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Review Article

REVIEW ARTICLE ON: CHEMICAL IMPORTANCE OF BRADY'S REAGENT

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ABSTRACT

Since the action of 2, 4-dinitrophenylhydrazine (Brady's reagent) on aldehydes and ketones was first investigated by Purgotti in 1894, its usefulness as an analytical reagent for carbonyl containing compounds has been thoroughly exploited. The 2, 4 -DNHP reagent is an orange crystalline solid melting at 199^{0}C. Its usefulness as a reagent stems from the fact that it forms crystalline derivatives which are easily purified and have melting points supposedly characteristic of the aldehyde or ketone used in preparing the derivative.

In principle, each aldehyde and ketone should form a single 2,4-dinitrophenylhydrazone (DNPH) with a characteristic melting point. In practice, however, a number of the aldehydes and ketones do not follow this general rule but form multiple derivatives, differing either in melting point, crystal structure, or both. Even the colors of pure DNPH's of a partîcular aldehyde or ketone are sometimes different.

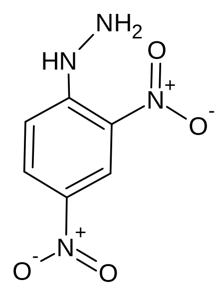
Keywords: 2,4-DNPH, Brady's reagent, 2, 4, - dinitrophenyl hydrazine.

INTRODUCTION

Aldehydes and ketones have been identified for a number of years by virtue of the fact that they form crystalline condensation products with a number of amines. One important example is 2,4-dinitrophenylhydrazine also called as Bradys reagent. The crystalline derivatives with their supposedly characteristic melting point provide a means of identification. The identifying aldehydes and ketones by the melting point of their 2,4-dinitrophenylhydrazones (DNPH's) has been shown to be unreliable in a number of Instances, as multiple DNPH's have been reported differing in melting point, crystal Structure, or both Draper, Heilman, Schoefer, Shine, and Shoolery observed that 2,4-Dexists in two crystal forms. Since the identification of aldehydes and ketones had previously been by the equivocal melting point method, a unequivocol x-ray method was considered desirable.

Structure of 2, 4-dinitrophenylhydrazine

Although the name sounds complicated, and its structure looks quite complicated.



(2, 4-dinitrophenyl) hydrazine

Properties of 2, 4-Dinitrophenylhydrazine

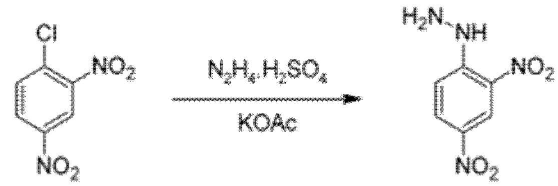
Molecular Formula - $C_6H_6N_4O_4$
Molar mass - 198.14
Appearance - Red or orange powder
Melting point - 198 - 202 °C.
Solubility in water - Slightly

Main hazard -Flammable, possible carcinogen

Hazards and safety precautions
2, 4-dinitrophenyl hydrazine may cause irritation and may be harmful if swallowed. Skin and eye irritant.

Brady's reagent
Dinitrophenylhydrazine is relatively sensitive to shock and friction; it is a shock explosive so care must be taken with its use. It is a red to orange solid, usually supplied wet to reduce its explosive hazard. It is a substituted hydrazine, and is often used to qualitatively test for carbonyl groups associated with aldehydes and ketones. The hydrazone derivatives can also be used as evidence toward the identity of the original compound.

Synthesis
2, 4-Dinitrophenylhydrazine is commercially available usually as a wet powder. It can be prepared by the reaction of hydrazine sulfate with 2, 4-dinitrochlorobenzene:

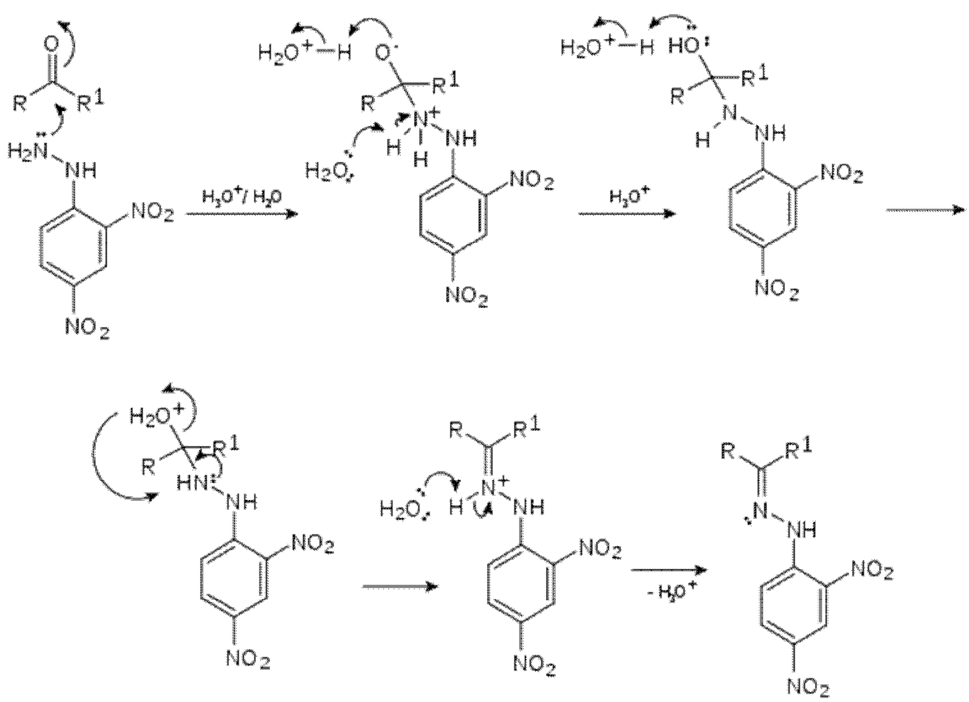


Brady's reagent is prepared by dissolving 2,4-dinitrophenylhydrazine in a solution containing methanol and some concentrated sulfuric acid.

Brady's test
2,4-Dinitrophenylhydrazine can be used to qualitatively detect the carbonyl functionality of a ketone or aldehyde functional group. A positive test is signaled by a yellow or red precipitate (known as a dinitrophenylhydrazone)

$RR'C{=}O + C_6H_3(NO_2)_2NHNH_2 \rightarrow C_6H_3(NO_2)_2NHNCRR' + H_2O$

This reaction can be described as a condensation reaction, with two molecules joining together with loss of water. It is also considered an addition-elimination reaction: nucleophilic addition of the $-NH_2$ group to the C=O carbonyl group, followed by the removal of a H_2O molecule.
The mechanism for the reaction between 2, 4-dinitrophenylhydrazine and an aldehyde or ketone is shown:



Crystals of different hydrazones have characteristic melting and boiling points, allowing the identity of a substance to be determined in a method known as derivatization. In particular, the use of 2, 4-dinitrophenylhydrazine was developed by Brady and Elsmie. Modern spectroscopic and spectrometric techniques have since superseded these techniques. Dinitrophenylhydrazine does not react with other carbonyl-containing functional groups such as carboxylic acids, amides, and esters. For carboxylic acids, amides and esters, there is resonance associated stability as a lone-pair of electrons interacts with the p-orbital of the carbonyl carbon resulting in increased delocalisation in the molecule. This stability would be lost by addition of a reagent to the carbonyl group. Hence, these compounds are more resistant to addition reactions.

Characterization Studies on 2,4-dinitrophenylhydrazine Single Crystal

Single crystal of an organic nonlinear optical (NLO) material, 2,4-Dnitrophenylhydrazine(DNPH), was grown by slow cooling method. Powder X-ray diffraction (PXRD), Fourier transforminfrared (FT-IR) FT-Raman and NMR studies have confirmed respectively the crystal structure and functional groups of the grown crystal. Crystalline perfection of single crystals was evaluated by high resolution X-ray diffractometry (HRXRD) using a multicrystal X–ray diffractometer and found that the grown crystals are nearly perfect. UV-Visible-NIR spectral analysis was used to determine the optical constants and band gap of DNPH. Fluorescence spectrum of DNPH was recorded.

The properties of hydrazides and hydrazones are of interest due to their biological activities and their use as metal extracting agents. The hydrazone derivatives are used as fungicides, and in the treatment of diseases such as tuberculosis, leprosy and mental disorders. The complexes of various hydrazones are reported to act as inhibitors of enzymes. Many substituted hydrazides are employed in the treatment of psychotic and psychoneurotic conditions. Carboxylic acid hydrazides are known to exhibit strong antibacterial activities which are enhanced by complexation with metal ions. The study of biological activity on 2,4-dinitrophenylhydrazine (DNPH) proved that DNPH is an important material for biological applications. 2, 4-dinitrophenylhydrazine is also an important constituent in various biomedical, pharmaceutical products and in toxicology. Single crystal 3-dimensional X-ray structure of DNPH was reported by Okabe et al. Wardell et al.have analyzed the molecular and supramolecular structures of DNPH. Chis et al. have reported a combined experimental and theoretical study on molecular structure of DNPH. Sundaraganesan et al. have investigated the vibrational spectra of this molecule and identified the various normal modes of vibrations. In this chapter the growth of DNPH and its characterization is presented.

Choice of Solvent and Solubility

Solvents offering moderate solubility-temperature gradient for a material and yielding prismatic growth habit will be considered as suitable solvents for growing crystal of that material. Another important factor influencing the habit of growing crystal is the polarity of the solvents and stirring the solution. Acetone (electric dipole moment 2.88 Debye) was found to yield prismatic transparent crystals and hence it was selected as the suitable solvent to grow DNPH.

Growth of DNPH Crystal

Recrystallized salt of DNPH was dissolved in acetone to prepare the saturated solution at 30 °C. About 300 ml of this solution was taken in a beaker and placed in a constant temperature bath(CTB) having an accuracy of ± 0.01 °C. Crystals were grown by the slow cooling method by reducing the temperature from 30 °C at the rate of 0.1 °C per day. Single crystal of dimension8x4x2mm3 was grown (Fig. 2) in a period of 7 days.

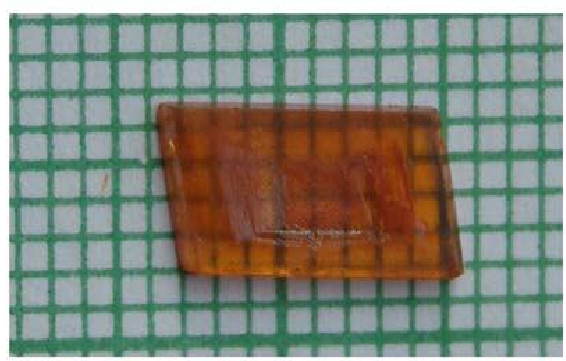
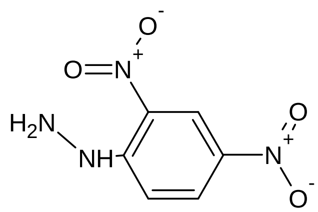


Fig. 1: Grown DNPH

The reactions of 2,4-dinitrophenylhydrazine

2,4-dinitrophenylhydrazine is often abbreviated to 2, 4-DNP or 2, 4-DNPH. A solution of 2, 4-dinitrophenylhydrazine in a mixture of methanol and sulphuric acid is known as Brady's reagent.

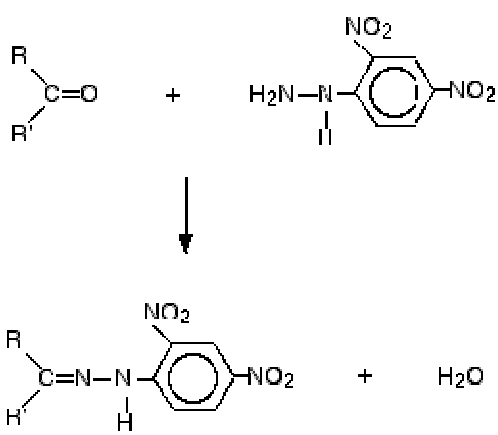
In 2, 4-dinitrophenylhydrazine, there are two nitro groups, attached to the phenyl group in the 2- and 4- positions. The corner with the nitrogen attached is counted as the number 1 position, and just number clockwise around the ring.



(2,4-dinitrophenyl)hydrazine

The chemistry of the reaction

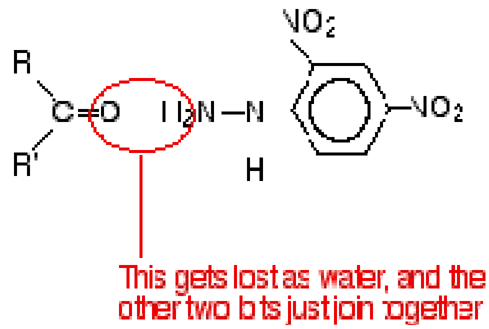
Brady's reagent (a solution of the 2,4-dinitrophenylhydrazine in methanol and sulphuric acid) add either a few drops of the aldehyde or ketone, or possibly a solution of the aldehyde or ketone in methanol, to the Brady's reagent. A bright orange or yellow precipitate shows the presence of the carbon-oxygen double bond in an aldehyde or ketone.This is the simplest test for an aldehyde or ketone.



Orange or Yellow ppt.

R and R' can be any combination of hydrogen or hydrocarbon groups (such as alkyl groups). If at least one of them is hydrogen, then the original compound is an aldehyde. If both are hydrocarbon groups, then it is a ketone.

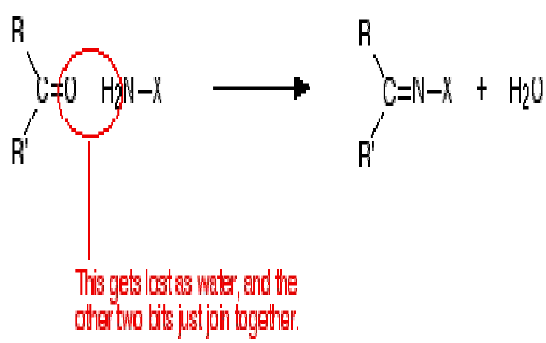
Look carefully at what has happened,



The product is known as a "2,4-dinitrophenylhydrazone". Notice that all that has changed is the ending from "-ine" to "-one". That's possibly confusing. The product from the reaction with ethanal would be called ethanal 2,4-dinitrophenylhydrazone; from propanone, you would get propanone 2,4-dinitrophenylhydrazone - and so on. That's not too difficult. The reaction is known as a **condensation reaction.**

A condensation reaction is one in which two molecules join together with the loss of a small molecule in the process. In this case, that small molecule is water. In terms of mechanisms, this is a **nucleophilic addition-elimination** reaction. The 2, 4-dinitrophenylhydrazine first adds across the carbon-oxygen double bond (the addition stage) to give an intermediate compound which then loses a molecule of water (the elimination stage).

2,4-dinitrophenylhydrazine changes during the reaction apart from the $-NH_2$ group. We can get a similar reaction if the $-NH_2$ group is attached to other things. In each case, the reaction would look like this –



In what follows, all that changes is the nature of the "X".

Experimental procedure

Two conical measures are each filled with 300 mL of the hydrochloric acid solution of 2, 4-dinitrophenyl hydrazine. 10 mL of acetone and benzaldehyde, respectively, are slowly added to the dinitrophenyl hydrazine solutions while stirring.

RESULTS

Copious crystalline precipitates are formed. Acetone gives a yellow precipitate and benzaldehyde gives a orange yellow precipitatee product is an "oxime" - for example ethanaloxime.

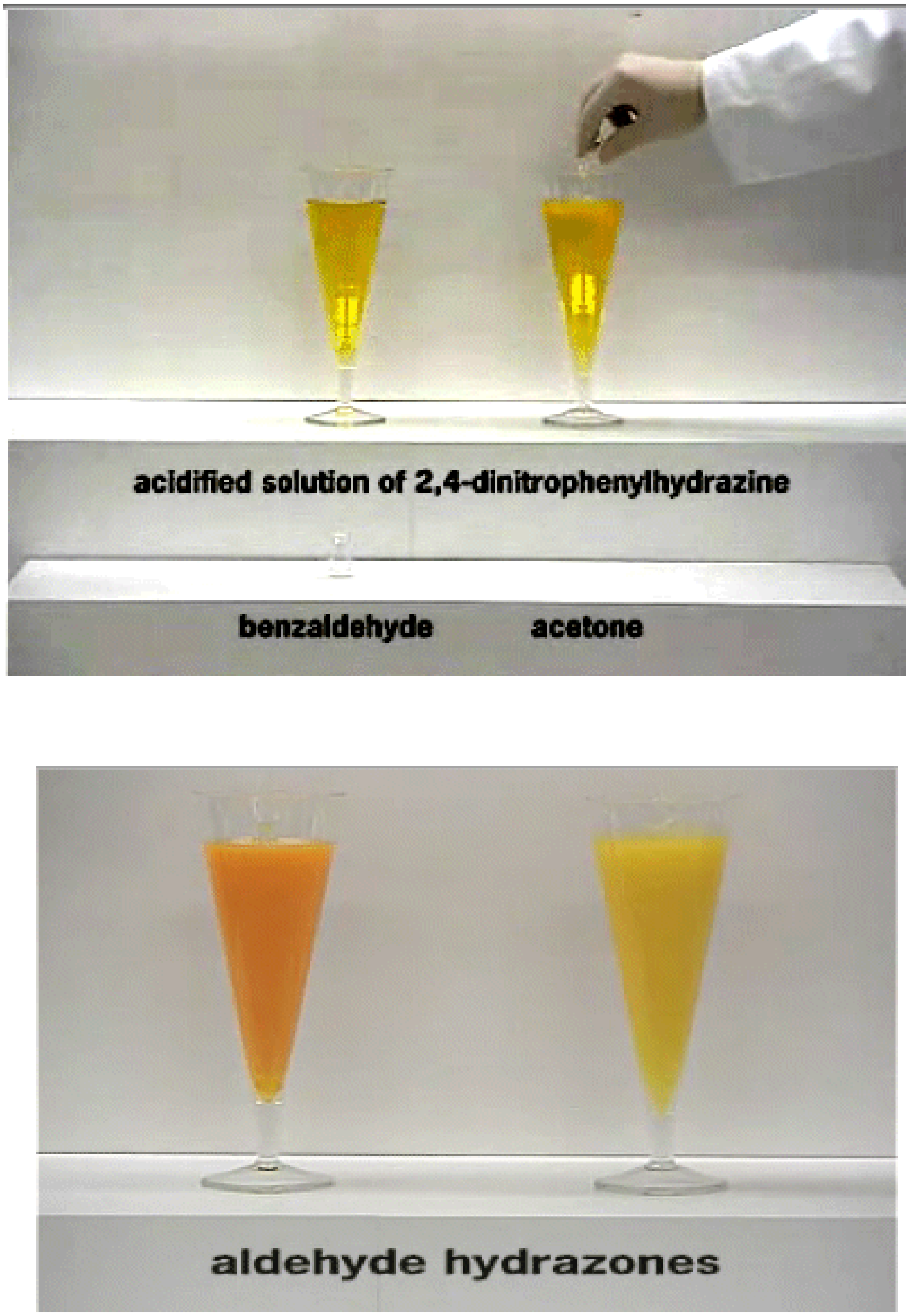
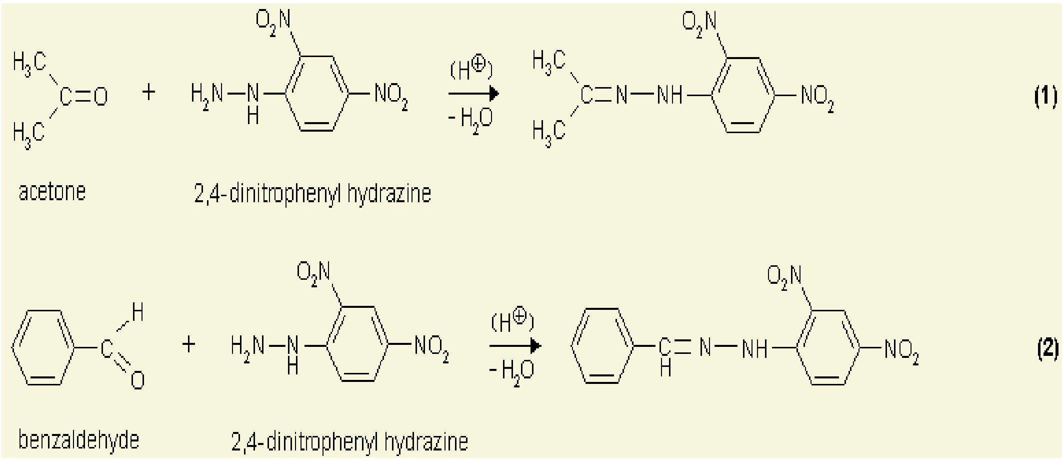


Fig. 2: Colour changes during reaction

DISCUSSION

The formation of this precipitate is a positive test for the carbonyl group of ketones and aldehydes. The ketone or aldehyde is converted to its hydrazone by reactionwith, dinitrophenylhydrazine.



A positive test is a yellow, orange, or red precipitate. Small crystals made from unconjugated aldehydes and ketones give precipitates toward the yellow end of the scale. Large crystals made from conjugated compounds tend to be redder. Hydrazones have a sharp melting point and can assist in identifying carbonyl compounds,

Uses of the reaction

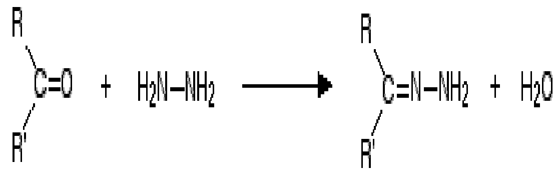
The reaction has two uses in testing for aldehydes and ketones.

- First, we can just use it to test for the presence of the carbon-oxygen double bond. You only get an orange or yellow precipitate from a carbon-oxygen double bond in an aldehyde or ketone.
- Secondly, we can use it to help to identify the specific aldehyde or ketone.

The precipitate is filtered and washed with, for example, methanol and then recrystallised from a suitable solvent which will vary depending on the nature of the aldehyde or ketone. For example, recrystallise the products from the small aldehydes and ketones from a mixture of ethanol and water. The crystals are dissolved in the minimum quantity of hot solvent. When the solution cools, the crystals are re-precipitated and can be filtered, washed with a small amount of solvent and dried. They should then be pure.

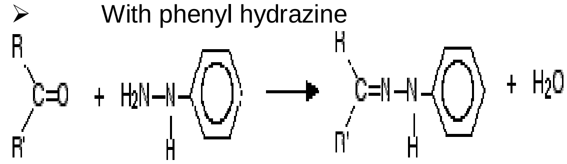
Some other similar reactions

➢ With hydrazine

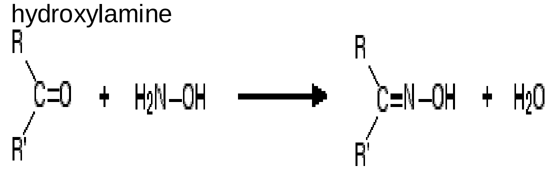


The product is a "hydrazone". If you started from propanone, it would be propanonehydrazone.

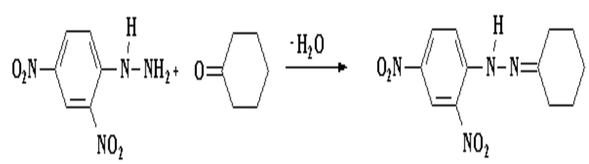
➢ With phenyl hydrazine



The product is a "phenylhydrazone" With hydroxylamine



Preparation of cyclohexanone 2, 4-dinitrophenylhydrazone



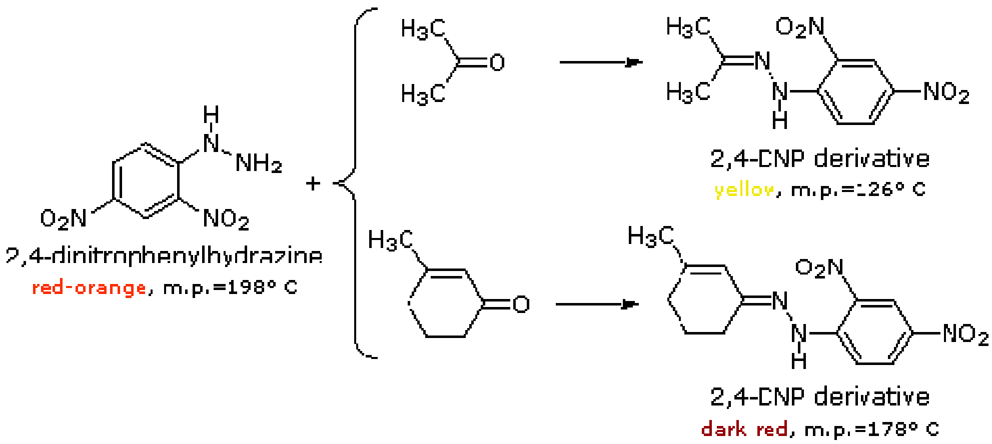
Derivatives of organic compounds are often prepared in order to confirm structures proposed. In this experiment a ketone will be converted to its 2, 4-dinitrophenylhydrazone derivative.

Procedure

Suspend 0.25 g of 2, 4-dinitrophenylhydrazine (toxic) in 5 ml of methanol and add 0.5 ml of concentrated sulphuric acid cautiously. Filter the warm solution if necessary and add a solution of 0.2 g cyclohexanone in 1 ml of methanol. Filter the derivative formed and recrystallise from methanol or ethanol. Use a Hirsch funnel for filtering the recrystallised material. Describe the mechanism of the reaction above.

Dinitrophenylhydrazones

Another commonly used carbonyl derivative is prepared from 2,4-dinitrophenylhydrazine, as shown below. The reagent and its hydrazone derivatives are distinctively colored solids, which can be isolated easily. Saturated ketones and aldehydes are usually yellow to light orange in color. Conjugation of the carbonyl group with a double bond or benzene ring shifts the color to shades of red.



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