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Reduction of Organomercurials by Sodium Dithionite

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The reaction between organomercuric salts and sodium dithionite was examined under various conditions. Several reactions occur, depending on the organofunctional classification of the mercurial. For simple hydrocarbon alkyls, one-electron reduction (probably involving the radical anion $\cdot SO_2^-$) is the predominant reaction, producing alkyl radicals and resulting in complete loss of any net enantiomeric (but not necessarily diastereomeric) resolution possessed by prochiral substrates. Aryl substrates undergo dithionite-induced symmetrization, and products of oxymercuration of simple alkenes undergo dithionite-induced reversion to the olefin. In both of the latter reactions, the free mercury(II) generated is rapidly reduced, although initially the role of dithionite is only that of any strong ligand.

Aqueous dithionite is an effective reducing agent of cobalt(III) and manganese(III) porphyrins[1] and alkylcobalt(III) chelates[2] (in-plane ligand = corrin, $(dmgH)_2$, and $(dpgH)_2$). The question of outer- or inner-sphere nature of the reduction has not been unambiguously established,[3] but an observed half-order dependence[4] of the rate on dithionite concentration has led to the hypothesis of rate-limiting *one*-electron reduction by the radical anion $\cdot SO_2^-$, formed via a dissociative equilibrium (eq 1).[5]

$$S_2O_4^{2-} \rightleftharpoons 2\,\cdot SO_2^- \qquad K(H_2O, 25\ °C) = 1.6 \times 10^{-10} \tag{1}$$

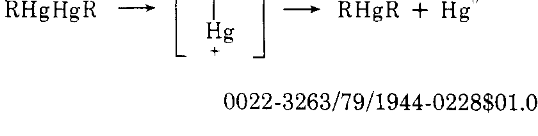
Recently, Todhunter and Currell[6] reported that organomercuric salts (but not diorganomercurials) could be reduced, viz., "symmetrized", by dithionite in ethanol, according to the stoichiometry shown in eq 2.

$$2RHgX + S_2O_4^{2-} \rightarrow RHgR + Hg^0 + 2Cl^- + 2SO_2 \tag{2}$$

These workers reported results only for one aromatic substrate (*p*-chloromercuribenzoic acid) and one aliphatic substrate (*exo*-*cis*-3-hydroxy-2-norbornylmercuric chloride). In the former case, styrene added to the initial solution was recovered from the reaction unchanged. In the latter case, the dialkylmercurial product was obtained with complete retention of configuration at both C–Hg centers. Consistent with these findings, Todhunter and Currell proposed a *two*-electron reduction mechanism (eq 3–5), in analogy to that proposed for magnesium metal induced "symmetrization".[7]

$$RHgX + 2e^- \longrightarrow RHg^- + X^- \tag{3}$$

$$RHg^- + RHgX \longrightarrow RHgHg + X^- \tag{4}$$



$$RHgHgR \longrightarrow \left[\begin{array}{c} R\overset{-}{H}gR \\ | \\ \underset{+}{Hg} \end{array}\right] \longrightarrow RHgR + Hg^0 \tag{5}$$

The magnesium reaction[7] is presently the only established method for converting chiral *hydrocarbon* alkylmercuric salts (e.g., (+)- or (−)-*sec*-butylmercuric bromide) as well as oxymercurated materials to the corresponding dialkylmercurials with complete retention of configuration at carbon. Thus, it was of interest to see if the scope of the dithionite reduction could be conveniently extended to include hydrocarbon alkylmercuric salts, and if so, whether or not the products obtained possess fully retained stereochemistry (thereby supporting the proposed two-electron reduction).

In contrast to the result obtained with the oxymercurial utilized by Todhunter and Currell,[6] we have found that hydrocarbon alkylmercuric halides (e.g., *n*-BuHgBr, *s*-BuHgBr, and cyclohexylmercuric bromide) are essentially inert to the prescribed reaction conditions (absolute ethanol, room temperature, under nitrogen or open to the air). However, it was found that the utilization of more suitable reaction conditions would allow reduction to take place. The selection of these conditions was based on several factors.

(i) Although ethanol is a reasonable compromise between the aqueous high solubility of $Na_2S_2O_4$ and the organic solubility of mercurials, the reaction system remained heterogeneous. Homogeneity would probably aid the reduction.

(ii) Prior coordination of the reductant to mercury is expected to facilitate reduction via an inner-sphere process. Alkylmercuric halides are covalent compounds wherein the mercury center possesses some, but not large, residual coordinating capacity. On the other hand, organomercuric salts with weak ligand anions (e.g., acetate and nitrate) are ionized or have substantial ionic character, such that the mercury center has a pronounced Lewis acidity, thus promoting coordination and reduction. Reduction might also be facilitated by an aprotic solvent, wherein an anionic reductant, e.g., $S_2O_4^{2-}$, will lack solvation via hydrogen bonding and thus will have a much greater tendency to coordinate to mercury.

(iii) The reducing potential of dithionite is greatly enhanced in basic media (eq 6 and 7).[6]

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$$HS_2O_4^- + 2H_2O \rightarrow 2e^- + 2H_2SO_3 + H^+ \qquad (6)$$

(pK_a 2.46)[8]

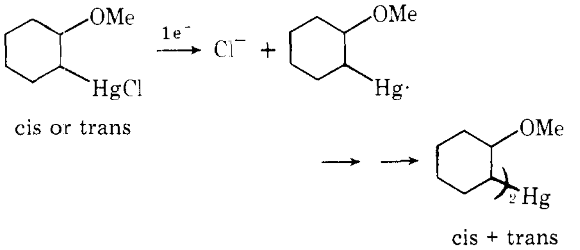
$$E°_{298} = 0.23 \text{ V}$$

$$S_2O_4^{2-} + 4OH^- \rightarrow 2e^- + 2SO_3^{2-} + 2H_2O \qquad (7)$$

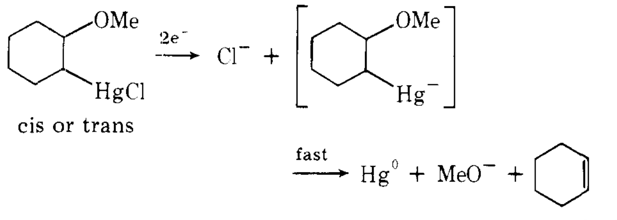
$$E°_{298} = 1.4 \text{ V}$$

Consistent with these proposals, hydrocarbon alkylmercurials were found in this work to be readily reduced by sodium dithionite via four (and many more are possible) alternative procedures: (i) alkylmercuric acetates in aqueous ethanol; (ii) alkylmercuric halides in methylene chloride with added R_4NOH (as a methanolic solution); (iii) alkylmercuric halides in aqueous ethanol with added NaOH; (iv) alkylmercuric nitrates in DMF or acetonitrile. Secondary alkylmercurials were found to react more sluggishly than primary substrates, implying the rather sensitive nature of the reduction to structural electronic and/or steric effects (primary alkyl is less electron-donating and less sterically hindered). Conversion of optically active *sec*-butylmercuric salts to di-*sec*-butylmercury via any of the above procedures resulted in complete loss of activity, suggesting the possible presence of free radicals and the operation of *one*-electron reduction. Direct evidence for such processes was the observation that the reaction of an equivalent each of $Na_2S_2O_4$, *n*-hexylmercuric nitrate, and 2,4,6-tri-*tert*-butylphenol resulted in the conversion of 17%[9] of the original *n*-hexyl groups to *n*-hexane. In serving as a good hydrogen atom donor, the phenol acts to trap some of the *n*-hexyl radicals that apparently are generated. The di-*n*-hexylmercury isolated accounted for 73%[9] of the *n*-hexyl groups. Alkylmercuric salts are known to be excellent radical traps, and such a process could partially account for the di-*n*-hexylmercury produced, vide infra (eq 19, 22).

Reduction of the diastereomeric 2-alkoxy(or 2-hydroxy)-cyclohexylmercuric salts has been proposed by Jensen and Rickborn[10] as a convenient test for discriminating between one- and two-electron reducing agents. Whereas one-electron reduction (e.g., with stannite or hydrazine) yields some dialkylmercurial, two-electron reduction (e.g., with magnesium) results entirely in β elimination, irrespective of which stereoisomer is utilized (eq 8 and 9).

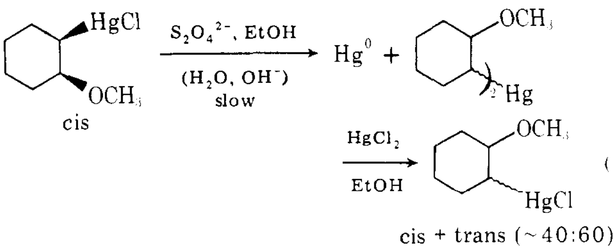


(8)



(9)

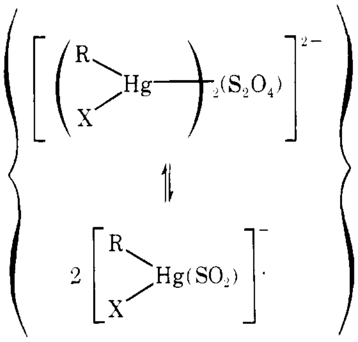
Treatment of *cis*-2-methoxycyclohexylmercuric chloride with $Na_2S_2O_4$ in ethanol (i.e., the conditions used by Todhunter and Currell[6] for reduction of *exo-cis*-3-hydroxy-2-norbornylmercuric chloride) yields mainly dialkylmercurial, with only a trace of cyclohexene. The reaction occurs slowly, but the rate is accelerated by the addition of aqueous base. Isolation of R_2Hg and conversion back to RHgCl with $HgCl_2$ in ethanol (which is known to give complete retention of configuration at carbon[11]) demonstrated that racemization had accompanied the initial reduction (eq 10).



(10)

These experimental results suggest that dithionite serves as a one-electron reductant of alkylmercuric salts in analogy with other (organo)metallic systems.[1-3] The kinetic reductant is presumably $\cdot SO_2^-$, but inner-sphere reduction could be accomplished by undissociated dithionite acting as a bidentate ligand (eq 11). If X^- is a strong ligand, an alternative depiction of reduction might be as shown in eq 12. The initially produced radical, RHg·, is unstable and will undergo further reaction in a variety of ways (eq 13–15), the most important being the generation of alkyl radicals by demercuration (eq 13).

$$\left\{\begin{array}{c} S_2O_4^{2-} \\ \upharpoonleft\downharpoonright \\ 2\cdot SO_2^- \end{array}\right\} + 2RHgX \rightleftharpoons 2X^- + \left\{\begin{array}{c} (RHg)_2(S_2O_4) \\ \upharpoonleft\downharpoonright \\ 2[RHg(SO_2)]\cdot \end{array}\right\} \longrightarrow 2SO_2 + 2RHg\cdot \qquad (11)$$



$$\longrightarrow 2SO_2 + 2X^- + 2RHg\cdot \qquad (12)$$

$$RHg\cdot \rightarrow Hg^0 + R\cdot \qquad (13)$$

$$RHg\cdot \xrightarrow{1e^-} RHg^- \xrightarrow[-X^-]{RHgX} RHgHgR \qquad (14)$$

$$2RHg\cdot \rightarrow RHgHgR \qquad (15)$$

The alkyl radicals can (i) undergo further reduction, (ii) combine with RHg·, (iii) attack the starting mercurial, or, when appropriate, (iv) be trapped by a hydrogen atom donor (ZH) (eq 16–20).

$$R\cdot \xrightarrow{1e^-} R^- \xrightarrow[-X^-]{RHgX} RHgR \qquad (16)$$

$$R\cdot + RHg\cdot \rightarrow RHgR \qquad (17)$$

$$R\cdot + [RHg(SO_2)]\cdot \rightarrow [R_2Hg(SO_2)] \rightarrow R_2Hg + SO_2 \qquad (18)$$

$$R\cdot + RHgX \rightleftharpoons [R_2HgX]\cdot \qquad (19)$$

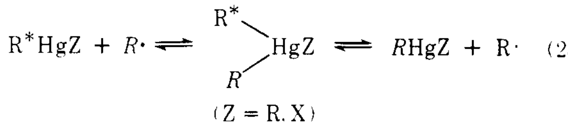
$$(R\cdot + ZH \rightarrow RH + Z\cdot) \qquad (20)$$

In addition to equations 16, 17, and 18, two remaining product-forming reactions are the decomposition of RHgHgR (eq 21) and possibly one-electron reduction of the radical addend formed in eq 19 (eq 22).

$$RHgHgR \rightarrow Hg^0 + RHgR \qquad (21)$$

$$[R_2HgX]\cdot \xrightarrow{1e^-} R_2Hg + X^- \qquad (22)$$

The production of dialkylmercurial depicted above would preserve optical activity in one of the two product C–Hg bonds according to equations 16, 17, 18, and 22, and in both product C–Hg bonds according to eq 21 (vide eq 14 and 15). The fact that *complete* racemization accompanies the reduction, however, is a common phenomenon in free-radical organomercury chemistry, wherein alkyl radicals can racemize either the starting alkylmercuric salt (via the equilibrium 19) or the product dialkylmercurial (eq 23).[12]

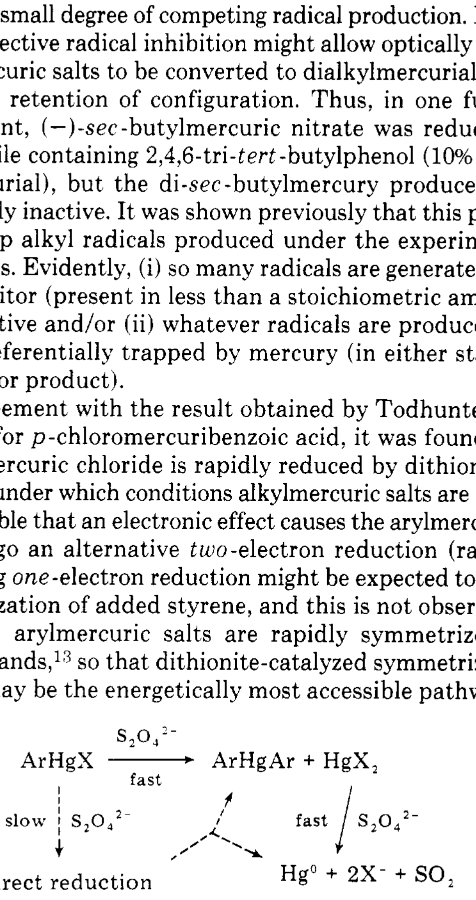


$$R^*HgZ + R\cdot \rightleftharpoons \overset{R^*}{\underset{R}{>}}HgZ \rightleftharpoons RHgZ + R\cdot \quad (23)$$

$$(Z = R, X)$$

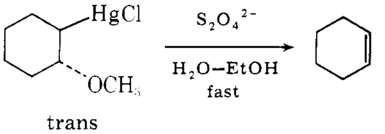
The racemizing action of alkyl radicals weakens, a priori, the interpretation of the experimental results in terms of one-electron reduction; viz., a predominant *two*-electron (presumably stereospecific) reduction could be camouflaged by only a small degree of competing radical production. In this event, selective radical inhibition might allow optically active alkylmercuric salts to be converted to dialkylmercurials with complete retention of configuration. Thus, in one further experiment, (−)-*sec*-butylmercuric nitrate was reduced in acetonitrile containing 2,4,6-tri-*tert*-butylphenol (10% based on mercurial), but the di-*sec*-butylmercury produced was completely inactive. It was shown previously that this phenol could trap alkyl radicals produced under the experimental conditions. Evidently, (i) so many radicals are generated that the inhibitor (present in less than a stoichiometric amount) is ineffective and/or (ii) whatever radicals are produced are being preferentially trapped by mercury (in either starting material or product).

In agreement with the result obtained by Todhunter and Currell[6] for *p*-chloromercuribenzoic acid, it was found that phenylmercuric chloride is rapidly reduced by dithionite in ethanol (under which conditions alkylmercuric salts are inert). It is possible that an electronic effect causes the arylmercurials to undergo an alternative *two*-electron reduction (radical-producing *one*-electron reduction might be expected to cause polymerization of added styrene, and this is not observed[6]). However, arylmercuric salts are rapidly symmetrized by strong ligands,[13] so that dithionite-catalyzed symmetrization (eq 24) may be the energetically most accessible pathway to Ar$_2$Hg. The free mercury(II) formed concurrently would be rapidly reduced[14] to mercury(0), so that the observed products are the same, irrespective of mechanism. The recovery of styrene unchanged from the reaction mixture is also expected according to the "symmetrization" mechanism since no free radicals are involved.



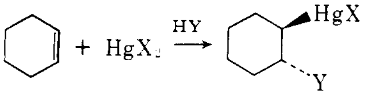
(24)

Whereas *cis*-2-methoxycyclohexylmercuric chloride undergoes slow dithionite reduction to racemized dialkylmercurial (eq 10), a quantitative yield of cyclohexene (as well as Hg^0) is rapidly obtained upon similar treatment of the trans isomer (eq 25). Although the latter is the expected outcome of two-electron reduction (vide supra), the contradictory behavior of the cis isomer requires an alternative interpretation for the trans case. A trans addition characterizes the oxymercuration of acyclic olefins and simple (unstrained) cycloalkenes,[15] e.g., eq 26. The reverse reaction (deoxymercuration) is readily brought about by strong ligands,[16] e.g., eq 27. Apparently, then, dithionite simply induces deoxymercuration of the trans isomer and the free mercury(II) generated thereby is rapidly reduced.[14]



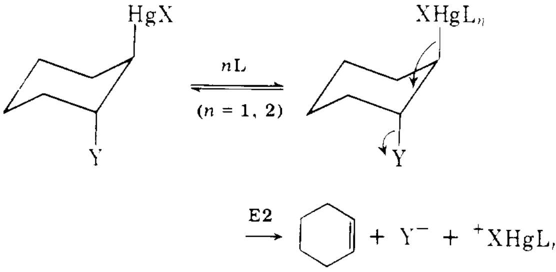
trans

(25)



(26)

(Y = OH, OR, OAc)



(27)

Discussed thus far has been the role of dithionite as a one-electron reductant of organomercuric salts, except for special cases in which an alternative energetically preferred reaction course is available (e.g., symmetrization and deoxymercuration). It remains to explain, then, the stereospecific result (100% retention) obtained by Todhunter and Currell[6] for *exo-cis*-3-hydroxy-2-norbornylmercuric chloride. This stereoisomer is that obtained upon oxymercuration of norbornene, so that one might expect dithionite to induce reversion to the alkene, as occurs with the *trans*-2-oxycyclohexylmercuric salts (vide supra). However, because of the increase in strain, olefin formation in the norbornyl case is relatively less favored than in the cyclohexyl case. Consequently, one-electron reduction becomes the pathway of comparable or lower energy of activation in the former case, whereas deoxymercuration remains the energetically preferred pathway in the latter case. The reaction between dithionite and *cis-exo*-3-methoxy-2-norbornylmercuric chloride in aqueous ethanol was examined and produced a small amount of norbornene in addition to dialkylmercurial. The experimental procedure of Todhunter and Currell[6] (reaction run open to the air for 24 h and then refluxed for 30 min) may not have permitted their detecting the highly volatile norbornene. The apparent stereospecific production of bis(*cis-exo*-3-hydroxy-2-norbornyl)mercury is not inconsistent with one-electron reduction (as recognized by Todhunter and Currell), since other free-radical reductions of these compounds proceed with greater than 95% retention of the thermodynamically favored cis-exo diastereomeric geometry.[17]

In conclusion, although kinetic studies have not been carried out, the results presented herein indicate that one-electron reduction (producing alkyl radicals) is the predominant course of reaction between Na$_2$S$_2$O$_4$ and hydrocarbon alkylmercuric salts. For arylmercurials or products of olefin oxymercuration, dithionite may initially serve a nonreducing role in ligand-induced symmetrization or ligand-induced deoxymercuration (respectively), but afterwards it does reduce the free mercury(II) generated in both cases.

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(9) These are *isolated* yields (totaling 90%), so that the actual yields are presumably about 5% higher for each of the two products.

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Metal Catalysis in Organic Reactions. 7. On the Role of Nickel Complexes in the Reaction of Triisobutylaluminum with Terminal Acetylenes

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The mechanism by which nickel(II) complexes catalyze the stoichiometric reaction between terminal aliphatic alkynes and triisobutylaluminum is discussed in the light of previous reports and new experimental findings. At room temperature (*E*)-2,4-dialkyl-1,3-butadiene along with 1,3,5-trialkyl- and 1,2,4-trialkylbenzenes are generally formed; the yields of the products were found to be dependent on the ligand originally present in the nickel complex. Deuteriolysis experiments have indicated clearly the occurrence of hydride nickel and nickelole species as reaction intermediates. On the basis of the results obtained, the proposed mechanism involves the formation of alkyl, hydride, and zerovalent nickel species, still containing, at least partially, the ligand. These catalytic species should give rise to the products through insertion and oxidative addition processes of the acetylenic substrate, followed by reductive elimination or alkyl exchange reactions with the excess organoaluminum compound.

Recently there is a renewed interest in the use of Ziegler-type catalysts for synthetic applications, and several useful processes such as metal-catalyzed coupling reactions have been reported.[1] Our investigations on nickel-promoted reactions of triisobutylaluminum with terminal acetylenes have led to a synthetically useful process as a route to (*E*)-2,4-dialkyl-1,3-butadienes and/or trialkylbenzenes.[2,3] In the following discussion we propose a mechanistic approach which is consistent with previously reported synthetic data[2] and the additional data presented herein.

Experimental Section

General. Triisobutylaluminum (Fluka A.G. Co., Buchs) and tris[(*S*)-2-methylbutyl]aluminum, $[\alpha]^{25}{}_D$ +27.01°, prepared as previously reported,[4] were carefully redistilled under nitrogen and stored in sealed capillary glass vials. Bis(acetylacetone)nickel [$Ni(acac)_2$], bis(*N*-methylsalicylaldimine)nickel [$Ni(mesal)_2$], and bis(ethylenediiminesalicylaldehyde)nickel [$Ni(salen)_2$] were prepared and purified as reported elsewhere.[5-7] Bis(triphenylphosphine)nickel dicarbonyl [$Ni(CO)_2(Ph_3P)_2$] was a commercial product (Strem Chemicals, U.S.A.), while bis(2-dimethylaminoethyl) sulfide nickel dibromide [$Ni(Me_4daes)Br_2$][8] and bis(2-dimethylaminoethyl)methylamine nickel dihalides [$Ni(dienMe)X_2$][9] were kindly supplied by Professor M. Ciampolini (Istituto di Chimica Generale, Università di Firenze). 1-Hexyne (Fluka A.G. Co., Buchs), (*R,S*)- and (*S*)-3-methyl-1-pentyne, $[\alpha]^{20}{}_D$ +35.69°,[10] and (*R,S*)- and (*S*)-3,4,4-trimethyl-1-pentyne, $[\alpha]^{25}{}_D$ + 7.93°,[11] were carefully distilled under nitrogen before use; 1-hexyne-1-*d* was obtained from 1-hexyne according to a published procedure.[12] GLC analyses were performed on Perkin-Elmer F 30 and 3920B instruments (flame ionization detectors; 200 × 0.30 cm columns packed with 2.5% silicone gum rubber E 301 on 60–80 mesh Chromosorb W at 40–200 °C; nitrogen flow rate 10 mL min^{-1}). Preparative GLC was carried out on a Perkin-Elmer F 21 chromatograph, using 300 × 0.80 cm columns filled with 20% Apiezon M on 45–60 mesh Chromosorb W. Optical rotations were measured with a Perkin-Elmer 142 polarimeter. Spectral measurements were determined with the following instruments: IR, Perkin-Elmer Model 225; NMR, Jeol JMN PS-100; mass spectra, Varian MAT CH 7.

General Procedure. All reactions were carried out at least in duplicate in a flame-dried, two-neck 25-mL flask equipped with a magnetic stirrer, a Versilic silicone cap, and a glass stopcock.[2] In a typical run, a weighed amount of $(i\text{-Bu})_3Al$ was transferred from the sealed capillary glass vial to a reaction flask containing the nickel complex, which was cooled at 0 °C. The 1-alkyne was injected by hypodermic syringe through the cap, and then the flask was placed in a thermostatic bath at 25 ± 0.3 °C. After 40 h, the residual reaction mixture was cautiously hydrolyzed with dilute sulfuric acid, extracted with pentane, and analyzed by GLC.

When 1-hexyne-*1-d* was used and in deuteriolysis experiments, the reactions were carried out as above, taking care that all glassware used was carefully dried. In these cases the hydrolysis was accomplished with water or deuterium oxide (>99.5% pure). The suspension obtained was diluted with 30 mL of dry pentane, stirred under nitrogen for 24 h, filtered, and washed with dry pentane. All of the deuterated compounds were identified through their mass spectra.

Reaction between Tris[(*S*)-2-methylbutyl]aluminum and 1-Hexyne. Tris[(*S*)-2-methylbutyl]aluminum (16.2 g, 67.4 mmol) was treated at 0 °C with 1-hexyne (5.5 g, 67.0 mmol), and the reaction flask was then held at 25 °C. After 40 h, the reaction mixture was diluted with dry pentane, cautiously hydrolyzed with dilute sulfuric

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