tert-butyl-4-nitro), 4074-25-3; A (R_x = 3,5-di-*tert*-butyl-4-bromo), 3975-77-7; A (R_x = 2,4,5-tri-*tert*-butyl), 796-97-4; A (R_x = 3,4,5-tri-*tert*-butyl), 40782-30-7; B (R_x = F_5), 363-72-4; B (R_x = F), 462-06-6; B (R_x = NH_2), 62-53-3; B (R_x = $CONH_2$), 55-21-0; B (R_x = NO_2), 98-95-3; B (R_x = $COCH_3$), 98-86-2; B (R_x = COOH), 65-85-0; B (R_x = *tert*-butyl), 98-06-6; B (R_x = *m*-di-*tert*-butyl), 1014-60-4; B (R_x = 1,3-di-*tert*-butyl-2-nitro), 15141-43-2; B (R_x = 1,3-di-*tert*-butyl-2-bromo), 19715-32-3; B (R_x = 1,2,4-tri-*tert*-butyl), 1459-11-6; B (R_x = 1,2,3-tri-*tert*-butyl), 40782-34-1; *tert*-butyl cation, 14804-25-2.

Cleavage of Allyloxycarbonyl Protecting Group from Oxygen and Nitrogen under Mild Conditions by Nickel Carbonyl

E. J. COREY* AND J. WILLIAM SUGGS

Department of Chemistry, Harvard University, Cambridge, Massachusetts 02138

Received May 15, 1973

This note outlines a method for the use of the allyloxycarbonyl group for protection of hydroxyl and amino functions.

Allyl and cinnamyl acetates have been reported to react with nickel carbonyl at 45–65° in tetrahydrofuran for 2–3 hr to form the allylic coupling products (1,5-hexadienes) in 30–50% yield.[1] Under these conditions nonallylic acetates and allylic alcohols or ethers are unreactive. These facts suggest that the allyloxycarbonyl group could be used for hydroxyl or amino protection in a way parallel to the well-known benzyloxycarbonyl (carbobenzoxy) group and removed under mild aprotic conditions by the action of nickel carbonyl or a related "allylophilic" reagent. Experimental verification of this possibility was readily obtained. The conversion of a variety of alcohols to alkyl (or cycloalkyl) allyl carbonates could be accomplished in high yield by reaction with allyl chloroformate (available from Polysciences, Inc., Warrington, Pa.) and pyridine in a suitable aprotic solvent [*e.g.*, ether or tetrahydrofuran (THF)]. Regeneration of alcohol from the corresponding alkyl allyl carbonate occurred upon exposure to nickel carbonyl, as expected, but it was found that the reaction could not be driven to completion even with an excess of the reagent. This difficulty could be overcome by the addition of *N,N'*-tetramethylethylenediamine to reaction mixtures in either acetonitrile or dimethylformamide (DMF) as solvent, although an excess of nickel carbonyl was found still to be necessary.[2] For optimal yields of alcohols from alkyl allyl carbonates, the following reaction conditions were typically employed: (a) *ca.* 5 equiv of nickel carbonyl and 3 equiv of tetramethylethylenediamine per equiv of allyl carbonate, (b) DMF [5–10 ml/ml of $Ni(CO)_4$] as solvent at 55°, (c) nitrogen or argon atmosphere, (d) *ca.* 4 hr reaction time. Under these quite mild conditions the following cleavages of alkyl allyl carbonates to alcohols were observed (yield in parentheses).

$$\mathrm{ROCOOCH_2CH{=}CH_2} \xrightarrow{\mathrm{Ni(CO)_4}} \mathrm{ROH}$$

R = *n*-decyl (95%)
R = *exo*-2-norbornyl (87%)
R = menthyl (91.5%)

To illustrate the use of the allyloxycarbonyl group for protection of amino nitrogen, two substrates, *N*-allyloxycarbonyl-*dl*-phenylalanine[3] and *N*-allyloxydicyclohexylamine, were prepared and treated with nickel carbonyl under the conditions outlined above except for the use of DMF–water (95:5) as medium and 10 equiv of nickel carbonyl. The expected free amino compounds, *dl*-phenylalanine and *N,N*-dicyclohexylamine, were obtained in 95 and 83% yield.

We expect that for large-scale preparative work where the use of excess nickel carbonyl may be unacceptable, the use of a carbon monoxide atmosphere under pressure is advisable to stabilize the reagent.

Experimental Section

The following procedures for the synthesis and cleavage of the allyloxycarbonyl derivative of 1-decanol could also be applied to *exo*-2-norborneol and menthol.

Decyl Allyl Carbonate.—A magnetically stirred solution of 1-decanol (3.24 g, 20.5 mmol) and pyridine (2.03 g, 25.7 mmol) in 75 ml of THF was cooled to 0°, and allyl chloroformate (3.097 g, 25.7 mmol) in 10 ml of THF was added dropwise. The reaction mixture was slowly warmed to room temperature, and after 2 hr at room temperature the solution was filtered and solvent was removed at reduced pressure. Ether (25 ml) was then added and the solution was filtered again, washed with water and brine, dried over anhydrous $MgSO_4$, then distilled to give 4.54 g (91%) of a pleasant-smelling liquid: bp 109–110° (0.5 mm); ir (neat) 1751 (s), 1647 (w), 1292 (sh), 1250 (s, b), 970 (m), 795 cm^{-1} (m); nmr (CCl_4) δ 6.34–5.70 (9-line multiplet, 1 H), 5.37 (ABC triplet, 2 H), 4.61 (d, J = 5 Hz, 2 H) (these three absorbances are due to the allyl group and are the same in all the carboallyloxy derivatives made), 4.14 (t, J = 6 Hz, 2 H), 1.33 (s, 16 H), 0.97 (m, 3 H); mass spectrum m/e 140 [$(CH_2)_{10}^+$].

1-Decanol.—(Nickel carbonyl is both volatile and toxic; all operations involving it were performed in a well-ventilated hood.) Into a 25-ml flask fitted with a side arm and reflux condenser topped by a three-way stopcock opened to an argon-filled balloon were placed *n*-decyl allyl carbonate (0.288 g, 1.19 mmol), tetramethylethylenediamine (0.417 g, 3.60 mmol), and 7 ml of dry, argon-saturated DMF. Nickel carbonyl (0.78 ml, 6.0 mmol) was added all at once, and the stirred mixture was warmed slowly to 55°. After 4 hr excess nickel carbonyl was removed by codistillation with ether into an ethereal iodine solution. The mixture was poured into 20 ml of water and extracted twice with 15 ml of pentane. The pentane layer was washed with 20 ml of 1 *N* hydrochloric acid and brine, and dried over anhydrous $MgSO_4$. Evaporation of the solvent at reduced pressure gave 0.177 g (95%) of 1-decanol, homogeneous by tlc and with spectral properties identical with those of authentic material.

Cleavage of Allyloxycarbonyl Amides. A. *N*-Allyloxycarbonyl-*N,N*-dicyclohexylamine.—The above procedure was followed except that 0.3 ml of water was also added to the reaction mixture, and 10 equiv of nickel carbonyl was used. After removal of excess nickel carbonyl, the reaction mixture was poured into 20 ml of 1 *N* HCl, and the solution was made basic with sodium carbonate and extracted thrice with pentane. These pentane extracts were dried over anhydrous magnesium sulfate and concentrated under reduced pressure to give dicyclohexylamine (95% yield).

B. *N*-Allyloxycarbonyl-*dl*-phenylalanine.—The reaction conditions were as described just above. After 5 hr excess nickel carbonyl and TMEDA were removed under reduced pressure. Then 50 ml of water was added and H_2S was bubbled through the solution for 10 min. The solution was brought to pH 6, heated

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(1) N. L. Bauld, *Tetrahedron Lett.*, 859 (1962).

(2) The role of tetramethylethylenediamine in this regard is unclear. It was originally considered that the formation of Ni(II) as a reaction product might somehow inhibit the reaction and that the diamine might prevent such inhibition by complexation. However, it has been observed that added nickel acetate has no effect on the rate or extent of reaction between alkyl allyl carbonate and nickel carbonyl alone.

(3) C. M. Stevens and R. Watanabe, *J. Amer. Chem. Soc.*, **72**, 725 (1950).

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.

Acknowledgment.—This work was assisted financially by the National Science Foundation.

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

E. J. Corey* and J. William Suggs

Department of Chemistry, Harvard University,
Cambridge, Massachusetts 02138

Received May 15, 1973

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]

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

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.

Acknowledgment.—This work was assisted financially by the National Science Foundation.

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.

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[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 $RhCl(PPh_3)_2CO$.