United States Patent Office 2,803,525 Patented Aug. 20, 1957

2,803,525

PROCESS FOR PREPARING CHROMIUM CARBONYL

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No Drawing. Application April 4, 1955, Serial No. 499,216

20 Claims. (Cl. 23—203)

The present invention relates to a novel process for preparing chromium carbonyl, $Cr(CO)_6$.

According to the text "Inorganic Syntheses," volume III, 1950, page 156: "Chromium hexacarbonyl has been prepared by the reaction of chromium (III) chloride with phenyl magnesium bromide in the presence of carbon monoxide. Unsatisfactory yields have been reported and difficulty experienced in repeating the synthesis. Unfortunately, no other methods for the preparation of this substance are recorded in the literature."

In accordance with the present invention, there is formed in a reaction vessel a mixture of at least one reducing metal higher than platinum in the electromotive series, such as magnesium, aluminum, zinc, copper, silver, sodium, calcium, iron, and manganese; and a chromium compound selected from the group consisting of chromium iodide, chromium chloride, and chromium bromide. When the mixture does not include chromium iodide, iodine must also be introduced into the mixture. Such iodine advantageously may be introduced as free iodine, as magnesium iodide, as aluminum iodide, or as zinc iodide. The ingredients mentioned above are mixed in a neutral oxygenated aliphatic Grignard-type solvent compound, such as an alkyl ether, alkyl ketone, or ethylene glycol ether.

Gaseous carbon monoxide is then introduced into the reaction vessel and reacted with the mixed ingredients at superatmospheric pressure. The pressure should be above 100 pounds per square inch gauge and the temperature should be between 0° C. and 160° C. for a yield of chromium carbonyl. Optimum conditions for a high yield are a pressure greater than 800 pounds per square inch, and a temperature between 30° C. and 50° C. It has also been found to be beneficial to carry out the process as a ball mill, or other type of attrition milling, operation in order to prevent the buildup of a coating on the surfaces of the solid reactant which tends to isolate the reactants and limit the extent of the reaction and the chromium carbonyl produced.

Recovery of the chromium carbonyl product from the reacted mixture can be accomplished in any suitable way, as by steam distillation or sublimation. Subsequently the carbonyl can be used as desired, for example being used to plate chromium metal onto metal surfaces by thermal decomposition of the carbonyl.

It is believed that the process described above proceeds through the reaction of chromium iodide with the reducing metal and carbon monoxide in the solvent compound, to yield chromium carbonyl. In this reaction chromium iodide can itself be the starting chromium compound. However, when the starting chromium compound is chromium chloride or chromium bromide, there must be present in the mixture a metal iodide which reacts with the chromium chloride or chromium bromide to form chromium iodide transitorially, which in turn reacts to yield the carbonyl as described above. The metal iodide can be added as such, or can be formed in situ by including in the reaction mixture free iodine which reacts with the reducing metals.

A number of examples of the novel process are described below. The metals used were in all cases so comminuted as to pass through a screen having 0.0083-inch openings. Some of them were also so fine as to pass through a screen having 0.0029-inch openings. The powder size is not critical, however, and both much coarser and much finer metal particles can be used successfully.

Example 1

8 grams of $CrCl_3$ (chromic chloride), 5 grams of Mg, 7 grams of free I_2, and 100 milliliters of ethyl ether were mixed together in a pressure vessel. Carbon monoxide was then pumped into the pressure vessel to an initial pressure of 880 pounds per square inch and the reaction was allowed to proceed at a temperature of 25° C. for 22 hours, after which the pressure had dropped to 590 pounds per square inch. The conversion of Cr to $Cr(CO)_6$ was 57.3%.

In contrast to Example 1, no carbonyl was obtained by mixing together 20 grams of chromic chloride and 20 grams of magnesium, and treating the mixture with carbon monoxide at a pressure of 7080 pounds per square inch for 45 hours at 350° C.

In further contrast to Example 1, no chromium carbonyl was obtained by mixing together $CrCl_3$, Mg, and ethyl ether and pressurizing the mixture with carbon monoxide under conditions which would have produced the carbonyl if iodine had been present.

Also in contrast to Example 1, no carbonyl was obtained by pressurizing 8 grams of chromium chloride, 5 grams of magnesium, 12 grams of free bromine, and 150 milliliters of ethyl ether with carbon monoxide at 880 pounds per square inch for 16 hours at 25° C.

Example 2

15.8 grams of (0.1 mol) $CrCl_3$, 5 grams of (0.02 mol) free iodine, 7.2 grams of magnesium, and 100 milliliters of ethyl ether were mixed together in a pressure vessel. Carbon monoxide was then pumped in to an initial pressure of 3000 pounds per square inch and the reaction was allowed to proceed for 64 hours at a temperature of 65° C. after which the pressure had dropped to 2800 pounds per square inch.

The conversion of Cr to $Cr(CO)_6$ was less than 2.3%, thus indicating that more than 1 mol of iodine should be present for each 5 mols of $CrCl_3$ for commercially acceptable yields.

The effect of temperature on the reaction is shown by Examples 3, 4, 5, and 6 below, which should be contrasted with Example 1.

Example 3

A mixture of 8 grams of $CrCl_3$, 4 grams of Mg, 5 grams of I_2, and 100 milliliters of ethyl ether was chilled to −78° C. and reacted with carbon monoxide under an initial pressure of 3000 pounds per square inch pressure for 18 hours. During the period of reaction, the mixture gradually warmed up to 25° C. Only about 3 grams of carbonyl was formed, indicating no advantage from sub-zero temperatures.

Example 4

A mixture of 8 grams of $CrCl_3$, 5 grams of Mg, 7 grams of I_2, and 100 milliliters of ethyl ether was reacted with carbon monoxide under an initial pressure of 4200 pounds per square inch pressure for 18 hours at 160° C. Only a trace of carbonyl was formed, indicating that the temperature should be no higher than 160° C.

Example 5

A mixture of 225 grams of $CrCl_3$, 90 grams of Mg, 190 grams of I_2, and 1100 milliliters ethyl ether was reacted with carbon monoxide under an initial pressure of 4700 pounds per square inch pressure for 16 hours at 100° C. Conversion of Cr to $Cr(CO)_6$ was 10.5%, thus indicating that the proper temperature limit for commercially acceptable yields is not much higher than 100° C., say 125° C.

Example 6

An autoclave was charged with 709 grams of $CrCl_3$, 593 grams of Mg, 593 grams of I_2, and 3½ gallons of ethyl ether. Carbon monoxide was pumped into the autoclave and a pressure of 2200 pounds per square inch was attained at the beginning of the heating period, which was between 4 and 8 hours. The experiment was conducted at six different temperatures with the results tabulated below, which indicate that the best yields occur in the range 30–50° C.

Operating Temp. °C.:	Percent conversion of Cr to $Cr(CO)_6$
9	29
22	38
31	51
40	69
50	58
60	20

With regard to pressure, it is advantageous to operate in excess of 800 pounds per square inch to obtain a satisfactory rate of reaction. Using reactants in approximately the amounts of Example 5, essentially the same conversions were obtained at 880, 1500, and 3000 pounds per square inch. The reaction took place, but lower conversions were obtained, at 300 pounds per square inch. No carbonyl has been obtained in experiments at atmospheric pressure, but a trace was formed at 100 pounds per square inch, as shown in the following example:

Example 7

8 grams of $CrCl_3$, 7 grams of Mg, 7.2 grams of I_2, and 150 milliliters of ethyl ether were reacted with carbon monoxide at 100 pounds per square inch and 25° C. for 66 hours. About 0.5 gram $Cr(CO)_6$ was obtained.

Among the solvent compounds which have been found operative in the process of the invention are ethyl ether, methyl ethyl ketone, and acetone and it has been found that any solvent suitable for use in prior Grignard-type reactions may be advantageously employed as the solvent in the process of the invention.

Under similar reaction conditions, using the reactants $CrCl_3$, Mg, I_2, and CO, a conversion of chromium to chromium carbonyl of 50 to 81% was obtained with ethyl ether, 9% with methyl ethyl ketone, and 2% with acetone.

Example 8

8 grams of $CrCl_3$, 7 grams of I_2, 8 grams of comminuted Al, and 100 milliliters of ethyl ether were reacted with carbon monoxide at an initial pressure of 3000 pounds per square inch and a temperature of 25° C. for 19 hours. 2.7% conversion of chromium to chromium carbonyl was obtained.

Example 9

32 grams of CrI_2, 4 grams of Mg, and 100 milliliters of ethyl ether were reacted for 16 hours with carbon monoxide at an initial pressure of 2600 pounds per square inch and a temperature of 25° C. Conversion of chromium to chromium carbonyl was 8%.

Example 10

15.8 grams of $CrCl_3$, 5 grams of Mg, 41 grams of AlI_3, and 110 milliliters of ethyl ether were reacted with carbon monoxide at an initial pressure of 3000 pounds per square inch and a temperature of 25° C. for 17 hours. Conversion of chromium to chromium carbonyl was 32%.

Example 11

8 grams of $CrCl_3$, 3 grams of Mg, 41.5 grams of ZnI_2 in 110 milliliters of ethyl ether were reacted with carbon monoxide for 16 hours at 25° C. and 3000 pounds per square inch. Conversion of chromium to chromium carbonyl was 40%.

Example 12

15.8 grams of $CrCl_3$, 4 grams of Mg, 50 milliliters of ethyl ether containing 22 grams MgI_2, and 60 milliliters of additional ethyl ether were reacted with carbon monoxide at an initial pressure of 2950 pounds per square inch and a temperature of 25° C. for 16 hours. Conversion of chromium to chromium carbonyl was 60%.

In contrast no carbonyl was obtained in a similar reaction, but wherein $MgBr_2$ was used instead of magnesium iodide.

Example 13

12.3 grams of $CrCl_2$ (chromous chloride), 3 grams of Mg, 25 milliliters of ethyl ether containing 11 grams of MgI_2, and 75 milliliters of additional ethyl ether were reacted with carbon monoxide at an initial pressure of 3000 pounds per square inch and a temperature of 25° C. for 64.5 hours. The final pressure was 1400 pounds per square inch. Conversion of chromium to chromium carbonyl was 71%.

Example 14

13.4 grams of CrI_2, 4.4 grams of Zn dust, and 100 milliliters of ethyl ether were reacted with carbon monoxide under a pressure of 3000 pounds per square inch for 18 hours at 25° C. Conversion of chromium to chromium carbonyl was 18%.

Example 15

158 grams of $CrCl_3$, 190.5 grams of Cu, 417 grams of MgI_2, and 1000 milliliters of ethyl ether were mixed together in a reaction vessel and reacted with carbon monoxide at a pressure of 2550 pounds per square inch. After 19 hours at 25° C., the conversion of chromium to chromium carbonyl was 71%.

Example 16

12.3 grams of $CrCl_2$, 19 grams of Cu powder, and 115 milliliters of an ethyl ether solution containing 36 grams of MgI_2, were mixed and reacted with carbon monoxide at a pressure of 3000 pounds per square inch. After 16 hours at 25° C. the pressure had dropped to 1500 pounds per square inch and the conversion of chromium to chromium carbonyl was 71.4%.

Example 17

32 grams of CrI_2, 12.7 grams of Cu powder, and 100 milliliters of ethyl ether were reacted with carbon monoxide at a pressure of 3000 pounds per square inch. After 20.5 hours at 25° C. the conversion of chromium to chromium carbonyl was 56%.

The chromium iodide (CrI_2) can be made from cuprous iodide and powdered chromium metal, and the reaction then proceeded as follows:

Example 18

20.8 grams of Cr and 28.1 grams of CuI were heated at 450° C. for 45 minutes. After cooling, 100 milliliters of ethyl ether were added. The mixture was reacted with carbon monoxide at a pressure of 3000 pounds per square inch. After 16 hours at 25° C. the pressure had dropped to 1900 pounds per square inch and the conversion of chromium to chromium carbonyl was 55.5%.

Example 19

15.3 grams of CrI_2, 10.8 grams of Ag powder and 100 milliliters of ethyl ether were reacted with carbon monoxide at a pressure of 3000 pounds per square inch

and a temperature of 25° C. for 17 hours. Conversion of chromium to chromium carbonyl was 67%.

Example 20

8 grams of $CrCl_3$, 5.5 grams of Mn, and 100 milliliters of MgI_2 were reacted with carbon monoxide for 17 hours at a pressure of 3000 pounds per square inch and a temperature of 25° C. Conversion of chromium to chromium carbonyl was 27%.

Example 21

Chromium bromide was prepared by heating chromium powder to 400–500° C. and then permitting the chromium powder to absorb 17.6 grams of bromine. 14.6 grams of the resulting product were suspended in ethyl ether along with 7 grams of I_2 and 7 grams of Mg. The mixture was reacted for 16 hours with carbon monoxide at a temperature of 25° C. and a pressure of 3000 pounds per square inch. The yield was 9.4 grams of chromium carbonyl.

In other examples of the process of the invention, iron, calcium and sodium have been employed as the reducing metal and n-butyl ether, ethylene glycol monomethyl ether, and ethylene glycol dimethyl ether have been employed as the neutral oxygenated aliphatic solvent compounds.

This is in part a continuation of our application Serial No. 238,196, filed July 23, 1951, now abandoned.

What is claimed is:

1. A process for preparing chromium carbonyl which comprises reacting together carbon monoxide, a chromium iodide, and at least one metal selected from the group consisting of magnesium, aluminum, zinc, copper, silver, sodium, calcium, iron, and manganese in the presence of a neutral oxygenated aliphatic solvent compound selected from the group consisting of alkyl ethers, allyl ketones, and ethylene glycol ethers and at a temperature between about 0° C. and 160° C., and at a superatmospheric pressure in excess of 100 pounds per square inch.

2. A process for preparing chromium carbonyl which comprises forming a mixture of the following ingredients: at least one metal selected from the group consisting of magnesium, aluminum, zinc, copper, silver, sodium, calcium, iron, and manganese; a compound selected from the group consisting of alkyl ethers, alkyl ketones, and ethylene glycol ethers; and a chromium compound selected from the group consisting of chromium bromide, and chromium chloride; said process also comprising providing metal iodide in said mixture to form chromium iodide; and said process also comprising reacting said mixture with carbon monoxide at a temperature between about 0° C. and 160° C., and at a superatmospheric pressure in excess of 100 pounds per square inch.

3. A process in accordance with claim 2 wherein said provided metal iodide is formed in situ by the reaction of free iodine and a selected group metal.

4. A process in accordance with claim 2, wherein said iodide is provided in said mixture as magnesium iodide, and said chromium compound is a chromium chloride.

5. A process in accordance with claim 2, wherein said iodide is provided in said mixture as magnesium iodide, and said chromium compound is a chromium bromide.

6. A process in accordance with claim 2, wherein said iodide is provided in said mixture as aluminum iodide, and said chromium compound is a chromium chloride.

7. A process in accordance with claim 2, wherein said iodide is provided in said mixture as zinc iodide, and said chromium compound is a chromium chloride.

8. A process for preparing chromium carbonyl which comprises mixing together a chromium chloride, free iodine, comminuted magnesium, and a compound selected from the group consisting of alkyl ethers, alkyl ketones and ethylene glycol ethers; and reacting said mixture with carbon monoxide at a temperature between about zero and about 160° C. and at a superatmospheric pressure in excess of 100 pounds per square inch.

9. A process for preparing chromium carbonyl which comprises mixing together a chromium chloride, free iodine, comminuted magnesium, and a compound selected from the group consisting of alkyl ethers, alkyl ketones and ethylene glycol ethers, said chromium chloride and said iodine being mixed in amounts to provide at least 1 mol of iodine for every 5 mols of chromium chloride; and reacting said mixture with carbon monoxide at a temperature between about zero and about 125° C. and at a superatmospheric pressure in excess of 100 pounds per square inch.

10. A process in accordance with claim 9, wherein said compound is ethyl ether.

11. A process for preparing chromium carbonyl which comprises mixing together a chromium chloride, free iodine, comminuted aluminum, and ethyl ether; and reacting said mixture with carbon monoxide at a temperature between about zero and about 160° C. and at a superatmospheric pressure in excess of 100 pounds per square inch.

12. A process for preparing chromium carbonyl which comprises mixing together a chromium iodide, comminuted magnesium, and ethyl ether; and reacting said mixture with carbon monoxide at a temperature between about zero and about 160° C. and at a superatmospheric pressure in excess of 100 pounds per square inch.

13. A process for preparing chromium carbonyl which comprises mixing together a chromium iodide, comminuted zinc, and ethyl ether; and reacting said mixture with carbon monoxide at a temperature between about 0° C. and 160° C., and a pressure in excess of 100 pounds per square inch.

14. A process for preparing chromium carbonyl which comprises mixing together chromic chloride, comminuted copper, an iodide of magnesium, and ethyl ether; and reacting said mixture with carbon monoxide at a temperature between about 0° C. and 160° C., and a pressure in excess of 100 pounds per square inch.

15. A process for preparing chromium carbonyl which comprises mixing together chromous chloride, comminuted copper, an iodide of magnesium, and ethyl ether; and reacting said mixture with carbon monoxide at a temperature between about 0° C. and 160° C., and a pressure in excess of 100 pounds per square inch.

16. A process for preparing chromium carbonyl which comprises mixing together a chromium iodide, comminuted copper, and ethyl ether; and reacting said mixture with carbon monoxide at a temperature between about 0° C. and 160° C., and a pressure in excess of 100 pounds per square inch.

17. A process for preparing chromium carbonyl which comprises mixing together a chromium chloride, magnesium iodide, comminuted manganese, and ethyl ether; and reacting said mixture with carbon monoxide at a temperature between about 0° C. and 160° C., and a pressure in excess of 100 pounds per square inch.

18. A process for preparing chromium carbonyl which comprises providing a mixture of the following ingredients: at least one metal selected from the group consisting of magnesium, aluminum, zinc, copper, silver, sodium, calcium, iron, and manganese; a compound selected from the group consisting of alkyl ethers, alkyl ketones and ethylene glycol ethers; and a chromium iodide; said process also comprising reacting said mixture with carbon monoxide at a temperature between about 0° C. and 160° C., and at a superatmospheric pressure in excess of 100 pounds per square inch.

19. A process for preparing chromium carbonyl which comprises mixing together chromium chloride, comminuted magnesium, magnesium iodide, and ethyl ether; and reacting said mixture with carbon monoxide at a temperature between about 0° C. and 160° C., and at a super-

atmospheric pressure in excess of 100 pounds per square inch.

20. A process for preparing chromium carbonyl which comprises reacting together carbon monoxide, chromium iodide, and at least one metal higher than platinum in the electromotive series in the presence of at least one solvent compound selected from the group consisting of alkyl ethers, alkyl ketones and ethylene glycol ethers and at a temperature between about 0° C. and 160° C., and

at a superatmospheric pressure in excess of 100 pounds per square inch.

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