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The Reaction Products of the Hydroformylation of Acrolein Acetals and Acetates*[1]

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The hydroformylation reactions of acrolein acetals and acetates were carried out in order to discuss the side reactions and any subsequent reactions. Acrolein cyclic acetals reacted with carbon monoxide and hydrogen in the presence of a dicobalt octacarbonyl catalyst to give *n*- and iso-aldehydes in a 2 : 1 ratio; they gave no further reaction products. Acrolein diethylacetal underwent hydroformylation using a rhodium catalyst to give *n*- and iso-aldehydes in a 1 : 2 ratio. In the presence of a cobalt catalyst, however, various products were obtained. As a result of the acidity of cobalt hydrocarbonyl and a high reaction temperature, *n*-aldehyde, first formed in benzene, underwent change to 2,5-diethoxytetrahydrofuran and 1,1,4-triethoxybutane. In ethanol, *n*- and iso-aldehydes gave the corresponding acetals. In the hydroformylation of acrolein acetate, only *n*-aldehyde was obtained. Iso-aldehyde seemed to be converted into 2-methyl-3-acetoxyacrolein by deacetylation. In ethanol, besides *n*-acetal, iso-acetal and propionaldehyde acetate, 2,5-diethoxytetrahydrofuran and 2-methyl-3-ethoxyacrolein were recognized. The former seemed to be formed from *n*-aldehyde by ring closure and ethanolysis. The latter seemed to be formed by the ethanolysis of 2-methyl-3-acetoxyacrolein. In ethyl orthoformate, no side reaction was observed and the yield of the main product, 1,1-diacetoxy-4,4-diethoxybutane, amounted to 80%.

Customarily hydroformylation is carried out using a cobalt carbonyl as the catalyst. The cobalt carbonyl shows an acidity under the reaction conditions.

In this case the aldehydes formed first undergo subsequent reactions to give various reaction products. It has been reported¹⁾ that acrolein diethylacetal absorbed 50—70% of the amount of hydrogen and carbon monoxide required for complete hydroformylation, but no aldehyde could be isolated from the reaction mixture. The present investigation of the hydroformylation of acrolein acetals and acrolein acetates was undertaken in order to confirm the by-products and propose a scheme for the subsequent reaction.

Results and Discussion

The Hydroformylation of Acrolein Cyclic Acetals. The treatment of acrolein cyclic acetals with hydrogen and carbon monoxide at 110°C and 200 atm in the presence of a cobalt carbonyl catalyst gave the usual hydroformylation products, *n*- and iso-aldehydes, in a 2 : 1 ratio. The results are summarized in Table 1. The hydroformylation products of acrolein cyclic acetals did not

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*[1] Presented in part at the 19th Annual Meeting of the Chemical Society of Japan, Yokohama, March, 1966.

1) H. Adkins and G. Krsek, *J. Am. Chem. Soc.*, **71**, 3051 (1949).

TABLE 1. THE HYDROFORMYLATION PRODUCTS OF ACROLEIN CYCLIC ACETALS

Acrolein cyclic acetal	Yield (%)	Bp °C/mmHg		Product Elementary analysis Found (%)	Product Elementary analysis Calcd (%)	G. C.* n : i	NMR n : i
2-Vinyl-4,4,6-trimethyl-1,3-dioxane	54.6	74—76/3	C H	64.35 9.87	64.49 9.74	2.18 : 1	2.34 : 1
2-Vinyl-4-methyl-1,3-dioxane	57.0	61—64/3	C H	60.61 9.11	60.74 8.92	2.01 : 1	2.00 : 1
2-Vinyl-1,3-dioxane	53.8	82/5	C H	57.93 8.52	58.31 8.39	—	2.25 : 1

* The ratios of normal aldehyde(*n*) and isomeric aldehyde(*i*) were measured by gas chromatographic (G. C.) and NMR analyses.

TABLE 2. THE HYDROFORMYLATION PRODUCTS OF ACROLEIN DIETHYLACETAL

	Reaction temperature	130°C				150°C			
	Solvent	Benzene		Ethanol		Benzene		Ethanol	
	Reaction time (hr)	1	2	1	2	1	2	1	2
Reaction products (mol%)	Acrolein acetal	62	35	62	28	1	1	0	0
	Propionaldehyde acetal	0	7	—	—	19	8	—	—
	2,5-Diethoxytetrahydrofuran	1	3	5	4	8	5	7	4
	1,1-Diethoxy-2-formylpropane	3	4	1	2	0	0	0	0
	1,1,4-Triethoxybutane	0	0	1	2	14	10	10	12
	1,1-Diethoxy-3-formylpropane	11	16	2	2	T	2	1	1
	1,1,3,3-Tetraethoxy-2-methylpropane	0	0	T	1	2	2	T	T
	1,1,4,4-Tetraethoxybutane	0	0	2	7	0	0	4	2
	X_1	0	0	T	+	+	+	+	++
	X_2	0	0	T	T	+	+	+	+
	X_3	0	0	+	+	0	+	++	+

Mol% of X_1, X_2 and X_3 were calculated by calibration curves of 2,5-diethoxytetrahydrofuran, 1,1,4-trithoxybutane and 1,1,4,4-tetraethoxybutane respectively.
+; 1—5 mol%, ++; 5—10 mol%, +++; 10—mol%, T; trace

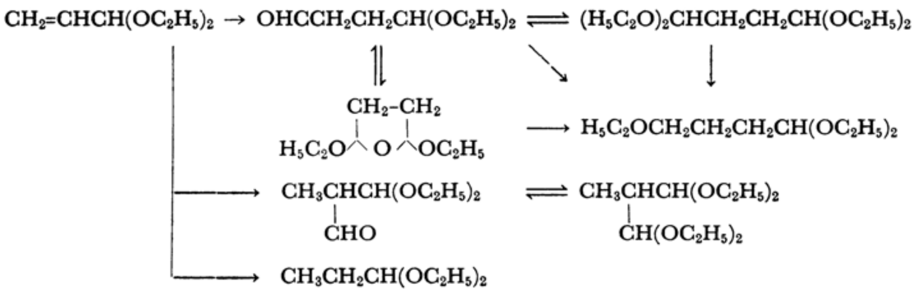
TABLE 3. THE SUBSEQUENT REACTION OF THE HYDROFORMYLATION PRODUCTS OF ACROLEIN DIETHYLACETAL

Starting material		2,5-Diethoxy-tetrahydrofuran	2,5-Diethoxy-tetrahydrofuran	1,1,4,4-Tetra-ethoxybutane	1,1,4,4-Tetra-ethoxybutane	1,1-Diethoxy-3-formylpropane
Reaction condition	Solvent	Ethanol	Ethanol	Ethanol	Benzene	Ethanol
	Temp. (°C)	150	130	150	150	150
	Time (hrs.)	2	2	2	2	2
Reaction products (mol%)	2,5-Diethoxytetra-hydrofuran	20	3	0	0	T
	1,1,4-Triethoxybutane	8	16	26	7	19
	1,1-Diethoxy-3-formyl-propane	2	1	1	2	2
	1,1,4,4-Tetraethoxy-butane	36	3	3	3	2
	X_1	+	T	+	+	+
	X_2	++	+	++	+	+
	X_3	0	+++	++	++	++

Measurements were similar to Table 2.

undergo any further, subsequent reaction because of their stability.

The Hydroformylation of Acrolein Diethylacetal. With a rhodium carbonyl catalyst, the hydroformylation of acrolein diethylacetal resulted in a mixture of aldehydes, *n*- and iso-aldehydes, in a 1 : 2 ratio. On the other hand, with a cobalt carbonyl catalyst various products were obtained.



Scheme I

Gas-chromatographic analysis showed 11 peaks. Eight of them were identified by mixed chromatography with authentic samples and by preparative chromatography. The results of gas chromatographs for various products obtained from acrolein diethylacetal by reactions at 130°C and 150°C with a cobalt carbonyl catalyst are given in Table 2. The yields of the products were calculated on the basis of the area of each peak in a gas chromatograph after a usual calibration using authentic samples.

In order to evolve a scheme consistent with all these observations, the present authors considered the possibility that 1,1-diethoxy-3-formylpropane and 1,1-diethoxy-2-formylpropane underwent subsequent reactions. To test this hypothesis, 1,1-diethoxy-3-formylpropane, 1,1,4,4-tetraethoxybutane, and 2,4-diethoxy-tetrahydrofuran were synthesized and then treated under the hydroformylation reaction conditions respectively. They were thus converted into several compounds, which were listed in Table 3.

These compounds were almost identical with the hydroformylation products of acrolein diethylacetal.

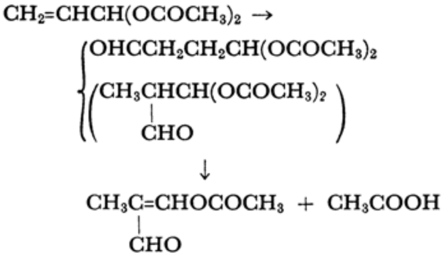
On the basis of these data, it seemed reasonable to assume that the hydroformylation products of acrolein diethylacetal were formed according to the scheme shown below (scheme I).

The Hydroformylation of Acrolein Acetates. It has previously been reported by Adkins[1] that acrolein acetate (1,1-diacetoxypropene) was converted to *n*-aldehyde (1,1-diacetoxy-3-formylpropane) alone by hydroformylation in benzene using a cobalt carbonyl catalyst. The present authors carried out the hydroformylation of acrolein acetate with a rhodium carbonyl catalyst in benzene. As the products, 2-methyl-3-acetoxyacrolein and acetic acid were obtained; iso-aldehyde with a branched chain structure could not be obtained. The NMR-spectrum analysis of the mixture of 2-methyl-3-acetoxyacrolein and acetic acid is shown in Table 4.

TABLE 4. NMR SPECTRUM OF THE MIXTURE OF 2-METHYL-3-ACETOXYACROLEIN AND ACETIC ACID

(TMS)	No. of H	Assignment
1.76	3.0	Methyl
2.04	1.5	Methyl of acetic acid
2.32	3.0	Methyl of ester
8.06	1.0	CH
8.54	0.5	H of acetic acid
9.50	1.0	H of aldehyde

The evidence thus obtained suggests that the isoaldehyde formed by the hydroformylation decomposed to 2-methyl-3-acetoxyacrolein and acetic acid.



In alcohol the yield of the *n*-aldehyde acetal did not exceed 50%.

The hydroformylations of various kinds of acrolein acetates were carried out in an alcohol solution with cobalt catalysts. The results are listed in Table 5. According to the reaction of acrolein acetates, the yields of the major products, 1,1-diacyloxy-4,4-dialkoxybutane, were 30—50%; the side reaction products were identified by gas-chromatographic and NMR spectra analyses. The results are given in Table 6.

On the basis of these data, it seemed reasonable to assume that the hydroformylation products of acrolein acetate formed first were *n*-aldehyde (1,1-diacetoxy-3-formylpropane, about 60%), iso-aldehyde (1,1-diacetoxy-2-formylpropane, about 5—10%), and propionaldehyde acetate (1,1-diacetoxypropane, about 5%). Then these aldehydes were converted to their acetals, and a part of the *n*-aldehyde was converted to 2,5-diethoxytetrahydrofuran (10%)[2] by the acidity of the cobalt catalyst, while the iso-aldehyde was decomposed to 2-methyl-3-acetoxyacrolein and acetic acid.

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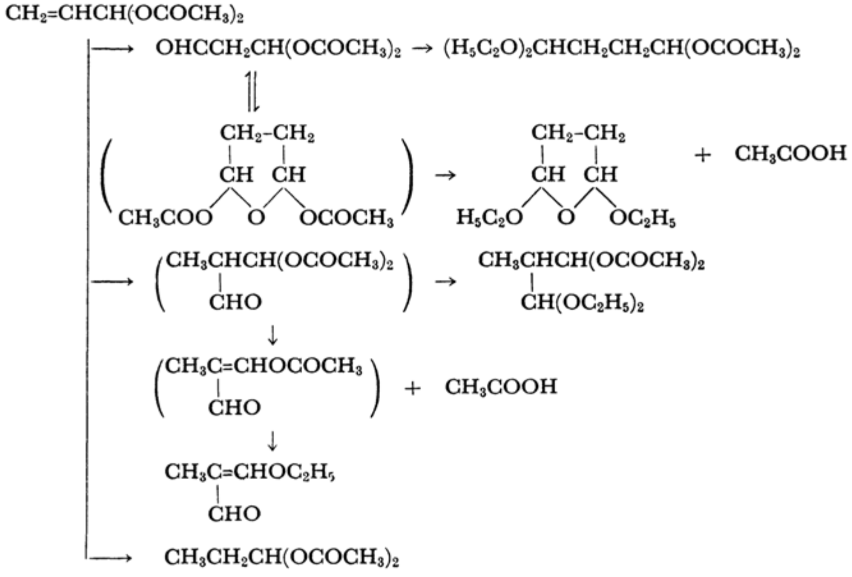
[2] W. R. Privette, H. W. Schulz and D. M. Yound, U. S. Pat. 2920081 (1960).



Scheme II

TABLE 5. THE HYDROFORMYLATION OF ACROLEIN ACETATES

$$CH_2=CHCH(OCOR)_2 \xrightarrow{R'OH} (R'O)_2CHCH_2CH_2CH(OCOR)_2$$

R	R′	Yield %	Concn. of $Co_2(CO)_8$ g/*l*	Bp °C/mmHg	Elementary analysis		Calcd %	Found %
CH_3	CH_3	44.6	4	119—120/5	$C_{10}H_{18}O_6$	C	51.27	51.60
						H	7.75	7.75
	C_2H_5	37.0	2	125—128/4	$C_{12}H_{22}O_6$	C	54.95	55.08
						H	8.45	8.53
	i-C_3H_7	34.8	3	130—132/3	$C_{14}H_{26}O_6$	C	57.91	57.53
						H	9.03	9.08
	C_4H_9	41.6	3	160—163/3	$C_{16}H_{30}O_6$	C	60.35	60.94
						H	9.50	9.79
C_2H_5	CH_3	36.2	3	128—130/3	$C_{12}H_{22}O_6$	C	54.95	55.01
						H	8.45	8.38
	C_2H_5	40.0	3	137—139/3	$C_{14}H_{26}O_6$	C	57.91	57.50
						H	9.03	9.00
	C_4H_9	46.3	3	160/1	$C_{18}H_{34}O_6$	C	62.40	62.38
						H	9.89	9.76
C_3H_7	CH_3	40.3	3	142—143/1	$C_{14}H_{26}O_6$	C	57.91	57.71
						H	9.03	8.97
	C_2H_5	49.3	3	153—156/3	$C_{16}H_{30}O_6$	C	60.35	60.81
						H	9.50	9.52

TABLE 6. THE HYDROFORMYLATION PRODUCTS OF 1,1-DIACETOXYPROPENE

Reaction product	Yield %
1,1-Diacetoxy-3-formylpropane	2.0
1,1-Diacetoxy-4,4-diethoxybutane	45.5
2,5-Diethoxytetrahydrofuran	10.3
1,1-Diacetoxy-2-methyl-3,3-diethoxypropane	0.8
2-Methyl-3-ethoxyacrolein	5—10
1,1-Diacetoxypropane	4.9

The overall reaction scheme may be illustrated as follows (Scheme II).

To prevent these side reactions and to promote the formation of 1,1-diacetoxy-4,4-diethoxybutane (I), the hydroformylation was carried out in the presence of ethyl orthoformate instead of ethanol. In these cases the formation of 1,1-diacetoxy-3-formylpropane, 2,5-diethoxytetrahydrofuran, 2-methyl-3-ethoxyacrolein and acetic acid were not seen, while 1,1-diacetoxy-2-methyl-2,3-diethoxypropane (II) and 1,1-diacetoxypropane were found as by-products. The presence of ethyl orthoformate was useful for the formation of I and II and reduced the formation of acetic acid. When ethyl orthoformate was used in excess to acrolein acetate, as shown in Table 7, the yield of main product, 1,1-diacetoxy-4,4-diethoxybutane, amounted to 80%.

TABLE 7. THE YIELD OF THE HYDROFORMYLATION PRODUCTS OF 1,1-DIACETOXYPROPENE IN THE PRESENCE OF ETHYL ORTHOFORMATE

Reaction temp.	110°C		130°C	
E. O/A. A*	I %	II %	I %	II %
0	37.7	1.6	36.5	—
0.5	55.4	3.0	56.9	1.3
1.0	68.6	5.4	69.7	2.0
1.0	—		74.2	2.9
1.2	75.0	6.3	76.0	2.7
1.4	—		78.6	3.0
1.5	—		80.0	3.9

* Mol ratio of ethyl orthoformate and acrolein acetate.

Experimental[*2]

Materials. These acrolein cyclic acetals (2-vinyl-4,4,6-trimethyl-1,3-dioxane, 2-vinyl-4-methyl-1,3-dioxane and 2-vinyl-1,3-dioxane) were prepared from acrolein and glycols according to the directions of Fischer and Smith.[3] The acrolein diethylacetal was prepared according to the procedures described in a previous paper.[4] These acrolein acetates (1,1-diacetoxypropene, 1,1-dipropoxypropene, and 1,1-dibutyroxypropene) were prepared from acrolein and acid anhydrides.[5] All of the above materials were shown by gas chromatographic analysis to have no impurity affecting the results.

Reaction Procedures. *(1) The Hydroformylation of Acrolein Cyclic Acetals.* Acrolein acetal (0.1 mol) and 9 m*l* of a dicobalt octacarbonyl solution in benzene (containing 17.8 g/*l* as cobalt) were put into an autoclave with a 100 m*l* capacity and equipped with a magnetic stirrer. Benzene was added until it filled half of the vessel. Hydrogen and carbon monoxide mixture (1 : 1) were then introduced to 200 kg/cm², using a compressor, after the air in the alutoclave had been replaced with their gases. The autoclave was kept at 110°C by electrical heating for about one hour, and then after the gauge pressure ceased to decline, it was chilled. The gas mixture was purged, and the carbonyl catalyst was decomposed by triphenylphosphine. The filtrate of the reaction mixture was distilled under reduced pressure. The analyses of the ratio of *n*- and iso-aldehydes were carried out on the reaction mixture by gas chromatography and NMR spectra.

(2) The Hydroformylation of Acrolein Diethylacetal. (a) With a rhodium carbonyl catalyst in benzene. Acrolein diethylacetal (39.0 g, 0.3 mol), rhodium oxide (129.6 mg, 0.5 g/*l* as Rh) and benzene (104 m*l*) were charged in a 300 m*l*, stainless-steel pressure reactor. The mixture was then treated in a manner similar to that used in the experiment described for (1) except that the reaction was carried out at 110°C for 30 min. After the solvent had been removed under reduced pressure, the mixture (29.9 g), consisting of 1,1-diethoxy-2-formylpropane (I) and 1,1-diethoxy-3-formylpropane (II), was distilled at 61—64°C/5 mmHg. Found: C, 60.00; H, 10.17%. Calcd for $C_8H_{16}O_3$: C, 59.98; H, 10.07%. The ratio of I and II was determined to be 1.82 : 1 by using the integral of the NMR spectra ($CHCl_3$); CHO, 0.40 τ. I and II were separated by preparative gas chromatography. I; n_D^{25} 1.4178, II; n_D^{25} 1.4167.

(b) With a cobalt carbonyl catalyst in benzene or ethanol. The method used here was virtually identical with that described for (a), but acrolein diethylacetal (13.0 g, 0.1 mol) and dicobalt octacarbonyl (4 g/*l* as cobalt) in benzene (or ethanol) were charged in a 100 m*l* autoclave. The benzene (or ethanol) was added until it filled half of the vessel. The reaction was carried out at 130°C (or 150°C) for one hour (or two hours).

(3) The Hydroformylation of Acrolein Acetates. (a) With a rhodium carbonyl catalyst in benzene or ethanol. Rhodium oxide (260 mg, 1 g/*l* as Rh), 1,1-diacetoxypropene (47.4 g, 0.3 mol), and 105.6 m*l* of benzene (or ethanol) were put into a 300 m*l*, stainless-steel autoclave. The reaction was similar to that described for (1), but the reaction temperature was kept at 100°C. The reaction mixture was filtered and diluted with benzene (or ethanol) to 200 m*l*, then the aldehydes were distilled

TABLE 8. THE HYDROFORMYLATION PRODUCTS OF 1,1-DIACETOXYPROPENE WITH COBALT CARBONYL IN ETHANOL

Fraction of the distillate	Weight	Substance	Weight calcd by gas chro. anal.	
I 26—62°C/5 mmHg	11.3 g	Acetic acid 2,5-Diethoxytetrahydrofuran	 6.4 g	6.6 g
II 62—95°C/5 mmHg	7.4 g	2,5-Diethoxytetrahydrofuran 2-Methyl-3-ethoxyacrolein Propionaldehyde acetate	0.2 g 2.4 g	
III 95—123°C/5 mmHg	2.8 g	Propionaldehyde acetate	1.1 g	3.5 g
IV 123—131°C/5 mmHg	49.9 g	1,1-Diacetoxy-4,4-diethoxybutane	47.7 g	

[*2] All boiling points are uncorrected.

[3] R. F. Fischer and C. W. Smith, *J. Org. Chem.*, **25**, 319 (1960).

[4] J. A. Van Allen, *Organic Syntheses*, **32**, 5 (1952).

[5] C. W. Smith, U. S. Pat. 2483852 (1949).

and analysis of the reaction products will be described in analytical procedures.

(b) With a cobalt carbonyl catalyst in ehtanol. A dicobalt octacarbonyl solution in ethanol (2—4 g/*l* as cobalt) and 1,1-diacyloxypropene (0.1 mol) were put into a 100 m*l* autoclave. The reaction was carried out according to the procedure described for (1), except that the reactor was kept at 110°C for 15 min after the gauge pressure ceased to decline. The contents of the autoclave were then filtered and diluted with ethanol to 100 m*l*. The distillation and analysis of aldehyde acetals and other reaction products will be described below.

(c) With a cobalt carbonyl catalyst in ethyl orthoformate. The method used here was identical with that described for (b), but ethyl orthoformate was added (0.5, 1, 1.1, 1.2, 1.4 and 1.5 mol per mol of 1,1-diacetoxypropene).

Analytical Procedures. *(1) The Hydroformylation of Acrolein Acetals.* (a) Authentic-sample preparation. The 2,5-diethoxy-tetrahydrofuran was prepared by the bromination of furan and its reduction.6) (Found: C, 60.05; H, 10.24%). By the Grignard reaction of acetylene and ethyl orthoformate,7) 1,1,4,4-tetraethoxybutyne-2 was prepared; it was then reduced to 1,1,4,4-tetraethoxybutane.8) (Found: C, 61.51; H, 11.00%). Propionaldehyde diethylacetal was prepared using the technique for acrolein acetal. 1,1-Diethoxy-2-formylpropane and 1,1-diethoxy-3-formylpropane were separated by preparative gas chromatography (the column packed with 10% Carbowax 20M coated on Diasolid M at 100°C) from their mixture prepared by the hydroformylation of acrolein diethylacetal with a rhodium carbonyl catalyst. From 1,1-diethoxy-2-formylpropane and ethyl orthoformate, 1,1,3,3-tetraethoxy-2-methylpropane was prepared. Found: C, 61.44; H, 11.19%. Calcd for $C_{12}H_{26}O_4$: C, 61.50; H, 11.18%. By preparative gas chromatography, 1,1,4-triethoxybutane was separated from the hydroformylation solution of acrolein diethylacetal with a cobalt carbonyl catalyst. The structure of 1,1,4-triethoxybutane was established by its IR and NMR spectra. Found: C, 63.08; H, 11.23%. Calcd for $C_{10}H_{22}O_3$: C, 63.01; H, 11.58%. n_D^{25} 1.4124.

(b) Gas chromatography was carried out with 5% carbowax 6000 on Diasolid M (4 mmϕ × 3 m; column temperature, 95°C; flow rate of He, 80 m*l*/min; internal standard, acetophenone). The individual peaks were identified by a comparison of their retention times with those of authentic samples. The low-boiling substances, propionaldehyde diethylacetal and acrolein diethylacetal, were analyzed with 20% β,β'-oxydipropionitrile on chromosorb W (4 mmϕ × 2 m; column temperature, 70°C; flow rate of He, 80 m*l*/min; internal standard, *n*-butanol).

(2) The Hydroformylation of Acrolein Acetates. The separation and identification of reaction products were performed by distillation and by gas chromatographic and NMR spectra analyses. The gas chromatography was carried out with 5 % polyethylene glycol 4000 on chromosorb T (4 mmϕ × 2 m; column temperature, 150°C; flow rate of He, 75 m*l*/min; internal standard, diethyl adipate).

(a) With a rhodium carbonyl catalyst in benzene. After the benzene had been removed, the reaction mixture was distilled under reduced pressure. By fractionating low-boiling fractions collected from several runs (bp 33—61°C/5 mmHg), the following compounds were isolated and identified. Gas chromatography showed two kinds of compounds; their NMR spectra showed that they were acetic acid and 2-methyl-3-acetoxyacrolein, is shown in Table 4. The next boiling fractions (bp 61—113°C/5 mmHg) were mixtures of acetic acid, 2-methyl-3-acetoxyacrolein and 1,1-diacetoxy-3-formylpropane. The only high-boiling fraction (bp 113—114°C/5 mmHg) was 1,1-diacetoxy-3-formylpropane. In gas chromatographic analysis, 1,1-diacetoxy-2-formylpropane was not found.

(b) With a rhodium carbonyl catalyst in ethanol. Five compounds were found in the distillate by gas-chromatographic analysis. In the fractions of the distillate, the following compounds were identified: Bp 54—117°C/7 mmHg, a mixture of acetic acid, 2-methyl-2-acetoxyacrolein, an unknown substance, 1,1-diacetoxy-2-formylpropane, and 1,1-diacetoxy-3- formylpropane; bp 118—124°C/7 mmHg, a mixture of 1,1-diacetoxy-2-formylpropane and 1,1-diacetoxy-3- formylpropane. Found: C, 50.67; H, 6.54%. Calcd for $C_8H_{12}O_5$: C, 51.06; H, 6.43%.

(c) With a cobalt carbonyl catalyst in ethanol. After the hydroformylation of 1,1-diacetoxypropene (0.4 mol), the reaction mixture was distilled. In the fractions of the distillate, the compounds as shown in Table 8 were identified and quantified by gas-chromatographic and NMR spectra analyses.

(d) With a cobalt carbonyl catalyst in ethyl orthoformate. After the hydroformylation of 1,1-diacetoxypropene (0.1 mol), the 1,1-diacetoxy-4,4-diethoxybutane and 1,1-diacetoxy-2-methyl-3,3-diethoxypropane were analyzed by gas chromatography. Gas chromatography was carried out with 5% carbowax 20 M on chromosorb T (4 mmϕ × 2 m; column temperature, 165°C; flow rate of He, 75 m*l*/min; internal standard, dimethyl terephthalate).

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6) J. Fakstorp, D. Raleigh and L. E. Schniepp, *J. Am. Chem. Soc.*, **72**, 869 (1950).

7) K. Henkel, *Ber.*, **76B**, 812 (1943).

8) A. Wohol and U. B. Mylo, *Ber.*, **45**, 839 (1912).