



Research Paper

Synthesis of a New Vat Dye

Okafor C. O.¹, *Nwokonkwo D.C.²

¹Department of Pure and Industrial Chemistry, University of Nigeria, Nsukka, NIGERIA.

²Department of Industrial Chemistry Faculty of Applied Physical Sciences,
Ebonyi State University Abakaliki, NIGERIA.

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Abstract - The importance of vat dyes especially those derived from indigo and its derivatives is still relevant and prompted this investigation. Disclosed hereby is the synthesis of a new vat dye from 2, 4-dinitroaniline which yielded a blue dye of indigo skeleton. 2, 4 dinitroaniline was treated with chloroacetic acid, in a base catalysed substitution nucleophilic bimolecular reaction using a high boiling non polar solvent such as nitrobenzene at a temperature above 300^oC. The intermediate compound that resulted was purified and this in turn was treated with admixture sodium hydroxide-potassium hydroxide - sodamide in a 5:5:1 ratio at a temperature of 120^oC to yield an indoxyl, in an intramolecular cyclization reaction. Oxidation of the indoxyl into the vat dye was brought about by treating the indoxyl with acidified solution of ferric chloride. The yield was excellent and the structure of this compound was established as 5, 5' 7, 7'-tetranitroindigo by chemical evidence: ultraviolet, infrared, nuclear magnetic resonance spectroscopy and mass spectrometry. Reduction of this compound with sodium dithionite (sodium hydrosulphite) and the ease of air oxidation back to the original colour made it applicable as vat dye.

Keywords: Synthesis, new vat dye, dinitroaniline, indigo dye, chemical evidence, reduction.

Introduction

Dyes and dye intermediates are used as indicators or in colouring foods, drugs, cosmetics, textiles, plastics, solvents, waxes, papers etc [1-9]. Indigo compounds are important compounds that are useful as dyes [10-11]. The presently employed industrial processes for the preparation of indigo comprise forming an N-phenylglycine salt from aniline and chloroacetic acid, converting this salt into an indoxyl compound by alkali fusion at elevated temperature, and then oxidizing this compound with air [12-19]. In this article, indigo dye, a vat dye was prepared by using 2, 4-dinitroaniline, chloroacetic acid to give an intermediate 2, 4-dinitrophenylglycine. This was fused with sodium hydroxide, potassium hydroxide and sodamide at a temperature between 110-120^oC to give an indoxyl. This indoxyl was oxidized using acidified solution of ferric chloride to form a blue vat dye [20-21].

Material and Methods

All reagents were of analytical grade, melting point was taken on Gallenkamp melting point apparatus in open capillaries and are reported uncorrected. Infrared was performed on Perkin-Elmer Model 337 from Central Research Laboratory University of Ibadan, Nigeria using potassium bromide discs and also dimethylsulphoxide was used where applicable. The ultraviolet-visible spectra were recorded on

UVI spectrophotometer Model 061408 using 1cm quartz cells. The solvent used were deuterated water, distilled water and dimethylsulphoxide at Central Science Laboratory Obafemi Awolowo University Ile-Ife Nigeria. ¹H- and ¹³C- were determined on FT model 65336 in deuterated dimethylsulphoxide using trimethylsilane as internal standard at ambient temperature at the chemical shifts were reported on the δ scale at Central Science Laboratory Obafemi Awolowo University Ile-Ife Nigeria Obafemi Awolowo University, Ile-Ife Nigeria. The mass Spectra were obtained on an AEIMS9 double focusing mass spectrometer at 70Ev at Usman Danfodio University Sokoto Nigeria.

Synthesis of the Intermediate: 2, 4-dinitrophenylglycine

2, 4-Dinitroaniline (20g, 0.11 moles) was introduced into a 500ml round bottomed flask, to this were added chloroacetic acid (30g, 0.32 moles) and sodium hydroxide (20g, 0.5mole). To this mixture was introduced 50ml of nitrobenzene and refluxed for six hrs at a temperature of approximately 300^oC. The colour progressively changed from yellow, red to black as heating continued. The slurry that formed was allowed to cool and washed with methanol (4 x 200ml). The crude product that was obtained, was a dirty white amorphous powder. This compound was soluble in water but insoluble in organic solvents like acetone. It was then dissolved in water, treated

with activated charcoal and filtered. A pure white powder weighing 20.4g crystallized out after distilling off the water. The melting point was 185-186°C. The UV: (EtOH) (nm) λ min 345, λ max 355, IR: (cm⁻¹) 3380 (d, NH), 3100 (s, OH, carboxylic), 1720 (s, C=O, carboxylic overtone) 1610-1420(C-H, arom.), 1300(s, NO₂). ¹H-: (CDCl₃) δ : 4.0 (d,NH), 4.0 (t,CH₂) 6.95 (¹H, d, =CH, arom), 8.36 (¹H,d,=CH, arom.), 8.36 (¹H,d), 8.90 (¹H,s), 11.0 (¹H,s,COOH). ¹³C: (CDCl₃) δ :45.0(CH₂),115.3(C-5,arom),119 (C-2,arom) , 128.0 (C-4,arom), 133.1 (C-1, arom.), 137.7 (C-3,arom.), 144.7 (C-6,arom),173.2 (COOH). MS m/e: 242.03 (1.1, M⁺⁺H) 243.04(1.6, M⁺⁺2H), 242.04(9.0, M⁺⁺H), 241.03 (M⁺, 100). Analytical Calculation for M m/e C₈H₇N₃O₆: C, 39.84, H, 2.93, N, 17.42, O, 39.81. Found C, 39.67, H, 2.83, N, 17.62, O, 39.71. The suggested reactions involved and the intermediate structure are shown as Figure 1 in Scheme 1.

Synthesis of 4, 4', 7, 7'-tetranitroindigo dye from 2, 4-dinitrophenylglycine

2,4-dinitrophenylglycine (6.0g 0.025 mole), sodium hydroxide (30.0 g, 0.75 mole), potassium hydroxide (30.0 g, 0.54 mole) and sod amide (6.0 g, 0.15 mole) were ground intimately in a mortar and introduced into a 250ml beaker. The mixture was moistened with 40ml nitrobenzene, corked and heated slowly for 1 hr.30 min. The colour changed progressed from colourless to yellow to deep yellow and finally to red-orange. As the temperature increased, the mixture gradually melted, became molten and solidified. The fused mixture was allowed to cool and dissolved in cold water, the solution was agitated for 1 hour and then treated with 100 ml of FeCl₃ solution acidified with concentrated HCl (50ml) to facilitate precipitation or oxidation of the dye. The blue dye that formed was recrystallized from acetone and dried. The melting point was > 390°. The UV (λ max nm)(DMSO) 720 (ϵ 1270), IR (cm⁻¹): 3130 (ring NH), 1320 (N=O), 1450 (aromatic), 1680-1750 (C=O), 1310-1295 (s,C=C), ¹H- (CDCl₃) δ :4.0 s (1,11-NH),8.88 s (4,41-1H) 9.15 s (6,61-1H), ¹³C- (CDCl₃) δ : 114.3 (2 C, arom, 30), 125.3 (2=CH), 127.7 (2 C, arom, 30), 131.7(2 C, arom,20), 136.4 (2C, arom), 139.8 (2C, arom,30), 149.1 (2C, arom,30), 187.0 (2 C=O).

The suggested reaction pathways and structures are shown as Figure 2 in Scheme 2.

Reduction of the dye

To 50ml dimethylsulphoxide (DMSO) solution of the 1.0g dye was added four molar equivalents of sodium hydrosulphite (Na₂S₂O₄) and the mixture heated under reflux for 2 hours, during which time the dye lost its colour as it is reduced to the dihydro derivative. The solution was poured into an iced cold solution of sodium hydrosulphite in 150 ml of water, the slurry was stirred and filtered. In the process, the reduced dye was re-oxidized to the original starting dye resulting in the regeneration of the original colour and isolation of a product which was characterized as the starting material.

Results

A blue compound of indigoid structure was prepared using 2, 4- dinitroaniline for the first time. This was treated with chloroacetic acid under alkaline condition in the usual and already established Heumann reaction pathway. An intermediate, 2,4-dinitrophenylglycine was obtained the melting point was 185-186°C. The intermediate product was treated with finely ground sodium hydroxide,

potassium hydroxide and sodamide. The solid mixture was heated at a temperature not exceeding 120°C, a blue compound was isolated after work-up. The choice of using acidified solution of ferric chloride to facilitate oxidation appeared most convenient and attractive [22-23]. Elemental analysis and mass spectroscopy are in agreement with the molecular formula C₁₆H₆N₆O₁₀. A band at 720nm characteristic of indigoid system was observed in the UV spectrum. The infrared spectrum showed a sharp band at 3130 cm⁻¹ due to the presence of secondary aromatic NH group [24-25], also there are significant bands at 1680-1750cm⁻¹. Further evidence of structure was provided by the proton and ¹³C NMR. MS m/e 442.01 (100%, M⁺), 443.02 (17.8%, M⁺+H), 443.01(2.2% M⁺+H), 444.02 (3.5% M⁺+2H). C, 43.45, H, 1.37, N, 19.00 and O, 36.18. The fastness of this compound to light, acid, base, organic solvents gave excellent results.

Discussion

The substitution nucleophilic bimolecular reaction, with chloroacetic acid reagent and 2, 4- dinitroaniline as the nucleophile under basic condition, yielded a chalky white powder of molecular weight C₈H₇N₃O₆ melting at 185-186°C. The molecular ion appeared in the mass spectrum m/e 241.03, molecular formula C₈H₇N₃O₆. The ultraviolet spectrum showed two maximum absorption bands at 345 and 355 nm. The infrared spectrum had strong bands at 3380 cm⁻¹ (d, NH, arom) for 2^o NH stretch, 3650 cm⁻¹ (b, OH) for O-H stretch of carboxylic acids, 1720 cm⁻¹ (s, CO) stretch of carboxylic acid, 1340 cm⁻¹ (s, NO₂) stretch for aromatic C-NO₂ and 1600-1300 cm⁻¹ (=CH, arom) characteristic aromatic vibrations. ¹H- chemical shift at 4.0 δ (s, 1H) showed NH proton, 4.0 δ (s,2H) for CH₂, 6.95 δ and 8.36 δ (d, 1H) methine protons –aromatic, 8.90 δ (s,¹H) methine proton, aromatic and 11.0 δ (s,¹H) for carboxylic acid. ¹³C- chemical shifts appeared at 128.0 (C5), 133.1 (C2) , 137.7 (C4), 144.7 (C1), 119.5 (C3) and 115.3 (C6) these are methine carbons of benzene. The molecular peak was found at m/e 241.03(M⁺, 100%) the parent ion which corresponded to molecular formula C₁₆H₆N₆O₁₀. This compound was given the name 2, 4-dinitrophenylglycine [21]. This compound under fusion with admixture NaNH₂: KOH: NaOH (1:5:5) at a moderate temperature of 120°C gave a blue compound. The melting point was above 390°C and the compound was soluble in dimethylsulphoxide, dimethylformamide and concentrated sulphuric acid: the same solubility properties as indigo. The Ultraviolet absorption maximum at 720 nm in DMSO was indicative of indigoid structure. The strong bands at 3280 cm⁻¹ (m, NH, arom) for 2^o NH stretch, 1725 cm⁻¹ (s, CO) stretch of ketones, 1340 cm⁻¹ (s, NO₂) stretch for aromatic C-NO₂, 1620cm⁻¹ (C=CH, arom, conjugated), 1570-1440 cm⁻¹ (C-H, arom) characteristic aromatic vibrations are characteristic vibrations. ¹H- chemical shift at 4.0 δ (s, 1H) showed NH proton, 4.0 δ (s,2H) for CH₂, 6.95 δ and 8.36 δ (d, ¹H) methine protons – aromatic, 8.90 δ (s,¹H) methine protons-aromatic and 11.0 δ (s, ¹H) for carboxylic acid. The absence of absorption band at 3650 cm⁻¹ confirmed the lost or absence of hydroxyl group of carboxylic acids (COOH) while the band at 1725 cm⁻¹ was for ketones, 1620 cm⁻¹ stretch showed the presence of conjugated C=C of aromatic compound. The ¹H- showed three peaks at 4.0 δ (s, 2NH), 8.88 δ (s, 2CH) and 9.15 δ (s, CH-NO₂). ¹³C- chemical shifts appeared at δ 127.7 (q,2C=C), δ 187.0 (2C=O) , δ 114.03 (q,2C) , δ 131.7 (d,2=CH), δ 139.8 (2C-NO₂) , δ 125.3 (d,2=CH), δ 136.4 (q,C-NO₂) and 149.1 (q,2=CH)

these are methine carbon of benzene and carbonyl shifts. The molecular peak was found at m/e 442.01(M^+ , 100%), the parent ion which corresponded to molecular formula $C_{16}H_6N_6O_{10}$: C, 43.45, H, 1.37, N, 19.00 and O, 36.18. From the proposed structural evidence, the compound was given the nomenclature 5, 5', 7, 7'-tetranitroindigo.

Conclusion

5, 5', 7, 7'-tetranitroindigo is a new indigo dye as suggested by and evidenced from the IR, UV and Mass spectrometry carried out. The chemical properties, physical properties as well as the dyeing properties are similar to those of commercial indigo dye in the market/circulation.

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Figure 1: The synthetic mechanistic pathway is illustrated in Scheme 1

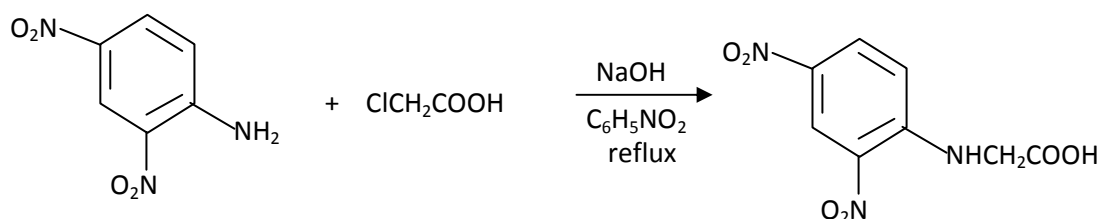


Figure 2: The synthetic mechanistic pathway is shown in Scheme 2

