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# Synthesis of 2,2′,4,4′,6,6′ Hexanitrostilbene

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**Abstract.** An economical method of synthesis of HNS has been developed in which solution of TNT is treated with 6 per cent sodium hypochlorite at $3\pm1°C$ to get the desired product. Effect of concentration as well as *pH* of sodium hypochlorite on the yield of HNS has also been studied. The solubility of HNS in various organic solvents has also been determined.

## 1. Introduction

2,2′,4,4′,6,6′ hexanitrostilbene (HNS) is one of the most important heat resistant explosives which can withstand temperature up to 300°C. It is sufficiently insensitive to heat, impact and electrostatic spark. It finds uses in plastic bonded explosives and in grain modification TNT or TNT based cast charges. It was first prepared by Shipp *et al.*[1-3] by treating the solution of TNT in tetrahydrofuran-methanol mixture with 5 per cent sodium hypochlorite at 0°C. Later on its synthesis was reported by Kompolthy *et al.*[4] in which they made cobalt complex with TNT and treated it with potassium hydroxide to get HNS. Recently Golding and Hayes[5] have done exhaustive study on the synthesis of HNS by oxidative coupling of 2,4,6 trinitro toluene in the presence of various metal catalysts. All the processes give a yield of 40-45 per cent. First process involves toxic and expensive solvent like THF and the other processes involve formation of metal complexes in which procedures are complicated. So attempt has been made in our laboratory to develop a simple method employing comparatively cheaper and less toxic solvents to get better yield of HNS.

## 2. Experimental Procedure

### (*a*) *Preparation of Sodium Hypochlorite (6 per cent)*

This is prepared by passing chlorine gas through the solution of sodium hydroxide (100 g) in cold water (1 litre) which is further cooled with ice. Strength of the solution is estimated iodometrically and made up to 6 per cent by diluting with water.

*(b) Preparation of HNS*

Sodium hypochlorite 6 per cent (1 liter) was taken in the two necked flask equipped with a magnetic stirrer, thermometer and double jacketted separating funnel. It was surrounded with ice bath to cool the solution to 3 ± 1°C with constant stirring. A solution of TNT (100 g) was prepared in mixed solvents of ethylacetate (1 litre) and ethylalcohol 95 per cent (1 litre) in the beaker cooled to 3 ± 1°C, and transferred to reaction flask through double jacketted funnel rapidly, keeping the temperature of reaction mixture at 15 ± 2°C. The reaction mixture was stirred for a few minutes and allowed to rest for about 4 hours at 15 ± 2°C. After this aging period, it was filtered and washed with ethylalcohol (95 per cent) until washings were colourless. The product was dried in vacuum oven. Similar experiments with different concentration of sodium hypochlorite at different *pH* and with different solvent systems were conducted (Tables 1, 2 and 4).

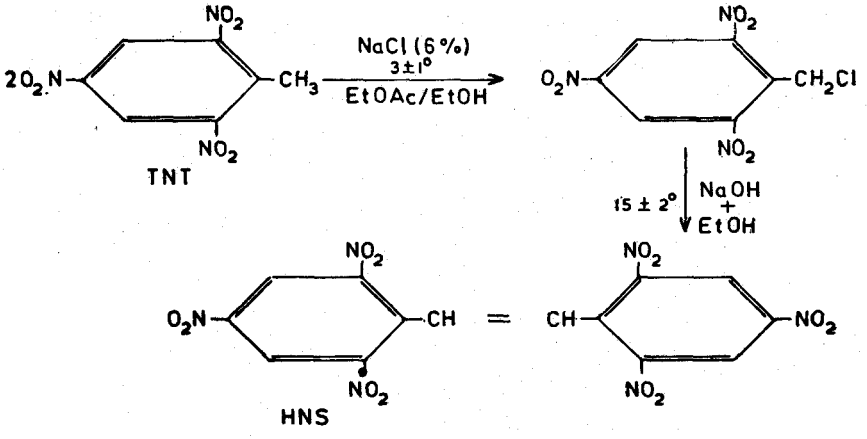
**Table 1.** Effect of various concentration of *NaOCl* on the yield of HNS based on 100 g TNT batch.

| Concentration of *NaOCl* | 3% | 4% | 5% | 6% | 7% | 8% |
|---|---|---|---|---|---|---|
| Yield of HNS (g) | 44 | 47 | 49 | 56 | 45 | 42 |
| Melting points range (°C) | 215-20 | 225-30 | 240-50 | 270-75 | 285-90 | 290.92 |

**Table 2.** Effect of *pH* of *NaOCl* solution (6%) on the yield of HNS based on 10 g TNT batch.

| *pH* | 8 | 9 | 10 | 11 | 11.5 | 12 |
|---|---|---|---|---|---|---|
| Yield of HNS (g) | 1.2 | 4 7 | 4.9 | 5.2 | 5.6 | 4.9 |

The overall reaction can be depicted as given below :



*Purificatian of HNS*

HNS thus prepared is found to be contaminated with undesirable impurities which had to be eliminated to get the pure product. So various chemicals were tried to remove or decompose the by products. Nitric acid (55 per cent) was found promising.

The crude HNS (5 g) was refluxed in 55 per cent nitric acid (100 ml) for half an hour. It was filtered through weighed sintered crucible, washed several times with distilled water to make it free from acid. The crucible was dried in vacuum oven to constant weight and 4.5g of pure HNS was obtained.

*Recrystallisation of HNS*

The pure product was further recrystallised with dimethyl formamide. The melting point of the recrystallised product was 316°C (dec). It was identified by mixed melting point with authentic sample of HNS prepared by the reported method[2]. It was further confirmed by TLC and I. R. Spectra.

The solubility of the product in various organic solvents at different temperatures was determined by usual evaporation method (Table 3).

**Table 3.** Solubility of HNS (g/100 ml of solvent) at various temperatures °C.

| Solvent | 30 | 40 | 50 |
|---|---|---|---|
| Nitrobenzene | 0.059 | 0.072 | 0.094 |
| Ethyl-methylketone | 0.035 | 0.052 | 0.061 |
| Acetone | 0.064 | 0.075 | 0.131 |
| Methanol | 0.003 | 0.006 | 0.008 |
| Dimethylformamide | 1.312 | 1.703 | 2.198 |
| Acetonitrile | 0.043 | 0.064 | 0.084 |
| Cyclohexanone | 0.118 | 0.156 | 0.206 |

## 3. Result and Discussion

From the Tables 1 & 2, it is evident that concentration as well as *pH* of *NaOCl* solution have profound effect on the yield and purity of HNS. From the Table 1, it is observed that yield of HNS first increases with the increase of concentration of *NaOCl* up to 6 per cent and then decreases at higher concentration, it is also noticed that purity of the product (melting point) increases with increase of concentration. So it is inferred that higher concentration of *NaOCl* favours comparatively purer product but with less yield.

On purifying the crude product with 55 per cent $HNO_3$ it was found that 6 per cent *NaOCl* gives maximum yield. When the experiments were conducted at different *pH*, maximum yield of HNS was obtained at *pH* 11.5 (Table 2). HNS is not much soluble in the organic solvents which poses problem for its recrystallisation. Since the solubility data is also not available in literature, its solubility was determined in several organic solvents at different temperatures (Table 3).

Table 4 which shows that the yield of HNS around 42 per cent can be obtained using Shipp Kaplan's solvent system. Many more solvent-systems were tried, of which Ethyl acetate/Ethanol (95 per cent) gave the encouraging result (56 per cent yield).

**Table 4.** Replacement of THF by other water miscible systems

| Solvent system | | Ratio | Yield of HNS (%) |
|---|---|---|---|
| Tetra Hydrofuran | Methanol | 2 : 1 | 42 |
| Tetra Hydrofuran | Methanol | 1 : 1 | 34 |
| Dioxane | Methanol | 2 : 1 | 35 |
| Acetone | Methanol | 2 : 1 | 15 |
| Methyl acetate | Methanol | 2 : 1 | 5 |
| Dioxane | Ethanol (95%) | 2 : 1 | 30 |
| Ethylacetate | Ethanol (95%) | 1 : 1 | 56 |

This solvent system has two advantages over Shipp-Kaplan Process. First it has replaced expensive and toxic solvent tetra hydrofuran with cheaper solvent system ethyl acetate/ethanol (95 per cent). Secondly the yield of HNS has increased. Recently a new approach to synthesise HNS by oxidative coupling of TNT in presence of metal catalysts has been reported[5] but the process is complicated and it does not contribute much improvement in the yield of HNS.

Our procedure is simple, rapid, comparatively cheap and gives a good yield of HNS (56 per cent of 90 per cent purity).

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