

interpreted in terms of the path leading to *R*-(–)-2 by internal rotation of the radical center with respect to the largest (ethyl) substituent ( $k_r$ ). This motion should be less sensitive to fluidity changes than the gross tumbling of the radical species.<sup>19</sup>

The  $k_r/k_c$  slope estimated from the data reported for the fluorenyl-diazanyl pair<sup>2</sup> (<1) is not readily reconciled with that found here (84) by purely rotational radius differences. We suggest that the difference is largely due to a lower  $k_c$  for the present system, which may be a result of the initial intervention of the CO<sub>2</sub> molecule between the radical pair.

**Acknowledgment.** We are grateful to the National Science Foundation and the E. I. Du Pont Company for financial support of this work.

$k_d$  corresponds to a particle of effective Stokes-Einstein diffusion radius of 4.7 Å.

(18) P. Debye, "Polar Molecules," Dover Publications, New York, N. Y., 1945, p 85.

(19) D. Gegiou, K. A. Muszkat, and E. Fischer, *J. Amer. Chem. Soc.*, **90**, 12 (1968). A referee has suggested this intercept is a measure of the rotation of the 2-butyl radical about its long axis which is certainly a possibility at this point.

T. Koenig,\* J. M. Owens

Department of Chemistry, University of Oregon  
Eugene, Oregon 97403

Received July 27, 1973

### Lithium Triethylborohydride as a Convenient Reagent for the Facile Reduction of Both Hindered and Bicyclic Epoxides Prone to Electrophilically Induced Rearrangement

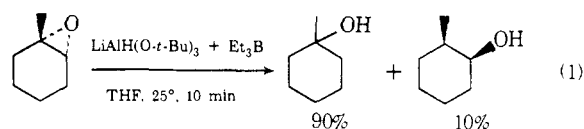
Sir:

Bicyclic epoxides, such as norbornene oxide and benzonorbornadiene oxide, are highly resistant to the usual reducing agents, reacting sluggishly, incompletely, and often with rearrangement. These epoxides, as well as highly hindered labile epoxides, can be reduced by lithium triethylborohydride relatively rapidly with exceptionally high regio- and stereospecificity, to the desired products.

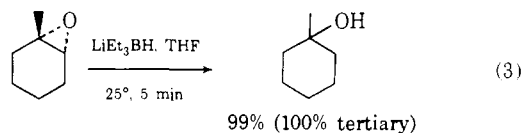
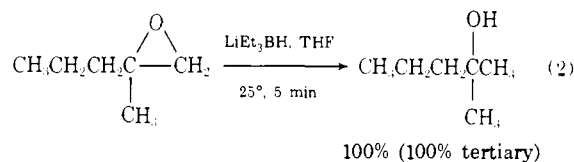
Difficulties are frequently encountered in the reductive opening of hindered and bicyclic epoxides with lithium aluminum hydride.<sup>1e,f,g</sup> In addition to the sluggishness of the reaction, there is frequently observed rearrangement. For example, treatment of *exo*-2,3-epoxynorbornane with lithium aluminum hydride in ether is reported to give a mixture of 7-norbornanol and *exo*-2-norbornanol.<sup>1a</sup>

Attempts to apply the reagent, lithium tri-*tert*-butoxyaluminumhydride, plus triethylborane<sup>2</sup> failed in the case of electrophilically labile epoxides. For example, both 1-methylcyclohexene oxide and styrene oxide gave significant amounts of the anti-Markovnikov

products. Evidently the monomeric aluminum *tert*-butoxide formed in the reaction is capable of inducing the electrophilic rearrangement of such epoxides<sup>3</sup> (eq 1).

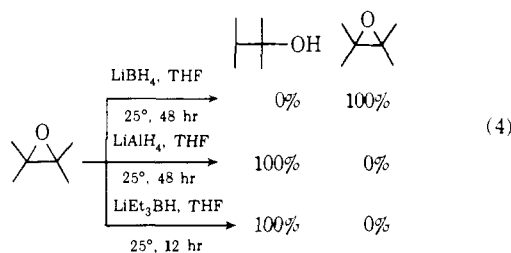


We recently reported that lithium triethylborohydride (LiEt<sub>3</sub>BH, "Super-Hydride") is the most powerful nucleophile known for S<sub>N</sub>2 displacement reactions with organic halides.<sup>4,5</sup> It appeared possible that LiEt<sub>3</sub>BH might overcome these difficulties. Indeed, we observed that the reduction of tertiary epoxides, such as 2-methyl-1-pentene oxide and 1-methylcyclohexene oxide, proceeds rapidly and cleanly at 25° (eq 2 and 3).



Yields are glpc values, except where the product was isolated, as indicated.

Even very hindered epoxides, such as 2,3-epoxy-2,3-dimethylbutane, react cleanly, considerably faster than with lithium aluminum hydride; under reflux the reaction is complete within 2 hr. Lithium borohydride was inert toward this epoxide (eq 4).



Moreover, lithium triethylborohydride reduces *exo*-2,3-epoxynorbornane reasonably rapidly, without rearrangement<sup>6</sup> (eq 5).

The advantage of the new reagent is especially evident for the reduction of bicyclic epoxides which are relatively labile. Thus, all of our attempts to reduce benzonorbornadiene oxide without rearrangement failed

(1) (a) P. D. Bartlett and W. P. Giddings, *J. Amer. Chem. Soc.*, **82**, 1240 (1960); (b) H. Kwart and T. Takeshita, *J. Org. Chem.*, **28**, 670 (1963); (c) H. C. Brown, S. Ikegami, and J. H. Kawakami, *ibid.*, **35**, 3243 (1970); (d) W. Hüchel and D. Volkman, *Justus Liebigs Ann. Chem.*, **664**, 31 (1963); (e) K. B. Wiberg, J. E. Hiatt, and G. Burgmaier, *Tetrahedron Lett.*, 5855 (1968); (f) P. G. Gassman and J. L. Marshall, *J. Amer. Chem. Soc.*, **88**, 2822 (1966); (g) L. A. Paquette and I. R. Dunkin, *ibid.*, **95**, 3067 (1973); (h) N. M. Yoon and H. C. Brown, *ibid.*, **90**, 2927 (1968).

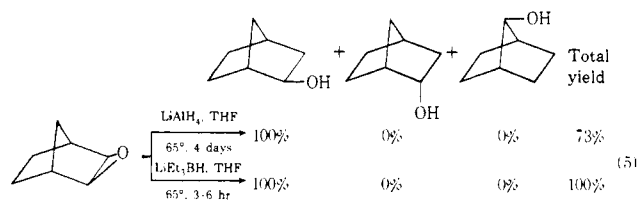
(2) H. C. Brown, S. Krishnamurthy, and R. A. Coleman, *J. Amer. Chem. Soc.*, **94**, 1750 (1972).

(3) H. C. Brown and S. Krishnamurthy, *J. Chem. Soc., Chem. Commun.*, 868 (1972).

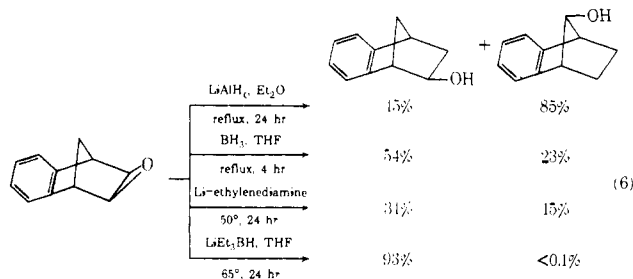
(4) H. C. Brown and S. Krishnamurthy, *J. Amer. Chem. Soc.*, **95**, 1669 (1973).

(5) Super-Hydride (lithium triethylborohydride) is now commercially available as 1 M solution in THF from Aldrich Chemical Co., Inc., Milwaukee, Wis.

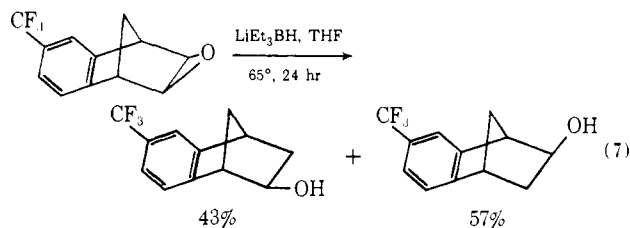
(6) Even at 25°, LiEt<sub>3</sub>BH-THF reduces *exo*-2,3-epoxynorbornane at a moderate rate, giving 37% of *exo*-2-norbornanol and 63% of the unreacted epoxide in 24 hr. However, LiAlH<sub>4</sub>-THF gives only 8% *exo*-2-norbornanol at 25°, after 10 days.



(eq 6). However, lithium triethylborohydride achieved



the clean reduction of this derivative to give 93% of *exo*-benzonorbornenol in >99.9% isomeric purity. Similar results were realized with the epoxide derived from 6-trifluoromethylbenzonorbornadiene (eq 7).



The following procedure for the reduction of 1-methylcyclohexene oxide is representative. An oven-dried 200-ml flask equipped with a side arm fitted with a Silicone rubber stopple, a magnetic stirring bar, and a reflux condenser connected to a mercury bubbler was cooled to room temperature under dry nitrogen. The flask was immersed in a water bath at 25°; then 25 ml of a 1.5 M solution in THF of LiEt<sub>3</sub>BH (37.5 mmol) was introduced into the reaction flask, followed by 3.1 ml (2.8 g, 25 mmol) of 1-methylcyclohexene oxide. The reaction mixture was stirred vigorously. After 2 min, glpc analysis of the reaction mixture indicated the completion of >99.5% reaction. The mixture was hydrolyzed and the organoborane oxidized. The aqueous phase was saturated with anhydrous potassium carbonate, the organic phase separated, and the aqueous phase extracted with two 20-ml portions of ether. The combined extracts were dried (K<sub>2</sub>CO<sub>3</sub>) and the solvents removed on a rotary evaporator. Upon distillation there was obtained 2.34 g (82%) of 1-methylcyclohexanol, bp 67° (21 mm), *n*<sub>D</sub><sup>20</sup> 1.4604 [lit.<sup>7</sup> bp 53–54° (7 mm), *n*<sub>D</sub><sup>20</sup> 1.4610].

In conclusion it should be emphasized that LiEt<sub>3</sub>BH provides a range of applicability far broader than the reducing agents previously available for such synthetic transformations. First, the reaction is rapid, clean, and gives excellent yields for a wide variety of epoxides. Second, the high regioselectivity and stereospecificity

(7) F. K. Signaigo and P. L. Cramer, *J. Amer. Chem. Soc.*, **55**, 3326 (1933).

of the reaction, especially with the labile bicyclic epoxides, enable us to use this reaction as a chemical tool to determine precisely the stereochemistry of epoxidation of such bicyclic olefins.<sup>8</sup> The present results make it clear that not only is lithium triethylborohydride an exceptionally powerful nucleophile in reductions but it is likewise remarkably free of electrophilic characteristics that sometimes complicate reduction by lithium aluminum hydride or other reagents.<sup>9</sup> We are continuing our active exploration in this area.<sup>10</sup>

(8) R. M. Schubert, Ph.D. Thesis, Purdue University, 1972.

(9) (a) L. W. Trevoy and W. G. Brown, *J. Amer. Chem. Soc.*, **71**, 1675 (1949); (b) E. L. Eliel and M. N. Rerick, *ibid.*, **82**, 1362 (1960); (c) M. N. Rerick and E. L. Eliel, *ibid.*, **84**, 2356 (1962); (d) E. C. Ashby and J. Prather, *ibid.*, **88**, 729 (1966); (e) D. K. Murphy, R. L. Alumbaugh, and B. Rickborn, *ibid.*, **91**, 2649 (1969), and the references cited therein; (f) H. C. Brown, P. M. Weissman, and N. M. Yoon, *ibid.*, **88**, 1458 (1966).

(10) Research in progress with Dr. S. Krishnamurthy and Mr. S. C. Kim.

(11) Postdoctoral Research Associate on Grant No. DA-ARO(D)-31-124-73-G1 supported by the U. S. Army Research Office (Durham).

(12) National Institutes of Health Predoctoral Fellow, 1967–1972.

S. Krishnamurthy,<sup>11</sup> Richard M. Schubert,<sup>12</sup> Herbert C. Brown\*

Richard B. Wetherill Laboratory, Purdue University  
West Lafayette, Indiana 47907

Received August 10, 1973

## Photochemistry in the Electronic Ground State. II. Selective Decomposition of *trans*-2-Butene by Pulsed Carbon Dioxide Laser

Sir:

The possibility to disturb the Boltzmann energy distribution by infrared (ir) lasers and thus control chemical reactions has already been discussed in the literature.<sup>1–7</sup> In all the cases which have been reported,<sup>7–10</sup> the interruption of chemical equilibrium by ir light was studied with compounds in which the energy of activation was equal to or smaller than the energy per einstein of the ir light beam. The most important problem in reactions induced by ir lasers is the competition between excitation and energy relaxation. In the past it was speculated that total redistribution of energy is expected within ten collisions in molecules with a number of atoms larger than ten. This assumption was based on shock-wave experiments.<sup>11,12</sup> Recently, it was shown in our laboratory by ir-ultraviolet (uv) double resonance experiments that thermal equilibrium was not reached within 10<sup>-5</sup> sec at pressures in the

(1) A. Yogev, R. M. J. Loewenstein, and D. Amar, *J. Amer. Chem. Soc.*, **94**, 1091 (1972).

(2) K. L. Kompa, *Z. Naturforsch. B*, **27**, 89 (1972).

(3) F. V. Bunkin, R. V. Karapetyan, and A. M. Prokhorov, *Sov. Phys. JETP*, **20**, 145 (1965).

(4) N. D. Artamonova, V. T. Platonenko, and P. V. Khokhlov, *Sov. Phys. JETP*, **31**, 1185 (1970).

(5) R. V. Ambartzumian, V. S. Letokhov, G. N. Makarov, and A. A. Puzetzkii, *Chem. Phys. Lett.*, **16**, 252 (1972).

(6) J. L. Lyman and R. J. Jensen, *J. Phys. Chem.*, **77**, 883 (1973).

(7) M. I. Buchwald, R. McFarlane, and S. H. Bauer, Third Conference on Chemical and Molecular Lasers, St. Louis, Mo., May 1–3, 1972.

(8) R. T. Hall and G. C. Pimentel, *J. Chem. Phys.*, **38**, 1889 (1963).

(9) S. W. Mayer, M. A. Kwok, R. W. F. Gross, and D. J. Spencer, *Appl. Phys. Lett.*, **17**, 516 (1970).

(10) T. J. Odiore, P. R. Brooks, and J. V. V. Kasper, *J. Chem. Phys.*, **55**, 1980 (1971).

(11) T. C. Cottrell and J. C. McCoubrey, "Molecular Energy Transfer in Gases," Butterworth, London, 1961.

(12) J. D. Lambert, *J. Chem. Soc., Faraday Trans.*, **68**, 364 (1972).