the reaction mixture was allowed to warm to room temperature. The xenon which evolved was collected in a storage can and the resulting solution was distilled at 25° under vacuum into another Kel-F tube at −196°. Comparison of GC retention times of the distillate on a 12 ft × 0.125 in. column packed with 2.5% Apiezon L on Chromosorb W at 150° with those of authentic samples showed the formation of 1-fluoronaphthalene (50%) and 2-fluoronaphthalene (11%). Further analysis of the redistilled reaction mixture on a GC–MS instrument, using the same GC column, indicated that each peak consisted of a single component and had the correct parent ion mass and fragmentation pattern expected for the particular monofluoro substituted naphthalene. No attempt was made to separate the isomers physically from the reaction mixture. Some unreacted naphthalene was also found.

Reaction of Anthracene with XeF_2. A degassed solution of 1.78 g (10 mmol) of anthracene in 15 ml of chloroform up to 10^{-5} Torr was introduced into an evacuated (5×10^{-6} Torr) Kel-F tube containing 0.67 g (ca. 4.0 mmol) of XeF_2 at −196°. After the gradual increase of the temperature to −12°, a light yellow solution formed which intensified into a deep green by increasing the temperature to 12° during a period of 4 hr. The reaction products were filtered through a glass wool plug into another Kel-F tube under vacuum. The course of reaction as followed by GC, using an 11 ft × 0.125 in. column packed with 2.5% Carbowax 20 mesh on Chromosorb G at 225° indicated no unreacted anthracene and comparison of the data with those of authentic samples showed the formation of 1-fluoroanthracene, 2-fluoroanthracene, and 9-fluoroanthracene in the relative ratio of 5:1:3, based on their relative retention times. The mass spectra (interfaced with GC) were used to identify the three components and analysis of the fragmentation patterns and maximum mass peaks of each component allowed assignment of three of the peaks to monofluoroanthracenes. The distillate was concentrated almost to dryness under reduced pressure and chromatographed on an 18 × 1.5 in. column packed with neutral alumina. By eluting the column with *n*-hexane, 9-fluoroanthracene, mp 102° (lit.[8] 103°), was obtained as light lemon-colored crystals, which sublimed under vacuum at 78° (yield 26%), followed by pale yellow crystals of 1-fluoroanthracene, mp 108° (lit.[9] 108°), which sublimed in vacuo at 80° (yield 45%). Further elution with *n*-hexane–chloroform (3:1) gave yellow, crystalline 2-fluoroanthracene, mp 212° (lit.[8] 212°), which was crystallized from ethanol to give sublimable yellow crystals (yield 9%). An unidentifiable dark brown solid was obtained by eluting the column with *n*-hexane–$CHCl_3$ (1:1), while another deep pink material, which did not dissolve even in tetrahydrofuran and methanol, remained behind.

Reaction of Phenanthrene with XeF_2. XeF_2 (0.43 g) contained in a Kel-F tube was allowed to react with a degassed solution of 1.1 g (ca. 6 mmol) of phenanthrene in 10 ml of methylene chloride at 10^{-5} Torr at −196°. The solution was gradually warmed from −196° to room temperature during a period of 2 hr by means of a series of baths to give a brown-green reaction mixture which was further warmed in a water bath at 60° to ensure complete reaction. The course of reaction, followed by GC, using the same column described for the anthracene reaction mixture, indicated the presence of one fluoro derivative in addition to some unreacted phenanthrene.

The reaction mixture was freed from the solvent as well as HF under reduced pressure and the deep green solid was chromatographed on an 18 × 1.5 in. column packed with Florisil. Elution with *n*-hexane gave a 40% yield of a colorless, crystalline compound, 9-fluorophenanthrene, which was crystallized from petroleum ether (bp 30–60°) to give colorless needles, mp 50° (lit.[10] 51–52°). The rest of the material, on further elution with *n*-hexane–CH_2Cl_2 (10:3), gave a bright yellow substance which was crystallized from petroleum ether–$CHCl_3$ (1:1) to give a yellow compound which decomposed at 181–182° to a brown mass and presumably is a difluorophenanthrene as inferred from the highest mass fragment obtained in its MS, *m/e* 214 (100%), $C_{14}H_8F_2$.

In another experiment, 0.51 g (2.8 mmol) of phenanthrene and 8 ml of CH_2Cl_2 were allowed to react with 0.5 g (ca. 3 mmol) of XeF_2 under similar conditions in the presence of 0.05 mmol of anhydrous HF. On warming the reaction mixture to 0°, an intense green color developed, with brisk evolution of xenon gas. At room temperature, the mixture turned to dark magenta after 15 min. The course of reaction as followed by GC indicated the absence of any phenanthrene and no formation of any monofluoro species as found in the previous experiment. The MS interfaced with GC indicated the formation of difluoro, trifluoro, and tetrafluoro addition products of phenanthrene. However, no polyfluoro compounds could be isolated either by column chromatography or crystallization. A separate analysis of the fragmentation patterns and maximum mass peaks of each component permitted identification of the di-, tri-, and tetrafluoro compounds.

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Registry No.—**1**, 529-85-1; **2**, 440-21-1; naphthalene, 91-20-3; XeF_2, 13709-36-9; 1-fluoronaphthalene, 321-38-0; 2-fluoronaphthalene, 323-09-1; anthracene, 120-12-7; 1-fluoroanthracene, 7651-80-1; 2-fluoroanthracene, 21454-60-4; phenanthrene, 85-01-8.

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Reduction of Bromohydrins to Olefins with Low Valent Titanium

John E. Mc Murry* and Tova Hoz

Thimann Laboratories, University of California, Santa Cruz, California 95064

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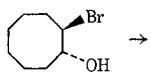
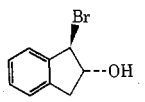
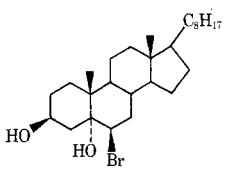
Although the reduction of bromohydrins to olefins is of some importance in synthesis, few direct methods have been devised to effect the reaction. To our knowledge, only the well-known zinc–acetic acid method has been used to any extent,[1] although chromous ion has been shown to be effective[2] and has been studied in some detail. Low valent tungsten halides also appear to work, but details are not available.[3]

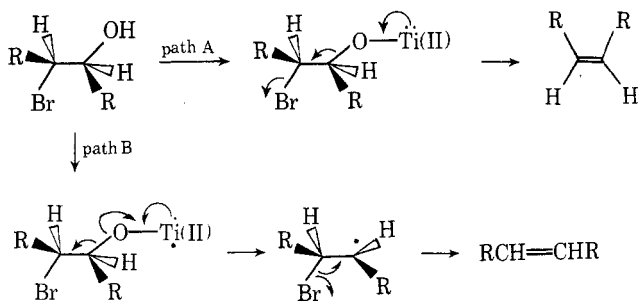
We have been involved recently in a study of low valent titanium reagents for use as reducing agents in organic synthesis,[4] and among the substrates we have examined have been some representative bromohydrins. We have found that a reagent prepared by mixing 1 molar equiv of $LiAlH_4$ with 0.25 molar equiv of $TiCl_3$ in tetrahydrofuran is extremely effective in reducing bromohydrins to olefins. Some of our results are given in Table I.

From a synthetic point of view, several comments should be made. The first is that all substrates studied reduced in high yields indicating the generality of the reaction. Second is the fact that the reaction conditions are nonacidic, making the method compatible with the presence of acid-sensitive functional groups and quite different from the other methods. Finally, we note from the reductions carried out on *erythro*- and *threo*-5-decene bromohydrins, that these reactions proceed with little stereoselectivity. In this respect, the results are similar to those obtained both with zinc[5] and with chromous ion.[2]

Table I
Reduction of Bromohydrins to Olefins with $TiCl_3$–$LiAlH_4$

	Yield, %
 → Cyclooctene	96
 → Indene	93
 → Cholesterol	79
2-Bromo-1-decanol → 1-Decene	74
2-Bromo-1-dodecanol → 1-Dodecene	91
erythro-5-Bromo-6-decanol → 5-Decene (4:1 trans/cis)	91
threo-5-Bromo-6-decanol → 5-Decene (2.3:1 trans/cis)	82

It had been our hope in initiating this study that titanium(II) might function as a two-electron reducing agent in the manner shown (path A). Should this occur, one would expect preferential trans elimination leading to specific olefin geometry (threo → cis; erythro → trans). Since this desired retention of geometry is not observed, however, we favor a mechanistic pathway involving one-electron transfer and the intermediacy of radicals, similar to that proposed for chromous ion[2] (path B).



Experimental Section

General Reaction Procedure. The reactive titanium(II) species was made in either of two ways.

Method A. $LiAlH_4$ (0.142 g, 3.75 mmol) was added to a stirred slurry of $TiCl_3$ (2.3 g, 15 mmol) in 70 ml of dry tetrahydrofuran (THF) under a nitrogen atmosphere. Hydrogen evolution was immediate, and the resulting black titanium(II) suspension was stirred for 10 min at room temperature before use.

Method B. Alternatively, a 4:1 premix of $TiCl_3$ and $LiAlH_4$[6] (effective mol wt 164, 2.46 g, 15.0 mmol) was added cautiously with stirring to 70 ml of dry THF at room temperature under a nitrogen atmosphere. The black titanium(II) suspension was stirred for 10 min before use.

The substrate bromohydrin (5.0 mmol) in 5 ml of THF was added to the Ti(II) suspension, and the reaction mixture was refluxed for 16 hr. After cooling, the reaction was quenched by addition of 60 ml of water, and then diluted with pentane. The organic layer was drawn off, washed with brine, dried ($MgSO_4$), and concentrated by distillation. Product yields were then determined by GLC using appropriate internal standards. Product identities were determined in all cases by comparison with authentic samples. In this manner, the following reactions were run.

***trans*-2-Bromocyclooctanol** gave **cyclooctene,** 96% as determined by GLC using indene as internal standard.

***trans*-1-Bromo-2-hydroxyindan** gave **indene,** 93% as determined by GLC using cyclooctene as internal standard.

6β-Bromo-3β,5α-dihydroxycholestane gave **cholesterol,** 79% isolated yield, mp 148° (lit. 148.5°).

2-Bromo-1-decanol gave **1-decene,** 74% as determined by GLC using 1-dodecene as internal standard.

2-Bromo-1-dodecanol gave **1-dodecene,** 91% as determined by GLC using 1-decene as internal standard.

***erythro*-5-Bromo-6-decanol** gave **5-decene,** 91% as determined by GLC using 1-decene as internal standard. The product 5-decene was analyzed for cis/trans composition by the following method (the cis and trans 5-decenes were inseparable by GLC under all conditions tried). Epoxidation of the olefin mixture with *m*-chloroperbenzoic acid ($CHCl_3$, room temperature) gave a mixture of isomeric epoxides which could be analyzed either by NMR integration [*cis*-5-decene epoxide, NMR (CCl_4) δ 2.91 (–CHO–, broad singlet); *trans*-5-decene epoxide, NMR (CCl_4) δ 2.67 (–CHO–, broad singlet)] or by GLC (12 ft × 0.25 in. 5% Carbowax 20M on Chromosorb P). A control experiment on a known cis/trans mixture established the validity of the analysis.

The 5-decene thus analyzed contained 80% trans olefin and 20% cis olefin.

***threo*-5-Bromo-6-decanol** gave **5-decene,** 82% as determined by GLC using 1-decene as internal standard. The product was 70 trans, 30% cis.

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Registry No.—*trans*-2-Bromocyclooctanol, 1502-14-3; *trans*-1-bromo-2-hydroxyindan, 56804-70-7; 6β-bromo-3β,5α-dihydroxycholestane, 1857-83-6; 2-bromo-1-decanol, 39579-74-3; 2-bromo-1-dodecanol, 56804-71-8; *erythro*-5-bromo-6-decanol, 56804-72-9; *threo*-5-bromo-6-decanol, 56804-73-0; cyclooctene, 931-88-4; indene, 95-13-6; cholesterol, 57-88-5; 1-decene, 872-05-9; 1-dodecene, 112-41-4; *trans*-5-decene, 7433-56-9; *cis*-5-decene, 7433-78-5.

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(6) This premix is sold commercially by Alfa Inorganics, Beverly, Mass.

Stereochemistry of Hydride Reductions. Participation by Heteroatoms

John N. Labows, Jr.,* and Nelson Landmesser

Wilkes College, Wilkes-Barre, Pennsylvania 18703

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The reduction of alkyl halides with hydride ion is generally believed to occur by an SN2 mechanism leading to inversion of configuration. Studies using $LiAlD_4$, $NaBD_4$ in HMPA, and $LiEt_3BD$ have shown exclusive inversion in the absence of any secondary factors.[1,2] However, a recent example of nitrogen participation through complexing with the hydride reagent has resulted in retention of configuration.[3]

We have studied the $LiAlD_4$ reduction of the isomeric *endo,endo-* and *exo,exo*-2,6-diiodo-9-oxabicyclo[3.3.1]nonanes[4,5] (structures 1 and 3). In each case reduction led to an identical product identified as *exo,exo*-2,6-dideuterio-9-oxabicyclo[3.3.1]nonane (2) by NMR, ir, and mass spectroscopy. In particular, the infrared spectrum showed C–D absorptions at 2140 and 2160 cm^{-1} which correspond to values reported for axial C–D stretch in 1,3-dioxanes.[6] The NMR was studied in detail by use of Eu(thd)$_3$. The 9-oxabicyclononanes have been found to form strong shift com-