Cbz-alanine deblocking was carried out at 25 °C with either 100 mg of Pd-PEI "ghosts" (1 mg of Pd), 10 mg of the Pd-carbon samples (1 mg of Pd), or 1 mg of Pd-black in 3 mL of $\mathrm{HCOOH/MeOH/H_2O}$ (14:28:58) containing 0.1 g of Cbz-alanine at the start of the reaction. The reaction mixture was agitated with a wrist-action shaker. The amount of free alanine was determined by amino acid analysis. Elution time was 13.8 min, using buffer B only on a Beckman 119CL amino acid analyzer.

L-Leucyl-L-alanylglycyl-L-valine. The synthesis was begun with Val-OMe. The other residues were successively added as the N-hydroxysuccinimide esters of the Cbz-amino acids.[6] Hydrogenolysis of the Cbz group was accomplished by using the following conditions: 1-5 mmol of peptide, 30 mL of THF, 30 mL of water, 6 mL of formic acid (97%), and about 5 g of Pd-PEI "ghosts". The reaction mixture was shaken in a round-bottom flask with a wrist-action shaker. A rotary evaporator may also be used for agitation.

Thin-layer chromatography was performed on silica gel G plates (Analtech) with $\mathrm{MeOH-CHCl_3}$ (1:50). After development, the plates were exposed to HBr-AcOH fumes for 15 min, heated at 100 °C for 10 min, sprayed with ninhydrin, and heated for 10 min at 100 °C.

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Registry No. PEI, 9002-98-6; Cbz-alanine, 1142-20-7; L-leucyl-L-alanylglycyl-L-valine, 17195-26-5.

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Rhodium(I)-Catalyzed Biphasic Isomerization of Allylic Alcohols

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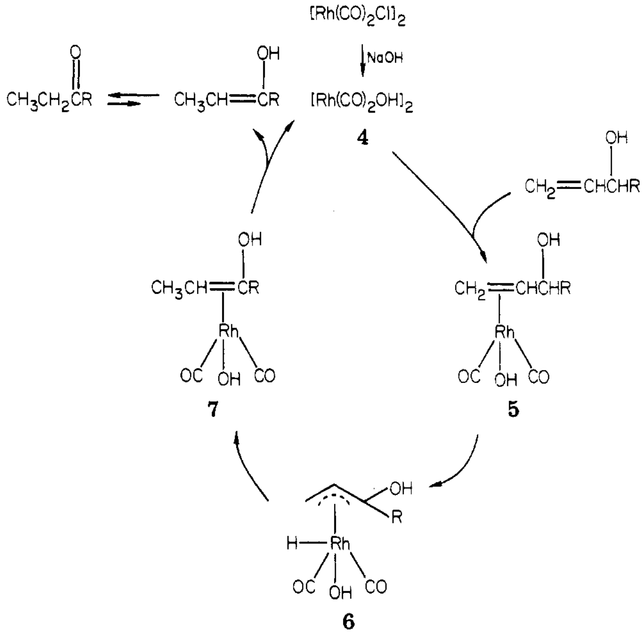
The isomerization of allylic alcohols to carbonyl compounds is an important reaction in organic chemistry. This transformation can be effected by thermolysis of the allyl alcohol at 302-368 °C.[1] Somewhat less drastic conditions could be used when the reaction was induced by metal species such as iron pentacarbonyl (130 °C, 16 h),[2] hydridochlorotris(triphenylphosphine)ruthenium(II) (110 °C, 1 h),[3] and hydridocarbonyltris(triphenylphosphine)rhodium(I) (70 °C, 3 h).[4] The use of 2 equiv of n-butyllithium also results in isomerization.[5]

Scheme I



We have been investigating the application of phase transfer catalysis to metal-catalyzed processes.[6-8] This note describes the rearrangement of allylic alcohols to carbonyl compounds under remarkably mild conditions by use of a two-phase system. This method does not generally require a phase-transfer catalyst, although the use of one results in cleaner reactions (no by-products).

Treatment of a methylene chloride solution of 1-hexen-3-ol (1) with a catalytic amount of chlorodicarbonyl-

$$\underset{\mathbf{1}}{\mathrm{CH_2{=}CHCH(OH)CH_2CH_2CH_3}} + \underset{\mathbf{2}}{\mathrm{[Rh(CO)_2Cl]_2}} \xrightarrow[\substack{\mathrm{CH_2Cl_2} \\ \mathrm{PhCH_2N(C_2H_5)_3{}^+Cl^-}}]{\mathrm{8\ M\ NaOH}} \underset{\mathbf{3}}{\mathrm{C_2H_5C(O)CH_2CH_2CH_3}}$$

rhodium(I) dimer (2) (50:1 ratio of 1:2), sodium hydroxide (8 M), and benzyltriethylammonium chloride as the phase-transfer catalyst, at room temperature for 6-10 h, affords 3-hexanone (3) in quantitative yield. Repetition of the experiment in the absence of the phase-transfer catalyst resulted in a 90-93% yield of 3-hexanone. The conversion of 3-penten-2-ol to 2-pentanone also proved to

Table I. Products Obtained from the Biphasic Rh(I)-Catalyzed Isomerization of Allylic Alcohols

allyl alcohol	$\mathrm{PhCH_2N(C_2H_5)_3{}^+Cl^-}$	product[a]	yield, %
$\mathrm{CH_2{=}CHCH(OH)C_3H_7}$ (1)	yes	$\mathrm{C_2H_5COC_3H_7}$ (3)	100
	no	$\mathrm{C_2H_5COC_3H_7}$	90-93
$\mathrm{CH_3CH{=}CHCH(OH)CH_3}$	yes	$\mathrm{CH_3CH_2CH_2COCH_3}$	98
	no	$\mathrm{CH_3CH_2CH_2COCH_3}$[b]	80
$\mathrm{PhCH(OH)CH{=}CH_2}$	no	$\mathrm{PhCOCH_2CH_3}$	71
$\mathrm{PhCH{=}CHCH(OH)CH_3}$	yes	$\mathrm{PhCH_2CH_2COCH_3}$	94
$\mathrm{CH_3CH(OH)CH{=}CHCH(OH)CH_3}$	no	$\mathrm{CH_3C(O)CH_2CH_2CH(OH)CH_3}$[b]	58

[a] Products were identified by comparison with authentic samples. [b] An unidentified by-product was also formed.

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be simpler in the presence rather than in the absence of the quaternary ammonium salt (Table I). Ketones were obtained in good yields from other allyl alcohols, including 3-hexene-2,5-diol. No reaction occurred when 1-phenylallyl alcohol in methylene chloride was exposed to NaOH in the absence of the rhodium(I) catalyst.

A possible pathway for this reaction is outlined in Scheme I. Hydroxide ion displacement of halide from rhodium(I) species **2** would generate the rhodium hydroxide **4**. The latter can then π-complex to the unsaturated alcohol to give **5**, which on subsequent allylic hydrogen abstraction leads to the π-allyl complex **6**. Delivery of the hydride to a terminal allylic carbon affords the enol complex **7**. Decomplexation regenerates the catalyst and gives the enol of the carbonyl.

In conclusion, the two-phase reaction described above constitutes a simple, and very mild, method for the isomerization of allyl alcohols.

Experimental Section

Chlorodicarbonylrhodium(I) dimer, benzyltriethylammonium chloride, and all but one of the allyl alcohols were commercial products. We are indebted to Mr. F. Houlihan for providing generous quantities of 1-phenylallyl alcohol. Spectral data were recorded with a Unicam SP-1100 infrared spectrometer and a Varian T-60 or HA-100 proton magnetic resonance spectrometer.

General Procedure for the Isomerization of Allylic Alcohols Catalyzed by Chlorodicarbonylrhodium(I) Dimer. A mixture of the allyl alcohol (5.0 mmol) and **2** (0.1–0.2 mmol) in methylene chloride (20–25 mL), 8 M NaOH (15–20 mL), and benzyltriethylammonium chloride (if used, 1.0–2.0 mmol) was stirred at 25–30 °C for 6–18 h (reactions were usually complete in 6 h or less, but were left stirring overnight). The layers were separated, and the organic phase was washed with water, dried (Na_2SO_4 or $MgSO_4$), and then concentrated to give the carbonyl compound, which was distilled.

Acknowledgment. We are grateful to Imperial Oil Ltd. and to the Natural Sciences and Engineering Research Council for support of this research.

Registry No. 1, 4798-44-1; **2**, 65629-74-5; **3**, 589-38-8; 3-penten-2-ol, 1569-50-2; 2-pentanone, 107-87-9; 1-phenylallyl alcohol, 4393-06-0; propiophenone, 93-55-0; 4-phenyl-3-buten-2-ol, 17488-65-2; 4-phenyl-2-butanone, 2550-26-7; 3-hexen-2,5-diol, 7319-23-5; 2-hydroxy-5-hexanone, 56745-61-0.

Facile One-Step Synthesis of Alkylphosphonothioic Dichlorides from Chloroaluminate Complexes, $(RPCl_3)^+(Al_2Cl_7)^-$

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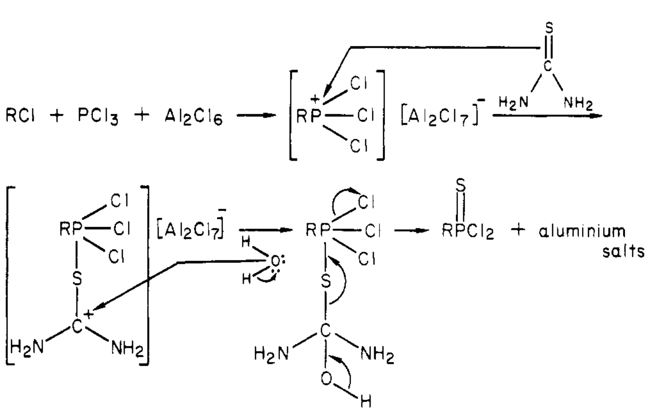
Alkylphosphonothioic dichlorides are intermediates of importance in insecticide synthesis. Among the reported procedures,[1] only two deserve mention here as convenient laboratory methods. The high-temperature reaction of phosphorus pentasulfide with alkylphosphonic dichlorides[2] invariably results in contamination by starting material while the second route makes use of less easily accessible dichlorophosphines.[3] A far more convenient procedure is reported here for the preparation of these compounds.

Scheme I



On hydrolysis with water, chloroaluminate (Kinnear–Perren) complexes[4] break up to yield alkylphosphonic dichlorides. Substitution of hydrogen sulfide in place of water, however, results in several side products along with the expected alkylphosphonothioic dichlorides, perhaps due to the greater nucleophilic reactivity of H_2S.[1c,4] In our modified method, the complex is treated with thiourea at room temperature followed by water to obtain pure alkylphosphonothioic dichloride in one step.

$$RCl + PCl_3 + Al_2Cl_6 \rightarrow (RPCl_3)^+(Al_2Cl_7)^- \xrightarrow[\text{2. water}]{\text{1. thiourea}} RP(S)Cl_2 \quad (1)$$

The starting alkyl halides, products, and yields are given in Table I. *n*-Butyl and 2-chloroethyl chlorides afforded rearranged products as expected from such reactions. The yields were moderate. This is probably inherent in $RCl-PCl_3-Al_2Cl_6$ complex formation[5] rather than in thiourea reaction. All alkylphosphonothioic dichlorides were characterized by comparing the boiling points and IR and NMR spectra with those of authentic samples and further confirmed by preparing diethyl derivatives.

In Scheme I, a plausible explanation for the formation of phosphonothioic dichloride is offered. The key step of the reaction is the attack of nucleophilic sulfur on phosphorus followed by reaction of water with this new complex. Elimination of urea affords the required product.[6]

Experimental Section

IR spectra were recorded on a Perkin-Elmer 577 instrument as neat liquid. ^1H NMR spectra in CCl_4 solutions were obtained with a Perkin-Elmer R-32 instrument with Me_4Si as internal standard. GC analyses were performed on a Varian Aerograph Model 2868 using an OV-17 column. TLC plates, 20 cm × 5 cm, were of silica gel. All alkyl halides were commercial products and were used after distillation. Thiourea (BDH) was dried at 110 °C for 5 h prior to use. Anhydrous aluminum chloride and phosphorus trichloride were commercial products and were used as such. The preparations of isopropylphosphonothioic dichloride and its diethyl derivative serve as typical procedures and are given below.

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(6) We thank one of the referees for modifying the mechanism suggested earlier by us.

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