[Contribution from the Laboratory of Organic Chemistry of the University of Wisconsin]

HYDROFORMYLATION OF CONJUGATED DIENES

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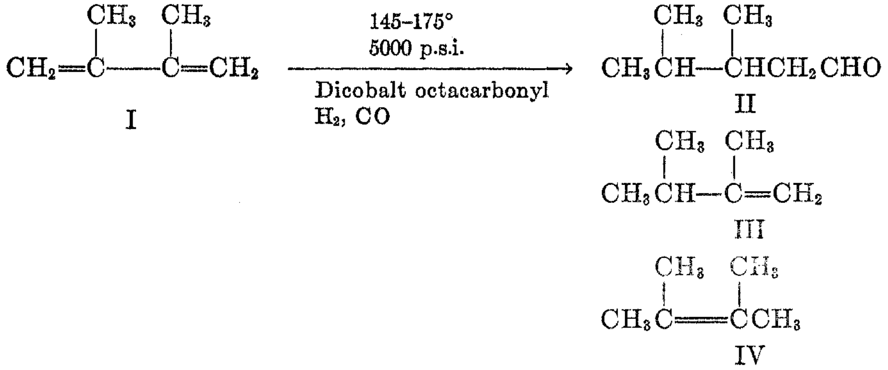
Application of the Oxo reaction to conjugated dienes has been previously reported by Natta and Beatti (1) who found that conjugated diolefins yielded not pure aldehydes but complicated side products. Recent investigators (2, 2a) reported that conjugated diolefins reacted with carbon monoxide and hydrogen over a hydrogenation catalyst to give products among which were aldehydes.

In this investigation 2,3-dimethyl-1,3-butadiene, 1,3-butadiene, isoprene, 3-methyl-1,3-pentadiene, cyclopentadiene, and 1-phenyl-1,3-butadiene reacted readily with carbon monoxide and hydrogen in the presence of dicobalt octacarbonyl under hydroformylation conditions described by Adkins and Krsek (3).

2,3-Dimethyl-1,3-butadiene (I) reacted with carbon monoxide and hydrogen in the presence of dicobalt octacarbonyl at 145–175° and 5000 p.s.i. to produce a single aldehyde, 3,4-dimethylvaleraldehyde (II), in 43% yield. In some cases the isomeric 2,3-dimethylbutenes (III and IV) were also isolated from the reaction mixture:



$$CH_2{=}\overset{CH_3}{\overset{|}{C}}-\overset{CH_3}{\overset{|}{C}}{=}CH_2 \xrightarrow[\text{Dicobalt octacarbonyl},\ H_2,\ CO]{145\text{–}175°,\ 5000\ \text{p.s.i.}} CH_3\overset{CH_3}{\overset{|}{C}}H-\overset{CH_3}{\overset{|}{C}}HCH_2CHO$$

I → II

$$CH_3\overset{CH_3}{\overset{|}{C}}H-\overset{CH_3}{\overset{|}{C}}{=}CH_2$$

III

$$CH_3\overset{CH_3}{\overset{|}{C}}{=}\overset{CH_3}{\overset{|}{C}}CH_3$$

IV

The production of olefin appeared only in reactions where a lower catalyst concentration was used. This appeared to be associated with longer reaction times and resulting corresponding decomposition of the catalyst. With comparatively high catalyst concentration no olefins were isolated from the reaction mixtures. The isomeric 2,3-dimethylbutenes were previously reported (4) to undergo the Oxo reaction utilizing a cobalt on kieselguhr catalyst to produce by subsequent reduction a single alcohol, 3,4-dimethylpentanol-1. The addition of carbon monoxide and hydrogen to 2,3-dimethyl-1-butene apparently took place in a direct manner, while with 2,3-dimethyl-2-butene it could only take place after a shift of the ofefinic bond from the 2 to the 1 position.

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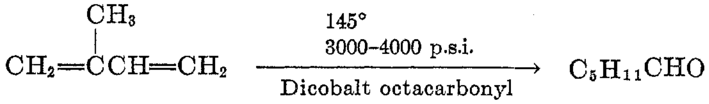
Hydroformylation of 2,3-dimethyl-1-butene (III) has been carried out in this investigation to produce the same aldehyde (II) as obtained by the hydroformylation of 2,3-dimethyl-1,3-butadiene. The 3,4-dimethylvaleraldehyde from both reaction schemes was reduced over platinum oxide to 3,4-dimethylpentanol-1, then oxidized with silver oxide to 3,4-dimethylvaleric acid, and found to be identical in both cases. Presumably hydroformylation of dienes took place by addition of the carbon monoxide and hydrogen, a shift of the remaining olefinic bond into the α,β-position followed by reduction to the saturated aldehyde.

1,3-Butadiene reacted readily with carbon monoxide and hydrogen in the presence of dicobalt octacarbonyl at 145–175° and 3000 to 4000 p.s.i. At 175° the reaction was violent and often became uncontrollable. In some cases the temperature and pressure rose to 250° and 6400 p.s.i. within a few seconds before the reaction subsided. Evidently dicobalt octacarbonyl was destroyed rapidly at temperatures in excess of 175° when a sufficiently reactive diene was present. This could be interpreted to mean that the catalyst could not be reformed at a rate equal to its disappearance while taking part in the hydroformylation reaction. Such reactions led to the presence of solid cobalt in the reaction mixture and the production of small amounts of the reduction products of 1,3-butadiene. The main portion of the reaction products consisted of a mixture of aldehydes and a higher-boiling fraction containing di-*n*-butyl ketone.

$$CH_2{=}CHCH{=}CH_2 \xrightarrow[\text{Dicobalt octacarbonyl}]{\substack{145\text{–}175^\circ \\ 3000\text{–}4000\text{ p.s.i}}} C_4H_9CHO + C_4H_9COC_4H_9$$

The aldehydes were identified by chromatographic separation of their 2,4-dinitorphenylhydrazones and found to be a mixture of approximately 50% *n*-valeraldehyde and 50% α-methylbutryaldehyde. Chromatographic separation of the 2,4-dinitrophenylhydrazones of the ketones was impossible since those derivatives were liquids even when resolved into bands. The semicarbazone of di-*n*-butyl ketone was obtained from the high-boiling fraction and was identified by the mixture melting point method.

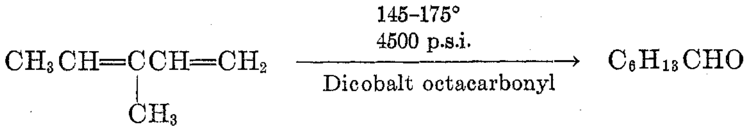
Isoprene reacted readily with carbon monoxide and hydrogen at 145° and 3000 to 4000 p.s.i. in the presence of dicobalt octacarbonyl to give a mixture of hexaldehydes and a higher-boiling fraction. The effect of the ratio of carbon monoxide to hydrogen in the reaction mixture upon the ratio of aldehyde to the high-boiling fraction was studied and found to be slight if any. However, when there was no hydrogen present in the reaction mixture, the reaction failed to proceed. In the case of isoprene, positions 1, 3, and 4 were sterically available for participation in the hydroformylation reaction. This could have conceivably led to the production of three isomeric aldehydes.



$$CH_2{=}\overset{\displaystyle CH_3}{\overset{|}{C}}CH{=}CH_2 \xrightarrow[\text{Dicobalt octacarbonyl}]{\substack{145^\circ \\ 3000\text{–}4000\text{ p.s.i.}}} C_5H_{11}CHO$$

No satisfactory separation of the 2,4-dinitrophenylhydrazones of the aldehyde fraction was carried out; however, isopropylmethylacetaldehyde is believed to be present. The analytical data for the mixed 2,4-dinitrophenylhydrazones of the aldehyde fraction indicated the formula $C_5H_{11}CHO$ for the corresponding aldehydes.

3-Methyl-1,3-pentadiene yielded only aldehydes under hydroformylation conditions.



$$\underset{\displaystyle CH_3}{CH_3CH{=}CCH{=}CH_2} \xrightarrow[\text{Dicobalt octacarbonyl}]{\substack{145\text{–}175^\circ \\ 4500\ \text{p.s.i.}}} C_6H_{13}CHO$$

The aldehyde material from this reaction was oxidized with silver oxide to the acid and the corresponding amide was prepared.

Cyclopentadiene reacted with carbon monoxide and hydrogen at 145–155° and 3700 p.s.i. in the presence of dicobalt octacarbonyl to give formylcyclopentane in 37% yield.

1-Phenyl-1,3-butadiene reacted rapidly under hydroformylation conditions at 145–150° and 3000 p.s.i. However, no aldehyde material was isolated from the reaction mixture. A small amount of *n*-butylbenzene was produced in the reaction, the greater part of the reaction product being polymeric in nature.

EXPERIMENTAL

Hydroformylation of 2,3-dimethyl-1,3-butadiene. 2,3-Dimethyl-1,3-butadiene was hydroformylated in the usual manner (3). Isolation of the reaction products was carried out by direct distillation and steam-distillation of the reaction mixture; the latter procedure proved the most satisfactory as it gave less higher-boiling, polymeric materials. Direct distillation led to the isolation of the two isomeric 2,3-dimethylbutenes in one particular experiment.

Following is a description of a typical run. A mixture of 16.5 g. (0.22 mole) of 2,3-dimethyl-1,3-butadiene and 2.5 g. of dicobalt octacarbonyl, in ether solution (total volume 120 cc.) was placed in a 270-cc. void steel reactor. Carbon monoxide was introduced to a pressure of 2300 p.s.i. followed by hydrogen to a pressure of 4600 p.s.i. The reactor was placed on a shaker and shaken for five minutes at which time the pressure was 4100 p.s.i. The temperature was raised to 175° over the course of 25 minutes and was accompanied by a pressure rise to 5600 p.s.i. After shaking for four hours at 175° the pressure had fallen to 3800 p.s.i. The reactor was then cooled to room temperature in an air blast; the pressure dropped to 2500 p.s.i. The contents of the reactor from two such runs were steam-distilled, after the addition of a few crystals of picric acid and 1.0 g. of hydroquinone, until no additional organic material distilled. The organic layer was separated and the aqueous layer was saturated with sodium chloride and extracted with two 50-cc. portions of ether. The combined extracts and organic layer were dried over magnesium sulfate and distilled. After the ether had distilled the residual liquid was distilled at reduced pressure through a 20-cm. helices-packed column to yield two fractions: (a) 20 g. (45.4%) of 3,4-dimethylvaleraldehyde (II), b.p. 64–66.5° (5 mm.), n_D^{25} 1.4147; (b) 2.0 g., b.p. 70–72° (3.0 mm.), n_D^{25} 1.4234.

Fractions a and b reacted with alcoholic 2,4-dinitrophenylhydrazine reagent. However, the 2,4-dinitrophenylhydrazone of fraction b was liquid. A small amount of fraction a was redistilled, b.p. 145–146°, n_D^{25} 1.4150, d_4^{25} 0.8226, for analysis.

Anal. Calc'd for $C_7H_{14}O$: C, 73.63; H, 12.36.
Found: C, 73.26; H, 12.25.

The *2,4-dinitrophenylhydrazone*, after recrystallization from ethanol, melted at 94°.

Anal. Calc'd for $C_{13}H_{16}N_4O_4$: C, 53.05; H, 6.16.
Found: C, 53.19; H, 5.96.

The *semicarbazone*, after three recrystallizations from ethanol and water, melted at 139–140°.

Anal. Calc'd for $C_8H_{17}N_3O$: C, 56.11; H, 10.01.

Found: C, 55.86; H, 9.95.

Oxidation of 3,4-dimethylvaleraldehyde. Oxidation of 11.3 g. (0.099 mole) of 3,4-dimethylvaleraldehyde (II) with 45.0 g. (0.26 mole) of silver nitrate and 14.5 g. (0.36 mole) of sodium hydroxide was carried out as described previously for α-methyl-β-propylacrolein (5). The yield of 3,4-dimethylvaleric acid, b.p. 81.5° (2 mm.), n_D^{25} 1.4255, d_4^{25} 0.9267, neutral equivalent 130.0 (calc'd 130.3), was 49%.

Anal. Calc'd for $C_7H_{14}O_2$: C, 64.57; H, 10.84.

Found: C, 64.52; H, 10.83.

The *amide* prepared from this acid melted at 138–138.5°.

Anal. Calc'd for $C_7H_{15}NO$: C, 65.08; H, 11.70.

Found: C, 65.29; H, 11.20.

Reduction of 4.5 g. (0.04 mole) of II over platinum oxide catalyst (1.0 g.) in 50 cc. of methylcyclohexane was carried out in the usual manner at 50 p.s.i. One mole of hydrogen was absorbed per mole of aldehyde. When the reduction had ceased, the catalyst was centrifuged and the clear solution distilled through a 15-cm. Vigreux column. After the methylcyclohexane had distilled, 2.1 g. (44%) of 3,4-dimethylpentanol-1 was collected, b.p. 163–170°, n_D^{25} 1.4281. Schmerling (6) reported this alcohol to have the following constants: b.p. 168–169°, n_D^{20} 1.4288.

2,3-Dimethyl-1-butene. Dimethylisopropylcarbinol was prepared from methyl isopropyl ketone and methylmagnesium iodide in 49% yield. Dehydration of the carbinol was accomplished in the following manner. Dimethylisopropylcarbinol (45 g.) was passed dropwise from a dropping-funnel at the rate of two drops per second through a 22-mm. o.d. Pyrex tube packed for a distance of 45 cm. with Harshaw $\frac{3}{32}$-in. alumina pellets and heated to 400° by an electrically heated jacket. The dehydration products were collected in a Dry Ice-trap. The organic layer was separated, dried over magnesium sulfate, and distilled through a 45-cm. helices-packed column equipped with a partial-take-off total-reflux head. The weight of the crude hydrocarbon prior to distillation was 36 g. The following fractions were obtained: (a) 17.5 g., b.p. 54–55.2°, n_D^{25} 1.3890; (b) 4.5 g., b.p. 55.5–70.5°, n_D^{25} 1.3991; (c) 6.0 g., b.p. 70.5–71.5°, n_D^{25} 1.4105. Fraction a was used for subsequent hydroformylation experiments. The following constants were recorded by Huntress and Mulliken (7) for the isomeric dimethylbutenes: 2,3-dimethyl-2-butene, b.p. 72.9–73.2°, n_D^{20} 1.4115; 2,3-dimethyl-1-butene, b.p. 56–56.5°, n_D^{25} 1.3995. This dehydration therefore yielded 62% of 2,3-dimethyl-1-butene and 38% of 2,3-dimethyl-2-butene. Shurman and Boord (8) reported the production of 20% of 2,3-dimethyl-1-butene and 80% of 2,3-dimethyl-2-butene by dehydration of the carbinol with oxalic acid.

Hydroformylation of 2,3-dimethyl-1-butene. A solution of 17.3 g. (0.21 mole) of 2,3-dimethyl-1-butene and 5.4 g. of dicobalt octacarbonyl in sufficient ether to make 120 cc. was placed in a 270-cc. void steel reaction vessel. Carbon monoxide was admitted to a pressure of 2000 p.s.i. followed by hydrogen to a pressure of 4000 p.s.i. The reactor was shaken for five minutes at room temperature (pressure 3700 p.s.i.) and heated to 135° during the course of 25 minutes at which time the pressure was 4650 p.s.i. After 2.75 hours the pressure had fallen to 3650 p.s.i. At room temperature the pressure was 2900 p.s.i. corresponding to a cold drop of 800 p.s.i. (theory 1050 p.s.i.). The reaction mixture was worked up by steam-distillation as described for 2,3-dimethyl-1,3-butadiene. The crude product was distilled through a 20-cm. helices-packed column at reduced pressure to yield 11.3 g. (45%) of 3,4-dimethylvaleraldehyde, b.p. 59°/45 mm., n_D^{25} 1.4144; *semicarbazone*, m.p. 140–141°. A mixture melting point with the semicarbazone of the aldehyde from the hydroformylation of 2,3-dimethyl-1,3-butadiene gave no depression.

Hydroformylation of 1,3-butadiene. Hydroformylation of 1,3-butadiene (Phillips Petroleum Company, Pure Grade) was carried out at temperatures ranging from 145–175°. In a tared, graduated 4-cm. by 20-cm. Pyrex tube there was placed approximately 15 g. of 1,3-

butadiene. The diene was allowed to boil off until 14 g. of 1,3-butadiene remained. The tube was then immersed in a Dry Ice-acetone bath and 45 cc. of a 10% solution of dicobalt octacarbonyl in benzene was added, followed by dry benzene to bring the volume to 100 cc. The contents of the tube were then poured into a 270-cc. void steel reaction vessel which had been precooled in a Dry Ice-methanol bath. The Pyrex tube was rinsed out with 20 cc. of

TABLE I

HYDROFORMYLATION OF 2,3-DIMETHYL-1,3-BUTADIENE

RUN	1	2	3, 4	5
Moles of diene	0.5	0.37	0.33	0.25
Catalyst, g.	2.4	1.2	1.8	5
Temperature, °C.	120	175	175	155
Yield of aldehyde, %	8.8$^{a, b}$	35.4^{b}	40.0^{c}	43.0^{c}
Initial cold pressure, p.s.i.	3850	3800	3900	3900
Cold drop, p.s.i.	2650	2300	1500	1700
Theoretical cold drop, p.s.i.	3880	2860	1700	1940
Time, hours	2.25	7.0	4.5	1.0

[a] Hydrocarbon, b.p. 0–10°, was isolated. [b] Isolated by direct distillation of the reaction mixture. [c] Isolated by the steam-distillation procedure.

TABLE II

HYDROFORMYLATION OF 1,3-BUTADIENE

RUN	DIENE		CATALYST, g.	TEMP. °C.	MAX. TEMP. °C.	YIELD		INITIAL COLD PRESSURE, p.s.i.	THEORETICAL COLD DROP. p.s.i.	COLD DROP, p.s.i.	TIME, HOURS
	g.	Mole				ALDEHYDE, %	HIGH-BOILING^{e} MATERIAL, %				
1	27.0	0.5	3.8	150	150	10.8	0	4000	3860	2800	4.30
2	27.0	0.5	10.0	150	200	0	30.8	3900	3860	2400	0.25
3	27.0	0.5	10.0	150	180			3800	3860	2200	1.00
4	27.0	0.5	10.0	150	183			3900	3860	2800	1.00
5	13.0	0.24	11.0	150	165	trace	15	4000	1860	1800	0.50
6	13.0	0.24	11.0	150	160			4100	1860	1800	1.0
7	27.0	0.5	10.0	145	220	^{f}		3800	(6400; at 220°)		
8	14.0	0.26	4.5	145	175	28.8	trace	3750	2000	1950	1.30
9	14.0	0.26	4.5	145	155	17	32	2900^{a}	2000	1600	1.25
10	14.0	0.26	4.5	145	150			2900^{a}	2000	1560	1.60
11	14.0	0.26	4.5	145	150			3050^{a}	2000	1700	2.30
12	14.0	0.26	4.5	140–170	170	trace		2900^{d}	2000	800	2.25
13	14.0	0.26	4.5	145	150	14.5	15.4	3000^{b}	2000	1500	0.50
14–17	14.0	0.26	4.5	150	154	23.3	23.8	3000 av.^{a}	2000	1600 av.	0.3 av.
18–21	14.0	0.26	4.5	150	175	23.8	11.5	3000 av.^{a}	2000	1700	1.00
23	14.0	0.26	10.0	145	180			4000^{c}		No reaction	4.0

[a] Hydrogen: carbon monoxide 1:1. [b] Hydrogen, 1000 p.s.i.; Carbon monoxide, 2000 p.s.i. [c] Hydrogen, 0 p.s.i.; Carbon monoxide, 4000 p.s.i. [d] Hydrogen, 650 p.s.i.; Carbon monoxide, 2250 p.s.i. [e] Calculated as dibutyl ketones. [f] Discarded; cobalt and polymer present in reactor. All other runs used hydrogen, 2000 p.s.i.; Carbon monoxide, 2000 p.s.i.

benzene into the reactor, which then was sealed as rapidly as possible and pressurized as indicated in Table II.

Careful control of the temperature was essential, since the hydroformylation was extremely exothermic. The fully charged reactor was shaken at room temperature for 5.0 minutes in order to obtain the initial cold pressure. Then the temperature was raised rapidly to 125° at which point the heat was turned off until the rapid rise of temperature had ceased. Heating then was resumed at the rate of 5° per ten minutes until the reaction became initiated, usually at 140–145°. Reaction of 1,3-butadiene usually took place completely within one-half hour. In some cases reaction times as short as two minutes resulted; however, for safety purposes this was not advisable. After the desired reaction time the reaction vessel was cooled rapidly in an air blast, opened, and the reaction products isolated.

From four combined runs each consisting of 14 g. (0.26 mole) of 1,3-butadiene and 4.5 g. of dicobalt octacarbonyl in 120 cc. of dry benzene treated for 1.0 hour with an equimolar quantity of carbon monoxide and hydrogen at 150–175° and 3000 p.s.i., there was obtained by the steam-distillation procedure the following fractions after distillation through a 45-cm. helices-packed column: (a) 21.0 g., (23.8%) of a mixture of five-carbon aldehydes, b.p. 34–39° (70 mm.) n_D^{25} 1.3910; and (b) 17.4 g., b.p. 52° (52 mm.) n_D^{25} 1.4133.

TABLE III

HYDROFORMYLATION OF ISOPRENE

RUN	1	2	3	4
Diene, g.	17.0	17.0	17.0	17.0
Moles	0.25	0.25	0.25	0.25
Catalyst, g.	9.0	9.5	9.5	9.5
Temperature, °C.	150	150	160	160
Initial cold pressure, p.s.i.	2800	3800	2800[a]	2900[a]
Cold drop, p.s.i.	1630	1700	1500	1550
Theoretical cold drop, p.s.i.	1930	1930	1950	1930
Aldehyde, yield, %	26	22	0	15.60[c]
High-boiling fraction,[b] yield, %	—	12.9	31.0	36.0
Time, hours	1	1.1	0.75	0.75

[a] Using a 2:1 ratio of hydrogen to carbon monoxide. [b] Calculated as diamyl ketones. [c] Run 4 was isolated by steam-distillation.

Fraction (a) consisted of aldehydes. Huntress and Mulliken (9) recorded for *n*-valeraldehyde, n_D^{20} 1.3944 and for α-methylbutyraldehyde, n_D^{20} 1.3896, *2,4-dinitrophenylhydrazone*, m.p. 120.5°. The 2,4-dinitrophenylhydrazone of fraction (a) melted at 98–101°. Chromatographic analysis of the 2,4-dinitrophenylhydrazone of fraction (a) by the procedure previously described (10) gave 50% by weight of the 2,4-dinitrophenylhydrazone of *n*-valeraldehyde, m.p. 104–107°, and 50% by weight of the 2,4-dinitrophenylhydrazone of α-methylbutyraldehyde, m.p. 115°.

Three combined runs each consisting of 27 g. (0.5 mole) of 1,3-butadiene, 10 g. of dicobalt octacarbonyl, and 120 cc. of dry benzene treated under hydroformylation conditions as in the above examples at 150–200° yielded no aldehyde by direct distillation; instead the following higher-boiling fractions were obtained: (a) 4.5 g., b.p. 68–72° (16 mm.), n_D^{25} 1.4185; (b) 7.0 g., b.p. 72–73° (16 mm.), n_D^{25} 1.4200; (c) 3.7 g., b.p. 67.5–68.5° (9 mm.), n_D^{25} 1.4200.

All fractions failed to give solid 2,4-dinitrophenylhydrazones. Fraction (c) yielded a *semicarbazone*, m.p. 88°, after three recrystallizations from alcohol-water. An authentic sample of the semicarbazone of di-*n*-butyl ketone melted at 89–89.5°. A mixture melting point of equal quantities of the two materials was not depressed.

Hydroformylation of isoprene. This reaction was carried out in dry benzene according to the procedure described for 2,3-dimethyl-1,3-butadiene employing both the steam-distillation technique and direct distillation. In the case of isoprene, higher-boiling fractions other than aldehydes were observed but were not characterized. In a typical run, 17 g. (0.25 mole) of isoprene and 9.5 g. of dicobalt octacarbonyl in sufficient dry benzene to make 120 cc., was treated with carbon monoxide and hydrogen at 160° and 4000 p.s.i. By distillation there was obtained 3.9 g. (15.6%) of isomeric hexaldehydes, b.p. 40–43.5° (47 mm.), n_D^{25} 1.4019–1.4060. Small higher-boiling fractions were obtained: b.p. 57° (17 mm.), n_D^{25} 1.4168; 57° (12 mm.), n_D^{25} 1.4187. A 2,4-dinitrophenylhydrazone mixture of the aldehyde fraction was prepared in almost quantitative yield, m.p. 89–91°.

Anal. Calc'd for $C_{12}H_{15}N_4O_4$: C, 51.61; H, 5.41.

Found: C, 51.53; H, 5.42.

Chromatographic analysis did not satisfactorily separate this material into identifiable fractions.

Hydroformylation of 3-methyl-1,3-pentadiene. In a typical run 26.2 g. (0.32 mole) of this diene (11) and 7.8 g. of dicobalt octacarbonyl in 120 cc. of dry ether was treated with an equimolar mixture of carbon monoxide and hydrogen at 145° and 4500 p.s.i. Two similar runs totaling 60.6 g. (0.53 mole) of diene yielded 22 g. (33%) of aldehydes, b.p. 52.5° (25 mm.), n_D^{25} 1.4140.

Anal. Calc'd for $C_7H_{14}O$: C, 73.63; H, 12.36.

Found: C, 73.13; H, 12.57.

The *2,4-dinitrophenylhydrazone* was prepared in 90% yield and melted at 58–63°. Chromatographic analysis yielded the following fractions: (a) m.p. 74–75°, 16%; (b) m.p. 72–75°, 25%; (c) m.p. 72–74°, 24%; (d) m.p. 71–74°, 24%.

The mixture melting point of a and b was 69–70°. The fractions were combined and submitted for analysis.

Anal. Calc'd for $C_{13}H_{20}N_4O_4$: C, 53.05; H, 6.16.

Found: C, 52.97; H, 5.93.

The *semicarbazone* of this material, after recrystallization from alcohol-water, melted at 106–107°.

Anal. Calc'd for $C_{18}H_{16}NO_3$: C, 56.11; H, 10.01.

Found: C, 56.03; H, 9.84.

A 10-g. portion of the (0.088 mole) aldehyde fraction was oxidized with 45 g. (0.26 mole) of silver nitrate and 14.5 g. (0.36 mole) of sodium hydroxide according to the procedure described for 3,4-dimethylvaleraldehyde (12) to produce 6.0 g. (45%) of acid, b.p. 72° (5 mm.), n_D^{25} 1.4233. An amide was prepared which melted at 97.5–98° after sublimation *in vacuo*. α-Methylcaproic acid was reported (12) to have the following constants: b.p. 215–216°, n_D^{20} 1.4227, amide, m.p. 99–100°.

Hydroformylation of cyclopentadiene. Hydroformylation of cyclopentadiene, prepared by thermal depolymerization of dicyclopentadiene (The Matheson Company, Paragon Division), was carried out at 145–155° and 3700 p.s.i. according to the procedure described above for 2,3-dimethyl-1,3-butadiene. The reactor was charged with 120 cc. of an ether solution of 16.5 g. (0.25 mole) of cyclopentadiene and 5 g. of dicobalt octacarbonyl. Carbon monoxide and hydrogen were introduced to give an equimolar mixture with final pressure of 3000 p.s.i. The reaction time was 50 minutes (cold drop 1500 p.s.i., calc'd 1930 p.s.i.) and 8 g. (37%) of formylcyclopentane, b.p. 49–50° (32 mm.), n_D^{25} 1.4410–1.4425, was obtained by the steam-distillation procedure. *p-Nitrophenylhydrazone*, m.p. 125–127°; *semicarbazone*, m.p. 140–141° after considerable shrinking at 123–125°. Adkins and Watkins (13) found m.p. 119–120.5° for the *p*-nitrophenylhydrazone and 138–139° for the semicarbazone.

Hydroformylation of 1-phenyl-1,3-butadiene. 1-Phenyl-1,3-butadiene (14) was hydroformylated in the above manner at 145–150°. The charge for a typical run consisted of 32.5 g. (0.25 mole) and 5 g. of dicobalt octacarbonyl dissolved in sufficient ether to make 120 cc. was placed in a steel bomb and pressurized with an equimolar mixture of carbon monoxide and hydrogen to 3000 p.s.i. The reaction time was one hour (cold drop 1300 p.s.i., calc'd 1930 p.s.i.). Steam-distillation yielded only 3 g. of *n*-butylbenzene, b.p. 91–95° (45 mm.), n_D^{25} 1.4887 (15). The remainder of the reaction product was polymeric in nature.

SUMMARY

Hydroformylation of 2,3-dimethyl-1,3-butadiene, 1,3-butadiene, isoprene, 3-methyl-1,3-pentadiene, and cyclopentadiene has been carried out with an equimolar mixture of hydrogen and carbon monoxide in the presence of dicobalt octacarbonyl. Monoaldehydes have been identified in the products.

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REFERENCES

(1) NATTA AND BEATTI, *Chimica e industria (Milan)*, **27**, 84 (1945); *Chem. Abstr.*, **41**, 708 (1947).
(2) GRESHAM, BRUNER, AND BROOKS, U. S. Patent 2,437,600.
(2a) BROOKS, U. S. Patent 2,517,383.
(3) ADKINS AND KRSEK, *J. Am. Chem. Soc.*, **70**, 383 (1948).
(4) KUELEMAN, KWANTES, AND VAN BAVEL, *Rec. trav. chim.*, **67**, 298 (1948).
(5) LICHTENBERGER AND NAFTALI, *Bull. soc. chim.*, [5], **4**, 325 (1937).
(6) SCHMERLING, *J. Am. Chem. Soc.*, **67**, 1438 (1945).
(7) HUNTRESS AND MULLIKEN, *Identification of Pure Organic Compounds*, John Wiley and Sons, New York, 1941, pp. 578 and 581.
(8) SHURMAN AND BOORD, *J. Am. Chem. Soc.*, **55**, 4930 (1933).
(9) HUNTRESS AND MULLIKEN, *Identification of Pure Organic Compounds*, John Wiley and Sons, New York, 1941, pp. 49 and 51.
(10) ADKINS AND KRSEK, *J. Am. Chem. Soc.*, **71**, 3051 (1949).
(11) NICHOL AND SANDIN, *J. Am. Chem. Soc.*, **69**, 2256 (1947).
(12) QUEBEDEAUX, WASH, NEY, AND LOCHTE, *J. Am. Chem. Soc.*, **65**, 767 (1945).
(13) ADKINS AND WATKINS, *J. Am. Chem. Soc.*, **73**, 2184 (1951).
(14) GRUMMITT AND BECKER, *J. Am. Chem. Soc.*, **70**, 149 (1948).
(15) HUNTRESS AND MULLIKEN, *Identification of Pure Organic Compounds*, John Wiley and Sons, New York, 1941, p. 535.