Faculty of Science
Chemistry Department

Utility of Iminoesters and IminoNitriles in synthesis of some new heterocyclic compounds and their application as disperse dyes.

A Thesis Submitted for the degree of Master of Science as a partial fulfillment for requirements of the Master of Science

Organic Chemistry

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Cairo, Egypt
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For M. Sc. Degree in Organic Chemistry

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Summary

The thesis aimed to prepare of new azo disperse dyes and test its ability to dyeing different types of fiber as poly ester, wool, nylon and cotton and its characterization. The structures were elucidated by Infrared,^{1}H- NMR, mass spectroscopic techniques and elemental analysis .

I) Using of 2-chloro-N-(3-cyano-4,5,6,7-tetrahydro- benzo-[b]thiophen-2-yl)acetamide in synthesis of new aromatic amines which used in preparation of new azo disperse dyes.

I.1-Preparation of ethyl 2-((4-amino-5, 6, 7, 8-tetrahydrobenzo [4,5] thieno[2,3-d]pyrimidin-2-yl)thio) acetate(3):-

Treatment of (2) with ammonium thiocyanate in dioxane/ethanol mixture under reflux conditions for four hours afforded ethyl 2-((4-amino-5, 6, 7, 8-tetrahydrobenzo [4,5] thieno[2,3-d]pyrimidin-2-yl)thio) acetate(3).Scheme(1).

Scheme(1)

I.1.1) Using free primary amino group of compound (3) in the formation of azo-dyes:

The diazonium salt of compound (3) was added drop wise to different nucleophilic reagents such as N,N dimethylaniline, resorcinol, and ethyl 2-((4-amino-5,6,7,8-tetrahydrobenzo [4,5]thieno[2,3-d]pyrimidin-2-yl)thio)acetate and formed three dyes according to(scheme 2).

Scheme 2

I.1.2) Using active methylene in azo-dyes formation:

The diazonium salt of aromatic amines namely 4-amino benzene sulphonic acid, *p*-toluidine, aniline, *o*-phenylene diamine

and α- naphthylamine were added to a solution of compound 3 to form a new series of azo dyes(8-12).

I.2.1) Preparation of 2-((4-aminophenyl)amino)-N-(3-cyano-4,5,6,7-tetrahydrobenzo[b]thiophen-2-yl) acetamide (13) :-

Treatment of (2) with p-phenlenediamine in dioxane as a solvent under reflux conditions for four hours afforded 2-((4-aminophenyl) amino)-N-(3-cyano-4, 5, 6, 7-tetrahydrobenzo [b]thiophen-2-yl) acetamide (13) and not isolated the dimer form.

I.2.1.1) 2-hydroxy-3-((4-((2-hydroxynaphthalen-1-yl)diazenyl) phenyl)- amino)-5,6,7,8-tetrahydrobenzo[4,5]thieno[2,3-b] pyridin -4(3H)-one (15)

compound (13) was dissolved in HCl then add sodium nitrite ,stirring for 1 hour in ice path. Dissolve β-Naphthol in NaOH(10%) the solution was cooled for 45 minute in 0-5 0c, the diazonium salt was added drop wise for 0.5 hr ,stirring for 4 hour in ice path.filtered, wash with diethyl ether to obtain orange crystals**.**

I.2.2) Preparation of 2-((4'-amino-[1, 1'-biphenyl]-4-yl) amino)-N-(3-cyano-4, 5, 6, 7-tetrahydro benzo[b]- thiophen-2-yl)acetamide (14):-

Treatment of (2) with Benzidine in dioxane under reflux conditions for four hours afforded 2-((4'-amino-[1,1'-biphenyl]-4-yl)amino)-N-(3-cyano-4,5,6,7-tetrahydrobenzo-[b]thiophen-2-yl)acetamide.

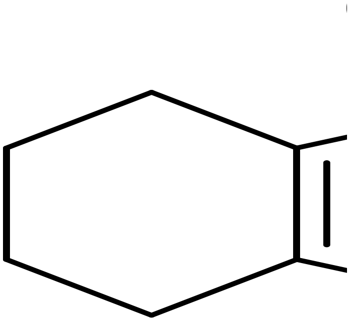
I.2.2.1)3-((4'-((4-(dimethylamino)phenyl)diazenyl)-[1,1'-biphenyl]-4-yl)amino)-2-hydroxy-5,6,7,8-tetrahydrobenzo [4,5] thieno- [2,3-b]pyridin-4(3H)-one (16)

Compound (14) was dissolved in HCl then add sodium nitrite ,stirring for 1 hour in ice path. Dissolve N,N Dimethylaniline in acetic acid the solution was cooled for 45 minute in 0-5 0c, the diazonium salt was added drop wise for 0.5 hr ,stirring for 4 hour in ice path.filtered, wash with diethyl ether to obtain orange crystals**.**

The study showed that the dyed fabric showed excellent light, washing, rubbing, and perspiration fastness.

II-Using of ethyl 2-amino-4, 5, 6, 7 tetrahydrobenzo[b]-thiophene-3-carboxylate in synthesis of new azo dyes

The synthesis of mono azodye by coupling of diazonium chloride of ethyl 2-amino-4,5,6,7 tetrahydrobenzo[b]- thiophene-3-carboxylate with 4-amino benzene sulphonic acid afforded 4-amino-3-((3-(ethoxycarbo- nyl)-4,5,6,7-tetrahydro-benzo [b] thio-phen-2-yl)diazenyl)benzene sulfonic acid. The aromatic amino group of (17) react with nitrous acid and forming the new diazonium salt, which able to couple with β-Naphthol, N,N-dimethyl aniline and resorcinol to forming the corresponding diazo dye products(20-23) respectively, which characterized by higher wave length in compared with the mono azodye (scheme 3).



Scheme (3)

The newly synthesized dyes were applied as dyes for wool and nylon fabric, where they exhibited very good dye ability and fastness properties.

Introduction

Disperse dyes are non-ionic chemicals with sparing solubility in water which, consequently, are able to retain comparatively better substantively for hydrophobic fibers, such as polyester, nylon and acetate. For the sake of efficient diffusion into textiles, the particles of disperse dye should be as fine as possible comprising low molecular weight molecules in the range of 400 – 600. It is essential for disperse dyes to be able to withstand various dyeing conditions, pH and temperature, resulting in negligible changes in shade and fastness [1,2].

Disperse dyes are often substituted azo, diphenylamine or anthraquinone compounds which are non-ionic and contain no water solubilizing groups. The dyes particles are thus held in dispersion by the surface-active agent and the dyes themselves are called disperse dyes. They are marketed in the form of either an easily dispersible powder or a concentrated aqueous dispersion and are now the main class of dye for certain synthetic fibers [3].

Azo dyes are the most important class, accounting for over 50% of all marketable dyes. Because of this, azo dyes have been studied more than any other class.Azo dyes contain at least one azo group (-N=N-). The azo group is attached to two radicals of which at least one but, more usually, both are aromatic. They exist in the transform and the bond angle is 120^0 ; the nitrogen atoms are Sp^2 hybridized[4].

INTRODUCTION

The most important amines compounds are 4-nitroaniline [100-01-6], 2-chloro-4-nitroaniline [121-87-9]*,2-cyano-4-nitroaniline [17420-30-3] *, 2,4-dinitroaniline[97-02-9] *,2,6-dichloro-4-nitroaniline [99-30-9] *,2-bromo- [1817-73-8] * and 2-chloro-4,6-di- nitroaniline [3531-19-9] *, and 2-bromo-6-cyano-4-nitroaniline[17601-94-4] *. The coupling components are derived from aniline, 3-aminotoluene [108-44-1],3-chloroaniline [108-42-9],3-aminoacetanilide [102-28-3], and 3-amino-4-alkoxyacetanilide by N-alkylation[5].

Disperse azodye became important for dyeing acetate fibers. It has been adapted to the requirements of polyester fibers and of different dyeing processes, mainly by varying the substituents R^1 and R^2[6].For example, the –hydroxyl alkyl groups (R^1 and/or R^2 = OH), typical of many acetate dyes, were replaced by less hydrophilic groups such as OCOR, CN, and COOR, which enhanced the affinity for polyester fibers and, in many instances, the fastness to light and sublimation [7, 8].

The shade of dyes with formula **(I)**depends largely on the substituents X, Y, A, B, R^1, and R^2. If the coupling component is kept constant and X = H, variation of Y results in a bathochromic shift, which increases in the following order: H, Cl, NO_2, CH_3SO_2, and CN.

*trade mark code

If X and Y are other than H, the situation is more complicated because of possible steric effects on the azobenzene system. For example, if X = Y = Cl, steric hindrance prevents a planar alignment of the azobenzene molecule, which leads to a hypochromic shift with simultaneous loss of clarity. This effect is exploited in the industry to produce brown shades. Cyano groups exert no steric effects, and the strongest bathochromic shifts can be obtained by using X = Y = CN; X = CN, Y = NO_2; and X = CN, Y = CH_3SO_2. For a given diazo component, a bathochromic shift occurs which increases in the order A = Cl, H, CH_3, NHCOR. The most extreme bathochromic effect is obtained when A = NHCOR and B = OR. In combination with 2-bromo- [*1817-73-8*] or 2-chloro-4,6-dinitroaniline [*3531-19-9*] as the diazo component, commercially important navy blue dyes are obtained; of all the monoazo dyes, these are produced in the largest quantity.The significant influence of R_1 and R_2 on color is quite surprising because these substituents are not components of the chromophore system. Ester and, especially, cyano groups in these positions cause a distinct hypsochromic shift [9].

(I)

This type of dye quickly became important for dyeing acetate fibers. It has been adapted to the requirements of polyester fibers and of different dyeing processes, mainly by varying the substituents R^1 and R^2[10, 11].For example, the-hydroxyl alkyl groups (R^1 and/or R^2= OH), typical of many acetate dyes, were replaced by less hydrophilic groups such as CN, O COR, and COOR, which enhanced the affinity for polyester fibers and, in many instances, the fastness to light and sublimation [12, 13].

The shade of dyes with formula(I) depends largely on the substituents X, Y, A, B, R_1, andR_2. If the coupling component is kept constant and X = H, variation of Y results in a bathochromic shift, which increases in the following order: H, Cl, NO_2, CH_3 SO_2, and CN. If X and Y are other than H, the situation is more complicated because of possible steric effects on the azobenzenesystem.For example, if X = Y = Cl, steric hindrance prevents a planar alignment of the azobenzene molecule, which leads to a hypsochromic shift with simultaneous loss of clarity. This effect is exploited in the industry to produce brown shades. Cyano groups exert no steric effects, and the strongest bathochromic shifts can be obtained by using X = Y =CN; X =CN, Y = NO_2; and X = CN, Y = CH_3 SO_2. For a given diazo component, a bathochromic shift occurs which increases in the order A = Cl, H, CH_3, NHCOR. The most extreme bathochromic effect is obtained when A = NHCOR and B = OR. In combination