

Green Synthesis of Sudan Dye 1 using Hydroxytriazenes under Sunlight Irradiation—a Photocatalytic Method

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Abstract-The present paper proposes a green synthesis of Sudan dye using hydroxytriazenes. The triazene moiety is an excellent stable intermediate for solid state synthesis of azo dyes. In the present investigation using five hydroxytriazenes Sudan dye 1 is synthesized through photocatalytic cleavage. The substituted hydroxytriazenes namely 3-ethyl-3-hydroxy-1-phenyltriazene, 3-hydroxy-1-phenyl-3-propyltriaz-1-ene, 3-hydroxy-1,3-diphenyltriazene, 3-hydroxy-3-(3-methylphenyl)-1-phenyltriazene, 3-hydroxy-3-(4-methylphenyl)-1-phenyltriazene were mixed with β -naphthol in equimolar ratio and were exposed to sunlight for 4-5 hr. In some cases the conversion into dye was initiated within 20 minutes of exposure. The dyes so formed were characterized and compared with the characterization data of product (Sudan dye 1) obtained by conventional method. The characterization techniques used were FTIR, ¹H NMR, UV VISIBLE, and TLC. The characterization data obtained for photocatalytic product agreed well with data obtained for conventional product thus proving that Sudan dye 1 can be prepared through solvent free, photocatalytic solid state synthesis. The present investigation is first report on green synthetic route for Sudan dye 1.

Keywords- Sudan dye 1; Hydroxytriazene; Photocatalytic cleavage.

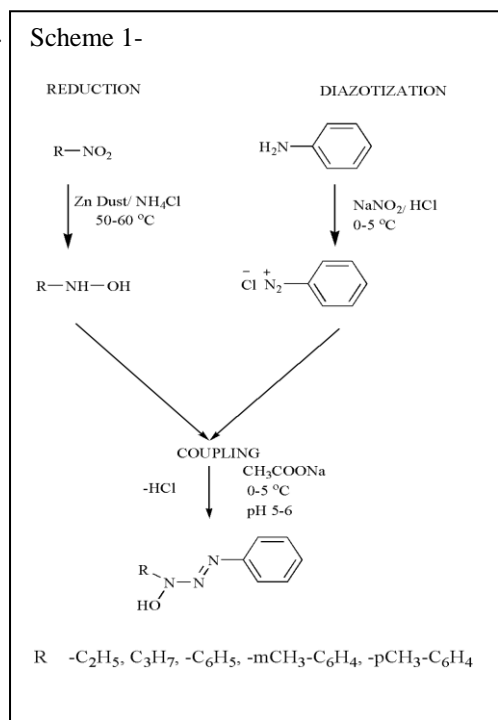
1. INTRODUCTION

Sudan dye 1 is classified as an azo dye and also named as Solvent Orange R. It is commonly used for colorizing oils, waxes, petrol, polishes and solvents. Application of solar energy to chemical synthesis is of late drawing much attention (1-5) of chemists. The solvent free or synthesis with minimum use of solvent is a greener approach. Further, the use of water as solvent adds another benefit to this route. Hydroxytriazenes (-N(OH)-N=N-) are compounds having a stable triazenic moiety which is an excellent synthetic scaffold for

preparative chemistry. Since they are stable reactive groups which are adaptable to a variety of synthetic transformation, they have been used for synthesis of various bioactive molecules having biological or pharmacological activities. We have been synthesizing such compounds having antibacterial, antifungal, and inflammatory, analgesic, wound healing and even cytotoxic activities (6-12). However for the first time the moiety has been used to prepare Sudan dye 1 through photocatalytic route. Thus it is first report for this dye via green route and can lead to a very interesting synthesis for such industrial products.

2. EXPERIMENTAL

We have synthesized 5 hydroxytriazenes (HDT-1, HDT-2, HDT-3, HDT-4, HDT-5) using method of Elkins and Hunter further modified by Sogani and Bhattacharya (12-14). The method involves reduction of alkyl or aryl nitro compounds to obtain respective hydroxyl amine which is coupled with diazonium salt obtained from diazotization of amino group of an aryl amine at 0–5 °C with constant magnetic stirring and occasional addition of sodium acetate solution to maintain the pH close



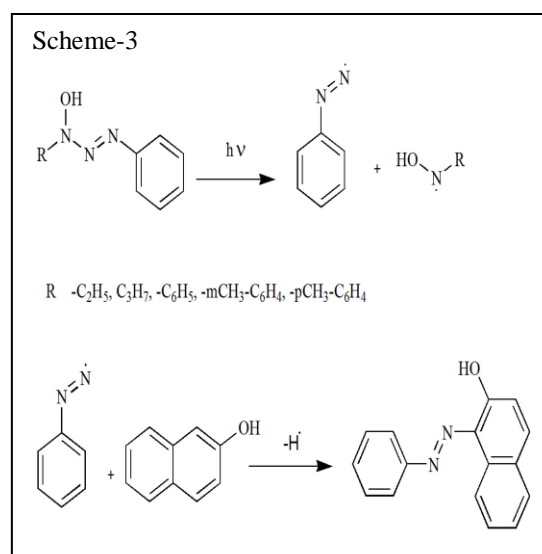
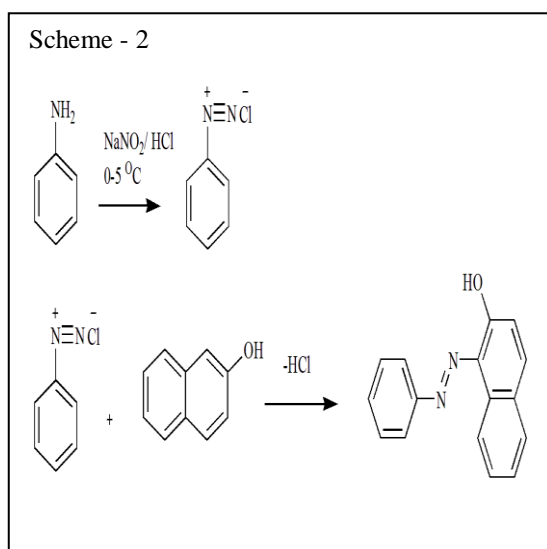
2.2. Synthesis of Sudan dye 1 using conventional method

The standard dye 1 was synthesized by the conventional chemical route for comparison

2.1. Synthesis of hydroxytriazenes

to 5. All synthesized compounds were purified by recrystallization from alcohol and methanol. Further, synthesized compounds were identified by recording their M.P. and IR spectra. Each of the hydroxytriazenes gave all four characteristic bands for hydroxytriazenes. The compounds gave bands for ν_{O-H} ($3,480\text{ cm}^{-1}$), ν_{N-H} ($3,190\text{ cm}^{-1}$), ν_{N-H} ($1,520\text{ cm}^{-1}$), and ν_{N-OH} ($1,070\text{ cm}^{-1}$) confirming the presence of the hydroxytriazene group. Scheme-1 represents synthesis of hydroxytriazene.

purposes and for identification of the photochemical product. Aniline (1.86 mL) was dissolved in mixture of 6 ml HCl and 10 ml distilled water. To this, a solution of 1.4 g sodium nitrite in 10 ml water was added drop wise at 0–5 °C and the mixture was stirred for 1 h at 0–5 °C. Separately, β -naphthol (2.8 g) was dissolved in 10 ml 10 % NaOH solution and cooled to 0–5 °C. To this solution, the solution of the diazotized compound prepared above was added drop wise with vigorous stirring. The mixture was stirred for an additional 30 min in an ice-bath. The precipitate obtained was isolated by filtration, initially purified by washing with water, and further purified by recrystallization from absolute alcohol. A dark orange red solid was obtained. Its structure was verified on the basis of physicochemical data such as IR, 1H NMR, and UV. The compound was found to be pure on the basis of these data. The characterization data of the product were used for comparison with the photocatalytic product. Scheme-2 represents synthesis of Sudan Dye 1.

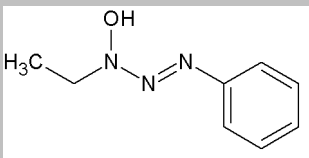
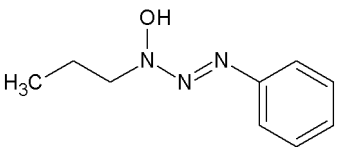


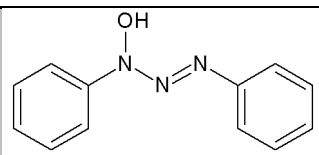
2.3. Synthesis of Sudan dye 1 via green route

Equimolar quantities each of hydroxytriazenes and 2-naphthol were taken and finely ground in a mortar and spread over Petri dishes. Each Petri dish was kept in open to expose to sunlight. After 1-1.5 h, the reaction mixtures (table no 1) gradually changed to bright orange color. Formation of dye via photoreactions was monitored by thin-layer chromatography using a 2:8 mixture of ethyl acetate and n-hexane as mobile phase, every hour to check initiation and completion of reaction. Each

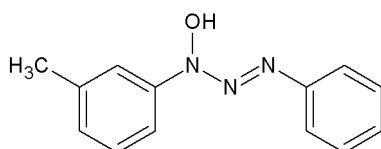
sample of hydroxytriazene and 2-naphthol mixture was treated with same procedure and separated by 2:8 ethyl acetate and n-hexane mixture as mobile phase from TLC. Further obtained Sudan dye 1 was characterized by various physicochemical techniques such as IR, UV and ¹H NMR. These results agreed well with the results of Sudan dye 1 obtained from conventional route. Scheme-3 represents photochemical reaction.

Table 1- Details of the photolysed mixtures.

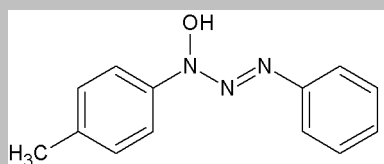
Code	Reaction Mixture	Color
HDT 1	3-ethyl-3-hydroxy-1-phenyltriazene 	+ 2-Naphthol Bright orange
HDT 2	3-hydroxy-1-phenyl-3-propyltriazene-1-ene 	+ 2-Naphthol Bright orange
HDT 3	3-hydroxy-1,3-diphenyltriazene	+ 2-Naphthol Bright orange



HDT 4 3-hydroxy-3-(3-methylphenyl)-1-phenyltriazeno + 2-Naphthol Bright orange



HDT 5 3-hydroxy-3-(4-methylphenyl)-1-phenyltriazeno + 2-Naphthol Bright orange



DYE CONVENTIONAL- IR frequencies (Bruker Optik GmbH Alpha Sample Compartment RT-DLa TGSZnSe HR 0.8) V_{O-H} (3492 cm^{-1}), $V_{N=N}$ (1424 cm^{-1}), V_{C-O} (1219 cm^{-1}), UV (Elico Double Beam SL 210 UV Vis Spectrophotometer) λ (477.5 nm) $^1\text{H NMR}$ (400 MHz, Chloroform D) δ 6.849-6.873 (1H, d), δ 7.250 - 7.741 (11H, m).

HDT 1- IR frequencies (Bruker Optik GmbH Alpha Sample Compartment RT-DLa TGSZnSe HR 0.8) V_{O-H} (3578 cm^{-1}), $V_{N=N}$ (1425 cm^{-1}), V_{C-O} (1220 cm^{-1}), UV (Elico Double Beam SL 210 UV Vis Spectrophotometer) λ (477.5 nm) $^1\text{H NMR}$ (400 MHz, Chloroform D) δ 6.848-6.876 (1H, d), δ 7.250 - 7.745 (11H, m).

HDT 2- IR frequencies (Bruker Optik GmbH Alpha Sample Compartment RT-DLa TGSZnSe HR 0.8) V_{O-H} (3495 cm^{-1}), $V_{N=N}$ (1425 cm^{-1}), V_{C-O} (1222 cm^{-1}), UV (Elico Double Beam SL 210 UV Vis Spectrophotometer) λ (477.5 nm) $^1\text{H NMR}$ (400 MHz, Chloroform D) δ 6.851- 6.875(1H, d) δ 7.249- 7.743 (11H, m).

HDT 3- IR frequencies (Bruker Optik GmbH Alpha Sample Compartment RT-DLa TGSZnSe HR 0.8) V_{O-H} (3506 cm^{-1}), $V_{N=N}$ (1425 cm^{-1}), V_{C-O} (1219 cm^{-1}), UV (Elico Double Beam SL 210 UV Vis Spectrophotometer) λ (477.5 nm) $^1\text{H NMR}$

(400 MHz, Chloroform D) δ 6.853-6.873 (1H, d), δ 7.252 - 7.741 (11H, m).

HDT 4- IR frequencies (Bruker Optik GmbH Alpha Sample Compartment RT-DLa TGSZnSe HR 0.8) V_{O-H} (3509 cm^{-1}), $V_{N=N}$ (1421 cm^{-1}), V_{C-O} (1222 cm^{-1}), UV (Elico Double Beam SL 210 UV Vis Spectrophotometer) λ (477.5 nm) $^1\text{H NMR}$ (400 MHz, Chloroform D) δ 6.846-6.877 (1H, d), δ 7.253 - 7.744 (11H, m).

HDT 5- IR frequencies (Bruker Optik GmbH Alpha Sample Compartment RT-DLa TGSZnSe HR 0.8) V_{O-H} ($3490\text{ cm}^{-1}\text{ cm}^{-1}$), $V_{N=N}$ (1423 cm^{-1}), V_{C-O} (1220 cm^{-1}), UV (Elico Double Beam SL 210 UV Vis Spectrophotometer) λ (477.5 nm) $^1\text{H NMR}$ (400 MHz, Chloroform D) δ 6.847-6.872 (1H, d), δ 7.251 - 7.744 (11H, m).

3. RESULTS AND DISCUSSION

The results for conventional and photochemical synthesis of Sudan dye have been described on the basis of IR, UV and $^1\text{HNMR}$. It is amply clear that there is excellent agreement in the characterization data which proves photocatalytic synthesis of Sudan dye 1. This makes it greener approach of using fewer chemicals and that too without an alkali. Minimum solvent is used to recover and crystallize the products. Almost entire synthesis of

hydroxytriazenes is water mediated, thus a greener way to obtain the diazo intermediate for coupling⁽¹⁵⁾. 2-naphthol in absence of NaOH, used for coupling is a good advantage over the conventional method. Thus this can be stated that the present method is an excellent green method to prepare Sudan dye, which can be further modified and scaled up. A tentative mechanism can be proposed for the photocatalytic synthesis. The data also reveal that the initial grinding of 2-naphthol and hydroxytriazenes immediately starts the reaction as indicated by change of color to light orange. In case of different hydroxytriazenes with alkyl substituent i.e. HDT 1 and HDT 2 in place of aryl on 3- side ($-N^1=N^2-N^3(OH)$ -alkyl) when exposed to sunlight, their mixture starts converting to product within 15 min. of exposure. In case of those with phenyl on 3- side ($-N^1=N^2-N^3(OH)$ -phenyl) the reaction visibly starts after one hour. It means that the alkyl group facilitates free radical formation faster as compared to phenyl which is evident from this reaction. In every case the reaction was complete after about 8 hours of exposure to sunlight which was verified by doing TLC of the product every hour. Thus present paper brings forward a green synthesis protocol for Sudan dye 1 via photocatalytic route.

4. ACKNOWLEDGMENT

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