was dried at 50 °C under vacuum to yield 0.6 g of perchlorate salt 8: IR (KBr) 1680 (C=O) cm^{-1}.

The yellow solid was suspended in methanol (25 mL) and cooled with an ice bath under nitrogen before the careful addition of sodium borohydride. The resultant mixture was stirred at 0 °C for 30 min and at ambient temperature for 1.5 h. The pale tan solution was quenched with the addition of 25 mL of saturated sodium bicarbonate solution. It was stirred for 2 h before it was partitioned between water–methylene chloride. The aqueous layer was extracted with a second portion of methylene chloride. The combined organic extracts were dried and concentrated to yield 0.58 g of clear tan oil which crystallized on sitting. Recrystallization from methanol yielded fine white needles, mp 184–190 °C. Except for a methoxyl singlet at δ 3.8, the ^1H NMR spectrum consisted of a series of unresolved humps from 2.0 to 7.4.

Anal. Calcd for $C_{20}H_{22}N_2O_3S$: C, 64.84; H, 5.99; N, 7.56; S, 8.66. Found: C, 65.02; H, 6.20; N, 7.38; S, 9.06.

Acknowledgments. Appreciation is extended to Mr. E. Zielinski and his group for microanalytical results, Ms. M. Magnuson for nomenclature advice, Ms. Roseann Gramlich for preparation of the manuscript, Dr. Richard Mueller for invaluable discussions and suggestions during the course of this work, and Dr. Bruce Maryanoff for comments on the manuscript.

Registry No. 2, 15964-79-1; 3, 70456-63-2; 4, 70456-64-3; 5, 70456-65-4; 6, 70456-66-5; 7, 70456-67-6; 8, 70456-69-8; 9, 70456-70-1; acetonitrile, 75-05-8; 2-aminothiophenol, 137-07-5; methyl bromoacetate, 96-32-2.

A Convenient Synthetic Sequence for the Deuterium Labeling of Olefins in the Allylic Position

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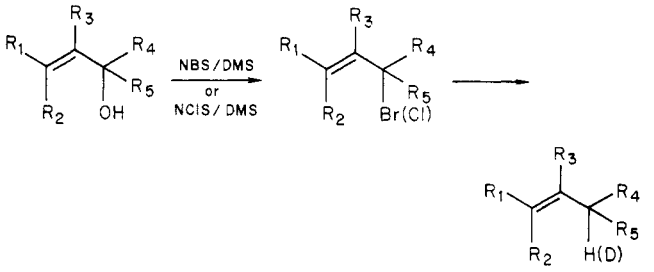
During the course of our studies of the mechanism of allylic functionalization[1] we have developed a convenient, high-yield, synthetic sequence which produces olefins isotopically labeled at the allylic positions. The established reaction sequence for such labeling generally involves synthesis of a mesylate or tosylate,[2] followed by lithium aluminum hydride (deuteride) reduction. This sequence proved to be impractical in the case of allylic alcohols due to the instability of these intermediates at temperatures required for the reduction reaction. By replacing the mesylates and tosylates with chlorides and/or bromides produced by Corey's method,[3] we have been able to produce labeled olefins in good yield.

Results and Discussion

The generalized reaction sequence employed is



The application of this technique to several olefins is summarized in Table I.

For primary allylic alcohols (R_4 = R_5 = H or D) the resulting allylic bromides or chlorides are both sufficiently stable to be handled conveniently and characterized by NMR (see Table I, entries 1 and 2). In the reduction of secondary allylic alcohols (R_4 = alkyl, R_5 = H or D), however, it is preferable to employ chlorides since the bromides undergo decomposition (see entries 5–7). The chlorides are also preferred for styrene derivatives (see entries 3 and 4). Only for primary allylic alcohols could the more traditional mesylate intermediate be employed, and here only if low temperatures were maintained through the workup and reduction. The mesylates of the secondary or styryl alcohols and of the diols (entries 8–10) were unstable[4] even at low temperatures and no olefin products could be isolated.

The solvent used in the second step of this sequence is chosen relative to the boiling point of the product olefin, diglyme being preferred for low-boiling olefins which can easily be distilled out of this solvent.

In the sequences which convert primary alcohols to the corresponding hydrocarbons, no evidence of cis–trans or allylic rearrangement could be detected in either step in the reaction sequence. This point could be examined with particular care for entries 2–4 and 10. For entries 2–4, careful examination of NMR spectra showed no evidence of rearrangement product. This point is strengthened by entry 10, where VPC analysis of the product olefin showed no evidence of rearrangement to *trans*-2-butene or to the allylic rearrangement isomer 1-butene.

Conversions involving secondary alcohols were somewhat less clean. For entries 5–7, conversion of the alcohols to the chlorides was accompanied by a few percent of allylic rearranged chloride (as revealed by NMR examination). Conversion of these chlorides to hydrocarbons showed a consistent 5–10% allylic rearrangement isomer, some of which apparently occurred in the reduction step. Thus, while this method appears to be suitable for secondary systems, it is not as unambiguously regiospecific as for the primary substrates.

In an attempt to assess the limits of applicability of this method, we have carried out these reactions on the benzylic/allylic alcohol shown in Scheme I. Both *E* and *Z* alcohols gave an allyl chloride whose structure is assigned by NMR as the rearrangement product. This is clearly the result of complete allylic rearrangement to the more stable species. Reduction of this compound gave the indicated mixture of olefins.

In summary this sequence offers the advantage of high regiospecificity for primary alcohols and represents a significant improvement in yield and convenience over the more traditional methods. With simple aliphatic secondary systems only small quantities of rearranged products were found. Materials labeled with deuterium and, in particular, methyl-labeled compounds are thus more generally

(1) (a) D. E. McClure, P. K. Sysak, and L. M. Stephenson, *J. Am. Chem. Soc.*, **95**, 7888 (1973); (b) D. L. Mattern and L. M. Stephenson, *J. Org. Chem.*, **41**, 3614 (1976); (c) D. R. Speth, J. E. Egnatchik, and L. M. Stephenson, *ibid.*, in press; (d) M. Orfanopoulos, M. B. Grdina, and L. M. Stephenson, *J. Am. Chem. Soc.*, in press.

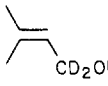
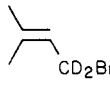
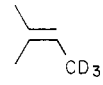
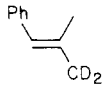
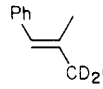
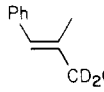
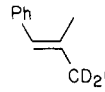
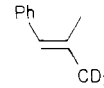
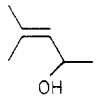
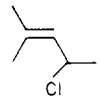
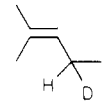
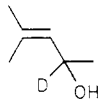
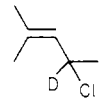
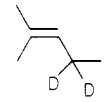
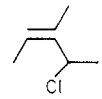
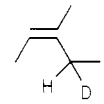
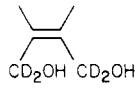
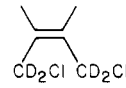
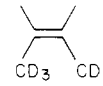
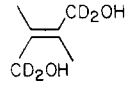
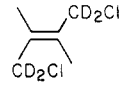
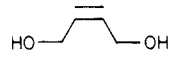
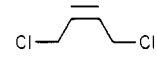
(2) R. K. Crossland and K. L. Servis, *J. Org. Chem.*, **35**, 3195 (1970).

(3) E. J. Corey, C. U. Kim, and Makoto Kakeda, *Tetrahedron Lett.*, 4339 (1972).

(4) Reaction mixtures turned black almost immediately even during careful low-temperature workups.

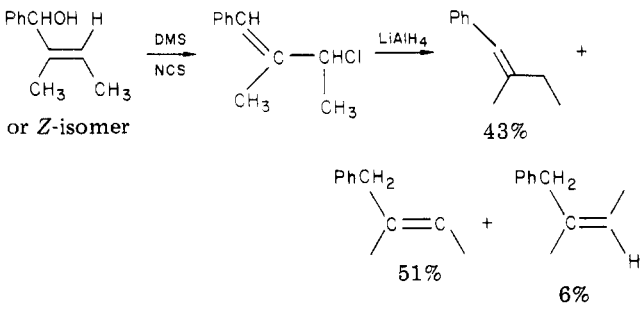
0022-3263/79/1944-2936$01.00/0

Table I. Deuterium Labeling of Olefins in the Allylic Position

entry	alcohol	allylic halide	% yield	reducing agent/solvent	olefin	% yield[a]
1			72	LAD/diglyme		88
2			70	LAD/diglyme		65
3			90	LAH/THF		60
4			90	Super D/THF		85
5			75	LAD/diglyme		85
6			76	LAD/diglyme		70
7			62	LAD/diglyme		66
8			80	LAD/diglyme		65
9			80	LAD/diglyme		65
10			70	LAH/diglyme		80

[a] Isolated crude yield. For our purposes these olefins were further purified by VPC giving lower yields than these recorded. No attempt was made to optimize yields.

Scheme I



available for mechanistic work involving allylic functionalization.

Experimental Section

Lithium aluminum deuteride, 99% D, was obtained from Norell, Inc., and Super D[5] (lithium triethylborodeuteride, 1 M solution in tetrahydrofuran) from Aldrich Chemical Co. Solvents were dried by standard procedures.[6] Nuclear magnetic resonance spectra were recorded on a Varian A-60A or Varian XL-100 spectrometer. Vapor phase chromatographic analyses or separations were performed with 20% OV-101 (10 ft × $^1/_8$ in. or 20 ft × $^3/_8$ in.) or 20% β,β-oxydipropionitrile (10 ft × $^1/_4$ in. or 18 ft × $^1/_8$ in.) columns. Detailed syntheses of several representative olefins and ^{1}H NMR spectral data for all olefins are given below (entries 1, 4, and 10).

1-Bromo-1,1-dideuterio-3-methyl-2-butene (Entry 1, Table I). To a solution of 80 mL of dichloromethane and 5.34 g (30 mmol) of *N*-bromosuccinimide at 0 °C was added 2.17 g (35 mmol) of dimethyl sulfide, and the mixture was stirred for an additional 0.5 h. To this solution at −20 °C 2 g (23 mmol) of the allylic alcohol 1,1-dideuterio-3-methyl-2-buten-1-ol was added dropwise (this dideuterioallylic alcohol was formed by reducing the corresponding ester with lithium aluminum hydride in diethyl ether). The solution was warmed slowly to room temperature and stirred for an additional hour. This reaction mixture was poured onto 20 g of ice, washed twice with saturated NaCl, and dried over $MgSO_4$. The solvent was removed under reduced pressure (40 mm), while the reaction mixture was maintained at 0 °C. The allylic bromide was obtained in 72% yield (2.5 g, 16 mmol).

1,1,1-Trideuterio-3-methyl-2-butene (Entry 1, Table I). The allylic bromide described above was used directly without further purification. To a solution of 0.33 g (8 mmol) of lithium aluminum deuteride in 16 mL of diglyme at −50 °C and under nitrogen was added dropwise 2.5 g (16 mmol) of allylic bromide. The solution was stirred and slowly warmed to room temperature. The product olefin was distilled directly from the reaction mixture. An 88% yield of 1,1,1-trideuterio-3-methyl-2-butene was obtained: ^{1}H NMR δ 1.6 (d, J = 1.5 Hz, CH_3), 1.68 (d, J = 1.5 Hz, CH_3), 5.17 (s, broad, =CH).

3,3-Dideuterio-3-chloro-2-methyl-1-phenylpropene (Entry 4, Table I). To a stirred dichloromethane suspension of 2 g (15

(5) H. C. Brown and S. Krishnamurthy, *J. Am. Chem. Soc.*, **95**, 1669 (1973).

(6) Diglyme was difficult to purify and maintain dry. Purification, under dry nitrogen, involved standing over solid KOH for a period of at least 1 week, followd by prolonged refluxing over sodium for 12–24 h, and then distillation from sodium directly into dried reaction glassware.

mmol) of *N*-chlorosuccinimide and 1.36 g (18 mmol) of dimethyl sulfide at −30 °C was added dropwise 1.5 g (10 mmol) of 3,3-dideuterio-3-hydroxy-2-methyl-1-phenylpropene. The solution was stirred until clear (1 h). It was then poured onto an ice–NaCl solution mixture, and the organic layer was washed twice with saturated NaCl solution and dried over Na_2CO_3. The solvent was removed by rotary evaporation to yield 1.6 g (9 mmol) of the allylic chloride: ^{1}H NMR δ 1.93 (d, J = 1.5 Hz, CH_3), 6.58 (d, broad, =CH), 7.38 (s, C_6H_5).

3,3,3-Trideuterio-2-methyl-1-phenylpropene (Entry 4, Table I). The styryl chloride from above (0.7 g (4 mmol)), dissolved in THF, was added dropwise to 5 mL (5 mmol) of 1 M Super D in THF. The solution was stirred for several hours, washed with saturated NaCl, and dried over Na_2CO_3. Olefin remaining after solvent removal amounted to 0.46 g (3.4 mmol): ^{1}H NMR δ 1.82 (d, J = 1 Hz, CH_3), 6.25 (s, broad, =CH), 7.2 (s, C_6H_5).

(*Z*)-1,3-Dichloro-2-butene (Entry 10, Table I). Dimethyl sulfide (5.3 mL (72 mmol)) was added dropwise to a stirred mixture of 8 g (60 mmol) of *N*-chlorosuccinimide in dichloromethane at 0 °C. The mixture turned milky and was cooled to −30 °C. A dichloromethane solution of 1.76 g (20 mmol) of 2-butene-1,4-diol (91% cis) was added dropwise to the milky suspension. The solution was stirred and maintained at temperatures below 0 °C until it became clear. It was then poured onto a mixture of ice and NaCl solution. The organic layer was washed twice with saturated NaCl and then dried over Na_2CO_3, and the solvent was removed by rotary evaporation yielding 1.75 g (14 mmol of the dichloride: ^{1}H NMR δ 4.05 (m, CH_2), 5.93 (m, =CH) (this spectrum matched Sadtler 9282M).

(*Z*)-2-Butene (Entry 10). A diglyme solution of 1.35 g (11 mmol) of the *cis*-1,4-dichloro-2-butene was added dropwise to a suspension of 2.05 g (54 mmol) of lithium aluminum hydride in 50 mL of diglyme at −50 °C. After the addition, the reaction mixture was brought slowly to room temperature. The *cis*-2-butene was distilled out of the diglyme into a flask cooled to −78 °C. Approximately 0.5 g of olefin was isolated. The identity (isomeric purity) was confirmed by VPC comparison with commerical cis and trans isomers: ^{1}H NMR δ 1.6 (m, CH_3), 5.45 (m, =CH).

Spectral Data for Other Olefins. Olefins from Table I were purified by preparative gas chromatography, in a few cases removing slight quantities of allylic rearrangement isomers (<10%). These spectral data confirm the absence of significant cis–trans isomerization.

(*E*)-1-Deuterio-2-methyl-2-butene (entry 2): ^{1}H NMR δ 1.57 (d, broad, CH_3), 1.63 (s, broad, CH_3 + CH_2D), 5.32 (q, broad, =CH).

(*E*)-3,3-Dideuterio-2-methyl-1-phenylpropene (entry 3): ^{1}H NMR δ 1.82 (d, J = 1 Hz, CH_3 + CHD_2), 6.25 (s, broad, =CH), 7.2 (s, C_6H_5).

2-Deuterio-2-methyl-2-pentene (entry 5): ^{1}H NMR δ 0.91 (dt, J_d = 7.5 Hz, J_t = 1 Hz, CH_3), 1.60 (s, broad, CH_3), 1.68 (s, broad, CH_3), 1.92 (m, CHD), 5.13 (d, broad, =CH).

2,2-Dideuterio-2-methyl-2-pentene (entry 6): ^{1}H NMR δ 0.90 (s, broad, $-CH_3$), 1.57 (d, J = 1.5 Hz, CH_3), 1.65 (d, J = 1.5 Hz, CH_3), 5.12 (s, broad, =CH).

(*Z*)-4-Deuterio-3-methyl-2-pentene (entry 7): ^{1}H NMR δ 0.95 (d, broad, CH_3), 1.55 (d, broad, CH_3), 1.60 (s, broad, CH_3), 2.0 (m, broad, CHD), 5.16 (q, broad, =CH).

(*E*)- and (*Z*)-1,1,1,4,4,4-hexadeuterio-2,3-dimethyl-2-butene (entries 8 and 9): ^{1}H NMR δ 1.63 (s, CH_3).

Acknowledgments. This work was supported by the National Science Foundation through Grant CHE-77-12744. We thank C. N. Sukenik for helpful advice and encouragement.

Registry No. 1,1-Dideuterio-3-methyl-2-buten-1-ol, 6158-92-5; 1-bromo-1,1-dideuterio-3-methyl-2-butene, 70576-39-5; 1,1,1-trideuterio-3-methyl-2-butene, 1560-58-3; (*E*)-2-methyl-2-buten-1-ol, 497-02-9; (*E*)-1-bromo-2-methyl-2-butene, 57253-30-2; (*E*)-1-deuterio-2-methyl-2-butene, 70576-40-8; (*E*)-1,1-dideuterio-2-methyl-3-phenyl-2-propen-1-ol, 70576-41-9; (*E*)-1-chloro-1,1-dideuterio-2-methyl-3-phenyl-2-propene, 70576-42-0; (*E*)-3,3-dideuterio-2-methyl-1-phenylpropene, 70576-43-1; (*E*)-3,3,3-trideuterio-2-methyl-1-phenylpropene, 70576-44-2; 4-methyl-3-penten-2-ol, 4325-82-0; 2-methyl-4-chloro-2-pentene, 21971-94-8; 2-methyl-4-deuterio-2-pentene, 70576-45-3; 2-deuterio-4-methyl-3-penten-2-ol, 70576-46-4; 2-methyl-4-chloro-4-deuterio-2-pentene, 70576-47-5; 2-methyl-4,4-dideuterio-2-pentene, 70576-48-6; (*Z*)-3-methyl-3-penten-2-ol, 64683-06-3; (*Z*)-3-methyl-4-chloro-2-pentene, 70576-49-7; (*Z*)-4-deuterio-3-methyl-2-pentene, 70576-50-0; (*Z*)-1,1,4,4-tetradeuterio-2,3-dimethyl-2-buten-1,4-diol, 70576-51-1; (*Z*)-1,1,4,4-tetradeuterio-1,1-dichloro-2,3-dimethyl-2-butene, 70576-52-2; (*Z*)-1,1,1,4,4,4-hexadeuterio-2,3-dimethyl-2-butene, 38132-19-3; (*E*)-1,1,4,4-tetradeuterio-2,3-dimethyl-2-buten-1,4-diol, 70576-53-3; (*E*)-1,1,4,4-tetradeuterio-1,4-dichloro-2,3-dimethyl-2-butene, 70576-54-4; (*E*)-1,1,1,4,4,4-hexadeuterio-2,3-dimethyl-2-butene, 38132-24-0; (*Z*)-2-butene-1,4-diol, 6117-80-2; (*Z*)-1,4-dichloro-2-butene, 1476-11-5; (*Z*)-2-butene, 590-18-1.

Electrosynthesis of Heteroatom–Heteroatom Bonds. 4. Direct Cross-Coupling of Dialkyl (or Diaryl) Phosphites with Disulfides by a Sodium Bromide Promoted Electrolytic Procedure

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Homologues of *S*-alkyl (or -aryl) *O,O*-dialkyl (or -diaryl) phosphorothiolates (**1**) are of interest as effective pesti-

$$\underset{\mathbf{2}}{(RO)_2P(O)H} + \underset{\mathbf{3}}{R'\text{-}S\text{-}S\text{-}R'} \xrightarrow[NaBr]{-e} \underset{\mathbf{1}}{(RO)_2P(O)\text{-}S\text{-}R'}$$

cides,[1] and a variety of synthetic procedures for **1** have been investigated.[2-8] As a result, the formation of the S–P bond of **1** has been achieved by the reaction of dialkyl (or diaryl) phosphites (**2**) with sulfenyl chlorides,[2] sulfenyl cyanides,[3] thiosulfonates,[4] disulfides,[5] and sulfur,[6] by the condensation of phosphorochloridate with thiols,[7] and by other reactions.[8]

In our preceding papers,[9a] we reported the electrolytic S–N bond-making reaction, yielding various sulfenamides from disulfides and amines. These results prompted us to extend the electrochemical procedure to making the S–P bond of **1** and we found that the direct cross-coupling of dialkyl (or diaryl) phosphites (**2**) with disulfides (**3**) proceeds smoothly by sodium bromide assisted electrolysis.

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