J. Text. Color. Polym. Sci., **Vol. 17***,* No. 1, pp 1-5 (2020)

Synthesis and Characterization of some Disperse Dyes based on Enaminones

Morsy. A. El-Apasery[a], Fathy. A. Yassin[b], Mohamed. H. M. Abd El-Azim[b], Mahmoud. E. A. Abdellatif [b]

[a]Dyeing, Printing and Textile Auxiliaries Department, Textile Industries Research Division, National Research Centre, 33 El Buhouth St., Cairo,and [b]Department of Chemistry, Faculty of Science, Zagazig University, Egypt.

3-DIMETHYL amino-1-phenyl propenone, 3-Dimethyl amino-1-p-tolyl-propenone and 1-(4-Bromo phenyl)-3-dimethyl amino-propenone 4a-c were gotten in a good yields by reaction of methyl ketones (acetophenone, p-methyl acetophenone, p-bromo acetophenone) with dimethyl formamide dimethyl acetal DMFDMA in para-xylene. Enaminones 4a-c were exposed to coupling process with arylidene diazonium chloride to afford the disperse dyes 7a-f. The substance structures were explained by various diagnostic procedures as well as elemental analysis, Fourier-transform infrared spectroscopy (FT-IR), and nuclear magnetic resonance ^{1}H-NMR spectra. These disperse dyes delivered of the coupling reaction has affirmed that these colors in the solid state they exists in the anti rather than syn-form.

Introduction

It should be noted that the use of Inaminone has become widespread during the past ten years because of its effective effect in preparing many organic compounds. It understood that enaminones are polydentate reactants that have large function in organic chemistry [1-4]. Enaminones have been utilized in the planning of different naturally dynamic compounds, just as dye intermediates [5]. In past investigations, we have depicted the utility of β-enaminones as forerunners to polyfunctional organic chemistry [6]. In the exertion portrayed beneath, we have tested the utility of the enaminones synthesis of new azo disperse dyes that could be utilized for dyeing polyester fabrics by various dyeing techniques.

Materials and Methods

All reactions were trailed by thin layer chromatography (TLC) utilizing Merck aluminum plates. NMR spectra were accounted for by a BRUKER AVANCE 400 spectrometer at 400 MHz; substance shifts were recorded in ppm comparative with tetramethylsilane inward standard. Fourier-change infrared (FT-IR) spectra were controlled by a JASCO FT/IR4700 spectrophotometer. Elemental analyses (C, H, N) was made utilizing PerkinElmer 2400 analyzer (PerkinElmer, Norwalk, CT, United States). Solvents utilized in this exploration study were gotten from Fluka and Aldrich for both of the synthesis processes and spectroscopic estimations.

General procedures for preparing of enaminones 4a-c.

Enaminones 4a-c were prepared according to the published procedures [7], a mixtures of methylketones (acetophenone, *p*-methylacetophenone, *p*-bromoacetophenone) 1a-c (0.01 mol) and DMFDMA (1.19 g, 0.01 mol) was refluxed for 12-16 h. Completion of the reactions was monitored by TLC. The reaction mixture left to cool to room temperature and then treated with petroleum ether. The solid product, so formed, was collected by filtration and crystalized from a proper solvent to afford compounds 3-Dimethylamino-1-phenylpropenone 4a, 3-Dimethylamino-1-*p*-tolyl-propenone 4b and 1-(4-Bromophenyl)-3-dimethylamino-propenone 4c as yellow crystals with 60% yields.

General procedures for preparing of disperse dyes 7a-f.

A cold solution of the diazonium salt (10 mmol) (prepared by adding a cold solution of

* *E-mail: elapaserym@yahoo.com*

DOI: 10.21608/jtcps.2020.22547.1034

sodium nitrite (0.7 g) in water (5 mL) to a solution of the aniline (10 mmol) in conc. hydrochloric acid (5 mL) was added to a cold solution of enaminone 4a-c (10 mmol) in ethanol (10 mL) containing sodium sulphate (2 g). The mixture was stirred at room temperature for 1 h, and the solid precipitate that formed was collected by filtration and crystallized from proper solvents to give yellow crystals.

2-[(4-Chlorophenyl)-hydrazono]-3-oxo-3-phenylpropionaldehyde 7a

Yield (92%); m.p. 92 °C

Anal. Calcd For $C_{15}H_{11}ClN_2O_2$:(286.71), C, 62.84; H, 3.87; N, 9.77. Found: C, 63.02, H, 3.53, N, 9.50; MS m/z $(M)^+$ = 286.20; IR: 3063, (NH), 1637 (CO); ^{1}H NMR (DMSO-d6): δ = 7.42-7.88 (m, 9H, arom-H), 10.00 (s, 1H, CHO), 14.11 (s, 1H, NH).

2-[(4-Chlorophenyl)-hydrazono]-3-oxo-3-p-tolyl-propionaldehyde7b

Yield (89%); m.p. 169 °C Anal. Calcd For $C_{16}H_{13}ClN_2O_2$:(300.74), C, 63.90; H, 4.36; N, 9.31. Found: C, 63.03, H, 4.07, N, 8.70; MS m/z $(M)^+$ = 300.18; IR: 3123, (NH), 1639 (CO); ^{1}H NMR (DMSO-d6): δ = 2.40 (t, 3H, CH_3), 7.33-7.84 (m, 8H, arom-H), 9.79 (s, 1H, CHO), 14.10 (s, 1H, NH).

3-(4-Bromophenyl)-2-[(4-chlorophenyl)-hydrazono]-3-oxo-propionaldehyde7c

Yield (85%); m.p. 162 °C Anal. Calcd For $C_{15}H_{10}BrN_2O_2$:(365.61), C, 49.28; H, 2.76; N, 7.66. Found: C, 50.66, H, 2.76, N, 7.92; MS m/z $(M)^+$ = 365.06; IR: 3069, (NH), 1645 (CO); ^{1}H NMR (DMSO-d6): δ = 7.44-7.83 (m, 8H, arom-H), 10.01 (s, 1H, CHO), 14.12 (s, 1H, NH).

2-[(3-Nitrophenyl)-hydrazono]-3-oxo-3-phenyl-propionaldehyde7d

Yield (90%); m.p. 167 °C Anal. Calcd For $C_{15}H_{11}N_3O_4$:(297.27), C, 60.61; H, 3.73; N, 14.14. Found: C, 60.04, H, 3.32, N, 14.16; MS m/z $(M)^+$ = 297.18; IR: 3177, (NH), 1638 (CO); ^{1}H NMR (DMSO-d6): δ = 7.54-7.99 (m, 9H, arom-H), 10.03 (s, 1H, CHO), 13.91 (s, 1H, NH).

2-[(3-Nitrophenyl)-hydrazono]-3-oxo-3-p-tolyl-propionaldehyde7e

Yield (83%); m.p. 153 °C Anal. Calcd For $C_{16}H_{13}N_3O_4$:(311.29), C, 61.73; H, 4.21; N, 13.50. Found: C, 61.73, H, 3.45, N, 13.84; MS m/z $(M)^+$ = 311.17; IR: 3088, (NH), 1637 (CO); ^{1}H NMR (DMSO-d6): δ = 2.42 (t, 3H, CH_3), 7.36-7.99 (m, 8H, arom-H), 10.00 (s, 1H, CHO), 13.97 (s, 1H, NH).

3-(4-Bromophenyl)-2-[(3-nitrophenyl)-hydrazono]-3-oxo-propionaldehyde7f

Yield (80%); m.p. 210 °C Anal. Calcd For $C_{15}H_{10}BrN_3O_4$:(376.16), C, 47.89; H, 2.68; N, 11.17. Found: C, 47.75, H, 2.50, N, 10.91; MS m/z $(M)^+$ = 376.10; IR: 3092, (NH), 1641 (CO); ^{1}H NMR (DMSO-d6): δ = 7.66-8.00 (m, 8H, arom-H), 10.01 (s, 1H, CHO), 13.96 (s, 1H, NH).

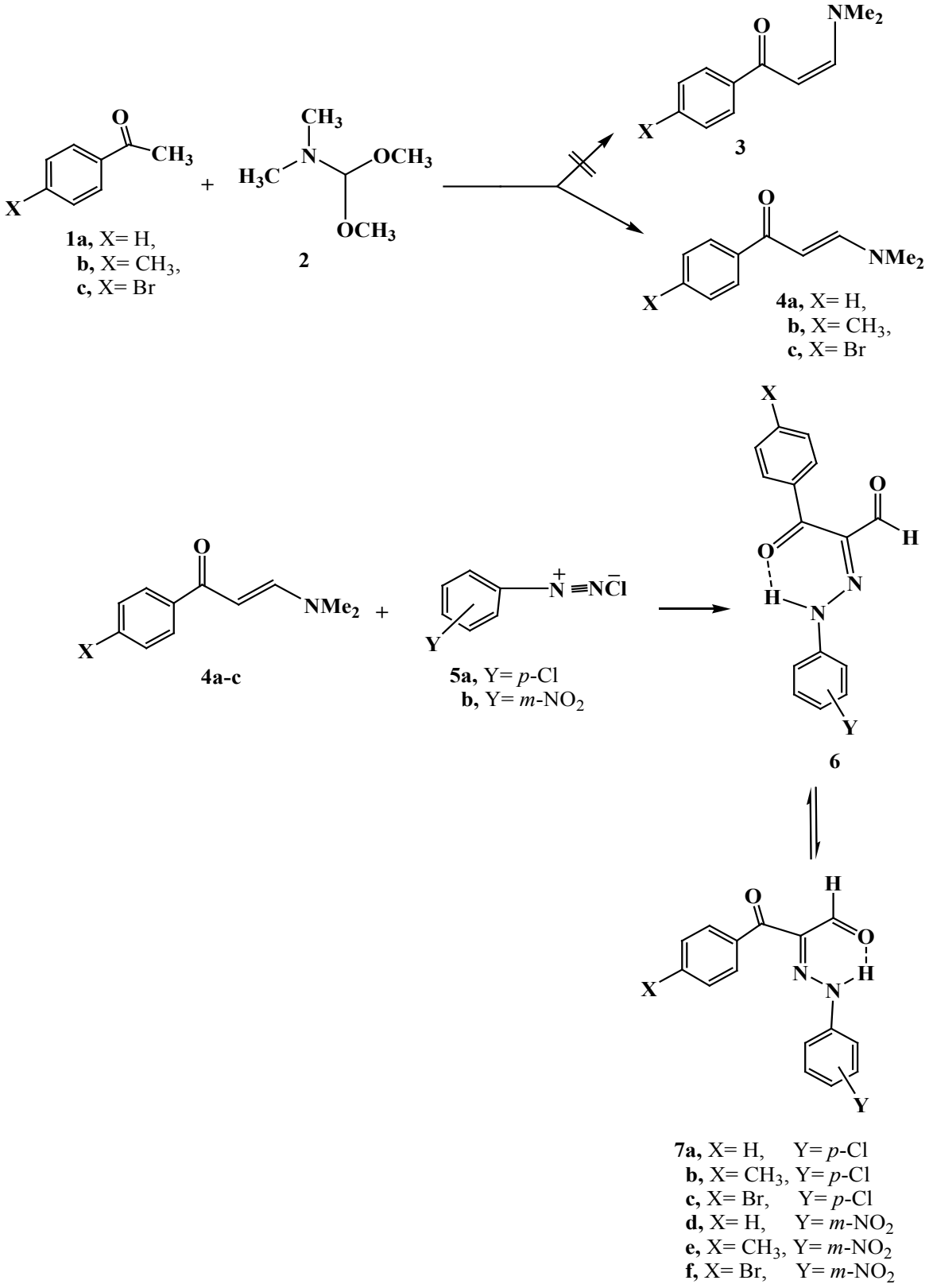
Result and Discussion

Scheme 1 shows that enaminones 4a-c were synthesized in acceptable yields by condensation reactions of methylketones 1a-c with dimethylformamide dimethyl acetal (DMFDMA) in *para*-xylene. It is essential that enaminone 7a was accounted for before to be framed as the trans structure is really delivered a suggestion that is affirmed by the X-ray crystallographic information [8-11]. However it was one report before our published the X-ray data indicated that enaminones were framed the cis-isomer, portrayed by investigation of olefinic proton coupling constants [12].

Conditions for the effective synthesis of enaminones from methylketones and DMFDMA including microwave heating have been accounted for earlier by us and all the more as of late by others [13-17]. We next examined the coupling reaction of enaminone 4a-c with arylidene diazonium chloride. This procedure managed new azo disperse dyes 7a-f, which is practically equivalent to substances that have been recently appeared to exist in the strong state in both *syn* and *anti*-forms [11]. As of late we have given X-ray crystallographic data exhibited that the disperse dyes delivered of the coupling reaction has affirmed that these colors in the solid state they exists in the *anti* rather than *syn*-form [18].

Conclusion

A new disperse were successfully incorporated in excellent yields and checked by mass spectroscopy, essential examination, FT-IR, and ^{1}H-NMR spectroscopy.



Scheme 1. Synthesis of azo disperse dyes 7a-f.

Acknowledgements

Authors are gratefully thankful for the technical support from both of National Research Centre, Cairo, Egypt. *and Zagazig University, Egypt.*

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(*Received 16* /1 /2020 ;
accepted 19 / 1 /2020)

توليف وتوصيف بعض الصبغات المنتشرة المرتكزة على الإينامينونات

مرسى الاباصيرى * فتحى ياسين , محمد عبد العظيم ومحمود عبد اللطيف
شعبة بحوث الصناعات النسيجية ، المركز القومي للبحوث ، القاهرة ، مصر
قسم الكيمياء , كلية العلوم , جامعة الزقازيق، مصر

تم تحضير وتوصيف بعض الصبغات المنتشرة وذلك من خلال تفاعل تكاثف بين مركب الميثيل كيتونات مع مركب ثنائى ميثل فورماميد ثنائى ميثل الاسيتال ثم اجراء عملية الازدواج بين هذه الاينامينونأت و املاح الايرليدنات. تم التحقق من التركيب الجزيئي بواسطة تقنيات تحليلية مختلفة تشمل تحليل العناصر, التحليل الطيفي بألشعة تحت الحمراء والرنين النووي المغناطيسي.