



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). 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.

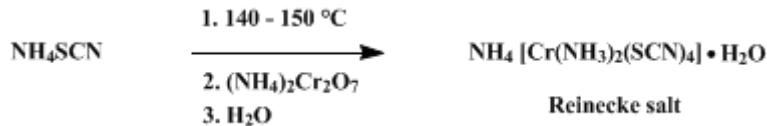
In some articles in *Organic Syntheses*, chemical-specific hazards are highlighted in red "Caution Notes" within a procedure. It is important to recognize that the absence of a caution note does not imply that no significant hazards are associated with the chemicals involved in that procedure. Prior to performing a reaction, a thorough risk assessment should be carried out that includes a review of the potential hazards associated with each chemical and experimental operation on the scale that is planned for the procedure. Guidelines for carrying out a risk assessment and for analyzing the hazards associated with chemicals can be found in Chapter 4 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.555 (1943); Vol. 15, p.74 (1935).

REINECKE SALT



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1. Procedure

Eight hundred grams (10.5 moles) of ammonium thiocyanate is gently heated, by means of three small flames (Note 1), in a white enameled cooking pot of about 4-l. capacity. The mass is stirred with a thermometer enclosed in a glass tube until the solid has partially melted and the temperature has reached 145–150°. At this point an intimate mixture of 170 g. (0.675 mole) of finely powdered ammonium dichromate and 200 g. (2.6 moles) of ammonium thiocyanate is added in portions of 10–12 g. with constant stirring. After about ten such portions have been added a fairly vigorous reaction takes place with evolution of ammonia and the temperature rises to 160°. The flames are extinguished, and the remainder of the mixture is added at such a rate that the heat of reaction maintains the temperature at 160° (Note 2). Stirring is continued while the mass cools, and any lumps of solid which form around the sides of the vessel are broken loose (Note 3).

The product, while still warm (Note 4), is finely powdered and stirred with 750 cc. of ice water in a large beaker. After fifteen minutes the insoluble portion is filtered by suction, freed as completely as possible from mother liquor without washing (Note 5), and stirred into 2.5 l. of water previously warmed to 65°. The temperature is then rapidly raised to 60° (Note 6), the solution is filtered at once through a hot-water funnel, and the filtrate is placed in a refrigerator overnight.

The resulting crystals are collected and the mother liquor employed for a second similar extraction of the residue at 60°. This yields a further crop of crystalline Reinecke salt. The mother liquor is finally concentrated to 250–300 cc. by evaporation at 40–50° under reduced pressure, when a small third crop (12–13 g.) is obtained. The total yield of air-dried crystals is 250–275 g. (52–57 per cent of the theoretical amount) (Note 7).

The undissolved residue from the second extraction consists chiefly of Morland salt (the guanidine salt of the Reinecke acid) and amounts to 130–135 g. (33–34 per cent of the theoretical amount) (Note 8).

2. Notes

1. Heat must be applied as uniformly as possible.
2. The addition of the mixture requires five to seven minutes.
3. The product is detached from the walls during cooling as it is difficult to remove when cold.
4. The material should be pulverized while warm before it has had an opportunity to attract moisture from the air.
5. The filtrate, which consists largely of unchanged ammonium thiocyanate and its decomposition products, contains too little Reinecke salt to repay further treatment.
6. Reinecke salt decomposes in aqueous solution with formation of a blue color and free hydrogen cyanide. At room temperature this decomposition occurs in about two weeks, and above 65° it takes place quite rapidly. A similar decomposition takes place in boiling alcohol.
7. Reinecke salt is of value as a precipitant for primary and secondary amines, proline and hydroxypyrolidine, and certain amino acids.¹
8. The Morland salt, which is soluble in acetone, contains a small proportion of a colorless sulfur compound insoluble in hot water. It can be partially converted into Reinecke salt by treatment in dilute

ammonia solution with a large excess of ammonium chloride, but the amounts so obtainable are unprofitably small.

3. Discussion

Reinecke salt has been prepared by adding either potassium dichromate² or ammonium dichromate¹,
³ to fused ammonium thiocyanate.

References and Notes

1. Kapfhammer and Eck, Z. physiol. Chem. **170**, 310 (1927); Grassmann and Lang, Biochem. Z. **269**, 223 (1934).
2. Reinecke, Ann. **126**, 113 (1863); Christensen, J. prakt. Chem. (2) **45**, 213 (1892); Zeleny and Gortner, J. Biol. Chem. **90**, 430 (1931).
3. Werner, Z. anorg. Chem. **15**, 260 (1897); Ann. **406**, 276 (1914).

Appendix Chemical Abstracts Nomenclature (Collective Index Number); (Registry Number)

REINECKE SALT

Morland salt (the guanidine salt of the Reinecke acid)

alcohol (64-17-5)

ammonia (7664-41-7)

ammonium chloride (12125-02-9)

ammonium thiocyanate (1762-95-4)

hydrogen cyanide (74-90-8)

acetone (67-64-1)

potassium dichromate (7778-50-9)

ammonium dichromate

proline (147-85-3)

hydroxyproline