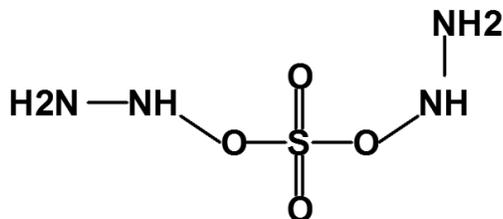


SYNTHESIS OF HYDRAZINE SULFATE via The Hoffmann Rearrangement Process on Urea (with Ketone Azine Final Workup)

by Hexavalent, SM Member



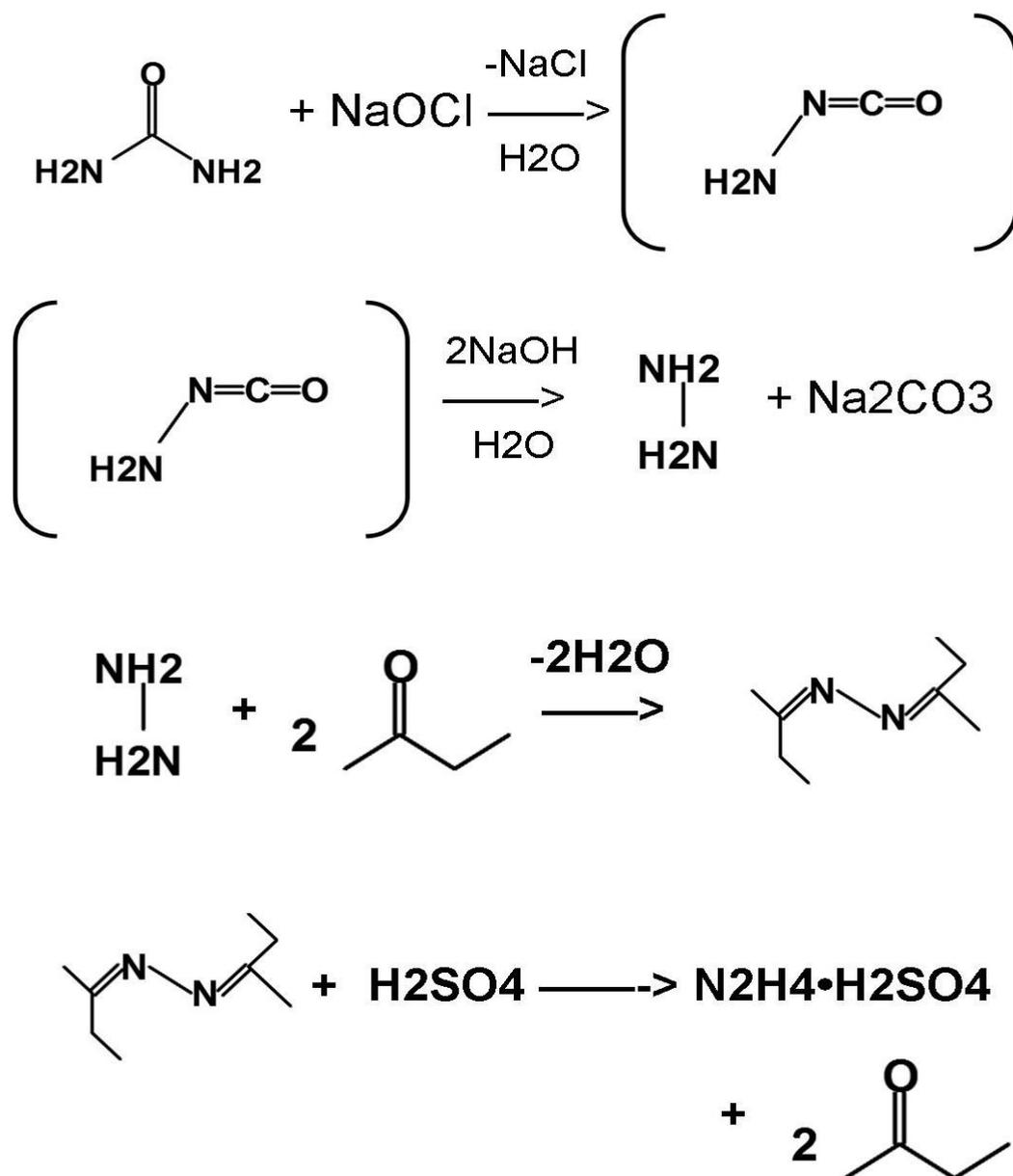
Abstract

Described in this document is an approach that was attempted in order to prepare Hydrazine Sulfate, a useful salt of N_2H_4 that is safer and easier to handle and store in an amateur setting than the pure liquid itself. All chemicals used were purchased easily from local stores or online (from eBay only).

WARNING – Hydrazine intermediates and salts are toxic, potentially carcinogenic, hazardous to the environment, potentially explosive and fairly reactive. All procedures described were carried out wearing full PPE and performed in a ducted fume cupboard or outside.

Introduction

The Hoffmann Rearrangement Process on Urea was attempted and was completed with a 42% yield as a glistening, free-flowing white crystalline powder. Simply, urea reacts with the hypochlorite ion in basic aqueous solution to generate an aminoisocyanate intermediate which is then hydrolysed to generate hydrazine and Na_2CO_3 . A ketone (MEK) is then added to form methyl ethyl ketazine (aka butanone azine) which is separated off and treated with sulfuric acid to precipitate Hydrazine Sulfate and free excess MEK.



Experimental

314g of 12.5% Sodium Hypochlorite (NaClO) solution was added to an Erlenmeyer flask and was chilled in an ice bath atop a magnetic stirrer. A stir bar was added and medium-speed stirring was begun.

53g (1.33 moles) of granular Sodium Hydroxide (NaOH) was slowly added in small portions. An exotherm is generated when this material dissolves, and NaClO degrades rapidly at increased temperatures so the ice bath is needed.

39g (0.65 moles) of recrystallized urea was then added to a 1L single-neck RBF with 600mg (0.6g) of gelatine alongside 50ml of distilled water. After the addition of some boiling stones, the mixture was slowly heated in the microwave on a low setting to help the solutes dissolve.

A setup was prepared as followed; a hotplate/magnetic stirrer, on top of it the RBF containing the urea/gelatine solution, with a claisen adapter attached; one neck connected to a pressure-equalizing dripping funnel and the other neck to a cooled reflux condenser. The basic hypochlorite solution was added to the dripping funnel and was allowed to fall into the flask at a rate of 1 drop/sec. Stirring was used continuously with the magnetic stirrer. NO heat was applied during this stage. The mixture turned to a yellow/brown colour at this stage.

After the basic hypochlorite solution was added, the mixture was slowly heated to 90°C whilst maintaining reflux. The yellow/brown colour slowly dissipated and when it goes clear the reaction has finished; the flask was pulled off the heat and allowed to cool to below 40°C.

77g of 99.9% (1.07 moles) of MEK was then simply poured through the condenser (the condenser was not removed from the flask to prevent leakage of hydrazine vapours) and the mixture was stirred vigorously for 3 hours for the layers to mix and form the azine.

After stirring, the mixture was transferred to a separating funnel and the two layers of butanone azine/excess MEK and water/other contaminants

were allowed to separate. Clean separation was observed as the aqueous layer was nearly saturated with NaCl, formed by the earlier reaction.

The organic phase was removed and transferred to a clean RBF flask. Then, in a separate vessel, 40ml of 18M (~98%) sulfuric acid was slowly added to 100ml of water with stirring. The two mixtures were combined with stirring in the RBF.

Some hydrazine sulfate crystallized out, but, the RBF was then set up for azeotropic distillation to remove any excess MEK and drive the precipitation reaction to completion. The fraction boiling at 77.3°C was taken (this was the MEK/H₂O azeotrope) and was recycled for another batch of this synthesis.

Post-distillation, the flask was cooled in an ice bath to obtain as much N₂H₄ – H₂SO₄ as possible. Then, it was vacuum filtered and air was pulled over the captured solid for 30 minutes to dry it on the frit.

The solid was then transferred into an amber glass storage vessel labeled appropriately. Again, a 42% yield based on hypochlorite was obtained, which equates to 29.229g or 0.225 moles of N₂H₄ • H₂SO₄ .

Experimenter's Notes

When adding the basic NaOCl sol'n to the urea/gelatine mixture, a large amount of foam was generated which subsided with powerful stirring and time.

Sources and References

- <http://www.youtube.com/watch?v=UB7vwIFCnR0> (NurdRage's video)
- <http://www.youtube.com/watch?v=JCrDttuw5co> (UnintentionalChaos' video)
- <http://www.sciencelab.com/msds.php?msdsId=9927191> (MSDS for Hydrazine Sulfate, by ScienceLab)
- http://en.wikipedia.org/wiki/Hydrazine_sulfate (Wikipedia Article)