Reduction of Epoxides. III. The Lithium Aluminum Hydride and Mixed Hydride Reduction of Some Secondary–Tertiary Epoxides[1]

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Abstract: The lithium aluminum hydride (LAH) and mixed LAH–aluminum chloride reductions of the epoxides of 1-methylcyclohexene, 1,2-dimethylcyclohexene, 1,4-dimethylcyclohexene, 1-methyl-4-*t*-butylcyclohexene, and *trans*-2-methyl-Δ^2-octalin in ether have been examined. In certain cases considerable product control is possible through choice of reagent. Energy parameters have been determined for the various factors which control the direction of opening of substituted cyclohexene oxides, *i.e.*, secondary *vs.* tertiary hydride attack, chair *vs.* twist transition state, and contributions from alternate half-chair epoxide conformations.

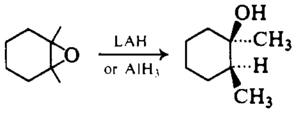
Recent work[3-5] with substituted cyclohexene oxides has shown that these systems are reduced by LAH or aluminum hydride[6] in a highly selective manner,[9] with products explicable entirely on the basis of *trans*-coplanar (diaxial) opening.[11] In fact, excluding *cis*-opening processes, we know of no well-authenticated example of "equatorial" opening of any cyclohexene oxide.[12] It is clear that a substantial energy difference favors diaxial opening over the hypothetical (but not yet observed) diequatorial opening mechanism.

However, equatorial products are not infrequently obtained in reactions of epoxides. When these are the products of a kinetically controlled reaction, as in the present study, one may readily rationalize their formation on the basis of some specific feature of the reactant epoxide, *e.g.*, steric effects or the absence of strong conformation-holding effects.

The purpose of the present work was to explore the interrelationships of the various factors which can affect the reduction of substituted cyclohexene oxides by LAH and aluminum hydride, if possible to quantify these factors, to determine the mechanism of equatorial alcohol formation, and to ascertain the degree of product control available through variation of the reducing species.

Results and Discussion

The classical work of Trevoy and Brown[14] first established that LAH reduction of 1,2-dimethylcyclohexene oxide (**1**) occurs with inversion of configuration. Although this work has been widely quoted, the analytical data (boiling point, refractive index, and density) do not allow a high degree of specificity to be assigned to this reduction. We have repeated this reaction, and, within the usual limits of vpc detection (0.1%), only alcohol **2** is formed.



1 **2**

The more electrophilic aluminum hydride could conceivably give rise to *cis* opening of **1**, but in fact this reagent also leads to exclusive formation of **2**.

1-Methylcyclohexene oxide (**3**) is of particular interest, as its reduction leads to a direct method for determining the degree of preference for hydride attack at a secondary over a tertiary carbon. Preliminary examination of two samples of this epoxide prepared by peracid treatment of the corresponding olefin indicated contamination by trace amounts (0.05 and 0.08%) of 2-methylcyclohexanone. A small amount of highly purified epoxide was obtained by preparative vpc for the LAH reduction. Although for all practical purposes this reaction leads to tertiary alcohol (**4**),[8] 0.63% of secondary alcohol is also formed. Separate analysis showed that this minor component consisted of 90.3% *cis*-2-methylcyclohexanol (**5**) and 9.7% of *trans*-2-methylcyclohexanol (**6**); this ratio is in accord with that observed in reductions of other cyclohexene epoxides,[9] and lends strong support to the

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

[3] Part II: B. Rickborn and W. E. Lamke, II, *J. Org. Chem.*, **32**, 537 (1967).

[4] B. Rickborn and J. Quartucci, *ibid.*, **29**, 3185 (1964).

[5] B. Rickborn and S. Lwo, *ibid.*, **30**, 2212 (1965).

[6] This term will be used in the present paper to designate the reagent that is formed on mixing LAH and aluminum chloride in a 3:1 molar ratio in ether. The complex nature of this reagent has been discussed by a number of authors.[7,8]

[7] (a) E. L. Eliel, *Record Chem. Progr. Kresge-Hooker Sci. Lib.*, **22**, 129 (1961); (b) E. C. Ashby and J. Prather, *J. Amer. Chem. Soc.*, **88**, 729 (1966).

[8] H. C. Brown and N. M. Yoon, *ibid.*, **88**, 1464 (1966).

[9] For example, the reduction of *trans*-4-*t*-butylcyclohexene oxide by LAH gives 90% *trans*-3-ol and 10% *cis*-3-ol.[4] The minor product arises from an "oxidative inversion" mechanism which has already been described,[4] and which appears to be a general phenomenon in cyclohexene[3,5] and larger cyclic olefin epoxide reductions with this reagent.[10] Although two products are formed, it is evident that the initial attack by hydride occurs with very high position specificity.

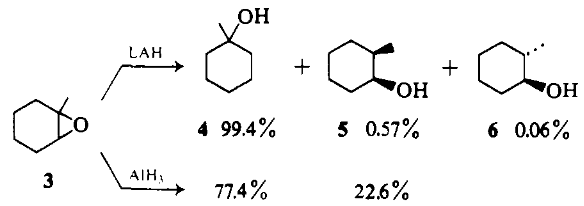
[10] A comparable result has been obtained in the reduction of a cyclodecene oxide; personal communication from Professor J. Sicher, Prague.

[11] A. Furst and P. A. Plattner, *Helv. Chim. Acta*, **32**, 275 (1949).

[12] The reported[13] formation of diequatorial diol in the reaction of *trans*-2,3-dimethyl-Δ^2-octalin oxide with aqueous acid has been shown to be in error; unpublished work of B. Rickborn and D. K. Murphy.

[13] H. B. Henbest, M. Smith, and A. Thomas, *J. Chem. Soc.*, 3293 (1958).

[14] L. W. Trevoy and W. G. Brown, *J. Am. Chem. Soc.*, **71**, 1675 (1949).

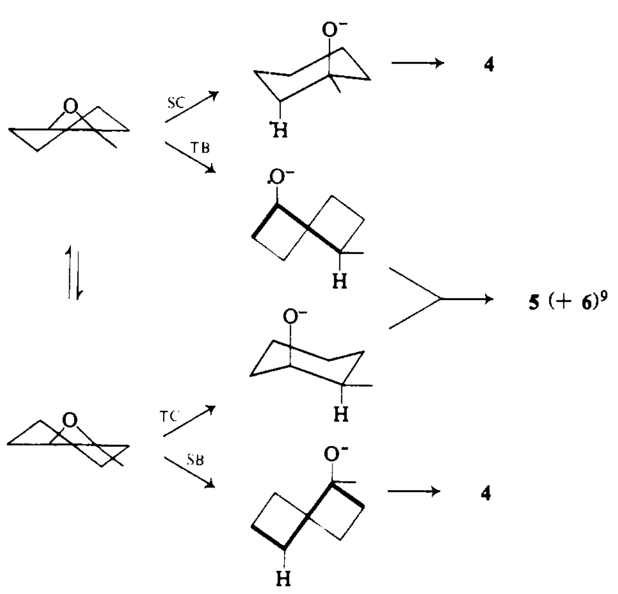


assignment of the secondary alcohols as direct products of LAH reduction of the epoxide.[15]

Aluminum hydride (in ether)[6] reduction of **3** gives a substantial amount of product derived from attack at the tertiary center. In agreement with the results from **1** this product is exclusively *cis* (**5**), formed by inversion of configuration at the cleaved center. As anticipated on the basis of earlier work,[4] no oxidative inversion[9] occurs with this reagent. Brown and Yoon have recently reported that reduction of **3** by aluminum hydride (prepared from LAH and 100% sulfuric acid) in tetrahydrofuran solvent yields only the tertiary alcohol **4**. We have carried out similar experiments using commercial concentrated (96%) sulfuric acid, and find that 9.9% of **5** is formed (using THF as solvent). The reagent prepared by this route in diethyl ether gives 13% (reproducibly ±1%) of **5**. These data are compatible with the Lewis base strengths of the solvents (THF > ether), and imply that the ether–LAH–$AlCl_3$ reagent is the most electrophilic of the series. Note, however, that secondary attack still predominates with this reagent; this behavior is to be contrasted with that of the strongly electrophilic materials obtained with higher $AlCl_3$ to LAH ratios, where rearrangements[16] and polymerization[4] of epoxides suggest the intermediacy of carbonium ions.

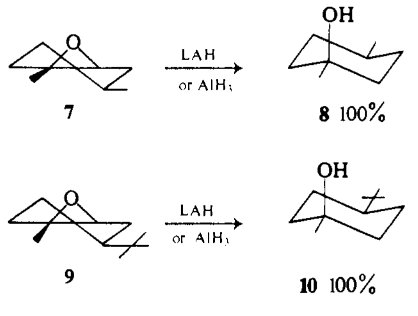
The mechanism of "abnormal" cyclohexene oxide opening has been the subject of speculation for some time. An important facet, given the strong preference for a *trans*-coplanar transition state, is whether the abnormal product arises from a twist-boat transition state, or by normal diaxial opening of the alternate half-chair epoxide conformation. The problem can be considered in terms of Scheme I, using 1-methylcyclohexene oxide to illustrate the available mechanistic pathways. The abbreviations are S for secondary hydride attack, T for tertiary attack, C for chair, and B for boat transition state. Thus tertiary alcohol **4** must arise by either path SC or SB; as we know from previous work with 4-*t*-butylcyclohexene oxide that B must be energetically unfavorable, we can discount (in this example) path SB and conclude that >99.5% of **4** is formed by route SC. By the same reasoning path TB can be ignored; consequently the ratio of secondary to tertiary alcohol formed in reduction of this system is a measure of the activation energy difference between paths TC and SC. Since both involve chair transition states, this further reduces to the difference between T and S attack.

Scheme I. Reduction Routes for 1-Methylcyclohexene Oxide



The $\Delta\Delta G^{\ddagger}$ (at 35°) values obtained in this manner are: for LAH, 3.1 kcal/mol; for AlH_3, 0.75 kcal/mol.

With these figures available, more complex systems can be analyzed. Turning first to the *cis*-epoxides **7** and **9**, it is evident that from the favored half-chair conformations shown, tertiary alcohols **8** and **10**, respectively, are the anticipated products. The alcohol formed in each instance is that arising from an SC pathway. The



LAH reduction of **9** has been previously reported by LeBel and Ecke,[17] and our results are in excellent agreement, *i.e.*, exclusive formation of tertiary alcohol **10**. Of greater interest here is the observation that the more electrophilic AlH_3 gives the same product with no indication of formation of secondary alcohol. This establishes a lower limit on the energy by which a C process is favored over a B mechanism (see later discussion).

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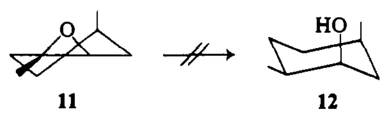
(15) Lithium salts can serve as efficient catalysts for the rearrangement of epoxides to ketones or aldehydes (B. Rickborn and R. M. Gerkin, *J. Amer. Chem. Soc.*, 90, 4193 (1968)). If the secondary alcohols here had arisen from ketone formed by electrophilic rearrangement, the *trans* alcohol would have predominated (72%).[3,7] On the other hand, assuming that the same intermediate (secondary) alkoxide is formed from **3** and *cis*-3-methylcyclohexene oxide[3] suggests that the *cis*/*trans* ratio should be 90/10, in good agreement with the observed value. Reduction of epoxide samples in which 2-methylcyclohexanone was present in known amounts gave the same results after correction for the ketone reduction products.

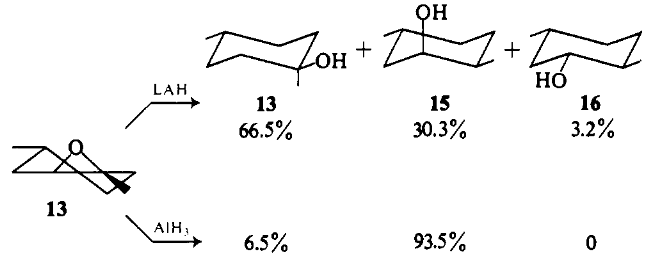
The possibility that the secondary alcohols result from reduction by aluminum hydride, conceivably generated from traces of water in either solvent or on the LAH surface, was also explored. It was shown that addition of 0.25 mol of water/mol of LAH gave some enhancement of *cis*-2-ol (3%) but no increase in *trans* material. When water was added to a mixture of LAH and lithium hydride, subsequent epoxide reduction gave the same results as LAH alone.

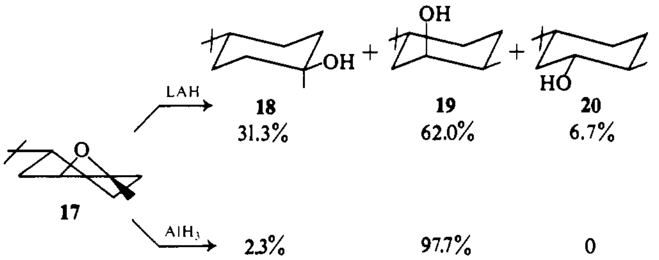
(16) E. L. Eliel and M. N. Rerick, *J. Amer. Chem. Soc.*, **82**, 1362 (1960).

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



It is less obvious that AlH_3 should give exclusively **8** on reduction of **7**; the alternate half-chair (**11**) has available a TC pathway with the added effect of an axial 4-methyl group. Since none of the secondary alcohol **12** is formed, it can be concluded that this group adds a steric interaction in the potential reduction transition state which is energetically unfavorable by ≥ 2.5 kcal/mol.[18]

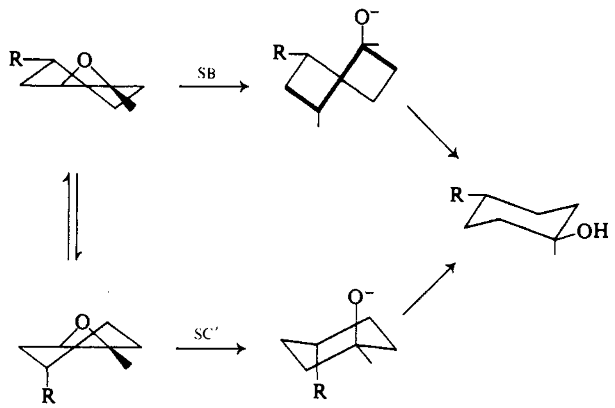


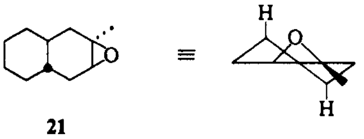


The pure *trans*-epoxides **13** and **17** behave very differently than the *cis* isomers on reduction. LeBel and Ecke[17] have already examined the LAH reduction of **17**, and again the results of these two studies are in excellent agreement. Several points can be made regarding the data presented above; from a synthetic viewpoint, the enhanced product specificity available through use of AlH_3 is particularly noteworthy.

The minor secondary alcohols (**16** and **20**) formed in the LAH reduction of **13** and **17**, respectively, clearly result from the oxidative inversion mechanism.[9] Since these arise *via* the same initial opening process as the major secondary alcohols **15** and **19**, further discussion and calculations will be based on the sum of the two secondary products in each instance.

A striking difference in the relative amounts of tertiary and secondary alcohol products is apparent in the LAH reduction of **13** and **17**. Two pathways need to be considered for formation of tertiary alcohol. Simply on the basis of bulk effects, one would expect path SC′ to be less favorable when R = *t*-butyl than where R = CH_3; consequently the higher percentage of tertiary alcohol **14** in the reduction of **13** (relative to **18** from **17**) is explicable in terms of a greater contribution of mechanism SC′ for **13**. However, this does not solve the more fundamental problem, *i.e.*, which route (SB or SC′) leads to tertiary alcohol in the reduction of **17**. This problem has been discussed previously by other authors, particularly with regard to opening reactions of anhydro sugars[19] and more recently terpene epoxides,[20,21] but no experimental evidence has been generated to allow a distinction between the two paths. We therefore undertook the study of *trans,cis*-2-methyl-Δ^2-octalin oxide (**21**).[22]





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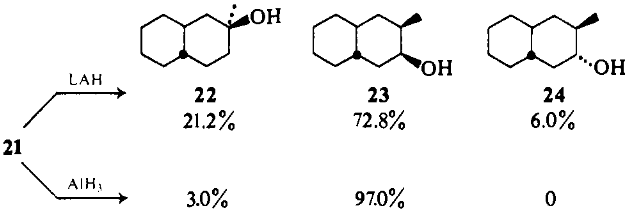
The *trans*-fused carbocyclic ring in **21** does not allow any contribution from the alternate half-chair (or from an SC′ transition state), and consequently any tertiary alcohol formed in reduction of this system must arise *via* a twist boat pathway (SB). The results are shown below.



Considering first the LAH results, we find that secondary alcohol predominates over tertiary by a factor similar to that observed with *trans*-1-methyl-4-*t*-butylcyclohexene oxide (**17**). This similarity suggests that **18** is also formed by an SB process; the somewhat greater percentage of **18** relative to **22** may imply some contribu-

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[18] Assuming that $\leq 0.5\%$ of this known retention time material might have escaped detection, this process is unfavorable by ≥ 3.2 kcal/mol relative to the observed $7 \rightarrow 8$ route. Subtracting 0.7 kcal/mol for the T, S difference leaves ≥ 2.5 kcal/mol for the transition-state interaction of the axial methyl group with the developing, bulky oxyaluminate group. It should be noted that this relatively large value is not a direct reflection of the ground state epoxide conformation populations (**7** and **11**), which probably differ much less in energy.

(19) (a) R. C. Cookson, *Chem. Ind.* (London), 223, 1512 (1954); (b) S. J. Angyal, *ibid.*, 1230 (1954); (c) W. G. Overend and G. Vaughan, *ibid.*, 995 (1955).

(20) (a) J. C. Leffingwell and E. E. Royals, *Tetrahedron Letters*, 3829 (1965); (b) E. E. Royals and J. C. Leffingwell, *J. Org. Chem.*, **31**, 1937 (1966).

(21) R. M. Bowman, A. Chambers, and W. R. Jackson, *J. Chem. Soc., C*, 612 (1966).

(22) Throughout this paper, stereochemical nomenclature refers to configuration relative to the functional group (either epoxygen or hydroxyl), and follows the usual numbering sequence.

tion from an SC′ pathway but this seems unlikely in view of the large steric interaction expected from the axial *t*-butyl group. More probably the reason for the small difference in product distributions from **17** and **21** is that the *t*-butyl group causes a deformation of the half-chair conformation. Distortion by this bulky group is well documented in the analogous olefin.[5,23,24]

The data from reduction of **21** can be used to calculate the energetic preference that a C process enjoys relative to a B process. Thus the ratio (**23** + **24**)/**22** leads to a factor (for LAH) of 0.80 kcal/mol for the difference SB − TC. Taking into account the T − S preference obtained from reduction of **3** (3.1 kcal/mol), we arrive at the conclusion that the C process is favored over the B process by 3.9 kcal/mol. Similar treatment of the data from reduction of **17** leads to a value of 3.6 kcal/mol for this B − C activation energy difference. The magnitude of this value is not unreasonably large, since its upper bound should correspond to the boat–chair enthalpy difference (4.9 kcal/mol).[25] A lower limit of 3.2 kcal/mol is established in the reduction of *trans*-4-*t*-butylcyclohexene oxide[4] (calculated by assuming that a generous 0.5% of product from the B process might have been missed in vpc analysis).

The question of the amount of tertiary alcohol arising from the less stable conformer of *trans*-1,4-dimethylcyclohexene oxide may now be answered. The octalin oxide system has established a ratio for the SB and TC pathways and, since the remote equatorial 4-methyl group of conformer **13** is not expected to cause an appreciable perturbation, the behavior of this conformer should be analogous to **21**. Thus, the amount of tertiary alcohol from path SB is calculated to be 9.1% leaving 57.4% as the amount formed by mechanism SC′. The ratio of products from paths SC′ and TC gives an energy difference between these two mechanisms of 0.33 kcal/mol, which, subtracted from the SC − TC value previously obtained gives 2.8 kcal/mol for the increase in activation energy caused by an axial *trans*-4-methyl group in LAH reduction. This energy parameter provides an additional argument for the exclusion of any process SC′ in the reduction of **17**.

The aluminum hydride reduction of **13**, **17**, and **21** yields data which may be handled in the same manner as the results from the LAH reductions. Both the octalin (**21**) and the *t*-butyl (**17**) system give small amounts of tertiary alcohol. Using the previously determined value for preference for attack at secondary *vs.* tertiary carbon (0.75 kcal/mol), the calculated preference for chair over boat transition state is 3.1 kcal/mol. This suggests that a small amount (*ca.* 0.5%) of SB pathway product should be formed in, for example, the reduction of 4-*t*-butylcyclohexene oxide. As indicated earlier, this amount could easily have escaped detection.[4] In the aluminum hydride reduction of mixed *cis*- and *trans*-4-methylcyclohexene oxide,[5] approximately 2% of equatorial alcohol was observed; this result is in keeping with the product distribution from **13**.[26]

The data from the aluminum hydride reduction of *trans*-1,4-dimethylcyclohexene oxide give (using the octalin oxide C − B energy difference) a value of 2.7 kcal/mol for the transition state energy destabilization factor due to the axial 4-methyl group. Interestingly this number is the same, within experimental error, as the value for LAH reduction. This suggests that ether-solvated aluminum hydride and LAH have similar bulk requirements.

Finally, it should be noted that in no instance in the present work was evidence for a *cis*-opening mechanism obtained. The absence of this intramolecular process is particularly significant in the reductions of **13**, **17**, and **21**, which are relatively slow, higher activation energy processes. *cis* opening may be unique to phenyl-substituted epoxides, both in hydride reductions[27] and other acid-catalyzed reactions.

Experimental Section

1,2-Dimethylcyclohexene Oxide. Grignard methylation of 2-methylcyclohexanone gave a mixture of *cis*-[22] (74%) and *trans*-1,2-dimethylcyclohexanol (26%) in 90% yield, bp 71–75° (15 mm). The *trans* isomer was characterized by hydroboration[28] of a sample of 1,2-dimethylcyclohexene.

Dehydration of the alcohol using 85% phosphoric acid gave a mixture of olefins containing about 60% of 1,2-dimethylcyclohexene. Fractionation was effected with a Teflon spinning annular band column to give 40% of the desired olefin, bp 137.5–138°.[29] Better yields were obtained in subsequent runs by using methanesulfonic acid in refluxing benzene for the dehydration.

Epoxidation with *m*-chloroperbenzoic acid in ether gave the desired product (bp 150–150.5°)[14] in nearly quantitative yield.

1-Methylcyclohexene Oxide. Similar treatment of 1-methylcyclohexene gave the epoxide (bp 137–138°) in high yield. Contrary to a recent report by Crandall and Lin,[30] the epoxide was also obtained using peracetic acid with sodium carbonate. Samples of highly purified epoxide, free of 2-methylcyclohexanone, were obtained by preparative vpc using a Carbowax 4000 column.

1,4-Dimethylcyclohexene Oxide. Phosphoric acid dehydration of the alcohol mixture obtained from Grignard methylation of 4-methylcyclohexanone gave a mixture of olefins. Careful fractional distillation gave 40% of 1,4-dimethylcyclohexene (bp 128–129°)[31] characterized by its nmr spectrum. Epoxidation with *m*-chloroperbenzoic acid gave in good yield a mixture of *trans*-[22] (55%) and *cis*-1,4-dimethylcyclohexene oxides (45%), bp 53° (20 mm).

The pure *trans*-epoxide was obtained by conversion to the chloro-*p*-nitrobenzoate,[32] which was recrystallized five times from methanol (14%, mp 132–133°). The epoxide was regenerated as described previously.[32]

1-Methyl-4-*t*-butylcyclohexene Oxide. As described by LeBel and Ecke,[17] methylation of 4-*t*-butylcyclohexanone gave a mixture of alcohols in which the *cis* predominated (63%). The *trans* material was further characterized by recrystallization from pentane to give material with mp 92–96°.[17] Dehydration with hot 85% phosphoric acid gave a mixture of olefins which were particularly difficult to separate by distillation. Methanesulfonic acid in refluxing benzene, however, gave 98% pure 1-methyl-4-*t*-butylcyclohexene in 85% yield. This material was treated directly with *m*-chloroperbenzoic acid to give the epoxide, bp 91–92° (9 mm),[17] in nearly quantitative yield.

Preliminary experiments indicated that the *trans*-epoxide reacted

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[23] B. Rickborn and J. H. Chan, *J. Org. Chem.*, **32**, 3576 (1967).

[24] D. J. Pasto and F. M. Klein, *ibid.*, **33**, 1468 (1968).

[25] N. L. Allinger, J. A. Hirsch, M. A. Miller, I. S. Tyminski, and F. A. Van-Catledge, *J. Amer. Chem. Soc.*, **90**, 1199 (1968).

[26] If the equatorial alcohol from 4-methylcyclohexene oxide were derived exclusively from either the *cis* or *trans* isomer, it would affect the previously calculated[5] conformational preference of 4-methylcyclohexene by as much as 0.3 kcal/mol. Pertinent data bearing on this question could in principle be obtained by comparison of the AlH_3 reduction products of **7** and **13**, but unfortunately we can only establish a lower limit on the SC′ process for **7**.[18]

[27] (a) P. T. Lansbury, D. J. Scharf, and V. A. Pattison, *J. Org. Chem.*, **32**, 1748 (1967); (b) E. C. Ashby and B. Cooke, *J. Amer. Chem. Soc.*, **90**, 1625 (1968).

[28] H. C. Brown and G. Zweifel, *ibid.*, **83**, 2544 (1961).

[29] C. H. Collins and G. S. Hammond, *J. Org. Chem.*, **25**, 911 (1960).

[30] J. K. Crandall and L. C. Lin, *ibid.*, **33**, 2375 (1968).

[31] S. Seigel, M. Dunkel, G. V. Smith, W. Halpern, and J. Cozort, *ibid.*, **31**, 2802 (1966).

[32] B. Rickborn and J. Quartucci, *ibid.*, **29**, 2476 (1964).

much more readily than *cis* material with *p*-nitrobenzoyl chloride, and a modified procedure was used to selectively form the chloro-*p*-nitrobenzoate. The epoxide mixture ($\sim$40% *trans*), 144.7 g (0.86 mol) was taken up in 1 l. of pyridine, and 112 g (0.60 mol) of *p*-nitrobenzoyl chloride was added. After stirring for 3 days a small amount of water was added to decompose any excess acid chloride, and the product was taken up in ether, washed with water and dilute acid, dried, and evaporated to give 20% of brown oil. This material was mulled with pentane at low temperature and filtered. The solid residue (85 g) was recrystallized three times from methanol to give 6.3 g (5.2% based on *trans*-epoxide), mp 120–121.5°, of the chloro-*p*-nitrobenzoate.

Evaporation of the pentane wash gave 128 g of yellow oil; retreatment with *p*-nitrobenzoyl chloride (61.5 g, 0.33 mol) in pyridine as described above gave 155 g of yellow semisolid. After washing with pentane and recrystallization from methanol, an additional 22.3 g of *trans*-epoxide derivative was obtained: mp 120–121.7°, combined yield 23.6%. The pure *trans*-epoxide was regenerated as described previously.[32]

The pentane solution from this second washing was evaporated to give 103 g of liquid residue. This product was distilled through a spinning-band column, bp 82–84° (3.5 mm), to give 41.5 g of nearly pure (97%) *cis*-epoxide (48% based on available *cis* material). Analysis was accomplished by LAH reduction and vpc examination of the alcohol products.

2-Methyl-Δ^2-octalin Oxide. The Diels–Alder adduct of isoprene and *p*-benzoquinone was reduced with zinc in acetic acid[33] to give 6-methyl-2,3,4a,5,8,8a-hexahydro-1,4-napthoquinone (84%), mp 84.0–84.5°[34] (recrystallized twice from ether). To 44 g of this material in 300 ml of ethylene glycol was added 65 ml of 85% hydrazine hydrate. After refluxing for 1 hr, 55 g of potassium hydroxide was added in portions; further heating caused the olefinic product to steam distill. The organic phase was dried and distilled to give 33.5 g (90%) of 2-methyl-Δ^2-octalin, bp 87° (10 mm).[34] The olefin was a mixture of *trans*-(69.2%) and *cis*-ring-fused (30.8%) material which was not further separated.

Treatment with *m*-chloroperbenzoic acid in ether gave a mixture of four epoxides which were tentatively identified on the basis of olefin composition and product distribution anticipated by comparison with other systems (*e.g.*, *cis*-4,5-dimethylcyclohexene[5]). In order of increasing vpc retention time (Carbowax 4M) these are: *cis,cis*[22] (1.6%); *trans,cis* (**21**, 35.7%); *cis,trans* (35.7%); *trans,trans* (26.0%).

This mixture (33 g, 0.2 mol) was subjected to the selective derivitization procedure described earlier, using 24 g (0.14 mol) of *p*-nitrobenzoyl chloride. A pasty yellow solid (44 g) was obtained. Four recrystallizations from methanol gave 7 g (0.02 mol) of pale yellow solid (mp 146.8–148°). Basic hydrolysis gave pure *trans,cis*-2-methyl-Δ^2-octalin oxide, bp 78° (4 mm).

Reduction Procedure. Reductions were in general carried in refluxing ether using a sevenfold molar excess of reducing agent. Potassium hydroxide solution was used to quench the excess hydride. The organic phase was dried and concentrated by evaporation through a Vigreux column prior to vpc analysis.

Product Identification. The tertiary alcohol products were prepared by methylation of the appropriate ketones. Samples of pure *trans*- (the major isomer from equilibration) and mixed *cis*- and *trans*-2,5-dimethylcyclohexanones were reduced by LAH to identify the 2,5-dimethylcyclohexanols. LeBel and Ecke's[17] results served to characterize the products from the 1-methyl-4-*t*-butylcyclohexene oxides. Grignard methylation of *trans*-2-decalone (69% axial alcohol), hydroboration of 2-methyl-Δ^2-octalin, and analogy with the 1-methyl-4-*t*-butylcyclohexene oxide were used to deduce the structures of the products from **21**.

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(33) W. S. Johnson, V. J. Bauer, J. L. Margrave, M. A. Frisch, L. H. Dreger, and W. N. Hubbard, *J. Amer. Chem. Soc.*, **83**, 606 (1961).

(34) R. T. LaLonde and M. A. Tobias, *ibid.*, **85**, 3771 (1963).

On the Mechanism of the Photoreduction of Aryl N-Alkylimines

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Abstract: The mechanism and scope of the photoreduction of some aryl N-alkylimines is described. Irradiation of a series of benzaldehyde N-alkylimines in 95% ethanol affords dihydro photodimers, whereas irradiation of several benzophenone N-alkylimines gives the reduced benzhydrylalkylamines. The excited states of the imines were shown not to be reactive intermediates but instead ketyl radicals were clearly implicated as the active reducing agent. These ketyl radicals were derived from carbonyl compounds present in the reaction mixture as an impurity, an added sensitizer, or as a photogenerated species. Comment is made regarding the relevance of these results to previous reports of imine photoreduction and photoalkylation.

One of the most active areas of organic photochemistry has been the study of systems which possess a carbonyl group.[2-5] As a result of these studies the photochemical transformations of organic molecules containing this functional group have been categorized into a number of primary photochemical processes.[6] This state of affairs contrasts sharply with the present status of the structurally related imine system, the photochemistry of which is mainly qualitative with relatively little available in the way of quantum yield data and kinetic studies. Even though the photochemistry of the C–N double bond has not been the subject of mechanistic studies, a considerable number of diverse reports have accumulated in the literature without critical review. Irradiation may lead to isomerization,[7,8] prototropy,[9] rearrangement,[10-12] addi-

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