possibly account for the difference in reactivity between I and II. However, it is noteworthy that if I is a mixture of *exo*- and *endo*-forms, these must have very similar solvolytic rate constants since the solvolysis of I follows the first-order rate law to well over 90% reaction as shown by Fig. 1.

Further experiments are in progress on the determination of the mechanisms of displacement reactions of norbornyl derivatives.

Acknowledgment.—We are indebted to Dr. R. C. Lord, Jr., and Mr. R. S. McDonald for the infrared determinations.

Experimental

Chlorination of Bicyclo[2,2,1]heptane.—A mixture of 48 g. of bicyclo[2,2,1]heptane,[11] 34 g. of sulfuryl chloride, 0.25 g. of benzoyl peroxide and 40 ml. of methylene chloride was refluxed (about five hours) until no further loss of weight was observed. The mixture was filtered and fractionally distilled through a 30-cm. Vigreux column. The yield of monochloride, b. p. 88–89° (74 mm.), was 23 g. (70% based on sulfuryl chloride). The weight of dichloride, b. p. 122–123° (75 mm.), was 4 g.

Anal. Calcd. for $C_7H_{10}Cl_2$ (dichloride): C, 50.93; H, 6.10. Found: C, 51.47; H, 6.27.

The monochloride (20 g.) was refluxed for five hours with a mixture of 50 ml. of water, 50 ml. of acetone and 50 g. of sodium carbonate. The recovered chloride amounted to 5 g., b. p. 79° (46 mm.).

Rate Determinations.—Weighed samples (0.5–1 g.) of the chlorides were made up to 50.0 ml. with aqueous alcohol (80% alcohol and 20% water by volume) at room temperature. Five-milliliter samples were sealed in soft glass test-tubes and heated in a thermostat at 85.0 ± 0.1°. The reaction rate was followed by titration of the liberated acid with standard alkali.

Summary

The peroxide-catalyzed chlorination of bicyclo-[2,2,1]heptane with sulfuryl chloride was found to give norbornyl chloride as the principal monochlorination product.

Norbornyl chloride solvolyzes in 80% ethanol at 85° nine times faster than cyclopentyl chloride.

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pentachloride. The properties b. p. 66–67° (25 mm.), m. p. −5° of the chloride prepared by Komppa and Beckman are very similar to those obtained in the present work.

[11] The bicyclo[2,2,1]heptane was prepared by low-pressure hydrogenation in acetic acid over platinum oxide of bicyclo[2,2,1]2-heptene made by the method of Joshel and Butz, THIS JOURNAL, **63**, 3350 (1941), as modified by Thomas, *Ind. Eng. Chem.*, **36**, 310 (1944). The low pressure hydrogenation process is somewhat more convenient than that described by Thomas and gives no methylcyclohexane.

[A COMMUNICATION FROM THE LABORATORY OF ORGANIC CHEMISTRY OF THE UNIVERSITY OF WISCONSIN]

Hydroformylation of Unsaturated Compounds with a Cobalt Carbonyl Catalyst

BY HOMER ADKINS AND GEORGE KRSEK[1]

Dicobalt octacarbonyl, $Co_2(CO)_8$, proved to be quite effective and useful[2] in catalyzing the formation of aldehydes through the addition of carbon monoxide and hydrogen (H_2CO) to alkene linkages. The present paper is concerned with improvements in the method and a survey of the usefulness and of the limitations of the hydroformylation reaction. The use of a soluble cobalt catalyst was developed from the earlier work[3–6] with a Fischer–Tropsch type of insoluble catalyst. Two publications on the use of the insoluble catalyst have appeared recently.[7,8]

The hydroformylation reaction has given good results with unsaturated compounds of quite diverse structures. Hydrocarbons of the types $RCH{=}CH_2$ and $RCH{=}CHR$, allyl ethers, α,β-unsaturated esters such as acrylates, crotonates and fumarates, and allyl and vinyl acetates and allylidene diacetate added the elements of formaldehyde in good to fair yields. A summary of the numerical results is given in Table I.

The yields of aldehydes reported in the tables are based upon distillation of the reaction mixtures, titration with hydroxylamine hydrochloride, determination of refractive indices, and the chromatographic separation of 2,4-dinitrophenylhydrazones, as described in the experimental part of this paper. Since it is difficult to isolate an aldehyde without considerable loss, the yields in Table I should be interpreted in consideration of the more detailed results given in the experimental part for representative syntheses.

The reactions were run at 120–125° in benzene, under a pressure of 100–150 atm. of hydrogen and 100–150 atm. of carbon monoxide, as measured at 23°. These conditions differ from those used earlier with dicobalt octacarbonyl, in that benzene rather than ether was the reaction medium, the total pressure was lower, and the ratio of carbon monoxide to hydrogen was 1:1 instead of 2:1. Benzene was chosen as the reaction medium after a comparison of several liquids. The hydroformylation of methyl undecylenate went twice as rapidly in benzene or methylcyclohexane as in diethyl ether and three times as rapidly as in methyl formate. The reaction went as rapidly

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[1] Socony-Vacuum Oil Co. Fellow, July, 1947–November, 1948.

[2] Adkins and Krsek, THIS JOURNAL, **70**, 383 (1948).

[3] Smith, Hawk and Golden, *ibid.*, **52**, 3221 (1930).

[4] Mittasch, Winkler and Urban, German Patent 539,900, *C. A.*, **26**, 2197 (1932).

[5] Otto Roelen, U. S. Patent 2,327,066 (1943).

[6] FIAT Final Report 1000. The Oxo Process. Issued by the Office of Military Government for Germany, through the Office of Technical Services of the U. S. Department of Commerce, PB81383.

[7] Keulemans, Kwantes and Van Bavel, *Rec. trav. chim.*, **67**, 299 (1948).

[8] Gresham, Brooks and Bruner, U. S. Patent 2,437,600 (1948).

in acetone as in benzene, but the yield of aldehyde isolated was lower, presumably due to condensation. The hydroformylation reaction proceeds well in a mixture of benzene and ethanol but the acetal of the aldehyde may be the chief product, as described later in the hydroformylation of ethyl acrylate.

The catalyst for hydroformylation is apparently not poisoned by sulfur compounds, as would be true of a catalytic metal such as cobalt. The reaction of carbon monoxide and hydrogen went almost as rapidly and gave approximately the same yield of aldehyde when diphenyl sulfide was present as when it was not.

The rate of reaction and temperatures required for hydroformylation, as shown by the data in Table I, are quite dependent upon the amount and ratio of catalyst to unsaturated compound. However, the yield of aldehyde isolated was usually about the same in a rapid reaction as in a slow one.

In several cases the compounds are unsymmetrically substituted derivatives of ethylene so that, depending on the direction of addition, there was a possibility of two isomeric aldehydes being produced. In four compounds of the type $RCH=CH_2$ where R was $—CO_2C_2H_5$, $—CH_2O_2CCH_3$ and $—CH(O_2CCH_3)_2$, addition of —CHO went exclusively to the terminal carbon, with the production of aldehydes of the type RCH_2CH_2CHO. In the case of two alkenes $(C_2H_5)_2C=CH_2$ and $C_2H_5C(CH_3)=CH_2$ addition of —CHO was also exclusively to the terminal carbon. In ethyl crotonate the addition of —CHO was apparently exclusively to the carbon carrying the methyl group rather than to the one adjacent to a carbethoxy group.

In contrast with these results four alkenes of the type $RCH=CH_2$, where R was phenyl, or α-naphthyl, or ethoxymethyl, or *n*-butoxy, showed addition of —CHO on the substituted carbon atom. The aldehydes isolated in good yields were of the structure $RCH(CH_3)CHO$. It is probable that the isomeric aldehydes, RCH_2CH_2CHO, were also produced, but with one exception they were not isolated. The absorption of hydrogen and carbon monoxide in the hydroformylation indicated a much higher yield of aldehyde than the 29–31% actually isolated in the four cases just mentioned.

Derivatives of ethylene of the type $RCH=CH_2$, where R was $n\text{-}C_4H_9\text{-}$, $n\text{-}C_{16}H_{33}\text{-}$, $—(CH_2)_8CO_2CH_3$, $—CH_2OC_6H_5$, $—CH_2OC_2H_5$ and $—O_2CCH_3$, all gave mixtures of aldehydes of the types RCH_2CH_2CHO and $RCH(CH_3)CHO$. The alkene $C_2H_5CH=CHCH_3$ also gave a mixture of $C_2H_5CH_2CH(CH_3)CHO$ and $(C_2H_5)_2CHCHO$. It is possible that the starting materials in the case of the hydrocarbons and methyl undecylenate were not homogeneous with respect to the position of the double bond, or that migration of the double bond took place during reaction.[7] However, there can be no doubt that vinyl acetate and the allyl ethers underwent simultaneous addition of —CHO at both the terminal and the secondary carbon atom.

Certain α,β-unsaturated carbonyl compounds were reduced without hydroformylation, through the action of hydrogen in the presence of cobalt carbonyls. Crotonaldehyde and acrolein were reduced to butyraldehyde and propionaldehyde, respectively, while methyl vinyl ketone and mesityl oxide gave methyl ethyl ketone and methyl isobutyl ketone. Similarly ethyl cinnamate and ethyl β-(2-furan)-acrylate gave ethyl β-phenylpropionate and ethyl β-(2-furan)-propionate. The yields with the aldehydes were 40–50% while with the ketones and esters they were in the range 70–90%. Higher yields could no doubt be obtained if the optimum conditions for the hydrogenation and isolation of the products were sought. The hydrogenation of the α,β-unsaturated carboxy compounds was apparently catalyzed by a compound soluble in benzene whose activity was not adversely affected by the addition of diphenyl sulfide (1.2 g.) to the cobalt carbonyl (1.6 g.).

Acrolein diethyl acetal, α-vinylfuran and acrylonitrile absorbed 50–75% of the amount of hydrogen and carbon monoxide required for complete hydroformylation. Apparently the desired reaction took place, but no aldehyde could be isolated from the reaction mixtures, although qualitative tests showed them to be present. It appeared that the aldehyde first formed underwent further reaction. 1,2-Dihydronaphthalene, 2-(4-methylphenyl)-propene-1,11-bromododecene-1, 5-bromo-pentene-1 and allyl chloride absorbed about 50% as much gas as required for complete hydroformylation but aldehydes were not found in the reaction mixture. In the case of the compounds containing a halogen, all of the cobalt present in the reaction mixture was converted to a cobalt halide. 1-Phenyl-butadiene-1,3, phenylacetylene, Δ^9-octalin, phenanthrene, furan and acetonylacetone did not react at an appreciable rate when exposed to carbon monoxide and hydrogen at 125° with dicobalt octacarbonyl in benzene.

Experimental Part

Attention is again called to the precautions necessary in handling carbon monoxide and metal carbonyls. The methods described in the preceding paper[2] were in general followed except that dicobalt carbonyl was prepared in benzene rather than in ether. Some of the unsaturated compounds were obtained from commercial sources, *i. e.*, butyl vinyl ether, $n^{25}D$ 1.3991, and allylidene diacetate, $n^{25}D$ 1.4172, from Carbide and Carbon Chemicals Corporation; allyl alcohol and acrolein from Shell Chemical Company; vinyl acetate, $n^{25}D$ 1.3934, from the Niacet Company; and ethyl acrylate, $n^{25}D$ 1.4037, from the Rohm and Haas Company. Several compounds were made by dehydration of alcohols over various catalysts: cyclopentanol over sulfuric acid to cyclopentene $n^{25}D$ 1.4183; 2-(1-naphthyl)-ethanol over potassium hydroxide at 165° (16 mm.) to α-vinylnaphthalene,[9] $n^{25}D$ 1.6420; and β-decalol over zinc chloride at 180° to a mixture of

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[9] Cohen and Warren, *J. Chem. Soc.*, 1318 (1937).

TABLE I

HYDROFORMYLATION OF CARBON TO CARBON DOUBLE BONDS

Compounds	Time, min.	Comp. cat., g./g.		% yield of aldehyde	B. p. °C.	B. p. Mm.	M. p., °C.	$n^{25}_{\rm D}$
Allyl acetate	32	60	1.8	75 γ-Acetoxybutyraldehyde				
Allyl acetate	80	60	1.2	70 γ-Acetoxybutyraldehyde				
Allyl acetate	300	60	0.3	55 γ-Acetoxybutyraldehyde				
Butyl vinyl ether	105	25	0.6	31 α-Butoxypropionaldehyde	55	26	78–79[c]	1.4150
Cyclopentene	100	23	0.6	65 Cyclopentanealdehyde[16]	133–136	746	123–124[a]	1.4406
Ethyl crotonate	80	50	0.6	71 Ethyl β-formylbutyrate	58–59	0.01	67–68[c]	1.4236
Diethyl fumarate	12	35	1.6	51 Diethyl α-formylsuccinate[18]	104–105	0.04	100–101[b]	1.4486
2-Ethyl-butene-1	120	42	2.0	55 β-Ethylvaleraldehyde	50–51	20	139–140[a]	1.4135
Styrene	53	26	3.6	30 Hydratropaldehyde[19]	76–77	0.08	153–154[a]	1.5148
Allyl alcohol	60	29	2.2	18 γ-Hydroxybutyraldehyde[20]	98–99	35		1.4284
α-Vinylnaphthalene	100	31	0.6	29 α-(1Naphthyl)-propionaldehyde[21]	142–143	3	206–207[a]	1.6086
2-Methyl-butene-1	140	25	0.6	53 β-Methylvaleraldehyde[22]	35–36	28	126–127[a] 93–94[c]	
Ethylene	25	5.6	7.8	50 Propionaldehyde[23]	45–51	746	123–124[b]	1.3614
Ethylene[e]	30	5.6	21.0	62 Propionaldehyde				
Allylidene diacetate	10	51	2.7	75 Succindialdehyde-1,1-diacetate				
Allylidene diacetate	90	51	0.5	75 Succindialdehyde-1,1-diacetate	102–103	0.04		1.4030
Ethyl acrylate	16	65	1.2	74 β-Carbethoxypropionaldehyde				
Ethyl acrylate	150	65	0.3	74 β-Carbethoxypropionaldehyde				
Ethyl acrylate[d]	30	65	1.3	71 β-Carbethoxypropionaldehyde[18]	68–69	7	136.5–137.5[a]	1.4212
Vinyl acetate	15	43	4.2	30 α-Acetoxypropionaldehyde[15]	41–42	8	162–163[a]	1.4160
				22 β-Acetoxypropionaldehyde				
Hexene-1	15	20	2.4	32 *n*-Heptaldehyde				
				32 2-Methylhexaldehyde	38–39	9		1.4088–1.4100
Pentene-2	33	25	2.2	75 C_6 Aldehydes	28–29	10		1.4009
Methyl undecylenate	25	30	1.6	71 C_{13} Aldehydes	134	0.6		1.4432
Octadecene-1	15	62	2.1	54 C_{19} Aldehydes	40–65	1		
Octalins	120	26	2.4	32 C_{11} Aldehydes				
Allyl phenyl ether	50	50	0.6	50 C_{10} Aldehydes				
Allyl ethyl ether	40	15	0.6	30 β-Ethoxyisobutyraldehyde[17]	64–65	743	77–78[c]	1.3856
				6 Methylacrolein				
				4 γ-Ethoxybutyraldehyde	59–60	1	102–103[c]	1.4245

[a] Semicarbazone. [b] *p*-Nitrophenylhydrazone. [c] 2,4-Dinitrophenylhydrazone. [d] Reaction at 70° with hydrogen only. [e] 1.2 g. of diphenyl sulfide in reaction mixture.

octalins,[10] $n^{25}_{\rm D}$ 1.4926–1.4955. Hexene-1, $n^{25}_{\rm D}$ 1.3863, 2-methylbutene-1, $n^{25}_{\rm D}$ 1.3760, octadecane-1, $n^{25}_{\rm D}$ 1.4435, and 2-ethylbutene-1, $n^{25}_{\rm D}$ 1.3952, were made by the pyrolysis of the acetates of the corresponding primary alcohols as described by Marvel and his associates.[11] Hexene-1 was also made by the reaction of allyl chloride and *n*-propylmagnesium bromide[12] and by the dehydration of *n*-hexanol through the Tschugaev reaction. The products from all three preparations had the same refractive index. Methyl undecylenate, $n^{25}_{\rm D}$ 1.4381, ethyl crotonate, $n^{25}_{\rm D}$ 1.4230, diethyl fumarate, $n^{25}_{\rm D}$ 1.4395, and allyl acetate, $n^{25}_{\rm D}$ 1.4026, were prepared by esterification of the alcohols with the acids or acetic anhydride. Allyl phenyl ether, $n^{25}_{\rm D}$ 1.5181, was prepared from allyl bromide and phenol in the presence of potassium bicarbonate and allyl ethyl ether, $n^{25}_{\rm D}$ 1.3856, from ethyl bromide and the sodium alkoxide of allyl alcohol.[13]

The distillation of aldehydes was usually carried out in an atmosphere of hydrogen, even when distillations were made at low pressures. In most cases about 0.1 g. of hydroquinone was added to a mixture before distillation. All distillations were made at as low a pressure and as rapidly as was feasible. Some of the physical properties of the products obtained and of their derivatives are given in Tables I and II.

The estimation of aldehydes by titration[14] was made as follows. A freshly prepared 4% solution (4 ml.) of hydroxylamine hydrochloride and 3 drops of a methyl orange solution were placed in a 50-ml. Erlenmeyer and the solution made neutral with dilute sodium hydroxide. About 0.002 mole of aldehyde was added and the solution allowed to stand about fifteen minutes in a stoppered flask. The free acid was then titrated with 0.1 *N* sodium hydroxide solution. The per cent. of aldehyde in the sample is given by the expression ml. of base × *N* of base × mol. wt. of aldehyde × 100 divided by the weight of the sample. In order to secure accurate results with the hydroxylamine method it is necessary that hydroxylamine hydrochloride be in about a 20% molecular excess over the aldehyde, so that in the directions given above the size of the sample titrated is specified in terms of the amount of aldehyde added and *not* in terms of the weight of sample. Thus in order to secure good results several titrations may be necessary before the proper weight of sample is ascertained. The method has given accurate results with pure samples of propionaldehyde, butyraldehyde and acetone.

Chromatographic Separation of 2,4-Dinitrophenylhydrazones.—Sixty grams of acid-washed alumina (Merck No. 8R1605) was placed in an absorbent column containing 50 ml. of dry petroleum ether. A column 1.4 × 25 cm. with a 19/22 ground glass joint and fritted glass plate, as designed by Zechmeister and sold by Scientific Glass Apparatus Co., was used. The alumina was added slowly through a funnel and the column was tapped gently during

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(10) Hückel, *Ann.*, **543**, 210 (1910).

(11) Marvel, Myers and Saunders, THIS JOURNAL, **70**, 1695 (1948).

(12) Kazanski, Lieberman, Plate, Rosengart and Tarasova, *C. A.*, **42**, 2226 (1948).

(13) "Organic Reactions," Vol. II, John Wiley and Sons, Inc., New York, N. Y., 1944, p. 26.

(14) Halasz, *Ann. chim.*, **14**, 336 (1940).

(15) Nef, *Ann.*, **335**, 266 (1904).

(16) Braun, Anton, Keller and Manz, *Ber.*, **67B**, 223 (1934).

(17) Bruhl, *Ann.*, **200**, 178 (1879).

(18) Stolle and Bolle, *Helv. Chim. Acta*, **21**, 1551 (1938).

(19) Wooten, *J. Chem. Soc.*, 409 (1910).

(20) Paul and Tchelitcheff, *Bull. soc. chim.*, 201 (1948).

(21) Fieser, Joshel and Seligman, THIS JOURNAL, **61**, 2137 (1939).

(22) Levene, Rothen and Kuna, *J. Biol. Chem.*, **111**, 744 (1935).

(23) Bruhl, *Ann.*, **200**, 80 (1880).

TABLE II

ANALYSES OF ALDEHYDES AND DERIVATIVES

Mol. form.	Carbon, % Calcd.	Carbon, % Found	Hydrogen, % Calcd.	Hydrogen, % Found
α-Butoxypropionaldehyde[c]				
$C_7H_{14}O_2$	64.6	64.4	10.9	10.7
$C_{13}H_{18}N_4O_5$[a]	50.3	50.5	5.9	6.0
Ethyl β-formylbutyrate[d]				
$C_7H_{12}O_3$	58.3	58.5	8.4	8.5
$C_{13}H_{16}N_4O_6$[a]	48.1	47.9	5.0	5.2
β-Ethylvaleraldehyde[e]				
$C_7H_{14}O$	73.6	73.4	12.4	12.6
$C_8H_{17}N_3O$[b]	57.4	57.2	10.0	10.0
Succindialdehyde-1,1-diacetate				
$C_8H_{12}O_5$	51.1	51.0	6.4	6.6
γ-Acetoxybutyraldehyde[f]				
$C_6H_{10}O_3$	55.4	55.4	7.8	8.0
$C_{12}H_{14}N_4O_6$[a]	46.4	46.1	4.6	4.7
γ-Acetoxybutyric acid				
$C_6H_{10}O_4$	49.3	49.3	6.7	7.1
β-Ethoxyisobutyraldehyde				
$C_{12}H_{16}N_4O_5$[a]	48.7	48.9	5.4	5.4

[a] 2,4-Dinitrophenylhydrazone. [b] Semicarbazone. [c] The aldehyde was converted by hydrogenation to 2-butoxypropanol-1, $n^{25}D$ 1.4184, b. p. 81° (24 mm.). [d] The aldehyde was converted by oxidation with air to monoethyl α-methylsuccinate. [e] The aldehyde and its derivatives were also prepared by a Grignard synthesis from 2-ethylbutanol-1 and orthoformic ester. [f] The aldehyde was converted by air oxidation to γ-acetoxybutyric acid, b. p. 113° (1 mm.), $n^{25}D$ 1.4343, and its lactone.

this addition. The hydrazone(s) (240 mg.) in petroleum ether (400 ml.) was passed into the column under a positive pressure of about 0.1 atm. The band of the absorbed hydrazone was 30–60 mm. in length depending upon the compound(s). Usually the band was developed with a solution of dry benzene in petroleum ether passed into the column under a pressure of 0.1 atm. The volume of solvent was 4–7 l. in most cases containing about 10% of benzene. However, there was considerable variation in the ratio of the solvents depending upon the solubility of the hydrazones. Petroleum ether (6 l.) without benzene was used with the hydrazone of γ-acetoxybutyraldehyde, while a solution (5 l.) containing 20% benzene was used with the hydrazone of α-butoxypropionaldehyde. The petroleum ether had a boiling range of 60–68°. The band was in most cases spread over almost all the length of the column. The column of alumina was removed from the tube and in most instances cut into five or six sections. Each section was extracted with diethyl ether and the 2,4-dinitrophenylhydrazone recovered for determination of m. p. and analysis where necessary. The weight of hydrazone recovered was usually of the order of 85–90% of that placed on the column.

Air Oxidation of Aldehydes.—Aldehydes were in several cases oxidized with air to the corresponding acids. A typical procedure was as follows: γ-acetoxybutyraldehyde (29.2 g., 94% pure) and 0.2 g. of manganese dioxide or cobalt acetate was placed above a fritted glass plate sealed in a U-tube so that air could be blown up through the plate and the sample of aldehyde. The U-tube was held in an oil-bath at 65 ± 5° and was provided with a reflux condenser. Air was passed in rapidly for a period of twenty-four hours. The crude acid (31 g.) after the removal of the manganese dioxide showed a neutral equivalent of 142. After fractionation γ-acetoxybutyric acid (25.5 g., b. p. 111–113° (1 mm.), $n^{25}D$ 1.4343) was obtained having a neutral equivalent of 144 and a saponification equivalent of 145. The calculated values for the pure acetoxy acid are 146.

Ethyl β-Formylbutyrate.—In a representative experiment 50 g. of ethyl crotonate and 0.6 g. of dicobalt octacarbonyl in 70 ml. of benzene were placed in a chrome vanadium steel reaction vessel having a void of 270 ml. Carbon monoxide was added to a pressure of 1800 p. s. i. and hydrogen to a total pressure of 3600 p. s. i. After shaking for one minute the total pressure was 3500 p. s. i. at 23°. The vessel with rocking was heated within twenty minutes to 125° and 4600 p. s. i. During eighty minutes with rocking, the pressure decreased to 2200 p. s. i. at 125°. The vessel was then allowed to cool to 23° when the pressure was 1600 p. s. i. The gases were then burned by releasing them through a Bunsen burner. The contents and washings of the reaction vessel were transferred to a 250-ml. bottle, stoppered and centrifuged. The solvent was distilled under reduced pressure and the product through a Vigreux column (1 cm. i. d., 15 cm. long). The product (50.1 g.) distilled at 96–100° (30 mm.), and was 95% pure according to titration. Upon refractionation the product had the properties given in Table I.

The 2,4-dinitrophenylhydrazone (120 mg.) was chromatographed as described above. After the alumina column was cut into six portions there was obtained six yellow crystalline portions of the derivative: 6.1 mg., no m. p.; 22.1 mg., m. p. 66–67°; 46.2 mg., m. p. 67–68°; 21.1 mg., m. p. 67–68°; 9.4 mg., m. p. 66–67°; and 5.2 mg., no m. p. These results indicate that the derivative of only one aldehyde was present.

Succindialdehyde-1,1-diacetate.—Allylidene diacetate (51 g.) and 0.5 g. of dicobalt octacarbonyl in 70 ml. of benzene, were subjected to conditions similar to those described above for ethyl crotonate. The original pressure at room temperature was 2650 p. s. i., the maximum observed pressure at 125° was 3400 p. s. i., and after reaction it was 1800 p. s. i. or 1200 p. s. i. at room temperature. The gas absorption was thus approximately 0.57 mole while 0.67 mole would be required if one mole each of hydrogen and carbon monoxide had been absorbed per mole of allylidene diacetate.

The distillation of the product was carried out in an apparatus consisting of two 250-ml. bulbs connected with a short piece of glass tubing 2.5 cm. in diameter. An opening for the insertion of a thermometer was provided in this tube. One bulb of the flask was placed in an oil-bath and the other was cooled with solid carbon dioxide. The second bulb was provided with a side-arm of glass tubing 2 mm. in diameter for connection to the oil pump and for pouring out the product after distillation. The product was distilled as rapidly as possible at 50–110° (0.8 mm.). The distillate (53.6 g.) showed 90% aldehyde by titration. Pure succinaldehyde-1,1-diacetate $n^{25}D$ 1.4030 was distilled at 102–103° (0.04) through a Vigreux column, as described above for ethyl β-formylbutyrate. If quantities as large as 50 g. are subjected to fractionation there is likely to be condensation before fractionation is complete. It was therefore necessary to carry out fractionations, intended to give pure aldehyde, upon quantities of the order of 10 g.

For purposes of characterization succindialdehyde-1,1-diacetate (0.5 g.) was hydrolyzed by shaking for five minutes in 9 ml. of a water solution containing 0.6 g. of sodium hydroxide and 3 ml. of alcohol. A solution of 1.5 g. of hydroxylamine hydrochloride in 8 ml. of water was added and the mixture warmed in a steam-bath for ten minutes. The crude dioxime of succindialdehyde was obtained by cooling the mixture in an ice-bath. After recrystallization from a mixture of water and ethanol the dioxime showed a m. p. 122–123°.(24) The 2,4-dinitrophenylhydrazone of succindialdehyde, m. p. 278–279°, was also prepared.(25)

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(24) Willstätter and Heubner, *Ber.*, **40**, 3872 (1907).

(25) Keagle and Hartung, THIS JOURNAL, **68**, 1609 (1948).

β-Carbethoxypropionaldehyde.—Ethyl acrylate (65 g.) and 1.2 g. of dicobalt octacarbonyl in 50 ml. of benzene was hydroformylated as described above in sixteen minutes. The pressures at room temperature were 3500 and 1100 p. s. i. at the beginning and end of the reaction with a maximum of 4550 p. s. i. at 125°. The gas absorption was 75–80% of the theoretical amount. A product of 61.7 g., b. p. 70–80° (10 mm.), and 98% pure was obtained. Refractionation gave a product which according to titration was 99% pure. In a similar experiment with 50 g. of ethyl acrylate and 1.3 g. of dicobalt octacarbonyl 1.5 g. of diphenyl sulfide was added to the reaction mixture. The absorption of hydrogen and carbon monoxide required thirty minutes and the yield of aldehyde was 71% of the theoretical as compared with 74% for the reaction mixture not containing diphenyl sulfide.

α-(1-Naphthyl)-propionaldehyde.—The hydroformylation of α-vinylnaphthalene (31 g.) was carried out in the usual way and the drop in pressure (1050 p. s. i. at 23°) corresponded to the absorption of approximately a mole each of hydrogen and carbon monoxide per mole of unsaturated compound. Fractionation of the product gave 26 g., b. p. 110–150° (3 mm.), which by titration was 45% aldehyde. Refractionation gave a product 142–143° (3 mm.) which was by titration 96% pure.

Ethoxybutyraldehydes.—Allyl ethyl ether (15 g.) was hydroformylated in the usual way. Distillation of the products gave 21 g., b. p. 30–70° (20 mm.), which by titration was 41% aldehydes. This corresponds to a 41% yield of ethoxybutyraldehydes. Another hydroformylation on 36 g. of allyl ethyl ether gave a 40% yield of aldehydes. Refractionation of the crude product gave a mixture which titrated 97% aldehyde, b. p. 51–54° (20 mm.), n^{25}D 1.4118. The mixture of 2,4-dinitrophenylhydrazones obtained from the mixture melted over the range 48–53°. Through chromatographing there was obtained, from 248 mg. of the mixture of hydrazones, 21.4 mg. (yellow) m. p. 88–89°, 28.3 mg. (red) m. p. 172–175°, 17.2 mg. (orange) m. p. 55–62°, 70 mg. (yellow) m. p. 75–76°, 87.7 mg. (yellow) m. p. 77–78° and 9.4 mg. of an oil. The derivative m. p. 88–89° corresponds to γ-ethoxybutyraldehyde,[26] while that of m. p. 77–78° is apparently that of β-ethoxyisobutyraldehyde. The α-ethoxybutyraldehyde has a much higher m. p. of 135°.[27]

α- and β-Acetoxy-propionaldehydes.—Vinyl acetate (45 g.) and 3.6 g. of dicobalt octacarbonyl in 70 ml. of benzene was hydroformylated in the usual way, the drop in pressure being from 3500 to 1700 p. s. i. as measured at 23°, corresponding to the absorption of about 0.7 mole of hydrogen and carbon monoxide for 0.5 mole of vinyl acetate. Distillation of the reaction mixture gave 31.1 g., b. p. 45–70° (8 mm.), which contained according to titration 91% of the aldehydes. Fractionation gave 15.4 g. b. p. 46–52° (8 mm.) and 9.0 g., b. p. 62–66° (8 mm.). These fractions each contain 90–94% aldehyde. Refractionation of the lower boiling sample gave α-acetoxypropionaldehyde 98% pure, b. p. 41–42° (8 mm.), n^{25}D 1.4160. The aldehyde was characterized by its semicarbazone, m. p. 162–163°. The higher boiling β-acetoxypropionaldehyde could not be purified beyond 90%. The compound was characterized by hydrogenation to propanediol-1,3 and the formation of the bis-phenylurethan, m. p. 136–137°, of the glycol.

Diethylacetal of β-Carbethoxypropionaldehyde.—Ethyl acrylate (50 g.) and 1.3 g. of dicobalt octacarbonyl in 20 ml. of benzene and 50 ml. of dry ethanol was hydroformylated in the usual way and the products separated by fractionation. There was obtained 28.6 g. (98% pure) of β-carbethoxypropionaldehyde b. p. 86–92° (15 mm.), and 23.3 g. of the diethylacetal of β-carbethoxypropionaldehyde, b. p. 100–103° (10 mm.), n^{25}D 1.4180.[28] Another experiment showed that β-carbethoxypropionaldehyde (46 g.) could be converted to its diethyl acetal (43.8 g.) under the conditions used for the hydroformylation. The formation of the acetal was avoided by carrying out the hydroformylation of ethyl acrylate in benzene free of alcohol.

Reduction of Ethyl 2-Furanacrylate with a Cobalt Carbonyl Catalyst.—Ethyl β-(2-furan)-acrylate (37 g.) and 0.6 g. of dicobalt octacarbonyl in 85 ml. of benzene, under a pressure of 4700 p. s. i. of equal parts hydrogen and carbon monoxide at 125° was rocked for six and one-half hours. The pressure dropped to 3700 p. s. i. during the period. After the usual procedures there was obtained 34.3 g. of ethyl β-(2-furan)-propionate b. p. 94–98° (4 mm.) n^{25}D 1.4812.[29] The saponification equivalent of the product was 167 as compared with a calculated value of 168.

Summary

The hydroformylation of several unsaturated hydrocarbons, ethers and esters, through the use of dicobalt octacarbonyl in benzene at 100–300 atmospheres of carbon monoxide and hydrogen, has given good yields of aldehydes free of isomers. The reaction of substituted ethylenes of the types $RCH{=}CH_2$ and $R_2C{=}CH_2$ have given in six cases aldehydes of the type RCH_2CH_2CHO and R_2CHCH_2CHO. However, where R was phenyl, 1-naphthyl, *n*-butoxy, acetoxy and ethoxymethyl, aldehydes of the type $RCH(CH_3)CHO$ were produced. Three alkenes of the type $RCH{=}CHR'$ have given good yields of a single aldehyde.

Some of the limitations of the reaction, due to the formation of mixtures of aldehydes or the failure of the hydroformylation reaction to take place, have been illustrated. The presence of a sulfur containing compound in the reaction mixture did not significantly poison the catalytic activity of the benzene soluble cobalt carbonyl catalyst. This catalyst has proven to be effective for the hydrogenation of the carbon to carbon double bond in certain α,β-unsaturated carbonyl compounds.

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[26] Paul and Tchelitcheff, *Bull. soc. chim.*, 201 (1948).

[27] Dworzak and Pierri, *Monatsh.*, **52**, 143 (1929).

[28] Carrière, *Ann. chim.*, **17**, 99 (1922).

[29] Hughes and Johnson, THIS JOURNAL, **53**, 742 (1931).