Anal. Calcd for $C_{19}H_{18}N_2OS$: C, 70.78; H, 5.63; N, 8.69. Found: C, 70.29; H, 5.40; N, 8.35.

F.—**4** had mp 218–219°; ν_{max} (KBr) 3120 (OH, broad) and 1047 cm^{-1} (CO); nmr (DMSO-d_6) δ 1.00 (s, 3 H, CH_3), 3.24 (m, 2 H, NCH_2), 4.11 (m, 2 H, $CHCH_3$ and CHOH), 5.67 (d, 1 H, OH), and 7.27 (center of multiplet, 10 H, ArH). Addition of trifluoroacetic acid resulted in disappearance of the δ 5.67 doublet. The mass spectrum gave a parent ion peak at *m/e* 322.

Anal. Calcd for $C_{19}H_{18}N_2OS$: C, 70.78; H, 5.63; N, 8.69. Found: C, 71.02; H, 5.54; N, 8.53.

G.—**6** had mp 237–238°; ν_{max} (KBr) 3140 (OH, broad) and 1078 cm^{-1} (CO); nmr (DMSO-d_6) δ 1.23 (s, 3 H, CH_3), 1.31 (s, 3 H, CH_3), 3.46 (m, 2 H, SCH_2), 3.90 (broad m, 1 H, CHOH), 5.75 (d, 1 H, OH), and bands centered at 7.14 and 7.47 (m, 10 H, ArH). Addition of trifluoroacetic acid resulted in disappearance of the δ 5.75 doublet. The mass spectrum gave a parent ion peak at *m/e* 336.

Anal. Calcd for $C_{20}H_{20}N_2OS$: C, 71.39; H, 5.99; N, 8.32. Found: C, 71.19; H, 6.16; N, 8.21.

Oxidation of 2 (R = R′ = C_6H_5) and 6.—Chromic oxide (5.1 mmol) was added, in small portions, to 8 ml of a well-stirred cold pyridine solution. The alcohol (1.7 mmol) was then added and the mixture was stirred at room temperature for 12–15 hr. The reaction mixture was poured into water and the ketone was extracted with methylene chloride. The methylene chloride extract was dried (Na_2SO_4), the solvent was evaporated *in vacuo*, and the residual oil was crystallized from pentane. Recrystallization from 70% aqueous ethanol gave analytically pure product.

A.—The oxidation product from **2** (R = R′ = C_6H_5) had mp 198–200°; ν_{max} (KBr) 1715 cm^{-1} (CO).

Anal. Calcd for $C_{18}H_{14}N_2OS$: C, 70.56; H, 4.60; N, 9.14. Found: C, 70.51; H, 4.91; N, 9.40.

B.—The oxidation product from **6** had mp 192–193°; ν_{max} (KBr) 1718 cm^{-1} (CO).

Anal. Calcd for $C_{20}H_{18}N_2OS$: C, 71.83; H, 5.43; N, 8.38. Found: C, 71.89; H, 5.87; N, 8.35.

Registry No.—2 (R = R′ = C_6H_5), 34035-39-7; 2 (R = R′ = C_6H_5) oxidation product, 34035-40-0; 2 (R = R′ = H), 34035-41-1; 2 (R = R′ = C_4H_4), 34035-42-2; 2 (R = R′ = $C_2H_2N_2$), 34035-43-3; **3**, 34035-44-4; **4**, 34035-45-5; **6**, 34035-46-6; **6** oxidation product, 34035-47-7.

Acknowledgment.—We are grateful to the Petroleum Research Fund, administered by the American Chemical Society, for support of this research.

Conversion of Allylic Alcohols to Chlorides without Rearrangement

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Received November 1, 1971

A recent report on the conversion of allylic alcohols to their chlorides without rearrangement[1] prompts us to report similar, limited observations made some time ago. The unique properties[2] of the triphenylphosphine–carbon tetrachloride reagent suggested its potential in specific allylic alcohol-chloride conversions. When the reaction was employed using the classic isomeric α- and γ-methallyl alcohol couple, the results substantiated our hopes based on prior experience (Table I).

TABLE I

CHLORIDE COMPOSITION FROM METHALLYL ALCOHOLS USING Ph_3P–CCl_4

Alcohol	CH_3CH= $CHCH_2Cl$	CH_3CHCl-CH=CH_2
CH_3CH=$CHCH_2OH$	100	0
$CH_3CHOHCH$=CH_2	11	89

The report of Meyers demonstrated that *primary* allylic alcohols can be converted to chlorides without formation of the secondary or tertiary isomer. Our results demonstrate that not only can the primary-primary conversion be achieved specifically, but also, and perhaps more importantly, the secondary-secondary conversion can be achieved with high specificity even in a system prone toward rearrangement.

Experimental Section[3]

3-Buten-2-ol was commercial material whose glpc trace showed no contamination by its allylic isomer. **2-Buten-1-ol** was a heart cut from distillation of commercial alcohol and was also free of its allylic isomer by glpc examination. Its nmr spectrum clearly showed a mixture of cis and trans isomers. Each alcohol (0.099 g, 1.37 mmol) was dissolved in 0.5 ml of carbon tetrachloride containing 0.36 g (1.4 mmol) of triphenylphosphine and kept at ambient temperature. After 48 hr the nmr spectrum of the 2-buten-1-ol mixture showed only a small amount of unreacted alcohol and 1-chloro-2-butene. High-gain examination showed the absence of signals at 264 Hz ($CH_3CHClCH$=CH_2). Examination by glpc showed 1-chloro-2-butene as the only chloride. Similarly, the nmr spectrum of the 3-buten-2-ol mixture showed some unreacted alcohol, a multiplet at 264 Hz, and a weak doublet at 236 and 228 Hz (CH_3CH=$CHCH_2Cl$) whose integral indicated 9% of the latter chloride. Examination by glpc showed that the chlorides consisted of 89% unrearranged secondary and 11% rearranged primary allylic chloride.

To determine whether the rearranged chloride from 3-buten-2-ol was a kinetic product or resulted from post-isomerization the following experiment was performed. To 1.00 g of alcohol in 6 ml of carbon tetrachloride was added 0.9 g of triphenylphosphine. After 4 hr an aliquot was removed and examined by glpc and another 0.9 g of phosphine was added. This was repeated twice more at intervals of 16 and 8 hr. The glpc results showed the presence of 8–12% primary chloride in all cases, suggesting that the latter was a kinetically controlled product.

Registry No.—3-Buten-2-ol, 598-32-3; *cis*-2-buten-1-ol, 4088-60-2; *trans*-2-buten-1-ol, 504-61-0; 1-chloro-2-butene, 591-97-9; 3-chloro-1-butene, 563-52-0.

Acknowledgment.—This work was supported by the National Science Foundation while the author was a guest at East Tennessee State University.

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(1) E. W. Collington and A. I. Meyers, *J. Org. Chem.*, **36**, 3044 (1971).

(2) R. G. Weiss and E. I. Snyder, *ibid.*, **36**, 403 (1971), and earlier work cited therein.

(3) Chloride analyses were performed on a FFAP column operated at 50°. Chemical shift data are with reference to internal TMS.