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BORANE REACTIONS—IX[1]

THE STEREOCHEMISTRY OF THE HYDROBORATION OF CYCLOHEX-2-ENONES, CYCLOHEX-2-ENOLS, CYCLOHEXAN-1,2 AND 1,3-DIONES

E. DUNKELBLUM,[2] R. LEVENE[3] and J. KLEIN[2]

Department of Organic Chemistry, The Hebrew University, Jerusalem, Israel

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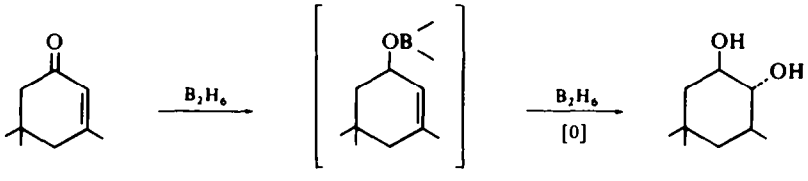
Abstract—The hydroboration of a number of substituted α,β-unsaturated cyclohexenones and cyclohexenols has been studied. The ketones and the pseudo equatorial alcohols yielded the diequatorial *trans*-1,2-diols in fair yields, accompanied by minor amounts of 1,3-diols. The directive effect of the intermediate allylic borate and the steric influence of ring substituents on this reaction has been established. The hydroboration of 1,3-cyclohexandiones has been shown to proceed mainly by an addition elimination process yielding diequatorial *trans*-1,2-cyclohexandiols, thus transforming a 1,3-dioxocyclohexane to a 1,2-dioxocyclohexane. 1,2-Cyclohexandione gave, on hydroboration, mainly *cis*-1,2-cyclohexandiol. Mechanisms for the hydroboration of 1,2 and 1,3-cyclohexandiones are proposed, both involving, to some extent, an unusual intramolecular displacement of borate or borane by hydrogen with retention of configuration.

THE HYDROBORATION of β-methyl substituted cyclohex-2-enones has been found to proceed in a stereospecific manner to yield the *trans*-1,2-diequatorial cyclohexandiols in 56–70% yield.[4] It has been established that the first step in this reaction is the reduction of the carbonyl group; the allylic borate generated directs the attack of diborane on the double bond *trans* to itself. This stereospecificity has been attributed to a combination of steric and polar effects of the borate group and to the fact that the intermediate *trans* borane-borates are much more stable to elimination than the *cis* isomers.[4, 5] Thus for example isophorone (**1**) gives the *trans*-diequatorial diol **2** in 65% yield.[4]



1 **2**

In order to estimate the directive power of the allylic borate group and evaluate the utility of this reaction as a new stereospecific cyclohexandiol synthesis a systematic study of the hydroboration of cyclohex-2-enones and cyclohex-2-enols was undertaken. The hydroboration of 1,2- and 1,3-cyclohexandiones was also studied as they represent a cyclohex-2-enone system in their enolic form, which is the preponderant one. These compounds were also of interest because they generally serve as the starting materials for the preparation of the cyclohex-2-enones and cyclohex-2-enols.

RESULTS

The following representative series of ring substituted cyclohex-2-enones, cyclohex-2-enols and cyclohexandiones was selected for the hydroboration study: cyclohex-2-enone (**3**), 5-phenylcyclohex-2-enone (**4**), *cis*-5-phenylcyclohex-2-enol (**5**), *trans*-5-phenylcyclohex-2-enol (**6**), 5-t-butylcyclohex-2-enone (**7**), *cis*-5-t-butylcyclohex-2-enol (**8**), 4-t-butylcyclohex-2-enone (**9**), *trans*-4-t-butylcyclohex-2-enol (**10**), *cis*-4-t-butylcyclohex-2-enol (**11**), 1,3-cyclohexandione (**12**), 5-phenyl-1,3-cyclohexandione (**13**), 5-t-butyl-1,3-cyclohexandione (**14**), 1,2-cyclohexandione (**15**) and 2-hydroxycyclohexanone (**16**). Some of the starting materials were commercial products, others were prepared according to known procedures. The main problem was the synthesis of the *cis*- and *trans*-cyclohex-2-enols **5**, **6**, **8**, **10** and **11**. They were prepared by aluminium isopropoxide reduction of the corresponding ketone and separation of the two isomers obtained through their benzoates or their *p*-nitrobenzoates. The thermodynamically more stable alcohols **5** and **8** were also prepared by direct reduction of the 1,3-diketones **13** and **14** with LAH. The structures of all the cyclohex-2-enols were confirmed by their NMR spectra, especially by examination of the protons α to the hydroxyls. The width at half height Wh/2 was 10–18 Hz for the pseudo axial proton and 6–8 Hz for the pseudo equatorial proton (experimental).

All the cyclohex-2-enones and cyclohex-2-enols have unsubstituted α and β positions. Both positions, therefore, are prone to diborane attack and the ratio of 1,2- and 1,3-diols in the product mixture is the combined result of the directive effect of the allylic borate group and of the ring substituent.

To simplify the identification of the diols obtained in the hydroboration reactions, a series of isomeric diols was prepared. The 1,2-diols were prepared by *cis* and *trans* hydroxylations of the appropriate cyclohexenes and the 1,3-diols by oxymercuration reduction of the corresponding allylic alcohols.[6] All the hydroboration reactions were performed in the usual manner using excess diborane. The diol fraction obtained was analyzed either by GLC or by TLC and the different cyclohexandiols were identified by comparison with authentic samples and by their NMR and IR spectra. The small amounts of monoalcohols which were present in all the reactions were not analyzed. The results of the hydroboration reactions are summarized in Table 1.

It was possible to distinguish between the 1,2-cyclohexandiols and the 1,3-cyclohexandiols by oxidation with $NaIO_4$. The 1,2-diols were cleaved readily, whereas the 1,3-diols were almost unaffected under the same conditions.[7]

Except for the unsubstituted cyclohexandiols **17**, **18**, **19** and **20** all the diols from the hydroboration reactions, and those prepared by other methods, have a preferred conformation. Due to the substituents chosen, the chair conformation with the bulky substituent in the equatorial position is energetically favoured by 2–5 kcal/mole. This fact simplified the NMR spectra of these compounds and enabled easy confirmation of all the proposed structures, especially when isomeric diols of known structure were available for comparison. The chemical shifts and the multiplicities of the signals of the protons α to the hydroxyls confirmed the structure assignments.[4] The structure of all the diols was further confirmed by their high dilution IR spectra in CCl_4.[4, 8] In the 1,2-cyclohexandiols only one band was present in the —OH region for the *trans* diaxial diols, whereas two bands were observed for the *cis* isomers and the *trans* diequatorial isomers. A greater separation between the two bands, $\Delta\nu$, was found for the *cis* diols in each isomeric series.[8] In the 1,3-cyclohexandiols only

TABLE 1. HYDROBORATION OF CYCLOHEX-2-ENONES, CYCLOHEX-2-ENOLS, 1,3-CYCLOHEXANDIONES AND 1,2-CYCLOHEXANDIONES

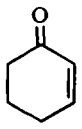
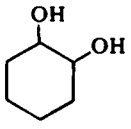
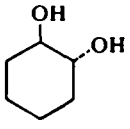
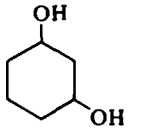
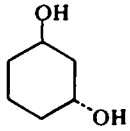
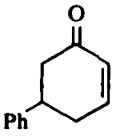
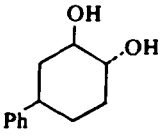
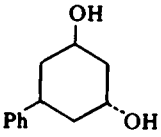
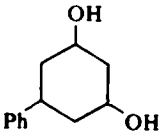
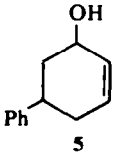
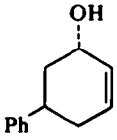
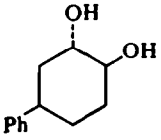
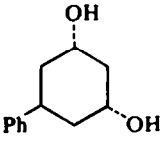
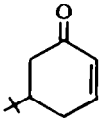
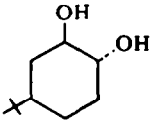
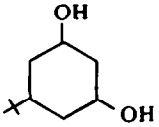
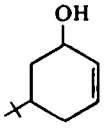
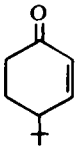
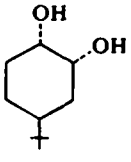
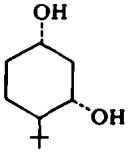
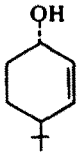
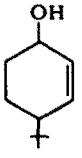
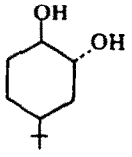
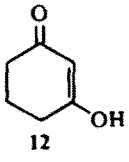
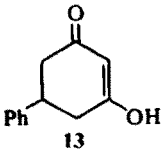
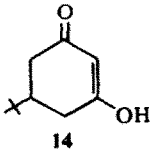
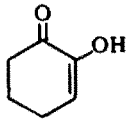
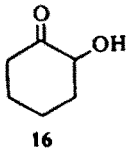
Starting material	Total yield of diols %	Isomer distribution (%)			
 3	60[a]	 17 (6)	 18 (86)	 19 +  20 8%	
 4	59[b]	 21 (76)	 12 (10)	 23 (14)	
 5	62[b]	21 (76)	22 (10)	23 (14)	
 6	34[b]	 24 (77)	 25 (5)	22 (18)	
 7	56[b]	 26 (81)	 27 (19)		
 8	58[b]	26 (81)	27 (19)		
 9	42[b]	 28 (41)	 29 (52)	26 (7)	

TABLE 1—*continued*

Starting material	Total yield of diols %	Isomer distribution (%)			
 **10**	45[b]	**28** (44)	**29** (49)	**26** (7)	
 **11**	24[b]	 **30**			
 **12**	74[c]	**17** (traces)	**18** (84)	**19** (8)	**20** (8)
 **13**	47[b]	**21** (53)	**22** (19)	**23** (28)	
 **14**	50[b]	**26** (60)	**27** (40)		
 **15**	45[a]	**17** (74)	**18** (22)	**19** (1)	**20** (3)
	45[a,d]	**17** (76)	**18** (24)	**19** + **20** traces	
 **16**	80[a]	**17** (42)	**18** (58)		

[a] Analysis by GLC.
[b] Analysis by TLC.
[c] This compound **11** contained 30% of its isomer **10**. The reaction mixture was very complex and only one product was isolated in pure form.
[d] Work-up without H_2O_2.

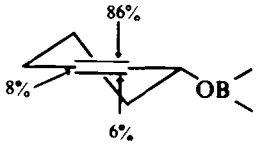
one band was present in the *trans* isomers and in the *cis* diequatorial isomers and two bands were observed for the *cis* diaxial isomers in each group.[9] The NMR and IR data of all the substituted cyclohexandiols are summarized in Table 2.

A combination of spectroscopic methods (NMR, IR) and chemical means (known structures of the starting allylic alcohols **5**, **6**, **8**, **10** and **11**) established the structure of all the diols except **31**. The *cis* diol **31** was prepared by the iodine-silver acetate-wet acetic acid hydroxylation[10] of 4-phenylcyclohexene (**44**). Two isomeric *cis*-1,2-diols could theoretically be obtained, but only one was isolated. The *cis-cis* structure **31** was assigned to the isolated product in accord with this hydroxylation mechanism.[10]

DISCUSSION

The most distinctive fact from Table 1 is the high and consistent regiospecificity[11] and stereospecificity observed in the hydroboration of all cyclohex-2-enones and cyclohex-2-enols with the exception of **9** and **10**. The main product in all these reactions was the *trans*-1,2-diol. The first step in the hydroboration of the α,β-unsaturated ketones is the reduction of the carbonyl function, as already proven in previous papers.[4, 12] The allylic borate formed is then further hydroborated to the final products.

In the case of the unsubstituted cyclohex-2-enone (**3**) there was only one allylic borate possible which was subsequently hydroborated to a mixture of cyclohexandiols consisting mainly of the *trans*-1,2-cyclohexandiol (**18**). The distribution of diborane attack on the intermediate allylic borate **35a**, as shown by the ratio of isolated diols, is demonstrated in Fig. 1. This ratio of isomers is very close to that which H. C. Brown obtained from the hydroboration (with diborane) of the disiamylborate ester of cyclohex-2-enol (**35**) (Fig. 2).[5] The similarity of these results is due either to the insensitivity of the hydroboration reaction to bulky groups on the oxygen or to the formation of dialkoxy boranes prior to the hydroboration step.



35a

FIG 1

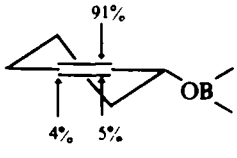
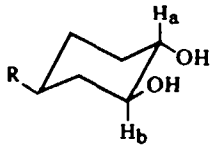
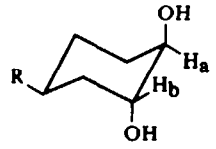
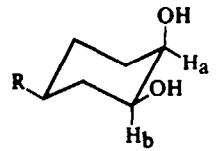
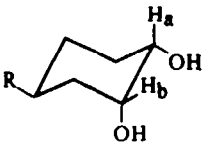
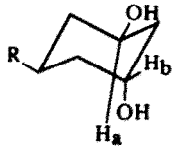
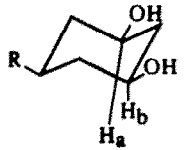
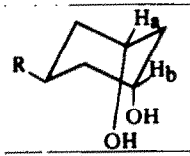
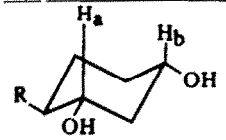
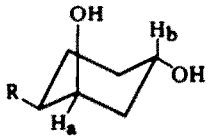


FIG 2

The 5-substituted cyclohex-2-enones **4** and **7** were particularly interesting because two allylic borates could be formed in each case by reduction of the keto group. In addition, the substituent keeps the molecule in one preferred conformation without directly interfering with the hydroborating agent. The stereochemistry of the diols formed (**21** and **26**) from the reaction of **4** and **7** with diborane showed that the reduction of the keto group gives the more stable pseudo equatorial esters. This fact is in accord with the observation that LAH reduces sterically unhindered cyclohex-2-enones to the thermodynamically more stable pseudo equatorial alcohols.[13] The stereochemistry of diborane reduction of cyclohexanones has been shown to be very

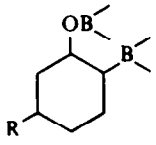
TABLE 2. NMR[a] AND IR[b] DATA OF THE 1,2- AND 1,3-CYCLOHEXANDIOLS

Compound	R	Ha(NMR) δ	W h/2 Hz	Hb(NMR) δ	W h/2 Hz	OH(IR) cm^{-1}	$\Delta\nu$ (cm^{-1})	Main Source
	**21** R = Ph	3·50[c]	Ha + Hb		17	3630 3600	30	Hydroboration of **4**, **5** and **13**
	26 R = CMe_3	3·35[c]	Ha + Hb		15	3631 3597	34	Hydroboration of **7**, **8** and **14**
	**24** R = Ph	3·74[c]	Ha + Hb		10	3632		Hydroxylation of 4-phenylcyclohexene (**44**). Hydroboration of **6**
	30 R = CMe_3	4·00[c]	Ha + Hb		13	3633		Hydroxylation of 4-t-butylcyclohexene. Hydroboration of **11**
	**31** R = Ph	4·30[c]	9	3·90	18	3632 3592	40	Hydroxylation of 4-phenylcyclohexene (**44**)
	32 R = CMe_3	3·96[c]	8	3·60	18	3629 3592	37	Hydroxylation of 4-t-butylcyclohexene
	**28** R = CMe_3	3·6[c]	18	4·05	7	3626 3588	38	Hydroboration of **9** and **10**

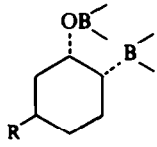
	**22** R = Ph	4·0[d]	20		4·20	10	3627[g]	Oxymercuration of **5**
	33 R = CMe_3	3·7[d]	~25		4·15	10	3619	Oxymercuration of **8**
	**23** R = Ph	3·9[e]		Ha + Hb		22	3623[g]	Hydroboration of **4**, **5** and **13**
	27 R = CMe_3	3·7[c]		Ha + Hb		17	3617	Hydroboration of **7**, **8** and **14**
	**25** R = Ph	4·23[c]		Ha + Hb		8	3627[g] 3548	79 Oxymercuration of **6**
	**29** R = CMe_3	3·6[c]		Ha + Hb		25	3620	Hydroboration of **10**
	**34** R = CMe_3	4·37[c]	8		4·0	20	3619	Oxymercuration of **10**

[a] Measurements were taken on a Varian A-60 with TMS as internal standard.
[b] Measurements were taken with 0·002–0·003 M solutions in CCl_4, on a Perkin-Elmer P.E. 621 spectrometer using a 20 mm long cell with KBr windows.
[c] Measured in $CDCl_3$.
[d] Measured in DMSO-d_6.
[e] Measured in MeCN-d_3.

similar to that of LAH.[14] This similarity also holds for the reduction of cyclohex-2-enones, as observed in this work. The intermediate pseudo equatorial borate esters were subsequently hydroborated in 60–65% yield, to a mixture of diols consisting mainly of the diequatorial *trans*-1,2-cyclohexandiols **21** and **26**. Hydroboration of the parent pseudo equatorial *cis*-cyclohex-2-enols **5** and **8** gave, in a comparable yield, the same mixture of diols as the ketones **4** and **7**, further proving the two step sequence in the hydroboration of α,β-unsaturated ketones. No diaxial *trans*-1,2-diols **24** and **30** could be detected in the hydroboration of both **4** and **7**. The absence of **24** and **30** in these reactions is due to the high stereospecificity of the first step and to the much faster elimination of the *trans*-diaxial borane-borate intermediate (which could be formed in small amounts) than that of the *trans*-diequatorial one. This fact was clearly demonstrated in the hydroboration of the pseudo axial *trans*-5-phenylcyclohex-2-enol (**6**). The total yield of the diols decreased to 34% as compared with 62% from the pseudo equatorial isomer **5** and the yield of the main product, namely the diaxial *trans*-5-phenylcyclohexan-1,2-diol (**24**), decreased to 26% as compared with a yield of 45% of the diequatorial *trans* isomer **21**. In all these cases no *cis* diols were isolated. The total yield of approximately 60% of diols in these reactions raised the question of the amount of hydroboration *cis* to the allylic borate group. Two *cis* borane borates could in principle be formed, namely **36** and **37**. The formation of **37** is probably not realized

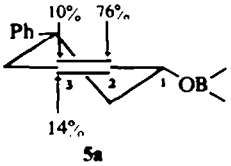


36

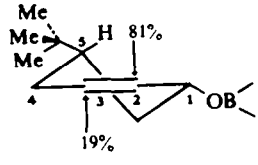


37

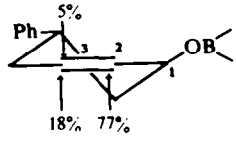
since hydroboration of the pseudo equatorial cyclohex-2-enols **5** and **8** gave almost exactly the same results as the conjugated ketones **4** and **7**. In addition it seems that the monoalcohols were not formed entirely from the *cis* borane borates with the equatorial borate group **36** *via* the olefin. We have previously shown that at least 50% of the monoalcohols formed in the hydroboration of cyclohex-2-enones were not formed from an intermediate olefin.[4] Moreover, losses during work-up and separation certainly account for at least 10% of the diols. Therefore, at the most, 15% of the intermediate allylic borate has undergone hydroboration *cis* to the allylic borate. The distribution of diols obtained in the hydroboration of **4** and **5**, **7** and **8** and **6** is outlined in Fig. 3.



5a



8a

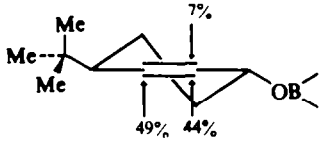


6a

FIG 3

Examination of **5a** clearly reveals the high stereospecificity of the hydroboration at position 2 and the low stereospecificity at position 3. On the other hand, in the case of **8a** high stereospecificity is observed for positions 2 and 3. The high regiospecificity and stereospecificity at position 2 in **3**, **4**, **5**, **6**, **7** and **8** is due to the strong inductive and polar directive effects of the allylic borate group as explained before.[4] The stereospecificity at position 3 in **8a**, as compared with **5a**, is due to a secondary factor, namely the steric effect of the t-butyl group at position 5. The unique steric effect of the t-butyl group, in the cyclohexane system, has been observed and explained in several papers.[15] Examination of the intermediate **8a** shows that the bulky t-butyl group forces the axial C_5 hydrogen closer to the center of the ring,[15] thus preventing the attack of diborane, at position 3, from the upper side.

The steric effect is very powerful, especially when the t-butyl group is in position 3 in relation to the attacked carbons. The steric course of the hydroboration of 4-t-butylcyclohex-2-enone (**9**) and *trans*-4-t-butylcyclohex-2-enol (**10**), which is entirely different from all the other hydroborations of substituted cyclohex-2-enones and cyclohex-2-enols, illustrates this interaction. The *syn* axial Me group of the t-butyl group in **9** and **10** produces a severe steric shielding of the side of the ring *cis* to this Me group and prevents diborane attack at both positions 2 and 3 from this side (Fig. 4). This strong effect overcomes the directive *trans* effect of the allylic borate



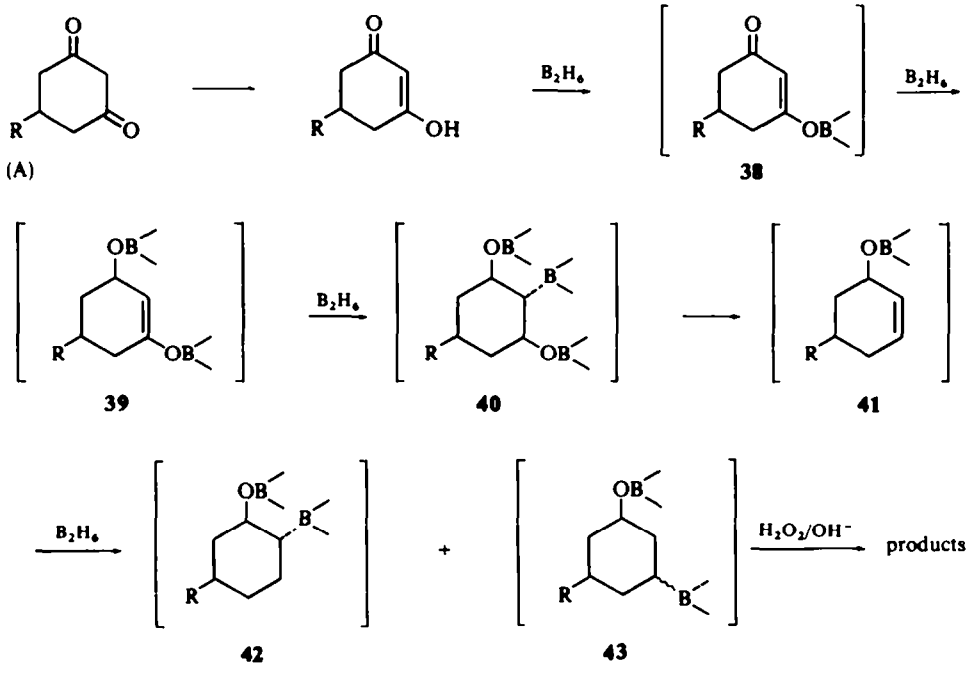
10a

FIG 4

group and the main diols obtained were, surprisingly, the *trans*-4-t-butyl-*cis*-1,2-cyclohexandiol (**28**) and the *trans*-4-butyl-*cis*-1,3-cyclohexandiol (**29**). On the other hand, hydroboration of *cis*-4-t-butylcyclohex-2-enol (**11**) (contaminated with 30% of the *trans* isomer **10**) gave, as the only identified product, the expected *trans*-4-t-butyl-*trans*-1,2-cyclohexandiol (**30**). Pasto examined recently the hydroboration of 3-t-butylcyclohexene, which is similar to intermediate **10a**, and found that 97% of the diborane attack was *trans* to the bulky t-butyl group,[15c] as compared with 93% *trans* attack to the t-butyl group in **10a**.

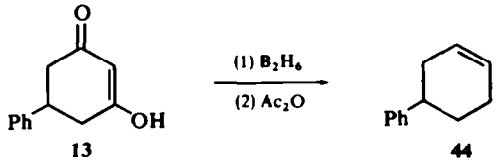
The relatively high yield (17–20%) of the *cis*-1,2-diol **28** from the hydroboration of **9** and **10** was surprising, since it was assumed in previous work that the *cis*-1,2-borane-borates are unstable under the reaction conditions.[4, 5] However, the present results prove that this assumption is not entirely accurate. The elimination of the *cis*-1,2-borane-borates is faster than that of the *trans* isomers, but not fast enough to destroy substantial amounts of them. This is also characteristic of compounds not containing a t-butyl group, as seen from the hydroboration of **3** (6% *cis*-1,2-diol) and **35** (5% *cis*-1,2-diol).[5]

The hydroboration of the 1,3-cyclohexandiones (Table 1) **12**, **13** and **14** gave to our surprise preponderantly the *trans*-1,2-cyclohexandiols **18**, **21** and **26**. The same diols were obtained in an overall yield of 45–50%, as compared with a yield of 60–65% from the corresponding cyclohex-2-enone. The yield of the 1,2-diols decreased and the yield of the 1,3-diols increased. The similarity of the results implies a mechanism which passes through an allylic borate, as in the case of the cyclohex-2-enones and cyclohex-2-enols. The following mechanism (A) is proposed to account for 70–75% of the total yield of the diols. The first step of the hydroboration of the enolized diketone is obviously the formation of an enol borate **38** (Evolution of hydrogen is observed).



The sequence of the next two steps was not determined, but reduction of the carbonyl group to yield **39** is probably the second step, as in the case of the cyclohex-2-enones. The trifunctional intermediate **40** which is formed undergoes fast *trans* elimination to yield the allylic borate **41** that is hydroborated in the normal manner as described above.

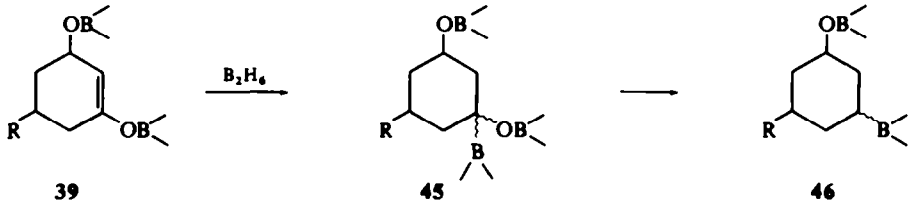
The hydroboration elimination of a 1,3-cyclohexandione was used, in one case, for an olefin synthesis. 5-Phenyl-1,3-cyclohexandione (**13**) was hydroborated with excess diborane and then refluxed with Ac_2O to yield 4-phenylcyclohexene (**44**) in



20% yield.* This olefin synthesis is similar to that previously described which involved hydroboration of a conjugated ketone and elimination with Ac_2O.[16]

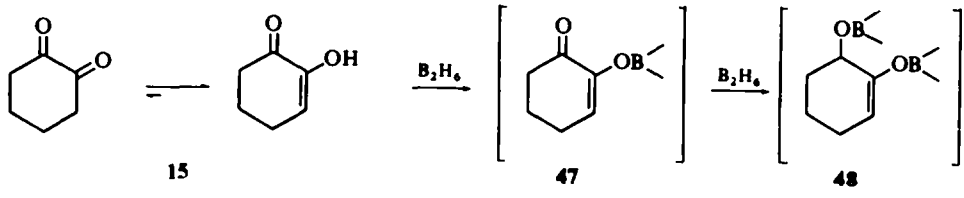
In order to account for the larger amounts of 1,3-cyclohexandiols obtained in the hydroboration of the 1,3-cyclohexandiones the following pathway (B) is assumed. Attack of diborane on intermediate **39** α to the enol borate yields **45**. The trifunctional intermediate **45** undergoes reduction to **46** which upon usual work-up gives the 1,3-diols. Displacement by hydrogen of chlorine[17] or acetoxy[18,19] in cyclohexane derivatives containing boron and chlorine[17] or boron and acetoxy[18,19] on the same carbon are known.

(B)



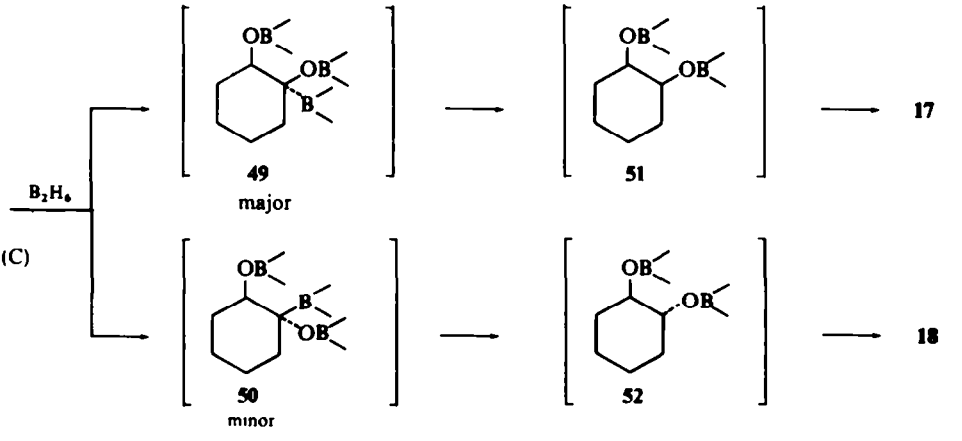
39 **45** **46**

Hydroboration of 1,2-cyclohexandione **15** gave unexpectedly a diol mixture containing *cis*-1,2-cyclohexandiol **17** as the main product (75–80% of the diol fraction). Formation of the *cis* diol **17** excludes an intermediate allylic borate (as in the case of the 1,3-diketones) which should yield predominantly the *trans*-1,2-cyclohexandiol (**18**). Direct reduction of **15** could also be excluded as the main



15 **47** **48**

(C)



* 4,4-Dimethylcyclohexene was prepared by the same procedure in 20% yield from dimedone, E. Dunkelblum and J. Klein, unpublished results

mechanism for this reaction for two reasons: (1) the diketone **15** is mainly in the enol form and addition of diborane evolves hydrogen; (2) hydroboration of 2-hydroxycyclohexanone (**16**) gave a different mixture of 1,2-cyclohexandiols (*cis* 42%, *trans* 58%). The following mechanism (C) is proposed for the hydroboration of **15**.

The first step is formation of an enol borate **47** which is reduced to **48**. Diborane attack, mainly *trans*, and to a small extent *cis*, to the allylic borate and α to the enol borate, gives intermediates **49** and **50**. Basic hydrolysis or intramolecular displacement by H of the borane group in **49** and **50** with retention* yields **51** and **52**. This mechanism implies that hydrogen peroxide is superfluous for the formation of the 1,2-cyclohexandiols, as 1,2-diborates **51** and **52** are the final intermediates.

Hydroboration of **15** and work-up without H_2O_2 indeed gave a comparable yield of 1,2-cyclohexandiols **17** and **18** with a similar isomer distribution. The very small yield of 1,3-cyclohexandiols **19** and **20** is due to hydroboration of **48** β to the enol borate and subsequent hydrogenolysis or elimination-hydroboration.

EXPERIMENTAL

Microanalyses were performed by Mrs. M. Goldstein of the microanalytical laboratory of the Hebrew University. B.ps and m.ps are uncorrected. NMR spectra were recorded on a Varian A-60 spectrometer with TMS as internal standard. They are reported in δ units, ppm/multiplicity (number of hydrogens). IR spectra were measured on a Perkin-Elmer Infracord 337 spectrometer. Gas liquid chromatography (GLC) was performed on an Aerograph A-700 or an F & M 720 apparatus. The column used was neopentylglycol succinate 20% on chromosorb W, 2·5 m long. Preparative TLC was carried out with 0·75 mm thick layers of GF 254 silica gel and C_6H_6:MeOH 85:15 was used for elution. The separated fractions were extracted with MeOH and purified if necessary by filtration of CH_2Cl_2 solutions. The accuracy of the TLC separations was ± 2%.

Sodium periodate oxidations of diols.[7] A 2×10^{-4}M aqueous solution (1·50 ml) of $NaIO_4$ was introduced into a UV cell and a 2×10^{-4} M aqueous solution (1·00 ml) of the diol was added. The solutions were mixed and the spectrum immediately measured over the range of 190–250 nm and repeated at 30 min intervals. Under these conditions a 1,2-diol caused the optical density of $NaIO_4$ (λ_{max} 221 nm) to decrease by 30–40% after one hr and by 50–60% after three hr. On the other hand, a 1,3-diol caused a fall of only 3–10% after three hr.

Starting materials. 1,2-Cyclohexandione (**15**) (Aldrich) was used without further purification. 1,3-Cyclohexandione (**12**) (Fluka) was crystallized from C_6H_6 before use. 2-Hydroxycyclohexanone (**16**) was prepared by distillation [b.p. 90–100° 30 mm] of the commercial dimer[20] (Aldrich). Cyclohex-2-enone (**3**) was prepared from cyclohexene.[21] 5-Phenyl-1,3-cyclohexandione (**13**) was synthesized from benzalacetone[22] and this was converted to 5-phenylcyclohex-2-enone (**4**).[23] 4-t-Butylcyclohex-2-enone (**9**) was prepared from 4-t-butylcyclohexanone.[24]

cis *and* trans-5-*Phenylcyclohex*-2-*enols* (**5**) *and* (**6**). Reduction of **4** with aluminium isopropoxide according to Macbeth and Mills[23e] gave a mixture of **5** and **6** in 70% yield, b.p. 113–117° 1 mm. This mixture (12·5 g, 72 mmol) was treated with benzoyl chloride (15 g, 110 mmol) in dry pyridine (30 ml) at room temp. Usual work-up gave 19·5 g (98%) of mixed benzoates. Crystallization from MeOH (200 ml) at 10° gave 13 g of the *cis*-benzoate, m.p. 94–97° and recrystallization from MeOH yielded 11 g, m.p. 97–98°. (Calc. for $C_{19}H_{12}O_2$: C, 82·0: H, 6·5. Found: C, 82·2: H, 6·3%.)

The mother liquors from the above crystallization were evaporated to dryness. The residue was crystallized twice from MeOH to yield 3·6 g of the *trans*-benzoate, m.p. 51–54°. (Calc. for $C_{19}H_{12}O_2$: C, 82·0: H, 6·5. Found: C, 81·7: H, 6·3%.)

* Displacement of chlorine[17] or acetoxy[18, 19] by hydrogen in diborane reactions was found previously to proceed with inversion[17–19]. The stereochemistry of our reaction and the different system from the ones previously studied suggest a different course of displacement. This problem is under current investigation.

The *cis*-benzoate (12 g) was hydrolyzed by refluxing for 3 hr with KOH (10 g) in MeOH (90 ml) and H_2O (20 ml) and yielded 6·5 g of **5**, m.p. 48–49° (hexane). IR (KBr) 3630, 1610 cm^{-1}. NMR (CCl_4): 7·22/s (5H), 5·67/bs (2H), 4·35/m, Wh/2 = 18 Hz (1H – α to OH), 3·9/bs (1H) exchanges with D_2O, 2·7/bm (1H), 2·5–1·5 (4H). (Calc. for $C_{12}H_{14}O$: C, 82·7; H, 8·0. Found: C, 82·6; H, 8·0%). According to the NMR spectrum this sample contained 5% of **6**.

The *trans*-benzoate (7·5 g) was hydrolyzed as described above and yielded 3·6 g of **6**, m.p. 42–45° (hexane). IR (KBr): 3600, 1600 cm^{-1}. NMR (CCl_4): 7·11/s (5H), 5·80/bs (2H), 4·14/m, Wh/2 = 6 Hz (1H – α to OH), 3·4/bs (1H) exchanges with D_2O, 3·0/bm (1H), 2·5–1·5 (4H). (Calc. for $C_{12}H_{14}O$: C, 82·7; H, 8·0 Found: C, 81·6; H, 7·9%). According to the NMR spectrum this sample contained 15% of **5**.

The *cis* isomer **5** was also prepared by the reduction of **13** with LAH according to the method of Dreiding and Hartmann[28] and was purified as described above.

5-t-Butyl-1,3-cyclohexandione (**14**). This dione was prepared from 5,5-dimethylhex-3-en-2-one[27]* and diethyl malonate as described for the phenyl analog **13**.[22] The yield was 57%, m.p. 147–148° (acetone). IR (CCl_4): 1720, 1600 cm^{-1}. NMR ($CDCl_3$): 10·6/bs (0·5H), 5·65/bs (0·5H), 2·8–1·7/m (6H), 1·00/s (9H). (Calc. for $C_{10}H_{16}O_2$: C, 71·5; H, 9·5. Found: C, 71·4; H, 9·4%).

cis-*5-t-Butylcyclohex-2-enol* (**8**). Reduction of **14** with LAH[26] gave **8** in 80–85% yield, b.p. 73–76° 1 mm, [lit.[25a] 110–112° 12 mm]. IR (neat): 3520, 1640 cm^{-1}. NMR (CCl_4): 5·62/bs (2H), 4·03/m (2H), on addition of D_2O, one proton was exchanged, remained: 4·10/m, $Wh/_2$ = 13 Hz, (1H), 2·20–1·05 (5H), 0·9/s (9H). (Calc. for $C_{10}H_{18}O$: C, 78·0; H, 11·7. Found: C, 77·9; H, 11·4%).

According to the NMR spectrum, **8** contained 11% of the *trans* isomer. Crystallization of the *p*-nitrobenzoate of **8** and subsequent hydrolysis, did not reduce the amount of the *trans* isomer.

5-t-Butylcyclohex-2-enone (**7**). This compound was prepared as described for **4**.[23] Methylation of **14** with MeOH in C_6H_6 catalyzed by *p*-TsOH gave 5-t-butyl-3-methoxycyclohex-2-enone in 50% yield, b.p. 101–102° 1 mm, m.p. 25–31° (hexane). The enol ether was reduced with LAH to give **7** in 60% yield, b.p. 125–128° 13 mm. IR (neat): 1725, 1680 cm^{-1}. NMR (CCl_4): 6·9/m (1H), 5·9/bd, J = 10, (1H), 2·65–1·85 (5H), 0·93/s (9H). (Calc. for $C_{10}H_{16}O$: C, 79·0; H, 10·5. Found: C, 79·1; H, 10·8%).

trans- *and* cis-*4-Butylcyclohex-2-enols* (**10**) *and* (**11**). Reduction of **9** with aluminium isopropoxide[23a] gave a mixture of **10** and **11** in 80% yield, b.p. 120–126 13 mm. The *trans*:*cis* ratio was 74:26 (NMR). This mixture (9g, 58 mmol) was treated with *p*-nitrobenzoylchloride (15 g, 80 mmol) in dry pyridine (30 ml) at room temp. Usual work-up gave 17·5 g (99%) of mixed *p*-nitrobenzoates. Two crystallizations from MeOH gave 7 g of the *p*-nitrobenzoate of **10**, m.p. 88–91°. (Calc for $C_{17}H_{21}NO_4$: C, 67·3; H, 6·9; N, 4·6. Found: C, 67·4; H, 7·0; N, 4·7%).

The mother liquors from the above crystallization were evaporated to dryness. The residue was crystallized from MeOH to yield 1·4 g of the *p*-nitrobenzoate of **11**, m.p. 38–43°. (Calc for $C_{17}H_{21}NO_4$: C, 67·3; H, 6·9; N, 4·6. Found: C, 67·0; H, 6·8; N, 5·1%).

The *trans-p*-nitrobenzoate (6·4 g) was hydrolyzed with KOH (5 g) in MeOH (50 ml) and H_2O (10 ml) at room temp. for 2·hr. Usual work-up and subsequent distillation gave 2·5 g of **10** which solidified on standing, m.p. 31–32°. IR (neat): 3300, 1650 cm^{-1}. NMR ($CDCl_3$): 5·75/bs (2H), 4·08, Wh/2 = 10 Hz, (1H-α to OH), 2·50/bs (1H) exchanges with D_2O, 2·3–1·2 (5H), 0·87 (9H). (Calc. for $H_{10}H_{18}O$: C, 78·0; H, 11·7. Found: C, 78·0; H, 11·7%).

The *cis-p*-nitrobenzoate (1·1 g) was hydrolyzed as described above and yielded 0·43 g of **11**, which solidified without distillation, m.p. 44–49°. IR (neat): 3300, 1650 cm^{-1}. NMR (CCl_4): 5·92/bs (2H), 4·10/m, Wh/2 = 6 Hz, (1H-α to OH), 2·50/bs (1H) exchanges with D_2O, 2·3–1·1 (5H), 0·92/s (9H). (Calc. for $C_{10}H_{18}O$: C, 78·0; H, 11·7. Found: C, 77·7; H, 11·3%). According to the NMR spectrum this sample contained 30% of the *trans* isomer **10**.

Comparison materials

cis-*1,2-Cyclohexandiol* (**17**) *and* trans-*1,2-cyclohexandiol* (**18**) were prepared by *cis* and *trans*-hydroxylation of cyclohexene.[28]

cis-*1,3-Cyclohexandiol* (**19**) *and* trans-*1,3-cyclohexandiol* (**20**) were separated from a commercial mixture (Fluka) through the dibenzoates[29] and subsequent hydrolysis with methanolic KOH.

The cyclohexandiols **17**, **18**, **19** and **20** were acetylated with Ac_2O and pyridine in the usual way and the diacetates used as GLC standards without distillation.

* 5,5-Dimethylhex-3-en-2-one was best prepared using NaOHaq rather than using anhydrous conditions.[27] The yield was 40%.

trans-3-*Hydroxy*-cis-5-*phenylcyclohexanol* (**22**). *cis*-5-Phenylcyclohex-2-enol (**5**) (1·74 g, 10 mmol) was subjected to oxymercuration-demercuration[6] according to Brown.[30] After 15 min at room temp. the mercury compound was reduced with $NaBH_4$ to yield 1·27 g of crude diol, m.p. 118–128°. Crystallization from EtOAc gave 1·15 g (60%) m.p. 131–133° (lit.[9] 132·5–133·5°). According to TLC, the crude product contained 8% of starting material **5**. The calculated yield of **22** from pure **5** (the starting material used contained 5% of **6**) was 75%. (Calc. for $C_{12}H_{16}O_2$: C, 75·0; H, 8·3. Found: C, 74·8; H, 8·2%).

4-*Phenylcyclohexene* (**44**). B_2H_6, generated by addition of a solution of 80 g BF_3 etherate in 50 ml diglyme to 12 g $NaBH_4$ in 50 ml diglyme, was bubbled during 1 hr at −10°–0° into a solution of 5-phenyl-1,3-cyclohexandione (**13**) (18·8 g, 100 mmol) in 200 ml diglyme. The mixture was stirred for 3 hr at −10°–0°, Ac_2O (60 ml) was added dropwise and the whole was refluxed for 1 hr. The mixture was concentrated to a small volume *in vacuo* and the residue stirred with sat. K_2CO_3 aq (150 ml) overnight. The product was extracted several times with hexane, washed with H_2O and dried. Distillation gave 3 g (19%) of **44**, b.p. 115–120° 20 mm; reported[31] b.p. 88–90° 16 mm. IR (neat) 3000, 2900, 1650 cm^{-1}. NMR (CCl_4) 7·22/bs (5H), 5·75/bs (2H), 2·65/bm (1H), 2·30–1·60 (6H). (Calc. for $H_{12}H_{14}$: C, 91·1; H, 8·9. Found: C, 91·0; H, 9·1%).

trans-2-*Hydroxy*-cis-4-*phenylcyclohexanol* (**24**). *trans*-Hydroxylation[4] of 4-phenylcyclohexene (**44**) (1·8 g, 11 mmol) yielded 1 g (48%) of **24**, m.p. 125–126° (EtOAc) reported[32] 126–127°. (Calc. for $C_{12}H_{16}O_2$: C, 75·0; H, 8·3. Found: C, 74·7; H, 8·6%).

cis-3-*Hydroxy*-trans-5-*phenylcyclohexanol* (**25**). *trans*-5-Phenylcyclohex-2-enol (**6**) (0·51 g, 3 mmol) was subjected to oxymercuration-demercuration.[6, 30] After 30 min at room temp. the mercury compound was reduced and gave 0·52 g of crude product which was purified by TLC. The yield of **25** was 0·28 g (49%) m.p. 132–134° (lit.[9] 135–136°). The calculated yield of **25**, corrected for the presence of 15% of **5** in **6**, was 58%. The diol **25** was also prepared according to the published procedure.[9] (Calc. for $C_{12}H_{16}O_2$: C, 75·0; H, 8·3. Found: C, 75·1; H, 8·4%).

In addition to **25**, the isomer **22** was isolated in 15% yield (5% calculated on pure **6**). Also, 8% of the starting material **6** was recovered. The rates of migration were in the order: **6** > **25** > **22**.

trans-2-*Hydroxy*-cis-4-*t-butylcyclohexanol* (**30**). *trans*-Hydroxylation[4] of 4-t-butylcyclohexene[33] (4·5 g, 33 mmol) yielded 3·2 g (57%) of **30**, m.p. 137–138° (EtOAc) reported 140–141°.[33] (Calc. for $C_{10}H_{20}O_2$: C, 69·8; H, 11·6. Found: C, 69·8; H, 11·7%).

cis-2-*Hydroxy*-cis-4-*phenylcyclohexanol* (**31**). *cis*-Hydroxylation[4, 10] of 4-phenylcyclohexene (**44**) (2 g, 12 mmol) yielded 1 g (43%) of a product b.p. 130–135° 2 mm. Two crystallizations from EtOAc hexane gave pure **31**, m.p. 90–91°. (Calc. for $C_{12}H_{16}O_2$: C, 75·0; H, 8·3. Found: C, 75·2; H, 8·4%).

cis-2-*Hydroxy*-cis-4-*t-butylcyclohexanol* (**32**). *cis*-Hydroxylation[4, 10] of 4-t-butylcyclohexene[33] (7 g, 50 mmol) yielded 3·5 g (41%) of a diol mixture, m.p. 83–88 (hexane). (Calc. for $C_{10}H_{20}O_2$: C, 69·8; H, 11·6. Found: C, 69·8; H, 11·5%). Two subsequent crystallizations from hexane gave pure **32** (TLC, NMR) m.p. 109–113°.

trans-2-*Hydroxy*-cis-5-*t-butylcyclohexanol** (**33**). *cis*-5-t-Butylcyclohex-2-enol (**8**) (1·54 g, 10 mmol) was subjected to oxymercuration-demercuration [6, 33] as described for the preparation of **25**. The crude product was crystallized from EtOAc to yield 0·6 g (35%) of **33**, m.p. 126·5–128·5°. (Calc. for $C_{10}H_{20}O_2$: C, 69·8; H, 11·6. Found: C, 69·5; H, 11·8%). The mother liquors from the crystallization were concentrated and subjected to TLC. Separation gave 0·22 g (13%) of **33** (the total yield of **33**, calculated on pure **8** was 54%) and approximately 4% of the all *cis* isomer **27** (was contaminated with **33**). Also isolated were 0·21 g (14%) starting material. The rates of migration were **8** > **33** > **27**.

cis-3-*Hydroxy*-trans-4-*t-butylcyclohexanol* (**34**). *trans*-4-t-Butylcyclohex-2-enol (**10**) (0·5 g, 3·3 mmol) was subjected to oxymercuration-demercuration[6, 30] for 24 hr under N_2. The crude product was distilled to yield 0·32 g, b.p. 140–160° 30 mm and this was subjected to TLC. Separation gave 0·093 g (18%) of **34**, m.p. 112–114° (EtOAc) and 0·105 g (21%) of starting material **10**. No isomeric cyclohexandiols could be detected (Calc. for $C_{10}H_{20}O_2$: C, 69·8; H, 11·6. Found: C, 70·0; H, 11·7%).

Hydroboration reactions[4, 34]

All the hydroboration reactions were carried out in THF with excess B_2H_6 (stock solutions in THF) under N_2. The B_2H_6 was added dropwise to the substrate at 0° and then stirred for 1 hr at room temp. Excess B_2H_6 was decomposed carefully with ice and the mixture oxidized with 10% NaOH and 30% H_2O_2. K_2CO_3 was added to saturation and the layers separated: the aqueous layer was extracted several times

* This compound was prepared independently[25b] by the same method

with CH_2Cl_2 and the combined extracts were dried and concentrated to dryness *in vacuo*. The residue was analyzed by GLC or TLC.

Hydroboration of cyclohex-2-enone (**3**) (2·4 g, 25 mmol) in 15 ml THF with B_2H_6 (20 ml, 1·3 M) gave 1·74 g (60%) of crude product. Analysis by GLC showed the following composition: 86% of **18**, 6% of **17** and 8% of **19** and **20**. Two crystallizations from EtOAc gave pure *trans*-1,2-cyclohexandiol (**18**), m.p. 101–102° (lit.[28] m.p. 102–103°). (Calc. for $C_6H_{12}O_2$: C, 62·1; H, 10·3. Found: C, 62·2; H, 10·6%).

Hydroboration of 5-phenylcyclohex-2-enone (**4**) (2·58 g, 15 mmol) in 10 ml THF with B_2H_6 (30 ml, 0·5 M) gave 0·76 g (26%) of **21**, m.p. 135–136° (two crystallizations from EtOAc). Calc. for $C_{12}H_{16}O_2$: C, 75·0; H, 8·3. Found: C, 74·9; H, 8·3%). Separation by TLC* gave a further amount (0·52 g) of **21** raising the total yield of **21** to 45%. Also isolated was a mixture (0·4 g, 14%) of 5-phenyl-1,3-cyclohexandiols. (Calc. for $C_{12}H_{16}O_2$: C, 75·0; H, 8·3. Found: C, 74·8; H, 8·1%). Partial TLC separation of this mixture gave 6% of **22**, m.p. 126–130°, identical with a sample prepared by oxymercuration of **5**. The second component, contaminated with **22**, was identified as **23** (8%), m.p. 147–155° (lit.[9] 160–161°). The rates of migration were **21** > **23** > **22**.

Hydroboration of cis-*5-phenylcyclohex-2-enol* (**5**) (3·5 g, 20 mmol) in 15 ml THF with B_2H_6 (40 ml, 0·5 M)

Hydroboration of trans-*5-phenylcyclohex-2-enol* (**6**) (3·3 g, calculated as 16 mmol pure **6**) in 15 ml THF with B_2H_6 (38 ml, 0·5 M) as described above gave 0·8 g (26%) of **24**, m.p. 121–123°, identical with a sample prepared by *trans*-hydroxylation of **44**. Also isolated (TLC) were 6% of **22**, m.p. 130–132° and 2% of **25**, m.p. 115–125° identical with a sample prepared by oxymercuration of **6** and by the method of Richer.[9] The rates of migration were **25** > **24** > **22**.

Hydroboration of 5-t-butylcyclohex-2-enone (**7**) (3·04 g, 20 mmol) in 15 ml THF with B_2H_6 (40 ml, 0·5 M) as described above gave 1·5 g (45%) of **26**, m.p. 102–105° (EtOAc); recrystallization gave the analytical sample, m.p. 103–105°. (Calc. for $C_{10}H_{20}O_2$: C, 69·8; H, 11·6. Found: C, 69·9; H, 11·5%). The only other diol isolated (TLC) was the slower migrating **27** (11%), m.p. 130–140° (EtOAc) contaminated by traces of **26**. (Calc. for $C_{10}H_{20}O_2$: C, 69·8; H, 11·6. Found: C, 69·7; H, 11·7%).

Hydroboration of cis-*5-t-butylcyclohex-2-enol* (**8**) (2·70 g, calculated as 16 mmol pure **8**) in 15 ml THF with B_2H_6 (27 ml, 0·65 M) gave, in an identical manner as for the hydroboration of **7**, 1·3 g (47%) of **26** and 11% of **27**.

Hydroboration of 4-t-butylcyclohexanone (**9**) (0·96 g, 6·3 mmol) in 5 ml THF with B_2H_6 (10 ml, 0·7 M) gave after TLC separation 0·18 g (17%) of **28**, m.p. 76–79°. (Calc. for $C_{10}H_{20}O_2$: C, 69·8; H, 11·6. Found: C, 69·9; H, 11·7%). The second main product was **29**, 0·24 g (22%), m.p. 108–120°. An additional TLC purification gave pure **29**, m.p. 124–126°. Also detected were approximately 3% of **26** identified by TLC comparison with a pure sample. Rates of migration were **28** > **26** > **29**.

Hydroboration of trans-*4-t-butylcyclohex-2-enol* (**10**) (1·0 g, 6·5 mmol) in 5 ml THF with B_2H_6 (10 ml, 0·7 M) gave, in an identical manner as above, 0·22 (20%) of **28**, 0·25 (22%) of **29** and approximately 3% of **26**.

Hydroboration of cis-*4-t-butylcyclohex-2-enol* (**11**) (0·3 g, contained 1·3 mmol of **11** and 0·6 mmol of **10**) in 1·5 ml THF with B_2H_6 (3 ml, 0·5 M) gave 56 mg (24%) of **30** (hexane-EtOAc) m.p. 139–141° (lit.[33] m.p. 140–141°). This was identical with an authentic sample prepared by *trans*-hydroxylation of 4-t-butylcyclohexene. No further amount of **30** or other diols could be isolated from the complex mixture either by crystallization or by TLC.

Hydroboration of 1,3-*cyclohexandione* (**12**) (3 g, 27 mmol) in 20 ml THF with B_2H_6 (24 ml, 1·2 M) gave 2·3 g crude product which solidified on standing. A small portion was converted to a mixture of diacetates. Analysis of the free diol mixture and of the diacetate mixture by GLC gave 62% of **18**, 6% of **19**, 6% of **20** and traces of **17**. GLC of the free diols did not separate **19** from **20**, but separated **17** from **18**. The opposite was the case for the diacetates. Therefore the ratio of **17**:**18**:**19** + **20** was found from the analysis of the free diols and the ratio 19:20 was determined from the diacetate analysis. The yields of the diols were calculated by GLC using a weighed amount of *trans*-2-hydroxy-*trans*-3-methylcyclohexanol[4] as internal standard.

Hydroboration of 5-*phenyl*-1,3-*cyclohexandione* (**13**) (3·76 g, 20 mmol) in 30 ml THF with B_2H_6 (30 ml, 1 M) and separation as for **4** gave 0·9 g (25%) of **21**, 0·35 g (9%) of **22** and 0·5 g (13%) of **23** (which was contaminated with traces of **22**).

* In all the hydroboration reactions subjected to TLC separations, varying amounts of unidentified fractions were isolated.

Hydroboration of 5-*t-butyl*-1,3-*cyclohexandione* (**14**) (3·36 g, 20 mmol) in 20 ml THF with B_2H_6 (60 ml, 0·5 M) and standard work-up gave 0·9 g (30%) of **26** and 0·6 g (20%) of **27**.

Hydroboration of 1,2-*cyclohexandione* (**15**) (3 g, 27 mmol) in 20 ml THF with B_2H_6 (24 ml, 1·2 M) and GLC separation as described for the hydroboration of **12** gave 33% of **17**, 10% of **18**, 0·5% of **19** and 1·5% of **20**. This reaction was repeated without H_2O_2 oxidation to give 34% of **17**, 11% of **18** and traces of **19** and **20**.

Reduction of 2-*hydroxycyclohexanone* (**16**) (3 g, 27 mmol) in 20 ml THF with B_2H_6 (22 ml, 1·25 M) for 2 hr at 0° and hydrolysis with NaOH aq gave 2·5 g (80%) of 1,2-cyclohexandiols. GLC analysis showed the presence of **17** and **18** in a ratio of 41:59.

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