General Procedure for Ozonolysis of Labeled Allylic Alcohols, Allylic Chlorides, and Coupling Products.—The procedure of Young and coworkers[14] for cleavage of allyl chloride was modified to allow milder conditions and to trap acetaldehyde as it was formed. Excess ozone was bubbled through a solution containing *ca.* 0.02 mol of the substrate in 30 ml of methylene chloride maintained at −15°. Solvent was removed with a rotary evaporator (without external heating) and the residue was added to 5 g of zinc dust and 50 ml of 10% aqueous acetic acid at room temperature. Acetaldehyde, thus generated, was swept by a stream of argon (30 ml/min) through an ice–water condenser and into a dimedone trap (*ca.* 300 ml of 0.1 *N* dimedone in sodium acetate–acetic acid buffer, adjusted to pH 5.8).[36] After *ca.* 30 min, the decomposition was complete; the contents of the trap were acidified to pH 4 with acetic acid. Typically, 80% (based upon dimedone) of the 1:2 derivative, mp 140–143°, was formed. Three recrystallizations from methanol–water followed by drying in a vacuum desiccator provided the pure derivative, mp 142–143°.

General Procedure for Reaction of Allylic Chlorides with Phenyllithium.—All reactions were performed by adding a 20% ethereal solution of 0.02–0.10 mol of freshly purified allylic chloride over 15 min to a twofold excess of 0.7–0.8 *N* phenyllithium in ether at room temperature. The reaction mixture was stirred for 2 hr and was hydrolyzed with water. The organic phase was washed with water, dried over Drierite, and concentrated. Quantitative glpc analysis for product yields (ethylbenzene, internal standard) and product distribution were performed on columns B or C for the monomethyl compounds and A or D for the dimethyl. All materials amounting to more than 1% of the total were purified by reduced pressure distillation followed by preparative glpc using columns M or U for the monomethyl compounds and columns S, T, Q, or U for the dimethyl. All products thus isolated were pure (>99%) and their structures were confirmed by nmr analysis and by comparison with authentic samples when available. For reactions in which low-boiling products (methyl-substituted butadienes and cyclopropenes) were anticipated, a stream of argon was swept through the reaction vessel into a Dry Ice–acetone trap whose contents were analyzed by glpc (column D); in every case, the only materials found were ether and unreacted allylic chloride. High-boiling materials (formed in low yield) which would not distil easily at reduced pressure were analyzed by nmr without further purification; they appeared to be mixtures of polymeric material and the coupling products from biphenyllithium and starting material.

Control Reactions.—All of the products were stable to the reaction conditions. In no case was phenyllithium-promoted isomerization to a substituted styrene detected, and alkenes with a benzylic deuterium showed no loss of label. All of the monomethyl allylic chlorides were subjected to the reaction conditions; analysis of aliquots removed at various times showed no isomerization (positional or geometric) and no conversion into allylic bromide (by reaction with LiBr present in phenyllithium). For the monomethyl allylic chlorides, inverse addition of phenyllithium gave no significant change in product yield or distribution nor did the use of halide-free phenyllithium.

Registry No.—**3**, 563-52-0; **4**, 563-47-3; **5**, 23009-73-6; **6**, 23009-74-7; **7**, 5166-35-8; **8**, 2190-48-9; **9**, 503-60-6; **10**, 18610-33-8; phenyllithium, 591-51-5.

(36) G. W. Gaffney, W. A. Williams, and H. McKennis, Jr., *Anal. Chem.*, **26**, 588 (1954).

The Coupling Reaction of Phenyllithium with Allylic Chlorides. The Stereochemistry of the Reaction[1a]

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The stereochemistry of γ coupling of phenyllithium with optically active 3-chloro-*cis*-1-butene-*1-d* has been determined. The results are interpreted in terms of a mechanism (concerted or stepwise) which proceeds greater than 95% by attack of phenyllithium syn to the leaving group.

In the preceding paper,[2] several mechanisms for the coupling of allylic chlorides with phenyllithium were discussed. Product and geometric isomer data from the reactions of mono- and dimethyl-substituted allylic chlorides led to the conclusion that the coupling at both the α and γ carbons either is a direct one-step process or involves intermediates (ionic or radical) which are separated from products by a relatively low energy barrier (*i.e.*, their lifetimes are not long enough to allow loss of memory of the structure and geometry of their precursors). In this paper, we report on the stereochemistry of the coupling reaction with optically active allylic chlorides.

Results

In order to fully elucidate the stereochemistry of the coupling reaction, a substrate which meets all of the following conditions is required.

1. It must have an asymmetric α-carbon atom. 2. Two different substituents must be present on the γ carbon, and the geometry of the double bond must be well defined. 3. Coupling reaction should occur at both allylic positions, and the α- and γ-coupling products must be cleanly separable, one from the other. 4. γ attack must produce a *separable* mixture of cis and trans olefins. 5. The absolute configuration and maximum rotation of the allylic chloride and of its coupling products should be able to be determined with a reasonable degree of accuracy.

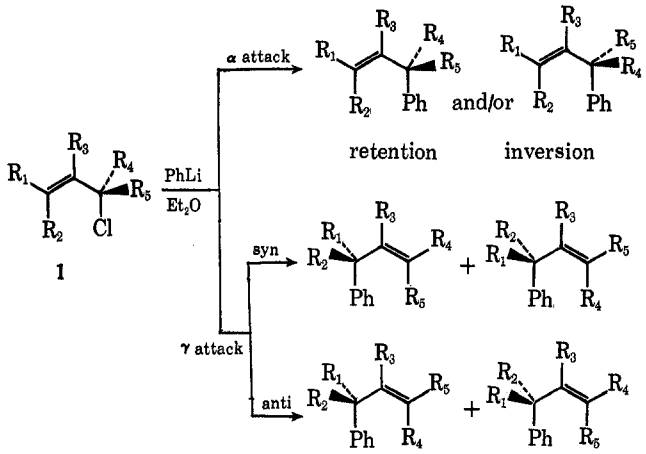
The reaction of phenyllithium with a substrate (of generalized structure **1**) meeting all of these conditions is illustrated in Scheme I.[3] Our initial plan was to use optically active 4-chloro-*trans*-2-pentene (**1**, $R_1 = R_4 = CH_3$; $R_2 = R_3 = R_5 = H$), unsymmetrically labeled with either ^2H or ^{14}C. Unfortunately, we were unable to prepare this material with a sufficiently large label spread and with clearly defined double bond geometry.[2] Furthermore, we were doubtful of the likelihood of obtaining this substance in an optically stable form in view

(1) (a) Partial support of this work by the Robert A. Welch Foundation is gratefully acknowledged, as is the assistance of the National Science Foundation in the purchase of a Varian Associates A-56/60A nmr spectrometer. (b) To whom inquiries should be addressed at the Department of Chemistry, The University of Tennessee, Knoxville, Tenn. 37916.

(2) R. M. Magid, E. C. Nieh, and R. D. Gandour, *J. Org. Chem.*, **36**, 2099 (1971).

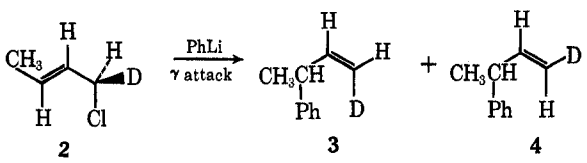
(3) The terms syn or anti used for γ attack refer to processes in which coupling occurs on the same or opposite side of the allylic system, respectively, as the departing chloride.

SCHEME I



of the known tendency of cyclic allylic chlorides to readily racemize *via* ion-pair formation.[4]

We were therefore forced to consider using a less reactive allylic chloride, one that is only monosubstituted. A substrate such as 1-chloro-*trans*-2-butene-*1-d* (**2**), or the corresponding cis isomer, satisfies all but condition 4. The two products of γ attack cannot be separated and, since the newly generated asymmetric centers of **3** and **4** would be of opposite chirality, the total sample would give no rotation.

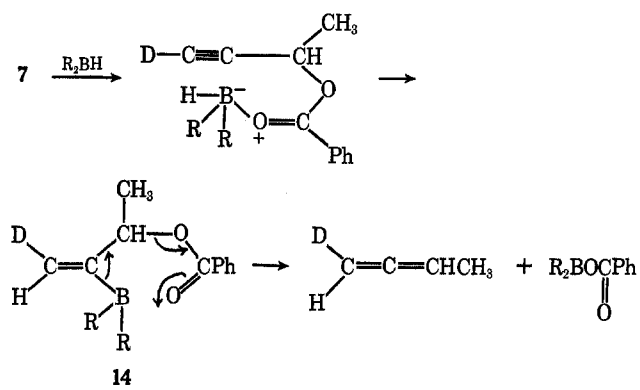


Thus, we turned our attention to optically active 3-chloro-*cis*-1-butene-*1-d* (**13**) as the substrate for this study. Unfortunately, 3-chloro-1-butene is known to couple almost exclusively by γ attack,[2] and thus condition 3 is not met. In order to determine the stereochemistry of α attack, a compound such as **2** is required. Since there are numerous reports on the coupling reactions of organometallic reagents with nonallylic chiral substances,[5] we concentrated our entire effort on the preparation and reactions of **13** for which the stereochemistry of allylic attack can be determined.

The synthesis of optically active 3-chloro-*cis*-1-butene-*1-d* (**13**) is summarized in Chart I. In general, these reactions were performed so as to obtain pure materials at each step; the yields reported in the Experimental Section are for the isolated, >99% pure, products of each reaction. Some of the steps of the synthesis merit a few words of explanation.

Conversion of alcohol **5** into benzoate **6** was necessary for two reasons. First, deuterium exchange on **5** is difficult because its miscibility with water makes isolation of **5** after each exchange laborious; use of **6** and the two-phase exchange system not only avoids this recovery problem but also allows the exchange to be conveniently monitored by nmr. Second, hydroboration of alcohol **5** produces none of the desired reduction product, whereas benzoate **6** gives quite acceptable yields.

The disiamylborane–protonolysis method for stereospecific cis reduction of an alkyne has been studied in some detail,[6] but the reproducibility of yields appears to be rather poor. For example, Brown and Zweifel[6a] claimed an 80% conversion of 1-hexyne into 1-hexene, but the same reaction in the hands of Murray and Williams[6b] gave only 40%. In the case of deuterated benzoate **7**, the literature procedure[6a] gives **8** in only 10–15% yield. We discovered, however, that, if both hydroboration and protonolysis are carried out at -5 to 0° and if protonolysis is performed immediately after completion of the first stage, quite acceptable yields (typically 40%) of **8** could be realized. One can speculate that the low yields with the literature procedure result from a competing reaction in which the initial adduct **14** undergoes intramolecularly catalyzed elimination to an allene before acetic acid is added; **7** proceeds regiospecifically to **14** because of the directing influence of the adjacent ester. A similar rationalization was



offered by Brown and Gallivan[7] in the hydroboration of allylic acetates; Zweifel, *et al.*,[6d] have indeed found that disiamylborane reduction of internal propargylic chlorides yields an intermediate which undergoes intermolecular base-catalyzed elimination to allenes.

That the reduction does, in fact, proceed stereospecifically cis is clearly demonstrated by first-order analysis of the nmr spectra of **8**, **9**, **10**, and **13** as compared to their undeuterated analogs (see Experimental Section for the complete spectral data). Briefly, (1) each of the labeled compounds is lacking the lower field of the two absorptions due to the terminal vinyl hydrogens in unlabeled material;[8] at most, 2% of the trans-reduced product is present. (2) The remaining pair of vinyl hydrogens gives J_{vic} = 10.0 Hz (typical of cis coupling); the other J_{vic} = 16.6–17.3 Hz found in the unlabeled compounds is absent.[9] (3) Each of the deuterated compounds shows coupling of the internal vinyl hydro-

(4) H. L. Goering, T. D. Nevitt, and E. F. Silversmith, *J. Amer. Chem. Soc.*, **77**, 5026 (1955).

(5) (a) J. Sauer and W. Braig, *Tetrahedron Lett.*, 4275 (1969); (b) W. D. Korte and L. Kinner, *ibid.*, 603 (1970); (c) L. H. Sommer and W. D. Korte, *J. Org. Chem.*, **35**, 22 (1970); (d) G. M. Whitesides, W. F. Fischer, Jr., J. S. Filippo, Jr., R. W. Bashe, and H. O. House, *J. Amer. Chem. Soc.*, **91**, 4871 (1969).

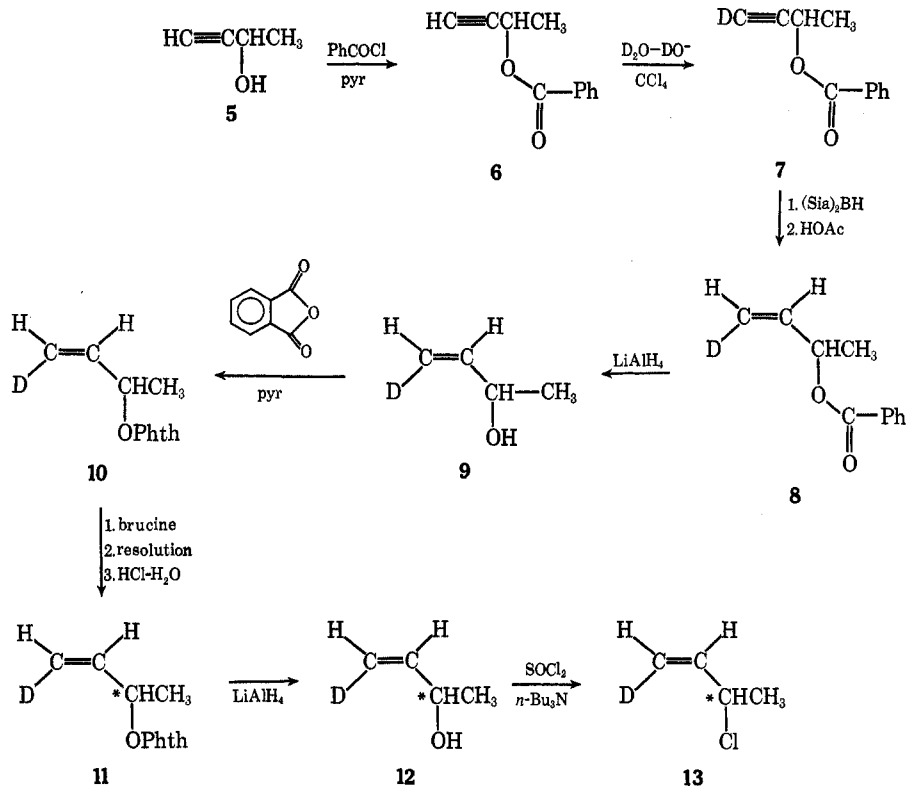
(6) (a) H. C. Brown and G. Zweifel, *ibid.*, **83**, 3833 (1961); (b) R. W. Murray and G. J. Williams, *J. Org. Chem.*, **34**, 1896 (1969); (c) A. Streitwieser, Jr., L. Verbit, and R. Bittman, *ibid.*, **32**, 1530 (1967); (d) G. Zweifel, A. Horng, and J. T. Snow, *J. Amer. Chem. Soc.*, **92**, 1427 (1970).

(7) H. C. Brown and R. M. Gallivan, Jr., *ibid.*, **90**, 2906 (1968).

(8) (a) U. E. Matter, C. Pascual, E. Pretsch, A. Pross, W. Simon, and S. Sternhell, *Tetrahedron*, **25**, 691 (1969); (b) S. W. Tobey, *J. Org. Chem.*, **34**, 1281 (1969).

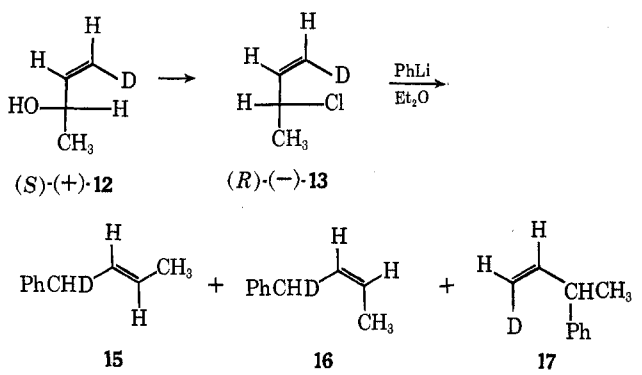
(9) (a) F. A. Bovey, "Nuclear Magnetic Resonance Spectroscopy," Academic Press, New York, N. Y., 1969, p 128 ff; (b) D. J. Pasto and C. R. Johnson, "Organic Structure Determination," Prentice-Hall, Englewood Cliffs, N. J., 1969, p 187 ff.

CHART I



gen to deuterium, J = 2.0–2.5 Hz, as expected for their trans relationship.[9]

Optically active (+)-phthalate **11** (75.6% optically pure[10]) yields (+)-alcohol **12**, known to have the *S* configuration[11a] (75.7% optically pure[11b]), which is converted into (*R*)-(−)-chloride **13** (50.4% optically pure[11]). Reaction of this chloride with phenyllithium produces three coupling products, **15**, **16**, and **17**, in a ratio of 86.0:13.5:0.5. Pure samples of **15** and **16** could be obtained by preparative glpc. Identification was based upon glpc and nmr comparisons with undeuterated materials; both products displayed a full deuterium atom at the benzylic position. The product of α coupling, **17**, could not be isolated but its identity



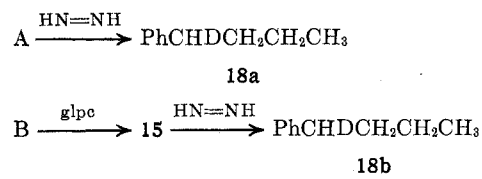
was established by glpc retention times on three different columns. Based upon the preservation of double bond geometry when γ-substituted allylic chlorides are converted into unrearranged coupling products,[2] the stereochemistry shown in **17** is assumed.

(10) J. Kenyon and D. R. Snellgrove, *J. Chem. Soc.*, 1169 (1925).

(11) (a) W. G. Young and F. F. Caserio, Jr., *J. Org. Chem.*, **26**, 245 (1961); (b) K. G. Oliver and W. G. Young, *J. Amer. Chem. Soc.*, **81**, 5811 (1959); (c) W. G. Young and J. S. Franklin, *ibid.*, **88**, 785 (1966).

Careful distillation of the crude reaction mixture afforded an 86.0:13.5:0.5 mixture of **15**, **16**, and **17**, 2.500 g of which was diluted to 9.500 g with a sample of authentic unlabeled racemic materials of exactly the same composition. Spinning band distillation then gave an 86.5:13.5 mixture of **15** and **16**, free of **17** whose removal is important because of its expected large rotation. This sample was diluted with an exactly equal weight of unlabeled racemic **15** and **16** in the same ratio. The mixture now contains 13.2% of deuterated materials.

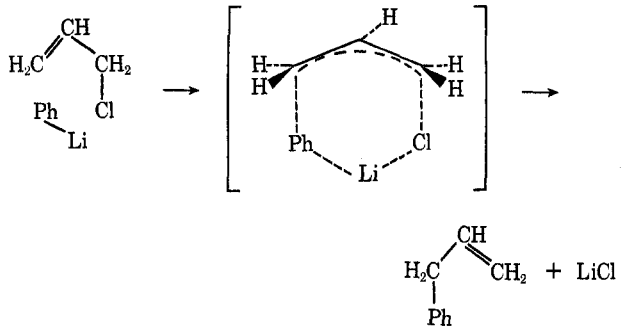
Since neither the absolute configuration nor maximum rotation of alkenes **15** and **16** is known, this sample was divided into two portions, A and B, which were treated as follows. A was reduced with diimide to (*R*)-(−)-1-phenylbutane-*1-d* (**18a**),[12] α^{27}D −0.0253 ± 0.0002° (neat, l = 0.298). B, by preparative glpc, yielded pure **15** which was similarly reduced to **18b**, α^{27}D −0.0329 ± 0.0002° (neat, l = 0.298). Adjustment of these observed rotations for the fact that the samples are only 13.2% deuterated leads to specific rotations: **18a**, $[\alpha]^{27}$D −0.780° (neat) and **18b**, $[\alpha]^{27}$D −1.02° (neat), corresponding to optical purities[12] of 35.0 and 45.6%, respectively.



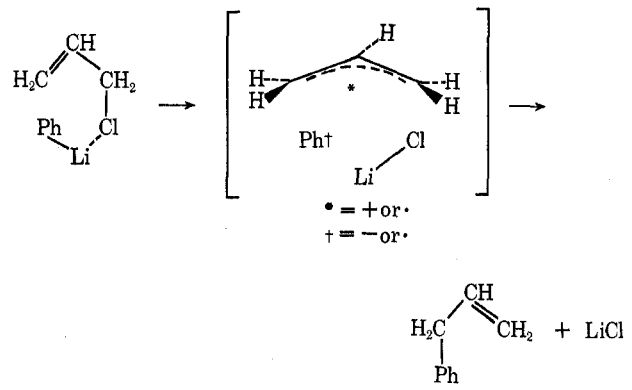
(12) (a) A. Streitwieser, Jr., J. R. Wolfe, Jr., and W. D. Schaeffer, *Tetrahedron*, **6**, 338 (1959); (b) V. E. Althouse, D. M. Feigl, W. A. Sanderson, and H. S. Mosher, *J. Amer. Chem. Soc.*, **88**, 3595 (1966); (c) L. Verbit, *Progr. Phys. Org. Chem.*, **7**, 51 (1970); (d) D. Arigoni and E. L. Eliel, *Top. Stereochem.*, **4**, 127 (1969).

Discussion

One of the plausible mechanisms for γ coupling discussed in the preceding paper[2] involves concerted C–Cl cleavage and C–C formation in a six-membered transition state. Were such a mechanism in fact



operative, the phenyl group would enter syn to the departing halide. Other mechanisms proceeding *via* ionic or radical intermediates could also result in syn attack if it is assumed that coordination of metal with halide is the initial step and that the intermediate collapses to product without rotation about the partial double bond.

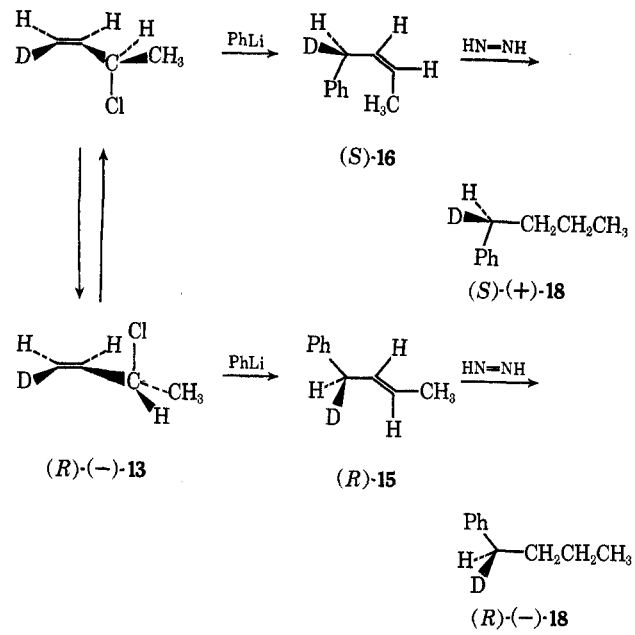


By either view, the mechanism resembles that for the reaction of secondary amines with allylic chlorides[13] for which syn attack has been established with a cyclic allylic ester.[14,15]

Only a relatively long-lived intermediate would fail to produce a highly stereospecific interaction of the reaction partners, and evidence presented earlier[2] would argue against such a situation. A possible variation of the above would involve coordination of phenyllithium to halide concerted with, or followed by, attack of a *second* molecule of phenyllithium either from above (anti) or below (syn) the plane.

The optical rotations observed for reaction of (*R*)-(−)-**13** with phenyllithium can easily be interpreted in terms of a mechanism proceeding by syn attack. Scheme II illustrates the expectations for such a process: cis product **16** should have the *S* configuration and on reduction should produce (*S*)-(+)-**18**, whereas trans olefin **15** should be *R* and should give (*R*)-(−)-**18**.

SCHEME II



Sample B, above, from which pure trans olefin **15** could be isolated, led to (*R*)-(−)-**18** which was 45.6% optically pure. Since starting chloride (*R*)-(−)-**13** was 50.4% optically pure, this corresponds to an asymmetric transfer to the extent of 91% (*i.e.*, >95% syn attack). Because of the uncertainty in the maximum rotation of **18**,[12] it is not unlikely that syn attack is the exclusive process.

Sample A containing **15** and **16** in a ratio of 86.5:13.5 produced (*R*)-(−)-**18** which was 35.0% optically pure. If one *assumes* 100% syn attack leading to the two components, then the result may be analyzed as follows. Product **18** should be composed of 86.5% of the (*R*)-(−) enantiomer and 13.5% of the (*S*)-(+). Since chloride **13** was only 50.4% optically pure, one expects a contribution of −0.97° from (*R*)-(−)-**18** [(−2.23)(0.504)(0.865)] and of +0.16° from (*S*)-(+)-**18** [(+2.23)(0.504)(0.135)] making the net rotation −0.81°, in excellent agreement with the observed $[\alpha]^{27}D$ −0.78°. To exactly reproduce this number, one need only assume that both reactions are stereospecific to the extent of 95%.

Thus the conclusions of the preceding paper[2] on the mechanism of coupling are reinforced: either the reaction is concerted or any intermediates go to products without suffering bond rotation.

Experimental Section

Instruments.—Analytical glpc was performed on a Perkin-Elmer Model 800 gas chromatograph (flame ionization detector) and utilized the following columns: A, 5.5 ft × 1/8 in., Carbowax 20M (10%) on Chromosorb W; B, 10 ft × 1/8 in., TCEP (10%) on Chromosorb W; C, 20 ft × 1/8 in., Carbowax 20M (20%) on Chromosorb P; D, 10 ft × 1/8 in., SE-30 (10%) on Chromosorb W. In those cases in which quantitative glpc was used for yield determinations, the internal standard method was employed. Peak areas (for yields or product ratios) were measured with a Disc integrator. Preparative glpc was performed on either a Varian Aerograph Model 202-1B gas chromatograph (thermal conductivity detector) or a Hewlett-Packard F & M PrepMaster Jr., Model 776 (flame ionization detector), and uti-

(13) (a) W. G. Young, I. D. Webb, and H. L. Goering, *J. Amer. Chem. Soc.*, **73**, 1076 (1951); (b) A. Fry, *Pure Appl. Chem.*, **8**, 409 (1964); (c) F. G. Bordwell, *Accounts Chem. Res.*, **3**, 281 (1970).

(14) G. Stork and W. N. White, *J. Amer. Chem. Soc.*, **78**, 4609 (1956).

(15) It is unfortunate that the stereochemistry of reaction with an acyclic substrate has not been determined, since the observed syn attack on the cyclohexenyl system[14] may be due to conformational factors (antiparallel attack) peculiar to such a cyclic system rather than to any inherent stereoelectronic preference of the S_N2' reaction.

lized the following columns: P, 8 ft × 1 in., Carbowax 20M (20%) on Chromosorb W; Q, 10 ft × 3/8 in., TCEP (15%) on Chromosorb W.

Nmr spectra were obtained on a Varian Associates A-56/60A spectrometer. Optical rotations were measured with a Bendix automatic polarimeter; the cell length was 0.298 dm. Rotations were taken either of solutions (reported as $[\alpha]^{T}D$) or of neat liquids (reported as $\alpha^{T}D$ adjusted to a path length of 1 dm or as $[\alpha]^{T}D$ adjusted for path length and density). All reactions involving lithium or organolithium reagents were run in an argon atmosphere.

Materials.—Reagent grade commercial materials were used without further purification except for the following: thionyl chloride (Matheson Coleman and Bell) was purified according to the method of Fieser and Fieser,[16] distilled through a glass helices packed column, and used directly; phenyllithium was prepared as in the preceding paper;[2] diglyme (Matheson Coleman and Bell) was purified according to the procedure of Zweifel and Brown;[17] disiamylborane was prepared according to the literature procedure.[17]

Preparation of Optically Active 3-Chloro-*cis*-1-butene-*1-d* (13).

A. 1-Butyn-3-yl Benzoate (6).—To a mixture of 210 g (3.0 mol) of 1-butyn-3-ol (**5**), 234 g (3.0 mol) of pyridine, and 300 ml of ether was added 415 g (3.0 mol) of benzoyl chloride over 20 min. The resulting solution was gently refluxed for 2 hr. Pyridine hydrochloride which precipitated upon cooling was removed, and the filtrate was washed with 300 ml of 1 *N* acetic acid, 300 ml of 5% Na_2CO_3, and 300 ml of water, and was dried ($CaSO_4$). Solvent was removed (rotary evaporator) and 1.5 l. of pentane was added. The white prisms which separated were combined with a second crop obtained by concentration of the mother liquor. The combined solids were crystallized once from pentane yielding 432 g (83%) of ester **6**: mp 46–47°; nmr (CCl_4) δ 1.60 (d, 3, J = 7 Hz, methyl), 2.38 (d, 1, J = 2 Hz, acetylenic), 5.54 (d of q, 1, J = 2 and 7 Hz, methine), and *ca.* 7.4 and 8.0 (m, 5, aromatic).

B. 1-Butyn-*1-d*-3-yl Benzoate (7).—Benzoate **6**, 430 g, was dissolved in 500 ml of CCl_4 and was stirred for 6 hr with 20 ml of a 1% solution of sodium methoxide in D_2O (99.8%, Stohler Isotope Chemicals). This procedure was repeated 12 times with fresh portions of D_2O solution until the area of the nmr acetylenic absorption peak had decreased to less than the area of one of the ^{13}C satellites of the methyl protons (*ca.* 98.5% exchanged). The organic layer was dried ($CaSO_4$), concentrated (rotary evaporator), and treated with pentane as above to induce deposition of the product. One crystallization from pentane afforded 414 g (96%) of deuterated ester **7**: mp 46–47°; nmr (CCl_4) δ 1.59 (d, 3, J = 7 Hz, methyl), 5.55 (q, 1, J = 7 Hz, methine), and *ca.* 7.4 and 8.0 (m, 5, aromatic).

C. *cis*-*1*-Buten-*1-d*-3-yl Benzoate (8).—By adaptation of the method of Brown and Zweifel,[6a] a solution of 51.0 g (0.29 mol) of acetylenic benzoate **7** in 100 ml of dried ether was added over 30 min to 400 ml of 0.9 *N* disiamylborane in THF[17] which was stirred under argon and maintained at −5 to 0°. The mixture was stirred at this temperature for an additional 15 min at which time glpc analysis (column A) showed that no starting material was left. With the temperature of the mixture held at −5 to 0°, 200 ml of glacial acetic acid was added over 25 min, and the resulting solution was stirred for an additional 4 hr at the same temperature. The solution was extracted thoroughly with several portions each of ice–water, saturated Na_2CO_3, and water, and was dried ($CaSO_4$). Removal of solvent (rotary evaporator) produced a residue which was distilled through a 14-in. glass helices packed column, and the fraction boiling from 65 to 85° (0.6 mm) was treated with 100 ml of 30% H_2O_2. The organic layer after washing and drying was distilled through a spinning band column giving allylic ester **8** in yields ranging from 30 to 46% (glpc yields, column A, before oxidation were typically 50 to 85%): bp 67–68° (0.5 mm); nmr (CCl_4) δ 1.41 (d, 3, J = 6.8 Hz, methyl), 5.03 (d of d, 1, J = 10.0 and 1.0 Hz, terminal vinyl), 5.52 (m, 1, consisting of a quartet, J = 6.8 Hz, each line of which is split into a doublet of doublets, J = 5.3 and 1.0 Hz, methine), 5.85 (m, 1, consisting of a doublet of doublets, J = 10.0 and 5.3 Hz, each line of which is further split into a 1:1:1 triplet, J = 2.5 Hz, internal vinyl), and *ca.* 7.3 and 7.9 (m, 5, aromatic).

D. 3-Hydroxy-*cis*-1-butene-*1-d* (9).—According to the method of Doering and Zeiss,[18] a solution of 140 g (0.79 mol) of ester **8** in 150 ml of dried ether was added dropwise over 1 hr to a stirred suspension of 25.0 g (0.66 mol) of $LiAlH_4$ in 500 ml of ether at 0–5°. The mixture was allowed to warm to room temperature and was stirred for an additional 1 hr. Saturated NH_4Cl was carefully added and the ether layer was decanted leaving a powdery residue which was thoroughly triturated with several 100-ml portions of ether. The combined ether solutions were washed with saturated NaCl, dried (BaO), and concentrated at atmospheric pressure through a 14-in. glass helices packed column. Distillation of the residue through a spinning band column gave 41.4 g (72%) of allylic alcohol **9**: bp 97–98° (lit.[10] bp 96–97° for 3-hydroxy-1-butene); glpc analysis (column B) >99% pure; nmr (CCl_4) δ 1.19 (d, 3, J = 6.5 Hz, methyl), *ca.* 3.8 (broad s, 1, hydroxyl, concentration-dependent chemical shift), 4.13 (m, 1, consisting of a quartet, J = 6.5 Hz, each line of which is further split into a doublet of doublets, J = 5.5 and 1.0 Hz, methine), 4.88 (d of d, 1, J = 10.0 and 1.0 Hz, terminal vinyl), and 5.75 (m, 1, consisting of a doublet of doublets, J = 10.0 and 5.5 Hz, each line of which is further split into a 1:1:1 triplet, J = 2.5 Hz, internal vinyl).

E. *cis*-1-Buten-*1-d*-3-yl Hydrogen Phthalate (10).—Following the procedure of Kenyon and Snellgrove,[10] a mixture of 41.0 g (0.56 mol) of labeled alcohol **9**, 44.5 g (0.56 mol) of pyridine, and 84.0 g (0.57 mol) of phthalic anhydride in 150 ml of dried ether was stirred at 50° for 5 hr. The cooled clear solution was poured into 500 ml of 2 *N* HCl at 0°. The resulting mixture was stirred vigorously for 5 min, the organic layer was separated, and the aqueous phase was extracted with several 100-ml portions of ether. The combined organic phases were dried ($CaSO_4$) and concentrated (rotary evaporator). Benzene (100 ml) was added and the small amount of phthalic anhydride which precipitated was removed. The solution was again concentrated (rotary evaporator) and the last trace of benzene was removed by heating at 40° (1 mm). The residue, 110 g (89%) of a colorless oil, was the desired phthalate **10**: nmr (CCl_4) δ 1.41 (d, 3, J = 6.3 Hz, methyl), 5.03 (d, 1, J = 10.0 Hz, terminal vinyl), 5.46 (m, 1, consisting of a quartet, J = 6.3 Hz, each line of which is further split into a doublet, J = 6.0 Hz, methine), 5.82 (m, 1, consisting of a doublet of doublets, J = 10.0 and 6.0 Hz, each line of which is further split into a 1:1:1 triplet, J = 2.0 Hz, internal vinyl), *ca.* 7.4 (m, 4, aromatic), and 12.3 (s, 1, carboxyl).

F. Optically Active *cis*-1-Buten-*1-d*-3-yl Hydrogen Phthalate (11).—According to the method of Kenyon and Snellgrove,[10] a solution of 110 g (0.50 mol) of phthalate **10** in 100 ml of acetone was added to 240 g (0.61 mol) of anhydrous brucine in 700 ml of warm acetone. The pale yellow solution was stirred and the white salt which precipitated was crystallized seven times to constant mp 160–162° (lit.[10] mp 120–122°), 43 g. Systematic work-up of the mother liquor yielded two more crops of the less soluble diastereomer, 55 g. Hydrolysis of the combined salts was accomplished by shaking with 400 ml of 4 *N* HCl at 0°. The solution was extracted with ten 50-ml portions of ether, and the combined extracts were dried ($CaSO_4$) and concentrated (rotary evaporator), and the last trace of ether was removed at 40° (1 mm). The residue, 32.5 g (30%), was the desired optically active ester **11**: nmr identical with that of racemic ester **10**; $[\alpha]^{30}D$ +30.6° (*c* 2.12, EtOH) (75.6% optically pure[10]).

The mother liquors from the fractional crystallization were concentrated and decomposed with 4 *N* HCl, as above, yielding 43.7 g (40%) of optically active ester **11**: $[\alpha]^{30}D$ −19.9° (*c* 5.03, EtOH) (49.2% optically pure[10]).

G. Optically Active 3-Hydroxy-*cis*-1-butene-*1-d* (12).—Optically active (−)-phthalate **11**, 44.0 g (0.20 mol), was treated with 22 g (0.58 mol) of $LiAlH_4$ according to the procedure described above for benzoate **8**. Work-up and spinning band distillation gave 9.8 g (67%) of optically active allylic alcohol **12**: bp 96–98°; $\alpha^{30}D$ −14.1° (neat) (51.1% optically pure[11]). Similarly, 33.2 g (0.15 mol) of (+)-phthalate gave 7.9 g (72%) of (+)-alcohol: $\alpha^{30}D$ +20.9° (neat) (75.7% optically pure[11]).

H. Optically Active 3-Chloro-*cis*-1-butene-*1-d* (13).—Following the procedure of Young, *et al.*,[19] 13.0 g (0.11 mol) of thionyl chloride in 30 ml of dried ether was added dropwise over 30 min to a solution of 7.7 g (0.11 mol) of (+)-alcohol **12** and 21.5 g (0.12 mol) of tri-*n*-butylamine in 180 ml of ether at −50°. The

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mixture was stirred for 3 hr during which time it slowly warmed to −20° and was flash-distilled into a Dry Ice–acetone trap. The distillate after drying ($CaSO_4$) was shown by glpc (column A) to contain a 69:31 ratio of 3-chloro-1-butene and 1-chloro-2-butene in an overall yield of 92%. Concentration of the solution followed by preparative glpc (column P) gave 4.6 g (48%) of (−)-chloride **13**: $\alpha^{30}D$ −30.8° (neat) (50.4% optically pure[11]); nmr (CCl_4) δ 1.58 (d, 3, J = 6.5 Hz, methyl), 4.42 (m, 1, consisting of a quartet, J = 6.5 Hz, each line of which is further split into a doublet of doublets, J = 7.0 and 0.8 Hz, methine), 5.00 (d of d, 1, J = 10.0 and 0.8 Hz, terminyl vinyl), and 5.86 (m, 1, consisting of a doublet of doublets, J = 10.0 and 7.0 Hz, each line of which is further split into a 1:1:1 triplet, J = 2.5 Hz, internal vinyl).

Reaction of Optically Active 3-Chloro-*cis*-1-butene-*1-d* (13) with Phenyllithium.—Optically active (−)-chloride **13**, 4.0 g (0.044 mol), in ether was added to 0.8 *N* phenyllithium in ether according to the general procedure of the previous paper.[2] Analysis of the crude reaction mixture by glpc (column B) revealed a 73% yield of three hydrocarbons in a ratio of 86.0:13.5:0.5. Preparative glpc (column Q) of a small portion of the crude product led to isolation of the major component, 1-phenyl-*trans*-2-butene-*1-d* (**15**), identified by comparison with unlabeled material and by its nmr spectrum (CCl_4) δ 1.65 (m, 3, methyl), 3.2 (m, 1, methine), 5.4 (m, 2, vinyl), and 7.0 (m, 5, aromatic). A small sample of the next most abundant product was similarly isolated and identified as 1-phenyl-*cis*-2-butene-*1-d* (**16**). The third component was not present in sufficient quantity to permit isolation, but its structure was confirmed as 3-phenyl-1-butene (presumably deuterated at C_1 with cis geometry, **17**) by glpc comparison (columns B, C, and D) with authentic unlabeled material.

Distillation of the crude product yielded 2.80 g of a mixture of **15**, **16**, and **17** in a ratio of 86.0:13.5:0.5, bp 62–64° (10 mm). A 2.500-g portion of this distillate was diluted to 9.500 g with a mixture of optically inactive compounds in exactly the same ratio. Careful distillation through a spinning band column gave 5.15 g of a mixture containing only hydrocarbons **15** and **16** in a ratio of 86.5:13.5 which was then diluted to twice its weight with 5.15 g of the identical mixture of unlabeled materials. This mixture (containing 13.2% of deuterated optically active hydrocarbons) was separated into two portions.

A 5.0-g portion (0.038 mol) was reduced by diimide [formed by treatment of 30.0 g of anhydrous hydrazine in 50 ml of ethanol (containing a few crystals of $CuSO_4$) with oxygen, 30 ml/min for 24 hr].[20] After the usual work-up, the organic layer was distilled through a 6-in. Vigreux column yielding 2.94 g (59%) of 1-phenylbutane-*1-d* (**18a**): bp 62° (10 mm); $[\alpha]^{27}D$ −0.780° (neat).

From a 5.3-g portion, preparative glpc (column Q) gave 4.30 g of pure trans olefin **15** which was reduced with diimide to 2.30 g (53%) of 1-phenylbutane-*1-d* (**18b**): bp 62° (10 mm); $[\alpha]^{27}D$ −1.02° (neat).

Registry No.—**6**, 29333-27-5; **7**, 29333-28-6; **8**, 29333-29-7; **9**, 29333-30-0; **10**, 29333-31-1; (+)-**11**, 29333-32-2; (+)-**12**, 29453-55-2; (−)-**13**, 29333-33-3; (−)-**18**, 29453-61-0; (+)-**18**, 14159-12-7; phenyllithium, 591-51-5.

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Reductions of Some Aliphatic β Diketones with Lithium Aluminum Hydride

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The reduction of β diketones with lithium aluminum hydride ($LiAlH_4$) under forcing conditions affords products of elimination as well as the expected 1,3-diols. The elimination products (unsaturated alcohols) are obtained in yields which correspond to the enol content of the starting diketone. The reaction is highly stereospecific, giving rise to trans olefins exclusively. The unsymmetrical diketone, 2,4-hexanedione, affords two unsaturated alcohols, 3-hexen-2-ol and 2-hexen-4-ol, with the former predominating. The ratio of these two products and their stereochemistry are discussed in light of the most likely reaction mechanism.

The reduction of enolizable β-keto esters,[1,2] malonic enolates,[3] and β diketones[1,4-6] with lithium aluminum hydride ($LiAlH_4$) gives rise to products of elimination as well as the expected 1,3-diols. In discussing the mechanism of the reaction, Dreiding and Hartman[1] proposed that the elimination products (unsaturated alcohols) resulted from the action of $LiAlH_4$ on the enol forms of the compounds, the diols arising from the nonenolized portions. The applicability of Dreiding and Hartman's mechanism to systems other than alicyclic or aromatic β-dicarbonyl compounds has been questioned by other investigators. Marshall, Andersen, and Hochstetler[3] reported that the proposed mechanism could not account for the saturated monoalcohols observed by them in the reduction of malonic enolates and suggested a considerably more complicated reaction scheme. Pohoryles, Sarel, and Ben-Shoshan[5] reacted acetylacetone with lithium aluminum hydride under forcing conditions and observed a higher ratio of elimination product to diol than would be expected from the enol content of acetylacetone. None of these investigators report on the stereochemistry of the unsaturated reaction products.

We have examined the reductions of acetylacetone and 2,4-hexanedione with $LiAlH_4$ in some detail. We were especially interested in identifying all reaction products, in determining the direction of the elimination in the case of the unsymmetrical dione, and in elucidating the stereochemistry of the reaction. This report describes our results and their bearing on the mechanism of the reduction–elimination reaction. Of especial interest is the stereochemical control exhibited during the elimination. The unsaturated reaction products are exclusively trans (Scheme I).

Results

Acetylacetone was a logical choice for most of our studies, because it is the most readily available, sym-

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