Synthesis of Azodisperse Dyes from Meldrum’s Acid for Dyeing Acetate and Other Fibres

A A FADDA*, M M YOUSIF, A M EL-HOUSINI† & M S EL-HOUSINI‡

Faculty of Science, Chemistry Department, Mansoura University, Mansoura, Egypt

Received 18 April 1984; accepted 20 July 1984

Some 5-arylazo-2,2-dimethyl-1,3-dioxane-4,6-diones have been prepared for use as dyestuffs. The effect of the nature and orientation of substituents in the diazonium component on the colour of azo dyes is discussed.

Although Davidson and Bernhard¹ reported a colour reaction of Meldrum’s acid with sodium nitrite in 1948, it was not until 1961 that two groups independently isolated the oxime as an unstable yellow solid².³. Its reduction provides the only known route to the 5-amino compound³, but otherwise the properties of this compound are unknown. Similarly, little studied are the hydrazones, prepared by coupling the appropriate diazo compounds⁴,⁵, or diazonium salts². The parent 4,5,6-trione of which these compounds are derivatives has not yet been prepared despite a number of attempts⁶,⁷.

The most important nitrogen-containing derivative of Meldrum’s acid is the diazo compound, formed by diazotization of the amine or, more conveniently, by direct reaction with p-toluenesulphonylazide⁵.

Diazonium salts undergo a coupling reaction with the active methylene group of 2,2-dimethyl-1,3-dioxane-4,6-dione to give azo Meldrum’s acid derivatives. However, no details of the dyeing behaviour of Meldrum’s acid azo derivatives as disperse dyes for acetate and/or other fibres are reported.

On the other hand, the application of disperse dyes to acetate fibres⁸, woollen fabrics⁹ and other synthetic fibres¹⁰ and the mechanism of dyeing¹¹ have been discussed thoroughly.

In accordance with the nomenclature of azo Meldrum’s acid, the general structural formula for 5-arylazo-2,2-dimethyl-1,3-dioxane-4,6-diones [1-14] should be as follows:

This can exist in the following tautomeric forms:

We, therefore, considered it worthwhile to prepare azodisperse dyes containing dioxane ring for dyeing cellulose acetate and/or other fibres. In the present investigation, fourteen 5-arylazo-2,2-dimethyl-1,3-dioxane-4,6-diones have been prepared by coupling 2,2-dimethyl-1,3-dioxane-4,6-dione (Meldrum’s acid) with the appropriate diazonium salts in ethanol containing sodium acetate. These dyes have been characterized by elemental analysis as well as spectral (ultraviolet, visible and infrared) analysis (Table I).

Results and Discussion

Most of the dyes show two main absorption bands. A wide band of relatively weak intensity appears at approx. 355 nm and the other absorption band of relatively high intensity in the region 370-410 nm (Table I). Substituents in the diazonium component have relatively less effect on the former band than on the latter.

The 350 nm band of the dioxane exhibits profound hypochromic shift, often disappearing from the measurable region, which is conceivably due to the cis arrangement of the dioxane ring and the aryl groups around - N = N - , bringing the aryl group sufficiently close to N and thus restricting the delocalization of its electron.

Generally, the variation in the colour of these dyes results from the alteration in the diazonium components. Within the series of 5-arylazo Meldrum’s acid dyes investigated, the relationship between the shifts, observed in the absorption maximum, and the polar characteristic of the substituent in the arylazo group, may be summarized as follows:
The introduction of an electron-donating group in the ortho or para position gives a bathochromic shift. This is clear from the comparison of the absorption maxima of dyes 4 and 6 with those of dye 1 (Table 1). The effect is more pronounced when the electron-donating groups are in the ortho position.

The introduction of a nitro group does not alter the absorption maxima. However, it gives a better exhaustion and marked depth of colour on dye (Table 1). The infrared measurements of 5-arylazo-2,2-dimethyl-1,3-dioxane-4,6-diones showed stretching frequencies at 1540 cm\(^{-1}\) for the azo group (\(-\text{N} = \text{N}\)-), and 1720 cm\(^{-1}\) for C=O.

**Experimental Procedure**

*Preparation of 5-arylazo Meldrum’s acid dyes*—A well-stirred solution of the base aromatic amine (0.1 mol) in 2\(N\) hydrochloride acid (125 ml) was cooled in an ice-salt bath and diazotized with 1\(N\) sodium nitrite solution (100 ml). The above cold diazonium solution was added slowly to a well-stirred solution of Meldrum’s acid (0.1 mol) in ethanol (150 ml) containing 10\(\%\) sodium acetate solution (50 ml), and the mixture was cooled in an ice-salt bath.

After the coupling reaction was complete, the reaction mixture was stirred for 15 min at room temperature to coagulate the dye particles. The crude product was filtered, dried, and recrystallized from acetic acid to give 5-arylazo-2,2-dimethyl-1,3-dioxane-4,6-dione (Table 1).

The details of obtaining analytical and spectral data are given in an earlier paper.\(^\text{13}\)
References

1 Davidson D & Bernhard S A, J Am chem Soc, 70 (1948) 3426.
