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Oxidation by Transition Metal Complexes. V. Oxidation of Vinyl Esters Catalyzed by Rhodium Complex.

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The oxidation of styryl acetate, vinyl acetate, vinyl propionate, methyl acrylate, and methyl cinnamate with $RhCl(PPh_3)_3$ catalyst has been studied. The reaction is remarkably affected by the substituent on an olefinic carbon atom. The oxidation mechanism was discussed in connection with decarbonylation.

Recently we reported on the oxidation of olefins catalyzed by rhodium complexes to give carbonyl compounds.[1] Oxidation products could be classified into two types, the carbon-carbon double bond cleavage products and the noncleavage products. The carbonyl compounds formed by olefin oxidation underwent decarbonylation.

We investigated rhodium complex catalyzed oxidation of some vinyl esters bearing a carbonyl group in connection with decarbonylation reaction. It was found that the formation of two type oxidation products is greatly affected by the site of the carbonyl group on olefins.

In this paper the oxidation of vinyl esters is described and discussed in relation to the substituent effect of olefins.

Results and Discussion

The olefin oxidation catalyzed by rhodium complex was carried out by heating mixtures of the reactant vinyl ester and the rhodium complex in toluene or ethanol for 8 hr under a constant bubbling of oxygen. The results are summarized in Table 1, showing that $RhCl(PPh_3)_3$ complex is a good catalyst.

Oxidation of Styryl Acetate. Heating of styryl ace-

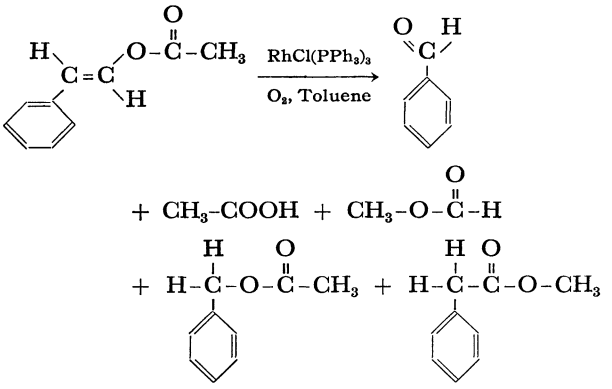
1) a) K. Takao, Y. Fujiwara, T. Imanaka, and S. Teranishi, This Bulletin, **43**, 1153 (1970); b) K. Takao, M. Wayaku, Y. Fujiwara, T. Imanaka, and S. Teranishi, *ibid.*, **43**, 3898 (1970); c) K. Takao, M. Wayaku, Y. Fujiwara, T. Imanaka, and S. Teranishi, *ibid.*, **45**, 1505 (1972).

Table 1. Oxidation of vinyl esters by $RhCl(PPh_3)_3$

Olefin	Solvent	Oxidation products: C=C bond cleavage	Oxidation products: Noncleavage	Decarbonylation products
Styryl acetate[b]	Toluene	Benzaldehyde (403%)[a]	Benzyl acetate (10%)	
		Acetic acid (240)	Methyl phenylacetate (trace)	
		Methyl formate (157)		
	Ethanol	Benzaldehyde (trace)	Benzyl acetate (56)	Benzyl methyl ketone (29%)
			Methyl phenylacetate (trace)	
Vinyl acetate[c]	Toluene		Methyl acetate (24)	Acetone (93)
				Propionaldehyde (15)
				Methyl vinyl ether (trace)
	Ethanol		Methyl acetate (238)	Acetone (110)
				Propionaldehyde (trace)
				Methyl vinylether (trace)
Vinyl propionate[c]	Toluene		Ethyl acetate (91)	Methyl ethyl ketone (83)
			Methyl propionate (trace)	Ethyl vinyl ether (10)
				Butyraldehyde (5)
Methyl cinnamate[b]	Toluene	Benzaldehyde (125)	Methyl phenylacetate (20)	
		Methyl formate (110)		
	Ethanol	Benzaldehyde (5)	Methyl phenylacetate (93)	
		Methyl formate (trace)		
Methyl acrylate[c]	Toluene		Methyl acetate (315)	
	Ethanol		Methyl acetate (837)	

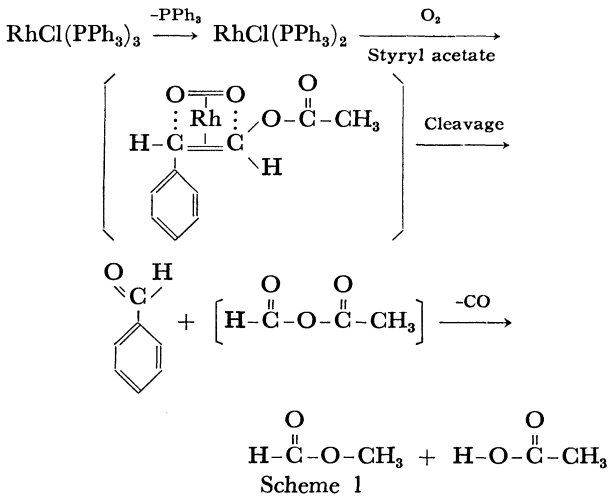
a) Yields are based on the catalyst utilized.
b) Olefin (30 mmol), $RhCl(PPh_3)_3$ (1.3 mmol), Reaction temp. 80°C, Reaction time 8 hr.
c) Olefin (60 mmol), $RhCl(PPh_3)_3$ (1. 3mmol),Reaction temp. 70°C, Reaction time 8 hr.

tate (*cis* and *trans* mixture) in toluene gave benzaldehyde (403%),[2] acetic acid (240%), and methyl formate (157%) as the main product with benzyl acetate (10%), and methyl phenylacetate (trace).



The formation of these oxidation products might be explained in the following way: The main products such as benzaldehyde, acetic acid and methyl formate are derived from the double bond cleavage of styryl acetate. Presumably a four-center intermediate in which both oxygen molecule and olefin coordinate to rhodium(I) is formed as shown in scheme 1.

The cleavage of C=C and O=O bonds of the intermediate would give benzaldehyde and acid anhydride of formic and acetic acids. This four-center type intermediate has been proposed in the reaction of singlet oxygen molecule and indene.[3] The acid anhydride of



Scheme 1

formic and acetic acids formed would undergo decarbonylation by the rhodium complex to give acetic acid and methyl formate. From the solid phase of the reaction mixture, $RhCl(CO)(PPh_3)_2$ and unidentified complexes (ν_{CO}: 2055 cm^{-1}) were obtained. We confirmed that acid anhydrides, such as acetic anhydride could be easily decarbonylated to give ester compounds by $RhCl(PPh_3)_3$.[4]

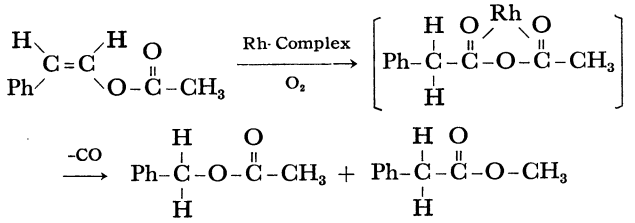
The formation of a small amount of benzyl acetate and methyl phenylacetate classified as the noncleavage oxidation products might take place in the following way: the addition of oxygen to bond of styryl acetate followed by a hydrogen shift would give an anhydride of acetic and phenylacetic acids. The anhydride would be further decarbonylated to benzyl ace-

2) Yields of the oxidation products which appear hereafter in this paper are all based on the amount of the complexes used.

3) W. Fenical, D. R. Kearns, and P. Radlick, *J. Amer. Chem. Soc.*, **91**, 3396 (1969).

4) J. Blum and Z. Lipshes, *J. Org. Chem.*, **34**, 3076 (1969).

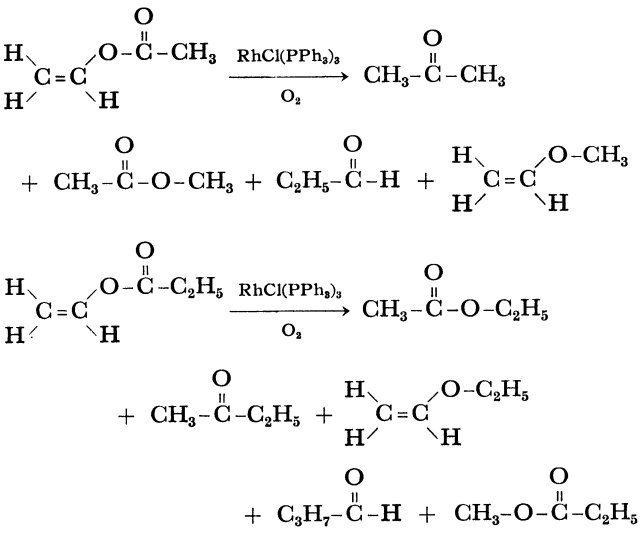
tate and methyl phenylacetate as shown below.



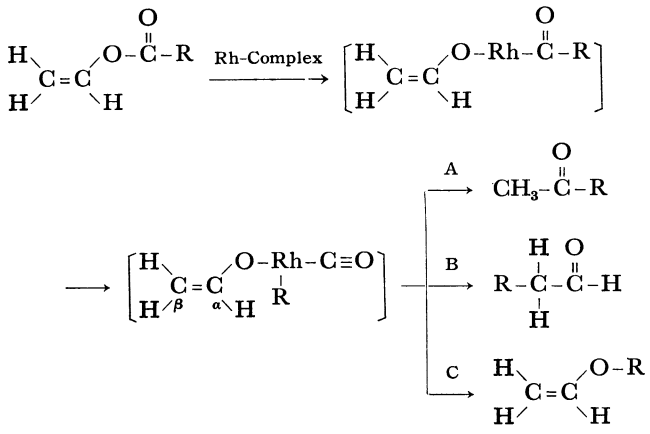
Scheme 2

Table 1 also shows that the oxidation of styryl acetate undergoes a similar remarkable solvent effect as styrene.[1b] In ethanol solvent, the double bond cleavage hardly takes place at all.

Oxydation of Vinyl Acetate and Propionate. In the oxidation of vinyl acetate and propionate in toluene, no double bond cleavage products were obtained. However, acetone (93%) and methyl ethyl ketone (83%) were obtained in marked contrast to the case of styryl acetate.



The products acetone, propionaldehyde and methyl vinyl ether from vinyl acetate, and methyl ethyl ketone, butyraldehyde and ethyl vinyl ether from vinyl propionate might be explained in terms of decarbonylation of the starting vinyl carboxylates as shown in scheme 3.



Scheme 3

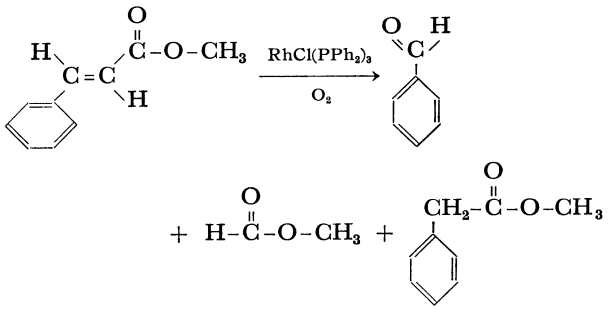
Presumably vinyl propionate is added oxidatively to the rhodium complex $RhCl(PPh_3)_2$ forming a vinyloxy acyl-rhodium complex. The acyl complex would then be converted into an alkyl carbonyl complex through acyl-alkyl rearrangement.[5] The decomposition of the complex followed by the recombination of the ligands would give the products.[6]

Ethyl acetate and methyl propionate may be derived from the noncleavage oxidation of vinyl propionate. Similarly methyl acetate from vinyl acetate as in the case of styryl acetate oxidation.

It should be noted that styryl acetate undergoes oxidation with the C=C bond cleavage, but not vinyl acetate or vinyl propionate. It might be that styryl acetate having an electron withdrawing phenyl group can form more easily the four-center intermediate described above than vinyl carboxylates.[7]

Oxydation of Methyl Cinnamate and Acrylate. Methyl cinnamate and acrylate were chosen as the reactant in order to investigate the conjugation effect between the C=C and C=O groups on oxidation and decarbonylation.

Oxidation of methyl cinnamate in toluene gave benzaldehyde (125%), methyl formate (110%) and methyl phenylacetate (20%). In contrast to the oxidation of vinyl esters bearing no carbonyl group on an olefinic atom, no decarbonylation products was obtained. No C=C bond cleavage oxidation was observed in the case of methyl acrylate which has no phenyl group on the olefinic carbon atom.



The result suggests that the conjugation of the carbonyl group with the C=C bond prevents decarbonylation reaction.

In conclusion, vinyl esters undergo oxidation smoothly by the rhodium triphenylphosphine complex, and the product distribution is influenced by the substituent on olefins.

Experimental

Materials and Analysis. All the temperatures were uncorrected. The IR spectra were recorded on a JASCO IR-E spectrometer. The NMR spectra were measured on a Japan Electron Optics JNM-4H-100 spectrometer. Chemical shifts are given in τ units together with splitting patterns

5) R. J. Mawby, F. Basolo, and R. G. Peason, *J. Amer. Chem. Soc.*, **86**, 5043 (1964).

6) No reaction occurring in argon atmosphere in place of O_2 suggests that O_2 plays an important role. Details of the behavior, however, are not apparent yet.

7) M. S. Kharash, R. C. Seyler, and F. R. Mayo, *J. Amer. Chem. Soc.*, **60**, 882 (1938).

and relative integrated area. Vpc analysis was carried out with a Yanagimoto G-8 gas chromatograph using Apiezon-L, Silicone OV-17, diethyl phthalate columms. $PhCl(PPh_3)_3$ was prepared by the method of Osborn *et al.*[8] Styryl acetate (*cis* and *trans* mixture) was prepared according to the method of Semmler.[9] Vinyl acetate, vinyl propionate, methyl cinnamate, and methyl acrylate were of commercial grade and dried over anhydrous magnesium sulfate and distilled before use. Toluene and ethanol were purified as mentioned previously.[1]

Oxidation of Styryl Acetate. In a flask described previously,[1] was charged a mixture of 1.21 g (1.3 mmol) of $RhCl(PPh_3)_3$, 4.96 g (30 mmol) of styryl acetate (*cis* and *trans* mixture) and 75 m*l* of toluene. The mixture was heated at 80°C with a constant bubbling of oxygen for 8 hr. The resulting mixture was concentrated and the liquid phase was analyzed and isolated by vpc to give 0.555 g (403%) of benzaldehyde (I), 0.187 g (240%) of acetic acid (II), 0.122 g (157%) of methyl formate (III), 0.020 g (10%) of benzyl acetate (IV) and a trace of methyl phenylacetate (V). These compounds were identified by comparison with authentic samples. Compound I: IR (neat): 685, 744, 1200, and 1675 cm^{-1}; NMR (CCl_4): 0.15 (s, 1) and 2.10—2.70 (m, 5). Compound II: NMR (CCl_4): −1.35 (s, 1) and 7.90 (s, 3). Compound III: NMR (CCl_4): 1.92 (s, 1) and 6.23 (s, 3). Compound IV: IR (neat): 710, 765, 1240, 1380, and 1740 cm^{-1}; NMR (CCl_4): 2.73 (s, 5), 4.99 (s, 2), 7.99 (s, 3).

The residual solid material was chromatographed on a silica gel column (50 g). Elution with benzene (300 m*l*) gave dark brown carbonyl complexes. Separation of the complexes by column chromatography (silica gel, 15 g) gave $RhCl(CO)(PPh_3)_2$ (0.1 g) and unidentified complexes (ν_{CO}: 2055 cm^{-1}) (0.5 g). Further elution with ether (300 m*l*) gave triphenylphosphine oxide.

Oxidation of Vinyl Acetate. The same procedure was used as for styryl acetate. Reaction products were methyl acetate (VI), acetone (VII), propionaldehyde (VIII), and methyl vinyl ether (IX). These compounds were assigned by comparison of NMR spectra and retention times with those of authentic samples. Compound VI: NMR (CCl_4): 6.35 (s, 3) and 7.99 (s, 3). Compound VII: NMR (CCl_4): 7.94 (s).

Oxidation of Vinyl Propionate. The same procedure was used as above. Reaction products were ethyl acetate (X), methyl ethyl ketone (XI), ethyl vinyl ether (XII), butyraldehyde (XIII), and methyl propionate (XIV). The compounds were identified by a comparison of NMR and retention time with those of authentic samples. Compound X: NMR (CCl_4): 5.94 (q, 2), 8.05 (s, 3), and 8.77 (t, 3). Compound XI: NMR (CCl_4): 7.53 (q, 2), 7.87 (s, 3), and 8.95 (t, 3).

Reaction of Acetic Anhydride with Rhodium Complex. In a flask as described above was placed a mixture containing 0.61 g (0.65 mmol) of $RhCl(PPh_3)_3$, 6.12 g (60 mmol) of acetic anhydride and 50 m*l* of toluene. The reaction was carried out at 80°C with a constant bubbling of oxygen for 8 hr. The resulting reaction mixture was treated as usual and the liquid phase was analyzed and separated by vpc to give 3.76 g (2.550%) of methyl acetate. The solid phase was chromatographed on silica gel (25 g) to give triphenylphosphine oxide and $RhCl(CO)(PPh_3)_2$ (0.40 g).

8) J. A. Osborn, F. H. Jardine, J. F. Young, and G. Wilkinson, *J. Chem. Soc., A*, **1966**, 1711.

9) F. W. Semmler, *Ber. Dtsch. Chem. Ges.*, **42**, 584 (1909).