



SYNTHESIS OF SOME NOVEL HETEROCYCLIC AZO-DYE BY USING MELDRUM'S ACID

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ABSTRACT:

A simple and efficient method has been devised for the synthesis of 2,2-dimethyl-5-(substituted phenyldiazenyl)-1,3-dioxane-4,6-dione (**3**) by reaction of Meldrum's acid and diazonium salt using catalytic amount of sodium acetate in ethanol. The structures of the products were confirmed by IR, ¹H and ¹³C NMR.

KEYWORDS: Aromatic primary amines, dioxane, azo coupling.

INTRODUCTION:

With increased ecological concern in recent years, the most essential role of organic chemistry has been to develop environmentally benign, economical and green chemical methods of synthesis ^[i]. Heterocyclic compounds of oxygen called pyrans play a significant role in the field of Drugs and Dyes. These compounds have attracted the interest of organic and medicinal chemists due to their useful biological and pharmacological properties. These include their ability to act as anti-coagulant, anti-cancer, anti-anaphylactin, spasmolytic and diuretic ^[ii-vii]. Some pyran derivatives also contribute to the structural unit of various natural products ^[viii-x], inhibit corrosion by acid ^[xi] and find application as photoactive materials ^[xii]

EXPERIMENTAL

Melting points of all synthesized compounds were determined in open capillary tubes on an electro thermal apparatus and are uncorrected. The purity of the compounds was monitored by TLC and UV light as visualizing agent. ¹H NMR and ¹³C NMR spectra were recorded on Varian 500 MHz NMR spectrophotometer using CDCl₃/DMSO-d₆ as solvent and TMS as an internal standard (chemical shifts in δ ppm).

General Procedure:

A mixture of Diazonium Salt, Meldrum's acid (1.25 mole) in ethanol & sodium acetate in catalytic amount was stirred in cold condition and progress of the reaction was monitored on TLC. On completion, the reaction mass was cooled at room temperature and filtered to obtain the solid product.

Compound 3a

2,2-dimethyl-5-(phenyldiazenyl)-1,3-dioxane-4,6-dione

Yield:68 %; m.p.=142-143 °C : IR (cm⁻¹): 1750(C=O) ¹H NMR(δ ppm): 1.78 (3H,s, 2xCH₃), 3.21 (1H,s,CH), 7.2-7.5 (5H, Ar- H), ¹³C NMR(δ ppm): 26.52(2xCH₃), 66.22(CH), 106.22(tetrahedral C), 122.3-148.2 (Ar-C & C=C), 170.4 (C=O) .

Compound 3b

2,2-dimethyl-5-(4-methylphenyldiazenyl)-1,3-dioxane-4,6-dione

Yield:68 %; m.p.=112-114 °C : IR (cm⁻¹): 1745(C=O) ¹H NMR(δ ppm): 1.77 (3H,s, 2xCH₃), 2.1 (3H, s, CH₃), 3.20 (1H,s,CH), 7.2-7.5 (4H, Ar- H), ¹³C NMR(δ ppm): 22.58(CH₃), 25.82(2xCH₃), 65.22(CH), 105.29(tetrahedral C), 120.8-147.2 (Ar-C & C=C), 170.4 (C=O) .

Compound 3c

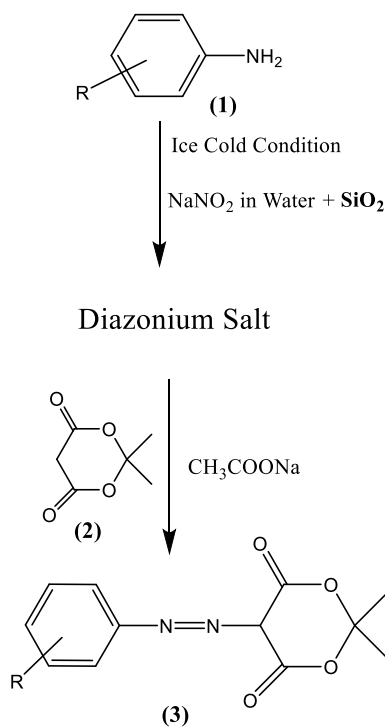
2,2-dimethyl-5-(4-chlorophenyldiazenyl)-1,3-dioxane-4,6-dione

Yield:68 %; m.p.=156-158 °C : IR (cm⁻¹): 1750(C=O) ¹H NMR(δ ppm): 1.79 (3H,s, 2xCH₃), 3.28 (1H,s,CH), 7.2-7.6 (4H, Ar- H), ¹³C NMR(δ ppm): 25.82(2xCH₃), 65.22(CH), 106.39(tetrahedral C), 121.9-148.2 (Ar-C & C=C), 171.2 (C=O) .

TABLE I : Characterization data of compounds 3

Compounds	R	Mol. Formula	m.p. °C	Yield %	Color
3a	H	C ₁₂ H ₁₂ N ₂ O ₄	142-143	68	Orange
3b	4-CH ₃	C ₁₃ H ₁₄ N ₂ O ₄	112-114	70	Yellow
3c	4-Cl	C ₁₂ H ₁₁ N ₂ O ₄ Cl	156-158	72	Orange
3d	2-NO ₂	C ₁₂ H ₁₁ N ₃ O ₆	100-102	75	Dark Brown
3e	4-NO ₂	C ₁₂ H ₁₁ N ₃ O ₆	135-136	78	Yellow

Reaction Scheme



RESULTS AND DISCUSSION

The target molecules 2,2-dimethyl-5-(substituted phenyldiazenyl)-1,3-dioxane-4,6-dione (3) (a-e) were synthesized in good yield by the reaction of Diazonium salt, Meldrum's acid in ethanol using catalytic amount of Sodium acetate.

CONCLUSIONS

New heterocyclic azo dyes were prepared in good yield, following a facile work-up process. The route is inexpensive and environment friendly.

ACKNOWLEDGEMENT:

Authors are thankful to Prof. A.E Lakdawala, Founder of Royal College; Management and Chemistry department of Royal College for constant encouragement and support with all necessary facilities. Authors are also thankful to The Director, UDC Mumbai for spectral data.

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Received on July 4, 2021.