Hole Transfer Promoted Hydrogenation: One-Electron Oxidation as a Strategy for Selective Reduction of π-Bonds

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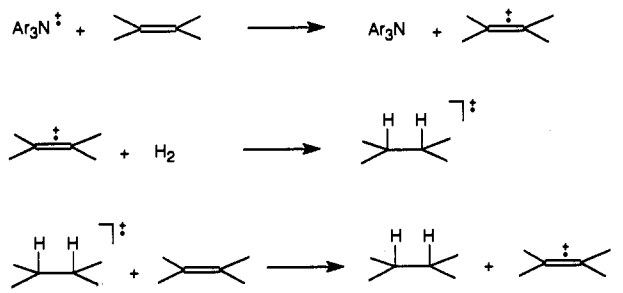
Abstract: One-electron oxidation is developed as a strategy for selective and efficient reduction of relatively ionizable functionalities, including conjugated dienes, styrenes, vinyl sulfides, aromatics, and even strained σ-bonds. Reduction is highly sensitive to substrate ionizability and permits selective reduction of the more ionizable function in a difunctional context. Ionization of the substrates to cation radicals is effected *via* the mild hole transfer agent tris(4-bromophenyl)-aminium hexachloroantimonate, and subsequent reduction of the cation radicals is accomplished by tributyltin hydride. The new reduction conditions provide a novel route for generating free radicals which may prove useful in the field of radical cyclizations. This is especially attractive in the case of phenyl vinyl sulfides since the phenylthio group, which remains intact subsequent to cyclization, provides versatile functionality for further synthetic operations.

One-electron oxidation is increasingly being recognized and exploited as a fundamental option for activating molecules toward a variety of rapid and selective chemistry.[1-9] The basic catalytic concept associated with one-electron oxidation has been termed hole transfer catalysis or, simply, hole catalysis.[1,2] Mechanistically, hole catalysis exploits the unique reactivity of cation radicals in the specific format of either a cation radical chain or a classic catalytic mechanism. Especially when a mild hole transfer catalyst such as tris(4-bromophenyl)aminium hexachloroantimonate ($1^{\bullet+}$) is used, hole formation and thus reactivity can be selectively directed to the most ionizable functionality of a multifunctional molecule. This promising strategy has been used recently to develop a new hole-catalyzed epoxidation reaction which is efficient, stereospecific, and highly site-selective.[9] The present paper describes the development of a new and similarly site-selective reduction reaction.[10]

Results and Discussion

Hole transfer activation of neutral reactant molecules ($R + HC^{\bullet+} \rightarrow R^{\bullet+} + HC$; where R = reactant, $HC^{\bullet+}$ = hole catalyst, and HC = hole conjugate of the catalyst) provides extraordinary kinetic impetus for many reactions (R → P; P = product) by providing access to the cation radical potential surface ($R^{\bullet+} \rightarrow P^{\bullet+}$), where activation energies are often vanishingly small. Because the product hole can subsequently be transferred to a new reactant molecule either directly ($P^{\bullet+} + R \rightarrow P + R^{\bullet+}$) or *via* the hole conjugate of the catalyst ($P^{\bullet+} + HC \rightarrow P + HC^{\bullet+}$; $HC^{\bullet+} + R \rightarrow HC + R^{\bullet+}$), these reactions quite often have the further advantage of propagation *via* a chain or classic catalytic format.[2,11,12] These two mechanistic formats are obviously very closely related since both provide substoichiometric acceleration *via* the cation radical potential surface and both have been properly considered to be catalytic in the general sense.[13] The mechanism illustrated in Scheme I appears to represent an attractive potential path for hole catalytic dihydrogenation. As has previously been noted for other hole-catalyzed additions, dihydrogenation of an alkene should have less *thermodynamic* driving force on the cation radical surface than on the neutral surface as a consequence of diminished delocalization of the hole in the product cation radical as compared to that in the reactant.[14] Nevertheless, ample precedent exists to show that hole catalysis is capable of delivering powerful *kinetic* impetus in spite of this effect. Consequently, the catalytic reduction of ionizable substrates by molecular hydrogen under aminium salt conditions was investigated. 1,1-Diphenylethene and *trans*-stilbene were selected as typical substrates since both of these efficiently undergo hole-catalyzed epoxidation[9] and cyclopropanation[15] under aminium salt conditions. However, no reduction was observed in either case, although the formation of the usual small amounts of hole-catalyzed dimers attested to the generation of substrate cation radicals. Possibly the inability of these cation radicals to react with dihydrogen is essentially a bond strength effect, the H–H bond dissociation energy being about 40 kcal/mol stronger than the carbon–carbon π-bonds usually involved in hole-catalyzed cycloadditions. This effect may be further accentuated by the

Scheme I. Hole Transfer Chain Catalyzed Dihydrogenation (Hypothetical)



(1) Bauld, N. L. *Tetrahedron* **1989**, *45*(17), 5307–5363.
(2) Bauld, N. L. *Advances in Electron Transfer Chemistry*, Vol. 2; Mariano, P. S., Ed.; JAI Press: Greenwich, 1992.
(3) Todd, W. P.; Dinnocenzo, J. P.; Farid, S.; Goodman, J. L.; Gould, I. R. *J. Am. Chem. Soc.* **1991**, *113*, 3601–3602.
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(8) Heidbreder, A.; Mattay, J. *Tetrahedron Lett.* **1992**, *33*, 1973–1976.
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(10) Mirazfal, G. A.; Bauld, N. L. *Ibid.* **1992**, *114*, 5457–5458.
(11) The classic catalytic mechanism has been strongly advocated by: Eberson, L.; Olofsson, B. *Acta Chem. Scand.* **1991**, *45*, 326–326.
(12) Evidence for the simultaneous operation of both chain and catalytic mechanisms has been presented by: Kim, T.; Pye, J.; Bauld, N. L. *J. Am. Chem. Soc.* **1990**, *112*, 6285–6290.
(13) Chanon, M. *Acc. Chem. Res.* **1987**, *20*, 214.
(14) Bauld, N. L.; Bellville, D. J.; Pabon, R.; Chelsky, R.; Green, G. *J. Am. Chem. Soc.* **1983**, *105*, 2378–2382.
(15) Bauld, N. L.; Stufflebeme, G. W.; Lorenz, K. T. *J. Phys. Org. Chem.* **1989**, *2*, 585–601.

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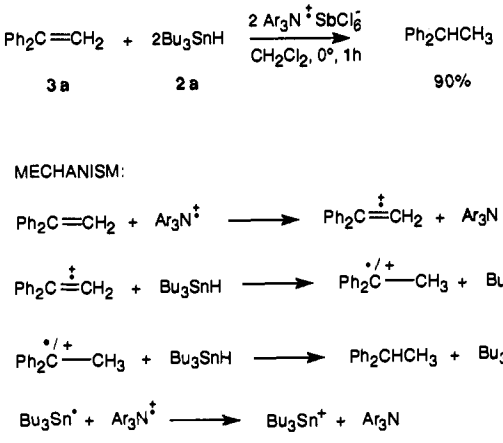
Scheme II. Hole-Promoted Dihydrogenation[a]

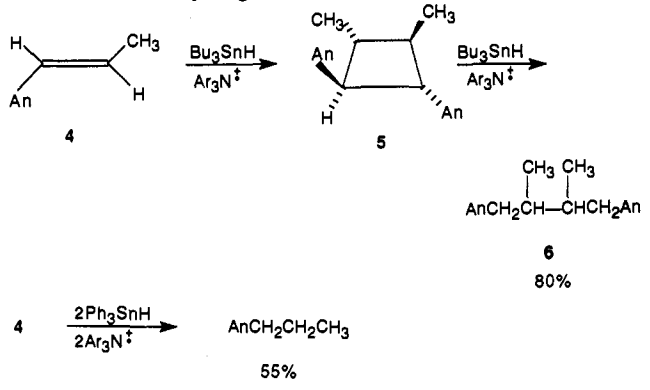


[a] +/· = carbocation *or* radical.

preference of hole-catalyzed reactions for highly nonsynchronous transition states.[14] In the present context, this would require that both the H–H bond and the partial π-bond of the substrate cation radical undergo cleavage with concomitant formation of essentially only one C–H bond.

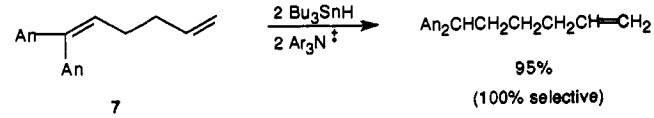
Hole-Promoted Hydrogenation. The acceleration and selectivity available on the cation radical potential surface nevertheless remains attractive even when not reinforced by a catalytic format. Hole-promoted chemistry, in which the hole "catalyst" is consumed stoichiometrically, would appear to be synthetically viable provided that the catalyst is readily available. Tris(4-bromophenyl)aminium hexachloroantimonate ($\mathbf{1}^{\bullet+}\mathbf{SbCl_6}^-$) is, of course, commercially available[16] and also readily prepared in quantity.[17] It can also be regenerated from recovered triarylamine **1** where desirable. The reduction of an alkene cation radical to an alkane formally requires the transfer of a hydrogen atom *and* a hydride ion to the cation radical. The hydrogen transfer agents found most effective in this work are tributyltin hydride (**2a**) and triphenyltin hydride (**2b**). The concept of promoting alkene *reduction* by initial one-electron *oxidation* is illustrated in Scheme II by the reduction of 1,1-diphenylethene (**3a**, E_{ox} = 1.22 V,[18] 90% yield). Because of the marked electronegativity difference between tin and carbon, it was tentatively projected that the initial hydrogen transferred would be a hydride ion, thus giving the tributyltin cation and the 1,1-diphenylethyl radical as opposed to an initial hydrogen-atom transfer, which would yield the tributyltin radical and the 1,1-diphenylethyl cation. This interesting mechanistic issue will be addressed in a subsequent section. The ability of $\mathbf{1}^{\bullet+}$ to ionize **3a** has previously been established[10] and is further confirmed by the formation of minor amounts (*ca.* 5%) of the hole-catalyzed dimer of **3a** under dihydrogenation conditions.[10] A major substituent effect, appropriate to the ionization of **3a**, is implicit in the complete unreactivity of the corresponding 4,4′-dichloro derivative **3b** under the same conditions as employed for **3a** (0 °C, 1 h). In contrast to both **3a** and **3b**, 4,4′-dimethoxy derivative **3c** was efficiently (93%) reduced essentially in the time of mixing (less than 1 min). A quantitative study of the competitive reduction of **3a** and its corresponding 4,4′-dimethyl derivative **3d** provided a relative rate ratio of 1:167, corresponding to a Hammett–Brown ρ value of –7.2, using $\sigma_p^+(CH_3)$ = –0.31. For comparison, a ρ value of –8.0 has been found for the generation of a full unit of positive charge in the equilibrium protonation of **3a**.[19] The possibility of a Bronsted acid catalyzed mechanism is, however, ruled out by the observation

Scheme III. Dihydrogenation of *trans*-Anethole[a]



[a] An = 4-MeOC$_6$H$_4$.

Scheme IV. Selectivity in Hole-Promoted Dihydrogenation[a]



[a] An = 4-MeOC$_6$H$_4$.

that excess 2,6-di-*tert*-butylpyridine fails to suppress the reaction.[1,2,20] Further, **3a** also undergoes dihydrogenation by **2a** under photosensitized electron transfer (PET) conditions, where the development of an acid catalyst is highly unlikely.[1,2,20] Finally, trapping experiments capable of detecting carbocation intermediates are discussed in a subsequent section. Consequently, the powerful electron withdrawal indicated by the large, negative ρ value can confidently be associated with the formation of a cation radical intermediate in or before the rate-determining step.

As noted in the case of **3a**, the formation of byproducts which are uniquely derived from hole catalytic chemistry unambiguously demonstrates the presence of cation radical intermediates under the dihydrogenation conditions and provides added support for a cation radical mechanism. Such products are formed in the case of virtually every successful hole promoted dihydrogenation, including those of 1,1-bicyclohexenyl and 1,3-cyclohexadiene, where the hole-catalyzed Diels–Alder dimers are especially well-known.[1,2] However, the reduction of 2,4-dimethyl-1,3-pentadiene is even more incisively diagnostic. The Diels–Alder cyclodimer formed under dihydrogenation conditions is exclusively a hole-catalyzed Diels-Alder dimer, and none of the acid-catalyzed Diels–Alder cyclodimer is formed.[1,2]

In the case of *trans*-anethole (**4**), the rapid hole-catalyzed cyclodimerization is strongly predominant, affording cyclobutadimer **5** (Scheme III).[1,2] However, since **5** is also relatively readily ionized, with the corresponding cation radical $\mathbf{5}^{\bullet+}$ being considered to have a long, one-electron bond,[21,22] reductive cleavage to **6** occurs efficiently (80%) in the presence of 4 mol of reductant (**2a**). Furthermore, the dihydrogenation of monomeric **5** could be accomplished through the simple expedient of using a better hydrogen transfer agent (**2b**; 55%).[23]

Simple alkenes such as 1-octene and norbornene are, of course, completely resistant to hole-promoted dihydrogenation. This makes it possible to selectively reduce a more ionizable double bond in the presence of a simple alkene moity, as is illustrated for **7** (Scheme IV, 95% yield). In view of the large, negative ρ value observed for **3**, it should be feasible to reduce, with virtual exclusivity, the more ionizable double bond even when the ionization potentials differ by as little as 0.1 eV. Conjugated dienes can also be readily dihydrogenated, as is illustrated for 1,1′-bicyclohexenyl (**8**) and *trans,trans*-1,4-diphenyl-1,3-buta-

(16) Available from Aldrich Chemical Company.
(17) Bell, F. A.; Ledwith, A.; Sherrington, D. C. *J. Chem. Soc. C* **1969**, 2719.
(18) Garrison, J. M.; Ostovic, D.; Bruice, T. C. *J. Am. Chem. Soc.* **1989**, *111*, 4960.
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(21) Bauld, N. L.; Pabon, R. *J. Am. Chem. Soc.* **1983**, *105*, 633–634.
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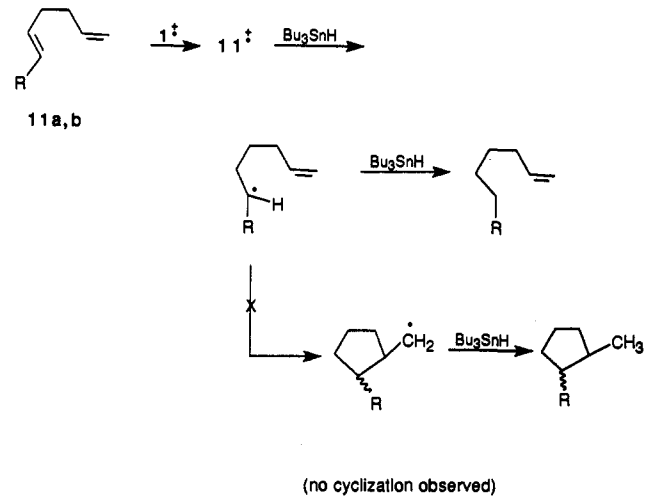
(23) Kuivila, H. G. *Synthesis* **1970**, *10*, 499–509.

Scheme V. 5-Hexenyl Radical Cyclization Probes[a]



[a] a, R = 4-MeOC$_6$H$_4$; b, R = PhS.

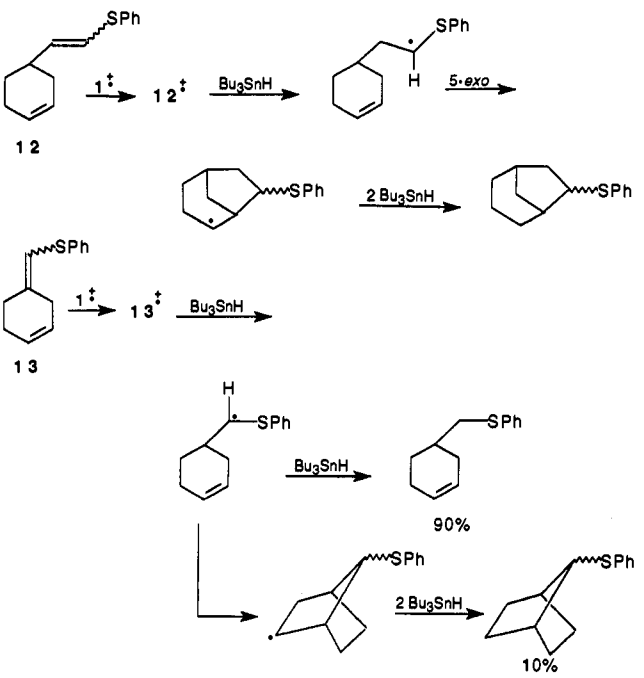
diene (**9**). The sole product of the reduction of **8** is cyclohexenylidenecyclohexane (90%), corresponding to exclusive 1,4-dihydrogenation. In contrast, **9** yields *trans*-1,4-diphenyl-2-butene and *trans*-1,4-diphenyl-1-butene in a 2:1 ratio (75%). These results both appear plausible for the abstraction of hydrogen atoms from **2a** by an intermediate allylic radical. Thus, selective 1,4 or 1,2 addition is not expected unless one allylic position is particularly hindered in the intermediate radical.

The reduction of suitably ionizable aromatics is also feasible. Anthracene, *e.g.*, is reduced to 9,10-dihydroanthracene in 75% yield, although less readily ionizable aromatics such as phenanthrene and naphthalene prove to be inert.

Among the electron-rich alkenes, vinyl sulfides are especially amenable to reduction, as would be expected.[24] An attractive feature of hole-promoted dihydrogenation of vinyl sulfides is the absence of hydrogenolysis of carbon–sulfur bonds. The reduction of ((phenylthio)methylene)cyclohexane (**10**) is efficient (88%), and the retention of the phenylthio group clearly contrasts with catalytic hydrogenation.

Detection of a Secondary Intermediate. Cation radicals are the primary intermediates involved in the proposed mechanism for hole-promoted dihydrogenation. Subsequent hydrogen transfer to the cation radical is proposed to yield, as a secondary intermediate, either a substituted alkyl radical (*via* hydride transfer) or a carbocation (*via* hydrogen atom transfer). Simple electronegativity considerations suggest that radical formation should be favored. To confirm this hypothesis, appropriate radical probe substrates (**11a,b**), which are based upon the familiar 5-*exo* and 6-*endo* cyclizations of the parent and substituted 5-hexenyl radicals, were synthesized (Scheme V).[25] The variation in carbocation stabilization available in **11a** vs **11b** (*p*-anisyl > phenylthio) was considered useful in view of the possibility that increasing carbocation stability could potentially engender a change to the carbocation mechanism. Somewhat surprisingly, the hole-promoted dihydrogenation of both **11a** and **11b** proceeded normally, *i.e.*, without detectable cyclization. Although this result superficially appears to be in conflict with the rather facile cyclizations reported for the 1-phenyl- and a variety of other 1-substituted-5-hexenyl radicals,[26,27] it should be noted that these latter cyclizations were typically conducted at elevated temperatures, usually above 80 °C, in contrast to the very mild conditions

Scheme VI. Improved Radical Probes



(0 °C) of the hole-promoted reactions. The successful cyclizations also appear to have been conducted either in the absence of an efficient hydrogen atom transfer agent such as tributyltin hydride or, at most, at low concentrations of the latter.

Since hole-promoted dihydrogenation could not be effected under conditions approaching the typical radical cyclization conditions, more efficient radical probes were sought. Tetrahydrobenzaldehyde derivative **12** was selected as a conveniently available and potentially efficient probe. Radical cyclization to form a five-membered ring (the 5-*exo* cyclization mode) was expected to be substantially faster in this system than in the case of **11a,b** since cyclization would afford a secondary radical in the case of **12** (Scheme VI) as opposed to the primary radical which would be generated from **11a,b** (Scheme V). Efficient cyclization was, in fact, realized in the hole-promoted dihydrogenation of **12**. The preferential formation of the bicyclo[3.2.1]octyl ring system *via* the 5-*exo* cyclization mode reflects the typical preference in radical cyclizations. The 6-*endo* cyclization mode, which would have produced bicyclo[2.2.2]octyl products, was not observed. The unusually high selectivity for the 5-*exo* mode presumably reflects the much milder conditions of the hole-promoted reaction. It is significant that in analogous carbocation cyclizations, bicyclo[2.2.2] and bicyclo[3.2.1] products are produced in virtually equal amounts.[28]

In contrast to the efficient cyclization observed in the case of **12**, in which none of the uncyclized dihydrogenation product was observed, the hole-promoted dihydrogenation of **13** yields predominantly an uncyclized dihydrogenation product (Scheme VI). However, 10% of a bicyclo[2.2.1]heptyl product is also formed. The relative difficulty of this latter cyclization appears consistent with the strain inherent in the bicyclo[2.2.1]heptyl ring system and the 5-*endo* cyclization mode required.

An Additional Carbocation Test. The hole-promoted dihydrogenations of 1-(*p*-anisyl)- and 1-(phenylthio)-4-phenyl-1-butene (**14a,b**) were also found to proceed without cyclization to the phenyl ring (Scheme VII). When the conditions of the hole-catalyzed reaction were simulated except that the hole promoter was replaced by a strong Bronsted acid catalyst (*p*-toluenesulfonic acid), the result was exclusive cyclization even though tributyltin hydride was present in the same concentration as in the hole-

(24) The oxidation potentials for phenyl vinyl sulfide, phenyl vinyl ether, and *N*-methyl-*N*-vinyl acetamide have been recorded as 1.42, 1.62, and 1.55 V vs SCE.[1,2]

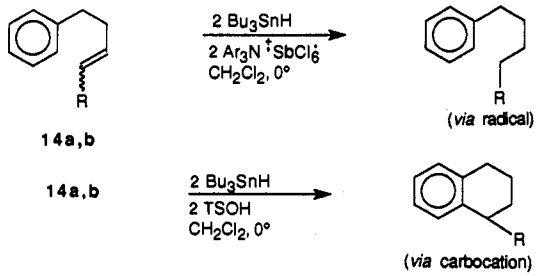
(25) Motherwell, W. B.; Crick, D. *Free radical Chain Reactions in Organic Synthesis*; Academic Press: New York, 1992.

(26) Motherwell, W. B.; Crick, D., ref 25, pp 213–157.

(27) Wilt, J. W.; Massie, S. N.; Dobek, R. B. *J. Org. Chem.* **1970**, *35*, 2803. Pines, H.; Sih, N. C.; Rosenfield, D. B. *J. Org. Chem.* **1966**, *31*, 2255.

(28) Winstein, S.; Carter, P. *J. Am. Chem. Soc.* **1961**, *83*, 4485–4486. Walborsky, H. M.; Baum, M. E.; Youssef, A. A. *Ibid.* 988.

Scheme VII. A Carbocation Probe[a]



[a] a, R = 4-MeOC$_6$H$_4$; b, R = PhS.

catalyzed reaction. The acid-catalyzed reaction is assumed to involve a carbocation intermediate (as the ion pair), which apparently cyclizes more rapidly than it is reduced by the hydride reagent.

Summary. One-electron oxidation is developed as a strategy for selective and efficient reduction of relatively ionizable functionalities, including conjugated dienes, styrenes, vinyl sulfides, aromatics, and even strained σ-bonds. Reduction is highly sensitive to substrate ionizability and permits selective reduction of the more ionizable function in a difunctional context. Ionization of the substrates to cation radicals is effected *via* the mild hole transfer agent tris(4-bromophenyl)aminium hexachloroantimonate, and subsequent reduction of the cation radicals is accomplished by tributyltin hydride. A variety of trapping experiments indicate the generation of free radicals as secondary intermediates formed by hydride ion transfer to substrate cation radicals. The subsequent reduction of these radicals presumably involves hydrogen atom abstraction from tributyltin hydride since the intermediacy of carbocations is decisively excluded. The new reduction conditions provide a novel route for generating free radicals which may prove useful in the field of radical cyclizations. This is especially attractive in the case of phenyl vinyl sulfides since the phenylthio group, which remains intact subsequent to cyclization, provides versatile functionality for further synthetic operations. One especially interesting operation, in view of the effectiveness of the phenylthio group for generating radical centers,[25] is the possibility of a double-barreled radical cyclization.

Experimental Section

Analysis. Proton magnetic resonance (^{1}H NMR) spectra were recorded on a General Electric QE-300 spectrometer as solutions in $CDCl_3$. Chemical shifts are reported in parts per million (ppm) downfield from the reference tetramethylsilane (TMS). Splitting patterns are designated as follows: s, singlet; d, doublet; t, triplet; q, quartet; p, pentet; m, multiplet. Low-resolution mass spectra (LRMS) were obtained on a Hewlett-Packard 5971A GC–MS spectrometer equipped with an HP-1 cross-linked methyl silicone GVM (12-m × 0.2-mm) capillary column. High-resolution mass spectra (HRMS) were recorded on a Dupont (CEC) 21-110B mass spectrometer. Analytical gas chromatographic (GC) analyses were performed on a Varian Model 3700 equipped with a flame ionization detector and a 12-M BP1 capillary column, using nitrogen as a carrier gas.

Reagents. Methylene chloride and HPLC grade acetonitrile were distilled from phosphorus pentoxide and stored over molecular sieves prior to use. Tris(4-bromophenyl)aminium hexachloroantimonate (Aldrich) was washed several times with cold anhydrous ether and dried *in vacuo* prior to use. 1,4-Dicyanobenzene (Aldrich) was twice recrystallized from benzene and dried *in vacuo* prior to use. Tributyltin hydride (Fluka) and triphenyltin hydride (Aldrich) were used as received without further purification. 1,2,3,6-Tetrahydrobenzaldehyde, Raney nickel, phosphorus pentoxide, 5% platinum on activated carbon, bicyclo[2.2.1]hept-2-ene, bicyclo[2.2.2]oct-2-ene, and bicyclo[3.2.1]octan-2-one were all purchased from Aldrich Chemical Co. Olefins were either synthesized or purchased from Aldrich Chemical Co. and independently passed through a short column of activated neutral alumina immediately prior to reaction to remove trace peroxides.

General Procedure for the Preparation of Olefins via Wittig Reaction. In a dry, 50-mL, three-necked round-bottomed flask equipped with a stirrer, nitrogen inlet, and additional funnel, 10 mmol of phosphonium salt and 25 mL of anhydrous diethyl ether were added. The solution was cooled to −10 °C and, with stirring, a solution of 9.5 mmol (2.5 M, 3.8 mL) of *n*-butyllithium in hexanes was added in a dropwise fashion to the reaction mixture. After all the *n*-butyllithium was added, the temperature of the reaction was allowed to rise to room temperature and then maintained as such for a period of 30–60 min. To the resulting ylide was added a solution of 8.5 mmol of substrate (ketone or aldehyde) in 10 mL of anhydrous diethyl ether in a dropwise fashion through the addition funnel. After the addition was completed, the reaction mixture was then allowed to stir for an additional 5–8 h. The resulting precipitates (triphenylphosphine oxide, etc.) were filtered and thoroughly washed with anhydrous diethyl ether. The combined ethereal filtrate was washed several times with water and then dried over anhydrous sodium sulfate. After filtration of sodium sulfate and removal of volatile material, the product(s) was(were) purified by flash silica gel column chromatography with hexanes:ethyl acetate (9:1 v/v) as eluent to give the desired product(s) upon removal of solvents. The following olefins were derived and isolated from their precursor Wittig phosphonium salt and carbonyl compound (aldehyde or ketone) in this fashion, producing the yields and spectral characteristics shown below.

1,1-Bis(*p*-tolyl)ethylene: isolated yield, 62%; mp 60–62 °C (lit.[29] mp 59–60 °C); ^{1}H NMR ($CDCl_3$) δ 7.23 (d, 8H, PhH), 5.40 (s, 2H), 2.37 (s, 6H); LRMS *m/e* 208 (base), 193, 178, 165, 152, 115, 91, 89, 65, 63.

1,1-Bis(*p*-methoxyphenyl)ethylene: isolated yield, 57%; mp 140–142 °C (lit.[29] mp 141–142 °C); ^{1}H NMR ($CDCl_3$) δ 7.32 (d, 4H, PhH), 6.89 (d, 4H, PhH), 5.31 (s, 2H), 3.83 (s, 6H); LRMS *m/e* 240 (base), 225, 209, 182, 165, 156, 139, 115, 89, 63.

1,1-Bis(*p*-chlorophenyl)ethylene: isolated yield, 65%; mp 80–82 °C (lit.[29] mp 84–86 °C); ^{1}H NMR ($CDCl_3$) δ 7.33 (s, 8H, PhH), 5.47 (s, 2H); LRMS *m/e* 248, 213, 178 (base), 151, 102, 88, 75.

1,1-Bis(*p*-methoxyphenyl)hexa-1,5-diene: isolated yield, 66%; ^{1}H NMR ($CDCl_3$) δ 7.0 (m, 8H, PhH), 5.96 (t, 1H), 5.72 (m, 1H), 5.01 (dd, 2H, J = 18, 10 Hz), 3.80 (s, 3H), 3.75 (s, 3H), 2.18 (t, 4 H); LRMS *m/e* 294, 253 (base), 222, 178, 145, 121, 91, 77; HRMS *m/e* calcd for $C_{20}H_{22}O_2$ 294.161980, found 294.162608.

((Phenylthio)methylene)cyclohexane: isolated yield, 40%; ^{1}H NMR ($CDCl_3$) δ 7.28 (s, 5H, PhH), 5.90 (s, 1H), 2.35 (m, 4H), 1.57 (s, 6H); LRMS *m/e* 204, 175, 147, 109, 91, 77 (base), 51; HRMS *m/e* calcd for $C_{13}H_{16}S$ 204.097272, found 204.097555.

1-(*p*-Methoxyphenyl)-4-phenyl-1-butene: isolated yield, 81%; ^{1}H NMR ($CDCl_3$) δ 7.34 (d, 2H, PhH, J = 9 Hz), 7.26 (s, 5H, PhH), 6.90 (d, 2H, PhH, J = 9 Hz), 6.40 (d, 1H, J = 18 Hz), 5.78 (m, 1H), 3.80 (s, 3H, OCH_3), 2.84–2.22 (m, 4H); LRMS *m/e* 238, 178, 147 (base), 131, 115, 91, 77, 65; HRMS *m/e* calcd for $C_{17}H_{18}O$ 238.135765, found 238.135870.

1-(Phenylthio)-4-phenyl-1-butene: isolated yield, 89%; ^{1}H NMR ($CDCl_3$) δ 7.26 (s, 5H, PhH), 7.22 (s, 5H, PhH), 6.18 (d, 1H, J = 16 Hz), 6.10–5.70 (dt, 1H), 2.84–2.31 (m, 4H); LRMS *m/e* 240, 149 (base), 134, 116, 115, 91, 77, 65; HRMS *m/e* calcd for $C_{16}H_{16}S$ 240.09727, found 240.096878.

4-(2-(Phenylthio)ethenyl)cyclohexene (12): isolated yield, 81%; ^{1}H NMR ($CDCl_3$) δ 7.30 (s, 5H, PhH), 6.24 (d, 1H, J = 16 Hz), 6.20–5.80 (dt, 1H), 5.68 (s, 2H), 2.48–1.22 (m, 7H); LRMS *m/e* 216, 162, 147, 129, 107, 85 (base), 79, 77, 51; HRMS *m/e* calcd for $C_{14}H_{16}S$ 216.097272, found 216.098688.

1-(Phenylthio)hexa-1,5-diene: isolated yield, 76%; ^{1}H NMR ($CDCl_3$) δ 7.36 (s, 5H, PhH), 6.23 (d, 1H, J = 16 Hz), 5.94 (m, 2H), 5.08 (dd, 2H, J = 18, 10 Hz), 2.24 (m, 4H); LRMS *m/e* 190, 149, 110, 109, 81, 80 (base), 79, 65, 53; HRMS *m/e* calcd for $C_{12}H_{14}S$ 190.081622, found 190.082031.

1-(*p*-Methoxyphenyl)hexa-1,5-diene: isolated yield, 75%; ^{1}H NMR ($CDCl_3$) δ 7.34 (d, 2H, PhH, J = 9 Hz), 6.90 (d, 2H, PhH, J = 9 Hz), 6.40 (d, 1H, J = 18 Hz), 5.78 (m, 2H), 5.07 (dd, 2H, J = 18, 10 Hz), 3.80 (s, 3H, OCH_3), 2.2 (m, 4H); LRMS *m/e* 188, 158, 147 (base), 131, 115, 91, 77, 51; HRMS *m/e* calcd for $C_{13}H_{16}O$ 188.120120, found 188.120135.

Preparation of 4-((Phenylthio)methylene)cyclohexene (13). To a stirred solution of 2.2 g (0.02 mol) of 1,2,3,6-tetrahydrobenzaldehyde and 2.2 g (0.02 mol) of thiophenol in 20 mL of benzene under an inert nitrogen atmosphere at room temperature was added 3.08 g (0.022 mol) of phosphorus pentoxide. The reaction mixture was then refluxed for a period of 30–60 min. After the solution was cooled to room temperature and the solid residue removed from the reaction mixture, the organic layer was condensed and the product was purified by flash silica gel

(29) Baldwin, J. E.; Kapeki, J. A. *J. Am. Chem. Soc.* **1970**, *92*(16), 4868.

column chromatography (hexanes:ethyl acetate, 8:2 v/v) to give product **13** upon removal of solvent: isolated yield, 55%; ^{1}H NMR ($CDCl_3$) δ 7.31 (s, 5H, PhH), 6.25 (s, 1H), 5.70 (s, 2H), 2.75 (d, 2H), 2.05 (m, 4H); LRMS *m/e* 202, 173, 154, 147, 109, 93 (base), 91, 77, 65, 51; HRMS *m/e* calcd for $C_{13}H_{14}S$ 202.081622, found 202.081658.

General Procedure for the Hydrogenation of Olefins with Tributyltin Hydride Promoted by Tris(4-bromophenyl)aminium Hexachloroantimonate (1$^{\bullet+}$). To a stirred solution of 0.292 mmol of olefin and 0.6424 mmol of tributyltin hydride in 2.0 mL of methylene chloride under an inert nitrogen atmosphere at 0 °C was added 477 mg (0.584 mmol, 200 mol %) of catalyst 1$^{\bullet+}$. The progress of the reaction was followed by GC and GC–MS spectrometry. After completion of the reaction (1–60 min), the reaction mixture was then quenched with a saturated aqueous solution of potassium carbonate in methanol (5 mL). The product(s) was(were) separated from the aqueous layer by extraction with diethyl ether and the aid of brine solution. The ethereal solution was then dried over anhydrous sodium sulfate. After filtration of sodium sulfate and removal of volatile material, the product(s) was(were) purified by flash silica gel column chromatography with hexanes followed by hexanes:ethyl acetate (8:2 v/v) eluent to give the corresponding hydrogenated product(s). The following hydrogenated products were derived and isolated from their precursor olefin in this fashion, producing the yields and spectral characteristics shown below.

1,1-Diphenylethane (a): reduction of 1,1-diphenylethene produced product **a** with a reaction time of 45–60 min; isolated yield, 90%; ^{1}H NMR ($CDCl_3$) δ 7.27 (s, 10H, PhH), 4.18 (q, 1H, J = 7.6 Hz), 1.64 (d, 3H, CH_3, J = 7.6 Hz); LRMS *m/e* 182, 167 (base), 152, 139, 103, 77.

1,1-Bis(*p*-tolyl)ethane (b): reduction of 1,1-bis(*p*-tolyl)ethene produced product **b** with a reaction time of 1–2 min; isolated yield, 95%; ^{1}H NMR ($CDCl_3$) δ 7.12 (m, 8H, PhH), 4.05 (q, 1H, J = 7.4 Hz), 2.25 (s, 6H, CH_3), 1.55 (d, 3H, CH_3, J = 7.4 H); LRMS *m/e* 210, 195 (base), 180, 165, 152, 139, 115, 91, 89, 65.

1,1-Bis(*p*-methoxyphenyl)ethane (c): reduction of 1,1-bis(*p*-methoxyphenyl)ethene produced product **c** with a reaction time of 1–2 min; isolated yield, 93%; ^{1}H NMR ($CDCl_3$) δ 6.98 (d, 4H, PhH, J = 9 Hz), 6.80 (d, 4H, PhH, J = 9 Hz), 3.93 (q, 1H, J = 7.1 Hz), 3.64 (s, 6H, OCH_3), 1.45 (d, 3H, CH_3, J = 7.1 Hz); LRMS *m/e* 242, 227 (base), 212, 197, 184, 153, 115, 91, 77.

Cyclohexenylidenecyclohexane (d): reduction of 1,1-bicyclohexylidene produced product **d** with a reaction time of 1–2 min; isolated yield, 90%; ^{1}H NMR ($CDCl_3$) δ 2.2 (t, 8H), 1.5 (m, 12H); LRMS *m/e* 164, 149, 135, 121, 107, 88, 82 (base), 81, 80, 79, 67, 55.

6,6-Bis(*p*-methoxyphenyl)-1-hexene (e): reduction of 1,1-bis(*p*-methoxyphenyl)hexa-1,5-diene produced product **e** with a reaction time of 1–2 min; isolated yield, 95%; ^{1}H NMR ($CDCl_3$) δ 7.08 (m, 8H, PhH), 5.75 (m, 1H), 4.97 (dd, 2H, J = 18, 10 Hz), 3.80 (t, 1H, J = 7.2 Hz), 3.75 (s, 6H, OCH_3), 2.03 (m, 4H), 1.36 (m, 2H); LRMS *m/e* 296, 253, 227 (base), 212, 181, 169, 141, 115, 108, 77, 53; HRMS *m/e* calcd for $C_{20}H_{24}O_2$ 296.177630, found 296.178494.

9,10-Dihydroanthracene (f): reduction of anthracene produced product **f** with a reaction time of 20–30 min; isolated yield, 70%; ^{1}H NMR ($CDCl_3$) δ 7.24 (s, 8H, PhH), 3.95 (s, 4H); LRMS *m/e* 180 (base), 179, 178, 165, 152, 139, 126, 115, 89, 76, 63, 51.

4-Propylanisole (g): reduction of *trans*-anethole by using triphenyltin hydride as reducing agent produced product **g** with a reaction time of 1–2 min; isolated yield, 55%; ^{1}H NMR ($CDCl_3$) δ 6.98 (d, 2H, PhH, J = 9 Hz), 6.70 (d, 2H, PhH, J = 9 Hz), 3.65 (s, 3H, OCH_3), 2.50 (t, 2H, J = 7.2 Hz), 1.93–1.11 (m, 2H), 0.91 (t, 3H, CH_3, J = 7.2 Hz); LRMS *m/e* 150, 121 (base), 105, 91, 77.

1,4-Bis(*p*-methoxyphenyl)-2,3-dimethylbutane (h): reduction of *trans*-anethole by using tributyltin hydride as reducing agent produced product **h** with a reaction time of 1–2 min; isolated yield, 80%; ^{1}H NMR ($CDCl_3$) δ 7.08 (d, 4H, PhH, J = 9 Hz), 6.86 (d, 4H, PhH, J = 9 Hz), 3.80 (s, 3H, OCH_3), 3.77 (s, 3H, OCH_3), 2.53 (dd, 4H, J = 7.2 Hz), 2.02–1.43 (m, 2H), 0.72 (d, 6H, CH_3, J = 7.2 Hz); LRMS *m/e* 298, 254, 208, 177, 149, 121 (base), 91, 77; HRMS *m/e* calcd for $C_{20}H_{26}O_2$ 298.193280, found 298.192221.

((Phenylthio)methyl)cyclohexane (i): reduction of ((phenylthio)-methylene)cyclohexane produced product **i** with a reaction time of 3–5 min; isolated yield, 88%; ^{1}H NMR ($CDCl_3$) δ 7.27 (s, 5H, PhH), 2.81 (d, 2H, J = 7 Hz), 2.1–1.0 (m, 11H); LRMS *m/e* 206, 135, 123, 110, 109 (base), 83, 77, 55; HRMS *m/e* calcd for $C_{13}H_{18}S$ 206.112923, found 206.111974.

6-(Phenylthio)-1-hexene (j): reduction of 1-(phenylthio)hexa-1,5-diene produced product **j** with a reaction time of 3–5 min; isolated yield, 25%; ^{1}H NMR ($CDCl_3$) δ 7.35 (s, 5H, PhH), 5.93 (m, 1H), 5.08 (dd, 2H, J = 18, 10 Hz), 2.97 (t, 2H, 7.1 Hz), 2.14 (m, 2H), 1.64 (m, 4H, J = 7.1 Hz); LRMS *m/e* 192, 151, 123, 109 (base), 83, 77, 55; HRMS *m/e* calcd for $C_{12}H_{16}S$ 192.097272, found 192.097312.

6-(*p*-Methoxyphenyl)-1-hexene (k): reduction of 1-(*p*-methoxyphenyl)-hexa-1,5-diene produced product **k** with a reaction time of 1–2 min; isolated yield, 88%; ^{1}H NMR ($CDCl_3$) δ 7.02 (d, 2H, PhH, J = 9 Hz), 6.74 (d, 2H, PhH, J = 9 Hz), 5.76 (m, 1H), 5.01 (dd, 2H, J = 18, 10 Hz), 3.70 (s, 3H, OCH_3), 2.51 (t, 2H, J = 7.2 Hz), 2.04 (m, 2H), 1.46 (m, 4H, J = 7.2 Hz); LRMS *m/e* 190, 147, 121 (base), 91, 77; HRMS *m/e* calcd for $C_{13}H_{18}O$ 190.135770, found 190.135812.

1-(Phenylthio)-4-phenylbutane (l): reduction of 1-(phenylthio)-4-phenyl-1-butene produced product **l** with a reaction time of 3–5 min; isolated yield, 28%; ^{1}H NMR ($CDCl_3$) δ 7.35 (s, 5H, PhH), 7.22 (s, 5H, PhH), 2.97 (t, 2H, J = 7.1 Hz), 2.83 (t, 2H, J = 7.2 Hz), 1.56 (m, 4H); LRMS *m/e* 242, 123, 109 (base), 91, 77; HRMS *m/e* calcd for $C_{16}H_{18}S$ 242.112922, found 242.112610.

1-(*p*-Methoxyphenyl)-4-phenylbutane (m): reduction of 1-(*p*-methoxyphenyl)-4-phenyl-1-butene produced product **m** with a reaction time of 1–2 min; isolated yield, 90%; ^{1}H NMR ($CDCl_3$) δ 7.21 (s, 5H, PhH), 7.01 (d, 2H, PhH, J = 9 Hz), 6.73 (d, 2H, PhH, J = 9 Hz), 3.68 (s, 3H, OCH_3), 2.84 (t, 2H, J = 7.2 Hz), 2.50 (t, 2H, J = 7.2 Hz), 1.55 (m, 4H); LRMS *m/e* 240, 177, 121 (base), 91; HRMS *m/e* calcd for $C_{17}H_{20}O$ 240.151420, found 240.151234.

Procedure for Competition Experiment in the Hydrogenation of 1,1-Diphenylethylene and 1,1-Ditolylethylene with Tributyltin Hydride Promoted by Tris(4-bromophenyl)aminium Hexachloroantimonate (1$^{\bullet+}$). To a stirred solution of 52.6 mg (0.292 mmol) of 1,1-diphenylethylene, 60.7 mg (0.292 mmol) of 1,1-ditolylethylene, and 187 mg (0.6424 mmol) of tributyltin hydride in 3.0 mL of methylene chloride under an inert nitrogen atmosphere at 0 °C was added 477 mg (0.584 mmol, 200 mol %) of catalyst 1$^{\bullet+}$. The reaction was quenched by placing 0.5 mL of a standard solution of potassium carbonate in methanol in a 3-mL syringe. This syringe was then used to withdraw a 0.25-mL aliquot from the reaction mixture. Aliquots were taken at approximately 5-s intervals for the first 20 s of reaction followed by 10-s intervals for the next minute of reaction and placed independently in 3-mL vials. A small amount of diethyl ether and water was then added to each vial, and organic layers were analyzed by GC and GC–MS spectrometry. Analysis of our data revealed that in the early stage of the reaction (10% conversion of starting materials to products), a relative rate ratio of 167:1 was obtained for 1,1-ditolylethane product (*m/e* = 210) over that of 1,1-diphenylethane product (*m/e* = 182). Accounting for the presence of both CH_3 groups in 1,1-ditolylethane product and using σ_p^+ (CH_3) = –0.31, we obtained a Hammett–Brown ρ value of –3.6.

Hydrogenation of 1-(*p*-Methoxyphenyl)-4-phenyl-1-butene (14a) with Tributyltin Hydride in the Presence of *p*-Toluenesulfonic Acid. To a stirred solution of 69.5 mg (0.292 mmol) of **14a** and 187 mg (0.6424 mmol) of tributyltin hydride in 2.0 mL of methylene chloride under an inert nitrogen atmosphere at 0 °C was added 25.1 mg (0.146 mmol) of *p*-toluenesulfonic acid. The reaction mixture was then allowed to warm up to room temperature and the reaction quenched with a saturated aqueous solution of potassium carbonate in methanol. After workup and purification of the product by flash silica gel column chromatography with hexanes: diethyl ether (8:2 v/v) eluent, the only product of the reaction was cyclized 1-(*p*-methoxyphenyl)-1,2,3,4-tetrahydronaphthalene having the following spectral characteristics: ^{1}H NMR ($CDCl_3$) δ 7.04 (m, 8H, PhH), 3.80 (s, 3H), 2.77 (t, 1H), 2.50 (q, 1H), 2.1–1.12 (m, 4H); LRMS *m/e* 238, 207, 178, 165, 130 (base), 104, 91, 69; HRMS *m/e* calcd for $C_{17}H_{18}O$ 238.135765, found 238.135200. The above cyclized product was also prepared by reaction of **14a** with 5% triflic acid in methylene chloride at 0 °C for a period of 5 min. Reduction of **14a** in the absence of *p*-toluenesulfonic acid and promotion by hole catalyst 1$^{\bullet+}$ yielded only an uncyclized reduced product corresponding to 1-(*p*-methoxyphenyl)-4-phenylbutane.

Hydrogenation of 4-(2-(Phenylthio)ethenyl)cyclohexene (12) with Tributyltin Hydride Promoted by Tris(4-bromophenyl)aminium Hexachloroantimonate (1$^{\bullet+}$). Using the same general procedure as that used for the hydrogenation of other olefins afforded, we obtained, as the only product of reaction, a cyclized product with the following spectral characteristics: ^{1}H NMR ($CDCl_3$) δ 7.28 (s, 5H, PhH), 3.17 (dt, 1H, 6.4 Hz), 2.26 (br s, 2H), 1.93–1.03 (m, 10H); LRMS *m/e* 218, 177, 135, 109 (base), 79, 67; HRMS *m/e* calcd for $C_{14}H_{18}S$ 218.112922, found 218.113120. To confirm the precise structure of this cyclized product, the above cyclized product was treated with an excess solution of Raney nickel in nickel in ethanol at room temperature and the resulting hydrocarbon was compared *via* GC analysis with coinjection to authentic

samples of the appropriate hydrocarbons. The product was found to be identical to bicyclo[3.2.1]octane, and no bicyclo[2.2.2]octane was present. The standard bicyclo[2.2.2]octane was prepared by reduction of bicyclo-[2.2.2]oct-2-ene with molecular hydrogen in the presence of 5% Pt/C catalyst at room temperature. Bicyclo[3.2.1]octane was prepared by Wolf–Kishner reduction of bicyclo[3.2.1]octan-2-one.

Hydrogenation of 4-((Phenylthio)methylene)cyclohexene (13) with Tributyltin Hydride Promoted by Tris(4-bromophenyl)aminium Hexachloroantimonate ($1^{\bullet+}$). Using the same general procedure as that used for the hydrogenation of other olefins afforded two reduced products with the following percent composition and spectral data. Analytical data for the uncyclized product 4-((phenylthio)methyl)cyclohexene (90%) are as follows: ^{1}H NMR ($CDCl_3$) δ 7.29 (s, 5H, PhH), 5.69 (s, 2H), 2.97 (t, 2H, J = 7.1 Hz), 2.04 (m, 4H), 1.45 (m, 3H, J = 7.1 Hz); LRMS m/e 204, 153, 123, 109 (base), 79, 65. The cyclized product 7-(phenylthio)-bicyclo[2.2.1]heptane (10%) gave the following mass analysis: LRMS m/e 204, 175, 149, 135, 110, 109, 95 (base), 77, 67. This minor product, when treated with an excess solution of Raney nickel in ethanol at room temperature, resulted in formation of a hydrocarbon with the same GC retention time as that found for the standard sample of bicyclo[2.2.1]-heptane.

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