



A Publication  
of Reliable Methods  
for the Preparation  
of Organic Compounds

## Working with Hazardous Chemicals

The procedures in *Organic Syntheses* are intended for use only by persons with proper training in experimental organic chemistry. All hazardous materials should be handled using the standard procedures for work with chemicals described in references such as "Prudent Practices in the Laboratory" (The National Academies Press, Washington, D.C., 2011; the full text can be accessed free of charge at [http://www.nap.edu/catalog.php?record\\_id=12654](http://www.nap.edu/catalog.php?record_id=12654)). All chemical waste should be disposed of in accordance with local regulations. For general guidelines for the management of chemical waste, see Chapter 8 of Prudent Practices.

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*These paragraphs were added in September 2014. The statements above do not supersede any specific hazard caution notes and safety instructions included in the procedure.*

*Organic Syntheses, Coll. Vol. 2, p.142 (1943); Vol. 19, p.31 (1939).*

## COPPER CHROMITE CATALYST



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### 1. Procedure

A mixture of 26 g. (0.1 mole) of c.p. [barium nitrate](#) and 800 cc. of distilled water is warmed to 70°. After solution is complete 218 g. (0.9 mole) of c.p. [copper nitrate trihydrate](#) is added and the mixture stirred at 70° until a clear solution results ([Note 2](#)).

A solution of [ammonium chromate](#) is prepared by dissolving 126 g. (0.5 mole) of c.p. [ammonium dichromate](#) in 600 cc. of distilled water and adding 150 cc. of 28 per cent aqueous [ammonia](#) (sp. gr. 0.9) ([Note 3](#)). The warm solution of the nitrates is stirred (hand stirring is adequate) while the [ammonium chromate](#) solution is poured into it in a thin stream. Stirring is continued for a few minutes, after which the reddish brown precipitate of [copper barium ammonium chromate](#) is collected ([Note 4](#)) and pressed in a 16-cm. Büchner funnel, and dried at 110°. This dry precipitate is placed in a loosely covered nickel pan ([Note 5](#)), or one or two small porcelain casseroles covered with watch glasses, and heated in a muffle furnace for one hour at 350–450° ([Note 6](#)). At this point the yield of chromite should be about 160 g. The ignition residue is pulverized in a mortar to break up any hard lumps that may be present ([Note 7](#)) and then transferred to a 2-l. beaker containing 1.2 l. of 10 per cent [acetic acid](#). After being stirred for ten minutes the mixture is allowed to settle. After about ten minutes, two-thirds or more of the spent acid solution is decanted and replaced by 1.2 l. of fresh 10 per cent [acetic acid](#), and the extraction is repeated. The residue is washed by repeating the extraction procedure four times with 1.2 l. of distilled water each time ([Note 8](#)). The insoluble portion is collected by filtering with suction on a Büchner funnel, dried at 110°, and ground in a mortar to a fine black powder ([Note 9](#)). The yield is 130–140 g. ([Note 10](#)) and ([Note 11](#)).

### 2. Notes

1. The reactions involved in this preparation cannot be expressed quantitatively in a simple equation. The process has been investigated by Gröger.<sup>1</sup>

2. [Barium nitrate](#) is sparingly soluble in cold water and even less soluble in [copper nitrate](#) solution. It is therefore necessary to heat the mixture in order to bring both salts into solution together.

3. The warm, freshly prepared [ammonium chromate](#) solution may be used for the precipitation at once or may be allowed to cool to room temperature. However, the solution prepared as indicated is supersaturated at room temperature and deposits crystals on standing. If a stock solution of [ammonium chromate](#) is to be held over from day to day, a portion of the [ammonia](#) should be withheld and added immediately before precipitation. [Chromic acid](#) may be used for the preparation of the [ammonium chromate](#) solution provided that the acid solution is kept cold while a sufficient quantity of [ammonia](#) is introduced below the surface.

4. The amount of [ammonia](#) used is calculated to give a mother liquid that is neutral to litmus, allowance being made for the basic character of the precipitate. While a deviation either way affects the yield adversely, it is better not to try to adjust the end point after precipitation, but to make a slight correction on the amount of [ammonia](#) to be used for the next batch. The mother liquor serves as its own indicator: if acid, the solution is yellow; if alkaline, a deep green.

5. A convenient-sized pan, 6 cm. deep, 19 cm. long, and 10 cm. wide, can be made from a sheet of nickel 1/32 inch thick.

6. The ignition of [copper ammonium chromate](#) causes a spontaneous exothermic reaction which proceeds with a rapid evolution of gas. Although the size of the charge ignited at one time is

unimportant, the retaining vessels should not be too full, else there will be considerable mechanical loss of product. It is also inadvisable to break up the lumps of dried precipitate, as the lumpy condition diminishes spraying of the chromite on ignition.

7. The unextracted catalyst should be a bluish black, friable powder. It is a satisfactory catalyst for the dehydrogenation of alcohols and for the less difficult hydrogenation reactions, such as the reduction of nitro compounds. This mixture of [copper chromite](#) and [copper oxide](#) is somewhat less active and more susceptible of reduction to metallic copper than the catalyst from which the [copper oxide](#) has been removed by acid extraction.

8. If the washing is unduly prolonged, the catalyst tends to become colloidal and is difficult to separate either by decantation or filtration.

9. No special precautions are necessary in handling or storing the [copper chromite](#) catalyst, since it is unharmed by exposure to air or moisture.

10. [Barium](#) has been included as a catalyst component on account of its protective action against sulfate poisoning and its reported stabilization of the catalyst against reduction. Alternatively, the above procedure may be used for the preparation of a [copper chromite](#) catalyst containing no [barium](#). In this case the [barium nitrate](#) is omitted and 242 g. (1 mole) of [copper nitrate](#) is used. All other details are the same as given above.

11. An alternative procedure described by Adkins<sup>2</sup> is as follows: Thirty-one grams of [barium nitrate](#) is dissolved in 820 cc. of distilled water which has been heated to 80°. To this hot solution is added 260 g. of [copper nitrate trihydrate](#), and the mixture is stirred and heated until solution is complete. Meanwhile, 151 g. of [ammonium dichromate](#) is dissolved in 600 cc. of distilled water and 225 cc. of 28 per cent aqueous [ammonia](#) added. The hot nitrate solution is poured in a thin stream with stirring into the [ammonium chromate](#) solution. The orange precipitate is collected on a filter, pressed, and sucked as dry as possible. It is dried in an oven at 75–80° for twelve hours, pulverized, and divided into three portions. Each portion is decomposed separately in a large porcelain casserole (15-cm. diameter) by heating over a free flame. The mass should be heated just hot enough to cause decomposition to take place at the minimum temperature. During the decomposition the powder is stirred continuously with a steel spatula, and the heating is regulated so that the evolution of gases does not become violent. This is accomplished by heating only one side of the casserole and by increasing the rate of stirring when the decomposition starts to spread throughout the mass. During this process the color of the powder changes from orange to brown and finally to black. When the entire mass has become black the evolution of gases ceases, and the powder is removed from the casserole and allowed to cool. The combined product is then stirred for thirty minutes with 600 cc. of 10 per cent [acetic acid](#) solution, collected on a filter, washed by suspending it six times in 100-cc. portions of water, dried for twelve hours at 125°, and pulverized. The yield of catalyst is 170 g.

### 3. Discussion

[Copper chromite](#) has been made by the ignition of basic [copper chromate](#) at a red heat and by the thermal decomposition of [copper ammonium chromate](#).<sup>1</sup> The procedure given here is a modification of the latter method<sup>3</sup> in which [barium ammonium chromate](#) is also incorporated.<sup>4</sup> [Copper-chromium oxide](#) hydrogenation catalysts have also been prepared by grinding or heating together [copper oxide](#) and chromium oxides, by the decomposition of copper ammonium chromium carbonates or copper-chromium nitrates,<sup>2, 4</sup> and by the low-temperature ignition of copper ammonium chromates.<sup>5</sup>

This preparation is referenced from:

- [Org. Syn. Coll. Vol. 2, 325](#)
- [Org. Syn. Coll. Vol. 3, 471](#)
- [Org. Syn. Coll. Vol. 3, 693](#)
- [Org. Syn. Coll. Vol. 4, 216](#)
- [Org. Syn. Coll. Vol. 4, 677](#)
- [Org. Syn. Coll. Vol. 4, 857](#)

1. Gröger, Z. anorg. Chem. **58**, 412 (1908); **76**, 30 (1912).
  2. Adkins, "Reactions of Hydrogen with Organic Compounds over Copper-Chromium Oxide and Nickel Catalysts," p. 12, University of Wisconsin Press, Madison, 1937.
  3. Lazier, U. S. pats. 1,746,782 and 1,746,783 [C. A. **24**, 1649 (1930)]; U. S. pat. 1,964,000 [C. A. **28**, 5075 (1934)].
  4. Connor, Folkers, and Adkins, J. Am. Chem. Soc. **53**, 2012 (1931); **54**, 1138 (1932)
  5. Calingaert and Edgar, Ind. Eng. Chem. **26**, 878 (1934).
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**Appendix**  
**Chemical Abstracts Nomenclature (Collective Index Number);**  
**(Registry Number)**

metallic copper

chromium oxides

copper ammonium chromium carbonates

copper-chromium nitrates

copper ammonium chromates

acetic acid (64-19-7)

ammonia (7664-41-7)

chromic acid (7738-94-5)

copper oxide (1317-38-0)

barium (7440-39-3)

COPPER CHROMITE

barium nitrate (10022-31-8)

copper nitrate trihydrate

ammonium chromate (7788-98-9)

ammonium dichromate

copper barium ammonium chromate

copper nitrate (3251-23-8)

copper ammonium chromate

Copper-Chromium Oxide

copper chromate

barium ammonium chromate

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