TABLE I

REDUCTION OF TERTIARY HALIDES TO HYDROCARBONS WITH SODIUM BOROHYDRIDE IN SULFOLANE

Compd	Registry no.	$NaBH_4$/compd, mol/mol	T ($NaBH_4$), °C	Time[a] ($NaBH_4$)	Yield of hydrocarbon[b]
3-Chloro-3-methyloctane	28320-88-9	1.0	100	2.5	45
		1.5	120	2.5	74
3-Chloro-3-ethylheptane	28320-89-0	2.0	120	2.5	84
1-Chloro-*n*-butylcyclohexane	28320-90-3	1.2	120	2.5	89
tert-Cumyl chloride	934-53-2	1.1	100	2.0[c]	78[d]
		6	100	2.0	9.5[d,e]
Triphenylmethyl chloride[f]	76-83-5	6	85	1.5	90.4[d,e]

[a] Reaction with borohydride followed by treatment with valeric acid at 190–200° for 18 hr. [b] Yields determined by glpc using standard solutions of the products. [c] Treatment with valeric acid for 2.5 hr at 190–200°. [d] Data from ref 2a. [e] Yield without valeric acid treatment. [f] Reaction in DMSO solvent.

method for synthetic applications. In addition, unlike corresponding reductions with lithium aluminum hydride[4] or sodium borohydride in aqueous diglyme,[5] the products are free of contaminating alkene side products. The reduction is not limited to tertiary halides containing an α hydrogen as illustrated by the reduction of triphenylmethyl chloride to triphenylmethane (Table I). In this case the reaction probably occurs by initial ionization followed by hydride capture.[6]

Experimental Section

Materials.—The materials were either obtained commercially and purified or synthesized by standard procedures. Sulfolane was distilled from calcium hydride and stored over 4A molecular sieves. Sodium borohydride was used as received from Alfa Inorganics, Inc.

General Reduction Procedure.—A solution of the tertiary chloride (0.009–0.015 mol) and $NaBH_4$ (0–1.0 mol excess) in 50 ml of sulfolane was prepared in a 500-ml one-neck flask equipped with a magnetic stirrer and a condenser attached at the top to a small Dry Ice–acetone trap which in turn was protected by a drying tube. The solution was heated at 100 or 120° for 2–2.5 hr. A tenfold molar excess of valeric acid was then cautiously added through the top of the condenser, and the temperature was raised to 190–200° and maintained for 18 hr. The solution was cooled, poured into water, and extracted thoroughly with cyclohexane. Yields were determined by diluting the cyclohexane solution to 100 ml and analyzing by glpc[7] (average of three to five determinations). The procedure is illustrated below for the reduction of 3-chloro-3-ethylheptane.

Reduction of 3-Chloro-3-ethylheptane.—The apparatus described above was charged with a solution of 3-chloro-3-ethylheptane (2.27 g, 0.0139 mol) and sodium borohydride (1.07 g, 0.0282 mol) in 50 ml of sulfolane and heated in an oil bath at 120° for 2.5 hr. Valeric acid (28.2 g, 0.282 mol, 30 ml) was slowly added through the top of the condenser and the oil bath temperature raised to 190–200° and maintained there for 18 hr. The mixture was cooled, poured into *ca.* 250 ml of water, and extracted several times with small portions of cyclohexane. The apparatus was washed with a few milliliters of cyclohexane and the combined organic solution diluted to 100 ml with cyclohexane. The product yield (84%) was determined by glpc[7] using a column temperature of 95° and a standard solution of 3-ethylheptane (Aldrich Chemical Co.). The cyclohexane solution was washed with two 100-ml portions of water and two 50-ml portions of 10% aqueous Na_2CO_3 and dried ($MgSO_4$). Solvent was removed on a rotary evaporator and the residue distilled at atmospheric pressure to obtain 1.1 g of 3-ethylheptane, bp 135–36°, $n^{28}{}_D$ 1.4076 [lit.[8] bp 143.1° (760 mm), $n^{20}{}_D$ 1.4090]. The ir spectrum was identical with that of an authentic sample.

Registry No.—Sodium borohydride, 16940-66-2.

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

(5) H. M. Bell and H. C. Brown, *ibid.*, **88**, 1473 (1966).

(6) S. Matsumura and N. Tokura, *Tetrahedron Lett.*, 363 (1969), have reported the reduction of aralkyl and triaryl tertiary halides to hydrocarbons with diborane or diisocamphenylborane in nitromethane. In this manner, the authors accomplished reduction of *tert*-cumyl and trityl chlorides to the hydrocarbons in 82 and 95–96% yields, respectively. The reactions were attributed to initial ionization followed by hydrogen capture and, at least in part for cumyl chloride, to elimination followed by hydroboration and subsequent protonation to the hydrocarbon by hydrogen chloride generated in the reaction. Our failure to observe substantial hydrocarbon formation in the absence of valeric acid treatment may be due to the destruction of HX by excess borohydride. See also, S. Matsumura and N. Tokura, *ibid.*, 4703 (1968).

(7) All glpc analyses were performed using Hewlett-Packard Model 5250B thermal conductivity chromatograph coupled to an Leeds & Northrup Model W recorder equipped with a Disc integrator. In all cases a 6-ft $^1/_8$-in. 10% OV-1 on 80–100 mesh Chromosorb W column was used.

(8) F. C. Whitmore and H. P. Orem, *J. Amer. Chem. Soc.*, **60**, 2573 (1938).

A Simple, Partial Resolution of *trans*-Cyclooctene

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Although one satisfactory asymmetric synthesis[1] and one complete resolution[2] of optically pure *trans*-cyclooctene have appeared in the literature, it should be reported that a more expeditious method of producing up to 20% optically pure olefin *via* Brown's asymmetric destruction method[3,4] is possible.

(−)-*sym*-Tetraisopinocampheyldiborane was prepared in triglyme at −10°. To this asymmetric hydroborating reagent was added an excess of racemic *trans*-cyclooctene, which was later partially recovered in optically enriched form by flash evaporation followed by silver nitrate extraction. Thus, based on starting (±)-*trans*-cyclooctene, it was possible to recover approximately 40% of the olefin in greater than 98% isomeric purity and up to 20% optical purity.

The data collected from many different runs suggest

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(1) E. J. Corey and J. I. Shulman, *Tetrahedron Lett.*, 3655 (1968).

(2) A. C. Cope, C. R. Ganellin, H. W. Johnson, T. V. Van Auken, and H. J. S. Winkler, *J. Amer. Chem. Soc.*, **85**, 3276 (1963).

(3) H. C. Brown, N. R. Ayyangar, and G. Zweifel, *ibid.*, **86**, 397 (1964), and references cited therein.

(4) For other examples of partial resolution by destructive asymmetric hydroboration, see S. I. Goldberg and F. L. Lam, *J. Org. Chem.*, **31**, 240 (1966); J. Furukawa, T. Kakuzen, H. Morikawa, R. Yawamoto, and O. Okuno, *Bull. Chem. Soc. Jap.*, **41**, 155 (1968); P. S. Wharton and R. A. Kretchmer, *J. Org. Chem.*, **33**, 4258 (1968); W. L. Waters and M. C. Caserio, *Tetrahedron Lett.*, 5233 (1968).

that the reaction is indeed complex.[5,6] However, it was found that lower temperatures, longer reagent preparation time, and smaller reaction volumes enhanced the resultant rotatory power of the partially resolved *trans*-cyclooctene.[7]

The overall results of these experiments indicate that partial resolution of *trans*-cyclooctene by kinetic asymmetric destruction (*via* asymmetric hydroboration) can be a valuable alternate[8] path to the optical enrichment of this unique olefin.

Experimental Section

Instrumentation.—All gas chromatographic analyses were performed on a Varian Aerograph Model 90-P instrument. Optical rotations were measured with a Ruldolph Model 80 polarimeter.

Materials.—(+)-α-Pinene (Aldrich) was distilled from crushed calcium hydride and collected at 152–155° (670 mm) [lit.[9] bp 156.2° (760 mm)], $[\alpha]^{27}D$ +57.1 ± 0.4° (*c* 5, $CHCl_3$). Boron trifluoride etherate (Eastman) was purified by distillation at 73° (59 mm) [lit.[9] bp 67° (43 mm)]. Triglyme (Ansul) was distilled at 216–217° (670 mm) [lit.[9] bp 220° (760 mm)] from $LiAlH_4$.

Preparation of (±)-*trans*-**Cyclooctene.**—The racemic olefin was prepared according to Cope's procedure[10] except that the *N,N,N*-trimethylcyclooctylammonium iodide was synthesized in one step from cyclooctylamine (Aldrich) using excess methyl iodide and base. In a typical run cyclooctylamine (50 g, 0.394 mol) was reacted with methyl iodide (228 g, 1.6 mol) in 200 ml of methanol. After the initial reaction had subsided, potassium carbonate (55 g, 0.4 mol) was carefully added and the mixture refluxed for 24 hr. After filtering, partially stripping, and cooling, the solution yielded 112 g (0.376 mol, 96%) of the tetraalkylammonium iodide. Following Cope's procedure,[10] 50 g (0.168 mol) of the iodide yielded 14.1 g (0.128 mol, 76%) of a 3:2 mixture of *trans*- and *cis*-cyclooctene, respectively. Extraction of the mixture with a 20% silver nitrate solution[10] yielded 7.2 g (0.065 mol, 37% overall yield from cyclooctylamine) of >98% pure (gc, 20 ft × $^3/_8$ in., 20% DEGS) *trans*-cyclooctene.

Partial Resolution of (±)-*trans*-**Cyclooctene.**—In a typical run, the asymmetric hydroborating reagent was prepared by mixing 0.379 g (0.01 mol) of $NaBH_4$ (12.0 ml of a 0.83 *M* solution in triglyme) and 2.68 g (0.197 mol) of (+)-α-pinene [$[\alpha]^{27}D$ +57.1 ± 0.4° (*c* 5, $CHCl_3$)] with 30 ml of dry triglyme. The solution was placed in a three-necked round-bottom flask, covered by N_2, and kept at −10°. Through a dropping funnel 1.39 g (0.0098 mol) of $BF_3 \cdot Et_2O$ (in 5 ml of triglyme) was slowly added to the rapidly stirred triglyme solution of $NaBH_4$ and α-pinene. After addition of the reagent was complete, the entire mixture was stirred an additional 30 hr at −10° after which 2.024 g (0.0184 mol) of (±)-*trans*-cyclooctene (containing 2.024 g of pentane as a gc standard) was added. This mixture was stirred 4 hr at −10° and then flash distilled at 50° (5 mm) into a Dry Ice–acetone trap until no more cyclooctene (by gc) remained in the reaction pot. Gc analysis of the raw flash distillate showed the presence of 0.87 g (0.0079 mol) of *trans*-cyclooctene. This raw yield represents 92% of the theoretically recoverable trans olefin.[11] Some *cis*-cyclooctene[12] and α-pinene[13] was also observed in the flash distillate.

Finally, the *trans*-cyclooctene was recovered in pure form from the flash distillate by the usual 20% $AgNO_3$ extraction.[10] After destruction of the silver complex with ammonium hydroxide, 0.685 g (0.0062 mol, 72%[10]) of *trans*-cyclooctene was obtained as a pentane solution. Removal of the pentane by distillation gave the pure trans olefin with $[\alpha]^{25}D$ −95.5 ± 0.5° (*c* 7, $CHCl_3$). Comparing the rotation in CH_2Cl_2 with that of Cope's[2] gives an optical purity of 20.8% for the partially resolved olefin.

Registry No.—(±)-*trans*-cyclooctene, 28541-65-3; (−)-*trans*-cyclooctene, 22770-27-0.

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(5) As with some of the more hindered olefins of Brown's, there is some ambiguity as to the exact nature of the asymmetric hydroborating species. See ref 6 and 7.

(6) D. J. Pasto, V. Balasubramaniyan, and P. W. Wojtkowski, *Inorg. Chem.*, **8**, 594 (1969). The authors proved that five different disproportionating equilibrium reactions exist simultaneously in certain alkylborane solutions.

(7) H. C. Brown and G. J. Klender, *ibid.*, **1**, 204 (1962). The authors showed that an appreciable equilibrium exists between tetraisopinocampheyldiborane and triisopinocampheyldiborane when the reagent is prepared in tetrahydrofuran. The trialkyldiborane is thought to be the cause of the reduced degree of resolution in the case of certain sterically hindered olefins. See H. C. Brown, N. R. Ayyangar, and G. Zweifel, *J. Amer. Chem. Soc.*, **86**, 1071 (1964). In diglyme the tetraalkyldiborane appears to precipitate, thereby shifting the equilibrium toward the more highly substituted diborane. Results in this lab indicate that this borane is more soluble in triglyme than in diglyme and that a more concentrated solution is required to effect precipitation.

(8) Since the synthesis of *dl-trans*-cyclooctene is relatively simple and inexpensive, loss of part of the trans olefin should not be objectionable. Moreover, the amount of the olefin "lost" can be reduced by the use of less hydroborating reagent. Of course, this would also result in lowered optical activity of the resolved *trans*-cyclooctene.

(9) D. D. Perrin, W. L. F. Armarego, and D. R. Perrin, "Purification of Laboratory Chemicals," Pergamon Press, New York City, N. Y., 1966.

(10) A. C. Cope, R. A. Pike, and C. F. Spencer, *J. Amer. Chem. Soc.*, **75**, 3212 (1953). The near-quantitative extraction procedure described by Cope has not yet been reproduced in this laboratory. Recovery of *ca.* 80% *trans*-cyclooctene by the $AgNO_3$ method represents this laboratory's best efforts.

(11) Generally, half of the *trans*-cyclooctene should have been returned unreacted.

(12) The exact origin of the cis olefin is unknown. However, gc analysis of the reaction mixture immediately after addition of the racemic olefin indicated almost immediate formation of this less strained alkene.

(13) α-Pinene has been found in varying amounts as a side product from the asymmetric hydroboration of bulky olefins, thereby inferring a preequilibrium between tetraisopinocampheyldiborane and triisopinocampheyldiborane plus α-pinene. See ref 7.

Catalysis by Molecular Sieves in the Preparation of Ketimines and Enamines[1]

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Ketimines and enamines can conveniently be prepared in high yield by the reaction of the appropriate ketones and amines in the presence of molecular sieves. The method is quite general and can be applied successfully even to medium-sized ring ketones and camphor, which are rather hindered. Since the method is so mild, it might be employed where more vigorous reagents (such as zinc chloride,[2a] titanium tetrachloride,[2b] or aluminum chloride[3]) may cause side reactions; since it is so simple, it may prove preferable to the use of acetals,[4] 1-amino-1-cyanoalkanes,[5] thioketones,[6] gem dichlorides,[7] or iminophosphorus compounds,[8] etc.,[9]

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(1) After this note had been submitted for publication, the authors saw the paper by E. P. Kyba, *Org. Prep. Proced.*, **2**, 149 (1970), on "An Improved Synthesis of Ketimines." Dr. Kyba used molecular sieves to shift the equilibrium in favor of the formation of six ketimines, three from acetone with various amines and three from methylamine with various methyl ketones. The present work extends that of Kyba to hindered ketones and further, in particular, reports the catalytic effects of molecular sieves in the formation of ketimines.

(2) (a) J. H. Billman and K. M. Tai, *J. Org. Chem.*, **23**, 535 (1958); (b) W. A. White and H. Weingarten, *ibid.*, **32**, 213 (1967).

(3) K. Taguchi, unpublished results.

(4) J. Claisen, *Ber.*, **29**, 2931 (1926); J. Hoch, *C. R. Acad. Sci., Ser. C*, 199, 1428 (1934).

(5) W. C. Bain, P. D. Richie, and A. E. Wright, *J. Chem. Soc.*, 1454 (1964); J. S. Walia, L. Heindl, H. Lader, and P. S. Walia, *Chem. Ind. (London)*, 155 (1968).

(6) A. Schoenberg and W. Urban, *J. Chem. Soc.*, 530 (1935).

(7) M. Pauly, *Justus Liebigs Ann. Chem.*, **187**, 196 (1877); D. Y. Curtin and J. W. Hausser, *J. Amer. Chem. Soc.*, **83**, 3474 (1961).

(8) R. Appel and A. Hauss, *Ber.*, **93**, 405 (1960); W. S. Wadsworth and W. D. Emmons, *J. Amer. Chem. Soc.*, **84**, 1316 (1962).

(9) P. A. Smith, "The Chemistry of Open-Chain Organic Nitrogen Compounds," Vol. I, W. A. Benjamin, New York, N. Y., 1965, p 295.