Anal. Calcd for $C_{12}H_{18}S_6$: C, 40.64; H, 5.12; S, 54.25. Found: C, 40.76; H, 5.04; S, 54.06.

13,13-Dimethyl-1,4,8,11-tetrathiadispiro[4.1.4.3]tetradecane 1,1,4,4,8,8,11,11-Octaoxide.—Trifluoroperoxyacetic acid was prepared by adding trifluoroacetic anhydride (84 ml, 0.398 mol) during 15 min to a stirred, ice-cold solution of 15 ml of chloroform and 14 ml (0.50 mol) of 90% hydrogen peroxide. After 20 min this solution was added during 30 min to a stirred, ice-cold suspension of 2.0 g (0.00684 mol) of 13,13-dimethyl-1,4,8,11-tetrathiadispiro[4.1.4.3]tetradecane, 7 g (0.049 mol) of disodium hydrogen phosphate and 20 ml of chloroform. The slurry was refluxed for 12 hr and poured into 500 ml of ice–water and 100 ml of chloroform. The heterogeneous solution was made neutral with sodium bicarbonate and shaken. Filtration and washing with chloroform and water gave 1.91 g of white microcrystalline 13,13-dimethyl-1,4,8,11-tetrathiadispiro[4.1.4.3]tetradecane 1,4,4,8,8,11,11-octaoxide (66%), mp 260–280° with sintering. The addition of methanol caused two crystalline modifications having different solvent properties to separate: methanol soluble, mp 230–245° with sintering; methanol insoluble, mp 260–280° with sintering. Their infrared spectra (KBr) were different in the 700–950-cm^{-1} region, but identical at 1125 and 1335 cm^{-1}, indicative of a sulfone.

Anal. Calcd for $C_{12}H_{20}S_4O_8$: C, 34.27; H, 4.79; S, 30.50. Found: C, 34.86; H, 5.09; S, 30.42.

Registry No.—**1,** 177-16-2; **2,** 7490-36-0; **3,** 15856-34-5; **4,** 15732-74-8; **5,** 15814-64-9; **6,** 311-37-5; 13,13-dimethyl-1,4,8,11-tetrathiodiaspiro[4.1.4.3]tetradecene 1,1,4,4,8,8,11,11-octaoxide, 15814-66-1.

Acknowledgment.—The authors gratefully acknowledge the support of this project by the National Institutes of Health, Grant NB 02733, and by the Parke-Davis Co.

Evaluation of Steric Effects in Additions to Substituted Cyclohexenes[1]

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A number of mono- and dialkylsubstituted cyclohexenes have been prepared and subjected to hydroboration under carefully controlled conditions. The alcohol product distributions, obtained on basic peroxide oxidation of the intermediate alkylborane mixtures, are used to assess the source of the steric effects involved in the addition of borane to the cyclohexenyl systems. It is found that in the 1-substituted 4-*t*-butylcyclohexenes, except the 1,4-di-*t*-butyl compound, there is a preference for addition *cis* to the 4-*t*-butyl group. This is attributed to a more prominent steric effect imposed by the axial 4-hydrogen, the effect of which is greater at the 2 position than at the 1 position, and the axial 5-hydrogen, the effect of which is greater at the 1 position than the 2 position. These steric effects are enhanced on substitution of methyl for hydrogen at these positions or by the use of bulky hydroborating agents. Alkyl groups in the 3 position give rise to direct steric effects, effects due to distortion about C_3, and inductive effects. The anomalous results obtained in the hydroboration of 1,4-di-*t*-butylcyclohexene are attributed to steric effects imposed by specific rotational conformations about the C_1-*t*-butyl carbon bond, an effect which is also present in 1-isopropylcyclohexenyl systems. The results are discussed in terms of the proposed distortion of the 4-*t*-butylcyclohexene system by Rickborn and Lwo, and the applicability of the Garbisch model for additions to substituted cyclohexenes in which torsional angle effects in going to the transition state are considered to be important.

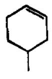
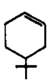
Numerous studies of the addition of a variety of reagents to simple substituted cyclohexenes have been reported in the literature. However, very few exhaustive kinetic and stereochemical studies involving these reactions have been carried out. Kwart and Miller[4] have measured the second-order rate constants for the addition of 2,4-dinitrobenzenesulfenyl chloride to a number of 4-mono- and 4,5-disubstituted cyclohexenes. These authors stated "the effect of the substituents of the 4-monosubstituted cyclohexenes on the rate of addition of 2,4-dinitrobenzenesulfenyl chloride is predominantly electronic in nature."[4] A portion of the data of Kwart and Miller is included in Table I for comparison with the relative rates of other addition reactions.

Rickborn and Lwo[5] have measured the rates and determined the stereochemistry of epoxidation of remotely substituted alkyl cyclohexenes (see Table I). These authors suggest "that the effects of remote alkyl groups are primarily steric rather than inductive in nature." The results for 4-methylcyclohexene were rationalized on the basis of a rate retarding steric effect contributed by the conformation with the *axial* methyl group. In order to explain the results of epoxidation of 4-*t*-butylcyclohexene, Rickborn and Lwo[5] invoked an unspecified distortion of the cyclohexene system by the bulky *t*-butyl group.

Consistent with the observation of Rickborn and Lwo on the stereochemistry of epoxidation of 4-*t*-

Table I

Relative Rates of Additions to 4-Substituted Cyclohexenes

	2,4-Dinitrobenzene-sulfenyl chloride 30° [a]	Epoxidation at 25° [b]	Diimide reduction at 80° [c]
	100	100	100
	81.2	81 (53.6% *trans* product)	90[d]
	89.7	94 (39.5% *trans* product)	95

[a] See ref 4. [b] See ref 5. [c] E. W. Garbisch, S. M. Schildkraut, and D. M. Patterson, *J. Amer. Chem. Soc.*, **87**, 2932 (1965). [d] Data derived from the 1-*t*-butylcyclohexene and 1-*t*-butyl-4-methylcyclohexene.

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[1] (a) Acknowledgment is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, for partial support of this work (PRF 1225-A1, 3). (b) Taken from the Ph.D. Thesis of F. M. K., University of Notre Dame, 1966. (c) Presented in part at the 153rd National Meeting of the American Chemical Society, Miami Beach, Fla., April 1967.

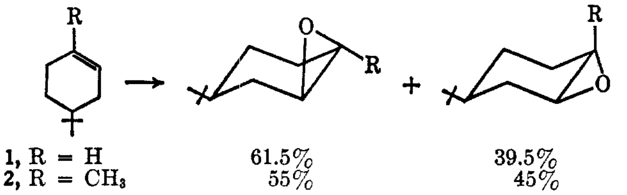
[2] Alfred P. Sloan Research Fellow, 1967–1969.

[3] National Science Foundation Predoctoral Fellow, 1963–1965; Lubrizol Fellow, 1965–1966.

[4] H. Kwart and L. J. Miller, *J. Amer. Chem. Soc.*, **83**, 4552 (1961).

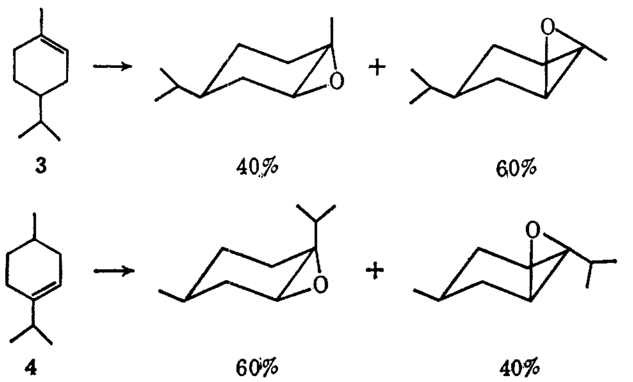
[5] B. Rickborn and S. Y. Lwo, *J. Org. Chem.*, **30**, 2212 (1965).

butylcyclohexene (1), LeBel and Ecke[6] observed that epoxidation of 1-methyl-4-*t*-butylcyclohexene (2) afforded a mixture of the 1-methyl-*trans*- and -*cis*-4-*t*-butylcyclohexene oxides in an approximate ratio of 45:55.



1, R = H
2, R = CH_3

Bowman and coworkers[7] have investigated the epoxidation of 1- and 3-*p*-menthene with perbenzoic acid. Epoxidation of 1-*p*-menthene (3) yields the 1-methyl-*cis*- and -*trans*-4-isopropylcyclohexene oxides in a 3:2 ratio whereas 3-*p*-methene (4) yields the 1-isopropyl-*cis*- and -*trans*-4-methylcyclohexene oxides in a 2:3 ratio.



3

4

Garbisch and coworkers[8] have investigated the reduction of cyclic, exocyclic, and acyclic olefins with diimide. Based on the assumption that the transition state for diimide reduction probably occurs fairly early along the reaction coordinate, these authors have proposed a model that suggests that the major factors which contribute to the observed reactivity differences are due to torsional strain, bond angle bending strain and α-alkyl substituent effects, with the assumption that steric factors (nonbonded repulsions) involved are likely to be small and hence were ignored. Calculations based on this model predict the relative reactivities of olefins with a remarkable degree of success, usually within a factor of 2.

Garbisch's model as applied to the analysis of the stereochemistry of attack on the cyclohexene ring system is illustrated in Figure 1. Approach of a reagent from side A (*trans* with respect to R'') leads to a reduction of angle τ, thus increasing the eclipsing strain between R and H, and an increase in angle τ' leading to a reduction in the eclipsing strain between R' and H'. Attack from side B results in opposite changes in τ and τ' and in the eclipsing strain energies. When R = R' = H, this model does not predict a preference for attack at either side A or B, whereas when R or R' are more bulky than H, attack would be expected to occur from sides B and A, respectively.

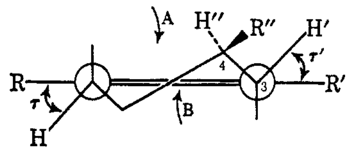


Figure 1.—Garbisch model for additions to substituted cyclohexenes.

The Garbisch model does not adequately explain the stereochemical results of Rickborn and Lwo.[5] The observed trend in the relative rates for epoxidation and diimide reduction[9] of 4-methyl and 4-*t*-butylcyclohexene relative to cyclohexene are not predicted by the Garbisch model although the changes in relative rates are within the sensitivity limits of the calculations.

Discussion

The nature of the steric effects giving rise to the trends observed in the data in Table I are not obvious and cannot be deduced from the reactions described thus far because of the symmetry of the attacking reagent (diimide), the intermediate (episulfonium ion in the addition of 2,4-dinitrobenzenesulfenyl chloride), or the final product (epoxide). In order to assess the steric factors operating in these reactions it is necessary to employ a sterically demanding, unsymmetrical reagent. The addition of borane to an olefin is uniquely well suited for such an investigation. The addition proceeds in a reasonably concerted, *cis* fashion[10,11] and subsequent oxidative work-up with alkaline hydrogen peroxide produces an alcohol in nearly quantitative yield in which the hydroxyl occupies the same site on the carbon atom that was occupied by the boron atom. The analysis of the products of hydroboration reactions can therefore be carried out on the much more easily handled alcohols rather than on the more reactive boranes. Furthermore, the hydroboration reaction has been shown to be quite sensitive to steric factors contained within the olefin[12-14] and the bulk of the hydroborating agent.[15]

In order to evaluate more critically the steric effects generated by remote alkyl groups in substituted cyclohexenes we have undertaken a study of the hydroboration of substituted cyclohexenes. The stereochemical results outlined in this paper are for the reaction of the substituted cyclohexene with an excess of borane in tetrahydrofuran to give predominantly (~95%) the monoalkylborane (see Experimental Section for the details of the analysis). Relativly few examples of the hydroboration of substituted cyclohexenes have been reported in the literature. These

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[6] N. A. LeBel and G. G. Ecke, *J. Org. Chem.*, **30**, 4316 (1965).

[7] R. M. Bowman, A. Chambers, and W. R. Jackson, *J. Chem. Soc., Sect. C*, 612 (1966).

[8] See Table I, footnote *c*.

[9] It might be argued that the transition state for epoxidation occurs considerably further along the reaction coordinate and thus the Garbisch model is not applicable. However, the similarity of the relative rates and stereochemistry of additions presented in Table I indicate a considerable degree of similarity exists despite the widely different types of reagents.

[10] H. C. Brown, "Hydroboration," W. A. Benjamin, Inc., New York, N. Y., 1962, p 130.

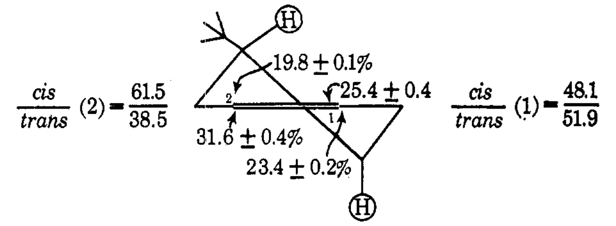
[11] W. G. Woods and P. L. Strong, *J. Amer. Chem. Soc.*, **88**, 4667 (1966).

[12] (a) N. Nussim, Y. Mazur, and F. Sondheimer, *J. Org. Chem.*, **29**, 1120 (1964); (b) L. Caglioti, G. Cainelli, G. Marna, and A. Selva, *Tetrahedron*, **20**, 957 (1964); (c) A. Hauser and C. Pillar, *J. Org. Chem.*, **27**, 2914 (1962).

[13] G. Zweifel and H. C. Brown, *J. Amer. Chem. Soc.*, **86**, 393 (1964).

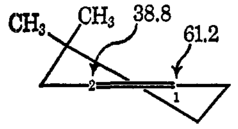
[14] W. Cocker, P. V. R. Shannon, and P. A. Stamland, *Tetrahedron Lett.*, 1409 (1966).

[15] H. C. Brown and G. Zweifel, *J. Amer. Chem. Soc.*, **82**, 3222 (1960); **83**, 1241 (1961).



1

Figure 2.—Positions of attack by boron in the hydroboration of 4-*t*-butylcyclohexene.



7

Figure 3.—Positions of attack by boron in the hydroboration of 4,4-dimethylcyclohexene (**7**).

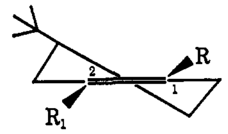
examples will be discussed in the appropriate sections of this article.

Hydroboration of 4-Substituted Cyclohexenes.[16]—The results from the hydroboration of 4-*t*-butylcyclohexene (**1**) are presented in Figure 2; the arrows indicate the position of attack by boron and the percentages indicate the average values for the extent of attack by boron at the indicated positions as determined from several independent experiments. The *cis/trans* ratios (relative to the 4-*t*-butyl group) for attack at the 1 and 2 positions are indicated beside the figure. The over-all *cis/trans* ratio relative to the 4-*t*-butyl group is 55:45, a slight, but nonetheless distinct, favoring of attack *cis* to the 4-*t*-butyl group. Closer inspection of the results presented in Figure 2 reveals that most of the stereochemical discrimination is at position 2. In fact, *trans* is very slightly favored at position 1. These stereochemical results are not predicted by the Garbisch model, and are consistent with the epoxidation results of Rickborn and Lwo[5] who observed a 60.5:39.5 *cis/trans* epoxidation ratio for **1**.

The stereochemical preferences for attack at positions 1 and 2 in **1** are *essentially* identical (within experimental limits) with those observed with 1-methyl-4-*t*-butylcyclohexene (**2**), 1-ethyl-4-*t*-butylcyclohexene (**5**), and 1-methyl-5-*t*-butylcyclohexene (**6**) (see Table II). The *cis/trans* ratios for attack at the 2 position of **2** and **5** are 62.2:37.8 and 64.7:35.2, respectively, compared to 61.5:38.5 for **1**. According to the Garbisch model, addition of borane to **2** and **5** should occur preferentially from the *cis* side (relative to the 4-*t*-butyl group). To this extent the prediction is correct. However, considering the changes in the prediction in going from **1** to **2** and **5**, we might have expected a greater preference for attack *cis* to the *t*-butyl group than observed in going from **1** to **2** and **5** in that the CH_3–H and C_2H_5–H eclipsing interactions in **2** and **5** should be greater than the H–H eclipsing interaction in **1** in which no stereochemical preference is expected. Again, it is interesting to note the similarity in the stereochemical results of hydroboration and epoxidation of **2**, the epoxidation leading to an approximate 55:45 *cis/trans* ratio.[6]

Table II

Stereochemistry of Attack by Borane on Substituted Cyclohexenes



Compd	Substituents	*cis*-1/*trans*-1	*cis*-2/*trans*-2
1	R = R_1 = H	48.1/51.9	61.5/38.5
2	R = CH_3; R_1 = H		62.2/37.8
5	R = C_2H_5; R_1 = H		64.7/35.3
6	R = H; R_1 = CH_3	49.3/50.7	

The results of the hydroboration of 1-methyl-5-*t*-butylcyclohexene (**6**) are also presented in Table II. The *cis/trans* ratio for attack at the 1 position in **6** is within experimental limits of the same value for **1**. In the case of **6**, the Garbisch model would have predicted a preference for *trans* addition relative to the 5-*t*-butyl group.

The excellent internal consistency of the results obtained with **1**, **2**, **5**, and **6** indicates that we are dealing with steric effects imposed by the 4-*t*-butylcyclohexenyl system itself, and does not involve steric interactions between the 1- and 2-alkyl groups and adjacent hydrogens on the ring.[17] Inspection of a molecular model of an undistorted half-chair form of 4-*t*-butylcyclohexene does not reveal an obvious basis for rationalizing the over-all *cis/trans* attack ratios. The axial hydrogens on carbons 4 and 5 (circled in Figure 2) might be expected to exert some steric influence on the relative amounts of attack at the 1 and 2 positions on each side of the cyclohexene ring. It therefore appears that Rickborn and Lwo's suggestion of a distorted 4-*t*-butylcyclohexene system[5] is necessary to rationalize the results.

Several distorted cyclohexene systems are conceivable. Such possibilities include a boat conformation and a pseudo-half-chair or "sofa" conformation. Thermodynamic calculations indicate that the boat conformation is less stable than the chair conformation by 2.7 kcal/mol,[18] and that the "sofa" conformation is less stable than the chair conformation by 1.2 kcal/mol.[19] Thus neither of these forms seems reasonable for the present system. A more reasonable possibility is that the bulky *t*-butyl group sterically interacts with the methine hydrogen attached to C_4 causing a distortion of the bond angles about C_4. This type of distortion is similar to the "*gem*-dialkyl" effect of Thorpe and Ingold[20] although in this case the

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[16] Subsequent to the completion of this study, J. Klein, E. Dunkelblum, and D. Avrahami [*J. Org. Chem.*, **32**, 935 (1967)] reported the results of the hydroboration of 4-methylcyclohexene which gave a mixture of *cis*-3- (28%), *trans*-3- (27%), *cis*-4- (20%), and *trans*-4-methylcyclohexyl alcohol (25%). This product distribution does not correlate well with the steric model developed in this paper. However, the product analysis is very difficult, requiring a partial separation of the alcohols followed by oxidation to the corresponding ketones for analysis, and the figures given might well suffer in accuracy from the procedure used in the analysis. We also attempted to analyze the products derived from the hydroboration of 4-methylcyclohexene but were never completely successful.

[17] It is interesting to note that the similarity of the results obtained from **1**, **2**, **5**, and **6** also indicates that the transition states for the addition of borane to the di- and trisubstituted double bonds must be quite similar, otherwise greater stereochemical preferences should be evident due to different degrees of rehybridization of carbons 1 and 2 in the transition state.

[18] C. W. Beckett, N. K. Freeman, and K. S. Pitzer, *J. Amer. Chem. Soc.*, **70**, 4227 (1948).

[19] R. Bucourt and D. Hainault, *Bull. Soc. Chim. Fr.*, 1366 (1965).

[20] R. M. Beesley, C. K. Ingold, and J. F. Thorpe, *J. Chem. Soc.*, **107**, 1080 (1915); C. K. Ingold, *ibid.*, **119**, 305 (1921). See also E. L. Eliel, "Stereochemistry of Carbon Compounds," McGraw-Hill Book Co., Inc., New York, N. Y., 1962, p 197.

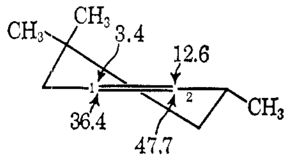

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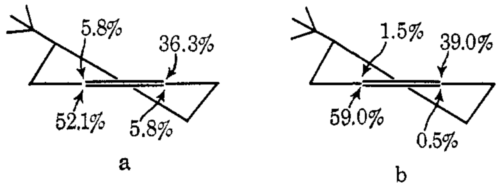
Figure 4.—Positions of attack by boron in the hydroboration of 3,5,5-trimethylcyclohexene (**8**).

distortion is due mainly to a single, very bulky group. Such a distortion would force the axial C_4 hydrogen (H_{4a}) (see Figure 2) closer to the center of the cyclohexene ring and should then shield the double bond from attack more than its C_5 axial hydrogen (H_{5a}) counterpart. The effect of H_{4a} should be felt more at C_2 than at C_1 owing to the closer proximity of H_{4a} to C_2 than to C_1. Experimentally this is observed with **1** giving rise to a *trans* 2:1 ratio of 44:56. The effect of H_{5a} should be felt more at C_1 than C_2. Again this is experimentally observed with **1** giving rise to a *cis* 1:2 ratio of 43:57.

Substitution of either H_{4a} or H_{5a} by methyl should enhance the steric interaction effects of these positions. Substitution of methyl for H_{4a} does result in a greater preference for attack at the 1 position. For example in the hydroboration of 4,4-dimethylcyclohexene (**7**) the 2:1 ratio is 38.8:61.2 (Figure 3) compared to 43:57 *cis* to H_{4a} in **1**. This value for **7** undoubtedly is not a true reflection of the effect of the 4-axial methyl group in that hydroboration *trans* to this group also occurs, which should favor position 2, thus tending to reduce the apparent effect of the C_4 axial methyl group.

A more informative, but more complex, case is illustrated by the results of the hydroboration of 3,5,5-trimethylcyclohexene (**8**) (see Figure 4).[21] Because of the severe 1,3-diaxial methyl interaction (3.7 kcal/mol in cyclohexane[22]), **8** can be considered as capable of existing essentially only in the conformation illustrated for **8** in Figure 4. The axial 5-methyl group *severely hinders attack cis to itself,* giving a *cis/trans* ratio of 16:84 compared to the corresponding ratio of 45:56 for H_{4a} in 1. Furthermore, the 2 to 1 position attack ratio *cis* to the axial 4-methyl group in **8** is 21:79 compared to the value of 44:56 in **1**, however there is also an increase in the extent of attack at position 1 *trans* to the axial-5 methyl group. This is not consistent solely with the steric effects outlined in the foregoing paragraphs. It appears that the 3-methyl group is exerting an inductive effect which leads to increased attack by boron at C_2. Evidence in support of this idea is derived from the hydroboration results of 3-methylcyclohexene (see later discussion).

Increasing the steric bulk of the attacking borane is reflected in increased steric interactions with groups in the 4 and 5 axial positions. Hydroboration of **1** by 2,3-dimethyl-2-butylborane (thexylborane[23]) resulted in a rather slow reaction to give the isomer distribution indicated in Figure 5a. The *cis/trans* ratio has increased slightly (57.9:42.1) relative to the hydroboration of **1** with borane (55:45), however the discrimination between the 1 and 2 positions has increased dramatically (compare with Figure 2). Hydroboration of **1** in a 2:1 olefin–borane ratio resulted in a rather slow formation of dialkylborane. The isomer distribution percentages presented in Figure 5b were determined by quenching the hydroboration reaction mixture with methanol, analyzing the amount of mono- and dialkylboron derivatives present by ^{11}B magnetic resonance followed by correcting the gross isomer distribution values for the amount of product formed by hydroboration of **1** to the monoalkyl stage (from Figure 2). In this instance a greater selectivity is observed than with 2,3-dimethyl-2-butylborane.



a b

Figure 5.—Positions of attack by boron in the hydroboration of 4-*t*-butylcyclohexene with 2,3-dimethyl-2-butylborane (**a**) and *t*-butylcyclohexylborane (**b**).

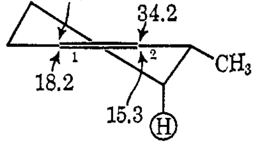


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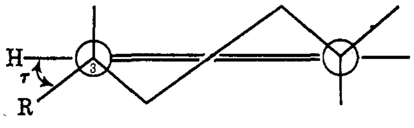
Figure 6.—Position of attack of boron in the hydroboration of 3-methylcyclohexene.

Hyroboration of 3-Alkylcyclohexenes.—The torsional angle effect model for additions to 3-alkylcyclohexenes would lead to the prediction that attack *trans* to the 3-alkyl group would be disfavored on the basis of eclipsing strain energies induced by changes in the angle τ. The results for the hydroboration of 3-methylcyclohexene (**9**) are presented in Figure 6.



These results are not in agreement with the torsional angle affect model prediction but are more consistent with a direct steric effect by the alkyl group. The interpretation of the results obtained with **9** is difficult owing to the possible existence of two conformations for **9** with the methyl in pseudo-axial or pseudo-equatorial positions. Talaty and Russell[24] have calculated a $-\Delta G$ value for the methyl in the cyclohexenyl system of 0.49 kcal/mol corresponding to approximately 29% of the pseudo-axial conformer at 0°. As we have no measure of the relative rates of hydroboration *cis*

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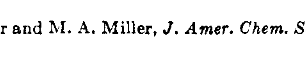
[21] Klein and coworkers have also examined the product distribution derived from the hydroboration of **7** (see ref 16). Their results are illustrated below and agree quite favorably with our results.



[22] N. A. Allinger and M. A. Miller, *J. Amer. Chem. Soc.*, **83**, 2145 (1961).

[23] H. C. Brown and G. Zweifel, *ibid.*, **85**, 2066 (1963).

[24] E. R. Talaty and G. A. Russell, *ibid.*, **87**, 4867 (1965).

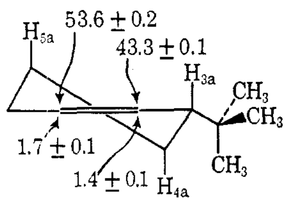


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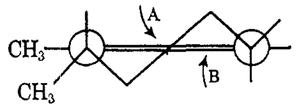
Figure 7.—Positions of attack by boron in the hydroboration of 3-*t*-butylcyclohexene in the most favorable conformation.



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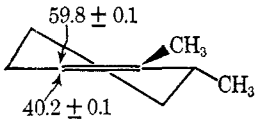

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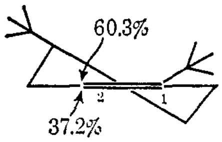
Figure 8.—Positions of attack by boron in the hydroboration of 1,6-dimethylcyclohexene.

and *trans* relative to the methyl group in the two conformations further interpretation of the results is not possible.

A further interesting observation can be made regarding the results given in Figure 6. The ratio of attack at the 1 and 2 positions (54:46) relative to H_{4a} (circled in Figure 6) *cis* to the methyl group is slightly less than the similar ratio in **1** (57:43) despite the added steric effect of the methyl group. This observation can be explained by invoking an inductive effect by the 3-methyl group resulting in a greater extent of attack by boron at C_2.[25] A similar effect is noted in Figure 4 for the attack at positions 1 and 2 *trans* to the *axial* 5-methyl group.

The results of the hydroboration of 3-*t*-butylcyclohexene (**10**) are given in Figure 7. 3-*t*-Butylcyclohexene should be a nearly conformationally homogeneous system, and the conformation that one must consider is that with the *t*-butyl group in a pseudo-equatorial position. The steric effect of H_{5a} is over-weighed by the steric effect of H_{3a} (see Figure 7). The increased steric prominence of H_{3a} in **10** compared to **9** is probably due to bond angle distortions about C_3, forcing H_{3a} into a position capable of shielding attack at C_2, similar to the distortion about C_4 in 4-*t*-butylcyclohexene in which the effect of H_{4a} is greater than that of H_{5a}.



12

Figure 9.—Positions of attack by boron in the hydroboration of 1,4-di-*t*-butylcyclohexene.

In addition to the steric effects of H_{3a} and H_{5a} in **10** the *t*-butyl group also obviously leads to an additional steric effect shielding the side of the ring *cis* to the *t*-butyl group. This would appear to be due to a preferred rotational conformation of the *t*-butyl group with respect to the substituents bonded to C_3 such that a staggered conformation exists about the C_3-*t*-butyl central carbon atom bond as is illustrated in Figure 7. In this conformation one of the methyl groups of the *t*-butyl group is *syn*-axial producing a severe steric shielding of the side of the ring *cis* to this methyl group (or the *t*-butyl group). The effect of this *syn*-axial-methyl group of the *t*-butyl group appears to be slightly greater than the steric shielding of the pseudo-axial C_5 methyl group in 3,5,5-trimethylcyclohexene. A similar rotational conformational effect must be invoked for the isopropyl and *t*-butyl groups appearing in the 1 position of cyclohexene (see later discussion on the hydroboration of 1,4-di-*t*-butylcyclohexene); however, the *t*-butyl group in the 4 position is too far away from the site of the reaction to produce a direct steric effect.

Hydroboration of 1,6-Dimethylcyclohexene.—In a final test of the applicability of the torsional angle affect model, we prepared 1,6-dimethylcyclohexene (**11**) and subjected it to hydroboration. Owing to the CH_3–CH_3 eclipsing strain developed by attack at side A of **11**, the torsional angle affect model would predict that attack would peferentially occur from side B. Experimentally, attack at side A is observed to predominate (see Figure 8). The *cis*/*trans* attack ratio, relative to the 6-methyl group, of 40.2:59.8 in **11** compares favorably with the *cis*/*trans* attack ratio at position 1 in **9** (36.2:63.8) indicating that the predominant factor operating in **11** is the steric effect of the 6-methyl group in the two conformations which are possible.

Hydroboration of 1,4-Di-*t*-butylcyclohexene.—Of the systems studied in the present work, only the results of the hydroboration of 1,4-di-*t*-butylcyclohexene[26] (**12**) (see Figure 9) are not in accord with our steric model or the Garbisch model. The introduction of a 1-*t*-butyl group in place of hydrogen or ethyl, in **1** and **5**, respectively, should not alter the conformation of the cyclohexene ring system and hence the effects of the 4-*t*-butylcyclohexenyl system. The effect produced by the 1-*t*-butyl group must be a consequence of extracyclic conformational steric effects produced by this group.

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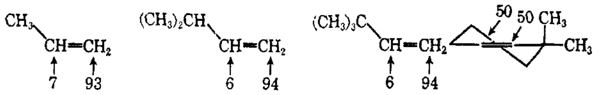
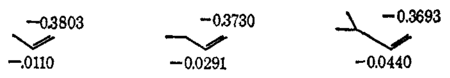
[25] Similar results have been obtained with acyclic olefins. As one increases the size of the alkyl group bonded to ethylene very little change in the direction of addition of borane is noted (see ref 10, pp 114 and 117). Furthermore, hydroboration of 3,3-dimethylcyclohexene leads to an equivalent extent of introduction of boron to both positions: H. C. Brown and G. Zweifel, *J. Amer. Chem. Soc.*, **83**, 2544 (1961).



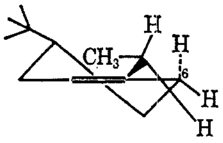
Theoretical support for the presence of an inductive effect is provided by extended Hückel calculations: R. Hoffmann, *J. Chem. Phys.*, **39**, 1397 (1963). As Δ_{12} (difference in charge density between C_1 and C_2 of the olefins) decreases, the discrimination in attack (assuming that the transition



state occurs early along the reaction coordinate such that the transition state highly resembles the ground state) should also diminish. Comparison of the observed hydroboranion results with the calculations indicates that in the simple acyclic olefins the steric, favoring terminal product, and inductive effects, favoring internal product, effectively cancel.

[26] D. J. Pasto and F. M. Klein, *Tetrahedron Lett.*, 963 (1967).

Conformational studies of 1-butene[27] have indicated that the preferred conformations involve eclipsing of the methylene C–H and C–CH_3 bond with the double bond. Incorporating the preferred 1-butene conformations in the structure of 1-ethyl-4-*t*-butylcyclohexene (**5**) gives conformations **13** and **14** (a third conformation is possible similar to **14** in which the methyl group is eclipsed with the other C_6 hydrogen). The C–H bonds of C_6 are positioned such that severe eclipsing between the methylene C–H and methyl bonds of the ethyl group occurs. As the eclipsing strain energy is least in **13**, compound **13** should be the preferred conformation. In this conformation the ethyl group does not offer steric resistance to attack at either side of the cyclohexene ring and hence the results obtained with **5** should be the same as obtained with the parent system (**1**) or the 1-methyl derivative (**2**). With 1,4-di-*t*-butylcyclohexene, however, maintaining eclipsing of one of the methyl groups with the double bond produces two CH_3–H eclipsing interactions with C_6. A slight rotation about the C_1-*t*-butyl carbon bond relieves the two severe CH_3–H eclipsing interactions, and, in what appears to be the most favorable rotational conformation, places one of the *t*-butyl methyls *syn*-axial, *cis* to the 4-*t*-butyl group (see **15**) giving rise to a substantial steric shielding of that side of the cyclohexene ring. The magnitude of this steric effect is quite large; **12** gives only a monoalkylborane in a relatively slow reaction and does not react with 2,3-dimethyl-2-butylborane.



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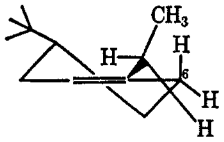

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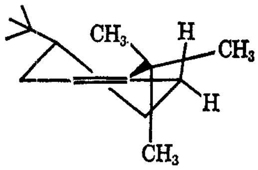

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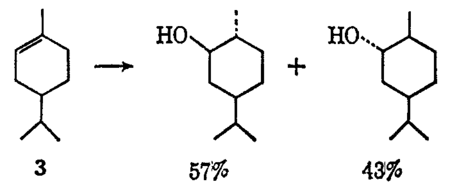
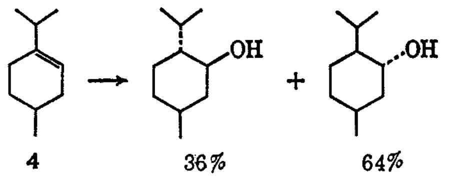
Although we were not successful in preparing 1-isopropyl-4-*t*-butylcyclohexene, the steric effects of the group in the 1 position can be inferred from the work of Shumway and Barnhurst[28] and Katsuhara and coworkers[29] which is illustrated in eq 1 and 2. It should be noted that the hydroboration of **3** is consistent with our ring substituent steric effect model, involving a slight distortion about C_4 caused by the isopropyl group, and that the hydroboration of **4** is not consistent with this model but compares favorably with the results obtained with 1,4-di-*t*-butylcyclohexene. (One should also note that the stereochemical results for the hydroboration of **3** and **4** almost exactly parallel the epoxidation stereochemistry results with **3** and **4**.[7] This indicates the operation of similar steric effects in both reactions.) The results derived with **4** (see Figure 10) may be explained on the basis of a rotational conformational effect with **16** being the most favorable rotational conformation providing steric hindrance to attack at the double bond *cis* to the 4-methyl group.



(1)



(2)

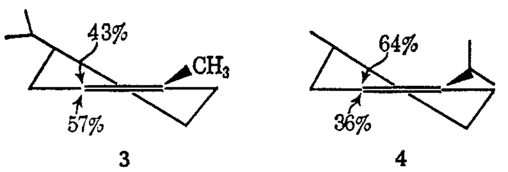
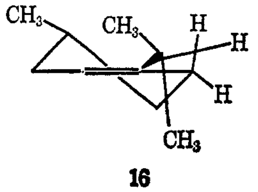


Figure 10.—Positions of attack by boron in the hydroboration of 1-*p*-menthene (**3**) and 3-*p*-menthene (**4**).



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The results presented in this paper indicate that in the hydroboration reaction steric factors imposed by remote functional groups play the predominant role in determining the stereochemistry of attack on the olefin, and that torsional angle effects as predicted by the Garbisch model are not important. This directly implies that very little rehybridization of the sp^2 olefinic carbon atoms has occurred in the transition state and hence the transition state for the hydroboration reaction must occur very early along the reaction coordinate.

Comparison of the kinetic and stereochemical data for the diimide reduction and epoxidation of these same olefins would indicate that the stereochemistry of attack on these olefins is also controlled by steric effects of remote functional groups and not by torsional angle effects.

Experimental Section

Preparation of Olefins. **4-*t*-Butylcyclohexene** was obtained from Professor E. L. Eliel's research group.

1-Methyl-4-*t*-butylcyclohexene was prepared following the procedure of DePuy and King[30] involving the addition of methylmagnesium iodide to 4-*t*-butylcyclohexanone followed by dehydration with iodine.

1-Ethyl-4-*t*-butylcyclohexene.—This compound, prepared from 10 g (0.065 mol) of 4-*t*-butylcyclohexanone on treatment with 0.07 mol of ethylmagnesium iodide, was dehydrated by distillation from 1 g of iodine. The distillate was dissolved in 150 ml of hexene and flushed successively through 20 × 15 cm Woelm activity II alumina and 21 × 2 cm Fluorisil columns.

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[27] A. A. Bothner-By, C. Naar-Colin, and H. Gunther, *J. Amer. Chem. Soc.*, **84**, 2748 (1962).

[28] D. K. Shumway and J. D. Barnhurst, *J. Org. Chem.*, **29**, 2320 (1964).

[29] J. Katsuhara, H. Wanatabe, K. Hashimota, and M. Kobayashi, *Bull. Chem. Soc. Jap.*, **39**, 617 (1966).

[30] C. H. DePuy and R. W. King, *J. Amer. Chem. Soc.*, **83**, 2743 (1961).

Final purification by distillation provided 8 g (74%) of 1-ethyl-4-*t*-butylcyclohexene, bp 75° (15 mm).

Anal. Calcd for $C_{12}H_{22}$: C, 86.67; H, 13.33. Found: C, 86.64; H, 13.25.

1,4-Di-*t*-butylcyclohexene was prepared by the procedure of Stolow and Ward.[31]

1-Methyl-5-*t*-butylcylohexene.—A solution of 20 g (0.12 mol) of 4-*t*-butyl-*o*-cresol (Aldrich Chemical Corp.) in 100 ml of glacial acetic acid was hydrogenated at room temperature on a Parr apparatus in the presence of 1 g of platinum oxide at an initial hydrogen pressure of 50 psi. The theoretical amount of hydrogen was taken up in 4 hr. The solution was poured into 150 ml of water and was extracted three times with 70-ml portions of ether. The combined ether extract was washed three times with 50-ml portions of water, twice with 50-ml portions of saturated sodium bicarbonate solution, and once with 50 ml of 10% hydrochloric acid solution, and dried over anhydrous magnesium sulfate. The solvent was removed on the flask evaporator, giving 17.4 g (84%) of soapy white crystals.

The mixture of isomeric 2-methyl-4-*t*-butylcyclohexanols was dehydrated in the presence of 0.2 go f iodine by refluxing for 5 hr followed by distillation. The olefin mixture was dissolved in 30 ml of pentane, washed with aqueous saturated sodium thiosulfate, dried over magnesium sulfate, and isolated by distillation at 69–80° (19 mm).

Analysis by glpc indicated the mixture contained three components in a ratio of 1:1.5:1.4. A portion of the mixture was separated on a Beckman Megachrom preparative gas chromatograph on a 48 m × 1.5 cm 1,2,3-tris(β-cyanoethoxy)propane column. The latter two fractions thus collected gave nmr spectra consistent with the desired olefin, however the spectra of these two compounds were almost superimposable. Each spectrum displayed singlets at −0.86 (9 H, *t*-butyl) and −1.63 (3 H, methyl), and a broad adsorption at −5.49 ppm (1 H, vinyl). Decoupling the methyl from the vinyl proton served to sharpen the vinyl peak of each spectrum, but did not reveal sufficient differences between the vinyl peaks to enable distinguishing the isomers. Final distinction between the compounds was made by analysis of their hydroboration products indicating that the second of these two olefins was 1-methyl-5-*t*-butylcyclohexene.

3-Methylcyclohexene was purchased from Aldrich Chemical Co. and was purified by distillation.

3-*t*-Butylcyclohexene.—Under a stream of nitrogen, 25 g (0.13 mol) of *cis*-2-*t*-butylcyclohexyl acetate (obtained from Professor E. Eliel) was pyrolyzed at 450° by dripping through a 50 cm × 2 cm, glass helices-packed column. The product, collected in Dry Ice–acetone cold traps, was taken up in 30 ml of ether, washed three times with 20-ml portions of water and twice with 15-ml portions of saturated sodium bicarbonate solutions and was dried over anhydrous magnesium sulfate. The solution was filtered, and the solvent was removed on the rotary flash evaporator. Distillation gave 4 g (23%) of a clear, colorless, liquid, bp 55.5–57° (15 mm) (lit.[32] 170.5° (746 mm)). Considerable unreacted acetate was also recovered.

4,4-Dimethylcyclopexene was purchased from Aldrich Chemical Co. and purified by distillation.

3,5,5-Trimethylcyclohexene was prepared according to the procedure of Sneen and Matheny.[33]

A mixture of 50 g (0.36 mol) of isophorone, 56.5 ml of 85% hydrazine hydrate, and 30 g (0.46 mol) of potassium hydroxide pellets was dissolved in 150 ml of ethylene glycol and refluxed for 4.6 hr. The reaction mixture was distilled directly. The organic phase of the distillate was separated from the aqueous phase by decantation, and was distilled from a few small pieces of sodium metal (0.2 g) through a 12-cm Vigreaux column. The material distilling at 120–135° was redistilled at 133–134°, giving 15 g (33%) of a mixture of 70% 2,4,4-trimethylcyclohexene and 30% 3,5,5-trimethylcyclohexene. A portion of this mixture was separated by preparative glpc on a 9.2 m × 0.6 cm adiponitrile column, giving pure 3,5,5-trimethylcyclohexene and 2,4,4-trimethylcyclohexene. The nmr spectrum of the 3,5,5-trimethylcyclohexene agrees with that reported by Sneen and Matheny.[33]

1,6-Dimethylcyclohexene.—To a stirred solution of methyl magnesium iodide in ether, prepared by the addition of 79.5 g (0.56 mol) of methyl iodide to 12.2 g (0.51 g-atom) of magnesium turnings in ether, was added slowly 50 g (0.45 mol) of 2-methylcyclohexanone in 200 ml of dry ether. After addition of the ketone, the mixture was refluxed 16 hr and then hydrolyzed with 100 ml of saturated ammonium chloride solution. The ether layer was decanted and the aqueous phase was extracted three times with 70-ml portions of ether. The combined ether extract was washed with 50 ml of saturated sodium thiosulfate solution, dried over anhydrous magnesium sulfate, and filtered. The solvent was removed on the rotary flash evaporator. The crude product (50 g, 88%) was distilled, bp 65–68° (15 mm) (lit.[34] *cis*-1,2-dimethylcyclohexanol, bp 95.7 (53 mm); *trans*-1,2-dimethylcyclohexanol 86.8° (52 mm)).

To a solution of 6.4 g (0.05 mol) of the product (a mixture of the *cis* and the *trans* isomers) in 30 ml of dimethylaniline at 0° was slowly added 7.1 ml (0.10 mol) of acetyl chloride. After all of the acetyl chloride has been added, the mixture was stirred at room temperature for 1 hr and on a steam bath for 3 hr. The solution was then cooled, poured onto 20 g of ice in 50 ml of 10% hydrochloric acid solution, and extracted three times with 35-ml portions of pentane. The combined pentane extract was washed with 20 ml of 10% hydrochloric acid solution and dried over anhydrous magnesium sulfate. After solvent removal *in vacuo*, 6.35 g (75%) of acetate was isolated.

Under a gentle stream of nitrogen, 12.8 g (0.075 mol) of the acetate was pyrolyzed by dropping slowly through a 2 cm × 50 cm glass helices packed column heated to 450°, collecting the effluent from the bottom of the column in Dry Ice–acetone traps. The product was poured into 20 ml of water and extracted with 60 ml of ether. The ether solution was washed twice with 20 ml of water, once with 20 ml of saturated sodium bicarbonate solution, and once with 20 ml of saturated sodium chloride solution, and dried over anhydrous magnesum sulfate. After removal of the solvent, the residue was distilled at 124–136° (750 mm) (lit.[34] 1,6-dimethylcyclohexene, bp 130.3–130.7° (745 mm); 1,2-dimethylcyclohexene, bp 136.2° (745 mm); 2-methylmethylenecyclohexane, bp 124.5 (745 mm)). Analysis by glpc showed this to be a mixture of approximately equal amounts of three components. Based on the results of Froemsdorf, *et al.*,[35] these components are assigned the structures of 2-methylmethylenecyclohexane, 1,2-dimethylcyclohexene, and 1,6-dimethylcyclohexene. The lack of adequate resolution impeded separation in large amounts. The mixture of olefins was used directly in the hydroboration studies in that only 1,6-dimethylcyclohexene is capable of giving rise to the isomeric 2,3-dimethylcyclohexanols, the products required for the desired stereochemical analysis.

Preparation of Compounds for Use as Glpc Standards. 3- and 4-*t*-Butylcyclohexyl Acetates.—Direct analysis of a mixture of 3- and 4-*t*-butylcyclohexyl alcohols (obtained from Professor E. Eliel) could not be accomplished by our available glpc techniques. The alcohols (0.2 g) were converted into the corresponding acetates by treatment with acetic anhydride (1 g) and pyridine (0.25 g). The pure acetates were isolated by pouring the reaction mixture into 10 ml of cold water and extraction with ether. The ether extracts were washed with 10% hydrochloric acid and dried over anhydrous magnesium sulfate. The solvent was removed under reduced pressure and the residues were purified by distillation in a micromolecular still. The pure acetates were used to determine the relative response ratios.

The crude alcohol mixtures from the hydroboration of 4-*t*-butylcyclohexene were treated with a tenfold excess of acetic anhydride and pyridine in ethereal solution and aliquots of this solution were analyzed directly by glpc. The quantitiveness of the procedure was demonstrated by acetylating a known mixture of the *cis*- and *trans*-3- and -4-*t*-butylcyclohexyl alcohols followed by glpc analysis and comparison of the results with the starting composition.

2-Methyl-5-*t*-butylcyclohexanols were obtained as a mixture of the isomers after hydroboration of 1-methyl-4-*t*-butylcyclohexene. Preparative separation of the two isomers by column chromatography or glpc could not be achieved.

The mixture of isomers was distilled, bp 60° (0.7 mm), and analyzed by nmr. Two peaks appear in the carbinol region of the spectrum, a broad peak at −3.07 ppm (axial carbinol proton) and a sharper peak at −3.79 ppm (equatorial carbinol proton). Planimeter integration of these two peaks gave the ratio of the

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[31] R. B. Stolow and J. A. Ward, *J. Org. Chem.*, **31**, 964 (1966).

[32] H. L. Goering, R. S. Reeves, and H. H. Espy, *J. Amer. Chem. Soc.*, **78**, 4926 (1956).

[33] R. A. Sneen and N. P. Matheny, *ibid.*, **86**, 5503 (1964).

[34] T. D. Nevitt and G. S. Hammond, *ibid.*, **76**, 4124 (1954).

[35] D. H. Froemsdorf, C. H. Collins, G. S. Hammond, and C. H. DePuy, *ibid.*, **81**, 643 (1959).

alcohols in this mixture. This known ratio was then used in calculating the response ratio for glpc analysis.

Anal. Calcd for $C_{11}H_{22}O$: C, 77.58; H, 13.02. Found: C, 76.96; H, 13.32.

2-Ethyl-5-*t*-butylcyclohexanols were obtained as a mixture of the isomers upon hydroboration of 1-ethyl-4-*t*-butylcyclohexene. Separation of the isomers by column chromatography or glpc could not be achieved.

The mixture of isomers was distilled on a microdistillation apparatus, bp 100° (12 mm). The nmr spectrum of the mixture shows two peaks in the carbinol region, one at −3.07 ppm, assigned to the axial proton, and at −3.82 ppm, assigned to the equatorial proton. As these isomers could not be separated by glpc, the analysis had to be carried out by nmr, comparing the areas of the two carbinol proton peaks mentioned above.

Anal. Calcd for $C_{12}H_{24}O$: C, 78.20; H, 13.12. Found: C, 78.45; H, 13.13.

2,5-Di-*t*-Butylcyclohexanols.—The separation, identification and analysis of the 2,5-di-*t*-butylcyclohexanols has been described separately.[26]

***trans*-2-Methyl-*cis*-4-*t*-butylcyclohexanol and *trans*-2-methyl-*trans*-4-*t*-4-*t*-butylcyclohexanol** were obtained from Professor Jiri Sicher.

***cis*- and *trans*-3- and *cis*- and *trans*-2-*t*-butylcyclohexanols** were obtained from Professor E. L. Eliel.

4,4-Dimethylcyclohexanol.—A mixture of 15 ml of Dowex 1 × 7.5 cation exchange resin (washed with sodium hydroxide), 10 ml of methanol, 7.2 g (0.1 mol) of isobutyraldehyde, and 7.0 g (0.1 mol) of methyl vinyl ketone was refluxed for 8 hr with stirring.[36] Distillation of the crude product gave 5.8 g (47%) of 4,4-dimethyl-2-cyclohexen-1-one, bp 92–96 (30–35 mm).

A solution of 4 g (0.032 mol) of 4,4-dimethyl-2-cyclohexen-1-one in 30 ml of glacial acetic acid and 6 ml of concentrated hydrochloric acid was hydrogenated on a Parr apparatus in the presence of 0.2 g of platinum oxide. When 2 molar equiv of hydrogen had been taken up, the sample was removed and poured onto 50 ml of ice and was extracted with four 75-ml portions of ether. The combined extract was dried over anhydrous magnesium sulfate and the solvent was removed under reduced pressure. The residue was refluxed for 4 hr with 10 ml of 15% aqueous ethanolic sodium hydroxide, poured onto 20 g of ice, and extracted with two 30-ml portions of ether. The extract was dried over anhydrous magnesium sulfate, and the ether was removed under reduced pressure. The residue was distilled giving pure (by glpc) 4,4-dimethylcyclohexanol, bp 102 (22 mm) (lit.[37] 83.5–83.8 (15 mm).

3,3-Dimethylcyclohexanols was prepared according to the procedure of Doering and Beringer.[38]

3,3- and 4,4-Dimethylcyclohexyl Acetates.—The 3,3- and 4,4-dimethylcyclohexanols were converted into the acetates employing the procedure outlined for the 3- and 4-*t*-butylcyclohexanols to facilitate analysis by glpc.

***cis*-Rich 2,4,4-Trimethylcyclohexanol.**—A mixture of 38 ml of Dowex 1 × 7.5 cation exchange resin (base-washed), 35 ml of methanol, 18 g (0.25 mol) of isobutyraldehyde, and 21 g (0.25 mol) of ethyl vinyl ketone was refluxed with stirring for 19 hr. The solution was poured into 550 ml of water and was extracted with 100 ml of ether. The aqueous phase was saturated with sodium chloride and was extracted with ether. The combined ether extract was washed with 25 ml of saturated sodium chloride solution, dried over anhydrous magnesium sulfate, and concentrated on the rotary flash evaporator. Distillation through a 50-cm spinning band column afforded 2.58 g (7.5%) of 2,4,4-trimethyl-2-cyclohexen-1-one, bp 79.5 (18 mm) (lit.[39] 190 (760 mm)).

A solution of 6.5 g (0.047 mol) of 2,4,4-trimethyl-2-cyclohexen-1-one in 5 ml of methanol was added to a suspension of 0.3 g of platinum oxide and subjected to hydrogenation with the absorption of 1 equiv of hydrogen. The solution was filtered and the methanol was removed by distillation. Distillation of the product at 70–71° (12 mm) (lit.[40] 87–89° (30 mm)) afforded 5.2 g (75%) of saturated ketone.

The saturated ketone was reduced following the procedure of Eliel and Doyle.[41] A mixture of 5.6 g (0.04 mol) of 2,4,4-trimethylcyclohexanone, 175 ml of 2-propanol, 14 ml of trimethylphosphite, and 50 ml of "Henbest catalyst"[42] was refluxed for 23 hr. The mixture was then stripped of 2-propanol and acetone under reduced pressure, diluted with 200 ml of water, and extracted with three 100-ml portions of ether. The ether extracts were combined, washed with water, and dried over potassium carbonate. After removal of the solvent on the rotary flash evaporator, the residue was distilled at 62° (16 mm) giving 5 g (89%) of alcohol, free of ketone by ir analysis and 95% pure by glpc. The nmr spectrum displays, in addition to the higher field absorption, a slightly broadened peak at −3.76 ppm, attributed to the equatorial carbinol proton, and a very broad, low-intensity absorption at −2.97 ppm due to the carbinol proton of the *trans* isomer, present as a minor impurity (~3% by glpc).

Anal. Calcd for $C_9H_{18}O$: C, 76.00; H, 12.70. Found: C, 75.80; H, 12.76.

***trans*-Rich 2,4,4-Trimethylcyclohexanol.**—An ether solution of 0.5 g (3.6 mmol) of 2,4,4-trimethylcyclohexanone was added to an ether suspension of lithium aluminum hydride and stirred for 1 hr at room temperature. The mixture was hydrolyzed with 10 ml of 10% hydrochloric acid solution and filtered. The ether was separated, washed with 10 ml of 10% hydrochloric acid solution, dried over anhydrous magnesium sulfate, and filtered. The solvent was removed on the rotary flash evaporator, and the residue was distilled on a microdistillation apparatus, bp 60–70° (16 mm) (lit.[43] 192–193° (760 mm)).

Glpc analysis of the product revealed it was a two-component mixture. The minor component (14%) is *cis*-2,4,4-trimethylcyclohexanol, and the major (86%) product is assigned the structure of *trans*-2,4,4-trimethylcyclohexanol. The latter compound was not obtained free of the other isomer. The nmr spectrum of the sample displays a broad peak at −2.97 ppm.

***cis*- and *trans*-3,3,5-trimethylcyclohexanol** were obtained from Professor E. Eliel.

***trans,cis*-Rich 2,3-dimethylcyclohexanol** was prepared according to the procedure of Ulery and Richards.[44]

***trans,trans*-2,3-Dimethylcyclohexanol.**—An attempt to prepare *trans,trans*-2,3-dimethylcyclohexanol by reduction of *cis*-2,3-dimethylcyclohexanone[35] with the "Henbest catalyst"[42] failed, producting instead a mixture containing only *cis,trans*- and *cis,cis*-2,3-dimethylcyclohexanol.[45]

Hydroboration of the Substituted Cyclohexenes.—The substituted cyclohexenes were subjected to hydroboration in tetrahydrofuran at 0° for 30 min employing a 1:2 olefin:borane-tetrahydrofuran ratio. The reaction mixtures were hydrolyzed and oxidized by the addition of a 50% excess of 20% sodium hydroxide and 30% hydrogen peroxide. After stirring at room temperature for 30 min the oxidized reaction mixtures were extracted three to five times with ether. The ether extract was dried over magnesium sulfate and concentrated by distillation employing a short Vigreaux column. The resulting ether solutions were analyzed directly by glpc, except in cases where prior acetylation was necessary, employing Carbowax columns at appropriate temperatures.

The results obtained with the individual olefins are indicated in the results and discussion section. Generally, several runs were made with each olefin, the values given being the average average values with an average deviation of generally less than 0.5%.

Determination of the Extent of Hydroboration.—Aliquots from several of the hydroboration reaction mixtures were removed and quenched with excess methanol. The samples were concentrated under reduced pressure and analyzed by ^{11}B magnetic resonance. All samples tested contained less than 5% dialkyl borinate as indicated by the intensity of the peak at −53 ppm,

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(37) E. L. Eliel and C. A. Lukach, *J. Amer. Chem. Soc.*, **79**, 5986 (1957).

(38) W. von E. Doering and F. M. Beringer, *ibid.*, **71**, 222 (1949).

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(42) A mixture of iridium trichloride, hydrochloric acid and water; *cf.* Y. M. Y. Haddad, H. B. Henbest, J. Hiesbands, and T. P. B. Mitchell, *Proc. Chem. Soc.*, 361 (1964).

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(44) H. E. Ulery and J. H. Richards, *J. Amer. Chem. Soc.*, **86**, 3113 (1964). Details of the modifications may be found in the Ph.D. Dissertation of F.K., University of Notre Dame, 1967.

(45) In view of the fact that the *trans,trans*-2,3-dimethylcyclohexanol could not be obtained in sufficiently pure form in order to determine the required accurate glpc response ratio, a response ratio was used corresponding to other *cis*- and *trans*-3-methylcyclohexanol systems. The error introduced is believed to be less than 5% of the final calculated composition percentages.

relative to boron trifluoride etherate, relative to the alkyl boronate peak at −32 ppm.

Registry No.—**1**, 2228-98-0; **2**, 3419-74-7; **5**, 15822-49-8; **6**, 15822-50-1; **7**, 14072-86-7; **8**, 933-12-0; **9**, 591-48-0; **10**, 14072-87-8; **11**, 1759-64-4; **12**, 5009-02-9; 2-methyl-5-*t*-butylcyclohexanol, 15822-55-6; 2-ethyl-5-*t*-butylcyclohexanol, 15822-56-7; *cis*-2,4,4-trimethylcyclohexanol, 15822-57-8.

Acknowledgment.—The authors wish to thank Professor E. L. Eliel and J. Sicher for kindly providing many of the compounds required in this investigation.

1,3-Bridged Aromatic Systems. III.[1,2] Ring-Opening Reactions of *gem*-Dihaloacetoxycyclopropanes

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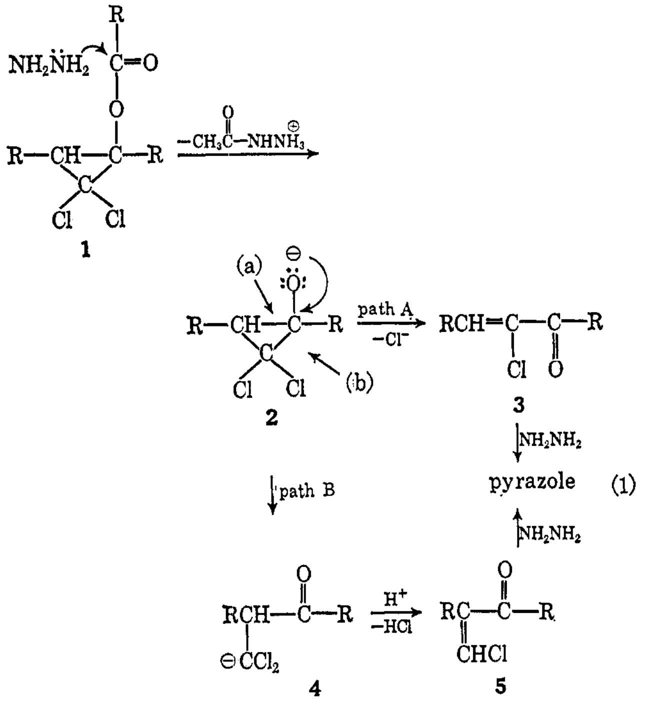
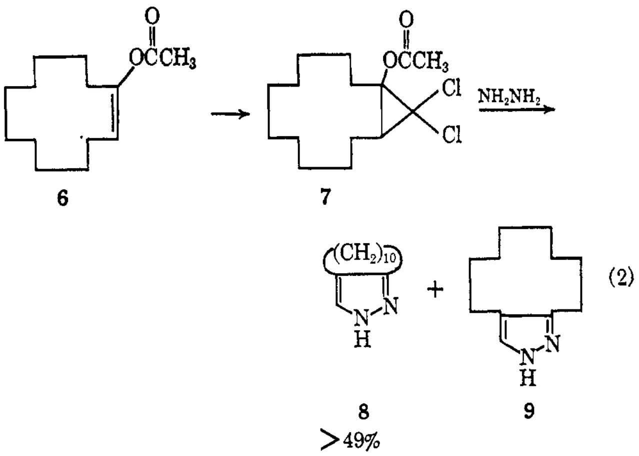
Reactions of hydrazine with dihalocyclopropanes derived from *cis*-2-buten-2-ol acetate, *trans*-2-buten-2-ol acetate, 1-cyclohexenyl acetate, and 1-cyclooctenyl acetate are described. A duality of mechanism is established for such reactions leading, in certain cases, to 3,4- and 3,5-disubstituted pyrazoles. The effect of stereochemistry and the effect of ring size on the course of reaction is considered.

We have previously reported[2a] that the reaction of dichlorocyclopropanes derived from enol acetates with hydrazine constitutes a new and useful synthesis of pyrazoles. Direct evidence for the reaction sequence shown in path A of eq 1 was provided by the observed formation of 3,5-pyrazoles with dichlorocyclopropanes derived from the enol acetates of desoxybenzoin and cyclododecanone. However, the formation of small quantities of the 3,4-substituted pyrazole **9** from **7**, in addition to the 3,5-metacyclophane **8**, suggested that[4] an alternate mechanism, as shown in path B of eq 1, may be operative. A study of the reactions of cyclopropanes **15a**, **15b**, **19b**, and **20** with hydrazine has now provided convincing evidence for the duality of mechanism as shown in eq 1, and the results of this study constitute the subject of this report.

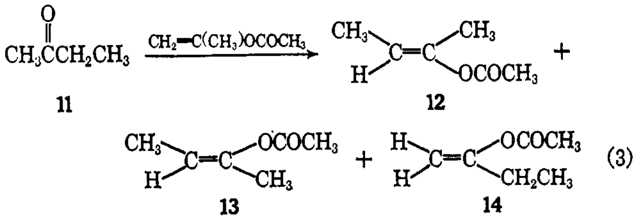


(1)



(2)

Treatment of butanone (**10**) with isopropenyl acetate (**11**) and *p*-toluenesulfonic acid afforded a mixture[5] of isomeric enol acetates (eq 3) which were separated by preparative vapor phase chromatography. The *cis* isomer **12** was obtained pure; however, **13** and **14** were not completely separated by glpc, and the mixture containing 77% of **13** and 23% of **14** was used in subsequent reactions.



(3)

The configurations of **12** and **13** were assigned on the basis of long-range coupling between the protons in the methyl groups, the differences in chemical shift for the β-olefinic protons, and comparison with model compounds. In this case homoallylic coupling between

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(1) Supported by the National Science Foundation Grant GP-6169X.

(2) For previous papers in this series, see (a) W. E. Parham and J. F. Dooley, *J. Amer. Chem. Soc.*, **89**, 985 (1967); (b) W. E. Parham and J. K. Rinehart, *ibid.*, **89**, 5668 (1967).

(3) Taken in part from the Ph.D. thesis of J. F. Dooley, University of Minnesota, 1967.

(4) Chloro ketones of type **3** and **5** are known to give 3,5- and 3,4-disubstituted pyrazoles, respectively, by reaction with hydrazine. *Cf.* K. V. Auwers and H. Broche, *Ber.*, **55**, 3880 (1922), and K. W. Auwers and R. Hugel, *J. Prakt. Chem.*, [2] **143**, 157 (1935).

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