

PREPARATION OF TRIAZOLE WITH THE HELP OF P-NITRO PHENYL ACETIC ACID

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This was prepared from p-nitro benzaldehyde by Azlactone synthesis.

INTRODUCTION

A mixture of p-nitro benzaldehyde (15.4 mL), hippuric acid (12 g) acetic anhydride (18mL) and anhydrous Sodium acetate (6 g) was heated under reflux when the mixture become homogenous in about half an hour. The resulting solution was boiled for a further one hour, cooled and then left in an ice chest overnight. The precipitated yellow solid was removed by filtration, washed several times with cold water and then with boiling water.

The azlactone obtained above was heated under reflux with solution of sodium hydroxide (25 g in 100 mL) for one hour.

The reaction mixture was then cooled with water (150 mL) and the saturated with sulphur dioxide. The reaction mixture was then filtered the filtrate was heated on a sodium bath in an open dish with conc. Hydrochloric acid (75 mL) and then cooled. The precipitated *p*-nitro phenyl pyruvic acid was collected and crystallized from benzene.

The crystals was collected by filtration and heated under reflux in a round bottom flask with excess of hydrogen peroxide.

The reaction mixture was cooled and the separated solid was collected by filtration. It was washed with cold water and recrystallised from hot water to give crystals of m-nitro phenyl acetic acid 12-6 g, (m.p. 151°C (U¹³⁵ – m.p. 152°C).

PREPARATION OF ETHYL-p-NITROPHENYL ACETATE

A mixture of p-nitrophenyl acetate acid (20 g) absolute alcohol (40 mL) and conc. sulphuric acid (2 mL) as heated on a water bath for two hours under the condition of reflux. The reaction mixture was then left a room temperature overnight. The excess of ethanol was removed by distillation water was used to wash the residual solution and then with (10%) sodium bicarbonate solution and again with water several times. The residual liquid was dried over excecated magnesium sulphate and distilled. The distilate on cooling overnight yellowish crystal was obtained m.pt. 64°C (Lit 131 m.p. – 63.3°C).

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PREPARATION OF -p-NITROPHENYL ACETATE HYDRAZIDE

This preparation was done by reacting ethyl-p-nitrophenyl acetate and hydrazine.

Following the standard method of Vogel¹³¹, ethyl p-nitrophenyl acetate (10 g) in ethanol (30 mL) was heated with hydrazine hydrate (5 mL 90%) for three hours till the volume of the solution was reduced half, pale yellow solid was separated out on cooling the solution. The solid was collected by filtration and recrystallisation from ethanol to furnish pure p-nitrophenyl acetylhydrazide (7.2 g) as pale yellow crystal m.p. 165°C (Lit¹²⁷ m.p. – 167°C).

Analysis

Found	N-20.90%
Calculated for C ₈ H ₉ N ₃ O ₃	21.53%

PREPARATION OF -p-NITROPHENYL ACETYLE CHLORIDE

Phosphorus pentachloride (4.5 g) was added to a solution of -p- nitrophenyl acetic acid (5 g) in dry chloroform (40 mL) and then mixture was heated on a water bath with shaking for two hours.

The excess of phosphorus oxy chloride was removed by distillation under reduced pressure. The residual liquid on cooling in the chest, gave solid which was separated by tetrahydrofuran to furnish pure crystals of p-nitrophenyl chloride (4.2 g)

m.p. 45°C (lit¹³¹ m.p. 46-47°C).

PREPARATION OF -p-NITROPHENYL ACETAMIDE

Place 3 mL of concentrated ammonia solution in a 18 mL flask and cool in ice. 1.0 g of redistilled carboxylic acid chloride drop by drop from a separatory funnel whilst shaking the flask frequently. Filter off the precipitated acid amide with a little cold water and recrystallised from hot water. The crystals were dried upon filter paper in the air. The yield of pure acid amide is 1.0 g. m.p.39°C (Lit m.p. 39°C).

PREPARATION OF -p-NITROPHENYL ACETHYDRAZIDE

(This preparation was done by reacting p-nitrophenyl acetic acid chloride and hydrazine).

Following the method of Vogel, p-nitrophenyl acetic acid chloride (3 g) in carbon tetrachloride (10 mL) was heated with hydrazine hydrate (5 mL 90%) for three hours under reflux, when homogeneous mixture was obtained. The volume of the solution was reduced to

half, this solution was then cooled, pale yellow solid was separated which was collected by filtration. Recrystallisation of the solid from methanol furnished p-nitrophenyl acethydrazide (2.1 g) as light yellow crystal m.p. 165°C (Lit¹³¹ m.p. 167°C).

PREPARATION OF 2, 5-di-(p-NITROBENZYL)- 1, 3, 4-TRIAZOLE

(By heating reaction between p-nitrophenyl acethydrazide and p-nitrophenyl acetamide).

This reaction was done under various conditions.

(a) With Phosphorus pentoxide :

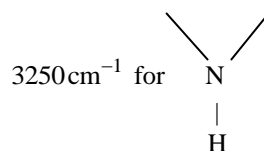
A mixture of p-nitrophenyl acethydrazide (0.5 g) p-nitrophenyl acetamide (0.3 g) phosphorus pentoxide (0.02 g) in carbon tetrachloride (2 mL) was heated on water bath for four hours. The completion of reaction was indicated by TLC examination. Reaction mixture was left at room temperature overnight. The separated solid was triturated with benzene and ethanol and then recrystallised from ethanol to furnish light yellow crystals of pure 2, 5-di-(p-nitrobenzyl)-1, 3, 4-triazole (0.40 g) m.p. 212°C.

Analysis

Found	20.15%
Calculated for C ₁₂ H ₁₃ N ₅ O ₅	20.77%

IR (Stretching frequencies)

KBr	1590 cm ⁻¹ for C=N stretching
V _{max}	2905 cm ⁻¹ for C-H stretching
	(Showing the pressure of -CH ₂ - grasping)
	... for C-N bending



1620 cm⁻¹ for showing disintitled bell zone

1540 cm⁻¹ for aromatic nitro group.

(b) With dry hydrogen chloride :

A mixture of a mixture of p-nitrophenyl acethydrazide (0.5 g) p-nitrophenyl acetamide (0.4 g) in benzene (2 mL) was heated under condition of reflux on water bath for five hours and dry hydrogen chloride gas was passed in this reaction mixture slowly. The progress of the reaction was carried out time to time by TLC examination.

The completion of was indicated by TLC examination and then reaction mixture was set aside at room temperature overnight. The yellow solid separating from the reaction mixture was triturated was aqueous sodium bicarbonate, washed with cold water and recrystallised from ethanol to furnish the pure triazole (0.45 g) m.p. and mixed m.p. 212°C.

(c) Direct on heating :

A mixture of p-nitrophenyl acetylhydrazide (0.5 g) p-nitrophenyl acetamide (0.4 g) in benzene (2 mL) was heated under reflux for six hours and placed at room temperature overnight. The yellow solid separating from the reaction mixture was obtained from filtration and recrystallised from ethanol to furnish the pure triazole (0.15 g) m.p. and mixed m.p. 211.5°C.

(d) In pyridine on heating :

A mixture of m-nitro phenyl acet hydrazide (0.5 g), m-nitro phenyl acetamide (0.4 g) and pyridine (1 mL) was heated on a water bath for four hours. The completion was indicated by TLC. The reaction mixture was then left overnight and yellow solid obtained. This was washed with benzene and ethanol, Recrystallisation of the solid from ethanol gave the pure triazole as yellow crystals (0.2 g) m.p. and mixed m.p. 167°C.

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