to break the nickel sulfide colloid, and filtered through Celite. The filtrate was evaporated under reduced pressure, and the residual solid was washed three times with acetone and dried to give pure *dl*-phenylalanine (83% yield) identified by comparison with an authentic sample.

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Registry No.—$Ni(CO)_4$, 13463-39-3; decyl allyl carbonate, 40940-42-9; 1-decanol, 112-30-1; allyl chloroformate, 2937-50-0; *N*-allyloxycarbonyl-*N*,*N*-dicyclohexylamine, 40940-43-0; *N*-allyloxycarbonyl-*dl*-phenylalanine, 40940-57-6.

Selective Cleavage of Allyl Ethers under Mild Conditions by Transition Metal Reagents

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The highly selective properties of various transition metal derived reagents would seem to recommend their application to the removal of suitable chosen protecting groups.[1] This note outlines a new method for the selective cleavage of allyl ethers to alcohols under conditions sufficiently mild so that alcohol derivatives such as alkyl ethers, aryl ethers, or esters, and also many of the common functional groups, would not be affected. Our findings suggest that protection of hydroxyl groups as allyl ethers may be a very useful technique for organic synthesis.

We have found that rhodium(I) complexes such as $RhCl(PPh_3)_3$ catalyze the isomerization of allyl ethers (**1**) to 1-propenyl ethers (**2**) under neutral aprotic conditions.[2] Hydrolysis of the enol ethers **2** occurs rapidly at pH 2 to form the free alcohols **3**. The generality of the process was demonstrated for the allyl ethers of methanol, 1-decanol, and cholesterol, all of which could be converted readily to the corresponding alcohols **3** in >90% yield. Benzyl ethers were found to be stable under the conditions which cleave allyl ethers. Tristriphenylphosphine rhodium chloride was considerably more active as a catalyst than $RhCl_3$,[3] which in turn was more active than $PdCl_2$, $RuCl_3$, or $IrCl_3$. Prior to this work the cleavage of allyl ethers has been effected by the conventional method using strong acids, by oxidation with SeO_2 in acetic acid–dioxane,[4] or by treatment with strong base to generate an enol ether followed by acid hydrolysis or oxidation.[2,5]

$$\underset{\mathbf{1}}{ROCH_2CH{=}CH_2} \xrightarrow{Rh(I)} \underset{\mathbf{2}}{ROCH{=}CHCH_3} \xrightarrow{pH\ 2} \underset{\mathbf{3}}{ROH} + CH_3CH_2CHO$$

Experimental Section

Cleavage of Allyl Ethers as Illustrated by Menthyl Allyl Ether → Menthol.—A solution of menthyl allyl ether (0.114 g, 0.58 mmol) (prepared from menthol, sodium hydride, and allyl bromide), $RhCl(PPh_3)_3$ (0.037 g, 0.040 mmol) (Alfa Inorganics), and diazabicyclo[2.2.2]octane (0.013 g, 0.120 mmol)[6] in 10% aqueous ethanol was heated at reflux for 3 hr. An aliquot was injected into 1 *N* HCl and after a few minutes was assayed by vpc analysis (10 ft × 0.125 in. 5% Carbowax 20M Chromosorb W, 130°) which showed only menthol and menthyl allyl ether in 93 and 7% yield, respectively. Work-up of a parallel reaction (by pouring into water, extracting with ether, washing the ether with brine acidified to pH 2, drying over anhydrous $MgSO_4$, concentration, and separation on silica gel) gave menthol in 93% yield. The same procedure was applied to the cleavage of the allyl ethers of 1-decanol and cholesterol to form the alcohols in 96 and 90% yield, respectively.

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Registry No.—$RhCl(PPh_3)_3$, 14694-95-2; menthyl allyl ether, 40940-58-7; allyl decyl ether, 3295-96-3; allyl cholesteryl ether, 25092-65-3.

(1) For an earlier application involving a metal-ion sensitive protecting group, see E. J. Corey and R. L. Dawson, *J. Amer. Chem. Soc.*, **84**, 4899 (1962).

(2) Allyl ethers have been found previously to be isomerized to 1-propenyl ethers under quite drastic conditions (potassium *tert*-butoxide in dimethyl sulfoxide at 100°). See J. Cunningham, R. Gigg, and C. D. Warren, *Tetrahedron Lett.*, 1191 (1964), and references cited therein.

(3) A. J. Birch and G. S. R. Rao, *Tetrahedron Lett.*, 3797 (1968); J. F. Biellmann and M. J. Jung, *J. Amer. Chem. Soc.*, **90**, 1673 (1968).

(4) K. Kariyone and H. Yazawa, *Tetrahedron Lett.*, 2885 (1970).

(5) R. Gigg and C. D. Warren, *J. Chem. Soc. C*, 1903 (1968).

(6) Added to inhibit premature hydrolysis of the intermediate enol ether. Free propionaldehyde reacts with $RhCl(PPh_3)_3$ to form the catalytically much less active $RhCl(PPh_3)_2CO$.