The Reaction of Organolithium Reagents with Allylic Alcohols[1a]

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Allyl alcohol adds a variety of organolithium reagents regiospecifically to give 2-substituted 1-propanols (**1**). Organolithium intermediate **2** was demonstrated. A similar reaction predominates with 3-buten-1-ol. On the other hand, 2-cyclopentenol undergoes replacement of the hydroxy group by the alkyl group of the organometallic species in a process which was demonstrated to proceed cleanly with double-bond rearrangement. The reactions of other allylic alcohols were similar but much less selective. The synthetic utility and mechanistic aspects of these organometallic transformations are briefly explored.

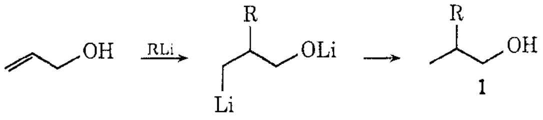
Although the initial observation that organolithium reagents add to nonconjugated olefins appeared some time ago,[2,3] this interesting reaction has not found general synthetic applicability. Thus, whereas ethylene adds secondary or tertiary organolithium reagents cleanly to give the corresponding chain-extended primary reagents,[4] high pressures[2,3] or catalysts such as *N*,*N*,*N'*,*N'*-tetramethylethylenediamine[5] (TMEDA) are required to promote the addition of primary alkyllithiums to this olefin. Under these conditions the initial organolithium product adds to ethylene at a similar rate, leading ultimately to polymeric products. With substituted olefins reaction either does not take place or results in polymers.[2,3,6] However, special instances of synthetically useful additions are observed when particularly stable carbanionic species are formed,[6,7] the starting olefin is strained,[6,8] or the reaction is intramolecular.[8,9]

Allylic ethers react with organolithium reagents by metalation followed by double-bond isomerization to vinyl ethers[10] or by replacement of the alkoxyl group by the organic moiety of the reagent[10,11] in a manner similar to that observed with allylic halides.[12] This substitution reaction appears to proceed with clean double-bond rearrangement probably in a cyclic process from a complex between the ether and the organometallic.[11]

Prior to our preliminary communication[13] and its independent discovery by Felkin and coworkers,[14] the reaction of organolithium reagents with allylic alcohols had not been reported. However, allylic and benzylic Grignard reagents are known to add slowly to both allylic and other unsaturated alcohols.[14,15] These particular Grignard reagents are exceptionally reactive toward double bonds, as shown by their addition to 1-octene as well as ethylene.[16] The present report examines the reaction between organolithium reagents and allylic alcohols as a function of structural change in each of the reaction partners.

Results

Allyl alcohol combines with a variety of organolithium reagents to give 2-substituted 1-propanols (**1**) in variable yield depending upon the organolithium and the reaction conditions. The isomeric alcohols derived from the alternative mode of addition are not formed.



1

2

- **a**, R = *tert*-butyl
- **b**, R = isopropyl
- **c**, R = *n*-butyl
- **d**, R = cyclopentyl
- **e**, R = phenyl
- **f**, R = benzyl

A study of yields of **1a–c** as a function of temperature and solvent revealed that the yields are at best moderate (20–50%) in hydrocarbon or ethereal solvents, and that raising the reaction temperature did not have a marked effect. However, a significant increase in yield, to 77% was achieved when 0.2 equiv of tetramethylethylenediamine (TMEDA) was used with *n*-butyllithium.[5] Subsequently, allyl alcohol was found to react with cyclopentyl-, phenyl-, and benzyllithium in the presence of TMEDA to give acceptable yields of **1d** (40%), **1e** (40%), and **1f** (52%).

Evidence for the existence of **2** as the organolithium precursor of **1** was obtained by the hydrolysis of reaction mixtures from *tert*-butyllithium and *n*-butyllithium with D_2O. Compounds **1a** and **1c** were ana-

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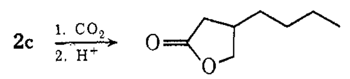
lyzed for deuterium content as the acetate and methyl ether, respectively. The acetate of **1a** did not have a large molecular ion, but the M − CH$_3$ ion was used for calculation, from which 86% deuterium incorporation was determined, assuming that the fragmentation leading to the M − CH$_2$D ion was negligible. The methyl ether of **1c** gave 83% deuterium incorporation, using the M − CH$_4$O ion. Additional evidence for intermediate **2c** was provided by the deuterium magnetic resonance spectrum of **1c** from the heavy water hydrolysis experiment which showed a single, broad resonance centered at δ 0.93, consistent only with deuterium on a methyl group.[17]

Two brief attempts to synthetically utilize **2c** were successful. When a reaction mixture containing **2c** was quenched by the addition of powdered Dry Ice and subsequently stirred with dilute acid, a 23% yield of β-*n*-butyl-γ-butyrolactone (**3**) was obtained in addition to **1c**. Development of this reaction sequence may provide a general synthesis of β-substituted γ-butyrolactones.



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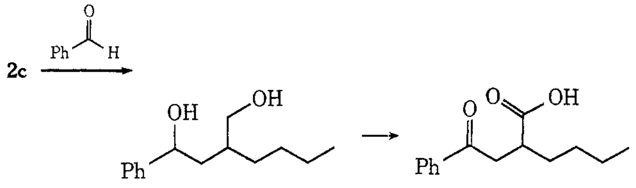
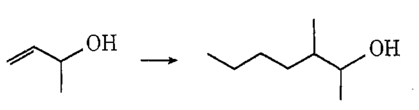
The addition of benzaldehyde to a reaction mixture containing **2c** gave a 43% yield of diol **4** as a mixture of diastereomers. This product was characterized by oxidation to keto acid **5**.



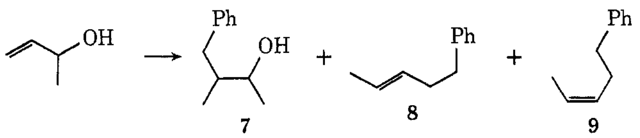
4 **5**

The reaction of 3-buten-2-ol with *n*-butyllithium or benzyllithium in the presence of TMEDA proceeds in a manner similar to that of allyl alcohol. *n*-Butyllithium gave a 66% yield of 3-methyl-2-heptanol (**6**),



6

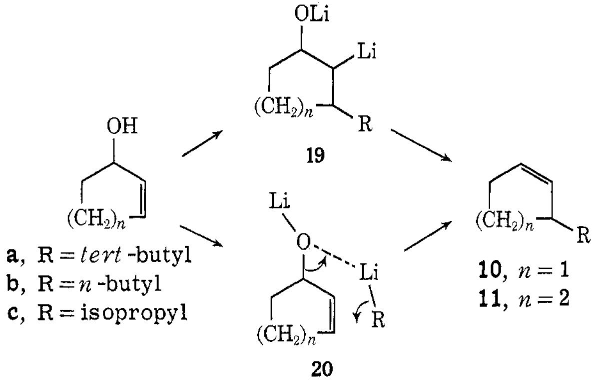
which may be a diastereomeric mixture,[14] but which was a single peak by all glpc methods tried. Benzyllithium afforded minor amounts of *trans*- and *cis*-5-phenyl-2-pentene, **8** and **9**, in addition to the expected product, 3-benzyl-2-butanol (**7**), in a ratio of 7:3:73.



7 **8** **9**

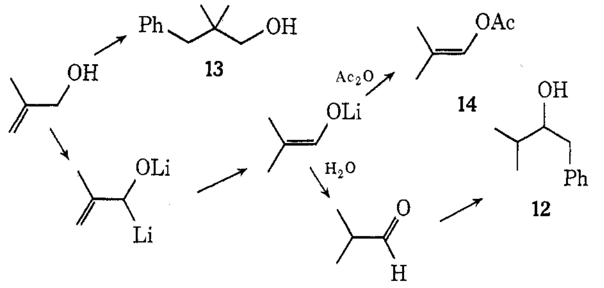
Alcohol **7** was shown by glpc to be a 4.5:1 mixture of threo and erythro isomers.[18] There was less than 0.1% of the isomeric olefin 3-benzyl-1-butene present.

Olefin formation is the predominate reaction of 2-cyclopentenol and 2-cyclohexenol which give 3-alkylcycloalkenes, **10a–c** and **11a,b**, respectively. The best results were obtained with *n*-butyllithium–TMEDA, which gave a 62% yield of **10b**. The efficacy of TMEDA in promoting reactions did not extend to *tert*-butyllithium; the yield of **10a** dropped from 35% to 10% with TMEDA. The reaction of *n*-butyllithium–TMEDA with 2-cyclohexenol proceeds sluggishly, but under forcing conditions substantial conversion to **11b** can be obtained, albeit accompanied by a number of unidentified by-products.



The mechanism of this reaction has been investigated briefly. The allylic hydroxyl group is requisite for the addition of *tert*-butyllithium to the double bond of 2-cyclopentenol, since neither 3-cyclopentenol nor a mixture of cyclopentene and cyclopentanol reacted with *tert*-butyllithium. Furthermore, treatment of 1-deuterio-2-cyclopentenol with *n*-butyllithium–TMEDA gave **10b**, which retained 98% of its deuterium label. The deuterium magnetic resonance spectrum of **10b** exhibited a single resonance at δ 5.76 indicating olefinic deuterium exclusively.

The reactions of 2-methyl-2-propen-1-ol with *n*-butyllithium and benzyllithium take quite different courses. *n*-Butyllithium in the presence of TMEDA led to a rapid darkening of the reaction mixture and formation of a plethora of products, none of which predominated. Benzyllithium, on the other hand, gave 30% of 3-methyl-1-phenyl-2-butanol (**12**) and 37% of 2,2-dimethyl-3-phenyl-1-propanol (**13**). The absence of 2-methyl-4-phenyl-1-butene and 3-methyl-1-phenyl-2-butene was demonstrated. When the reaction mixture was quenched by the addition of deuterium oxide, the nmr spectrum of **12** revealed that the unique isopropyl hydrogen had been replaced by deuterium. Detailed analysis by dmr showed that extensive deuterium incorporation also occurred at the aromatic and benzylic carbons, and a small amount of deuterium was even seen at the isopropyl methyl positions. Finally,



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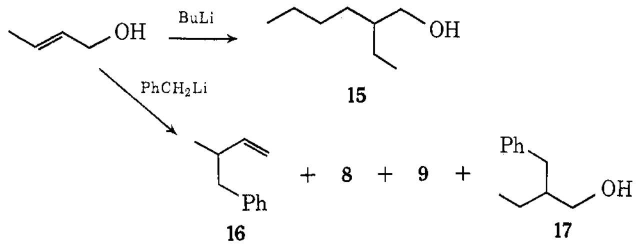
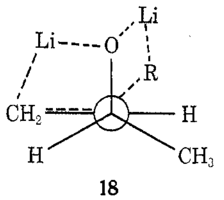
quenching the reaction mixture with acetic anhydride gave a product mixture in which neither **12** nor its acetate was present. However a new product, enol acetate **14**, was observed along with the acetates of **13** and starting material.

The reactions of *trans*-2-buten-1-ol with *n*-butyllithium and benzyllithium also differ markedly. *n*-Butyllithium–TMEDA reacts to give 2-ethyl-1-hexanol (**15**) as 67% of the volatile products. Glpc analysis revealed at most trace amounts of C_8 olefins. Benzyllithium–TMEDA, however, gives a mixture of olefins **16**, **8**, and **9**, and the addition product, 2-benzyl-1-butanol, **17**, in a 41:14:14:9 ratio. The product mixture from a similar reaction with *cis*-2-buten-1-ol was a 9:48:41:2 mixture of the same four compounds. However, the overall yields of these reactions were low. Quenching the reaction with acetic anhydride gave no enol acetate and quenching with deuterium oxide gave undeuterated olefins. The reaction of *trans*-1,1-dideuterio-2-buten-1-ol with benzyllithium gave **16** retaining 97% of its deuterium at the terminal vinyl position and a mixture of **8** and **9** retaining 93% of their label at the allylic methylene position. It was further shown that olefin **8** was inert to the reaction conditions, and that, as expected, the saturated alcohol, *n*-butyl alcohol, did not couple with benzyllithium.



Discussion

The regiospecific addition of organolithium reagents to allylic alcohols with unsubstituted vinyl groups appears to be a general and reasonably effective route to **1** proceeding by way of a primary organolithium intermediate **2**, potentially capable of further synthetic transformations. The orientation of the addition is presumably dictated mainly by the greater stability of **2** compared to the secondary organolithium species that would be formed by the alternate mode of addition. Felkin and coworkers[14] have independently witnessed similar reactions and have commented upon the preference for α-substituted allylic alcohols to yield threo alcohols. This is in direct contrast to the addition of allylic Grignard reagents,[15] a reaction which gives preferentially the erythro isomers. The stereochemistry of the organolithium reaction has been explained in terms of a transition state such as **18**, in which the attacking organometallic takes advantage of prior coordination at the lithium alkoxide function in order to add to the double bond by a cyclic mechanism. This explanation accounts for the greater reactivity of allylic alcohols with organolithium reagents as compared to the corresponding simple olefins. Furthermore, the stereochemical preference for threo alcohol is accounted for by the greater stability of transition state **18** over the diastereomeric one with the H and CH_3 groups of the carbinol carbon interchanged. This is apparently because of steric interactions between the CH_3 and the developing organometallic center.



18

It is well known that both lithium alkoxides and organolithium compounds exist as oligomeric species in hydrocarbons solvents and that mixed aggregates result from a combination of the two.[19] Since the alkoxides of both starting and product alcohols are present during the course of the reaction, the situation is quite complicated. The ability of tertiary amines in general, and TMEDA in particular, to increase the reactivity of organolithium species by breaking up oligomeric structures and polarizing the carbon–metal bond has been observed in a number of instances, and the facilitating effect of the amine can undoubtedly be ascribed to a similar action in the present instance. However, a specific picture of the effect of TMEDA in these complicated systems is less clear. In structure **18** the new carbon–lithium bond is viewed as being generated in concert with the new carbon–carbon linkage so that high-energy carbanionic intermediates are avoided. For simplicity, a lithium originally bound to the reacting oxygen atom is utilized, although the lithium could equally well come from a more remote site in a more complex aggregate or even from a second organolithium species.

The addition reaction with 2-methyl-2-propen-1-ol is also capable of producing a primary organolithium product. However, the presence of a methyl group on the double bond apparently inhibits this reaction with respect to other processes, although reasonable amounts of the expected product were observed with benzyllithium. The competing process here is obviously metalation which results principally in double-bond migration similar to that of allylic ethers[10] to give the enolate of isobutyraldehyde, as indicated by the D_2O quenching experiment, the formation of enol acetate **14** upon quenching with acetic anhydride, and the presence of **12** in hydrolyzed reactions. The latter alcohol results from addition of excess benzyllithium to the aldehyde during the hydrolysis process. The heterogeneity of the reaction mixture undoubtedly contributes to this unusual reaction. Metalation apparently becomes more important in the case of 2-methyl-2-propen-1-ol because of retardation of the addition reaction by the methyl substituent, probably the result of steric interactions.

In the reaction of 3-buten-2-ol with benzyllithium small amounts of olefins **8** and **9** were formed by replacements of the alcohol function by the benzyl group with concomitant double-bond migration. This reaction is the only important one with 2-cyclopentenol and alkyllithium reagents. This substitution process also occurs with clean double-bond migration, as demonstrated by using deuterium-labeled cyclopentenol.

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Two reasonable mechanisms can be visualized for the substitution reaction. The first of these is simply a modification of the addition reaction, which now occurs with the opposite regiospecificity to give intermediate **19**. This species would be expected to undergo ready elimination of lithium oxide to yield the observed olefin.[20] The reversal in regiospecificity in the addition reaction is at least partially accountable for by the fact that a secondary organometallic is necessarily formed by either mode of addition. Furthermore, the rigid cyclic structure may prevent attainment of the optimum geometry required for the addition process indicated by structure **18**. The second mechanism for the substitution reaction involves concerted bond forming and bond breaking as shown in structure **20**. Arguments similar to those given above rationalize the change in reaction pathway with change in substrate. This substitution reaction is analogous to the aforementioned reactions of allylic ethers.[10,11]

Since the 2-buten-1-ols have the same substitution pattern on the double bond as 2-cyclopentenol, a similar reactivity might have been expected for these materials. However, the acyclic compounds behave in a more complex manner. Even the nature of the organolithium appears to be important in determining the course of the reaction. *n*-Butyllithium resulted in predominance of the addition reaction with little, if any, substitution reaction. However, the use of benzyllithium gave only small amounts of the alcohol derived from addition; the major products are the olefins resulting from substitution of the hydroxy function by the benzyl moiety. These materials are formed both with and without double-bond migration in contrast to the very selective cyclopentenol and 3-buten-2-ol reactions, which follow the former course exclusively. Furthermore, the relative proportions of the three olefins varied substantially depending upon whether the cis or trans isomer of the starting alcohol was utilized. Extensive mechanistic study was rendered pointless by the low product yields, but experiments with deuterium-labeled *trans*-2-buten-1-ol ruled out processes involving metalation at the carbinol position, formation of and addition to butadiene, etc. The apparent difference between butyl- and benzyllithium in this reaction raises the possibility of an electron-transfer process[21] being important in the olefin-forming reaction with benzyllithium, but further discussion of this reaction must await more incisive experimentation.

Experimental Section

General.—Infrared spectra (ir) were obtained with Perkin-Elmer Model 137 and 137G Infracord spectrometers as liquid films. Nuclear magnetic resonance spectra (nmr) were obtained with Varian Associates A-60 and HR-100 spectrometers in carbon tetrachloride solution. Deuterium magnetic resonance spectra (dmr) were obtained with a Varian Associates HR-100 spectrometer operating at 15.35 MHz as chloroform solutions with tetramethylsilane-d_3 as an external reference. Mass spectra were recorded with AEI MS-9, Varian MAT CH-7, CEC 21-620, and CEC 21-110b spectrometers at 70 eV. The glpc inlet system of the Varian MAT CH-7 mass spectrometer consisted of a Varian Associates Model 1200 gas chromatograph coupled through a Biemann-Watson separator to the solid probe inlet. A 10 ft × 0.125 in. column packed with 5% Carbowax 20M on Chromosorb P was used with the glpc inlet. Analytical columns were 10 or 20 ft × 0.125 in. of 15 or 20% Carbowax 20M on 60/80 Chromosorb W. Percentage composition data were estimated by peak areas and were uncorrected unless specified otherwise. Preparative gas chromatography was performed on Aerograph Model A-700 and A 90-P3 chromatographs' with 10 or 20 ft × 0.375 in. of 30% Carbowax 20M on Chromosorb W, 10 ft × 0.375 in. of 30% Lac-2-r-446 on Chromosorb W, and 5 ft × 0.375 in. of 30% SE-30 on Chromosorb W. Anhydrous magnesium sulfate was used for all drying operations. Microanalyses were performed by Midwest Microlabs, Inc., Indianapolis, Ind.

All reactions with air-sensitive reagents were run in sealed tubes as described below or in a three-necked, round-bottomed flask equipped with a serum cap and a reflux condenser under a positive pressure of either nitrogen or argon. Prior to the introduction of reactants, the apparatus was dried by heating with a Bunsen burner flame while being flushed with inert gas.

tert-Butyllithium and isopropyllithium were obtained as *ca.* 1.6 and 2.1 *M* pentane solutions from Alfa Inorganics, Inc., Beverly, Mass. Solutions of *ca.* 1.7 *M* methyllithium in ether, *ca.* 1.5 *M* *n*-butyllithium in hexane or pentane, and *ca.* 2.2 *M* cyclopentyllithium in cyclohexane were obtained from Foote Mineral Co., Exton, Pa. Solutions of *n*-butyllithium were generally titrated prior to use.[22] Phenyllithium and benzyllithium were made by the metalation of benzene or toluene with a mixture of *n*-butyllithium and TMEDA.[5]

Sealed-Tube Reactions with Alkyllithiums.—Reactions were performed in Pyrex ampoules which were flushed with nitrogen prior to the addition of reactants (and until just before the ampoules were evacuated and sealed). The alkyllithium solutions were introduced by syringe and cooled to −78° prior to the cautious addition of substrate. The sealed ampoules were generally allowed to warm to room temperature before being placed in a loosely covered steel pot filled with water, maintained at *ca.* 97° by placing the pot in a steam bath. The ampoules were cooled in an ice bath and opened, and the reaction was quenched by the addition of distilled water. The layers were separated, the aqueous layer was extracted with several portions of pentane, and the combined organic extracts were washed with distilled water and dried. For those reactions in which TMEDA was used, the organic layer was washed with dilute hydrochloric acid. (A similar work-up procedure was also used for most organolithium reactions and is referred to as the usual work-up procedure.)

Reaction of *tert*-butyllithium for 7 hr at room temperature gave 17% of **1a**; 3 equiv of TMEDA in a similar experiment resulted in a 25% yield; a reaction at 97° for 2.5 hr gave 22%. The addition of isopropyllithium under the latter conditions gave a 48% yield of **1b**; *n*-butyllithium produced **1c** in only 5% yield. The addition of 9 equiv of either raised the yield of **1c** to 20%, while 0.2 equiv of TMEDA produced 77% of **1c** after 8 hr at room temperature.

Reaction of Allyl Alcohol with *tert*-Butyllithium.—To 36 ml of a 1.5 *M* *tert*-butyllithium solution under nitrogen was added dropwise 1.00 g of allyl alcohol. The reaction mixture was heated to 40° with stirring for 15 hr. Analysis by glpc showed one major product which was identified spectroscopically as 2,3,3-trimethyl-1-butanol (**1a**): ir 3.00, 7.18, 7.34, 9.72 μ; nmr δ 0.88 (s, 9), 0.91 (d, 3), 1.28 (m, 1), 3.45 (eight-line multiplet, 2), 4.00 (s, 1, OH).

Reaction of Allyl Alcohol with Isopropyllithium.—A mixture of 6.2 ml of a 2.1 *M* isopropyllithium solution and 253 mg of allyl alcohol was heated in a sealed tube at 97° for 1.7 hr, allowed to remain at room temperature for 22 hr, and worked up. Glpc analysis revealed three products in a 14:83:3 ratio. The 83% product was identified as 2,3-dimethyl-1-butanol (**1b**) by its ir spectrum.[23] Neither the 14% product, ir 3.73, 5.94, 6.08, 7.12, 7.36, 8.2, 9.6 μ, nor the 3% product was identified.

2-Methyl-1-hexanol (1c).—To an ice-cold solution of 980 mg of lithium hydride and 5.03 g of allyl alcohol in 70 ml of pentane under nitrogen, which had been stirred at room temperature for 30 min, was added 20 g of TMEDA and 123 ml of a 1.4 *M* *n*-butyllithium solution. The reaction mixture was stirred at room temperature for 2 hr and worked up. Distillation gave 7.24 g (72%) of **1c**: bp 166°; ir 3.06, 7.26, 9.64 μ; nmr δ 0.88 (m, 6), 1.38 (m, 7), 3.33 (d, 2), 5.14 (s, 1, OH).

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[22] S. C. Watson and J. F. Eastham, *J. Organometal. Chem.*, **9**, 165 (1967).

[23] Sadtler Index: ir 3432.

Reaction of Cyclopentyllithium with Allyl Alcohol.—To an ice-cold mixture of 54 ml of a 2.2 *M* cyclopentyllithium solution and 2.69 g of TMEDA under nitrogen was added dropwise 2.88 g of allyl alcohol. The reaction mixture was stirred at room temperature for 4 hr, heated to 79° for 1.5 hr, and worked up to give 3.8 g of crude product. Glpc analysis showed four products in the ratio 20:8:4:68. The 68% product was identified spectroscopically as 2-cyclopentyl-1-propanol (**1d**): ir 3.1, 7.24, 9.75 μ; nmr δ 0.90 (d, 3), 1.0–2.0 (m, 10), 3.45 (eight-line multiplet, 2), 4.3 (s, 1, –OH). The 20 and 8% products were shown to be saturated hydrocarbons of molecular weight 180 by their ir, nmr, and mass spectra.

Reaction of Phenyllithium with Allyl Alcohol.—To an ice-cold phenyllithium solution (formed by refluxing a mixture of 100 ml of benzene, 69 ml of a 1.6 *M* *n*-butyllithium solution, and 3.49 g of TMEDA under nitrogen for 1.5 hr) was added 2.88 g of allyl alcohol. The reaction mixture was heated to 61° for 18 hr and worked up. Distillation gave 3.23 g of product, bp 121° (20 mm). Glpc analysis showed three components present in a 3:14:83 ratio. Preparative glpc gave a pure sample of **1e**: ir 3.08, 6.24, 7.25, 9.7, 13.2, 14.4 μ; nmr δ 1.18 (d, 2), 2.75 (sextet, 1), 3.47 (four-line multiplet, 2), 3.98 (s, 1), 7.1 (s, 5). The 14% component was identified as **1c**.

Reaction of Benzyllithium with Allyl Alcohol.—To an ice-cold benzyllithium solution (formed by heating a mixture of 100 ml of toluene, 65 ml of a 1.6 *M* *n*-butyllithium solution, and 3.29 g of TMEDA at 70° with stirring for 2.0 hr under argon) was added 2.54 g of allyl alcohol. The reaction mixture was heated to 65° for 11 hr and worked up. The crude product was distilled to give 4.15 g of 2-benzyl-1-propanol (**1f**): bp 91° (1.65 mm); ir 3.06, 6.24, 7.26, 9.70, 13.6, 14.4 μ; nmr δ 0.86 (d, 3), 1.88 (sextet, 1), 2.53 (eight-line multiplet, 2), 3.40 (d, 2), 4.39 (s, 1, –OH), 7.1 (s, 5). Glpc analysis showed the distilled product to be 83% pure; the remaining 17% was comprised of a dozen minor products, the largest of which was 5%.

1-Acetoxy-2-deuteriomethyl-3,3-dimethylbutane.—To 11 ml of a 1.4 *M* *tert*-butyllithium solution at −78° under nitrogen was added 296 mg of allyl alcohol. The reaction mixture was warmed to room temperature for 8 hr, quenched by the addition of 1 ml of deuterium oxide, and worked up. A mixture of the crude product, 590 mg of isopropenyl acetate, and 1 drop of concentrated sulfuric acid was stirred at 60° for 1 hr, diluted with pentane, and washed with saturated sodium bicarbonate solution. The organic layer was dried, filtered, and concentrated. Glpc analysis showed one major product which was identified spectroscopically as 1-acetoxy-2-deuteriomethyl-3,3-dimethylbutane: ir 4.59, 5.75, 7.22, 7.34, 8.10, 9.70 μ; mass spectrum *m/e* (rel intensity) 144 (0.4), 104 (7), 103 (12), 102 (12), 99 (6), 84 (55), 62 (25), 61 (87), 57 (87), 56 (100), 43 (82), 41 (29). Since there was no molecular ion, the extent of deuteration was calculated using *m/e* 143, 144, and 145. Assuming that the loss of a CH_2D radical from the molecular ion was negligible, it was calculated that the acetate was 86% d_1.

2-Deuteriomethyl-1-methoxyhexane.—To an ice-cold slurry of 48 mg of lithium hydride and 371 mg of allyl alcohol, which had been stirred at room temperature for 1 hr under nitrogen, was added 85 mg of TMEDA and 9 ml of a 1.6 *M* *n*-butyllithium solution. The reaction mixture was stirred at room temperature for 3.5 hr, cooled in an ice bath, quenched by the addition of 4 ml of deuterium oxide, and worked up. Glpc analysis showed one product which was identified spectroscopically as 2-deuteriomethyl-1-hexanol, ir 2.97, 4.57, 7.24, 9.64 μ. The deuterium magnetic resonance spectrum showed a single resonance at δ 0.93.

A solution of 251 mg of 2-deuteriomethyl-1-hexanol and 211 mg of sodium hydride in 20 ml of *N*,*N*-dimethylformamide was refluxed on a steam bath under nitrogen for 1.25 hr. Approximately 1 ml of methyl iodide was added, and the mixture was refluxed for 15 hr, poured into distilled water, and extracted with pentane. The combined organic extracts were dried, filtered, and concentrated. Preparative glpc gave a pure sample of 2-deuteriomethyl-1-methoxyhexane: mass spectrum *m/e* (rel intensity) 131 (0.6), 99 (30), 85 (18), 71 (20), 70 (26), 69 (14), 57 (43), 56 (49), 45 (100), 44 (45), 43 (60). Because of the small size of the molecular ion, the extent of deuterium incorporation was calculated using the set of ions resulting from the loss of methanol from the molecular ion. Assuming that no loss of deuterated methanol from the molecular ion occurred, an estimate of 83% d_1 was obtained.

β-*n*-Butyl-γ-butyrolactone (**3**).—To a slurry of 406 mg of lithium hydride in 10 ml of pentane at room temperature under nitrogen was added 2.5 g of allyl alcohol. The mixture was stirred until hydrogen evolution ceased and cooled in an ice bath, and 5 g of TMEDA and 30 ml of 1.4 *M* *n*-butyllithium solution were added. The reaction mixture was stirred at room temperature for 2 hr and quenched by the addition of an excess of freshly crushed Dry Ice. The reaction mixture was stirred for 30 min, acidified with 1 *N* hydrochloric acid, and stirred for an additional 2.5 hr. The layers were separated, and the aqueous layer was saturated with sodium chloride and extracted with pentane. The combined organic layers were dried, filtered, and concentrated, The residue was distilled to give 1.4 g (23%) of **3**: bp 120° (10 mm); ir 5.61, 7.24, 8.54, 9.8 μ; nmr δ 0.90 (t, 3), 1.23 (m, 6), 1.9–2.8 (m, 3), 3.65–4.5 (m, 2); mass spectrum *m/e* (rel intensity) 142 (3), 114 (6), 111 (6), 95 (3), 84 (12), 70 (14), 69 (23), 55 (38), 56 (100), 57 (15), 43 (24), 42 (35), 41 (61), 39 (24).

Anal. Calcd for $C_8H_{14}O_2$: C, 67.57; H, 9.92. Found: C, 67.89; H, 9.90.

3-Hydroxymethyl-1-phenyl-1-heptanol (**4**).—To an ice-cold, stirred solution of 1.38 g of TMEDA in 75 ml of a 1.4 *M* *n*-butyllithium solution under argon was added 2.65 g of allyl alcohol. After the reaction mixture had been stirred at room temperature for 7.4 hr, 8.5 ml of benzaldehyde was added. The reaction mixture was stirred at room temperature for 12 hr, quenched by the addition of saturated ammonium chloride solution, and worked up. The crude material was chromatographed on silica gel to give 4.33 g (43%) of **4**: ir 3.05, 6.24, 7.3, 9.65, 13.2, 14.3 μ; nmr δ 0.85 (t, 3), 1.15 (m, 6), 1.6 (m, 3), 3.35 (m, 2), 4.54 (m, 1), 5.35 (m, 2), 7.15 (s, 5).

3-Carboxyheptanophenone (**5**).—To an ice-cold, stirred solution of 902 mg of **4** in 60 ml of acetone was added dropwise 8 *N* chromic acid until an orange color persisted. The reaction mixture was stirred at room temperature for 15 min and quenched with isopropyl alcohol. The green sludge was dissolved with water and the mixture was extracted with ether. The ether layer was extracted with 10% sodium hydroxide solution and discarded. The basic layer was acidified with 3 *N* hydrochloric acid and extracted with ether. The combined ethereal extracts were washed with water until neutral, dried, filtered, and concentrated to give 721 mg of a viscous residue which was recrystallized from carbon tetrachloride and sublimed (70°, 10^{-2} mm) to give a pure sample of **5**: mp 72.7–73.3°; ir (CCl_4) 3.27, 5.84, 5.90, 6.24, 6.31, 7.33, 14.5 μ; nmr δ 0.90 (t, 3), 1.4 (m, 6), 2.68–3.68 (m, 3), 7.4 (m, 3), 7.86 (m, 2), 12.1 (s, 1); mass spectrum *m/e* (rel intensity) 234 (2), 216 (6), 178 (2), 160 (2), 133 (2), 120 (68), 105 (100), 91 (1), 77 (41), 55 (3), 51 (10).

Anal. Calcd for $C_{14}H_{18}O_3$: C, 71.77; H, 7.74. Found: C, 71.95; H, 7.89.

Reaction of 3-Buten-2-ol with *n*-Butyllithium.—To an ice-cold slurry of 5.58 g of 3-buten-2-ol and 895 mg of lithium hydride, which had been warmed to 50° with stirring for 1 hr under argon, was added 80 ml of pentane, 1.71 g of TMEDA, and 100 ml of a 1.6 *M* *n*-butyllithium solution. The reaction mixture was stirred at room temperature for 22 hr and worked up. Distillation of the residue through a 4-in. glass helices column gave 6.7 g (66%) of 3-methyl-2-heptanol (**6**), bp 82–83° (20 mm).[24]

Reaction of 3-Buten-2-ol with Benzyllithium.—To an ice-cold benzyllithium solution (200 ml of toluene, 120 ml of 1.6 *M* *n*-butyllithium solution, and 3.3 g of TMEDA) was added 4.45 g of 3-buten-2-ol. The reaction mixture was warmed to room temperature for 2.5 hr, heated to 70° for 12 hr, and worked up. Glpc analysis of the residue revealed nine products.

Two products, accounting for 13 and 60% of the volatile products, were identified as *erythro*- and *threo*-3-benzyl-2-butanol (**7**): ir 3.0, 6.24, 7.3, 9.25, 13.6, 14.3 μ; nmr δ 0.89 (d, 3), 1.14 (d, 3), 1.75 (m, 1), 2.0–3.1 (eight-line multiplet, 2), 3.47 (s, 1, –OH), 3.60 (pentet, 1). Chromic acid oxidation of **7** gave 3-benzyl-2-butanone: ir 5.85, 6.24, 7.4, 13.3, 13.6, 14.3 μ; nmr δ 1.0 (d, 3), 1.95 (s, 3), 2.17–3.17 (m, 3), 7.12 (s, 5).

Two other products, accounting for 7 and 3% of the volatile products, were identified as *trans*- and *cis*-5-phenyl-2-pentene: ir 6.24, 7.3, 10.37, 13.5, 14.4 μ; nmr δ 1.58 (m, 3), 2.0–2.78 (m, 4), 5.37 (m, 2), 7.07 (s, 5). Glpc analysis showed two additional products (6 and 4%) to be **1c** and bibenzyl. The amount of **16** present was less than 0.1%.

Reaction of 2-Cyclopentenol with *tert*-Butyllithium.—A mixture of 300 mg of 2-cyclopentenol[25] and 7.2 ml of 1.5 *M* *tert*-butyllithium solution in a sealed tube was heated to 97° for 2 hr. Glpc

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(24) Sadtler Index: ir 7402, nmr 2844.

(25) K. Alder and F. H. Flock, *Chem. Ber.*, **89**, 1732 (1956).

showed only one product. Preparative glpc afforded 70 mg of 3-*tert*-butylcyclopentene (**10a**): ir 3.24, 6.15, 7.2, 7.35 μ; nmr δ 0.85 (s, 9), 1.3–1.95 (m, 2), 2.05–2.65 (m, 3), 5.66 (m, 2); mass spectrum *m/e* (rel intensity) 124 (5), 109 (12), 68 (12), 67 (43), 66 (48), 57 (100), 41 (25). The ir and nmr spectra were identical with those of an authentic sample of **10a** prepared from the reaction of 3-chlorocyclopentene with *tert*-butyllithium.

Reaction of 2-Cyclopentenol with *tert*-Butyllithium–TMEDA.—A mixture of 51 mg of 2-cyclopentenol, 78 mg of cyclooctane, 210 mg of TMEDA, and 1.2 ml of a 1.5 *M* *tert*-butyllithium solution in a sealed tube was allowed to react at room temperature for 16 hr. Glpc analysis of the product after work-up showed a 10% yield of **10a**. A similar reaction carried out without TMEDA gave a 35% yield of **10a**.

Reaction of *tert*-Butyllithium with a Mixture of Cyclopentene and Cyclopentanol.—A mixture of 157 mg of cyclopentene, 153 mg of cyclopentanol, and 8.2 ml of a 1.5 *M* *tert*-butyllithium solution was heated in a sealed tube at 97° for 2 hr. Glp analysis after work-up showed no appreciable loss of cyclopentene and no products of significance.

Reaction of 2-Cyclopentenol with Isopropyllithium.—A mixture of 300 mg of 2-cyclopentenol and 5 ml of a 2.1 *M* isopropyllithium solution in a sealed tube was heated to 97° for 2 hr. Glpc analysis of the crude product after work-up showed only one product, 3-isopropylcyclopentene (**10c**): ir 3.24, 6.18, 7.21, 7.30, 14.0 μ; nmr δ 0.88 (two overlapping doublets, 6), 1.1–2.6 (m, 6), 5.65 (s, 2).

Reaction of 2-Cyclopentenol with *n*-Butyllithium.—To a stirred solution of 6.79 g of 2-cyclopentenol and 914 mg of TMEDA in 20 ml of pentane at −78° under nitrogen was added by syringe 140 ml of a 1.6 *M* *n*-butyllithium solution over a period of 15 min. The reaction mixture was allowed to warm to room temperature over a period of 3 hr and worked up. Glpc analysis showed two components in a 96:4 ratio. Distillation gave 6.27 g (62%) of 3-*n*-butylcyclopentene (**10b**): bp 137°; ir 3.25, 6.19, 7.26, 7.38, 14.0 μ; nmr δ 0.88 (t, 3), 1.3 (m, 6), 1.65–2.75 (m, 5), 5.60 (s, 2); mass spectrum *m/e* (rel intensity) 124 (10), 95 (4), 82 (12), 67 (100), 41 (11). The spectral properties were identical with those of an authentic sample of **10b** prepared by the reaction of 3-chlorocyclopentene with *n*-butyllithium.

1-Deuterio-2-cyclopentenol.—To an ice-cold, stirred solution of 234 mg of lithium aluminum deuteride in 10 ml of anhydrous ether was added dropwise a solution of 840 mg of 2-cyclopentenone in 10 ml of anhydrous ether. The reaction mixture was stirred at room temperature for 12 hr, cooled in an ice bath, quenched by the addition of water, stirred for 30 min, and filtered. The precipitate was washed with anhydrous ether and the filtrate was dried and concentrated. Preparative glpc afforded 424 mg of 1-deuterio-2-cyclopentenol: ir 4.69 μ; nmr δ 1.37–2.75 (m, 4), 4.61 (s, 1, -OH), 5.75 (m, 2). The deuterium magnetic resonance spectrum showed a single peak at δ 4.84.

Reaction of 1-Deuterio-2-cyclopentenol with *n*-Butyllithium.—To an ice-cold, stirred solution of 211 mg of 1-deuterio-2-cyclopentenol and 887 mg of TMEDA in 10 ml of pentane under nitrogen was added 5 ml of a 1.5 *M* *n*-butyllithium solution. The reaction mixture was stirred at room temperature 2 hr and worked up. Preparative glpc gave a pure sample of 1-deuterio-3-*n*-butylcyclopentene: ir 4.38 μ; nmr (TMS external) δ 0.62 (t, 3), 1.05 (m, 6), 1.4–2.6 (m, 4), 5.37 (s, 1). The deuterium magnetic resonance spectrum contained only one peak centered at δ 5.76. The mass spectrum showed the product to be 98% d_1.

Reaction of 2-Cyclohexenol with *tert*-Butyllithium.—A mixture of 305 mg of 2-cyclohexenol and 6.2 ml of a 1.5 *M* *tert*-butyllithium solution in a sealed tube was heated to 97° for 3 hr. Glpc analysis of the product solution after work-up showed a mixture of about 20 products with three components in the ratio 50:9.4:40 making up the majority of the volatile products. The major product was identified spectroscopically as 3-*tert*-butylcyclohexene (**11a**): ir 3.28, 7.18, 7.32 μ; nmr δ 0.85 (s, 9), 1.1–2.1 (m, 7), 5.65 (s, 2). The next largest component was identified by glpc retention time as starting material. The minor product was not characterized.

Reaction of 2-Cyclohexenol with *n*-Butyllithium.—To a slurry of 2.45 g of 2-cyclohexenol and 251 mg of lithium hydride, which had been stirred at room temperature for 4 hr under nitrogen, was added 3.37 g of TMEDA and 21 ml of a 1.4 *M* *n*-butyllithium solution. The reaction mixture was refluxed for 15 hr and then worked up. Glpc analysis of the product solution showed five components. The major product accounted for 88% of the volatile products and was identified as 3-*n*-butylcyclohexene (**11b**): ir 3.38, 6.06, 7.25, 14.0 μ; nmr δ 0.90 (t, 3), 1.3 (m, 6), 1.4–2.3 (m, 7), 5.54 (s, 2); mass spectrum *m/e* (rel intensity) 138 (21), 123 (0.4), 109 (6), 96 (52), 82 (30), 81 (100), 67 (30), 41 (20), 39 (10). The spectral properties of **11b** were identical with those of a sample prepared by the reaction of 3-bromocyclohexene with *n*-butyllithium.

Reaction of 2-Methyl-2-propen-1-ol with *n*-Butyllithium.—To an ice-cold mixture of 10 ml of a 1.6 *M* *n*-butyllithium solution and 144 mg of TMEDA under nitrogen was added 357 mg of 2-methyl-2-propen-1-ol. The reaction mixture was stirred at room temperature for 19 hr, during which time the color changed from yellow to dark red, and worked up. Glpc analysis showed a plethora of products, none of which were characterized.

Reaction of 2-Methyl-2-propen-1-ol with Benzyllithium.—To an ice-cold benzyllithium solution (200 ml of toluene, 120 ml of 1.5 *M* *n*-butyllithium solution, and 3.36 g of TMEDA) was added 4.45 g of 2-methyl-2-propen-1-ol. The reaction mixture was stirred at 76° for 18 hr and worked up. Glpc analysis showed a dozen products. The major product, accounting for 37% of the volatile products, was identified spectroscopically as 2,2-dimethyl-3-phenyl-1-propanol (**13**): ir 2.9, 6.24, 7.25, 7.37, 9.6, 13.7, 14.2 μ; nmr δ 0.86 (s, 6), 2.55 (s, 2), 3.26 (s, 2), 3.75 (s, 1, -OH), 7.12 (s, 5). Another product, accounting for 30% of the volatile products, was identified spectroscopically as 3-methyl-1-phenyl-2-butanol (**12**): ir 2.93, 6.24, 7.25, 7.35, 9.7, 10.1, 13.5, 14.4 μ; nmr δ 0.89 (d, 3), 1.55 (m, 1), 2.4 (s, 1, -OH), 2.55 (m, 2), 3.36 (doublet of triplets, 1), 7.08 (s, 5); mass spectrum *m/e* (rel intensity) 164 (2), 121 (8), 102 (12), 93 (33), 92 (100), 91 (44), 73 (19), 55 (27), 42 (12). Chromic acid oxidation of **12** gave 3-methyl-1-phenyl-2-butanone.[26] Glpc analysis identified a third product as bibenzyl (16%) and confirmed the absence of 2-methyl-4-phenyl-1-butene and 3-methyl-1-phenyl-2-butene.

Deuterium Oxide Quenching of the Reaction of 2-Methyl-2-propen-1-ol with Benzyllithium.—To a benzyllithium solution (60 ml of toluene, 35 ml of a 1.5 *M* *n*-butyllithium solution, and 985 mg of TMEDA) at room temperature was added 1.01 g of 2-methyl-2-propen-1-ol. The reaction mixture was stirred at 88° for 17 hr, cooled in an ice bath, and quenched by the addition of 4 ml of deuterium oxide. The solution was stirred for an additional 2.5 hr at room temperature and worked up. Glpc analysis showed a 54:14:32 mixture of **12**, **13**, and bibenzyl. The residue was chromatographed on silica gel. Toluene, bibenzyl, and other hydrocarbon impurities were eluted with pentane; and the alcohols were eluted with anhydrous ether. Preparative glpc of the combined alcoholic fractions afforded a sample of **12**: nmr δ 0.90 (s, 5.2), 2.04 (s, 0.8), 2.3–2.85 (m, 1.4), 3.38 (m, 1.0), 7.1 (s, 3.6). The extensive deuterium incorporation which the nmr integration suggests was supported by the dmr spectrum: δ 1.30 (0.3), 1.96 (1.0), 2.85 (1.2), 7.47 (1.0).

Acetic Anhydride Quenching of the Reaction of 2-Methyl-2-propen-1-ol with Benzyllithium.—To a benzyllithium solution (30 ml of toluene, 19 ml of a 1.5 *M* *n*-butyllithium solution, and 503 mg of TMEDA) at room temperature was added 516 mg of 2-methyl-2-propen-1-ol. The reaction mixture was stirred at 80° for 19 hr, cooled to room temperature, quenched by the addition of 4 g of acetic anhydride, stirred at room temperature for 2.5 hr, heated to 80° for 1.5 hr, hydrolyzed, and worked up. Glpc analysis revealed the presence of the acetate of the starting alcohol, **14**, the acetate of **13**, **13**, and bibenzyl in a 17:55:13:1:14 ratio. Neither **12** nor its acetate was present. The residue was chromatographed on silica gel. Toluene, bibenzyl, and other hydrocarbon impurities were eluted with pentane, and the acetates were eluted with ether. Preparative glpc of the combined acetate fractions afforded a sample of **14**, which was spectroscopically identical with an authentic sample.

Reaction of *trans*-2-Buten-1-ol with *n*-Butyllithium.—To an ice-cold mixture of 10 ml of a 1.6 *M* *n*-butyllithium solution and 143 mg of TMEDA under nitrogen was added 368 mg of *trans*-2-buten-ol. The reaction mixture was stirred at room temperature for 50 hr and worked up. Glpc analysis showed at most traces of C_8 olefins and nine major products, one of which made up 67% of the volatile products. Preparative glpc gave 100 mg of the major product, which was identified as 2-ethyl-1-hexanol (**15**).[27]

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[26] Sadtler Index: ir 2747.

[27] Sadtler Index: ir 1472, nmr 98.

Reaction of *trans*-2-Buten-1-ol with Benzyllithium.—To an ice-cold, stirred benzyllithium solution (200 ml of toluene, 120 ml of a 1.6 *M* *n*-butyllithium solution, and 3.34 g of TMEDA) was added 4.43 g of *trans*-2-buten-1-ol. The reaction mixture was stirred at 73° for 19 hr and worked up. Glpc analysis showed nine products.

The major product, accounting for 41% of the volatile products, was identified as 3-methyl-4-phenyl-1-butene (**16**): ir 6.10, 6.24, 7.32, 11.0, 13.5, 14.3 μ; nmr δ 0.96 (d, 3), 2.2–2.8 (m, 3), 4.7–5.1 (m, 2), 5.40–6.07 (m, 1), 7.1 (s, 5); mass spectrum *m/e* (rel intensity) 146 (14), 131 (4), 117 (4), 115 (3), 104 (4), 91 (100), 77 (3), 65 (16), 55 (12), 39 (11). Two other products, accounting for 14% each of the volatile products, were identified as **8** and **9**. The nmr spectrum was virtually identical with that of an authentic sample of **8** and the second compound was found to be coincident with the product obtained from the photoisomerization of **8**. (Ozonolysis of a mixture of **8** and **9** in methylene chloride at −78° followed by lithium aluminum hydride reduction of the resulting ozonides gave one major product which was identified unambiguously as 3-phenyl-1-propanol by its characteristic ir and nmr spectra.[28]) A 7% product was identified as bibenzyl and a 9% product as 2-benzyl-1-butanol (**17**): ir 3.03, 6.24, 7.28, 9.6, 13.6, 14.3 μ; nmr δ 0.90 (t, 3), 1.1–1.9 (m, 3), 2.48–2.70 (m, 2), 3.0 (s, 1, -OH), 3.40 (d, 2), 7.10 (s, 5).

In a similar reaction using *sec*-butylbenzene as an internal standard, the yields of **8**, **9**, and **16** were 4.3, 4.9, and 6.7%, respectively. In another reaction in which slightly more than 1 equiv of TMEDA was used per 1 equiv of *n*-butyllithium and the reaction mixture was diluted with hexane to completely dissolve the benzyllithium–TMEDA complex, **8**, **9**, and **16** were obtained in 11, 12, and 2% yield, respectively.

***cis*-2-Buten-1-ol.**—A solution of 7.80 g of *trans*-2-buten-1-ol in 600 ml of benzene was irradiated for 30 hr with a vicor-filtered 450-W Hanovia type L medium-pressure mercury arc in a water-cooled quartz immersion well. Glpc analysis of the reaction mixture showed a 59:41 mixture of *trans*- and *cis*-2-buten-1-ol. The crude reaction mixture was chromatographed on silica gel with anhydrous ether. Preparative glpc gave a pure sample of *cis*-2-buten-1-ol: ir 3.04, 3.35, 6.03, 9.7, 10.24 μ; nmr δ 1.64 (d, 3), 3.78 (s, 1, OH), 4.09 (d, 2), 5.51 (m, 2).

Reaction of *cis*-2-Buten-1-ol with Benzyllithium.—To a benzyllithium solution (5 ml of toluene, 3 ml of a 1.6 *M* solution of *n*-butyllithium, and 113 mg of TMEDA) at room temperature was added a solution of 87 mg of *cis*-2-buten-1-ol in 1 ml of pentane. The reaction mixture was heated to 72° for 14 hr and worked up. Analysis by glpc revealed **16**, **8**, **9**, bibenzyl, and **17** in a 8:44:37:9:2 ratio.

***trans*-5-Phenyl-2-pentene (8).**—To an ice-cold, stirred benzyllithium solution (10 ml of toluene, 5 ml of 1.6 *M* solution of *n*-butyllithium, and 203 mg of TMEDA) was added 229 mg of crotyl chloride. The reaction mixture was heated with stirring to 60° for 15 min, stirred at room temperature for 2 hr, and worked up. Preparative glpc afforded a pure sample of **8**: ir 6.24, 7.3, 10.3, 13.6, 14.4 μ; nmr δ 1.6 (m, 3), 2.0–2.8 (m, 4), 5.4 (m, 2), 7.1 (s, 5).

A solution of 20 mg of **8** in 1.5 ml of spectral-grade benzene in a quartz test tube was irradiated in a Rayonet photochemical reactor at 2537 Å for 5.5 hr. Glpc analysis showed a mixture of 52% trans and 48% cis olefin. The yellow photolysis solution was suction filtered through fluorosil and concentrated. The ir of the residue showed a substantial reduction in the size of the 10.3-μ band. This sample was used for glpc comparison with the reaction products from the reaction of benzyllithium with 3-buten-2-ol and 2-buten-1-ol.

Reaction of 8 with Benzyllithium.—To a stirred benzyllithium solution (5 ml of toluene, 3 ml of 1.6 *M* *n*-butyllithium solution, and 123 mg of TMEDA) at room temperature was added a solution of 31 mg of **8** and 20 mg of decane in 1 ml of pentane. The reaction mixture was stirred at 77° for 19 hr and worked up. Glpc comparison of the starting mixture of trans olefin and decane with the reaction product showed that neither isomerization to the cis olefin nor loss of olefin had taken place.

***trans*-1,1-Dideuterio-2-buten-1-ol.**—To an ice-cold solution of 430 mg of lithium aluminum deuteride in 10 ml of anhydrous ether under a nitrogen atmosphere was added dropwise 1.51 g of methyl-2-butenoate. The reaction mixture was stirred at room temperature for 13 hr, cooled in an ice bath, and quenched by the addition of 1.7 ml of distilled water. Anhydrous magnesium sulfate was added and the resulting suspension was filtered. The precipitate was washed with anhydrous ether, and the dried filtrate was concentrated to give 879 mg (79%) of *trans*-1,1-dideuterio-2-buten-1-ol: nmr δ 1.68 (m, 3), 4.83 (s, 1, OH), 5.55 (m, 2).

Reaction of *trans*-1,1-Dideuterio-2-buten-1-ol with Benzyllithium.—To an ice-cold benzyllithium solution (80 ml of toluene, 45 ml of 1.6 *M* *n*-butyllithium solution, and 1.22 g of TMEDA) was added 879 mg of *trans*-1,1-dideuterio-2-buten-1-ol. The reaction mixture was stirred at 74° for 18 hr. Glpc analysis showed **16**, **8**, **9**, and bibenzyl in a 36:21:23:20 ratio. However, only trace amounts of **17** were observed.

The 36% product was identified as 1,1-dideuterio-3-benzyl-1-butene: nmr δ 0.96 (d, 3), 2.3–2.8 (m, 3), 5.72 (m, 1), 7.08 (s, 5). The relative intensities of the peaks in the molecular ion region of the mass spectrum indicated the composition to be 97% d_2, 3% d_1. The 21 and 23% products were isolated as a mixture and identified as *trans*- and *cis*-4,4-dideuterio-5-phenyl-2-pentene: nmr δ 1.60 (m, 3), 2.62 (m, 2), 5.4 (m, 2), 7.1 (s, 5). The relative intensities of the peaks in the molecular ion region of the mass spectrum indicated the composition to be 93% d_2, 7% d_1.

Deuterium Oxide Quenching of the Reaction of *trans*-2-Buten-1-ol with Benzyllithium.—To an ice-cold benzyllithium solution (100 ml of toluene, 60 ml of a 1.6 *M* *n*-butyllithium solution, and 1.55 g of TMEDA) was added 2.21 g of *trans*-2-buten-1-ol. The reaction mixture was stirred at 78° for 18 hr, cooled in an ice bath, and quenched by the addition of 5 ml of deuterium oxide. Hydrolysis was completed by stirring the solution at room temperature for 2 hr followed by work-up. Glpc analysis showed **16**, **8**, **9**, bibenzyl, and **17** in a 29:24:24:16:7 ratio. The mass spectra of **16** and a mixture of **8** and **9** showed negligible deuterium incorporation.

Acetic Anhydride Quenching of the Reaction of *trans*-2-Buten-1-ol with Benzyllithium.—To an ice-cold benzyllithium solution (30 ml of toluene, 20 ml of 1.4 *M* *n*-butyllithium solution, and 515 mg of TMEDA) was added 501 mg of *trans*-2-buten-1-ol at room temperature. The mixture was stirred at 82° for 18 hr, cooled in an ice bath, and treated with 4 ml of acetic anhydride. The resulting mixture was stirred at room temperature for 3 hr, heated to 75° for 2.5 hr, and quenched by the addition of saturated ammonium chloride solution. Glpc analysis after work-up revealed the presence of 1-acetoxy-1-butene,[29] 1-acetoxy-2-butene, **16**, **8**, and **9** in a 0.4:7:40:26:27 ratio.

Registry No.—**1a**, 36794-64-6; **1c**, 624-22-6; **1d**, 36794-65-7; **1e**, 1123-85-9; **1f**, 7384-80-7; **3**, 22530-99-0; **4**, 36794-69-1; **5**, 36794-70-4; **6**, 31367-46-1; *erythro*-**7**, 1499-64-5; *threo*-**7**, 1499-63-4; **8**, 16091-23-9; **10a**, 6189-88-4; **10b**, 22531-00-6; **10c**, 4276-45-3; **11a**, 14072-87-8; **11b**, 3983-07-1; **12**, 705-58-8; **13**, 13351-61-6; **16**, 1647-06-9; **17**, 3968-87-4; allyl alcohol, 107-18-6; *tert*-butyllithium, 594-19-4; isopropyllithium, 1888-75-1; cyclopentyllithium, 23473-12-3; phenyllithium, 591-51-5; benzyllithium, 766-04-1; 1-acetoxy-2-deuteriomethyl-3,3-dimethylbutane, 36794-81-7; 2-deuteriomethyl-1-hexanol, 36794-82-8; 2-deuteriomethyl-1-methoxyhexane, 36794-83-9; 3-buten-2-ol, 627-27-0; 3-benzyl-2-butanone, 2550-27-8; *trans*-5-phenyl-2-pentene, 16091-23-9; *cis*-5-phenyl-2-pentene, 16487-65-3; 2-cyclopentenol, 3212-60-0; cyclopentene, 142-29-0; cyclopentanol, 96-41-0; 1-deuterio-2-cyclopentenol, 20826-91-9; 1-deuterio-3-*n*-butylcyclopentene, 36794-85-1; 2-cyclohexenol, 822-67-3; 2-methyl-2-propen-1-ol, 513-42-8; *trans*-2-buten-1-ol, 504-61-0; *cis*-2-buten-1-ol, 4088-60-2; *trans*-1,1-dideuterio-2-buten-1-ol, 36807-25-7; 1,1-dideuterio-3-benzyl-1-butene, 36794-86-2; *trans*-4,4-dideuterio-5-phenyl-2-pentene, 36807-26-8; *cis*-4,4-dideuterio-5-phenyl-2-pentene, 36807-27-9; *n*-butyllithium 109-72-8.

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(28) Sadtler Index: ir 1651, nmr 116.

(29) D. B. Bigley and D. W. Payling, *J. Chem. Soc.*, 3974 (1965).