Cis–Trans Isomerizations of 1-Lithio-1-phenyl-1-butene. Solvent Effects on the Rate of Isomerization and on Nuclear Magnetic Resonance Spectra[1]

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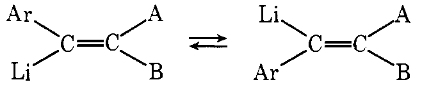
Abstract: (*Z*)- and (*E*)-1-lithio-1-phenyl-1-butene (**1** and **2**, respectively) are formed stereospecifically by lithium-halogen exchange reactions between *n*-butyllithium and (*E*)- and (*Z*)-1-bromo-1-phenyl-1-butene, respectively. Both **1** and **2** are configurationally stable at room temperature in hexane solutions containing less than 1 equiv of THF. Cis-trans isomerization of **1** and **2** occurs in hexane–THF mixture solutions at +35° when more than 1 equiv of THF has been added and at −30° when more than 5 equiv of THF has been added. The effect of different donor solvents on the rate of cis-trans isomerization of **1**, TMEDA > DME > THF > diethyl ether, suggests that the cis-trans isomerization proceeds via ion pair intermediates. Changes in the ^{1}H NMR spectra of **1** and **2** in hexane solutions as THF is added support this conclusion.

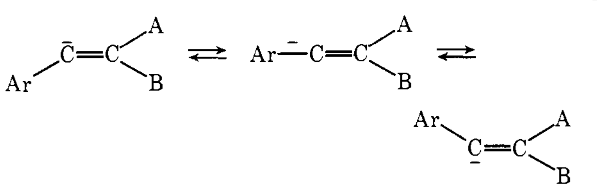
Vinyllithium compounds substituted in the α position with aryl groups will undergo cis-trans isomerization in the presence of coordinating base solvents (eq 1).[3] Those substituted in the α position with alkyl groups[3,4] or hydrogen[5] do not isomerize. These cis-trans isomerizations are ground-state reactions that occur readily at low temperatures and thus do not involve rotation about the tetra-substituted carbon-carbon double bond.



(1)

Two general mechanisms can be proposed for these isomerizations. One mechanism is similar to the mechanism for inversion in primary alkyl organometallics[6,7] in which an alkyl-bridged dimeric aggregate is associated with the transition state for inversion.[7b] The rates of these inversions generally increase with increasing temperature, increasing concentration, and with decreasing solvent coordinating ability. For example, the rate of inversion of 3,3-dimethylbutylmagnesium chloride shows the following solvent dependence: diethyl ether > tetrahydrofuran > diglyme.[6b]

The second mechanism involves, as key steps, formation of ion pairs from the covalent vinyllithium compounds by coordination of the Lewis base solvent to the lithium cation and cis-trans isomerization of the vinyl anions. This cis-trans isomerization probably occurs via the linear carbanion which is either an intermediate or transition state in eq 2.[8]



(2)

It is also necessary for the solvated lithium cation to migrate during the isomerization.

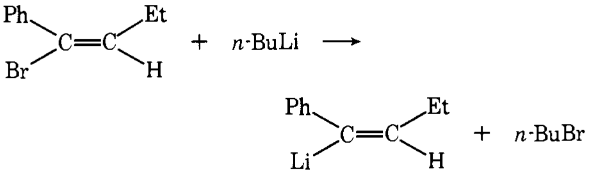
The necessity of α-aryl substituents for cis-trans isomerization suggests that the latter mechanism applies. Resonance stabilized carbanions typically exist as ion pairs,[9] and the linear carbanion is stabilized by the aryl substituent.[8] Since, if the ion pair mechanism applies, the rate of isomerization should increase with increasing solvent coordinating ability,[9] the two mechanisms can be readily distinguished by their opposite solvent effects.

We have determined the relative effectiveness of diethyl ether, tetrahydrofuran (THF), *N,N,N′,N′*-tetramethylethylenediamine (TMEDA), and 1,2-dimethoxyethane (DME) at catalyzing the cis-trans isomerization of (*Z*)-1-lithio-1-phenyl-1-butene (**1**). The relative rates at which equilibrium will be established for these solvents if the ion pair mechanism applies are TMEDA $\sim$ DME > THF > diethyl ether.[9] We have also studied the influence of a small amount of THF on the ^{1}H NMR spectra of **1** and its *E* diastereomer, **2**, as hexane solutions at ambient and low temperatures in order to ascertain the changes in solvation and aggregation[10] of the vinyllithium compounds necessary for cis-trans isomerization.

Results

Preparation and Characterization of 1 and 2. The vinyl bromides necessary for preparation of the vinyllithium compounds were synthesized by standard methods (Scheme I). The erythro and threo dibromides are separated by fractional crystallization from hexane and column chromatography (alumina-hexane). They were characterized by the magnitude of the coupling constant between the protons on carbon-1 and carbon-2 (J = 10.8 Hz, erythro; J = 5.5 Hz, threo).[11] The configurations of the vinyl bromides were anticipated on the basis of trans elimination and confirmed by ^{1}H NMR.[12]

(*E*)- and (*Z*)-1-lithio-1-phenyl-1-butene are formed with retention of configuration about the carbon-carbon double bond by lithium-halogen exchange reactions between *n*-butyllithium and (*Z*)- and (*E*)-1-bromo-1-phenyl-1-butene, respectively, in THF solution at −78° (eq 3). The formation of **1** from the *E* vinyl bromide was confirmed by ^{1}H NMR spectra (see below), reaction with ethanol to yield *cis*-1-phenyl-1-butene,[13] and reaction with 1,2-dibromoethane[14] to yield (*E*)-1-bromo-1-phenyl-1-butene. The *E* vinyllithium compound was characterized in similar fashion with the reactions yielding the diastereomeric products.



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The retention of configuration in these lithium-halogen exchange reactions demonstrates that free vinyl radicals are

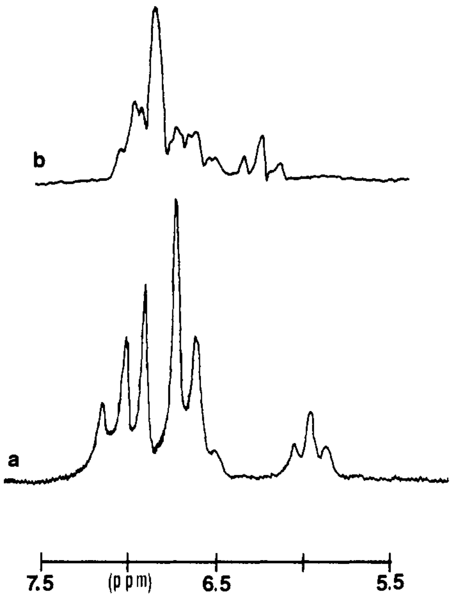
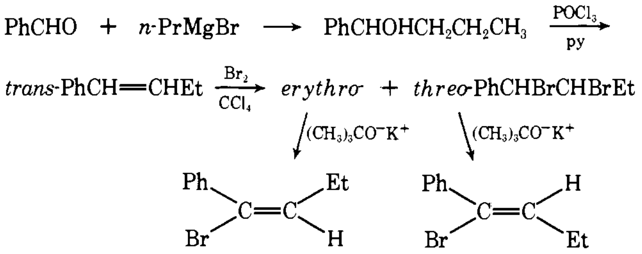


Figure 1. ^{1}H NMR spectra (60 MHz) at −30° of **1** (a) and **2** (b) in hexane solution with 3.0 equiv of THF present.

Scheme I



not intermediates. If they were, extensive isomerization should have occurred.[15] This contrasts with the lithium-halogen exchange reactions of alkyl iodides where free alkyl radicals have been detected as intermediates by ESR,[16] CIDNP NMR experiments,[17] and chemical trapping of the radicals.[18]

Upon warming these THF solutions containing the vinyllithium compounds and *n*-butyl bromide to −60°, cis-trans isomerization of the vinyllithium compounds and coupling of the vinyllithium compounds and *n*-butyl bromide to form (*E*)- and (*Z*)-4-phenyl-3-octene occurred. Thus it is necessary to prepare solutions of the vinyllithium compounds which do not contain alkyl halides for these studies.

The lithium-halogen exchange reaction between (*E*)-1-bromo-1-phenyl-1-butene and *n*-butyllithium occurs rapidly in hexane solution at room temperature without loss of configuration about the carbon-carbon double bond.[19] The hexane and *n*-butyl bromide can be removed by vacuum distillation to yield, after adding the desired solvent, a solution of the vinyllithium compound free of *n*-butyl bromide.

Similar reactions of (*Z*)-1-bromo-1-phenyl-1-butene occur much slower, and mixtures of **1** and **2** are formed. The unreacted vinyl bromide in these reactions is not isomerized. Thus the vinyllithium compound must be isomerizing. The slower rate of this lithium-halogen exchange reaction is presumably due to steric interference since the ethyl group rather than the hydrogen is cis to the bromine. The reaction of (*Z*)-1-bromo-1-phenyl-1-butene with *n*-butyllithium containing 0.4-0.5 equiv of THF proceeds rapidly at room temperature to form **2**. The *n*-butyl bromide can be removed by vacuum distillation.

The vinyllithium compounds are configurationally stable in hexane solutions containing less than 1 equiv of THF for at least 4 hr at room temperature. This is indicated by GLC analysis for *cis*- and *trans*-1-phenyl-1-butene in aliquots of these solutions quenched with ethanol and by ^{1}H NMR spectra. The vinyl and aromatic proton regions of the ^{1}H NMR spectra of these compounds are shown in Figure 1. The triplets at δ 6.35 (**2**, J = 6.8 Hz) and δ 5.95 (**1**, J = 6.0 Hz) are assigned to the vinyl protons. Irradiation at ca. δ 2.0 (ethyl group CH_2 absorption) collapses these triplets to singlets and does not change the appearance of the aromatic protons. Since the vinyl protons have sufficiently different chemical shifts, the course of cis-trans isomerization can be readily followed by ^{1}H NMR.

Table I. Solvent Effects on the Rate of Cis-Trans Isomerization of **1** at 22°[a]

Solvent (equiv)	Time,[b] sec	% **2**[c]
TMEDA (10)	15	36
	55	42
	135	43
	250	43
	370	43
TMEDA (5)	12	31
	60	41
	115	43
	240	44
	360	44
	600	44
THF (10)	12	20
	50	44
	120	55
	210	59
	315	59
	600	58
DME (10)	15	52
	70	63
	150	63
	300	62
DME (5)	15	36
	75	50
	195	60
	310	61
	480	61
Ether (10)	15	16
	150	22
	300	27
	600	36
	1170	50
	2460	62
	3570	66
	5010	68
	6000	68

[a] The reactions are in hexane solutions, 0.2 *N* in **1** and 2.0 or 1.0 *M* in added solvent. The solutions were prepared by volume, and the ratios of solvent to **1** + **2** checked by ^{1}H NMR integration. GLC analysis of ethanol quenches of the hexane solutions before addition of the solvent indicated 95–97% **1** and 3–5% **2** present. These are points from single runs. At least two runs were done for each solvent mixture, and essentially identical results were obtained. [b] The time when 1,2-dibromoethane is added. [c] Relative yield determined by GLC analysis of the vinyl bromides (see text).

Solvent effects on the rate of cis-trans isomerization of 1 at 22° in hexane-Lewis base mixture solutions are summarized in Table I. The amounts of **1** and **2** present were determined by GLC analysis for (*E*)- and (*Z*)-1-bromo-1-phenyl-1-butene, respectively, in aliquots quenched with 1,2-dibromoethane. The total yield of vinyl bromides relative to *tert*-butylbenzene as an internal standard is greater than 95% in all cases. The relative rates at which equilibrium is established are: solvent (solvent/**1** molar ratio), TMEDA (10) ~ TMEDA (5) ~ DME (10) > DME (5) ~ THF (10) > diethyl ether (10). Comparison of the TMEDA and DME results illustrates the larger formation constant for the TMEDA-lithium cation complex since 5 and 10 equiv of TMEDA have the same effect, whereas 5 and 10 equiv of DME do not.[20] This ordering of solvent effect is consistent with the ion pair mechanism.[9]

Discrete ^{1}H NMR spectra are obtained for the **1** and **2** present in these mixture solutions during and after the establishment of equilibrium at +35°. The sharp patterns observed for the vinyl protons indicate that cis-trans isomerization is slow on the ^{1}H NMR time scale at this temperature, and that the linear vinyl carbanion in eq 2 is a transition state or a transient intermediate present in low concentration. Integration of the vinyl proton signals after equilibrium is reached gives these compositions: TMEDA (10),

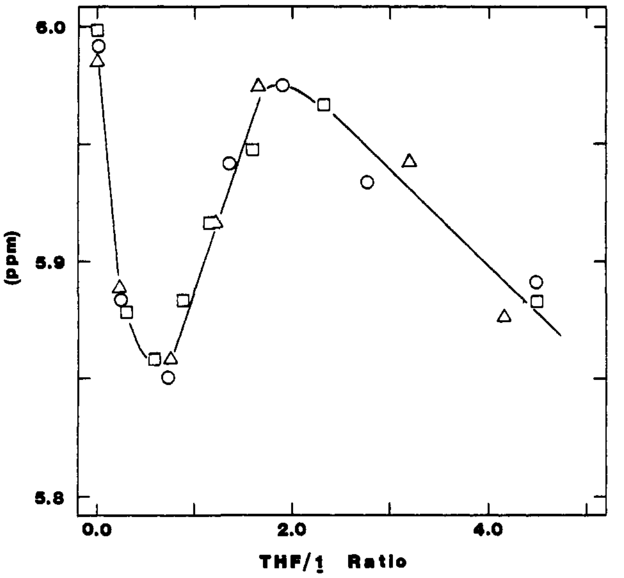


Figure 2. Change in the chemical shift of the vinyl proton of **1** at −30° in hexane solution as a function of added THF; ○, □, and △ refer to separate experiments.

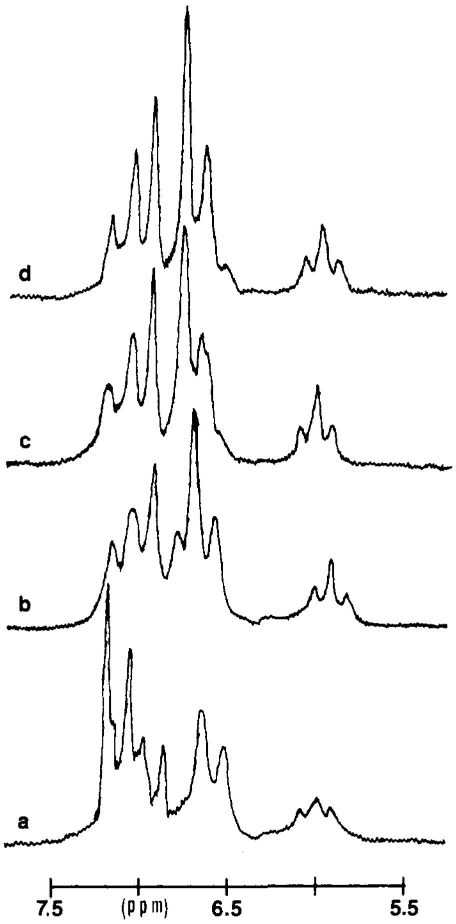


Figure 3. ^1H NMR spectra (60 MHz) at −30° of **1** as a function of added THF: (a) 0.0 equiv; (b) 1.2 equiv; (c) 2.0 equiv; and (d) 3.2 equiv.

45% **2**; DME (10), 60% **2**; THF (10), 60% **2**; diethyl ether (10) 69% **2**. These are the same compositions obtained by the 1,2-dibromoethane quenches. Thus both methods of analysis accurately measure the amounts of **1** and **2** present.

The influence of temperature and the amount of THF present on the rate at which equilibrium is established and the equilibrium position was studied by the ^1H NMR method. Cis-trans isomerization occurs at +35° when more than ca 1.1 equiv of THF is added to hexane solutions of **1** and **2**. At −30 and −50° isomerization does not occur until more than 5 equiv of THF has been added. Equilibration is also established at a much slower rate at these low temperatures. When 6.0 equiv of THF are present, equilibrium is established within 5 min at +35° (57% **2**), in ca. 30 min at −30° (60% **2**), and in ca. 60 min at −50° (60% **2**). The equilibrium position at +35° is a function of the amount of THF present when less than 6 equiv is present: 1.5 equiv, 31% **2**; 2.5, 41% **2**; 3.5, 48% **2**; 5.0, 54% **2**, 8.0, 58% **2**. The equilibrium position is not a function of temperature.

Changes in the ^1H NMR spectra of the vinyl and aromatic protons of 1 and 2 as a function of added THF were monitored to ascertain changes in the aggregation and solvation of **1** and **2**. The curious changes in the chemical shift of the vinyl proton of (*Z*)-1-lithio-1-phenyl-1-butene as THF is added at −30° are shown in Figure 2. The same changes occur at +35° for this isomer and at −30° for the *E* isomer. The maximum upfield shift is observed at a THF/RLi ratio of ca. 0.6. This suggests that a complex of stoichiometry 2RLi·THF is formed. Complexes of this stoichiometry between alkyllithium compounds and THF have different reactivities than the unsolvated alkyllithium compounds.[21] Since more than 1.1 equiv of THF is necessary for cis-trans isomerization at +35°, formation of a 2 RLi·THF complex is not sufficient for the isomerization. The downfield shift of the vinyl proton upon adding THF to a THF/RLi ratio of ca. 1.9 may be due to deaggregation of the vinyllithium compound. One can envision aggregates in which the vinyl proton is shielded by the phenyl rings. Changes in aggregation and solvation will change the effective electronegativity of the lithium atom. This also has an effect on the chemical shift of the vinyl proton.[12a]

Changes in the aromatic proton region of **1** at −30° as THF is added indicate that the nature of the carbon-lithium bond is changing (Figure 3). In pure hexane solution, the aromatic region consists of a downfield multiplet (3 H) and a two-line pattern (2 H) upfield. As THF is added, the appearance of the aromatic proton region changes until a limiting spectrum is reached at a THF/RLi ratio of ca. 3.0. The aromatic proton region now consists of two 3-line patterns with the upfield pattern integrating for 3 H. Assuming there is free rotation about the carbon-1-phenyl bond, the two ortho protons and the two meta protons should be equivalent. A first-order analysis of the observed splitting patterns indicates that the ortho protons are upfield of the meta protons. Thus the para proton shifts upfield on the addition of THF. This conclusion is confirmed by our observations on 1-(3,5-dimethylphenyl)-1-lithio-2-methyl-1-propene.[22] The aromatic proton region of the ^1H NMR spectrum consists of two broadened singlets at δ 6.53 (1 H) and 6.33 (2 H) at +35° in hexane solution containing 0.7 equiv of THF. When 6.0 equiv of THF are present, the two peaks have essentially merged into one peak at δ 6.34. The ordering of chemical shifts observed for **1** in the presence of >3.0 equiv of THF ($\delta_{meta} > \delta_{ortho} \sim \delta_{para}$) resembles those observed for benzyllithium[23] and indicates that the carbon-lithium bond is now more ionic than in pure hexane solution.

This species is not formed until enough THF has been added to occupy three of the four primary coordination sites about the lithium cation.[24] It may be the monomeric vinyllithium compound or a contact ion pair. However this species is best described, it has the geometry of a tetrasubstituted vinyl compound since **1** and **2** have different ^1H NMR spectra at all the conditions studied.

Discussion

The solvent effects on the rate at which equilibrium is established and the changes observed in the ^{1}H NMR spectra of **1** and **2** on the addition of THF at −30° are consistent with the ion pair mechanism for cis-trans isomerization. Additional support for this hypothesis is gained by comparison of the solvent effects for isomerization of **1** and the hindered rotation of benzylic[25] and allylic[26] metal compounds.

Benzylic and allylic metal compounds typically exist as ion pairs in coordinating solvents.[9,25,26] The planarity of and hindered rotation in these carbanions is indicated by the nonequivalence of protons in ^{1}H NMR spectra. The rotational barrier for a given carbanion is a function of cation and solvent. Conditions which increase the interaction between the cation and carbanion (increase the carbon-metal bond localization) decrease the rotational barrier. Since the solvent effects seen in these hindered rotation studies are the opposite of those obtained here for cis-trans isomerization of **1**, decreased carbon-metal bond localization is necessary for isomerization. One way of decreasing the interaction between the metal cation and the carbanion is to form ion pairs.

The results reported here suggest that the effectiveness of different coordinating agents for lithium (and other) cations can be compared on a quantitative basis by determining their effects on the rate of cis-trans isomerization of vinyllithium compounds. This method should provide an attractive alternative to the polymerization initiation[27] and metalation[28] rate studies which have been used to study the effects of different solvents on the reactivities of covalent organolithium compounds.

We are continuing our study of the influence of various coordinating agents on the ^{1}H NMR spectra of aryl methylated and deuterated analogs of **1** and **2** in order to follow more precisely the changes which occur in the aromatic proton region and to determine if there is hindered rotation about the aryl-vinyl bond at some conditions.

Experimental Section

General Methods. All reactions involving organometallic compounds were carried out under atmospheres of prepurified nitrogen. Ether and TMEDA were distilled from lithium aluminum hydride under a nitrogen atmosphere immediately before use. THF and DME were distilled from a dark-purple solution of sodium benzophenone dianion under a nitrogen atmosphere immediately before use. Hexane (freed of olefins by permanganate) was distilled from a suspension of sodium benzophenone ketyl under a nitrogen atmosphere immediately before use. Melting points were obtained using a Laboratory Devices Mel-Temp capillary melting point apparatus and are uncorrected. Boiling points are uncorrected. ^{1}H NMR spectra of all compounds except **1** and **2** were run as carbon tetrachloride solutions on a JEOL MH-100 spectrometer; chemical shifts are reported in parts per million downfield from internal tetramethylsilane and coupling constants in hertz. ^{1}H NMR spectra of **1** and **2** were run on JEOL MH-100 and C-60HL spectrometers as 0.1–0.4 *N* solutions; chemical shifts are reported in parts per million downfield from internal tetramethylsilane (benzene was used as a secondary internal standard). Temperatures were determined using a methanol sample. Microanalyses were performed by Galbraith Laboratories, Inc., Knoxville, Tenn.

Analytical GLC analyses were performed on a Gow-Mac Model 750 (flame ionization detector) instrument. The products of reactions of **1** and **2** with ethanol and 1,2-dibromoethane were analyzed using a 4-ft 10% DC-200 on Chromosorb P column operating at 116°. Compounds could be identified by ^{1}H NMR spectra of the crude reaction mixtures.

Materials. 1-Phenyl-1-butyne was purchased from Chemical Samples Co., and *n*-butyllithium as a hexane solution was purchased from Lithium Corporation of America. Concentrations of organolithium compounds in hexane solution were determined by titration with standard acid and in the mixture solutions by the Gilman double titration method with 1,2-dibromoethane.[29]

1-Phenyl-1-butanol was prepared by reaction of benzaldehyde (90.0 g, 0.85 mol) with an ether solution of *n*-propylmagnesium bromide, prepared from 130 g (1.06 mol) of 1-bromopropane and 24.2 g (1.0 g-atom) of magnesium. Hydrolysis of the reaction mixture with saturated ammonium chloride followed by a standard work-up and vacuum distillation yielded 112.2 g (88% yield) of alcohol: bp 118–120° (19 mm) [lit.[13] bp 233° (760 mm)]; ^{1}H NMR (CCl_4) δ 7.12 (s, 5 H, phenyl), 4.64 (s, 1 H, OH), 4.41 (m, 1 H, CH), 1.72–1.44 (m, 2 H, CH_2) 1.40–1.04 (m, 2 H, CH_2), 0.78 (t, J = 7.0 Hz, 3 H, CH_3).

***trans*-1-Phenyl-1-butene** was synthesized by dehydration of 1-phenyl-1-butanol using phosphorus oxychloride and pyridine following the general method of Rinehart and Perkins.[30] Phosphorus oxychloride (20.0 g, 0.13 mol) was added dropwise to a stirred mixture of 1-phenyl-1-butanol (45.0 g, 0.30 mol) and pyridine (25.0 g, 0.95 mol). A reflux period of 4 hr followed by a conventional work-up yielded 38 g of crude product. GLC analysis of the crude product indicated 3% cis olefin, 96% trans olefin, and 1% alcohol. Fractional distillation yielded a fraction weighing 32.9 g (83% yield, 99% trans by GLC): bp 102–106° (40 mm) [lit.[13] bp 198.7° (760 mm)]; ^{1}H NMR (CCl_4) δ 7.30–7.00 (m, 5 H, phenyl), 6.28 (d, J = 16.4 Hz, 1 H, vinyl), 6.02 (t of d, J_t = 5.6, J_d = 16.4 Hz, 1 H, vinyl), 2.04 (q, J = 6.5 Hz, 2 H, CH_2), 0.96 (t, J = 7.0 Hz, 3 H, CH_3).

***cis*-1-Phenyl-1-butene.** 1-Phenyl-1-butyne (40 g) dissolved in enough absolute ethanol to give a volume of 174 ml with 1.1 g of 10% palladium on charcoal was hydrogenated on a previously calibrated Parr hydrogenation apparatus.[31] The hydrogenation was interupted after 1 equiv of hydrogen reacted. GLC analysis of the crude product (38 g) indicated 24% *n*-butylbenzene, 56% cis olefin, 3% trans olefin, and 17% acetylene. An atmospheric pressure distillation from hydroquinone yielded a fraction (9.3 g) which contained greater than 98% *cis*-1-phenyl-1-butene: bp 180–194° [lit.[13] 187.1° (760 mm)]; ^{1}H NMR (CCl_4) δ 7.0 (s, 5 H, phenyl), 6.20 (d of t, J_d = 11.5, J_t = 1.5 Hz, 1 H, vinyl), 5.40 (d of t, J_d = 11.5, J_t = 7.2 Hz, 1 H, vinyl), 2.16 (q of d, J_q = 7.1, J_d = 1.5 Hz, 2 H, CH_2), 0.86 (t, J = 7.1 Hz, 3 H, CH_3).

***erythro*- and *threo*-1,2-Dibromo-1-phenylbutane.** Bromine (24.5 g, 0.153 mol) is added dropwise in the dark to a stirred and cooled (ice bath) solution of *trans*-1-phenyl-1-butene (20.2 g, 0.153 mol) in carbon tetrachloride (80 ml). The bromine addition is stopped when bromine persists in the solution. Addition of carbon tetrachloride (160 ml) and water (120 ml) is followed by the addition of sodium sulfite to destroy the excess bromine. After separating the layers and an additional extraction of the aqueous layer, the combined carbon tetrachloride layers are dried (magnesium sulfate). Evaporation of the solvent on a rotary evaporator yields a mixture of the dibromides (42.4 g, 94% yield) which is 85% erythro and 15% threo by ^{1}H NMR.[11] A similar reaction with *cis*-1-phenyl-1-butene yields a mixture of dibromides which is 72% threo and 28% erythro.

erythro-1,2-Dibromo-1-phenylbutane can be isolated by fractional crystallization of the dibromide mixture from hexane: mp 70–71° (lit.[32] mp 71°); ^{1}H NMR (CCl_4) δ 7.20 (s, 5 H, phenyl), 4.96 (d, J = 10.8 Hz, 1 H, benzylic H), 4.36 (7 lines, J = 10.8, J = 8.0, J = 3.2 Hz, 1 H, C_2H), 2.36 (6 lines, J = 15.2, J = 7.6, J = 3.2 Hz, 1 H, C_3H), 2.04 (7 lines, J = 15.2, J = 7.8, J = 7.6 Hz, 1 H, C_3H), 1.12 (t, J = 7.6 Hz, 3 H, CH_3).

Anal. Calcd for $C_{10}H_{12}Br_2$: C, 41.12; H, 4.14; Br, 54.73. Found: C, 41.16; H, 4.08; Br, 54.64.

Chromatography on an alumina column (~100 g) of a mixture of the dibromides (5 g) using *n*-hexane as an eluent separates the diastereomers. *threo*-1,2-Dibromo-1-phenylbutane, eluted second, is isolated as a colorless oil: ^{1}H NMR (CCl_4) δ 7.40–7.18 (m, 5 H, phenyl), 5.18 (d, J = 5.5 Hz, 1 H, benzylic H), 4.24 (8 lines, J = 11.2, J = 5.5, J = 4.0 Hz, 1 H, C_2H), 2.06 (10 lines, J = 6.4, J = 4.0, J = 3.2 Hz, 1 H, C_3H), 1.60 (12 lines, J = 11.2, J = 6.4, J = 3.2 Hz, 1 H, C_3H), 1.01 (t, J = 6.4 Hz, 3 H, CH_3).

Anal. Calcd for $C_{10}H_{12}Br_2$: C, 41.12; H, 4.14; Br, 54.73. Found: C, 41.21; H, 4.13; Br, 54.62.

(*E*)-1-Bromo-1-phenyl-1-butene is synthesized by reacting potassium *tert*-butoxide (0.90 g, 8.0 mmol) with *erythro*-1,2-dibromo-1-phenylbutane (2.34 g, 8.0 mmol) in *tert*-butyl alcohol solution (25 ml) at room temperature for 24 hr.[33] A standard work-up yields 1.7 g (100% yield) of vinyl bromide as a colorless liquid: ^{1}H

NMR (CCl_4) δ 7.24 (s, 5 H, phenyl), 6.09 (t, J = 7.5 Hz, 1 H, vinyl), 1.99 (q, J = 7.5 Hz, 2 H, CH_2), 0.95 (t, J = 7.5 Hz, 3 H, CH_3).

Anal. Calcd for $C_{10}H_{11}Br$: C, 56.89; H, 5.25; Br, 37.86. Found: C, 56.70; H, 4.97; Br, 37.83.

(*Z*)-1-Bromo-1-phenyl-1-butene is synthesized from *threo*-1,2-dibromo-1-phenylbutane by the same method illustrated for the *E* vinyl bromide. It is isolated as a colorless liquid: ^{1}H NMR (CCl_4) δ 7.7–7.5 (m, 2 H, phenyl), 7.5–7.2 (m, 3 H, phenyl), 6.17 (t, J = 7.5 Hz, 1 H, vinyl), 2.36 (q, J = 7.5 Hz, 2 H, CH_2), 1.08 (t, J = 7.5 Hz, 3 H, CH_3).

Anal. Calcd for $C_{10}H_{11}Br$: C, 56.89; H, 5.25; Br, 37.86. Found: C, 56.77; H, 5.40; Br, 37.76.

(*Z*)-1-Lithio-1-phenyl-1-butene (1). (*E*)-1-Bromo-1-phenyl-1-butene (0.63 g, 3.0 mmol) is added by syringe to a stirred and cooled (Dry Ice-acetone) mixture of THF (3.5 ml) and *n*-butyllithium (2.0 ml of 1.6 *N* hexane solution, 3.2 mmol). The reaction mixture was stirred for 2 min and then reacted with 1,2-dibromoethane or cooled ethanol. GLC analysis and ^{1}H NMR spectra of the products of these reactions detected only (*E*)-1-bromo-1-phenyl-1-butene or *cis*-1-phenyl-1-butene, respectively.

For the ^{1}H NMR spectra and isomerization studies, **1** was prepared as *n*-butyl bromide free hexane solutions in a side-arm flask attached to a nitrogen-vacuum manifold. The flask was cleaned by sacrificing ca. 1 ml of *n*-butyllithium in hexane. The flask was then charged with 2.5 ml of 1.6 *N n*-butyllithium in hexane (4.0 mmol) and a hexane solution (4 ml) of (*E*)-1-bromo-1-phenyl-1-butene (0.74 g, 3.5 mmol). After allowing the reaction to proceed ca. 5 min at room temperature, the hexane and *n*-butyl bromide were removed by vacuum distillation. The resulting viscous, light-yellow liquid was dissolved in ca. 8.5 ml of *n*-hexane to yield an approximately 0.4 *N* solution of **1.**

These solutions were transferred by cannula to dry, nitrogen flushed NMR tubes capped with No-Air stoppers for the ^{1}H NMR experiments. THF was added by microliter syringe and the relative amounts of **1** and THF present were determined by integration.

The hexane solutions of **1** were transferred by cannula to dry, nitrogen flushed calibrated centrifuge tubes capped with No-Air stoppers and diluted with hexane and coordinating solvent to yield 0.2 *N* solutions of **1** for the isomerization studies. Timing was started when the coordinating solvent was added.

(*E*)-1-Lithio-1-phenyl-1-butene (2) is prepared in THF solution at −78° from (*Z*)-1-bromo-1-phenyl-1-butene as described for the preparation of **1.** Reactions of these solutions of **2** with 1,2-dibromoethane or cooled ethanol yielded (*Z*)-1-bromo-1-phenyl-1-butene or *trans*-1-phenyl-1-butene, respectively, as indicated by GLC analysis or ^{1}H NMR spectra.

A hexane-THF mixture solution of **2** free of *n*-butyl bromide was prepared in a side-arm flask attached to a nitrogen-vacuum manifold as illustrated before. A hexane solution (1 ml) containing 0.21 g (1.0 mmol) of (*Z*)-1-bromo-1-phenyl-1-butene and 60 μl (0.4 mmol) of THF is added to 750 μl of 1.6 *N n*-butyllithium (1.2 mmol) in the side-arm flask. The viscous, light-yellow liquid remaining after the hexane and *n*-butyl bromide were removed by vacuum distillation is dissolved in 2.0 ml of hexane to yield an approximately 0.5 *N* solution of **2.** This solution is transferred by cannula to dry, nitrogen flushed NMR tubes capped with No-Air stoppers.

Acknowledgment. The Tulane University Chemistry Department and the organizations mentioned in ref 2 are thanked for their support.

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