[CONTRIBUTION OF THE BRANCH OF COAL-TO-OIL RESEARCH, BUREAU OF MINES, U. S. DEPARTMENT OF THE INTERIOR AND THE DEPARTMENT OF CHEMISTRY OF THE UNIVERSITY OF PITTSBURGH]*

The Reaction of Allenes with Dicobalt Octacarbonyl[1]

HAROLD GREENFIELD,[2] IRVING WENDER,[2] AND JOHN H. WOTIZ[3]

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Certain allenic compounds react with dicobalt octacarbonyl at room temperature. It appears that an organocobalt complex is formed that can catalyze the polymerization of allenes.

The recent report that alkynes react with dicobalt octacarbonyl to give a new type of organometallic compound[4] (equation 1) prompted the present investigation of the reaction of allenes with the same carbonyl.

We wish to report that certain allenes react with dicobalt octacarbonyl at room temperature with the evolution of carbon monoxide; the primary

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

product of this reaction, which has not been identified, then catalyzes the polymerization of allenes. That the polymerization catalyst is probably an organometallic complex is supported by the isolation of organometallic compounds from the reaction of acetylenes with dicobalt octacarbonyl[4] and by the accumulation of evidence that olefins also form organometallic complexes with dicobalt octacarbonyl under the conditions of the hydroformylation reaction.[5-8]

Allenes having a hydrogen atom bonded to an allenic carbon atom (allene, 1,2-heptadiene, 2-butyl-2,3-butadienoic acid, and 2-butyl-2,3-pentadienoic acid) reacted with dicobalt octacarbonyl at room temperature. Tetraphenylallene, which does not have a hydrogen atom on an allenic carbon atom, did not react. No reaction took place at room temperature between dicobalt octacarbonyl and a monoölefin, 1-dodecene, and between the carbonyl and a conjugated diolefin, 1,4-diphenyl-1,3-butadiene.

THE STOICHIOMETRY OF THE REACTION OF ALLENES WITH DICOBALT OCTACARBONYL

The results of gasometric experiments with excess allene and with excess 1,2-heptadiene indicate that terminal allenes displace one mole of carbon monoxide from one mole of dicobalt octacarbonyl. The excess terminal allene polymerizes, either after the reaction with dicobalt octacarbonyl or concurrently with this reaction. For example, the infrared spectrum of the product of the reaction with a 50-fold molar excess of 1,2-heptadiene showed the absence of any 1,2-heptadiene. In the reaction with excess allene the polymerization was demonstrated directly by the absorption of large quantities of gaseous allene to form first a liquid and then a solid product. Because of the polymerization, it was not possible to determine the number of moles of an allene associated with the evolution of one mole of carbon monoxide from one mole of dicobalt octacarbonyl.

THE NATURE OF THE PRODUCTS OF THE REACTION OF DICOBALT OCTACARBONYL WITH TERMINAL ALLENES

An infrared spectrum was obtained from the dark, viscous oil resulting from the reaction of dicobalt octacarbonyl with allene after approximately eight moles of the allene had been absorbed per mole of dicobalt octacarbonyl. The spectrum indicated the absence of dicobalt octacarbonyl and of an allenic group. The spectrum had bands at 6.06 μ, characteristic of the C═C stretching frequency, and at 11.14 μ, characteristic of a terminal methylene group. There were also bands at 4.86 and 5.04 μ that could not be accounted for by any of the known carbonyls of cobalt.

The reaction mixture obtained from treating dicobalt octacarbonyl with excess 1,2-heptadiene was also subjected to infrared analysis. As in the case with allene, the spectrum indicated the absence of dicobalt octacarbonyl and of an allenic group, and had bands at 6.08 and 11.18 μ. There were also bands at 4.88, 4.95, 4.97, and 5.04 μ. This latter group of bands and the absorption at 4.86 and 5.04 μ for the product obtained from allene suggest the presence of compounds possessing terminal carbonyl groups of the type found in dicobalt octacarbonyl and the acetylenic dicobalt hexacarbonyls.[4]

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(2) Branch of Coal-to-Oil Research, Bureau of Mines, Bruceton, Pa.

(3) Department of Chemistry, University of Pittsburgh.

(4) (a) Sternberg, Greenfield, Friedel, Wotiz, Markby, and Wender, *J. Am. Chem. Soc.*, **76**, 1457 (1954); (b) Greenfield, Sternberg, Friedel, Wotiz, Markby, and Wender, *J. Am. Chem. Soc.*, **78**, 120 (1956).

(5) Natta, Ercoli, Castellano, and Barbieri, *J. Am. Chem. Soc.*, **76**, 4049 (1954).

(6) Greenfield, Metlin, and Wender, paper presented at the 126th Meeting of the American Chemical Society, New York, N. Y., September 1954.

(7) Martin, *Chemistry & Industry*, 1536 (1954).

(8) Wender, Metlin, Ergun, and Greenfield, to be submitted for publication.

In one experiment gaseous allene was allowed to react with dicobalt octacarbonyl until about 5.5 moles of allene had been absorbed per mole of dicobalt octacarbonyl. An attempt was made to distill the reaction mixture—a dark, viscous oil. None of the material was volatile at 45° and 1 mm. pressure. This suggests the absence of any hydrocarbons possessing less than 12 to 13 carbon atoms.[9] Thus it appears that this polymeric material derived from allene did not contain any dimers, trimers, or tetramers.

The results of the investigation of the reactions of dicobalt octacarbonyl with allene and with 1,2-heptadiene suggest that the initial product is an organocobalt compound that can catalytically polymerize allenes under very mild conditions. The polymerization products appear to be high-molecular-weight substances. The progressive transformation of the reaction product derived from solid dicobalt octacarbonyl and gaseous allene from an oil to a solid suggests that the degree of polymerization increases with further addition of allene.

An infrared spectrum was obtained of the reaction mixture resulting from the treatment of 2-butyl-2,3-butadienoic acid with excess dicobalt octacarbonyl. The spectrum showed the presence of unreacted dicobalt octacarbonyl and the absence of any absorption bands that could be attributed either to allenic groups or to carboxy groups. It thus appears that the reaction of the allenic acid with dicobalt octacarbonyl involved both the allenic group and the carboxylic acid group.

THE ATTEMPTED POLYMERIZATION OF MONOÖLEFINS

It was apparent that a product of the reaction of allene and dicobalt octacarbonyl was able to catalyze the polymerization of additional allene over a period of several days. It was of interest to ascertain whether this material could also catalyze the polymerization of a simple olefin. Experiments with propylene and with ethylene showed that the catalyst for the polymerization of allene was not able to effect the polymerization of simple monoölefins under the same reaction conditions.

EXPERIMENTAL

Dicobalt octacarbonyl,[10] 1,2-heptadiene,[11] 1,4-diphenyl-1,3-butadiene,[12] 2-butyl-2,3-butadienoic acid,[13] and 2-butyl-2,3-pentadienoic acid[14] were prepared by methods described in the literature.

Allene was purchased from the Chemicals Procurement Company. A mass spectroscopic analysis gave: allene, 93.8%; carbon dioxide, 5.1%; diethyl ether, 1.1%. Tetraphenylallene was purchased from the Eastern Chemical Corporation. Hexadecane and 1-dodecene were purchased from Humphrey-Wilkinson, Inc., and were distilled before use.

Unless otherwise stated, the following experiments were carried out at room temperature under an atmosphere of carbon monoxide or synthesis gas in a gasometric apparatus consisting of a reaction flask connected to a 25-ml. gas burette. The flask was fitted with a serum stopper for the injection of liquids and was provided with an arrangement for magnetic stirring.

THE STABILITY OF DICOBALT OCTACARBONYL

A. Solid dicobalt octacarbonyl. Under an atmosphere of carbon monoxide, 0.1854 g. (5.42×10^{-4} moles) of solid dicobalt octacarbonyl evolved 3.7×10^{-5} moles of gas (0.07 mole of gas per mole of dicobalt octacarbonyl) in a period of 65 hours. Illumination of the flask with ultraviolet light resulted in the evolution of an additional 8.4×10^{-5} moles of gas (0.16 mole of gas per mole of dicobalt octacarbonyl) in 5 hours and a further 5.3×10^{-5} moles of gas (0.10 mole of gas per mole of dicobalt octacarbonyl) in another 3.5 hours. After removal of the ultraviolet light the rate of gas evolution decreased, with an additional 8.7×10^{-5} moles of gas (0.16 mole of gas per mole of dicobalt octacarbonyl) coming off in an additional 16 hours.

B. Dicobalt octacarbonyl in hexadecane. A stirred solution of 0.1012 g. (2.96×10^{-4} moles) of dicobalt octacarbonyl in 0.9 ml. of hexadecane under an atmosphere of carbon monoxide evolved 0.4×10^{-5} moles of gas (0.01 mole of gas per mole of dicobalt octacarbonyl) in 2.5 hours. A total of 5.2×10^{-5} moles of gas (0.18 mole of gas per mole of dicobalt octacarbonyl) was evolved in a total of 19 hours. Illumination with a fluorescent light increased the rate of evolution to an additional 2.6×10^{-5} moles of gas (0.09 mole of gas per mole of dicobalt octacarbonyl) in an additional 4 hours. Illumination with ultraviolet light further increased the rate of evolution to an additional 6.5×10^{-5} moles of gas (0.18 mole of gas per mole of dicobalt octacarbonyl) in an additional 4 hours.

REACTIONS OF DICOBALT OCTACARBONYL

The attempted reaction of dicobalt octacarbonyl and 1-dodecene. A stirred solution of 0.130 g. (3.80×10^{-4} moles) of dicobalt octacarbonyl in 2 ml. (*ca.* 9×10^{-3} moles) of 1-dodecene under an atmosphere of carbon monoxide evolved 1.1×10^{-4} moles of gas (0.29 mole of gas per mole of dicobalt octacarbonyl) in a period of 7 hours. After standing for an additional 17 hours without stirring, an additional 0.1×10^{-4} moles of gas (0.03 mole of gas per mole of dicobalt octacarbonyl) was evolved.

The attempted reaction of dicobalt octacarbonyl and 1,4-diphenyl-1,3-butadiene. A stirred solution of 0.13 g. (6.3×10^{-4} moles) of 1,4-diphenyl-1,3-butadiene and 0.111 g. (3.24×10^{-4} moles) of dicobalt octacarbonyl in 2 ml. of toluene under an atmosphere of carbon monoxide evolved 5.4×10^{-6} moles of gas (0.02 mole of gas per mole of dicobalt octacarbonyl) in 5.5 hours. After standing for an additional 16.5 hours without stirring, a total of 2.5×10^{-5} moles of gas (0.08 mole of gas per mole of dicobalt octacarbonyl) was evolved.

The attempted reaction of dicobalt octacarbonyl with tetraphenylallene. A stirred solution of 0.1368 g. (4.00×10^{-4} moles) of dicobalt octacarbonyl and 0.3184 g. (9.25×10^{-4} moles) of tetraphenylallene in 4 ml. of toluene under an atmosphere of 0.25:1 synthesis gas evolved little or no gas in a period of 30 minutes. After the reaction mixture had stood for a total of 44 hours, 3.36×10^{-5} moles of gas (0.08 mole of gas per mole of dicobalt octacarbonyl) had been evolved.

Pyridine (10 ml.) was added to the reaction mixture in

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[9] Egloff, *Physical Constants of Hydrocarbons*, Reinhold Publishing Corp., New York, 1939, Vol. I.

[10] Wender, Greenfield, and Orchin, *J. Am. Chem. Soc.*, **73**, 2656 (1951).

[11] Wotiz, *J. Am. Chem. Soc.*, **73**, 693 (1951).

[12] Corson, *Org. Syntheses*, **Coll. Vol. 2**, 229 (1943).

[13] Wotiz, *J. Am. Chem. Soc.*, **72**, 1639 (1950).

[14] Wotiz and Palchak, *J. Am. Chem. Soc.*, **73**, 1971 (1951).

order to decompose the dicobalt octacarbonyl.[15] There was a rapid evolution of gas and a change in color from dark brown to amber. The reaction mixture then was transferred to a separatory-funnel. After the addition of 25 ml. of benzene, the organic phase was washed with dilute hydrochloric acid to remove the pyridine and the cobalt salts and then washed with water until the water washings were neutral. The organic solution was taken to dryness in a stream of nitrogen. The residue consisted of a quantitative recovery of tetraphenylallene, melting point 163.2 to 165.4°. There was no depression on a mixture melting point with an authentic sample.

The reaction of dicobalt octacarbonyl and 1,2-heptadiene. A. A stirred solution of 0.3386 g. (9.90×10^{-4} moles) of dicobalt octacarbonyl and 0.0323 g. (3.36×10^{-4} moles) of 1,2-heptadiene in 2 ml. of toluene under an atmosphere of carbon monoxide evolved 9.7×10^{-5} moles of gas (0.29 mole of gas per mole of 1,2-heptadiene) in 2 minutes, a total of 1.45×10^{-4} moles of gas (0.43 mole of gas per mole of 1,2-heptadiene) in 5 minutes and a total of 1.6×10^{-4} moles of gas (0.47 mole of gas per mole of 1,2-heptadiene) in 2.5 hours.

Infrared spectroscopic examination of the reaction mixture showed the absence of any allenic absorption bands, the presence of dicobalt octacarbonyl and probable presence of some type of an organocobalt compound.

B. A stirred solution of 0.101 g. (2.95×10^{-4} moles) of dicobalt octacarbonyl in 2 ml. (*ca.* 0.015 mole) of 1,2-heptadiene under an atmosphere of carbon monoxide evolved 3.3×10^{-4} moles of gas (1.11 moles of gas per mole of dicobalt octacarbonyl) in 7 minutes. After 3 hours the total amount of gas evolved had decreased to 2.7×10^{-4} moles (0.91 mole of gas per mole of dicobalt octacarbonyl). After 25 hours the value had further decreased to 2.6×10^{-4} moles of gas (0.87 mole of gas per mole of dicobalt octacarbonyl). The reaction product was a viscous, reddish-amber liquid.

Infrared spectroscopic examination of the reaction mixture showed the absence of dicobalt octacarbonyl and of any allenic absorption band. The infrared spectrum also indicated the presence of some kind of an organocobalt compound with absorption bands at 4.88, 4.95, 4.97, and 5.04 μ that are similar to those of the acetylenic dicobalt hexacarbonyls but at longer wavelengths.

The reaction of dicobalt octacarbonyl with 2-butyl-2,3-butadienoic acid. A. A solution of 0.0700 g. (4.99×10^{-4} moles) of 2-butyl-2,3-butadienoic acid and 0.360 g. (10.5×10^{-4} moles) of dicobalt octacarbonyl in 6 ml. of toluene under an atmosphere of carbon monoxide evolved 3.2×10^{-4} moles of gas (0.64 mole of gas per mole of 2-butyl-2,3-butadienoic acid) in 21 hours and a total of 3.3×10^{-4} moles of gas (0.66 mole of gas per mole of 2-butyl-2,3-butadienoic acid) over a period of 24 hours.

Infrared spectroscopic examination of the reaction mixture showed the presence of dicobalt octacarbonyl and the absence of both allenic and carboxy absorption bands.

B. A stirred solution of 0.4062 g. (11.9×10^{-4} moles) of dicobalt octacarbonyl and 0.1060 g. (7.56×10^{-4} moles) of 2-butyl-2,3-butadienoic acid in 2 ml. of toluene under an atmosphere of 0.7:1 synthesis gas evolved 0.90×10^{-4} moles of gas (0.12 mole of gas per mole of 2-butyl-2,3-butadienoic acid) in 6 minutes, 1.28×10^{-4} moles of gas in 10 minutes, 1.55×10^{-4} moles of gas in 13 minutes, 2.59×10^{-4} moles of gas (0.34 mole of gas per mole of 2-butyl-2,3-butadienoic acid) in 35 minutes, 2.96×10^{-4} moles of gas in 60 minutes, 3.25×10^{-4} moles of gas (0.43 mole of gas per mole of 2-butyl-2,3-butadienoic acid) in 135 minutes, and 3.36×10^{-4} moles of gas (0.44 mole of gas per mole of 2-butyl-2,3-butadienoic acid) in 24 hours.

The reaction of dicobalt octacarbonyl with 2-butyl-2,3-pentadienoic acid. A stirred solution of 0.3209 g. (9.38×10^{-4} moles) of dicobalt octacarbonyl and 0.1029 g. (6.67×10^{-4} moles) of 2-butyl-2,3-pentadienoic acid in 2 ml. of toluene under an atmosphere of 0.25:1 synthesis gas evolved 0.48×10^{-4} moles of gas (0.07 mole of gas per mole of 2-butyl-2,3-pentadienoic acid) in 2 minutes, 0.90×10^{-4} moles of gas in 12 minutes, 1.15×10^{-4} moles of gas (0.17 mole of gas per mole of 2-butyl-2,3-pentadienoic acid) in 17 minutes, 1.22×10^{-4} moles of gas in 32 minutes, 1.33×10^{-4} moles of gas (0.20 mole of gas per mole of 2-butyl-2,3-pentadienoic acid) in 62 minutes, and 1.44×10^{-4} moles of gas (0.22 mole of gas per mole of 2-butyl-2,3-pentadienoic acid) in 212 minutes.

The reaction of dicobalt octacarbonyl with allene. The experiments in which allene was used were conducted in a gasometric apparatus consisting of a 125-ml. reaction flask attached to a 250-ml. gas burette. Gaseous allene was added to the burette from a cylinder of allene. The total gas pressure, consisting of the partial pressure of the allene plus the partial pressure of an inert gas in the system, was kept close to one atmosphere by means of a mercury leveling bulb. Allene was added in portions in quantities of 100 to 200 ml. of gaseous allene whenever most of the allene in the system had been absorbed.

A. To 0.41 g. (1.2×10^{-3} moles) of solid dicobalt octacarbonyl in an atmosphere of helium was added gaseous allene. After a 24-hour period 4.8×10^{-3} moles of gas (4.0 moles of gas per mole of dicobalt octacarbonyl) had been absorbed. A gas sample was taken at this point. A mass spectroscopic analysis of the gas indicated the presence of allene, helium, and carbon monoxide, and the absence of any C_6 hydrocarbons. From the analysis it was calculated that 1.2×10^{-3} moles of carbon monoxide (1.0 mole of carbon monoxide per mole of dicobalt octacarbonyl) had been evolved and 6.0×10^{-3} moles of allene (5.0 moles of allene per mole of dicobalt octacarbonyl) had been absorbed.

More allene was added to the gasometric apparatus and the experiment was continued. In an additional 4 hours another 3.5×10^{-3} moles of gas was absorbed. Thus, a total of 9.5×10^{-3} moles of allene (7.9 moles of allene per mole of dicobalt octacarbonyl) had been absorbed. The reaction product was a dark, viscous oil. Its infrared spectrum had bands at 4.86 and 5.04 μ, attributable to the carbonyl groups of an organocobalt compound; at 6.06 μ, characteristic of the C=C stretching frequency; and at 11.14 μ, characteristic of a terminal methylene group.

B. To 0.30 g. (8.8×10^{-4} moles) of solid dicobalt octacarbonyl in an atmosphere of 1:1 synthesis gas was added gaseous allene. About 1×10^{-3} mole of gas was absorbed in 2 hours, and droplets were visible. At the end of 24 hours about 3×10^{-3} moles of gas was absorbed, and the product was a dark-red oil. At the end of three days 9.3×10^{-3} moles of gas (about 11 moles of allene per mole of dicobalt octacarbonyl) had been absorbed. An infrared spectrum of the reaction product, a dark, viscous oil, was very similar to that obtained from experiment A.

C. To 1.6 g. (4.7×10^{-3} moles) of solid dicobalt octacarbonyl in an atmosphere of 1:1 synthesis gas was added gaseous allene. At the end of 1 week, 21×10^{-3} moles of gas (about 5.5 moles of allene per mole of dicobalt octacarbonyl) had been absorbed. An attempt was made to distill the reaction mixture, a very viscous, dark oil. None of the product was volatile at 45° and 1 mm. pressure in a period of 2 hours. Some of the product then was sublimed at 40° and 10^{-5} mm. pressure. The sublimate was a black, oily, crystalline material. Its infrared spectrum contained the same bands characteristic of the reaction products from experiments *A* and *B*. In addition, there were several new bands in the 5 μ region.

D. To 0.30 g. (8.8×10^{-4} moles) of solid dicobalt octacarbonyl in an atmosphere of 1:1 synthesis gas was added gaseous allene. After the absorption of about 5×10^{-3} moles

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[15] Wender, Sternberg, and Orchin, *J. Am. Chem. Soc.*, **74,** 1216 (1952).

of gas (about 7 moles of allene per mole of dicobalt octacarbonyl) the apparatus was flushed with helium. The gasometric burette then was filled with propylene. No absorption of gas took place in a period of 3 days. The propylene then was replaced with ethylene. No absorption took place in a period of 18 days. The apparatus then was flushed with helium, and allene then was added. In a 3-day period 21 × 10^{-3} moles of gas (24 moles of allene per mole of dicobalt octacarbonyl) were absorbed. At this point the reaction mixture appeared to have solidified. After an additional 16 days during which time allene was added and absorbed, a total of about 80 moles of allene was absorbed per mole of dicobalt octacarbonyl. The reaction product appeared to be a non-homogeneous solid. Most of the solid was brownish-yellow, and some black material was also present.

BRUCETON, PENNSYLVANIA
PITTSBURGH 13, PENNSYLVANIA