mately equal parts of 2-ethyl-1-butanol, b.p. 149–151°, and 1-hexanol, b.p. 156–158°, identified as their 3,5-dinitrobenzoates.

Acidification of the steam distillation residue with sulfuric acid followed by further steam distillation effected isolation of the carboxylic acids produced during higher alcohol formation. Titration showed a total of 0.035 equivalents to be present, which represents a ratio of higher alcohol to carboxylic acid of approximately 20:1.

When the reaction time was extended to 16 hr., no appreciable increase in conversion was realized. This was also the case when, at the end of 8 hr., additional quantities of potassium carbonate, magnesium oxide, and copper chromite were added and the reaction continued an additional 8 hr. In another experiment, at the end of 8 hr. the reaction mixture was subjected to distillation and ethanol-water distilled until no more water came over. The mixture was made up to the original volume with dry ethanol and subjected to an additional 8 hr. reaction time. Recovery of ethanol and isolation of the higher alcohol in the previously described manner resulted in a 35% conversion and a 76% yield of higher alcohols.

Condensation of 1-butanol by potassium carbonate, magnesium oxide and copper chromite. The autoclave was charged with 370 g. (5.0 moles) of 1-butanol, 18.5 g. of anhydrous potassium carbonate, 18.5 g. of magnesium oxide (light powder), and 18.5 g. of copper chromite. It was heated rapidly with stirring to 245–250° and maintained at this temperature for 8 hr. during which time the pressure registered 700–800 p.s.i.g. At the end of the heating period the autoclave was cooled and its contents were subjected to steam distillation to recover butanol and higher alcohols. Redistillation of the organic phase resulted in a recovery of 278 g. 1-butanol and 58.6 g. of 2-ethyl-1-hexanol, b.p. 180–182° (18% conversion, 70% yield on the 1-butanol actually used). A very small amount of higher boiling alcoholic residue remained from this distillation.

ST. LOUIS, MO.

[CONTRIBUTION FROM CENTRAL EXPERIMENT STATION, BUREAU OF MINES, U. S. DEPARTMENT OF THE INTERIOR, AND THE DEPARTMENT OF CHEMISTRY OF THE UNIVERSITY OF PITTSBURGH[1]]

Reactions of Acetylenic Compounds under Hydroformylation Conditions[2]

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The reaction of 1-pentyne with carbon monoxide and hydrogen in the presence of a cobalt catalyst at elevated temperatures and pressures produces low yields of the same C_6 alcohols as are obtained from the hydroformylation of 1-pentene. Under these conditions, diphenylacetylene is hydrogenated to 1,2-diphenylethane.

The reaction of acetylene with stoichiometric quantities of cobalt hydrocarbonyl at room temperature and atmospheric pressure results in the formation of propionaldehyde.

All simple olefins undergo the hydroformylation (oxo) reaction. This involves the addition of carbon monoxide and hydrogen to an olefin in the presence of a cobalt carbonyl catalyst at elevated temperatures and pressures to produce aldehydes containing one carbon atom more than the starting olefin.[5-8] For example, propylene yields a mixture of butyraldehyde and isobutyraldehyde.

Although the hydroformylation of olefins has received considerable attention and is of industrial importance, little work has been done on acetylenes. It has been reported that a mixture of high boiling, unidentified products was produced by the reaction of acetylene with carbon monoxide and hydrogen in the presence of metallic cobalt catalysts at 120° to 150° and 200 to 300 atm. pressure[9]. This reaction took place at a slower rate than does the hydroformylation of olefins.

In the present work we have investigated the reactions of 1-pentyne and of diphenylacetylene under hydroformylation conditions. We have studied the effect of small amounts of alkynes on several reactions of nonacetylenic compounds that take place under hydroformylation conditions. We have also reacted acetylene with stoichiometric amounts of cobalt hydrocarbonyl at room temperature and atmospheric pressure.

Reaction of 1-pentyne under hydroformylation conditions. The 1-pentyne began to absorb gas at about 130°. The temperature was then raised to about 185° in order to convert any aldehydes into the corresponding alcohols[10] which are less reactive and easier to isolate. A 6% yield of 1-hexanol and a 5.5% yield of 2-methyl-1-pentanol were obtained. The remainder of the product was higher-boiling material. Infrared and mass spectroscopic analyses showed the presence of C_{12} esters in a fraction distilling at

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[1] Contribution No. 1001.

[2] This paper is based, in part, on the Ph.D. thesis of Harold Greenfield, University of Pittsburgh, 1955.

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

[6] H. Adkins and G. Krsek, *J. Am. Chem. Soc.*, **70**, 383 (1948).

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

[8] I. Wender and M. Orchin, *U. S. Bur. Mines Rept. Invest. No. 4270* (1948).

[9] G. Natta and P. Pino, paper presented at the 12th International Congress of Pure and Applied Chemistry, New York, N. Y., September 1951.

[10] I. Wender, R. Levine, and M. Orchin, *J. Am. Soc.*, **72**, 4375 (1950).

113°–116° at 20 mm. Such esters could be formed by the reaction of 1-pentyne with carbon monoxide and a C_6 alcohol.[11–14]

There are two likely reaction paths for the formation of 1-hexanol and 2-methyl-1-pentanol from 1-pentyne. In the first case, if the 1-pentyne were hydrogenated to 1-pentene, the olefin would react further to yield the usual hydroformylation products, hexanal and 2-methylpentanal. These aldehydes would then be hydrogenated to the corresponding alcohols.[10] In the second case, if the alkyne were first hydroformylated to give α,β-unsaturated aldehydes, both the conjugated olefinic linkages[7] and the carbonyl groups[10] would be hydrogenated to yield 1-hexanol and 2-methyl-1-pentanol.

It is interesting to note that, whereas 1-pentyne began to react at about 130°, the corresponding olefin, 1-pentene, starts to react at about 90° under similar conditions.[15] This confirms the earlier observation that acetylene reacts more slowly than do olefins under hydroformylation conditions.[9] The double bond generally is more reactive than the comparably situated triple bond toward electrophilic reagents, as in electrophilic halogen additions,[16] and toward free radicals, such as the trichloromethyl radical,[17] while the reverse holds true for nucleophilic reagents, such as the methoxide ion.[18] With regard to the hydroformylation reaction, however, mechanistic inferences based on the relative reactivities of alkenes and alkynes are complicated by the fact that alkynes, in contrast to alkenes, react readily with dicobalt octacarbonyl at room temperature.[19] The alkyne replaces two carbonyl groups in dicobalt octacarbonyl and forms an acetylenic dicobalt hexacarbonyl, a stable organometallic compound,[20,21] as shown in Equation (1).

$$RC{\equiv}CR' + Co_2(CO)_8 \longrightarrow RC_2R'Co_2(CO)_6 + 2CO \quad (1)$$

Use of alkynes as inhibitors of reactions occurring under hydroformylation conditions. Dicobalt octacarbonyl is probably the catalyst, or the catalyst precursor, for reactions taking place under hydroformylation conditions.[19] A possible explanation of the fact that acetylene[9] and 1-pentyne appear less reactive than the corresponding olefins is that the catalyst has been removed by reaction with the alkynes to form acetylenic dicobalt hexacarbonyls (Equation 1). If the organometallic compound thus formed were not a catalyst, no hydroformylation or hydrogenation should occur until it was transformed into an active catalyst. This point was investigated by using acetylenic dicobalt hexacarbonyls instead of dicobalt octacarbonyl in the following reactions under hydroformylation conditions: the hydroformylation of cyclohexene, the hydroformylation of 1-heptene, the hydrogenation of crotonaldehyde to butyraldehyde,[7] the hydrogenolysis of *p*-methoxybenzhydrol to *p*-methoxydiphenylmethane,[22] and the hydrogenolysis and homologation of *p*-methoxybenzyl alcohol to *p*-methoxytoluene and 2-(*p*-methoxyphenyl)ethanol.[23]

In each of the above cases, the temperature of initial reaction was increased when an acetylenic dicobalt hexacarbonyl was used instead of dicobalt octacarbonyl. The temperature at which reaction took place was different for the various acetylenic dicobalt hexacarbonyls. These results suggest that the above reactions did not occur until the acetylenic dicobalt hexacarbonyl had been converted to an active catalyst. It is not clear whether this transformation entails a thermal decomposition, a reaction of the acetylenic dicobalt hexacarbonyl with carbon monoxide and/or hydrogen, or a reaction of the acetylenic dicobalt hexacarbonyl with the organic substrate. Experiments with nonacetylenic substrates in the presence of both an acetylenic dicobalt hexacarbonyl and dicobalt octacarbonyl did not show any inhibition. This indicates that the previously observed inhibition was due to the absence of dicobalt octacarbonyl rather than to any inhibiting effect of the acetylenic dicobalt hexacarbonyl *per se.*

The addition of catalytic amounts of an alkyne makes it possible to run reactions in batch autoclaves above the ordinary reaction temperature under hydroformylation conditions. It is likely that such a procedure would change the product distribution and might be used to obtain higher yields of desired products in certain cases.

This effect of alkynes on reactions that are homogeneously catalyzed by cobalt carbonyls has an interesting analogue in heterogeneous catalysis. It is

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(20) H. W. Sternberg, H. Greenfield, R. A. Friedel, J. H. Wotiz, R. Markby, and I. Wender, *J. Am. Chem. Soc.*, **76** 1457 (1954).

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(22) I. Wender, R. Markby, and H. Greenfield, unpublished work.

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well known that alkynes inhibit the metal-catalyzed, heterogeneous hydrogenation of olefins.[24,25] Apparently the alkyne monopolizes the catalyst surface because of its greater strength of chemisorption. In this connection, it is interesting to note the similarity between the intermediates produced by the associative adsorption of unsaturated hydrocarbons on dual surface sites of metals[25–27] and the complexes formed in the reaction of dicobalt octacarbonyl with alkynes[21] and olefins.[19d]

Reaction of diphenylacetylene under hydroformylation conditions. The reaction of diphenylacetylene began at approximately 170°. The temperature was maintained at 180°–195° for about 2 hr. An 80% yield of 1,2-diphenylethane was obtained. Presumably, the course of the reaction was as shown in Equation 2

$$C_6H_5{-}C{\equiv}C{-}C_6H_5 \longrightarrow C_6H_5{-}CH{=}CH{-}C_6H_5 \longrightarrow C_6H_5{-}CH_2CH_2{-}C_6H_5 \quad (2)$$

Cis-stilbene also yields 1,2-diphenylethane as the major product under similar conditions.[22]

Stoichiometric reaction of acetylene with cobalt hydrocarbonyl. It has been shown that some catalytic reactions which take place under hydroformylation conditions also can be effected by stoichiometric amounts of cobalt hydrocarbonyl at atmospheric pressure and room temperature.[28,29] It was therefore of interest to determine whether alkynes as well as alkenes undergo a stoichiometric reaction with cobalt hydrocarbonyl.

Acetylene gas was allowed to stand for 24 hr. with cobalt hydrocarbonyl, carbon monoxide, and hydrogen at room temperature and atmospheric pressure. Infrared and mass spectroscopic analyses showed the absence of cobalt hydrocarbonyl and the presence of acetylene, acetylene dicobalt hexacarbonyl, and propionaldehyde. Presumably, the acetylene dicobalt hexacarbonyl arose from the reaction of acetylene and dicobalt octacarbonyl, the latter being the known product of the decomposition of cobalt hydrocarbonyl.[30]

Thus, alkynes can give rise to aldehydes containing one carbon atom more than the starting alkyne under both catalytic hydroformylation conditions at elevated temperatures and pressures and also with stoichiometric amounts of cobalt hydrocarbonyl at room temperature and atmospheric pressure.

EXPERIMENTAL

Melting points are corrected.

Phenylacetylene, 1-pentyne, and 1-hexyne were purchased from the Farchan Research Laboratories. Diphenylacetylene was purchased from Metro Industries and from Organic Specialties, Inc. Cyclohexene and crotonaldehyde were purchased from Distillation Products Industries. 1-Heptene was purchased from Humphrey-Wilkinson, Inc.

p-Methoxybenzyl alcohol,[23] *p*-methoxybenzhydrol,[31] cobalt hydrocarbonyl[32] and dicobalt octacarbonyl[33] were prepared by methods described in the literature. Synthesis gas (a mixture of hydrogen and carbon monoxide) was manufactured and compressed by the Bureau of Mines at Bruceton, Pa.

Autoclave experiments were performed in type 347 stainless steel, rocking autoclaves. A 500-ml. autoclave with a free space of 492 ml., purchased from the American Instrument Company, or a 200-ml. autoclave with a free space of 185 ml., fabricated by the Bureau of Mines at Bruceton, Pa., was used.

Reaction of 1-pentyne under hydroformylation conditions. To a solution of 5.0 g. (1.5×10^{-2} mole) of dicobalt octacarbonyl in 55 ml. of benzene in an Erlenmeyer flask equipped with a water-cooled condenser were added 88.0 g. (1.3 moles) of 1-pentyne. The evolved carbon monoxide was allowed to escape through a mercury valve at the top of the condenser. After standing overnight, the benzene solution containing 1-pentyne and 1.5×10^{-2} mole of 1-pentyne dicobalt hexacarbonyl was transferred to a 500-ml. autoclave and an additional 45 ml. of benzene were added. The reaction mixture was then pressured to 3865 p.s.i. with 1:1 synthesis gas and rocking and heating were begun.

A reaction began at about 130° and proceeded smoothly for 135 min. with the temperature rising to 184° and the pressure falling to 3800 p.s.i. At this point an exotherm occurred with the temperature rising to 200° and the pressure falling to 1800 p.s.i. in a 1 min. interval. The temperature rapidly fell to 186°. The reaction mixture was then repressured at 185° from 1680 p.s.i. to 3350 p.s.i. with 1:1 synthesis gas, and the temperature was maintained at 185–188° for 1.5 hr., during which time 250 p.s.i. of gas were absorbed. The final pressure at room temperature was 1940 p.s.i. A total of about 1.9 moles of gas per mole of 1-pentyne had been absorbed.

The reaction mixture was removed from the autoclave and distilled from a Claisen flask up to a boiling point of 192° at 4 mm. pressure and a pot temperature of 240°. The distillate was then fractionated in a 2-ft. long, 8-mm. i.d., Heli-grid packed Podbielniak column at a reflux ratio of 120:1. The following fractions were obtained:

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(25) G. C. Bond, Chap. 4 in "Catalysis," Vol. III, edited by P. H. Emmett, Reinhold Publishing Corp., New York, 1955.

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(27) G. C. Bond, *Quart. Rev. (London)*, **8**, 279 (1954).

(28) I. Wender, H. W. Sternberg, and M. Orchin, *J. Am. Chem. Soc.*, **75**, 3041 (1953).

(29) I. Wender, H. Greenfield, and H. W. Sternberg, paper presented at the 125th Meeting of the AMERICAN CHEMICAL SOCIETY, Kansas City, Mo., March 1954.

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(32) H. W. Sternberg, I. Wender, R. A. Friedel, and M. Orchin, *J. Am. Chem. Soc.*, **75**, 2717 (1953).

(33) I. Wender, H. Greenfield, and M. Orchin, *J. Am. Chem. Soc.*, **73**, 2656 (1951).

Fraction	Weight, g.	Boiling Point, °C.	Refractive Index, n_D^{20}
1	3.2	25–89.5 at 100 mm.	1.4752–1.4225
2	1.2	89.5–94 at 100 mm.	1.4152
3	3.8	94–94.5 at 100 mm.	1.4183
4	2.3	94.5–102 at 100 mm.	1.4185–1.4175
5	5.8	102–104 at 100 mm.	1.4173–1.4177
6	0.9	104–132 at 100 mm.	1.4190
7	1.0	132–136 at 100 mm.	1.4205
8	1.1	136–142 at 100 mm.	1.4209
9	1.0	142–151 at 100 mm.	1.4282
10	1.3	151 at 100 mm. to 108 at 20 mm.	1.4330
11	1.4	108–113 at 20 mm.	1.4347
12	8.2	113–116 at 20 mm.	1.4413–1.4405
13	2.0	116–118 at 20 mm.	1.4377
14	3.4	118–122 at 20 mm.	1.4377–1.4399
15	2.5	122–133 at 20 mm.	1.4413–1.4432
16	4.9	133 at 20 mm. to 122 at 10 mm.	1.4620–1.4833
17	3.6	120–144 at 10 mm.	1.4810–1.4605
Residue	36.8	>144 at 10 mm.	—

Fractions 3 and 5 were fairly pure 2-methyl-1-pentanol and 1-hexanol, respectively. The 2-methyl-1-pentanol and 1-hexanol were identified by their α-naphthylurethans and by comparison of their infrared spectra with those of authentic samples. The α-naphthylurethan of 2-methyl-1-pentanol from fraction 3 melted at 75.0–75.8° after recrystallization from petroleum ether (b.p. 60–68°C.), and the α-naphthylurethan of 1-hexanol from fraction 5 melted at 58.6–59.0° after recrystallization from petroleum ether (b.p. 60–68°). The literature values are 75–76°[34] and 59°,[35] respectively.

Fractions 1 through 9 were subjected to mass spectroscopic analyses for 2-methyl-1-pentanol and 1-hexanol, and from the mass spectroscopic analyses, boiling points and refractive indices of these fractions, the yields of 2-methyl-1-pentanol and 1-hexanol were estimated to be 7.3 g. (5.5%) and 8.0 g. (6.0%), respectively.

Infrared and mass spectroscopic analyses of fraction 12 indicated the presence of C_{12} esters.

Reaction of diphenylacetylene under hydroformylation conditions. In a 200-ml. autoclave, 17.8 g. (0.10 mole) of diphenylacetylene, 3.0 g. (8.8×10^{-3} mole) of dicobalt octacarbonyl and 60 ml. of cyclohexane were pressured to 3500 p.s.i. with 1:1 synthesis gas. The reaction mixture was heated to 129° in about 1 hr., kept at 129° for 1.5 hr., at 130–140° for about 1 hr. and at 140–150° for about 1 hr. without any pressure drop or other sign of reaction. The temperature was then raised to 175° in about 1.5 hr. The maximum pressure reached was 4510 p.s.i. at 168°, after which there was a small pressure drop. At 185° there was an 11° exotherm to 196° and a rapid pressure drop from 4350 to 3800 p.s.i. The temperature was kept at 180–195° for about 2 hr. The final pressure at room temperature was 2680 p.s.i.

The reaction mixture was removed from the autoclave and subjected to elution chromatography on an alumina column.

(a) The Skellysolve eluant yielded two fractions, 12.3 g. of a tan semi-solid and 4.9 g. of a slightly oily, white solid that melted at 46.6–48.6°.

(b) The Skellysolve-benzene (1:1) eluant yielded 0.9 g. of a white semi-solid.

(c) The benzene eluant yielded 0.13 g. of a colorless oil. The infrared absorption spectrum of this material indicated the presence of a non-conjugated ketonic carbonyl group. An attempt to prepare a 2,4-dinitrophenylhydrazone was unsuccessful.

(d) The benzene-ethanol (4:1) eluant yielded 1.3 g. of a pale brown oil which was shown to contain aliphatic hydroxyl groups by means of its infrared and ultraviolet absorption spectra. Attempts to prepare a phenylurethan and an α-naphthylurethan were unsuccessful.

Fractions (a) and (b) from the Skellysolve and Skellysolve-benzene (1:1) eluants were combined. Recrystallization from pentane yielded 14.6 g. (80%) of 1,2-diphenylethane, melting point 49–51°. There was no depression of the mixed melting point upon mixture with an authentic sample, and the infrared spectra of the two samples were identical.

Effect of acetylenic dicobalt hexacarbonyls on reactions occurring under hydroformylation conditions. Effect of acetylenic dicobalt hexacarbonyls on the hydroformylation of olefins. In each of the following experiments, varying amounts of an alkyne were added to a mixture of the olefin, the solvent, and dicobalt octacarbonyl. The reaction mixture was allowed to stand at room temperature for 1 hr. in a flask fitted with a mercury valve to allow the escape of carbon monoxide which was evolved from the reaction of the alkyne with dicobalt octacarbonyl. The reaction mixture was then transferred to a 500-ml. autoclave and pressured with 1:1 synthesis gas to 3500 p.s.i. at room temperature. Rocking and heating of the autoclave were then begun. The same rate of heating was used in each experiment; a temperature of approximately 50° was reached in about 30 min., and thereafter the temperature rose at a rate of approximately 2° per min. The point of initial reaction was taken to be that temperature at which gas absorption started.

All time intervals refer to total heating time and not to time at a particular temperature.

Experiment 1. Cyclohexene and dicobalt octacarbonyl. The reaction mixture consisted of 41.1 g. (0.50 mole) of cyclohexene, 65 ml. of methylcyclohexane and 2.8 g. (8.2×10^{-3} mole) of dicobalt octacarbonyl. Reaction began at about 105°. The highest pressure reached was 4560 p.s.i. at 120° after 58 min., and the first pressure drop occurred at 120–124°.

Experiment 2. Cyclohexene and 1-hexyne dicobalt hexacarbonyl. Experiment 1 was repeated in the presence of 0.69 g. (8.4×10^{-3} mole) of 1-hexyne, so that the dicobalt octacarbonyl was converted to 1-hexyne dicobalt hexacarbonyl (8.2×10^{-3} mole). Reaction began at about 115°. The highest pressure reached was 4660 p.s.i. at 117° after 61 min., and the first pressure drop occurred at 117–126°.

Experiment 3. Cyclohexene and phenylacetylene dicobalt hexacarbonyl. Experiment 1 was repeated in the presence of 0.86 g. (8.4×10^{-3} mole) of phenylacetylene, so that the dicobalt octacarbonyl was converted to phenylacetylene dicobalt hexacarbonyl (8.2×10^{-3} mole). Reaction began at about 130°. The highest pressure reached was 4950 p.s.i. at 134° after 68 min., and the first pressure drop occurred at 138–140°.

Experiment 4. Cyclohexene and diphenylacetylene dicobalt hexacarbonyl (DDH). Experiment 1 was repeated in the presence of 1.50 g. (8.4×10^{-3} mole) of diphenylacetylene, so that the dicobalt octacarbonyl was converted to DDH (8.2×10^{-3} mole). Reaction began at about 140°. The highest pressure reached was 4970 p.s.i. at 145° after 71 min., and the first pressure drop occurred at 145–147°. At 150° there was an exotherm with the temperature rising to 178° and the pressure falling from 4900 to 3750 p.s.i. in a 3-min. interval.

Experiment 5. Cyclohexene, dicobalt octacarbonyl, and diphenylacetylene dicobalt hexacarbonyl. Experiment 1 was repeated with 4.2 g. (12.3×10^{-3} mole) of dicobalt octacarbonyl in the presence of 0.73 g. (4.1×10^{-3} mole) of diphenylacetylene, so that the reaction mixture contained 2.8 g. (8.2×10^{-3} mole) of dicobalt octacarbonyl and 4.1 ×

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(34) A. Magnani and S. M. McElvain, *J. Am. Chem. Soc.*, **60**, 813 (1938).

(35) D. W. Adamson and J. Kenner, *J. Chem. Soc.*, 838 (1934).

10^{-3} mole of DDH. The reaction proceeded in a manner that was indistinguishable from Experiment 1.

Experiment 6. Cyclohexene, diphenylacetylene dicobalt hexacarbonyl, and diphenylacetylene. Experiment 1 was repeated in the presence of 3.0 g. (16.8×10^{-3} mole) of diphenylacetylene, so that the reaction mixture contained 8.2×10^{-3} mole of DDH and 1.50 g. (8.4×10^{-3} mole) of diphenylacetylene. Reaction began at 172° after 90 min. At this point there was an exotherm with the temperature rising to 221° in a 1-min. interval and the pressure falling from 5250 p.s.i. at 172° to 3810 p.s.i. at 220° in a 2-min. interval.

Experiment 7. 1-Heptene and dicobalt octacarbonyl. The reaction mixture consisted of 24.5 g. (0.25 mole) of 1-heptene, 33 ml. of methylcyclohexane and 1.4 g. (4.1×10^{-3} mole) of dicobalt octacarbonyl. Reaction began at about 90°. The highest pressure reached was 4425 p.s.i. at 111° after 56 min., and the first pressure drop occurred at 111–114°.

Experiment 8. 1-Heptene and diphenylacetylene dicobalt hexacarbonyl. Experiment 7 was repeated in the presence of 0.75 g. (4.2×10^{-3} mole) of diphenylacetylene, so that the dicobalt octacarbonyl was converted to DDH (4.1×10^{-3} mole). Reaction began at about 140°. The highest pressure reached was 5010 p.s.i. at 148° after 72 min., and the first pressure drop occurred at 152–157°.

Experiment 9. 1-Heptene, dicobalt octacarbonyl, and diphenylacetylene dicobalt hexacarbonyl. Experiment 7 was repeated with 2.8 g. (8.2×10^{-3} mole) of dicobalt octacarbonyl in the presence of 0.73 g. (4.1×10^{-3} mole) of diphenylacetylene, so that the reaction mixture contained 1.4 g. (4.1×10^{-3} mole) of dicobalt octacarbonyl and 4.1×10^{-3} mole of DDH. The reaction proceeded in a manner that was indistinguishable from Experiment 7.

Effect of diphenylacetylene dicobalt hexacarbonyl on the hydrogenation of the olefinic bond in crotonaldehyde. Each experiment was conducted in a 500-ml. autoclave with an initial pressure of 3500 p.s.i. of 1:1 synthesis gas at room temperature. The experimental procedures and the rate of heating were the same as have been described for Experiments 1–9.

Experiment 10. Crotonaldehyde and dicobalt octacarbonyl. The reaction mixture consisted of 35.0 g. (0.50 mole) of crotonaldehyde, 65 ml. of methylcyclohexane and 2.8 g. (8.2×10^{-3} mole) of dicobalt octacarbonyl. Reaction began at about 125°. The highest pressure reached was 4700 p.s.i. at 135° after 75 min., and the first pressure drop occurred at 140–143°.

Experiment 11. Crotonaldehyde and diphenylacetylene dicobalt hexacarbonyl. Reaction 10 was repeated in the presence of 1.50 g. (8.4×10^{-3} mole) of diphenylacetylene, so that the dicobalt octacarbonyl was converted to DDH (8.2×10^{-3} mole). Reaction began at about 145–150°. The highest pressure reached was 5060 p.s.i. at 159° after 79 min., and the first pressure drop occurred at 159–162°. At 162° there was an exotherm with the temperature rising to 182° and the pressure falling from 5050 to 4450 p.s.i. in a 4-min. interval.

Experiment 12. Crotonaldehyde, dicobalt octacarbonyl, and diphenylacetylene dicobalt hexacarbonyl. Experiment 10 was repeated with 5.6 g. (16.4×10^{-3} mole) of dicobalt octacarbonyl in the presence of 1.46 g. (8.2×10^{-3} mole) of diphenylacetylene, so that the reaction mixture contained 8.2×10^{-3} mole of dicobalt octacarbonyl and 8.2×10^{-3} mole of DDH. The reaction proceeded in a manner that was indistinguishable from Experiment 10.

Effect of diphenylacetylene dicobalt hexacarbonyl on the hydrogenolysis of p-methoxybenzhydrol. Each experiment was conducted in a 200-ml. autoclave with an initial pressure of 3500 p.s.i. of 1:1 synthesis gas at room temperature. Rocking of the autoclave was begun when the temperature reached 75°. The temperature then rose at a rate of approximately 2° per min. in each experiment.

Experiment 13. p-Methoxybenzhydrol and dicobalt octacarbonyl. The reaction mixture consisted of 36.0 g. (0.17 mole) of *p*-methoxybenzhydrol, 50 ml. of benzene and 2.8 g. (8.2×10^{-3} mole) of dicobalt octacarbonyl. The maximum pressure reached was 4400 p.s.i. at 116° after 64 min. The first pressure drop occurred at 116–120°.

Experiment 14. p-Methoxybenzhydrol and diphenylacetylene dicobalt hexacarbonyl. Experiment 13 was repeated in the presence of 1.50 g. (8.4×10^{-3} mole) of diphenylacetylene, so that the dicobalt octacarbonyl was converted to DDH (8.2×10^{-3} mole). The maximum pressure reached was 4945 p.s.i. at 147° after 80 min. The first pressure drop occurred at 150–152°.

Experiment 15. p-Methoxybenzhydrol, dicobalt octacarbonyl, and diphenylacetylene dicobalt hexacarbonyl. Experiment 13 was repeated with 5.6 g. (16.4×10^{-3} mole) of dicobalt octacarbonyl and 1.46 g. (8.2×10^{-3} mole) of diphenylacetylene, so that the reaction mixture contained 8.2×10^{-3} mole of dicobalt octacarbonyl and 8.2×10^{-3} mole of DDH. The reaction proceeded in a manner that was indistinguishable from Experiment 13.

Effect of diphenylacetylene dicobalt hexacarbonyl on the hydrogenolysis and homologation of p-methoxybenzyl alcohol. Experiment 16. p-Methoxybenzyl alcohol and diphenylacetylene dicobalt hexacarbonyl. A solution of 69.1 g. (0.50 mole) of *p*-methoxybenzyl alcohol and 8.2×10^{-3} mole of DDH [prepared *in situ* from 2.8 g. (8.2×10^{-3} mole) of dicobalt octacarbonyl and 1.50 g. (8.4×10^{-3} mole) of diphenylacetylene] in 65 ml. of benzene was placed in the 500-ml. autoclave. The reaction mixture was pressured to 3500 p.s.i. at room temperature with 2:1 synthesis gas ($2H_2$:1CO). Reaction began at about 140°. The maximum pressure reached was 4940 p.s.i. at 140° after 70 min. The first pressure drop occurred at 146–149°.

In the absence of the acetylenic compound, the temperature of initial reaction would have been at about 70°.[23]

Reaction of cobalt hydrocarbonyl with acetylene. A 1-l. round-bottom flask was evacuated and then filled with 1 atmosphere of acetylene gas at room temperature. The 1-l. flask was then equilibrated with an evacuated 12-l. round-bottom flask. The 12-l. flask, containing acetylene gas under reduced pressure, was filled to atmospheric pressure with 1:1 synthesis gas which contained cobalt hydrocarbonyl.[32]

A gas sample was immediately withdrawn and subjected to infrared spectroscopic analysis. Its infrared spectrum showed the presence of acetylene and cobalt hydrocarbonyl, and indicated the absence of aldehydes. A second gas sample was withdrawn after a period of 24 hr. Infrared and mass spectroscopic analyses showed the absence of cobalt hydrocarbonyl and the presence of acetylene, acetylene dicobalt hexacarbonyl, and propionaldehyde.

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