

of lithium aluminum hydride. The mixture was refluxed for 2 hr. with magnetic stirring and under exclusion of moisture and then cooled in an ice bath; the excess reductant was destroyed by careful addition of tetrahydrofuran-water (10:1). The inorganic solid was removed and washed with chloroform, and the combined solutions were evaporated to furnish a colorless oil. The oil was taken up in 1 ml. of methanol, and picric acid (145 mg.) in hot methanol (3 ml.) was added. Dropwise addition of water to incipient turbidity and cooling produced yellow crystals that were isolated and washed with water-containing, cold methanol. After drying, the crude picrate of XVII, m.p. 143–146°, weighed 87 mg. (a second crop, of lesser purity, was obtained from the mother liquor). The crude picrate was triturated, in a centrifuge tube, with 0.3 ml. of warm methanol, decanted, and washed twice with 0.2 ml. of cold methanol, and then melted at 154–156°.

Recrystallization from methanol raised the melting point to 156–157°.

In one experiment, the picrate of XVII which had remained in the mother liquor was converted into the hydrochloride by passage over a small column containing an anion-exchange resin, Dowex-1, in the chloride form. The hydrochloride of XVII formed colorless needles, m.p. 178°.

Witkop¹⁷ reported m.p. 150° for the picrate, and m.p. 183° for the hydrochloride, of *cis*-decahydroisoquinoline, and m.p. 177° and 224°, respectively, for the corresponding *trans* derivatives.

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Stereochemistry and Mechanism of Lithium Aluminum Hydride and Mixed Hydride Reduction of 4-*t*-Butylcyclohexene Oxide¹

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Lithium aluminum hydride reduction of *trans*-4-*t*-butylcyclohexene oxide gives only *trans*- (90%) and *cis*-3-*t*-butylcyclohexanol (10%). The *cis* epoxide affords only 4-ols, in a comparable ratio (90% *cis*, 10% *trans*). Deuterium distribution in the products derived from lithium aluminum deuteride reduction suggests that the minor product arises by a novel rearrangement to ketone which is subsequently converted to alcohols. In contrast, mixtures of lithium aluminum hydride and aluminum chloride give very stereospecific reduction, the product from each epoxide being essentially pure axial alcohol.

Epoxide ring-opening reactions involving numerous reagents have been studied, and this subject has been reviewed by Parker and Isaacs.² Lithium aluminum hydride has been widely used for the reduction of epoxides to alcohols; the steric effects observed when this reagent is applied to unsymmetrical epoxides,² and the general observation of inversion of configuration at the attacked carbon³ support the view that reduction occurs through nucleophilic displacement of oxygen by a hydride-donor species. Stereochemical implications were further explored by Fürst and Plattner⁴ with steroidal epoxides, where it was demonstrated that axial alcohols are formed in high yield by lithium aluminum hydride reduction. Inversion of configuration at the carbon attacked by hydride would thus correspond to formation of the new carbon-hydrogen bond in the axial position. The resultant "rule of diaxial opening"⁵ appears to be a specific statement of the energetically favorable *trans*-coplanar transition state associated with both additions to olefins and the reverse elimination reactions. The opening of an epoxide ring may in fact be viewed as analogous to the latter stages of any addition reaction involving the intermediacy of a three-membered ring.

The purpose of the present study was to examine in detail, with the aid of modern analytical techniques, the nature of the products formed on reduction of a flexible cyclohexene oxide system (Table I). Extension of the rule of diaxial opening from conformationally frozen steroidal epoxides is not obvious; the limited data pertaining to this question involve for the most

part reactions of anhydro sugars.^{6–8} Results from these studies indicate that the major product is that arising from diaxial opening, but the alternate isomer is formed in varying amounts.⁸ The process leading to the minor product has been the subject of speculation for some time, but at present the literature contains no data allowing a choice from among the several mechanistic alternatives.⁹ Cookson¹⁰ and Angyal¹¹ have suggested that the controlling feature is the conformation of the epoxide through which reaction occurs, and that the minor product is formed through the less stable, half-chair, cyclohexene oxide conformation. An alternate, and in many ways more attractive, explanation involves reaction through the most stable half-chair to give the minor product initially formed in the boat conformation. Both mechanisms allow for major and minor products to be formed by *trans*-diaxial opening of the epoxide ring. It was in the hope of distinguishing between these two possibilities that we undertook a study of the hydride reduction of *trans*- and *cis*-4-*t*-butylcyclohexene oxide. The former isomer is readily available in pure form,¹² and all four potential alcohol products are separable (as the acetates) by vapor phase chromatography.

An entirely unexpected result was obtained when *trans*-4-*t*-butylcyclohexene oxide was reduced with lithium aluminum hydride in ether. The major product,

(6) A. K. Bose, D. K. R. Chaudhuri, and A. K. Bhattacharyya, *Chem. Ind. (London)*, 869 (1953).

(7) F. H. Newth, *ibid.*, 1257 (1953).

(8) W. G. Overend and G. Vaughn, *ibid.*, 995 (1955).

(9) This topic is discussed and the literature is summarized by E. L. Eliel, "Steric Effects in Organic Chemistry," M. Newman, Ed., John Wiley and Sons, Inc., New York, N. Y., 1956, pp. 130–134, and "Stereochemistry of Carbon Compounds," McGraw-Hill Book Co., Inc., New York, N. Y., 1962, p. 230.

(10) R. C. Cookson, *Chem. Ind. (London)*, 223 (1954); 1512 (1954).

(11) S. J. Angyal, *ibid.*, 1230 (1954).

(12) See reference in footnote b, Table I.

(1) Support by The Petroleum Research Fund, administered by the American Chemical Society, is gratefully acknowledged.

(2) R. E. Parker and N. S. Isaacs, *Chem. Rev.*, **59**, 737 (1959).

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

(4) A. Fürst and P. A. Plattner, *Helv. Chim. Acta*, **32**, 275 (1949).

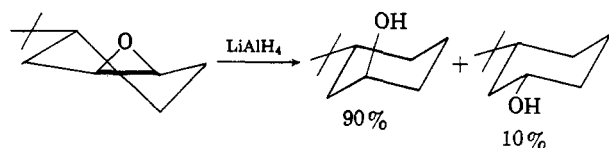
(5) A. Fürst and P. A. Plattner, Abstracts, 12th International Congress of Pure and Applied Chemistry, New York, N. Y., 1951, p. 409.

TABLE I
PRODUCT DISTRIBUTION FROM LITHIUM ALUMINUM HYDRIDE IN ETHER REDUCTION OF EPOXIDE ISOMERS

| 4- <i>t</i> -Butyl- cyclohexene oxide, <i>cis-trans</i> ^{a,b} | Reducing ^c agent | <i>t</i> -Butylcyclohexanols, % | | | |
|---|---|---------------------------------|---------------------|---------------------|-----------------------|
| | | <i>trans</i> -3 (ax.) | <i>cis</i> -3 (eq.) | <i>cis</i> -4 (ax.) | <i>trans</i> -4 (eq.) |
| 0:100 | LiAlH ₄ | 90 ± 1 | 10 ± 1 | ... | ... |
| 60:40 | LiAlH ₄ | 37 | 4 | 53 | 6 |
| 80:20 | LiAlH ₄ | 19 | 2 | 72 | 7 |
| 0:100 | LiAlD ₄ | 89 | 11 | ... | ... |
| 0:100 | LiAlH ₄ -AlCl ₃ = 3 | >99 | <i>d</i> | ... | <i>d</i> |

^a Isomeric epoxide ratios determined by v.p.c. analysis, 8-m. triscyanoethoxypropane column, 110°. ^b The *cis* epoxide has the shorter retention time [B. Rickborn and J. Quartucci, *J. Org. Chem.*, **29**, 2476 (1964)]. ^c When hydride alone was used, molar ratios of lithium aluminum hydride to epoxide were varied from 2.0 to 15 without a measurable effect on product distribution. ^d Insufficient minor product was formed with the mixed hydride for isolation and identification; v.p.c. retention time of the acetate in this case indicated that the material is *trans*-4-*t*-butylcyclohexanol.

in keeping with the rule of diaxial opening, is *trans*-3-*t*-butylcyclohexanol (90 ± 1%); however, the material formed in lesser amount is not the anticipated *trans*-4-*t*-butylcyclohexanol, but rather *cis*-3-*t*-butylcyclohexanol (10 ± 1%).



The very unlikely possibility that the product involving inversion of the oxygen-bearing carbon had been formed by subsequent isomerization of axial alcohol was ruled out by varying lengths of time in reducing media, and by adding a known mixture of these alcohols (rich in *trans*) to the reducing agent and subjecting the solution to a normal isolation procedure. All evidence pointed to complete stability of products once formed under the reaction conditions used here (large excess of hydride).

Substantiated examples of rearrangement during reduction of epoxides by lithium aluminum hydride are unknown, with one exception. Kwart and Takeshita¹³ have shown that *exo*-norbornene oxide gives varying amounts, depending on solvent, of 7-norborneol. The corresponding *endo* isomer is reduced normally to 2-*endo*-norborneol. Thus it appears that this lone example of rearrangement may be attributed to special constraints of the geometry of the substrate epoxide.

If the inversion of the oxygen-bearing carbon, observed in lithium aluminum hydride reduction, were due to electrophilically assisted rearrangement to ketone intermediate, added aluminum chloride would be expected to facilitate this process.^{14,15} The opposite effect is found.

Mixed hydride reduction of *trans*-4-*t*-butylcyclohexene oxide occurs with higher specificity than is found in the absence of added aluminum chloride. The dependence of specificity on hydride-aluminum chloride ratio is shown by the data in Table II. In all cases the total reducing agent represents a large molar excess over epoxide concentration. The effects of added aluminum chloride appear even at ratios as high as 18.4, where the product consists of 96% axial alcohol as opposed to 90% in the absence of the aluminum halide. The specificity approaches a maximum of >99% axial alco-

TABLE II
SPECIFICITY OF MIXED HYDRIDE REDUCTION OF
4-*t*-BUTYLCYCLOHEXENE OXIDE^a

| LiAlH ₄ -AlCl ₃ ^b | % axial alcohol ^c |
|--|------------------------------|
| ∞ | 90 ± 1 |
| 18.4 | 96.1 |
| 10 | 98.2 |
| 4.0 | 98.8 |
| 3.0 | >99 |
| 2.9 | >99 ^d |
| 2.2 | >99 ^e |
| 1.5 | >99 ^e |
| 1.0 | >99 ^e |
| 0.74 | >99 ^e |
| 0.4 | ... |
| 0.3 | ... |

^a A mixture consisting of 60% *cis* and 40% *trans* epoxide was used. ^b The mole ratio of reagents is reported; for various mixtures, mole ratios of lithium aluminum hydride to epoxide from 5 to 100 were used without altering the results. ^c A diethylene glycol succinate column was used at 150° for analysis; this gave a clean separation of axial from equatorial alcohols, but did not separate the positional isomers. ^d At this ratio and above, the over-all yield of alcohol products was essentially quantitative. ^e Alcohol yields diminished with decreasing hydride-aluminum chloride ratios: at 1.0, 60%; at 0.4, trace amounts. The product is apparently a polyether.

hol at a ratio of 3.0; below this the high specificity is maintained, but the over-all yield of alcohol product is diminished. At ratios below 0.4, *i.e.*, in the region where Eliel has observed the striking reversal of the direction of unsymmetrical epoxide opening, only trace amounts of alcohol are obtained. The product in this instance is a viscous, apparently polymeric material which shows a very weak absorption in the O-H stretch region of the infrared. It appears that, with increasing electrophilic and decreasing nucleophilic character of the reducing agent, the epoxide competes favorably with hydride donor for opening of the oxirane ring.

The extensive work of Eliel and his co-workers^{14,15} on lithium aluminum hydride and hydride-aluminum chloride reduction of epoxides has demonstrated that several mechanisms may be operative in these reactions, depending on the nature of the substrate and reducing species. With the particular unsymmetrical epoxides used by Rerick and Eliel,¹⁵ it was found that the sole product from lithium aluminum hydride reduction is that derived from attack at the least hindered carbon atom; this result is particularly striking in the case of triphenylethylene oxide, where the potential for electrophilic opening (or assistance) is presumably far greater than in simple aliphatic epoxides. Mixed hy-

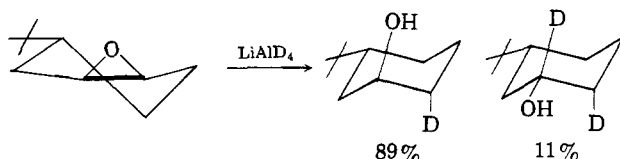
(13) H. Kwart and T. Takeshita, *J. Org. Chem.*, **28**, 670 (1963).

(14) E. L. Eliel, *Record Chem. Progr.*, **22**, 129 (1961).

(15) M. N. Rerick and E. L. Eliel, *J. Am. Chem. Soc.*, **84**, 2356 (1962).

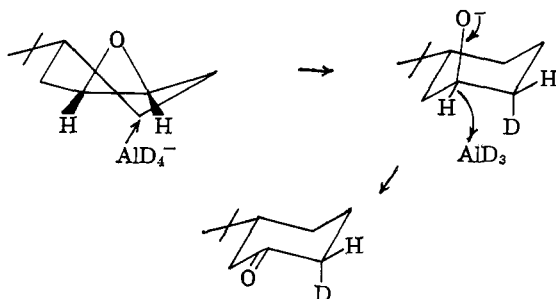
drude treatment of this material, on the other hand, gives various products depending on the hydride to aluminum chloride ratio,¹⁵ indicative of the enhanced electrophilicity of the active species in solution.

Lithium aluminum deuteride reduction of *trans*-4-*t*-butylcyclohexene oxide was undertaken to shed some light on the mechanism of formation of the *cis*-3-*t*-butylcyclohexanol. The two alcohol products were separated by preparative vapor phase chromatography. The axial alcohol contained one deuterium atom per molecule, as expected; the equatorial alcohol was shown to contain two deuterium atoms per molecule, one of which was attached to the carbinol carbon. Analyses



were accomplished by infrared, nuclear magnetic resonance, and combustion methods. None of these, unfortunately, was able to distinguish the configuration of deuterium in the products; we have tentatively assigned the structures shown on the basis of (1) diaxial opening for the major product, and (2) the proposed mechanism for formation of the minor product.

We feel that the reduction by lithium aluminum hydride is largely unassisted by electrophilic attack on oxygen, and as a consequence the initially formed oxanion is a good hydride donor. Formed in close proximity to the hydride-accepting species aluminum hydride, this oxanion may be oxidized to ketone. Subsequent reduction of the ketone will produce largely equatorial alcohol (91%).¹⁶



The enhanced specificity of the mixed hydride reduction may thus be attributed to electrophilically assisted opening of the oxirane system to give a metallated oxygen species which is not an effective hydride donor. This facet of the proposed mechanism is required since, with the particular mixture (ratio of 3.0) that we have found to be particularly effective in terms of specificity and yield, aluminum hydride is presumed to be the predominant reductant in solution.¹⁴ Calling on aluminum hydride as a hydride acceptor in the lithium aluminum hydride reduction therefore requires a variation in the nature of the potential hydride donor.¹⁷

(16) Eliel (ref. 14) has shown that 3-*t*-butylcyclohexanone gives 91% *cis*-3-*t*-butylcyclohexanol on reduction with lithium aluminum hydride. Hydride and aluminum chloride in a ratio of 1:4 gives 70% equatorial alcohol. In our system, ketone intermediate would give rise to a negligible (~1%) amount of axial alcohol containing two deuterium atoms per molecule.

An attempt to test this hypothesis by treating the potassium salt of the axial alcohol with aluminum deuteride failed to give useful information. Treatment of the alcohol in ether with potassium metal (under nitrogen) led to the formation of some ketone and consequent extensive equilibration of the alcohol.¹⁸

The results reported here are not a vagary of 4-*t*-butylcyclohexene oxide, as we have observed this same diminished specificity with both the 4-methyl- and *cis*-4,5-dimethylcyclohexene oxides¹⁹ on lithium aluminum hydride reduction. Extension to noncyclic systems does not appear to be valid, however, as Leroux and Lucas²⁰ have found that optically pure D-(+)-2,3-epoxybutane gives 99% optically pure L-(-)-2-butanol on lithium aluminum hydride reduction, thus precluding any appreciable inversion of oxygen-bearing carbon. This difference may be associated with more facile rotation of the carbon skeleton in the open-chain system, allowing ready formation of aluminum salt.

Returning to the general question of formation of "nondiaxial" product in epoxide-opening reactions, it is evident that the hydride-reduction results are not generally applicable to other reagents. However, when these reagents are potential hydride acceptors, rearrangement of the type observed here must be considered. We are currently investigating a number of ring-opening reactions in order to establish the generality of the present observations.

Experimental

4-*t*-Butylcyclohexanol, 4-*t*-butylcyclohexene, and *trans*-4-*t*-butylcyclohexene oxide were prepared as described previously.¹²

3-*t*-Butylcyclohexanol.—Distillation of commercial 3-*t*-butylphenol, b.p. 97–99° (3 mm.), followed by catalytic reduction (5% rhodium on alumina)¹² gave a mixture of *cis*- (44%) and *trans*-3-*t*-butylcyclohexanol (56%) in essentially quantitative yield.^{21,22}

Acetates.—The acetates of the 3-ols and 4-ols were prepared in pyridine, using a large excess of acetic anhydride and allowing the mixture to stand at room temperature for 24 hr. The products were shown by infrared and vapor phase chromatography to be free of alcohol starting materials. Analysis by v.p.c. (various columns) gave results in good agreement with those noted for the alcohol mixtures.

Reduction of Epoxides.—Filtered ethereal solutions of lithium aluminum hydride and aluminum chloride were prepared and stored in containers protected from the atmosphere. The lithium aluminum hydride was analyzed (0.75 *M*) by measuring the hydrogen evolved on treating a known volume of solution with benzyl alcohol. Gravimetric analysis was used for the aluminum chloride solution (2.76 *M*), after a known volume had been added to water.

(17) An alternate explanation, in which alkoxide is oxidized by reducing unreacted epoxide, has been suggested by a referee. We had considered this possibility, but viewed it improbable on two accounts. First, the rate of reaction appears unusually rapid for a Meerwein-Ponndorf-Verley reduction of an epoxide, which presumably would be less reactive than a ketone. A stronger argument is found in the insensitivity of product ratio to lithium aluminum hydride concentration; this observation rules out competing bimolecular reactions unless both are equally dependent on hydride concentration.

(18) S. V. Vitt and N. S. Martinkova [Izv. Akad. Nauk SSSR, Ser. Khim., 524 (1964); Chem. Abstr., 60, 15696 (1964)] have recently reported that benzhydrol-1-*d* and its potassium salt when heated under nitrogen with diglyme, toluene, and lithium aluminum hydride give recovered benzhydrol with some loss of deuterium.

(19) Unpublished results of Sharon Lwo.

(20) P. J. Leroux and H. J. Lucas, *J. Am. Chem. Soc.*, 73, 41 (1951).

(21) S. Weinstein and H. Holness, *ibid.*, 77, 5562 (1955).

(22) The preponderance of *trans* (less stable) isomer from this reduction is somewhat surprising in view of the usual *cis* selectivity of rhodium as a catalyst, as shown in the reduction of 4-*t*-butylphenol,¹² and even more pronounced in other aromatic reductions (personal communication from F. R. Jensen).

These solutions were transferred by syringe in the proper proportions to a reaction flask immersed in an ice bath. Total volumes of solution were approximately 20 ml. Typically the reductions were carried out using 0.1 ml. of epoxide, which was added dropwise to the reducing solution at 0°. For more accurate yield determinations, a few reductions were carried out on a larger scale.

The solution, after being stirred for 0.5 hr., was decomposed with excess dilute hydrochloric acid. The ethereal layer was separated, washed with water and bicarbonate solution, dried over magnesium sulfate, and evaporated. The residue was examined directly by vapor phase chromatography, using an 8-m. diethylene glycol succinate column at 140°.

The retention times of the axial alcohols (*trans*-3- and *cis*-4-*t*-butylcyclohexanol) were too similar for direct analysis, and consequently this analysis gave only axial to equatorial ratios. On this same column, however, the acetates of all four isomeric alcohols were cleanly separated, and these were used for exact product measurements.

Reduction of *trans*-4-*t*-Butylcyclohexene Oxide with Lithium Aluminum Deuteride.—To a solution of 2.0 g. (0.048 mole) of lithium aluminum deuteride²³ in ether at 0° was added 2.0 g. (0.013 mole) of *trans*-4-*t*-butylcyclohexene oxide over a period of 0.25 hr. The mixture was stirred for 2 hr., then decomposed, washed, dried, and evaporated as described for the normal isotope reduction. Preparative vapor phase chromatographic separation was accomplished using the 8-m. diethylene glycol succinate column and 0.2-ml. injections.

The major product (1) after collection was analyzed and found to contain $95.6 \pm 0.5\%$ *trans*-3-*t*-butylcyclohexanol and $4.4 \pm 0.5\%$ *cis*-3-*t*-butylcyclohexanol.

The minor product (2, 11% of original material) analyzed after collection contained $90.1 \pm 0.3\%$ *cis*-3-*t*-butylcyclohexanol and $9.9 \pm 0.3\%$ *trans*-3-*t*-butylcyclohexanol. Further analyses involved these somewhat isomerically impure materials 1 and 2.

The nuclear magnetic resonance spectrum of 1 was very similar to that of *trans*-3-*t*-butylcyclohexanol prepared by reduction of 3-*t*-butylcyclohexanone and isolated by preparative v.p.c. The only notable difference was a decrease in the ring proton peak at ca. 1.65 p.p.m. (from tetramethylsilane), expected for substitution by deuterium. The carbinol carbon proton at 4.10 p.p.m. was present, and integration indicated no measurable deuterium at this position.

(23) Metal Hydrides' 97% material was used; we wish to thank Professor G. O. Pritchard for a timely gift of this material.

The spectrum of 2 contained no peak at 3.38 p.p.m. (C-1 proton), and showed slight differences in the ring proton region, when compared with that of an isotopically normal sample.

The infrared spectrum of 1 contained a sharp single peak at $4.63 \pm 0.01 \mu$ with a very weak shoulder at $4.71 \pm 0.02 \mu$. The C-D stretching region for 2 showed a clear doublet, the stronger peak at $4.64 \pm 0.01 \mu$, another at $4.74 \pm 0.1 \mu$. A sample of 3-*t*-butylcyclohexanone was reduced with lithium aluminum deuteride, and the product (90% *cis*-3-*t*-butylcyclohexanol-1-*d*)¹⁴ showed a somewhat broadened peak at $4.74 \pm 0.01 \mu$ with a weak shoulder at $4.59 \pm 0.02 \mu$.

Since nuclear magnetic resonance had indicated C-1 deuterium substitution in 2, borne out by the infrared absorption at 4.74μ , the other C-D stretch must be assigned to the adjacent ring position. Although the excellent wave-length agreement for these peaks in 1 and 2 (4.63 and 4.64μ) might suggest assignment of like (axial) conformations to the substituents, such speculation may not be valid.²⁴ Combustion analyses²⁵ of samples 1 and 2 indicate that 1 is 98% monodeuterated and 2 is 94% dideuterated.

Anal. Calcd.²⁶ atom % excess D for C₁₀H₁₈DO (1): 5.06. Found: 4.96.

Anal. Calcd.²⁷ atom % excess D for C₁₀H₁₈D₂O (2): 9.22. Found: 8.65, 8.70.

Controls.—Known mixtures of *cis*- and *trans*-4-*t*-butylcyclohexanol were added to lithium aluminum hydride and hydride-aluminum chloride (3:1) in ether. After 24 hr. these mixtures were recovered, by an extraction procedure identical with that described for the reductions. In all cases the alcohol mixtures were unchanged, thus precluding equilibration, preferential destruction, or loss in work-up of either isomer.

(24) A. Streitwieser, Jr., and C. E. Coverdale [*J. Am. Chem. Soc.*, **81**, 4275 (1959)] have reported C-D stretching frequencies of 4.60 and 4.66 μ , respectively, for *trans*- and *cis*-cyclohexanol-2-*d*. These materials were prepared by lithium aluminum deuteride reduction of cyclohexene oxide and presumably contain about 10% C-1-deuterated material. These spectra were obtained from thin-film neat samples while we used carbon tetrachloride solutions, and hence direct comparison is not possible. Nevertheless, the very slight shift associated with deuterium conformation would make a structural assignment on such a basis very questionable.

(25) Analyses were by Josef Nemeth, Urbana, Ill.

(26) Corrected for the purity (97%) of lithium aluminum deuteride and for the inclusion of 4.4% C₁₀H₁₈D₂O in the sample.

(27) Corrected for purity of lithium aluminum deuteride and for the inclusion of 9.9% of C₁₀H₁₈DO in the sample. Isotope effects have necessarily been ignored. These corrections cannot alter the gross conclusion that 1 is monodeuterated and 2 is dideuterated.

Cleavage of 1,2-Diazetidiones by Bases. The Reaction of 1,2,4,4-Tetraphenyl-1,2-diazetidione with Alkoxides, Organolithium Compounds, and Lithium Aluminum Hydride

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Reaction of 1,2,4,4-tetraphenyl-1,2-diazetidione (I) with sodium ethoxide or sodium *t*-butoxide, followed by hydrolysis, results in cleavage of the C-N bonds to give azobenzene and diphenylacetic acid. In contrast, reaction of I with methylolithium results in cleavage of the N-N and C-C bonds to give benzophenone anil and acetanilide. Similarly, I reacts with phenyllithium to give benzophenone anil and benzanilide. Lithium aluminum hydride cleaves I to give azobenzene and diphenylacetaldehyde as the major products along with smaller amounts of 1,1-diphenylethylene glycol, 2,2-diphenylethanol, and aniline.

The type of products formed in the base-induced cleavage of the 1,2-diazetidione ring system has been found to depend on the nature of the base used and the structure of the 1,2-diazetidione. Ingold and Weaver¹ reported that ethyl 1,4,4-triphenyl-1,2-diazetidione-2-carboxylate underwent rapid amide cleavage when treated with 2% sodium hydroxide in aqueous ethanol. The structure of their starting material has been recently reinvestigated by Bird² and has been shown to

have the alternate ethyl 2,4,4-triphenyl-1,2-diazetidione-1-carboxylate (IIa) structure, which on basic hydrolysis would give the acid IIIa. Schenck and Engelhard³ reported that 1,2-diphenyl-1,2-diazetidione (IIb) was rapidly cleaved by cold, dilute sodium hydroxide solution to give the acid IIIb. Similarly, Cook and Jones⁴ reported the easy base hydrolysis of IIc to IIIc,

(2) C. W. Bird, *ibid.*, 674 (1963).

(3) G. O. Schenck and N. Engelhard, *Angew. Chem.*, **68**, 71 (1956).

(4) A. H. Cook and D. G. Jones, *J. Chem. Soc.*, 184 (1941).

(1) C. K. Ingold and S. D. Weaver, *J. Chem. Soc.*, **127**, 378 (1925).