be stereospecific, yielding the 3β, 4α-cholestanediol.[5] Similarly, a *trans* diol was obtained on hydroboration of verbenone.[6] The steric course of both these reactions is easily understood, since an attack on the CO group and the double bond by diborane *trans* to the axial Me in the steroid[7] and *trans* to the bridge in the bicyclic terpene[8] is expected.

The hydroboration of conjugated cyclohexenones, where either no steric influence was present, or where the interfering group sterically directed the reaction towards the formation of *cis*-diols was investigated. The ketones studied were: isophorone (I), 3-methylcyclohex-2-enone (II) and piperitone (III). All of them contain a Me group on the double bond β to the carbonyl, to ensure the formation of 1,2 diols. An open chain conjugated ketone, mesityl oxide (IV), was also submitted to hydroboration for sake of comparison with the cyclic ketones.

The hydroboration of isophorone proceeded stepwise, the carbonyl beiny the first group attacked. Interruption of the reaction after short periods yielded mostly the allylic alcohol (V). After longer reaction times two products were obtained: (1) a crystailine diol obtained in 65% yield and shown to be a single isomer by chromatographic methods and (2) a mixture of isomeric monoalcohols (15% yield). The diol was different from the isomeric cyclohexanediols (VI and VII).



I



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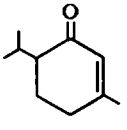
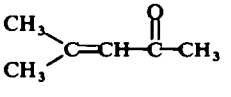
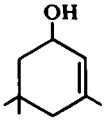


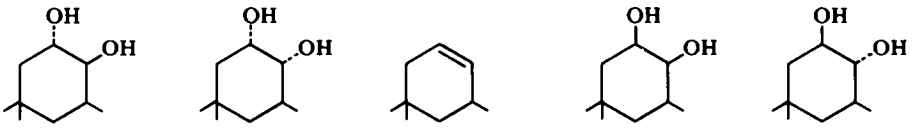
III



IV



V



VI VII VIII IX X

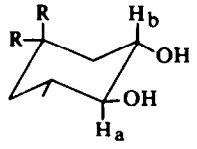
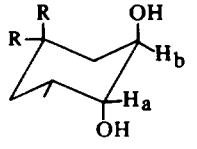
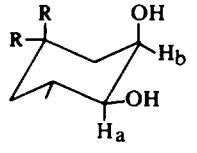
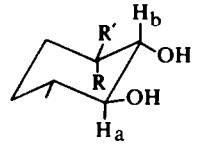
The first of these diols was prepared by hydroxylation of 3,5,5-trimethylcyclohexene (VIII) with hydrogen peroxide and formic acid and its structure follows from the rule of diaxial opening of epoxides.[9] The diol VII was obtained using the Woodward–Brutcher procedure[10] of oxidation with iodine and silver acetate in wet acetic acid. This method usually gives *cis* diols, having the hydroxyls on the more hindered side of the molecule. Since a third isomeric 1,2-diol (IX) is excluded as a possible product of hydroboration in view of the known *cis* addition of boron and hydrogen to the double bond, we assigned the structure X to the diol obtained on hydroboration.

All these structure assignments were confirmed by physical methods. The NMR spectrum of VI shows a triplet (J = 3·5 c/s) and a quartet (J = 3·5 c/s) for the hydrogens α to the hydroxyls. The molecule is therefore predominantly in one conformation (Table 1) with both hydroxyls axial. The triplet at 6·18 τ is assigned to the equatorial Ha having two vicinal protons and the quartet at 6·52 τ to Hb with three vicinal protons. The diol VII is also mostly in one conformation since two different α protons are present: Ha—at 6·9 τ as a doublet of doublets with two widely separated coupling constants of 10 and 3 c/s proving its axial disposition with two vicinal protons, one axial and one equatorial, and Hb at 6·07 τ which shows as a quartet (J = 3 c/s) and is evidently placed in an equatorial position and has three vicinal protons. A preferred conformation is also found in the diol X, with both hydroxyls equatorial, since Ha appears as a triplet at 7·12 τ (J = 9 c/s) and Hb as a broad multiplet at 6·48 τ, with a width of 30 c/s at half-height. The conformational preferences of all these diols are evidently determined in such a manner as to avoid an axial-axial interaction between two methyls.

The structures assigned to the diols VI, VII and X are furthermore confirmed by their high dilution IR spectra in carbon tetrachloride solution[11] (Table 1). Thus, only one band is observed in the OH region for the diol VI and its position at 3638 cm^{-1} corresponds to hydroxyls which are not hydrogen-bonded. Such a spectrum is characteristic of a diaxial vicinal diol.[11] Both other diols show two bands, one due to non-bonded and the other to hydrogen-bonded hydroxyls. The separation between these bands is different for the two isomers, being 53 cm^{-1} for VII and 37 cm^{-1} for X. The higher difference corresponding to a stronger hydrogen bond[11] confirms a *cis* disposition of the two hydroxyls in VII, whereas the lower separation is characteristic of a *trans* diequatorial diol in X.

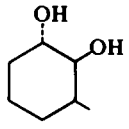
The hydroboration of II yielded similarly a single diol in 70% yield in addition to a smaller monoalcohol fraction (17%). This diol was shown to be different from its isomers XI and XII obtained from 3-methylcyclohexene respectively by hydrogen peroxide–formic acid oxidation[12] and the Woodward[10] procedure. Structure XIII was therefore assigned to the product of hydroboration. A different configuration of the hydroxyls, shown in XIV can be attributed to the product of hydroxylation with iodine–silver acetate in wet acetic acid. The same compound obtained from the

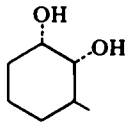
TABLE 1. NMR[a] AND IR[b] OF SUBSTITUTED 1,2-CYCLOHEXANDIOLS

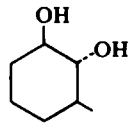
Compound	R; R′	H_a(NMR)		H_b(NMR)		OH(IR) cm^{-1}
		τ	J c/s	τ	J c/s	
	X R = CH_3	7·12	(t) 9	6·48	(m)	3636 3599
	XIII R = H	7·20	(t) 9	6·52	(m)	3630 3592
	VI R = CH_3	6·18	(t) 3·5	6·52	(q) 3·5	3638
	XI R = H		complex			3629 3594
	VII R = CH_3	6·90	(d, d) 10;3	6·07	(q) 3	3634 3581
	XII R = H	6·80	(d, d) 9;2	6·02	(m)	3630 3580
	XV R = H R′ = isopr.	6·80	H_a + H_b (t)	9		3645 3600
	XVI R = isopr. R′ = H	6·3	(t) 8·5	6·02	(d, d) 8·5;3	3640 3595

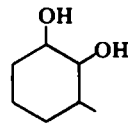
[a] Measurements were taken in deuterochloroform with TMS as internal standard on a Varian A-60.
[b] Measurements were taken with 0·002–0·003 M solution in CCl_4 on a Beckman IR 7.

Woodward reaction was prepared previously in low yield by potassium permanganate oxidation of 3-methylcyclohexene,[13] but its configuration was not established. Its structure and that of the other isomers follows however from their spectral properties (Table 1). The NMR spectrum of XI shows a complicated pattern due to an equilibrium between two conformations with similar energies, one having the hydroxyls in the


XI

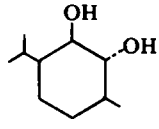

XII

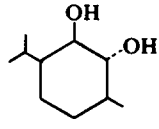

XIII


XIV

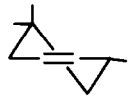
diaxial, and the other having them in the diequatorial position. This is supported by the IR spectrum, which shows two bands with 35 cm^{-1} separation, but the intensity of the hydrogen-bonded band is lower than in other diequatorial diols.

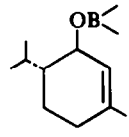
The hydroboration of piperitone (III) yielded two diols in almost equal amounts (53:47). The structures XV and XVI respectively were assigned to these compounds, both with the hydroxyl in *trans* diequatorial positions. The assignments are based on their NMR and IR spectra.

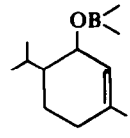

XV


XVI

The hydroboration of all three cyclohexenones studied gave exclusively diequatorial vicinal diols. This should be compared with the lack of stereoselectivity in the hydroboration of alkylcyclohexenes.[8,14] Since the carbonyl is reduced first and an oxygen-boron link is formed, it is this group that determines the course of the reaction. The directing power of the borate group is evident in the reaction of isophorone with diborane. The intermediate borate of the allylic alcohol (V) has a structure similar to the olefin (VIII), the borate of V corresponding to the Me at position 3 in VIII. The presence of this preferred conformation is supported by the NMR spectrum of the allylic alcohol (V) which shows the hydrogens at position 6 as two doublets at 8·85 τ and 8·58 τ with coupling constants respectively of 4 and 10 c/s. Hydroboration of of VIII was found[4] to proceed 87% *cis* to the 3-Me and this was attributed to the steric interference of the axial Me at position 5 with diborane attacking perpendicularly to the double bond of VIII in conformation XVII.


XVII


XVIII

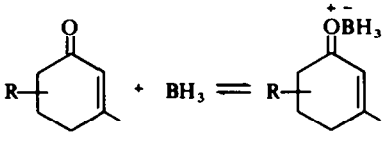

XIX

The borate ester of V with a similar structure to VIII should give also predominantly hydroboration *cis* to the borate group. However, the opposite is observed. In the case of 3-methylcyclohexenone (II) or piperitone (III) almost no steric influence is expected (no steric influence was found for 3-methylcyclohexene[8]), yet product stereospecificity is complete.

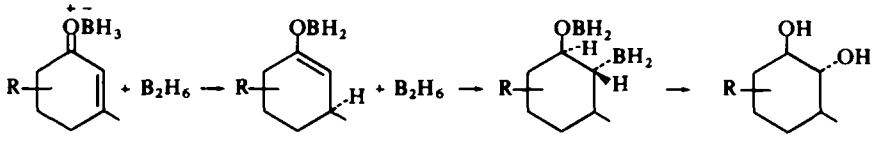
The stereoselectivity of the diol formation is even more spectacular in the case of piperitone (III). The steric course of the hydroboration of III is determined by the first step, which consists of the reduction of the carbonyl group. This step by itself is

devoid almost totally of stereospecificity, yielding an almost equal amount of the two isomeric allylic alcohols. This reaction reflects the similar energies of these two compounds (XVIII and XIX) since the reduction of ketones with diborane obeys[15] the "product development control" rule.[16] (A *cis* isopropyl-borate 1,2-interaction in XIX is compensated by a 1,3-interaction between an axial hydrogen and pseudo-axial borate group in XVIII). The hydroboration, however, of both isomers (XVIII and XIX) is stereospecific, and diborane attacks in both cases *trans* to the borate group. It seems to us that this stereospecificity is due to a combination of steric and polar effects of the $OB\langle$ group.

There is an alternate simple explanation assuming a 1,4 addition of a hydride ion and boron to the conjugated system (1) with subsequent hydroboration of the enol borate ester. However, this possibility can be eliminated, since the allylic alcohol (V) yielded on hydroboration the same diol (X) as the conjugated ketone (I) and in the

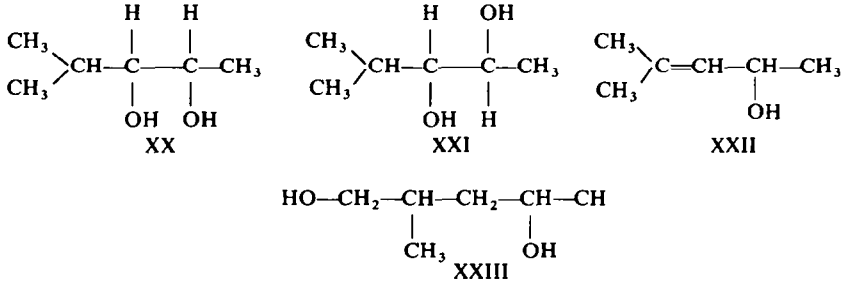


(1)



same yield. In this case no conjugated addition is possible. The *trans* directive effect of a hydroxyl or borate group in allylic alcohols is different from the reported increase of the extent of *cis* attack with diborane in presence of a homoallylic OH group, e.g. in cholesterol.[17]

The reaction of the open-chain conjugated ketone (IV) with diborane did not show stereoselectivity and the two possible diols (40% yield) erythro (XX) and threo (XXI) were obtained in equal amounts. This hydroboration was carried out at lower



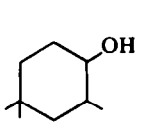
temperature than other reactions, since much elimination occurred at usual conditions giving a lower yield (25%). Approximately the same ratio of diastereoisomers was obtained in the two reactions, showing that it corresponds to the ratio formed initially. An additional diol is formed during this reaction (5–10% of diol fraction). This is

probably XXIII, the product of hydroboration of 2-methyl-1-pentenone-4, which is present in mesityl oxide in that amount. The separation of XXIII from XX and XXI was difficult.

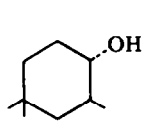
The erythro isomer (XX) was prepared for comparison by iodine-silver acetate oxidation in wet acetic acid[10] of *cis*-4-methylpentene-2 and the threo isomer (XXI) by formic acid-hydrogen peroxide hydroxylation of the same olefin.

The unexpected lack of stereospecificity in the hydroboration of mesityl oxide can be ascribed to the reaction of the borate of the allylic alcohol (XXII) in a conformation, where the oxygen is eclipsed with the double bond. The directive effect of the borate group cannot be effective in this conformation. Since the transition state is probably similar in its structure to that of the olefin,[14] the directive effect will be ineffective also in the transition state. Bonds between allylic atoms and groups linked to them were found to be eclipsed with the double bond.[18]

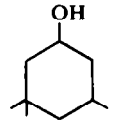
Subsequently we turned our attention to the composition of the monoalcohol fraction. It was reasonable to assume, that these alcohols are formed by hydroboration of the olefin (VIII) formed by a borane–borate elimination.[19] The four expected isomers (XXIV, XXV, XXVI and XXVII) should be found in a proportion similar to the products of hydroboration of isophorone and the olefin (VIII).[14] This expectation, however, was not fulfilled. The composition of the monoalcohol fraction of the products of hydroboration of VIII, of isophorone (I) and of a series of its derivatives is summarized in Table 2.



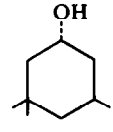
XXIV



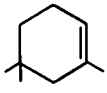
XXV



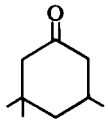
XXVI



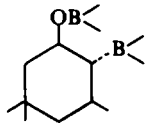
XXVII



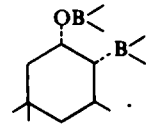
XXVIII



XXIX



XXX



XXXI

Since XXIV cannot be formed directly from I in view of the *cis* addition of borane, it can be assumed that compound XXIV is formed via VIII. Not more than 55% of the monoalcohols obtained during the uncatalyzed hydroboration of I or V are formed therefore by the intermediate of VIII, but 90% of the monoalcohols are formed via VIII in the hydroboration of the acetate of V. In the hydroboration of I in presence of BF_3 or $AlCl_3$ only 10–25% of the monoalcohols are accounted for by VIII, although their total yield and the percentage of the isomer (XXV) increases. Most of the last product has obviously its origin in the hydroboration of XXVIII, which is formed by the hydrogenolysis of the originally formed borate of V. This kind of reaction was studied by Eliel.[20]

Similar results were obtained in the monoalcohol fraction obtained on hydroboration-oxidation of II. Here also, not all these monoalcohols come from 3-methylcyclohexene. The proportion of this fraction increases in the BF_3 and $AlCl_3$ catalyzed reaction.

TABLE 2. COMPOSITION OF MONOALCOHOLS (%)[a]

Starting material \ Products	(XXIV)	(XXV)	(XXVI)	(XXVII)	Total yield monoalcohols %	(X) %
VIII[14]	47	16	34	3	85	—
I 1 hr	25	21	45	9	15	65
I 4 hr	25	20	50	5	15	—
I 20 hr	27	23	40	10	15	—
I $+BF_3OEt_2$	12	52	20	16	40	up to 5
I $+AlCl_3$	4	57	14	25	40	up to 5
V	28	30	33	9	15	60
V 1 hr + ¼ LAH	22	39	39	9	35	—
Acetate of V	43	18	33	6	35	45

[a] Analysis by GLC (Ref. 14).

The formation of the intermediate VIII requires comment. The yield in momoalcohols does not increase by increasing the reaction time from 30 min to 24 hr. This observation proves, that the bulk of monoalcohol is not derived from compound XXX which yields the diol. The most plausible explanation is to assume the formation of an isomeric borane–borate (XXXI) which yields VIII in a rapid *cis* elimination reaction. The *trans* isomer (XXX) does not undergo elimination under these conditions. A *cis* borane–borate elimination has been proved in open-chain compounds.[21]

The assumption that XXXI is one of the primary products of hydroboration of I shows that this primary reaction is not stereospecific in an absolute manner. Its stereospecificity remains high however. The ratio of XXX:XXXI is 8:1, since the ratio of the yields of diol and monoalcohols is 4:1 and XXXI via VIII accounts for half of the monoalcohols. The combination however of the high ratio of (XXX:XXXI) and the fast elimination step from XXXI contributes to the high yield and exclusive formation of only one of four or two of eight possible cyclohexanediols from I, II and III respectively.

The hydroboration of all conjugated ketones studied gave 1,2-diols exclusively. This could be ascribed to the directive effect of the Me group on the β-position of the double bond. A preliminary study of cyclohexenones without an alkyl on the double bond has shown however, that in their case also, only 1,2- and not 1,3-diols are formed. The oxygen containing group on the allylic carbon therefore exerts a powerful positional directive effect. The hydroboration of conjugated cyclohexenones is therefore a general method for the preparation of diequatorial 1,2-diols. To our knowledge, this is the only method which gives access to these compounds without major contamination by other isomers.

EXPERIMENTAL

Isophorone (Fluka), 3-methylcyclohexene and *cis*-4-methyl-2-pentene (Aldrich), piperitone (Todd) and mesityl oxide (Light) were commercial products. 3-*methylcyclohex-2-enone* (II) was prepared according to a published procedure.[22] The alcohols XXIV, XXV, XXVI and XXVII and 3,5,5-cyclohexene (VIII) were prepared as reported previously.[14]

3,5,5-*Trimethylcyclohex-2-enol* (V). A soln of 56 g isophorone in 150 ml dry ether was added dropwise to a suspension of 6 g LAH in 200 ml ether at a rate that maintained ebullition of the reaction mixture. This mixture was then refluxed for 2 additional hr. Excess hydride was decomposed with EtOAc and then ice and HCl were added. The aqueous layer was extracted with ether, the ether layers combined, washed with water, dried and distilled, yielding 30 g of V b.p. 95–100° (25 mm); $\bar{\nu}_{max}$ 3320, 1660 cm^{-1} (neat); n_D^{24} 1·4731. (Found: C, 77·1; H, 11.4. Calc. for $C_9H_{16}O$: C, 77·1; H, 11·4%).

3,5,5-*Trimethylcyclohex-2-enyl acetate*. Ac_2O (30 g) was added to a soln of 14 g of V in 75 ml dry pyridine cooled in an ice bath. The soln was left overnight at room temp, then cooled in an ice bath and 10% HCl was added. The product was extracted 4 times with CH_2Cl_2 and the organic layer washed with Na_2CO_3 aq. Distillation yielded 13 g of the acetate, b.p. 102–105 (25 mm); $\bar{\nu}_{max}$ 1730 cm^{-1} (neat), n_D^{24} 1·4577. (Found: C, 73·0; H, 10·2. Calc. for $C_{11}H_{18}O_2$: C, 72·5; H, 9·9%).

trans 3,5,5-*Trimethyl*-trans-2-*hydroxycyclohexanol* (VI). H_2O_2 (4·5 ml, 30%) was added to a soln of VIII (2 g) in 98% formic acid (35 ml). The reaction mixture was heated for 2 hr on a water bath and the formic acid was evaporated *in vacuo*. 20 ml of 20% NaOH aq was added to the residue and the mixture heated for 1 hr on a water bath, cooled, neutralized with dil HCl aq and extracted several times with ether. Distillation of the dried organic layer gave 1·5 g of VI b.p. 85° (0·6 mm) which solidified on standing. Crystallization from hexane yielded a product, m.p. 52–53°, reported 58–59°.[23] (Found: C, 67·5; H, 11·6. Calc. for $C_9H_{18}O_2$: C, 67·5; H, 11·5%).

trans 3,5,5-*Trimethyl*-cis-2-*hydroxycyclohexanol* (VII). AcOAg (7 g) was added during 10 min with stirring to a soln of VIII (3 g) in AcOH (74 ml) followed by 5 g powdered I_2 during 25 min. A 4% AcOH soln in water (33 ml) was then added, the reaction mixture heated on a water bath for 3 hr, and then cooled. NaCl (16 g) was added, the mixture stirred for 30 min, and the soln filtered. The ppt was washed with 30 ml warm benzene and the solns combined. The solvents were distilled off *in vacuo*, the solid residue was treated with a soln of 3 g KOH in 25 ml MeOH and stirred overnight under a blanket of N_2. MeOH was distilled off under reduced press, 40 ml of water added and the product extracted several times with ether. The dried ethereal soln was distilled yielding VII (2 g), b.p. 110° (4 mm) which solidified on standing. The product was crystallized from hexane, m.p. 36–37°. (Found: C, 67·8; H, 11·6. Calc. for $C_9H_{18}O_2$: C, 67·5; H, 11·5%).

trans-3-*Methyl*-trans-2-*hydroxycyclohexanol* (XI). The treatment of 3-methylcyclohexene (3 g) with H_2O_2 (8 ml) and formic acid (30 ml) was carried out as for VIII. The hydroxyformate obtained was treated with a soln of 6 g KOH in 30 ml MeOH for 4 hr at room temp. The solvent was distilled off at reduced press, 50 ml water was added and the product extracted several times with CH_2Cl_2. Distillation of the solvent left a solid residue, which was crystallized from MeOAc giving 2 g of XI m.p. 89–90° reported m.p. 96°.[12] (Found: C, 64·6; H, 10·8. Calc. for $C_7H_{14}O_2$: C, 64·4; H, 10·8%).

trans-3-*Methyl*-cis-2-*hydroxycyclohexanol* (XII). (a) A mixture of $KMnO_4$ (8 g) $MgSO_4$ (6 g) and 180 ml water was added during 90 min with stirring to a soln of 3-methylcyclohexene (7 g) in 150 ml EtOH cooled with a ice salt bath at −10°–15°. The soln was filtered, the ppt washed with EtOH and the solvent distilled off from the filtrate under reduced press. Water (50 ml) was added to the residue and the product extracted several times with CH_2Cl_2. Evaporation of the solvent left a solid residue which yielded, on crystallization from EtOAc, 1 g of XII m.p. 77–78°, reported 81–82°.[13] (Found: C, 64·6; H, 10·9. Calc. for $C_7H_{14}O_2$: C, 64·6; H, 10·8%).

(b) The reaction of 3-methylcyclohexene (4 g) with silver acetate–iodine as described for VIII yielded 1·5 g of a diol m.p. 75–76° (hexane), identical with the product obtained by $KMnO_4$ treatment (GLC, NMR).

Hydroboration of isophorone (I). (a) A stream of diborane, generated from 8 g $NaBH_4$ and 60 g BF_3–etherate in diglyme was passed through a soln of 28 g isophorone in 100 ml THF cooled at 0° in an ice-bath. The soln was left, after completion of diborane addition, for 1 hr at room temp and excess diborane decomposed by slow addition of 60 ml water; 60 ml of a 10% NaOH aq were then added, followed by dropwise addition of 60 ml 30% H_2O_2 and the reaction mixture stirred for 1 hr at room temp. K_2CO_3 was then added until saturation of the soln, the layer separated and the aqueous layer extracted several times with

ether. The dried combined organic layers gave on distillation a mixture of monoalcohols (3 g) b.p. 60–85/0·7 and 17 g X b.p. 90–95° (0·6 mm), which solidified. Crystallization from hexane or EtOAc gave a product, m.p. 103–104°. (Found: C, 67·7; H, 11·3. Calc. for $C_9H_{18}O_2$: C, 67·5; H, 11·5%).

(b) A 1·4M soln of diborane in THF (7 ml) was added dropwise to a stirred soln of 1·4 g isophorone in 5 ml THF, cooled in an ice bath. The soln was then left at room temp for 1 hr, cooled, 5 ml water added dropwise, followed by 5 ml of 10% NaOH aq, then treated by dropwise addition of 5 ml 30% H_2O_2. Work-up as above and analysis by GLC showed a yield of 15% of monoalcohols (XXIV, XXV, XXVI and XXVII) in the ratio summarized in Table 2 and a yield of (65%) of diol X. This analysis was performed on a 5 ft × $\frac{1}{4}$ in column of 10% Versamide 900 on Chromosorb P, using weighed amounts of cyclohexanol and of XI as internal standards.

(c) To a soln of 13·8 g isophorone in 50 ml THF cooled in an ice bath, 35 ml of a 1M soln of diborane in THF was added. The reaction mixture was left for 45 min at room temp, then treated dropwise with 10% NaOH aq until alkaline. The layers were separated after 15 min and the aqueous layer extracted with ether. Distillation of the organic layer gave 9·5 g of a mixture of isophorone and V b.p. 100–105° (30 mm). The residue was oxidized with H_2O_2 and NaOH and gave 1·2 g of X m.p. 90–91°.

Hydroboration of I *in presence of catalysts.* (a) A 1·4M soln of diborane (15 ml) in THF were added dropwise to a cooled soln of (2·8 g) and BF_3-etherate (6·2 g) in 10 ml THF. The work-up was as described above, yields given in Table 2.

(b) A 1·4M soln of diborane (15 ml) in THF were reacted as above with a soln of I (2·8 g) and $AlCl_3$ (5·2 g) in 50 ml THF, yields given in Table 2.

Hydroboration of V was carried out as in the case of I (procedure b) using 2·8 of V in 10 ml THF and 15 ml of diborane soln (1·4M) yields are given in Table 2.

Hydroboration of acetate of V was carried out by the same procedure using 3·6 g acetate of V in 10 ml THF and 15 ml 1·4M diborane solution, yields are given in Table 2.

Hydroboration of 3-methylcyclohex-2-enone II. (a) A 1·4M diborane soln (45 ml) in THF was added dropwise to a soln of II (6·6 g) in 25 ml THF. Treatment with 25 ml water, then 25 ml 10% NaOH aq and 25 ml 30% H_2O_2 and the work up as in the case of I gave 2 g, b.p. 80–90° (25 mm) and 4 g of XIII b.p. 90–95 (1 mm) which solidified, m.p. 39°–40° from hexane. (Found: C, 64·9; H, 11·1. Calc. for $C_7H_{14}O_2$: C, 64·6; H, 10·8%).

(b) For GLC analysis, the reaction was performed on a solution of II (1·1 g) with 1·4M diborane (7 ml). Oxidation and work-up as in procedure (b) of the same reaction (with I) gave 70% of XIII and 17% of a monoalcohol fraction. The analyses were performed on a 5 ft × $\frac{1}{4}$ in column of 10% Versamide 900 on Chromosorb P using weighed amounts of cyclohexanol and of X as internal standards.

Hydroboration of piperitone (III). Piperitone (2 g) in 10 ml THF was hydroborated with 10 ml of a 1·25M soln of diborane in THF and then treated with 10 ml water, 10 ml 10% NaOH aq and 10 ml 30% H_2O_2 as described above. Distillation at 100–105° (0·8 mm) gave 1·5 g of XV and XVI. (Found: C, 69·7; H, 11·5. Calc. for $C_{10}H_{20}O_2$: C, 69·8; H, 11·6%). These diols were separated by GLC on a 2 m column of 20% neopentyl glycol succinate on Chromosorb P at 175°, the first eluted being XV m.p. 86–87° (hexane) then XVI m.p. 73–74° (hexane).

Hydroboration of mesityl oxide (IV). A soln of IV (10 g) in 20 ml THF was hydroborated with 1·5M diborane (50 ml) in THF at −5°–0° by dropwise addition of the diborane solution. The reaction mixture was kept for 2 hr in an ice-bath and then treated with water (20 ml), 10% NaOH (20 ml) and 30% H_2O_2 (40 ml) as described above. Distillation of the dichloromethane soln gave 4 g of XX and XXI, b.p. 110–120° (35 mm); $\bar{\nu}_{max}$ 3350 cm^{-1}. (Found: C, 60·4; H, 12·1. Calc. for $C_6H_{14}O_2$: C, 60·5; H, 11·9%). The composition of the diol mixture was analyzed by GLC on a 5 m column of 10% diglycerol on Chromosorb P at 140°. A third compound (5–10%) was present in the mixture, but the separation was not very satisfactory. A better separation between XX and XXI was achieved on a Versamide 1·5 m column and on a Ethylene Glycol Succinate 1·5 m column at 130° but the third compound was eluted with XX on the first column and with XXI on the second one.

Erythro-2-methyl-3,4-pentanediol (XX) was obtained by treating 7 g 4-methyl-*cis*-2-pentene with 12 g AcOAg by the method described above, yield: 1 g, b.p. 115–120° (35 mm) (reported m.p. 49–40°[25]). ν_{max} 3370 cm^{-1}. (Found: C, 60·7; H, 11·8. Calc. for $C_6H_{14}O_2$: C, 60·5; H, 11·9. This isomer was also prepared by $KMnO_4$ hydroxylation of the same olefin according to a published procedure[25] yielding a liquid diol (5%) (solidified only on cooling). identical with the former compound by GLC.

Threo 2-methyl-3,4-pentanediol (XXI) was prepared by treating 7 g of 4-methyl-*cis*-2-pentene with 15 ml 30% H_2O_2 and 50 ml formic acid as described above, yielding 5 g of XXI, b.p. 110–112° (35 mm) which

solidified, m.p. 52–53° from hexane (reported 59–60°[24]) ν_{max} 3360 cm^{-1}. (Found: C, 60·4; H, 11·7. Calc. for $C_6H_{14}O_2$: C, 60·5; H, 11·9%).

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