TABLE II

HYDROGEN EVOLUTION FROM REACTIONS OF *o*-DINITROSOBENZENE (DNB) AND OF *o*-BENZOQUINONE DIOXIME (BQD) WITH SODIUM BOROHYDRIDE (SBH)

Compound[a]	G.	Mmole	SBH,[a,b] mmole	Hydrogen evolved during reaction[c] Cc.	Mmole	Hydrogen evolved by acid Cc.	Mmole	Excess SBH,[d] mmole	SBH consumed in reaction, mmole
DNB	0.0890	0.654	0.745	12.5	0.509[e]	18.7	0.761	0.190	0.555
DNB	.0902	.663	.745	13.5	.550	18.8	.765	.191	.554
BQD	.0839	.608	.701	20.4	.833	14.2	.580	.145	.556
BQD	.0350	.254	.701	9.2	.375	39.1	1.59	.398	.303

[a] Samples dissolved in 3 ml. of diglyme purified by distillation from lithium aluminum hydride and redistilled, b.p. 88–90° (52 mm.). [b] SBH (0.769 mmole) which assayed 97.0% used with DNB; SBH (0.769 mmole) which assayed 91.2% used with BQD. [c] Blank runs with sodium borohydride in purified diglyme gave no more than 0.1 cc. of evolved gas after 2.5 hours at 35–40°. For DNB, reaction time was 3 hours at 35–40°; for BQD, reaction time was 1.5 hours at 35–40°; hydrogen measured at 27° (762 mm.). [d] One-fourth of the mmoles of hydrogen evolved by acid according to the equation $NaBH_4 + H_2SO_4 + 3H_2O \rightarrow 4H_2 + H_3BO_3 + NaHSO_4$. [e] Sample calculation: $n = (762/760)0.0125/0.08205\ (300) = 0.000509$ mole = 0.509 mmole.

ranged from 0–30%. The initially acidified reaction mixture was made strongly alkaline with sodium hydroxide with the precipitation of 0.1–0.2 g. of a yellow or brown solid which did not melt below 300° and was insoluble in hot methylene chloride or *n*-hexane but very soluble in hot ethanol. It dissolved readily in cold concentrated hydrochloric acid or glacial acetic acid and gave a wine colored solution in each case; it was insoluble in cold 10% sodium hydroxide. It could be sublimed with difficulty at 170–180° (0.02 mm.) whereupon a red-orange solid which did not melt below 300° was obtained.

Reduction of nitroso derivatives and furoxans is summarized in Table I.

In two experiments, *o*-dinitrosobenzene was treated with excess sodium borohydride (assayed by hydrogen evolution in a reaction with sulfuric acid) in diglyme following a procedure[13] which allowed the collection over mercury of evolved hydrogen. Excess borohydride was removed with dilute sulfuric acid. Based on hydrogen evolution measured before and after treatment with acid, the amount of sodium borohydride used in reduction was calculated. A sample of the gas collected above water during the reduction burned explosively in air and gave negative tests for the presence of boron compounds. Under similar conditions *o*-benzoquinone dioxime was treated with sodium borohydride. The results obtained with each compound are described in Table II.

Reaction of Bis-(α-hydroxybenzyl)-furoxan with Sodium Hydroxide.—A suspension of 0.30 g. (1.0 mmole) of the furoxan in 15 ml. (38.0 mmoles) of 10% sodium hydroxide solution was stirred at room temperature for 45 minutes. The solid slowly dissolved as the solution became pink and finally yellow and the odor of benzaldehyde was noted. After acidifying with 5 ml. of glacial acetic acid, a solution of 2,4-dinitrophenylhydrazine was added, the mixture was heated to the boiling point, cooled to 0° and filtered. The crude product recrystallized from methanolic hydrochloric acid as small orange plates of benzaldehyde 2,4-dinitrophenylhydrazone, m.p. and mixture m.p. 243–245°, 0.12 g. (21%).

NEW ORLEANS 18, LA.

(13) J. C. Rankin and C. L. Mehltretter, *Anal. Chem.*, **28**, 1012 (1956).

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, THE UNIVERSITY OF FLORIDA]

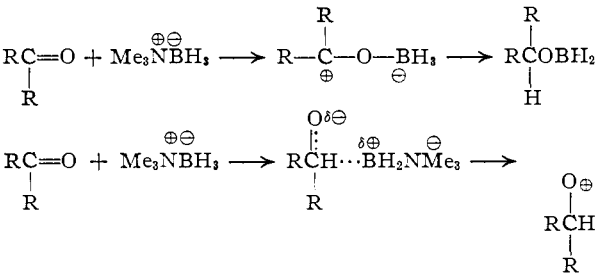
Amine Borane Reductions. The Stereochemistry of the Reduction of 4-*t*-Butylcyclohexanone with Trimethylamine Borane in the Presence and Absence of Boron Fluoride

BY W. M. JONES

RECEIVED OCTOBER 9, 1959

The reduction to the alcohol of 4-*t*-butylcyclohexanone with trimethylamine borane and diborane in neutral, non-aqueous solvents was found to give approximately 16% of the *cis* isomer in each case. These results suggest that the two reactions have a common intermediate. On the other hand, the reduction of 4-*t*-butylcyclohexanone with trimethylamine borane and diborane in the presence of boron fluoride gave, under the same conditions, 46–52% and 16% *cis*-4-*t*-butylcyclohexanol, respectively. These results are rationalized in terms of the trimethylamine borane reduction proceeding by initial complexing of the boron fluoride with the carbonyl oxygen followed by intermolecular hydride transfer from the amine borane. Evidence is also presented which indicates that the resulting ionic intermediate I decompose to 4-*t*-butylcyclohexyldifluoroboronite II and III.

Of the many substituted boranes and borohydrides that have been found in the past few years to be effective reducing agents[1] one which we feel has potential for becoming especially useful due to its stability[1b,2] and convenience to deal with is trimethylamine borane.[3] The possibility that carbonyl reductions involving this reagent might well proceed by either of the general paths



(1) (a) N. G. Gaylord, "Reduction with Complex Metal Hydrides," Interscience Publishers, Inc., New York, N. Y., 1956; (b) Callery Chemical Co., Technical Bulletin C-200, Callery, Penna., April 1, 1958.

(2) A. B. Burg and H. I. Schlesinger, THIS JOURNAL, **59**, 780 (1939).

(3) Commercially available from Callery Chemical Co., Callery, Penna. The trimethylamine borane employed in these investigations was most generously supplied by this company.

intrigued us to undertake a rather thorough examination of this reaction. The first approach which we elected to pursue was the stereochemical consequences of the reduction of 4-*t*-butylcyclohexanone[4] in the presence and absence of Lewis acids.[5]

Reduction of 4-*t*-Butylcyclohexanone with Trimethylamine Borane and Diborane in the Absence of Lewis Acids.—The reduction of 4-*t*-butylcyclohexanone with trimethylamine borane in neutral, non-aqueous solvents (diglyme, benzene) was found to be quite slow even at steam-bath temperature. The stereochemical consequences of this reaction were not appreciably different in the two solvents, the reductions in benzene and diglyme being found to give mixtures of the two isomeric alcohols consisting of 15% and 17% *cis*-4-*t*-butylcyclohexanol, respectively. Reduction of the ketone was also effected in diglyme by employing diborane as the reducing agent.[6] Whereas at low temperature (ice-bath) diborane caused quantitative reduction to a mixture of 8.5% *cis*-4-*t*-butylcyclohexanol and 91.5% of the *trans* isomer, reduction effected by passing diborane into a hot solution (steam-bath) of the ketone in diglyme gave a mixture of 16% *cis*-5-*t*-butylcyclohexanol and 84% of the *trans* alcohol.

Reduction in the Presence of Lewis Acids.—In the presence of added BF_3 (as the etherate), trimethylamine borane was found to be a much more effective reducing agent. Not only was the rate of the reduction drastically increased, but the stereochemistry of the reduction was found to be quite different from that observed in the absence of added Lewis acid. Thus, for example, when ketone, trimethylamine borane and boron fluoride etherate were mixed in a 1:1:1 molar ratio, the ketone was quantitatively reduced to 4-*t*-butylcyclohexanol in a matter of seconds. The product was found to contain 46% of the *cis*-alcohol and 54% of the *trans* isomer. It was also found that the amount of reduction (in two minutes) was not affected by changing the molar ratios of starting materials as long as the acid was kept equal to or in excess of the ketone and as long as the trimethylamine borane:ketone ratio was one-half or greater. The stereochemical consequences of the reduction were not affected by changes in the concentration of trimethylamine borane as long as the trimethylamine borane:ketone ratio was equal to or greater than one. Reduction of this ratio below one caused small increases in the amount of the *cis* isomer produced (see Discussion).

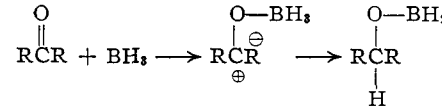
Exploratory reductions were also run with other Lewis acids; *e.g.*, aluminum chloride. Although the majority of these results will be reported in a future paper, it is of interest and perhaps significant that the aluminum chloride-catalyzed reduction gave a mixture of alcohols consisting of 25% *cis*-4-*t*-butylcyclohexanol and 75% of the *trans*-alcohol.

TABLE I

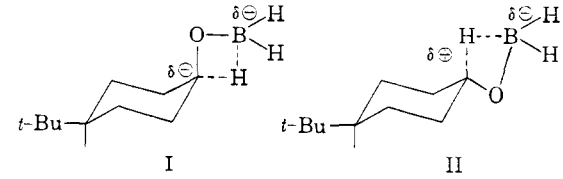
Molar ratio: Ketone	Trimethylamine borane	Boron fluoride	Reduction time	Reduction, %	*cis*-Alcohol, %	*trans*-Alcohol, %
1.0	1.0	1.0	2 min.	100	46	54
1.0	2.0	1.0	30 min.	100	46	54
1.0	4.0	1.0	30 min.	100	46	54
1.0	2.0	3.0	30 min.	100	46	54
1.0	0.2	1.0	1 min.	39		
1.0	.2	1.0	12 min.	40		
1.0	.33	1.0	2 min.	68	49	51
1.0	.33	0.67	2 min.	67	49	51
1 0	.33	1.0	16 hr.	100	52	48
1.0	1.0	0.3	1 min.	31		
1.0	1.0	.33	10 min.	35		
1.0	0.33	.33	10 sec.	31		
1.0	.33	.33	20 min.	35		
1.0	.33	.44	1 min.	42		
1.0	.33	.44	12 min.	45		

Discussion

Diborane and Uncatalyzed Trimethylamine Borane Reductions.—Brown, Schlesinger[6b] and Burg have suggested that diborane reductions of ketones most likely proceed by an initial complexing of the BH_3 moiety with the carbonyl oxygen followed by intramolecular hydride shift.



This mechanism gives a reasonable explanation for the stereochemical consequences of the diborane reduction of 4-*t*-butylcyclohexanone in diglyme. Since the product-determining transition state is reminiscent of the product, it would be expected that II would be favored over I and the *trans* isomer would predominate. The fact



I II

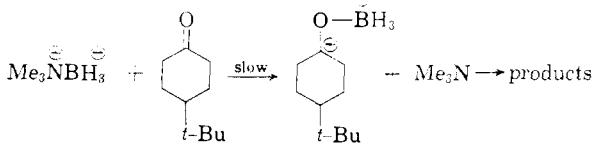
that the diborane and the uncatalyzed trimethylamine borane reductions gave essentially identical ratios of isomeric alcohols (17% *cis* and 16% *cis*, respectively) suggests that the two reactions might well have a common intermediate. Thus, it is suggested that the uncatalyzed reduction of 4-*t*-butylcyclohexanone with trimethylamine borane proceeds by initial slow formation of the ketone–borane complex by either initial dissociation of the Me_3NBH_3 or, perhaps, by participation of the carbonyl oxygen, followed by rapid intramolecular hydride shift.

Kinetic investigations are in progress to gain further evidence for this suggested reaction path as well as to determine the role of the ketone, if any, in the breaking of the boron–nitrogen bond.

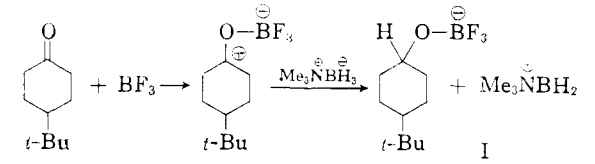
(4) This ketone was selected in order to ensure the formation of conformationally pure *cis*- and *trans*-cyclohexanol products; *cf.* S. Winstein and N. J. Holness, THIS JOURNAL, **77**, 5562 (1955).

(5) E. L. Eliel and M. N. Rerick (*ibid.*, **82**, 1362 (1960)) have recently reported a similar study of the effect of aluminum chloride on the stereochemistry of cyclohexanone reductions employing lithium aluminum hydride as the reducing agent.

(6) (a) H. C. Brown and B. C. Subba Rao, *J. Org. Chem.*, **22**, 1135 (1957); (b) H. C. Brown, H. I. Schlesinger and A. B. Burg, THIS JOURNAL, **61**, 673 (1939).



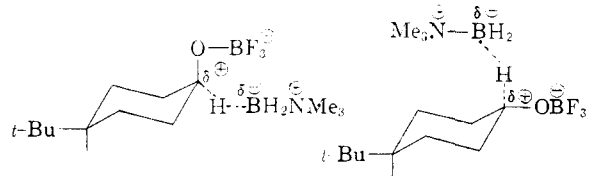
Lewis Acid-catalyzed Reductions.—The catalytic effect of boron fluoride in the trimethylamine borane reductions apparently does not arise from initial reaction of the Lewis acid with the amine borane to give diborane[1b] followed by reduction since this reaction should lead to the same stereochemical results as the reduction with diborane. Instead, as indicated in Table I, this reaction gave a mixture consisting of 46% *cis*-4-*t*-butylcyclohexanol and 54% of the *trans* isomer. The known facile reaction of ketones with boron fluoride[6b,7] suggests that the reaction probably proceeds by initial complexing of the carbonyl oxygen with the acid followed by an intermolecular hydride transfer from the amine borane.



I

The stereochemistry of the reaction is then readily explained by the sequence summarized by Dauben, Fonken and Noyce.[8] These investigators pointed out that the stereochemical consequences of the reduction of a cyclohexanone proceeding by an intermolecular hydride transfer should be governed by two competing factors which they chose to call "*steric approach control* and "*product development control.*" It was suggested that steric approach control should favor formation of the *axial*-alcohol due to interference arising from interaction between the incoming reducing species and 3,5-*axial* hydrogens. On the other hand, product development control should favor formation of the thermodynamically more stable alcohol (in this case, the *trans* product).[9]

Thus, applying this idea to hydride transfer to the complexed ketone, two possible transition states need to be considered.



In view of the bulky nature of the reducing agent it might have been expected that steric approach control would be even more important than was observed. However, in the present case we are reckoning with a rather large "effective oxygen" size (oxygen complexed with BF_3) which apparently offsets the steric control enough to make the two effects of about equal importance.

Consistent with these suggestions is the fact that reduction in the presence of aluminum chloride, which should create even a larger effective oxygen size, was found to give a mixture of 25% *cis*- and 75% *trans*-alcohols. Thus, applying the above ideas, in this case the product development control becomes appreciably more important than the steric approach control.

To this point, the discussion on acid-catalyzed reductions has dealt with only one of the three potential reducing hydrogens of trimethylamine borane. It was therefore of interest to investigate this reaction further in an attempt to determine the number of amine borane hydrogens actually involved in the reduction with an excess of the amine borane as well as to determine the conditions necessary for employing all three of these available hydrogens.

It was mentioned earlier that the amount of reduction (in two minutes) was not affected by changing the molar ratios of starting materials as long as fluoride was kept in excess and the amine borane:ketone ratio was 0.5 or greater. If, however, this ratio was made less than one-half, reduction was not complete in a few minutes and the amount of reduction was found to be equal to twice the amount of amine borane present. For example, in the presence of a full mole of BF_3 and ketone, 0.2 mole of amine borane led to 40% reduction in one minute or twelve minutes; one-third of a mole of the amine borane led to 68% reduction, etc. Thus, it is clear that in a short time and in the presence of a limited amount of amine borane, only two of the available reducing hydrogens are employed. Further, it is obvious that in the presence of excess amine borane, at most two of the hydrogens are used and possibly only one.

To gain information on the relative rates of the first two steps, the products from the reductions involving a limited amount of trimethylamine borane were analyzed. It was found that in those cases where the amine borane was forced to use two of its reducing hydrogens, the reduction gave a mixture of the stereoisomeric alcohols consisting of 49% of the *cis* isomer and 51% of the *trans* material. Although this is just outside the region of experimental error (±1%), these results were consistently obtained and we feel real confidence in their validity. This change in stereochemistry can be explained by assuming that, in the presence of excess trimethylamine borane, reduction involves only one of the amine borane reducing hydrogens to give 46% *cis*-alcohol[10]; however,

2 trimethylamine borane + $2BF_3 \longrightarrow B_2H_6 + 2Me_3NBF_3$

(7) V. Gasselin, *Ann. chim. phys.*, [7] **3**, 58 (1894).

(8) W. G. Dauben, G. J. Fonken and D. S. Noyce, THIS JOURNAL, **78**, 2579 (1956).

(9) K. D. Hardy and R. J. Wicker (*ibid.*, **80**, 640 (1958)), have recently pointed out that this argument does not lead to a totally consistent explanation of the observed stereochemistry of cyclohexanone reductions with lithium aluminum hydride, sodium borohydride and various other reducing agents. However, we still feel that it offers a reasonable approach to the system under question.

(10) The possibility that reduction in the presence of excess trimethylamine borane actually involves competing reactions employing both the first and second available hydrogens was eliminated by varying the amine borane:ketone ratio (to as high as 4:1). It was found that the stereochemistry of the reaction was insensitive to these changes.

These observations also eliminate the possibility that the decrease in the amount of *cis* isomer formed upon increasing the trimethylamine

in the presence of a limited amount of amine borane, the second hydrogen is also employed in a somewhat slower reaction which gives 52% of the *cis* isomer.

Finally, it was found that the reaction of ketone, trimethylamine borane and BF_3 in the molar ratio 1.0:0.33:1.0, when allowed to remain at room temperature for several hours, gave quantitative reduction to a mixture of 52% *cis*-4-*t*-butylcyclohexanol and 48% of the *trans* isomer. Thus, the third reducing hydrogen can be utilized under the proper conditions to give approximately 58% of the *cis* isomer. These results also imply an increase in the importance of steric approach control in the second and third reducing steps.

In an attempt to gain some information on the fate of the suggested intermediate I, experiments were conducted in which the amount of boron fluoride was limited. Intermediate I might be expected to decompose in any of the following ways.

$$\overset{\ominus}{\mathrm{ROBF_3}} + \overset{\oplus}{\mathrm{Me_3N}}\mathrm{BH_2} \longrightarrow \overset{\oplus\ominus}{\mathrm{Me_3NBH_2OR}} + \mathrm{BF_3} \quad (1)$$

$$\overset{\ominus}{\mathrm{ROBF_3}} + \overset{\oplus}{\mathrm{Me_3N}}\mathrm{BH_2} \longrightarrow \mathrm{ROBH_2} + \overset{\oplus\ominus}{\mathrm{Me_3NBF_3}} \quad (2)$$

$$\overset{\ominus}{\mathrm{ROBF_3}} + \overset{\oplus}{\mathrm{Me_3N}}\mathrm{BH_2} \longrightarrow \underset{\mathrm{II}}{\mathrm{ROBF_2}} + \underset{\mathrm{III}}{\overset{\oplus\ominus}{\mathrm{Me_3NBH_2F}}} \quad (3)$$

R = 4-*t*-butylcyclohexyl

Path 1 is obviated by the observation that, in the first step of the reduction, boron fluoride is not regenerated. Thus, it was found that, in the presence of excess trimethylamine borane, the amount of reduction effected in a short period of time was directly proportional to the amount of the Lewis acid present. For example, a decrease in the boron fluoride:ketone ratio to one-third caused the amount of reduction to drop to one-third in one minute and ten minutes (31 ± 3% and 35 ± 3%, respectively). Experiments of this type (Table I) also shed some doubt on path 2 since non-catalyzed reduction involving the second reducing hydrogen on the original trimethylamine borane is much slower than might be anticipated for a monoalkoxy borine.[6] Further evidence for the exclusion of this path was the absence of the relatively insoluble trimethylamine boron fluoride complex.

At the present time, it is therefore suggested that the boron fluoride-catalyzed reduction of 4-*t*-butylcyclohexanone proceeds by initial completing between the boron fluoride and the carbonyl oxygen followed by intermolecular hydride transfer to give intermediate I. It is further suggested that this intermediate decomposes by fluorine transfer[11] to give 4-*t*-butylcyclohexyl difluoroboronite II and III.

In the presence of excess boron fluoride and limited trimethylamine borane the suggested product III can then effect further reduction in a slower step than the initial hydride transfer. Finally, it was particularly interesting that reduction in the presence of a ketone:trimethylamine borane: boron fluoride ratio of 1.0:0.33:0.44 stopped after approximately 44% reduction had occurred (Table I). Thus, when the second reducing hydrogen is forced to take part in the reaction, not only does it require a molecule of boron fluoride, but, again, the boron fluoride is lost from the reaction.

borane:ketone ratio from 0.5 to 1.0 resulted from a competing reaction with diborane since, again, a further increase in this ratio should have effected still a further decrease in the amount of *cis*-alcohol formed.

(11) Fluorine transfers from boron are not at all uncommon; *e.g.* see H. G. Cook, J. D. Ilett, B. C. Saunders and G. J. Stacey, *J. Chem. Soc.*, 3125 (1950), V. Gasselin, *Ann. chim. phys.*, **3**, 5 (1894); M. F. Lappert, *J. Chem. Soc.*, 784 (1955).

Experimental

The Reaction of 4-*t*-Butylcyclohexanone with Trimethylamine Borane.—In a typical run, equimolar amounts of 4-*t*-butylcyclohexanone (0.40 g., 2.6 millimoles) and trimethylamine borane (0.188 g., 2.6 millimoles) were dissolved in 4.0 ml. of very dry diethylene glycol dimethyl ether[12] and the resulting clear solution was warmed on a steam-bath. After 3 days the mixture was cooled, poured into 5% sodium bicarbonate solution and extracted with pentane. The pentane extract was then washed several times with water, dried over sodium sulfate and evaporated to dryness. The residual colorless oil was dissolved in 10 ml. of ethanol and excess 2,4-dinitrophenylhydrazine solution[13] was added. After several hours, the precipitated 4-*t*-butylcyclohexanone-2,4-dinitrophenylhydrazone was removed by filtration (0.390 g., 55% reduction) and the filtrate was poured into water. The aqueous solution was extracted with pentane and the light yellow pentane solution was washed several times with water, dried over sodium sulfate and evaporated to dryness. The residue was analyzed by gas chromatography techniques employing an 18-foot column of 60–80 mesh commercial detergent[14] in a Perkin–Elmer 154-B vapor fractometer at 188° at an internal pressure of 16 p.s.i. and a recorder range of 1. Employing peak heights which were found, in this case, to be far more reliable than integrated intensities the mixture was found to contain in three chromatography runs: 16.5%, 15.5% and 16.0% *cis*-4-*t*-butylcyclohexanol.[15]

Some of the above experimental details deserve brief further discussion. In some of the earlier experiments, the crude reaction mixtures resulting from the reductions were decomposed in aqueous acid. However, it was found that in those cases in which reduction was not complete this created difficulties due to very rapid reduction of the ketone in aqueous acid solution. This rapid reduction did not occur in alkaline solution. Resorting to this method did introduce one potential problem in that dilute base does not decompose trimethylamine borane at a very rapid rate. However, trimethylamine borane is more soluble in water than it is in pentane[1b] and it was found that a few washings with water removed virtually all of the unreacted trimethylamine borane. One other difficulty was the fact that, under the chromatography conditions outlined above, 4-*t*-butylcyclohexanone has approximately the same retention time as *cis*-4-*t*-butylcyclohexanol. This problem was effectively eliminated by precipitating the ketone as its 2,4-dinitrophenylhydrazone before analysis. Precipitation of the ketone as its 2,4-dinitrophenylhydrazone was also employed to determine the extent of reduction.

Reaction of Trimethylamine Borane with 4-*t*-Butylcyclohexanone in the Presence of Added BF_3.—In a typical run, equimolar amounts of 4-*t*-butylcyclohexanone (0.40 g., 2.6 millimoles) and trimethylamine borane (0.188 g., 2.6 millimoles) were dissolved in 4.0 ml. of dry diglyme. The mixture was cooled in an ice-bath and swept well with dry nitrogen. Boron fluoride etherate (0.26 ml., 2.6 millimoles) was introduced. After an appropriate time interval, the clear solution was poured into 5% sodium bicarbonate solution and extracted with pentane. After drying the pentane solution over sodium sulfate, the mixture was evaporated to dry-

(12) H. C. Brown, E. J. Mead and B. C. Subba Rao, THIS JOURNAL, **77**, 6209 (1955).

(13) R. L. Shriner and R. C. Fuson, "The Systematic Identification of Organic Compounds," John Wiley and Sons, Inc., New York, N. Y., p. 171.

(14) This material was graciously donated by the Procter and Gamble Co. of Cincinnati, Ohio; *cf.* E. L. Eliel and R. S. Ro, THIS JOURNAL, **79**, 5992 (1957).

(15) For calibration purposes, pure *cis*- and *trans*-4-*t*-butylcyclohexanols were synthesized by the method of Winstein and Holness.[4]

ness. The residual product gave a negative 2,4-dinitrophenylhydrazine reaction and, upon analysis by gas chromatography, was found to contain, in two runs, 46.5% and 46.0% *cis*-4-*t*-butylcyclohexanol.

Reduction of 4-*t*-Butylcyclohexanone with Diborane.—Dry diborane (from trimethylamine borane and boron fluoride)[15] was bubbled into a cold, rapidly stirred solution of 4-*t*-butylcyclohexanone in diglyme (under nitrogen). An acetone trap was used to catch and destroy any unreacted diborane.[6a] The diborane addition was continued until the carbonyl absorption of the unreacted ketone had disappeared. The solution was then poured into water, extracted with pentane, dried over sodium sulfate and evaporated to dryness. Gas chromatographic analysis of the product showed 8.5% *cis*-4-*t*-butylcyclohexanol and 91.5% of the *trans*-product.

When the same reaction was effected at steam-bath temperatures, it was found that the carbonyl absorption disappeared very slowly. This was probably due to insolubility of the diborane in diglyme at this elevated temperature. The reaction was finally stopped, worked up as usual and the unreacted ketone precipitated as the 2,4-dinitrophenylhydrazone. The filtrate was poured into water, extracted with pentane, dried and evaporated. Analysis of the residue showed it to contain 16% *cis*-4-*t*-butylcyclohexanol and 84% of the *trans* isomer.

Reduction of the 4-*t*-Butylcyclohexanone with Diborane in the Presence of BF_3.—In a typical run, equimolar amounts of 4-*t*-butylcyclohexanone (0.40 g., 2.6 millimoles) and boron fluoride ethyl ether (0.26 ml., 2.6 millimoles) were dissolved in 4.0 ml. of dry diglyme. The mixture was swept well with nitrogen and cooled in an ice-bath. Diborane was bubbled into the solution until the carbonyl absorption had disappeared. The mixture was then worked up and analyzed. It was found to contain, in two runs, 15.0 and 15.5% of the *cis*-alcohol.

Acknowledgments.—The author is indebted to Dr. G. E. Ryschkewitsch for his many helpful discussions on this work.

GAINESVILLE, FLA.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, IOWA STATE UNIVERSITY]

Electronic Effects in Elimination Reactions. IV. Elimination of β-Phenylethyl Derivatives in *t*-Butyl Alcohol[1,2]

BY C. H. DEPUY AND C. A. BISHOP

RECEIVED SEPTEMBER 26, 1959

Rates of bimolecular elimination reactions of a series of *m*- and *p*-substituted β-phenylethyl bromides, iodides and tosylates have been determined in *t*-butyl alcohol with *t*-butoxide and ethoxide as the bases. By use of the Hammett treatment it is shown that the halides undergo a more highly concerted elimination than do the tosylates. A theory is advanced to account for the low reactivity of the tosylates in this elimination, and the nature of the transition state in E_2 reactions of halides and tosylates is discussed in the light of this work and the recent work of Saunders and Edison[3] on kinetic deuterium isotope effects in this system. Rho values for the SN2 reaction of β-phenylethyl tosylates with ethoxide are also reported and briefly discussed.

Recent studies on the E_2 reaction of β-phenylethyl compounds have shown that in the transition state of this bimolecular elimination reaction a great deal of carbanionic character develops on the benzyl carbon.[4,5] Thus for a series of *m*- and *p*-substituted β-phenylethyl bromides and iodides the Hammett ρ-values[6,7] for eliminations by ethoxide ion in ethanol were +2.1, and this value rose to +2.7 for the corresponding sulfonium salts. At the same time it was recognized that a certain amount of double-bond character was present in the transition state, for the rigid stereochemical requirements of the reaction[8] and the sensitivity of the rate of elimination to the nature of the leaving group show that carbon–hydrogen and carbon–halogen bond breaking are highly synchronous. Although in the cases studied the acidity of the hydrogen atom being removed was very important in determining the rate of the reaction, other evidence has accumulated that the transition state in E_2 eliminations may be altered with a change in the leaving group or the base. Thus it was shown[9] that the relative rates of the E_2 reaction of diastereomeric 1,2-diphenyl-1-propyl chlorides and bromides were a function of the base used, the stronger base giving rise to a transition state with more double bond character and hence with greater eclipsing of adjacent groups. More recently Saunders and Edison[3] studied the kinetic isotope effect in the elimination of β,β-dideuterio-β-phenylethyl derivatives and showed that the extent of bond-breaking in the transition state varied with the leaving group and the strength of the base used (*vide infra*).

In an attempt to delineate more precisely the course of the reaction, and especially the timing of the bond-breaking processes, we have studied the rates of the E_2 reaction of substituted β-phenylethyl bromides, iodides and tosylates with potassium *t*-butoxide in *t*-butyl alcohol and with potassium ethoxide in *t*-butyl alcohol. It was hoped that a study of substituent effects with the stronger base would shed more light on the removal of the hydrogen and, at the same time, elucidate the reasons for the abnormally slow eliminations of the tosylates[4] in this system. Both of these hopes have, to an extent, been realized.

The rates of the E_2 reactions for the unsubstituted, *p*-methoxy-, *p*-chloro-and *m*-bromo-β-phe-

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(2) This research was supported by a grant from the Petroleum Research Fund administered by the American Chemical Society. Grateful acknowledgment is hereby made to the donors of these funds.

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