The Mechanism of Hydride Attack in the Reduction of *trans*-1-*t*-Butyl-3-phenylallyl[1] and 1-*t*-Butyl-3-phenylpropargyl Alcohols

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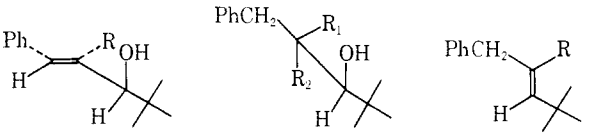
Abstract: Hydride delivery in the reduction of *trans*-1-*t*-butyl-3-phenylallyl alcohol (**1**) is shown to be intramolecular through the analysis of the stereochemistry of the product **2** by nmr and also by a stereospecific elimination from **2** to give **3**. Under certain conditions in the preparation of **1** from 1-*t*-butyl-3-phenylpropargyl alcohol (**4**) by hydride reduction, the corresponding *cis* alcohol (**5**) can be isolated. Evidence is presented which suggests both *cis* and *trans* alcohols are produced by intramolecular hydride attack.

Interest in the mechanism of the lithium aluminum hydride (LAH) reduction of propargylic to the corresponding allylic alcohols[1,2] has been aroused by the reports that with certain substrates it is possible by the addition of Lewis acids and bases to direct the position of initial hydride attack,[3,4] and, in the presence of sufficient amounts of $AlCl_3$, to obtain only allenic products.[4,5] In elucidating the mechanisms of these interesting reactions, a point of principal interest is the role played by the oxygen in activating proximate multiple bonds to attack.[6,7] The first step in these reactions is almost certainly the formation of an oxygen–aluminum bond as evidenced by the immediate liberation of hydrogen on mixing an alcohol with LAH.[8] Therefore, the principal mechanistic question is whether the function of the aluminum bound to the oxygen is to donate a hydride intramolecularly to the multiple bond or to facilitate intermolecular donation from another aluminum.

Results and Discussion

Reduction of *trans*-1-*t*-Butyl-3-phenylallyl Alcohol. An allylic alcohol, designed to provide a stereochemical approach to the solution of this problem, was initially chosen for study. Previous results[9] had shown that 1-*t*-butyl substituted allylic alcohols exist in essentially one conformation with the *t*-butyl and vinyl groups in a transoid disposition. In the reduction of an allylic alcohol, phenyl substituted at C-3 (both to activate the double bond to hydride attack[1] and to cause donation to occur at C-2), distinguishing by isotopic labeling which of the diastereotopic hydrogens at C-2 in the product originated from the LAH seemed a promising method for ascertaining whether the hydride was donated from the side of the molecule occupied by the oxygen (required for intramolecular attack) or from the opposite side (intermolecular donation).[1] Specifically, if the intramolecular mechanism is operative, the reduction of **1a** with LAD or **1b** with LAH should give **2a** and **2b**, respectively, while the reverse is anticipated if attack is intermolecular.



1a, R = H
b, R = D

2a, R_1 = D; R_2 = H
b, R_1 = H; R_2 = D
c, R_1 = R_2 = H

3a, R = H
b, R = D

The allylic alcohols **1a** and **1b** were synthesized by reduction of 1-*t*-butyl-3-phenylprogargyl alcohol[10] (**4**) in tetrahydrofuran (THF) with, respectively, LAH and LAD. Treatment of **1a** in ether with 2 mol of LAH followed by hydrolysis of the intermediate gave the saturated alcohol **2c** in 98% yield. When the hydrolysis was carried out with D_2O, nmr showed all the deuterium to be located at C-3, as expected for hydride attack occurring at C-2 under the directive influence of the phenyl group. In both the deuterated and undeuterated material the methine proton appeared as part of an ABB′ pattern at δ 3.2 with J_{AB} = 10 cps and $J_{AB'}$ = 3 cps. From the preferred conformation of **2** and the Karplus relationship for the dependence of J on dihedral angle[11] the larger coupling is assigned to H_1 and the smaller to H_2.[1]

When the reduction of **1a** was carried out with LAD, the nmr spectrum showed the 10-cps coupling to have collapsed, indicating that **2a** had been produced. Similarly, when **1b** was allowed to react with LAH in ether, the nmr of the product showed the doublet with the 10-cps splitting expected from **2b**, with no trace of **2a** detectable, even when the reaction was carried out in refluxing THF. In order to see if the presence of $AlCl_3$ would alter the stereochemical course of the reduction, as it does in certain propargylic systems,[3] the reaction of **1b** with LAH was run as before but

(1) Preliminary communication: W. T. Borden, *J. Amer. Chem. Soc.*, **90**, 2197 (1968).
(2) B. B. Molloy and K. Hauser, *Chem. Commun.*, 1017 (1968).
(3) E. J. Corey, J. A. Katzenellenbogen, and G. H. Posner, *J. Amer. Chem. Soc.*, **89**, 4245 (1967).
(4) J. A. Katzenellenbogen, Ph.D. Thesis, Harvard University, 1969.
(5) W. T. Borden and E. J. Corey, *Tetrahedron Lett.*, 313 (1969).
(6) Alkynes and conjugated alkenes are also reduced by LAH, but much more severe conditions are required. E. F. Magoon and L. H. Slaugh, *Tetrahedron*, **23**, 4304 (1967).
(7) The proximity of the hydroxyl group to the unsaturated linkage is very important in determining the rate of reduction. F. Bohlmann, R. Enkleman, and W. Plettner, *Chem. Ber.*, **97**, 2118 (1964).
(8) This point seems to have been overlooked by Molloy and Hauser in their mechanistic conjectures.[2]
(9) W. T. Borden, Ph.D. Thesis, Harvard University, 1968.
(10) E. E. Smissman, R. H. Johnson, A. W. Carlson, and B. F. Aycock, *J. Amer. Chem. Soc.*, **78**, 3395 (1956).
(11) M. Karplus, *J. Chem. Phys.*, **30**, 11 (1959).

with a trace of $AlCl_3$ added. The product was again **2b** but the reaction proceeded more slowly.[12]

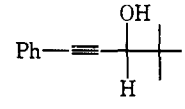
The above experiments demonstrate that hydride donation in the reduction of **1** is stereospecific. Moreover, if the assignment of structures of the diastereomers **2a** and **2b** from nmr is correct, it is H_1 that comes from the reducing agent, indicating that hydride attack is intramolecular.

Chemical confirmation of the spectroscopic assignment of the structures of the diastereomeric alcohols was sought by preparation and pyrolysis of the corresponding xanthates. The alcohols were converted to their lithium salts with *n*-butyllithium and treated in succession with carbon disulfide and methyl iodide to give the crude xanthates in 95% yield. These were pyrolyzed in a flow system, and the *trans*-1-*t*-butyl-3-phenylpropene (**3**) produced was trapped. The crude pyrolysates, obtained in 97% yield, were nearly pure, and trace impurities (<1%) could be removed by preparative glpc on a Carbowax 20M column. The expected *trans* stereochemistry of the double bond in **3** was confirmed by the presence in the ir spectrum of a strong absorption at 10.28 μ. The nmr spectra of the pyrolysates made apparent the difference between the olefins synthesized from the two alcohols. Whereas **3a**, obtained from the alcohol assigned structure **2a** and identical with that synthesized from **2c**, showed two vinyl protons at δ 5.50 and a triplet at 3.30 for the methylene protons, the olefin **3b**, produced from **2b**, displayed only one vinyl proton and a broad singlet for the methylene hydrogens. The mass spectrum of the latter olefin (**3b**) showed the molecular ion at *m/e* 175, with only a trace of a peak at 174, where the molecular ion of the olefin (**3a**) obtained from **2a** and **2c** appears. This confirms the nmr structural assignments of **2a** and **2b**, since xanthate pyrolysis, resulting in the elimination of H_1, is expected to produce **3a** from **2a** and **3b** from **2b**, as is observed.

One consequence of this finding that hydride donation in a cinnamyl system proceeds intramolecularly is that the rate of hydride reduction should, to a first approximation, be independent of LAH concentration, provided at least 1 mol equiv is added. In fact, when **1** is stirred at room temperature in ether for 6 hr with 2.5 and 5.0 mol of LAH, the extent of reaction is, respectively, 49 and 53%.[13] In THF both reactions are nearly complete within 1 hr under the same conditions.[14]

Reduction of 1-*t*-Butyl-3-phenylpropargyl Alcohol. In one preparation of **1** for the study described above, 1-*t*-butyl-3-phenylpropargyl alcohol (**4**) was reduced by stirring overnight with LAH in ether instead of in THF. The nmr spectrum of the crude product revealed, in addition to the expected *trans*-allylic alcohol (**1**), 25% of another compound which was isolated by preparative glpc. Its nmr spectrum was similar to that of the *trans* compound, but the methine proton appeared at lower field and the C-2 vinyl proton at higher field (suggesting, respectively, greater and lesser proximity to the phenyl) than in the *trans*, and J_{vinyl} was 12 cps, compared to 15 cps in the *trans*. The ir spectrum of the new product was also quite similar to that of **1**, except that the *cis*-CH bend at 14.5 μ was more intense and the *trans*-CH bend at 10.3 μ was absent. From the spectroscopic data the structure of the minor product was assigned as *cis*-1-*t*-butyl-3-phenylallyl alcohol (**5**) and confirmed chemically by reduction of the mixture of **1** and **5** with LAH to give the saturated alcohol (**2c**).

This is the first time, to the best of our knowledge, that an allylic alcohol of *cis* stereochemistry has been isolated from the LAH reduction of a propargylic alcohol. That it should be observed first in a system with two bulky substituents makes it even more startling. Nevertheless, the reaction appears to be general in 3-phenyl-substituted propargylic alcohols, for about 25% of the *cis* allylic alcohol results when 1,3-diphenylpropargyl alcohol is stirred in ether with LAH.[9]



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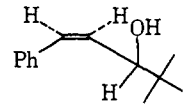


5

To test the possibility that the intermediate which leads to **5** might also be formed in THF, but undergoes subsequent conversion to that from which **1** arises, an equal volume of THF was added to a solution of the complex formed by LAH reduction in ether of **4**. As a control, another reduction was run in a 1:1 ether–THF solvent, in which the product is 98% pure *trans* alcohol (**1**), produced with a half-time of 3 min. When the first reaction was hydrolyzed with D_2O, 7 hr after the addition of the THF, the nmr of the product showed complete incorporation of deuterium into the 3 position, demonstrating that the intermediate had not been hydrolyzed by adventitious water prior to work-up. Yet, the product contained 25% *cis* alcohol (**5**), the same amount found in an aliquot removed before addition of the THF. Therefore, **1** and **5** must be produced from different intermediates, which do not equilibrate once formed.

Since the electrophilic cleavage of vinyl carbon–metal bonds proceeds with retention of configuration,[15] the intermediate which leads to **5** must also have the phenyl and neopentyl substituents disposed in a *cis* geometry. Therefore, the *cis* product cannot arise from a cyclic organoaluminum intermediate formed in an intramolecular fashion, for this intermediate would contain an impossibly strained *trans*-double bond in a five-membered ring.

Although an organoaluminum compound containing a five-membered ring cannot be dismissed on purely geometric grounds as the precursor of the *trans* olefin **1**, dilution experiments could be undertaken to test whether such an intramolecularly formed heterocycle is actually an intermediate. If it were, increasingly dilute solutions would favor its production over the intermolecular formation of the complex leading to **5**. However, it was found that in ether fourfold dilution left the ratio of **1** to **5** unchanged.

(12) $AlCl_3$ is known to inhibit the reduction of cinnamyl systems, presumably by forming a trivalent hydride species which is preferentially bound to the oxygen and is less effective in reduction of the double bond: M. J. Jorgenson, *Tetrahedron Lett.*, 559 (1962).

(13) This finding is totally inconsistent with the proposal by Molloy and Hauser[2] that the rate-determining step is oxygen–aluminum bond formation.

(14) A more extensive study of the effect of solvent on the rate of hydride reduction of cinnamyl alcohols has been carried out by M. J. Jorgenson and A. F. Thatcher, *Chem. Commun.*, 973 (1968).

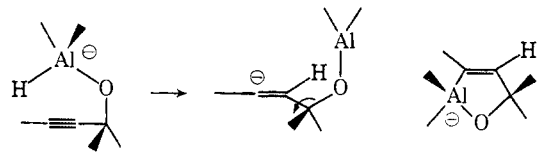
(15) H. G. Kuivila, W. Rahman, and R. H. Fish, *J. Amer. Chem. Soc.*, **87**, 2835 (1965).

Thus, one is forced to conclude that when the reduction of **4** with LAH is carried out in ether, a cyclic organoaluminum intermediate is not formed, at least not initially.

A possible explanation of why the thermodynamically less-favored **5** is formed in ether and not THF is that in the weaker Lewis base,[16] ether, the various Lewis acids are less solvated. Therefore, trapping of the carbanionic species generated by hydride attack is expected to be more exothermic in ether; hence, according to Hammond's postulate,[17] the transition state should resemble more closely the reactants. If the phenyl-stabilized vinyl carbanion intermediate is nearly linear or has a low barrier to inversion, then in ether the difference in the energy of the transition states leading to the intermediates which are the precursors of **1** and **5** might be expected to be small.

That the role of aluminum bound to the alcohol oxygen in the 3-phenyl-substituted propargylic system is to deliver the hydride may be deduced from the formation of *cis*-allylic alcohol (**5**). It is sterically impossible for this compound to be produced with deuterium incorporated into the 3 position, as is observed, if the function of the aluminum is to activate the multiple bond to attack by coordination to it, for this would involve an impossibly strained five-membered ring, as discussed earlier. Thus, if the production of **5** shows that the aluminum does not activate the triple bond to attack, the only role left to assign to it is that of deliverer of the hydride in the genesis of this compound. Nor can one argue that a duality of mechanisms obtains, where the *trans* compound is produced by intermolecular and the *cis* by intramolecular hydride attack, for this possibility is ruled out by the dilution studies (assuming, of course, that the rate-limiting step in the intermolecular mechanism would be hydride donation). Therefore, one concludes from the experimental data what one might have guessed, reasoning by analogy from the results in the cinnamyl system that hydride attack in 3-phenyl-substituted propargylic alcohols is intramolecular. Once again, consistent with this conclusion is the result that after 35 min in ether at room temperature, 1-*t*-butyl-3-phenylpropargyl alcohol (**4**) is 38% reduced whether 3 or 6 mol of LAH are used.[13]

Mechanistic Conclusions. The result which emerges most clearly from these studies is that in 3-phenyl-substituted allylic and propargylic alcohols the function of the aluminum bound to the oxygen is to deliver a hydride to C-2. In the propargylic systems it appears that the resulting carbanion reacts initially in an intermolecular fashion with Lewis acids in solution to form an intermediate which leads quantatively in THF and preferentially in ether to the *trans*-cinnamyl alcohol. The reason that the carbanion does not react immediately in an intramolecular fashion with the aluminum may be that this reaction requires rotation about a C–C bond to bring the aluminum to the opposite side of the molecule, as shown below. Although the dilution studies show that the five-membered ring organoaluminum intermediate is not formed initially, this intermediate could be formed in a subsequent step.



In the allylic systems, the fate of the initially formed benzylic carbanion is not so certain. In an elegant experiment Snyder has demonstrated that *erythro*- and *threo*-$C_6H_5CHDCHDCD_2OH$ are produced in equal amounts in the LAD reduction of methyl cinnamate, followed by deuterolysis.[18] However, as Snyder points out, the results do not differentiate between a number of possible mechanisms which would explain the observed lack of specificity in the relative stereochemistry of addition. Snyder seems to favor rapid equilibrium of the first-formed organoaluminum intermediate with its diastereomer by C–Al bond fission.[18] Nevertheless, it is also possible that stereochemistry is lost prior to reaction of the benzylic carbanion with a Lewis acid.

The powerful directive influence of the phenyl group at C-3 in the systems we have studied apparently overcomes the tendency of trivalent aluminum species[3-5] to direct hydride attack to C-3, since in both the allylic (**1**) and propargylic (**4**) systems all the hydride attack occurs at C-2 within experimental error. Rather than altering the position of hydride attack, added $AlCl_3$ seems to slow the rate of reduction in these systems.[12]

If the hydride species, produced by addition of $AlCl_3$ to the reaction mixture, is much less efficient than LAH in donating a hydride to C-2, why does its efficiency in producing attack at C-3 exceed that of LAH? The answer may be that trivalent aluminum bound to oxygen does not deliver hydride to C-3 but perhaps coordinates to the triple bond,[19] thus activating it to intermolecular attack by external hydride. Attack would necessarily proceed at C-3, since the geometric constraints of the triple bond would enforce intramolecular aluminum coordination at C-2. In this mechanism the effect of Lewis bases[3,4] in directing hydride attack to C-2 could be interpreted in terms of scavenging trivalent aluminum species present in LAH.[20] Intramolecular coordination and intermolecular hydride delivery would also explain how under certain circumstances allene formation in the reaction of 1,3-di-*t*-butylpropargyl alcohol with LAH–$AlCl_3$ can occur with the hydride being delivered to the side of the molecule opposite that from which the oxygen and aluminum bound to it depart.[5]

Further evidence regarding the correctness of the above mechanistic hypothesis is currently being sought.

Experimental Section

General. Ether used was Mallinckrodt anhydrous, opened just prior to use, and THF was distilled from LAH under an argon atmosphere. All glassware was dried at 120° for at least 1 hr prior to use, and all reactions were run under an atmosphere of purified nitrogen. LAH and LAD were obtained from Metal Hydrides Co.

(16) R. J. Gritter in "The Chemistry of the Ether Linkage," S. Patai, Ed., Interscience Publishers, New York, N. Y., 1967, pp 378–380.
(17) G. S. Hammond, *J. Amer. Chem. Soc.*, 77, 334 (1955).
(18) E. I. Snyder, *J. Org. Chem.*, 32, 3531 (1967).
(19) The intramolecular interaction between trivalent aluminum and a double bond has been detected by G. Hata, *Chem. Commun.*, 7 (1968).
(20) B. Franzus and E. I. Snyder, *J. Amer. Chem. Soc.*, 87, 3423 (1965). See also ref 18.

Whether or not filtered solutions were used seemed to have little effect on the results, provided the LAH weighed out had not been exposed to moist air for long periods of time.

1-*t*-Butyl-3-phenylpropargyl Alcohol (4).[10] Phenylacetylene (Aldrich) was converted into its lithium salt by adding to a solution of 10.2 g (100 mmol) of the alkyne in 50 ml of THF at 0° 62.5 ml of 1.6 *M* *n*-butyllithium in hexane (100 mmol). After stirring for 15 min under N_2, 8.60 g (100 mmol) of pivaldehyde was added slowly, the solution was allowed to warm to 25°, and was stirred for an additional 2 hr. Most of the solvent was removed at reduced pressure and the residue taken up in ether, which was washed with water, dried, and evaporated. The residue was distilled at 84–87° (0.2 mm). On standing the distillate crystallized. Analytical glpc detected no impurities. The material when recrystallized from methanol–water had mp 43.5–45.5° (lit.[7] mp 45–46° from petroleum ether); nmr ($CDCl_3$) δ 1.05 (s, 9), 2.52 (s, 1), 4.23 (s, 1), and 7.3 (m, 5); and ir (neat) showing OH (2.95 μ), C≡C (4.55 μ), and monosubstituted benzene. The yield was 15.6 g (83%).

Anal. Calcd for $C_{13}H_{16}O$: C, 82.94; H, 8.57. Found: C, 82.97; H, 8.55.

***trans*-1-*t*-Butyl-3-phenylallyl Alcohol (1).** Ten millimoles (1.88 g) of the propargylic alcohol was refluxed in 25 ml of THF with 11 mmol (420 mg) of LAH for 6 hr. The intermediate was hydrolyzed by the 1:1:3 method (0.42 ml of water added cautiously, then 0.42 ml of 15% aqueous NaOH, and finally 1.26 ml of water),[21] the aluminum hydroxide precipitate filtered and washed with ether, the solvent dried over $MgSO_4$, and evaporated. The 1.84 g (98%) of oil obtained was >98% pure by glpc on a 6 ft × 1/8 in. 10% SE-30 on 80–100 Diatoport S column operated at 160°. The ir (neat) showed conjugated C=C at 6.08 μ and *trans*-CH at 10.30 μ; and the nmr ($CDCl_3$) δ 0.95 (s, 9), 1.95 (s, 1), 3.85 (d, 1, J = 7 cps), 6.2 (q, 1, J = 7 and 15 cps), 6.58 (d, 1, J = 15 cps), and 7.3 (m, 5); exact mass of $C_{13}H_{20}O$, 192.1509 (calcd 192.1514); mp as the benzoate ester, 83.0–84.0°.

Anal. Calcd for $C_{20}H_{22}O_2$: C, 81.60; H, 7.53. Found: C, 81.53; H, 7.58.

1-*t*-Butyl-3-phenylpropanol (2c). One millimole (190 mg) of the allylic alcohol was stirred in ether with 56 mg (1.5 mmol) of LAH for 18 hr. The product was isolated as described above, and glpc under the same conditions as above showed >99% purity. The yield was 170 mg (90%). The ir was consistent with that expected for a phenyl-substituted saturated alcohol, and the nmr ($CDCl_3$) had signals at δ 0.88 (s, 9), 1.5–2.0 (m, 3), 2.3–3.0 (m, 2), 3.2 (q, 1, J = 3 and 10 cps), and 7.24 (s, 5).

Anal. Calcd for $C_{13}H_{20}O$: C, 81.20; H, 10.48. Found: C, 80.92; H, 10.38.

When the intermediate was hydrolyzed with D_2O, the splitting pattern at δ 3.2 remained unaltered.

1-*t*-Butyl-3-phenylpropanol-2-d_1 (2a). The same reaction was stirred for 30 hr, substituting LAD for LAH. The product was >99% pure by glpc. Its ir was similar to that of the undeuterated material except for a weak band at 4.68 μ (CD stretch), and its nmr differed in the following respects: δ 1.5–2.0 (m, 2) and 3.2 (s, 1), both of which were much broadened as was the somewhat altered multiplet between 2.3 and 3.0; exact mass of $C_{13}H_{19}DO$, 193.1565 (calcd 193.1577).

Anal. Calcd for $C_{13}H_{19}DO$: C, 80.77; H, 10.95. Found: C, 80.79; H, 10.98.

***trans*-1-*t*-Butyl-3-phenylallyl Alcohol-2-d_1 (1b).** The reaction was carried out in a fashion completely analogous to that for the preparation of the undeuterated compound, except LAD was substituted for LAH. The nmr spectrum of the product differed from that of the undeuterated material in the absence of the proton at δ 6.2 and the appearance of the remaining vinyl and the allylic proton as broad singlets.

1-*t*-Butyl-3-phenylpropanol-2-d_1 (2b). The reaction was carried out as in the preparation of **2a**, except that the deuterated allylic alcohol (**1b**) was allowed to react with LAH. The important differences in the nmr spectra are discussed in the text. The reaction was also carried out for 5 hr, substituting refluxing THF for ether as reaction solvent. The nmr of the product was unchanged.

Reduction of *trans*-1-*t*-Butyl-3-allyl Alcohol in the Presence of $AlCl_3$. The same reaction that produces **2a** was run with the addition of 13 mg of $AlCl_3$ (0.10 mmol). The product was again **2a**, but only about 70% of the starting material had reacted, as determined by nmr.

Preparation of 1-*t*-Butyl-3-phenylpropyl Methyl Xanthate and the Diastereomeric 2-d_1 Labeled Xanthates. One millimole of alcohol was converted to its lithium salt by stirring for 0.5 hr with 1.1 mmol of *n*-butyllithium at 0° in THF. Addition of 114 mg (1.5 mmol) of carbon disulfide was followed 0.5 hr later by 282 mg (2.0 mmol) of methyl iodide. After another hour at 25° the reaction mixture was poured into ether and extracted with several portions of water. The ether was dried with saturated brine and anhydrous magnesium sulfate and evaporated to give the xanthate in 95% yield. The ir spectrum (neat) showed strong absorptions at 8.12, 8.38, and 9.50 μ; nmr ($CDCl_3$) δ 0.95 (s, 9), 1.6–3.8 (m, 4), 2.5 (s, 3), 5.80 (t, 1), 7.17 (s, 5) for the xanthate prepared from **2c**. The apparent coupling constant for the methine triplet was J = 5 cps. When the xanthate of **2a** was prepared, the nmr was altered by the broadening and reduction to a three-proton integration of the methylene protons. Also, the methine proton appeared as a broad singlet, whereas in the xanthate derived from **2b**, it appeared as a doublet with J = 10 cps.

Pyrolysis of the Xanthates. A flow system pyrolysis apparatus was constructed by wrapping a 25 cm × 1 cm Pyrex tube with nichrome wire and asbestos, with provision of a thermometer well for measuring the temperature of the tube wall. The tube was packed with glass helices, the top fitted with a serum cap for injection of samples and a nitrogen inlet, and the bottom attached to a mercury bubbler and a trap packed with glass wool and cooled to −196°. The tube was heated to 300°, and the xanthates injected as 1 *M* hexane solutions in a dropwise fashion. The tube was washed with several more milliliters of hexane and the solvent was removed on a rotary evaporator, giving the olefin in 97% yield, 92% overall from the alcohol.

The nmr ($CDCl_3$) of the pyrolysate detected only trace amounts of impurity. It showed resonances at δ 1.01 (s, 9), 3.30 (t, 2), 5.50 (t, 2), and 7.17 (s, 5). Pure *trans*-1-*t*-butyl-3-phenylpropene was obtained by preparative glpc on a 10 ft × 3/8 in. 10% Carbowax 20M on Diatoport S column, and less than 1% of volatile impurity was detected. The purity of the collected material was further indicated by reinjection onto an FS 1265 analytical column. A single peak was observed under conditions such that it had an 18-min retention time. The ir spectrum (neat) of the collected material showed a strong *trans*-CH absorption at 10.29 μ. The mass spectrum showed a molecular ion at *m/e* 174.

Anal. Calcd for $C_{13}H_{18}$: C, 89.59; H, 10.41. Found: C, 89.28; H, 10.60.

The olefin obtained by the pyrolysis of the deuterioxanthate synthesized from **2a** was identical in all respects with that produced from undeuterated xanthate. However, the nmr of the xanthate pyrolysate derived from **2b** showed the resonance at δ 3.30 to have collapsed to a broad singlet, and that at δ 5.50 to have become a very broad triplet with J = 2 cps, integrating to only *1.0* proton. The mass spectrum of this material showed the molecular ion at 175, with a peak of less than 5% its size at *m/e* 174.

***cis*-1-*t*-Butyl-3-phenylpropargyl Alcohol (5).** The reaction of 1.88 g (10 mmol) of the propargylic alcohol with 0.50 g LAH (1.3 mmol) was carried out by stirring in 20 ml of ether for 12 hr. The yield of product isolated was 1.84 g (98%), which proved to be a 3:1 mixture. This ratio remained unchanged when the reaction was carried out in four times the volume of ether. The minor component was isolated by preparative scale glpc on a 7 ft × 3/8 in. 15% SE-30 on Diatoport S column at *160*°, He flow *200* ml/min, which cleanly separated it from the major product, the *trans* alcohol. The chief features of the ir of the *cis* compound are discussed in the text. The nmr ($CDCl_3$) showed resonances at 0.92 (s, 9), 1.68 (s, 1), 4.23 (d, 1, J = 10 cps), 5.77 (g, 1, J = 10 and 12 cps), 6.67 (d, 1, J = 12 cps), and 7.33 (s, 5); exact mass of $C_{13}H_{18}O$ 190.1358 (calcd 190.1357).

Stability of the Complex Leading to *cis*-1-*t*-Butyl-3-phenylallyl Alcohol in THF. Reaction of 76 mg of LAH (2.0 mmol) with 282 mg of 1-*t*-butyl-3-phenylpropargyl alcohol (1.5 mmol) in a 1:1 THF–ether solvent was half-complete in 3 min, and the product was >98% *trans*-allylic alcohol, as determined by analytical vpc. When the reaction was run in ether, a 1-ml aliquot removed after 16 hr, and 1 ml of THF added to the remainder, which was then stirred for 7 hr longer, the nmr spectra of the products isolated from the two solutions were identical, each showing 3:1 *trans–cis* product.

Acknowledgment. I wish to thank Professors E. J. Corey and John Katzenellenbogen for stimulating discussions.

(21) V. N. Mićović and M. L. Mihailović, *J. Org. Chem.*, **18**, 1190 (1959).