olution MS of adduct fractions separated by preparative GC, on a 15% SE-30 column (~6.4 mm × 2 m, 112 °C), were performed on an AEI MS50. GC/FTIR experiments were performed with the same SE-52 column (145 °C) interfaced to a Nicolet 7199 FTIR. All 400-MHz $^1H$ and 100-MHz $^{13}C$ spectra were recorded on a Bruker WH-400 NMR spectrometer. To detect the $^{13}C$ resonance of the quaternary carbon atoms in **12a** and **12b**, a total of 88000 scans were performed on a Bruker WH-200 NMR spectrometer. This comparatively large number of scans was required since these carbon atoms having no attached hydrogens possess longer relaxation times.

**NMR Data.**[23] 100-MHz $^{13}C$ ($\delta$): **8**, 197.5 (C=O), 138.4 (=CH), 77.4 (—HC—O—), 40.8 (—HC—CHO), 30.1 (—HC—C); **9**, 195.6 (C=O), 131.5 (=CH), 78.8 (—HC—O—), 46.5 (—HC—CHO), 24.8 (—HC—C); **12a**, 199.7 (C=O), 141.4 (=$CH_2$), 135.2 (=$CH_A$*), 133.0 (=$CH_B$*), 107.5 (C=), 82.6, 79.8 (—HC—O—), 57.1 (—HC—CHO); **12b**, 199.7 (C=O), 144.7 (=$CH_2$), 136.2 (=$CH_J$*), 134.5 (=$CH_I$*), 109.0 (C=), 81.9, 80.2 (—HC—O—), 56.0 (—HC—CHO) [*tentative assignments based on the well-known $\gamma$-gauche steric interaction[24,25]]. 400-MHz $^1H$ ($\delta$): **12a**, 9.08 (H), 3.47 (G), 5.02 (F), 5.24 (E), 5.21 (D), 5.17 (C), 6.51 (A, B); **12b**, 9.49 (Q), 2.81 (P), 5.06 (N), 5.33 (M), 5.15 (L), 5.29 (K), 6.41 (J), 6.52 (I).

**Acknowledgment.** We thank the Natural Sciences and Engineering Research Council of Canada for continuing financial support and the Alberta Heritage Scholarship Fund (W.A.R.). We also thank Dr. T. Nakashima and the NMR laboratory, Dr. A. Hogg and the MS laboratory, and J. Hoyle (GC/FTIR) for technical assistance. The assistance of Prof. G. Toth in the interpretation of some of the NMR data is gratefully acknowledged.

**Registry No.** 8, 97334-54-8; **9**, 97334-55-9; **12a**, 97277-62-8; **12b**, 97277-63-9; $CH_2$=C=CHCHO, 53268-92-1; furan, 110-00-9; cyclopropene-3-carboxaldehyde, 36998-21-7.

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# Weak Base Promoted $\beta$-Elimination Reactions in 1-Phenyl-1-propyl Derivatives. Evidence for an Intermediate in the E2C Reaction

Harold Kwart† and Kazimiera A. Wilk*‡

*Department of Chemistry, The University of Delaware, Newark, Delaware 19711*

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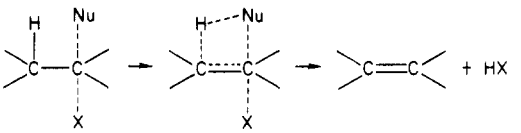
We describe the observation of a nucleophile trigger mechanism in the case of the weak base promoted $\beta$-elimination (E2C process) and suggest permutational isomerism of TBP intermediates. Weak bases, namely, bromide and fluoride ions, bring about elimination in a bent transition state to which only a small fraction of a covalent bond to the nucleophile–base and some leaving group departure must be achieved in an orienting intermediate. These studies provide evidence for a TBP structure surrounding C-$\alpha$ in the 1-phenyl-1-propyl system and attribute the equal availability of abstractable H and D of both diastereoisomers to the action of the promoter bases.

The E2C mechanism has been the subject of vigorous controversy for many years, and several proposals for the transition state (TS) have been advanced.[1-3] Several contributors to the field of elimination mechanisms concluded that E2C-like transition states were utilized by strong carbon but weak hydrogen bases (e.g., $Br^-$, $Cl^-$, $RS^-$) in their reaction with very weakly acidic compounds containing good leaving groups.[1,4,5] It has been postulated that these eliminations occurred in a trans-periplanar fashion,[1d,e,6] with the base anti to the leaving group (Scheme I). Such transition states were "loose", with the double bond well developed and the base bound to both $\beta$-hydrogen and $\alpha$-carbon.

Recently, we defined the E2C mechanism in fluoride ion promoted elimination of $\beta$-phenylethyl substrates in an aprotic medium.[7] Other evidence for an E2C mechanism was found in the course of bromide[8] and amine base[9] promoted eliminations in $\alpha$-bromo ester substrates. From the latter, the E2C mechanism is not $S_N2$-like but may be regarded as a well-precedented nucleophilic trigger[10] mechanism involving a trigonal bipyramid carbon intermediate (TBP).

Scheme I. The E2C Process




The principal purpose of the present work was to adduce further evidence for TBP carbon intermediate invoked by triggering the E2C mechanism with weak bases and focused at C-$\alpha$ of the substrate.

†Deceased, March 31, 1983.
‡Address correspondence to Institute of Organic and Polymer Technology, Technical University of Wroclaw, 50370 Wroclaw, Poland.

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(3) (a) McLennan, D. J. *Tetrahedron* **1975**, *31*, 2999. (b) Ford, W. T. *Acc. Chem. Res.* **1973**, *6*, 410.
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**Table I. Product Composition and Deuterium Isotope Effects in the Halide-Promoted β-Elimination Reaction of the *threo*- and *erythro*-1-Phenyl-1-propyl-2-$d_1$ *p*-Nitrobenzoates in Acetonitrile**

| base | diastereoisomer | elimination product composition,[a] %  |  | temp,[b] °C | $k_H/k_D$ | mean $k_H/k_D$ |
|---|---|---|---|---|---|---|
| Br | threo | 33.0 | 67.0 | 105.00 | 2.03 ± 0.02 | 2.02 ± 0.02 |
| | | 33.2 | 66.8 | 120.00 | 2.01 ± 0.02 | |
| | | 33.2 | 66.8 | 130.00 | 2.01 ± 0.02 | |
| | | 33.0 | 67.0 | 153.50 | 2.03 ± 0.02 | |
| | erythro | 33.0 | 66.7 | 105.00 | 2.00 ± 0.02 | 2.01 ± 0.02 |
| | | 33.1 | 66.9 | 120.00 | 2.02 ± 0.02 | |
| | | 33.1 | 66.9 | 130.00 | 2.02 ± 0.02 | |
| | | 33.1 | 66.9 | 153.50 | 2.02 ± 0.02 | |
| F | threo | 29.5 | 70.5 | 100.00 | 2.39 ± 0.02 | 2.38 ± 0.02 |
| | | 29.7 | 70.3 | 120.00 | 2.37 ± 0.02 | |
| | | 29.6 | 70.4 | 130.00 | 2.38 ± 0.02 | |
| | | 29.5 | 70.5 | 150.00 | 2.39 ± 0.02 | |
| | erythro | 29.7 | 70.3 | 100.00 | 2.37 ± 0.02 | 2.38 ± 0.02 |
| | | 29.4 | 70.6 | 120.00 | 2.40 ± 0.02 | |
| | | 29.5 | 70.5 | 130.00 | 2.39 ± 0.02 | |
| | | 29.6 | 70.4 | 150.00 | 2.38 ± 0.02 | |

[a] The uncertainty of the product composition determination is about 1%. [b] ±0.05 °C.

Fluoride and bromide ions in acetonitrile, which have previously been used in promoting β-elimination,[1e,7,8,11,12] were selected as the weak-base reagents. These bases, with high charge density in a polar solvent, can interact with C-α and thus stabilize the ensuing E2 TS. Threo and erythro diastereoisomers of 1-phenyl-1-propyl-2-$d_1$ *p*-nitrobenzoate were chosen as model compounds to study the mechanism and the course of the E2 reaction promoted by weak bases.

## Results and Discussion

Diastereoisomeric 1-phenyl-1-propan-2-$d_1$-ol esters were obtained by methods described in the Experimental Section. High-resolution NMR analysis confirmed the structures and stereochemical purity (>98%) of threo and erythro derivatives. The kinetic isotope effects and product compositions were determined for erythro and threo isomers at four temperatures with $Et_4NBr$ or $Bu_4NF$ in acetonitrile solvent. All runs were done in the presence of excess 2,6-lutidine, which traps the liberated acid as the kinetically inactive lutidinium salt.[13] After the reaction had been completed, the products were isolated and submitted to GC and NMR analysis. The results of NMR measurements with determinations made over a 50 °C range are gathered in Table I.

In the eliminations promoted by bromide ion, the only products of the reaction derived from either of the diastereoisomers of 1-phenyl-1-propyl-2-$d_1$ *p*-nitrobenzoate and detectable by GC were *trans*-propenylbenzene (>97%) and less than 3% of *cis*-propenylbenzene. The same isomers reacted with $Bu_4NF$ in acetonitrile to give 55% of *trans*-propenylbenzene and 45% of substitution product. The fluoride formed by substitution undergoes elimination much more slowly than either of the *p*-nitrobenzoates; this secondary elimination reaction is therefore not a complication and does not change the picture of the stereochemistry. It was further established that isomerization of *cis*-propenylbenzene to the more stable trans isomer does not occur under the reaction conditions. Thus, the latter is the kinetic product in these reactions, as concluded also by Winstein.[1a]

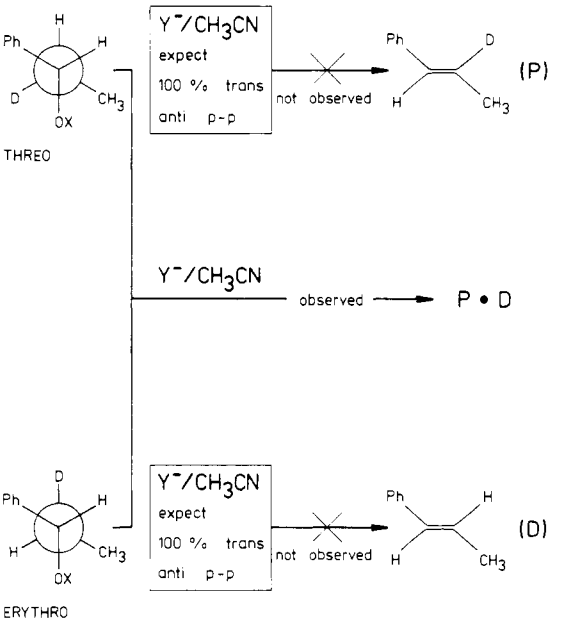


**Figure 1.**

A major finding of this work is the identical isotope distribution in the elimination product obtained from *both* diastereoisomers: 33.1 ± 0.4% $PhCH{=}CHCH_3$ and 66.9 ± 0.7% $PhCH{=}CDCH_3$ with bromide ion and 29.6 ± 0.4% and 70.5 ± 0.7%, respectively, with fluoride. The fact that H and D are lost at the same rate in each substrate demonstrates that antiperiplanar geometry is not maintained in these reactions (Figure 1).

Primary deuterium isotope effects were determined for *threo*- and *erythro*-1-phenyl-1-propyl-2-$d_1$ *p*-nitrobenzoates by high-resolution NMR. The $k_H/k_D$ values are virtually identical for the threo and erythro isomer in each base system and are greater than 1.2 (Table I). The isotopic activation energy differences approach zero, and the isotope effects equal the isotopic ratio of preexponential factors, i.e., $[E_a]_D{}^H \simeq 0$, and $k_H/k_D = A_H/A_D$. A temperature-independent isotope effect that is essentially the same for both diastereoisomers has been suggested to

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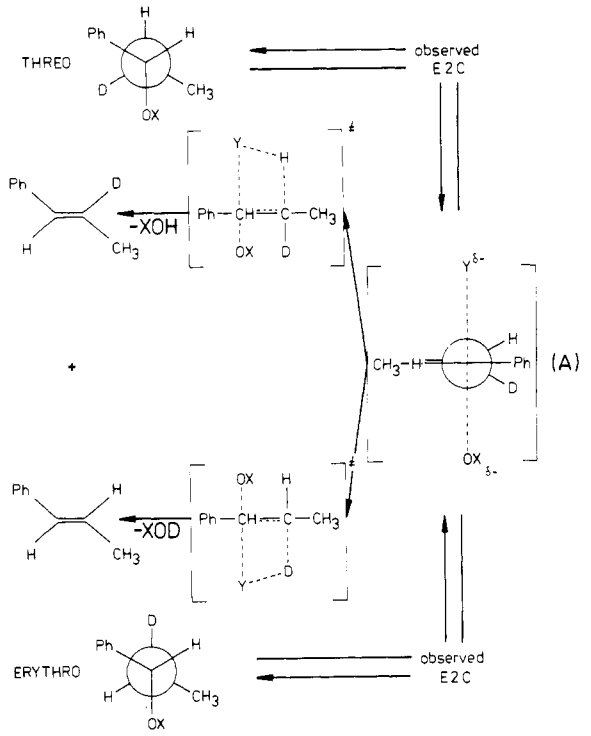



**Figure 2.** Permutational isomerism in the E2C mechanism of $\beta$-elimination.

signify nonlinear H transfer[14] for a reaction with a single rate-determining step. The $k_H/k_D$ values at each temperature of the fluoride-promoted $\beta$-elimination are found to be similar to that effected by the bromide ion, differing only by a factor 1.18. It can be concluded, therefore, that changing the base promoter, i.e., $F^-$ or $Br^-$, appears to be without a significant effect on the TS structure. The low values of $A_H/A_D$, i.e., 2.02 and 2.38 respectively for bromide and fluoride ions, indicate looser transition states in this E2C investigated reaction. It is in close agreement with our earlier observation and interpretation of some data corresponding to the halide ion promoted eliminations in $\beta$-phenylethyl and bromo ester[8] substrates in an aprotic medium.

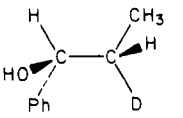
The equal availability of abstractable H and D in the TS, taken together with the same isotope effect for both threo and erythro isomers, implies that the two elimination reactions proceed through a similar equilibrating intermediate focused at C-$\alpha$ of the 1-phenyl-1-propyl system. Generally speaking, our results call for the reaction model depicted in Figure 2 that has already been conceived by Winstein.[1a] Both halide ions ($F^-$ or $Br^-$) are to cause C-$\alpha$ epimerization by forming the TBP intermediate of substrate via positional exchanges of C-$\alpha$ ligands. Strictly speaking, the TBP intermediate (A) undergoes polytopal rearrangement[15] by some mode of a permutational isomerism that equilibrates the apically bonded promoter base ($Y^-$) and nucleofugal group (OX). The bending vibrations of these bonds, longer and weaker than required in the TS, become indistinguishable and undergo rapid energy exchanges, i.e., permutational isomerism over a low barrier. Passage of the intermediate (A) to the respective transition states for nonlinear H and D abstraction is determined primarily by the zero-point energy and entropy factors responsible for isotope effects as it has previously been considered in our papers.[8,9] If equilibrating permutational isomerism is achieved prior to anti elimination, the rate ratio ($k_H/k_D$) of the threo and erythro isomers should be identical, which was achieved in the present work.

Although the concept of a TBP intermediate is not part of the classical picture of elimination mechanisms, such structures have been invoked in several other situations. Several examples of relatively stable pentacoordinate compounds, i.e., $CH_5^+$ (in mass spectroscopy[16a] and fairly stable in "magic acid"), $CCl_5^-$,[16b] as well as theoretical work yielding stability estimates for the model systems $CH_5^-$[16c] and $CH_3F_2^-$[16d] have appeared in the literature. CNDO calculations[17] indicate that the transition states of the $S_N2$ reactions $CH_3OH + F^-$ and $CH_3CN + F^-$ are actually potential energy minima, making them formally intermediates. Ugi and co-workers[18] elaborated a quantitative and qualitative treatment requiring the species with the pentacoordinated carbon atom to be an intermediate. Such an intermediate has recently been found as a relatively stable entity by Forbus and Martin.[19]

We feel that the metastable intermediate indicated in Figure 2 meets the requirements of our experimental findings and provides a rational basis for understanding the course of the E2C reaction.

## Experimental Section

**A. Synthesis of Substrates. *erythro*-1-Phenyl-1-propan-2-$d_1$-ol.** This alcohol was prepared by a hydroboration–oxidation procedure.[20] Under a dry nitrogen atmosphere 0.04 mol of sodium borodeuteride (99 atom % D) was placed in a 500-mL flask. *cis*-Propenylbenzene (0.15 mol) was introduced, followed by 100 mL of dry tetrahydrofuran. After the mixture



was cooled to 10–20 °C, 0.55 mol (7.0 mL) of boron trifluoride etherate was added to the well-stirred suspension over a period of 1 h while the temperature was maintained at 25 °C. The reaction mixture was then stirred for 6 h at room temperature. The solution was again cooled to 0 °C, and 10 mL of water was added cautiously to destroy residual hydride. The organoborane was oxidized at 30–40 °C by the addition of 17 mL of a 3 M solution of sodium hydroxide, followed by the careful dropwise addition of 17 mL of 30% hydrogen peroxide. The reaction product was obtained in a yield of 60%, bp 104–108 °C (18 mm), by fractional distillation: NMR (250 MHz, $CCl_4$) $\delta$ 7.17–7.10 (m, 5 H, aromatic protons), 4.27 (d, $J$ = 5.8 Hz, 1 H, methine proton at C-1), 4.07 (s, 1 H, hydroxyl proton), 1.77–1.6 (m, 1 H, methine proton at C-2), 0.75 (d, $J$ = 7.4 Hz, 3 H, methyl protons). According to the high-resolution NMR analysis the deuteroboration product consisted of 88.5 ± 0.8% of 1-phenyl-propan-2-$d_1$-ol and 11.5 ± 0.2% of 1-phenyl-2-propan-1-$d_1$-ol.

***threo*-1-Phenyl-1-propan-2-$d_1$-ol.** The same procedure was applied as before. *trans*-Propenylbenzene was used as a substrate:

(14) (a) Kwart, H. *Acc. Chem. Res.* **1982**, *15*, 401. (b) The identification of a nonlinear TS for proton transfer by means of a temperature-independent isotope effect has been challenged by: Vitale, A. A.; San Filippo, J., Jr. *J. Am. Chem. Soc.* **1982**, *104*, 7341.

(15) (a) Berry, R. S. *J. Chem. Phys.* **1960**, *32*, 933. (b) Ugi, I.; Marquarding, D.; Klusacek, M.; Gillespie, P.; Ramirez, F. *Acc. Chem. Res.* **1971**, *4*, 288. (c) Gillespie, P.; Hoffman, P.; Klusacek, H.; Marquarding, D.; Pfohl, S.; Ramirez, F.; Tsolis, E. A.; Ugi, I. *Angew. Chem., Int. Ed. Engl.* **1971**, *10*, 689.

(16) (a) Olah, G. A.; Klopman, G. Schlosberg, R. H. *J. Am. Chem. Soc.* **1969**, *91*, 3261. (b) McDaniel, D. H.; Dieters, R. H. *J. Am. Chem. Soc.* **1966**, *88*, 2607. (c) Allinger, N. L.; Tai, J. C.; Wu, F. T. *J. Am. Chem. Soc.* **1970**, *92*, 579. (d) Berthier, G.; David, D. J.; Veillard, A. *Theor. Chim. Acta* **1969**, *14*, 329.

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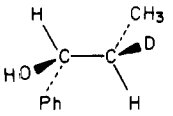
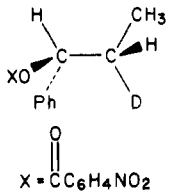


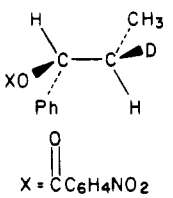
bp 104–106 °C (18 mm); NMR (250 MHz, $CCl_4$) δ 7.19–7.10 (m, 5 H, aromatic protons), 4.27 (d, $J$ = 5.8 Hz, 1 H, methine proton at C-1), 4.13 (s, 1 H, hydroxyl proton), 1.68–1.5 (m, 1 H, methine proton at C-2), 0.74 (d, $J$ = 7.4 Hz, 3 H, methyl protons). NMR analysis shows that the deuteroboration product consisted of 93 ± 0.9% 1-phenyl-1-propan-2-$d_1$-ol and 7.0 ± 0.1% of 1-phenyl-2-propan-1-$d_1$-ol.

***erythro*-1-Phenyl-1-propyl-2-$d_1$ *p*-Nitrobenzoate.** This compound was prepared from the erythro alcohol by reaction of the lithium alkoxide with *p*-nitrobenzoyl chloride in tetrahydrofuran.[21] A solution of 0.06 mol of alcohol and 30 mL of



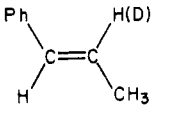
tetrahydrofuran was placed in a reaction flask under nitrogen. *n*-Butyllithium solution (0.06 mol) was added dropwise at 0 °C. After the reaction mixture was stirred for 2 h, it was cooled to −30 °C, and a 1.0 M solution of *p*-nitrobenzoyl chloride in THF was added. The reaction mixture was allowed to warm to room temperature and stirred for an additional 3 h. After a workup in the usual manner, the *p*-nitrobenzoate was crystallized fractionally from hexane to constant melting point: mp 56.5–56.7 °C (lit.[22] mp 56.5–57.5 °C); NMR (250 MHz, $CCl_4$) δ 8.18 (d, $J$ = 2.0 Hz, 4 H, aromatic protons), 7.37–7.20 (m, 5 H, aromatic protons), 5.87 (d, $J$ = 6.8 Hz, 1 H, methine proton at C-1), 2.06 (p, $J$ = 7.3 Hz, 1 H, methine proton at C-2), 0.94 (d, $J$ = 7.4 Hz, 3 H, methyl protons).

***threo*-1-Phenyl-1-propyl-2-$d_1$ *p*-Nitrobenzoate.** This compound was synthesized from the threo alcohol with the same procedure as before: mp 56.9–57.2 °C; NMR (250 MHz, $CCl_4$)



δ 8.18 (d, $J$ = 2.0 Hz, 4 H, aromatic protons), 7.37–7.20 (m, 5 H, aromatic protons), 5.87 (d, $J$ = 6.8 Hz, 1 H, methine protons at C-1), 1.93 (p, $J$ = 7.3 Hz, 1 H, methine proton at C-2), 0.94 (d, $J$ = 7.4 Hz, 3 H, methyl protons).

**B. Elimination Studies.** Acetonitrile solutions, i.e., 0.05–0.10 M in the corresponding *p*-nitrobenzoate, 0.055–0.105 M in 2,6-lutidine, and 0.5–1.0 M in $Et_4NBr$ or $Bu_4NF$, were allowed to react to completion at four temperatures over a range of 50 °C. The



resulting solutions were poured into 1 N $HNO_3$ and extracted with petroleum ether. The combined extracts were washed with water, separated, dried, and stripped of solvent. The isolated products (preparative GC) were analyzed by chromatography and high-resolution NMR: NMR (250 MHz, $CCl_4$) δ 7.22–7.10 (m, 5 H, aromatic protons), 6.32–6.29 (m, 1 H, methine proton at C-1), 6.17–6.13 (m, 1 H, methine proton at C-2), 1.88 (br s, 3 H, methyl protons).

The 1-phenyl-1-propyl fluoride was found in our preliminary experiments as a $S_N2$ displacement product (in 45% yield) in the bimolecular reaction of 1-phenyl-1-propyl *p*-nitrobenzoate with fluoride ion in acetonitrile. This compound, bp 40–41 °C (5 mm) $n^{29}_D$ 1.4622 (lit.[23] bp 39 °C (4 mm), $m^{30}_D$ 1.4623), was submitted to elimination with fluoride ion in acetonitrile at 130 °C. Less than 5% of conversion was noticed after the time of completion for the *p*-nitrobenzoate elimination promoted by $Bu_4NF$–$CH_3CN$.

Additionally, 1-phenyl-1-propyl *p*-nitrobenzoate along with 50% of *cis*-propenylbenzene and *o*-xylene as a standard was submitted to elimination conditions (130 and 150 °C, $Et_4NBr$–$CH_3CN$, 2,6-lutidine). After the required time for the reaction completion, the product was isolated and analyzed by gas chromatographic procedure. The *cis*-propenylbenzene did not isomerize.

It was found that tetra-*n*-butylammonium fluoride (commercially available from Aldrich, 1 M solution in tetrahydrofuran) loses its reactivity in promoting the elimination if the reaction mixture is contaminated with water. $Bu_4NF$ was stored in a vacuum desiccator, and all experiments were performed under dry nitrogen.

**C. Instrumental Procedures.** Gas chromatographic quantitative analyses were conducted on a F and M 5750 chromatograph connected to a Hewlett-Packard 3370A electronic integrator. Standard conditions were as follows: column, (305 × 0.32) × $10^{-2}$ m, 10% SE-30 on Chromosorb W; oven temperature, 110 °C; detector and injection port temperatures, 200 and 220 °C, respectively. Preparative gas chromatography was performed on a F and M dual-column gas chromatograph. Standard conditions were as follows: column, (305 × 0.64) × $10^{-2}$ m, 10% SE-30 on Chromosorb W; oven temperature, 140 °C. $^1H$ NMR spectra were obtained on a Bruker Spectroscopin Model WM 250 using $Me_4Si$ as the reference.

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**Registry No.** $Et_4NBr$, 71-91-0; $Bu_4NF$, 429-41-4; Br, 24959-67-9; F, 16984-48-8; $D_2$, 7782-39-0; *erythro*-1-phenyl-1-propanol-2-$d_1$, 96792-45-9; *cis*-propenylbenzene, 766-90-5; *threo*-1-phenyl-1-propanol-2-$d_1$, 96792-46-0; *trans*-propenylbenzene, 873-66-5; *erythro*-1-phenyl-1-propyl-2-$d_1$ *p*-nitrobenzoate, 96792-44-8; *erythro*-1-phenyl-1-propanol-2-$d_1$ (lithium alkoxide deriv.), 96792-47-1; *p*-nitrobenzoyl chloride, 122-04-3; *threo*-1-phenyl-1-propyl-2-$d_1$ *p*-nitrobenzoate, 96792-43-7.

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