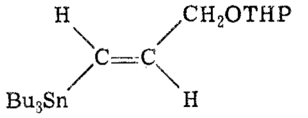
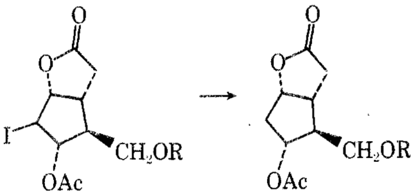
Table I

Substrate (mmol)	Product	Mmol of $NaBH_4$	R, R_3SnCl (mmol)	Conditions	Yield, %
$PhCH_2CH_2CH_2Br$ (1)	$PhCH_2CH_2CH_3$	2	Bu (0.1)	2.5 hr, 25°	86[b]
$PhCH_2CH_2CH_2Br$ (1)	$PhCH_2CH_2CH_3$	2	Bu (0.1)	0.5 hr, 25°, $h\nu$	88[b]
Ia (0.27)	IIa	0.41	Bu (0.027)	20 min, 10°, $h\nu$	93[a]
Ia (0.156)	IIa	0.195	Me (0.032)	20 min, 15°, $h\nu$	94[a]
n-$C_{14}H_{29}Br$ (0.35)	n-$C_{14}H_{30}$	0.56	Bu (0.035)	0.5 hr, 25°, $h\nu$	100[b]
Ib (0.078)	IIb	0.117	Me (0.026)	15 min, 15°, $h\nu$	88[a]
p-BrC_6H_4NHAc (0.08)	C_6H_5NHAc	0.1	Bu (0.008)	3 hr, 25°, $h\nu$	96[a]
$HC{\equiv}CCH_2OTHP$ (5.64)	 III	6.1	Bu (6.1)	3 hr, reflux	73.5[a]

[a] Isolated yields. [b] Yields determined by VPC.



Ia, R = CH_3 IIa, R = CH_3
b, R = $CH_2C_6H_5$ b, R = $CH_2C_6H_5$

ly tin hydrides have usually been employed in stoichiometric amounts (either preformed or generated in situ from the nonvolatile polymethylhydrosiloxane and trialkyltin oxides).[1,2] The product, once formed by these procedures, must be separated from a full 1 equiv of trialkyltin halide. A catalytic method has been described using stoichiometric amounts of lithium aluminum hydride;[1] however, the reactivity of lithium aluminum hydride greatly limits the method's usefulness.

In our procedure the organic halide and 0.1–0.3 equiv of the trialkyltin chloride are dissolved in absolute ethanol and a solution of sodium borohydride in ethanol is added rapidly. In most experiments the reaction was carried out in Pyrex with irradiation by a 100-W mercury floodlamp so that reaction occurred rapidly at or below room temperature. The catalytic cycle is given in eq 1 and 2.

$$2R_3SnX + 2NaBH_4 \longrightarrow 2R_3SnH + 2NaCl + B_2H_6 \quad (1)$$

$$R_3SnH + R'X \longrightarrow R_3SnX + R'H \quad (2)$$

Ethanol is used as the solvent in order to trap the resulting diborane.[3]

Our results are summarized in Table I. As can be seen, ester and lactone functions do not interfere with this procedure.[4] The ethanolic solution of tributyltin hydride produced by our method also can be used in the hydrostannation reaction, illustrated by the preparation of the synthetically useful[5] *trans*-1-tri-*n*-butylstannyl-1-propene-3-tetrahydropyranyl ether (III).

Experimental Section

All reactions were performed under argon with carefully degassed solvents.

2-Oxa-3-oxo-6-*syn*-methoxymethyl-7-*anti*-acetoxy-*cis*-bicyclo[3.3.0]octane (IIa). To the iodide Ia (0.0553 g, 0.156 mmol) and trimethyltin chloride (0.0063 g, 0.0316 mmol) in 3 ml of air-free absolute ethanol cooled to 15° was rapidly added via syringe sodium borohydride (0.0076 g, 0.195 mmol) dissolved in 1.5 ml of ethanol. The solution was irradiated with a 100-W mercury floodlamp. Initially gas was rapidly evolved. After 20 min no starting material remained. Oxalic acid (0.0010 g) was added (to convert any trimethyltin hydride to the tin ester) followed 5 min later by 20 ml of CH_2Cl_2. The solution was washed once with saturated sodium bicarbonate and dried over anhydrous magnesium sulfate and the solvent was evaporated to give as a slightly yellow oil a mixture of hexamethylditin and IIa. Chromatographic separation on silica gel (eluent 1:1 benzene–ether) gave 0.0336 g (94%) of IIa, the spectral data for which were identical with those for authentic material.[6]

***trans*-1-Tri-*n*-butylstannyl-1-propene-3-tetrahydropyranyl Ether (III).** To tri-*n*-butyltin chloride (2.00 g, 6.1 mmol) in 5 ml of absolute ethanol was added dropwise sodium borohydride (0.23 g, 6.1 mmol) in 10 ml of ethanol. The solution became warm, gas was vigorously evolved, and sodium chloride precipitated. After stirring at 25° for 10 min, propargyl tetrahydropyranyl ether (0.790 g, 5.46 mmol) was added and the solution was refluxed for 3.5 hr, cooled, treated with 30 ml of pentane, and filtered. Evaporation of the solvent gave a clear oil containing (by ir and NMR) only III and tri-*n*-butyltin hydride. Distillation gave 1.78 g (73.5%) of III, bp 140–150° (0.1 mm), identical with material prepared by the direct reaction of isolated tri-*n*-butyltin hydride with propargyl tetrahydropyranyl ether.

Registry No.—Ia, 55721-21-6; Ib, 55721-22-7; IIa, 37745-51-0; IIb, 52689-80-2; III, 55723-10-9; $PhCH_2CH_2CH_2Br$, 637-59-2; n-$C_{14}H_{29}Br$, 112-71-0; p-BrC_6H_4NHAc, 103-88-8; $HC{\equiv}CCH_2OTHP$, 6089-04-9; $PhCH_2CH_2CH_3$, 103-65-1; n-$C_{14}H_{30}$, 629-59-4; C_6H_5HNAc, 103-84-4; $NaBH_4$, 16940-66-2; Bu_3SnCl, 1461-22-9; Me_3SnCl, 1066-45-1.

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(3) See E. R. Birnbaum and P. H. Javora, *J. Organomet. Chem.*, **9**, 379 (1967).
(4) Some reduction is observed if unnecessarily extended reaction times are used.
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(6) E. J. Corey, T. K. Schaaf, W. Huber, U. Koelliker, and N. M. Weinshenker, *J. Am. Chem. Soc.*, **92**, 397 (1970).
(7) This study was assisted financially by a grant from the National Science Foundation.

Reduction of Epoxides to Olefins with Low Valent Titanium

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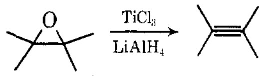
The reduction of epoxides to olefins is of some importance in synthesis, and a variety of methods have been devised to accomplish the transformation.[1] Among these methods has been the use of strongly reducing metals or

Table I
Reduction of Epoxides to Olefins with $TiCl_3$-$LiAlH_4$

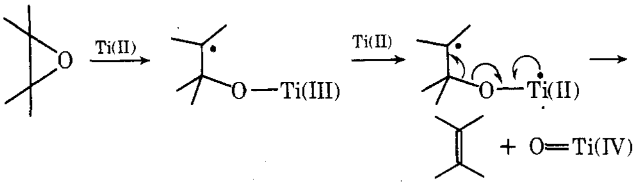


Substrate	Registry no.	Yield, %	Registry no.
α-Methylstyrene oxide	2085-88-3	36	98-83-9
Cyclooctene oxide	286-62-4	53	931-88-4
1-Dodecene oxide	2855-19-8	69	112-41-4
1-Decene oxide	2404-44-6	65	872-05-9
Cholesterol oxide	55700-78-2	75	57-88-5
cis-5-Decene oxide	36229-64-8	70 (4:1 trans/cis)	7433-78-5 (cis)
trans-5-Decene oxide	2165-61-9	70 (4:1 trans/cis)	7433-56-9 (trans)

metal salts including chromous ion,[2] zinc–copper couple,[3] magnesium amalgam,[4] zinc,[5] low valent tungsten complexes,[6] and $FeCl_3$–BuLi.[7] We have recently been studying the use of low valent titanium species as reducing agents for organic systems[8] and therefore examined the possible reduction of some epoxides.

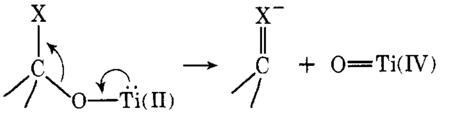
We have found that Ti(II), prepared by reaction of dry $TiCl_3$ with 0.25 molar equiv of $LiAlH_4$ in tetrahydrofuran, is a convenient and efficient reagent for converting epoxides to olefins. Some of our results are given in Table I.

The mechanism of epoxide reduction with Ti(II) is probably similar to that proposed by Kochi[2] for the chromous ion reduction. Central to this postulate is the implication



that the reaction must proceed with loss of olefin stereochemistry, as observed for reductions with chromous ion[2] and ion,[7] but not with low-valent tungsten.[6] This is in fact observed as shown in Table I. Both *cis*- and *trans*-5-decene oxide give the identical 81:19 mixture of *trans*- and *cis*-5-decene on treatment with $TiCl_3$-$LiAlH_4$. A control experiment established the stability of *cis*-5-decene under the reaction conditions.

Yet a further implication of this mechanistic postulate is the expectation that whenever a Ti(II)–oxygen bond is formed next to a group, X, which can stabilize free radicals, then deoxygenation should occur. We have confirmed this expectation in reactions with halohydrins (X = CBr) and cyanohydrins (X = CN), and we are currently studying these and other cases in detail.[9]



From a synthetic point of view, use of $TiCl_3$-$LiAlH_4$ for epoxide reduction appears competitive with use of other reagents. A major advantage of the present procedure, however, is the ease with which the reagent may be prepared. A 4:1 ball-milled mixture of $TiCl_3$ and $LiAlH_4$ prepared for our evaluation by Alfa Inorganics has proven to be indefinitely stable in the absence of solvent and extremely convenient to use as a one-bottle source of reagent.[10]

Experimental Section

General Reaction Procedure. The titanium reagent was prepared in either of two ways.

Method A. Lithium aluminum hydride (0.20 g, 5.0 mmol) was added in small portions to a stirred slurry of $TiCl_3$ (3.08 g, 20.0 mmol) in 60 ml of dry tetrahydrofuran under an inert atmosphere (argon or nitrogen) at room temperature. Hydrogen evolution was immediate, and the resulting fine black suspension was stirred for 15 min before use.

Method B. Alternatively, a 4:1 premix of $TiCl_3$ and $LiAlH_4$[10] (effective mol wt 164, 3.28 g, 20.0 mmol) was added with stirring and in small portions to 60 ml of dry THF at room temperature under an inert atmosphere. Hydrogen evolution occurred immediately and the fine black suspension was stirred 15 min before use.

A solution of epoxide (10 mmol) in 10 ml of dry THF was added to the Ti(II) reagent, and the reaction mixture was refluxed for 3 hr. The reaction mixture was then cooled to room temperature and quenched by addition of 60 ml of water. The organic layer was diluted with ether, then drawn off, washed with water and with brine, dried ($MgSO_4$), and concentrated to yield the product. With the exception of cholesterol, yields were determined by GLC with appropriate internal standards added. Products were identified by comparison with authentic samples. The results are presented in Table I.

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(10) We thank Mr. Robert Wade, Alfa Inorganics, Beverly, Mass., for preparing this premix, which is commercially available as "Mc Murry's Reagent".

A Simple One-Step Alternative to the Malonic Ester Synthesis

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The classical malonic ester synthesis involving discrete alkylation and decarbalkoxylation steps remains, in spite of attempts at replacement, the standard method for effecting two-carbon homologation of alkyl halides. Although nor-