

The C–O Bond Cleavage of Allyl Ethers by Rhodium Compounds

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Synopsis. Allyl ethers were cleaved by rhodium compounds under mild conditions to give aldehydes and hydrocarbons. This reaction can be extended to allyl esters.

The cleavage of allyl or benzyl ethers has hitherto been known—*e.g.*, i) by hydrogenolysis over Raney-nickel,¹⁾ ii) by treatment with strong bases or rhodium compounds to generate an enol ether followed by acid

hydrolysis or oxidation,²⁾ and iii) by oxidation with SeO₂ in acetic acid.³⁾ The reaction products were usually alcohols and aldehydes. Also, the reactions of allyl ethers with transition metals are known to give a metal hydride or π -allyl complex.⁴⁾

In this paper, we wish to report that the C–O bonds of cinnamyl and benzyl ethers have been easily cleaved to the corresponding aldehydes and hydrocarbons in

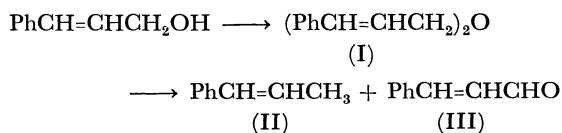
TABLE I. THE CLEAVAGE OF CINNAMYL AND BENZYL ETHERS

	Catalyst	Solvent	Reaction		Products and yields, % ^{a)}
			time, hr	temp, °C	
Cinnamyl ethers					
Dicinnamyl ether 1.2 mmol	RhCl ₃ -PPh ₃ -EtOH	Dioxane	2	100	(II), 97 (III), 96
<i>p</i> -Methylcinnamyl hydrocinnamyl ether 1.2 mmol	RhCl ₃ -PPh ₃ -EtOH	Dioxane	2	100	<i>p</i> , <i>β</i> -Dimethylstyrene, 48 β-Phenylpropionaldehyde, 41 <i>p</i> -Methylcinnamaldehyde, 27 <i>n</i> -Propylbenzene, 21 Allylbenzene, 14
Cinnamyl <i>n</i> -propyl ether 3.0 mmol	RhCl ₃ -PPh ₃ -EtOH	Dioxane	2	100	(II), 40 (III), 37 Cinnamyl alcohol, 3.3 Propionaldehyde, Propane Propylene
Cinnamyl isopropyl ether 3.0 mmol	RhCl ₃ -PPh ₃ -EtOH	Dioxane	2	100	(II), 33 (III), 17 Acetone, Propane, Propylene
Cinnamyl allyl ether 5.0 mmol	RhCl ₃ -PPh ₃ -EtOH	Tetrahydrofuran	2	60	(II), 44 (III), 34 Acrolein, Propylene
	RhCl(PPh ₃) ₃	Tetrahydrofuran	2	60	(II), 12 (III), 9.5
	RhCl(CO)(PPh ₃) ₂	Tetrahydrofuran	2	60	(II), 19 (III), 18
Benzyl ethers					
Dibenzyl ether ^{c)} 1.2 mmol	RhCl ₃ -PPh ₃ -EtOH	Dioxane	8	100	Toluene, 3.0 Benzaldehyde, 2.4
<i>p</i> -Anisyl benzyl ether 1.2 mmol	RhCl ₃ -PPh ₃ -EtOH	Dioxane	8	100	<i>p</i> -Methylanisole, 17 Benzaldehyde, 16 <i>p</i> -Anisaldehyde, 4.5 Toluene, 3.6
<i>p</i> -Nitrobenzyl benzyl ether 1.2 mmol	RhCl ₃ -PPh ₃ -EtOH	Dioxane	8	100	<i>p</i> -Nitrobenzaldehyde, 16 Toluene, 15 Benzaldehyde, 0.6 <i>p</i> -Nitrotoluene, 0.5
Benzyl allyl ether 5.0 mmol	RhCl ₃ -PPh ₃ -EtOH	Tetrahydrofuran	16	60	Toluene, 24 Benzaldehyde, 17 Propylene, Acrolein
Cyclic ethers^{b)}					
2,5-Dihydrofuran 5.0 mmol	RhCl ₃ -PPh ₃ -MeOH	Tetrahydrofuran	16	60	Crotonaldehyde, 21
	RhCl(PPh ₃) ₃	Tetrahydrofuran	16	60	Crotonaldehyde, 15
Cinnamyl esters					
Cinnamyl <i>n</i> -butyrate 5.0 mmol	RhCl(CO)(PPh ₃) ₂	—	6	150	(II), 34 (III), 22 Styrene, 2.5 Cinnamyl <i>n</i> -propyl ether, trace
Cinnamyl isobutyrate 5.0 mmol	RhCl(CO)(PPh ₃) ₂	—	6	150	(II), 37 (III), 15 Styrene, 1.1 Cinnamyl isopropyl ether, trace
Cinnamyl acetate 5.0 mmol	RhCl(CO)(PPh ₃) ₂	—	6	150	(II), 23 (III), 16 Cinnamyl methyl ether, trace
Benzyl ester					
Benzyl acetate ^{c)} 5.0 mmol	RhCl(CO)(PPh ₃) ₂	—	24	150	Benzyl methyl ether, 4.0 Toluene, 1.2 Benzaldehyde, 0.9

a) Yields are based on the reactants. b) Cyclic ethers such as tetrahydrofuran, tetrahydropyran, and 3,4-dihydro- α -pyran were not cleaved under these conditions. c) Unreacted ether and ester were recovered.

the presence of rhodium compounds under mild conditions.

The reaction of cinnamyl alcohol with RhCl_3 and PPh_3 in dioxane gave dicinnamyl ether (I), β -methylstyrene (II), and cinnamaldehyde (III). In an early stage of the reaction, the ether formation was remarkable. Therefore, the reaction of ether (I) with RhCl_3 and PPh_3 was carried out. As expected, C–O bond cleavage products (II) and (III) were obtained in high yields.⁵⁾



$\text{RhCl}(\text{PPh}_3)_3$ and $\text{RhCl}(\text{CO})(\text{PPh}_3)_2$ were also active as catalysts, but PdCl_2 , RuCl_3 , and IrCl_3 were not good catalysts.

The generality of this cleavage reaction was demonstrated for cinnamyl alkyl, cinnamyl allyl, dibenzyl, and benzyl allyl ethers. In the case of *p*-substituted benzyl ethers, the bonds between the carbon of a benzyl group containing a more electron-donating substituent and oxygen were selectively cleaved. However, non-allylic ethers, such as hydrocinnamyl isopropyl and dihydrocinnamyl ether, did not react. The cleavage of cyclic allyl ether to unsaturated aldehyde was also observed.

In addition, this reaction could also be applied to allyl esters. Cinnamyl *n*-butyrate afforded (II), (III), propionaldehyde, propylene, and cinnamyl propyl ether. The reaction was accompanied by a decarbonylation of the ester to ether. These results are summarized in Table I.

This C–O bond cleavage reaction is characteristic of allyl and benzyl ethers. Presumably the allyl rhodium complex might play an important role as an intermediate species.

Experimental

Materials. The dibenzyl ether, 2,5-dihydrofuran, and benzyl acetate were purchased from Nakarai Kagaku. The

other ethers and esters were prepared by the methods of the literature.⁶⁾

Cleavage of Cinnamyl or Benzyl Ethers. To a solution of $\text{RhCl}_3 \cdot 3\text{H}_2\text{O}$ (0.25 mmol) and PPh_3 (0.25 mmol) in ethanol (2.5 mmol) and dioxane or tetrahydrofuran (5 ml), we added cinnamyl or benzyl ether (1.2–5.0 mmol). After 2 hr (or 8 hr) of refluxing under a nitrogen stream, the solvent was removed and the residue was treated by gas chromatography (25% Apiezon grease L on Neopak) to isolate the products. The structures of the products were determined by means of the IR and NMR spectra. From cinnamyl allyl ether, β -methylstyrene (II) (2.30 mmol), cinnamaldehyde (III) (1.72 mmol), acrolein, and propylene were obtained.

Decarbonylation of Cinnamyl or Benzyl Esters. A mixture of the ester (5 mmol) and $\text{RhCl}(\text{CO})(\text{PPh}_3)_2$ was heated at 150 °C for 6 hr. The resulting solution was treated as has been mentioned above. $\text{RhCl}(\text{CO})(\text{PPh}_3)_2$ was recovered quantitatively.

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