Reaction of *p*-Toluenesulfonyl Isocyanate with Tetramethyl-2-tetrazene.—Tetramethyl-2-tetrazene (2.95 g, 25 mmol) was dissolved in 50 ml of Spectrograde carbon tetrachloride and placed in a flask fitted with reflux condenser, drying tube, and syringe septum. *p*-Toluenesulfonyl isocyanate (5.00 g, 25 mmol) dissolved in 25 ml of Spectrograde carbon tetrachloride was introduced gradually into the tetrazene solution by syringe. The solution immediately turned orange and then yellow, and a solid separated out. Enough heat was evolved to cause the solution to reflux. The mixture was stirred for 0.5 hr. An infrared spectrum of the reaction mixture at this time showed no band for *p*-toluenesulfonyl isocyanate (4.4 μ). Methylene chloride was added to dissolve the precipitated solid, and the resulting mixture was extracted with three 50-ml portions of saturated aqueous sodium bicarbonate solution. These extracts were acidified with 2 *N* hydrochloric acid and extracted with three 50-ml portions of methylene chloride. Drying the latter extracts over magnesium sulfate and evaporation left 3.72 g (62%) of 1-(*p*-toluenesulfonyl)-3,3-dimethylurea (**7**) as a white solid, mp 146–160° dec. In another run, **7** was collected by filtration of the acidified sodium bicarbonate extracts. On standing the filtrate precipitated further solid, which was collected and dried, giving 0.28 g (5%) of 1-(*p*-toluenesulfonyl)-3-methylurea (**9**): mp 160–171° dec (lit.[10] mp 170–172°); ir (Nujol) 2.97 (m, N-H), 6.02 (s, C=O), 6.39 (m), 7.50 (m, $-SO_2-$), 8.59 (s, $-SO_2-$), 9.16 (w), 10.42 (m), 11.07 (m), 11.37 (m), and 12.27 μ (m); nmr (DMSO-d_6) δ 2.34 (s, 3 H), 2.60 (s, 3 H), 7.39 (d, 2 H), 7.93 (d, 2 H).

An authentic sample of **7** was prepared by reaction of *p*-toluenesulfonyl isocyanate with dimethylamine in chloroform and isolated by the extraction procedure described above: mp 156–170° dec; ir (Nujol) 3.03 (m, N-H), 5.90 (s, C=O), 6.25 (w), 7.43 (m, SO_2), 8.37 (w), 8.49 (m), 8.73 (s, $-SO_2-$) 9.16 (s), 9.78 (w), 11.09 (w), 11.65 (m), 12.29 (m), 13.27 (m), and 14.20 μ (w); nmr ($CDCl_3$) δ 2.41 (s, 3 H), 2.88 (s, 6 H), 7.29 (d, 2 H), 7.95 (d, 2 H).

Anal. Calcd for $C_{10}H_{14}N_2O_3S$: C, 49.58; H, 5.78; N, 11.57; S, 13.22. Found: C, 49.30; H, 5.91; N, 11.70; S, 12.99.

Melting of **7** was accompanied by evolution of a gas, presumably dimethylamine, which turned wet pH paper blue-green.

Reaction of Phenyl Isocyanate with Tetrabenzyltetrazene.—Tetrabenzyltetrazene (4.20 g, 0.010 mol) and phenyl isocyanate (1.12 g, 0.009 mol) were dissolved in 75 ml of carbon tetrachloride in a 125-ml erlenmeyer flask fitted with a reflux condenser and drying tube, and rubber septum fitted to a small side arm for ir sampling. After 11.5 days of stirring at room temperature, the isocyanate was consumed, as judged by ir. The solvent was stripped off, and the residue was chromatographed on silica gel. This yielded (a) unreacted tetrabenzyltetrazene (0.94 g, 23%, eluted with pentane–benzene mixtures) and (b) a pale yellow solid, eluted with benzene, mp 156–158° after recrystallization from ethanol (0.248 g, 6%), identified as **10** by its ir and nmr spectra (see text).

Anal. Calcd for $C_{28}H_{27}N_5O$: C, 74.83; H, 6.01; N, 15.59; mol wt, 449. Found: C, 75.51, 75.20; H, 5.99, 6.16; N, 15.72; mol wt, 420 (osmometric in chloroform).

The residue from evaporating the mother liquor from the recrystallization of **10** gave 0.145 g (5%) of benzaldehyde 2,4-dinitrophenylhydrazone on treatment with 2,4-dinitrophenylhydrazine reagent.

Further elution of the chromatography column with ether–benzene mixtures yielded (c) 1,1-dibenzyl-3-phenylurea, 0.243 g, (8%), mp 126–128° after recrystallization from benzene–ligroin (lit.[11] mp 125°).

Registry No.—**1**, 6130-87-6; **7**, 26093-79-8; **8**, 28321-01-9; **9**, 13909-69-8; **10**, 28321-03-1; diphenylketene, 525-06-4.

Acknowledgments.—We gratefully acknowledge financial support from Rohm and Haas, and a NASA traineeship to T. J. R.

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[10] H. Ruschig, *Arzneim.-Forsch.*, **8**, 448 (1958); *cf. Chem. Abstr.*, **53**, 1316*i* (1959).

[11] T. Mukaiyama, S. Ozaki, and Y. Hobayashi, *Bull Chem. Soc Jap.*, **29**, 51 (1956).

Reduction of Tertiary Halides to Hydrocarbons with Sodium Borohydride in Sulfolane

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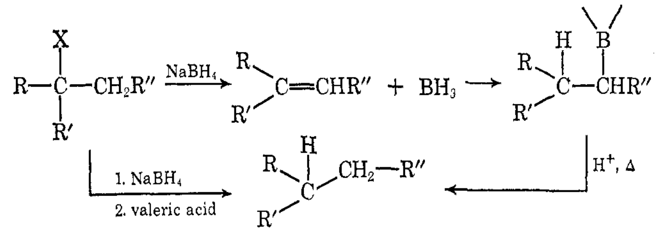
The use of sodium borohydride in polar aprotic solvents as convenient systems for the selective removal of aliphatic halides and tosylates was recently reported from our laboratories[2a] and also independently by Bell and coworkers,[2b] and more recently, by Vol'pin, Dvolaitzky, and Levitin.[2c] In the course of our study, the tertiary halide cumyl chloride was observed to undergo dehydrohalogenation followed by hydroboration. The intermediate alkylborane could be converted to the expected alcohol with alkaline peroxide or to isopropylbenzene by refluxing with valeric acid. This latter procedure results in overall reduction of tertiary halides to the hydrocarbon as shown in Scheme I.

Scheme I



This note describes the utility of sodium borohydride in sulfolane as a convenient one-step procedure for direct removal of tertiary halides by way of elimination, hydroboration, and protonolysis. Recently, Jacobus[3] has reported use of the procedure (in DMSO) to reduce 3-chloro-3,7-dimethyloctane to 2,6-dimethyloctane in unspecified yield.

After conducting some preliminary experimentation, the general reaction conditions represented in Table I were chosen to provide adequate yields with reasonable reaction times. The use of a large excess of borohydride does not appear to be necessary as borohydride/compound ratios of 1:1 to 2:1 were entirely sufficient. Using temperatures of 120° for reaction with borohydride (100° for the benzyl halide, cumyl chloride) and 190–200° (reflux) for the subsequent protonolysis, a total reaction time of about 20 hr was realized. The reaction mixtures were worked up by simply pouring into water and extracting with cyclohexane or ether. Isolation is easily accomplished by washing the organic solution with water and dilute carbonate, drying, and removing the solvent.

The ease of the reductive procedure coupled with the good to excellent yields obtainable recommends the

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[1] (a) Undergraduate Research Participant, 1969–1970; (b) Undergraduate Research Participant, 1968–1969.

[2] (a) R. O. Hutchins, D. Hoke, J. Keogh, and D. Koharski, *Tetrahedron Lett.*, 3495 (1969); (b) H. M. Bell, C. W. Vanderslice, and A. Spehar, *J. Org. Chem.*, **34**, 3923 (1969); (c) M. Vol'pin, M. Dvolaitzky, and H. Levitin, *Bull. Soc. Chim. Fr.*, 1526 (1970).

[3] J. Jacobus, *Chem. Commun.*, 338 (1970).

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$_2$CO$_3$ 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).