

**SYNTHESIS AND SPECTRAL STUDIES OF NOVEL BIS-CHROMENE BY THE
CYCLIZATION OF N, N'-METHYLENEBIS(2-CHLOROACETAMIDE) WITH
SALICYLDEHYDE**

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Abstract: 1, 2-diaminoethane react with chloroacetyl chloride to form N, N'-methylenebis(2-chloroacetamide), which exist in tautomeric equilibrium in DMSO-d₆ solution. N, N'-bis(3-chloro-chromen)methanediamine was obtained by cyclocondensation of N, N'-methylenebis(2-chloroacetamide) with salicyldehyde in the presence of KOH. The synthesis of novel heterocyclic azo disperse dye bis[3-chloro-4(substituted)phenylazo-2H-chromene-2-iminyl]ethane derived from N, N'-bis(3-chloro-chromen)methanediamine and by using various diazonium salt. The structures of the newly synthesized compounds were confirmed by spectral data such as IR and NMR.

Keywords: Chromene, cyclocondensation, salicyldehyde, azo dyes

Introduction

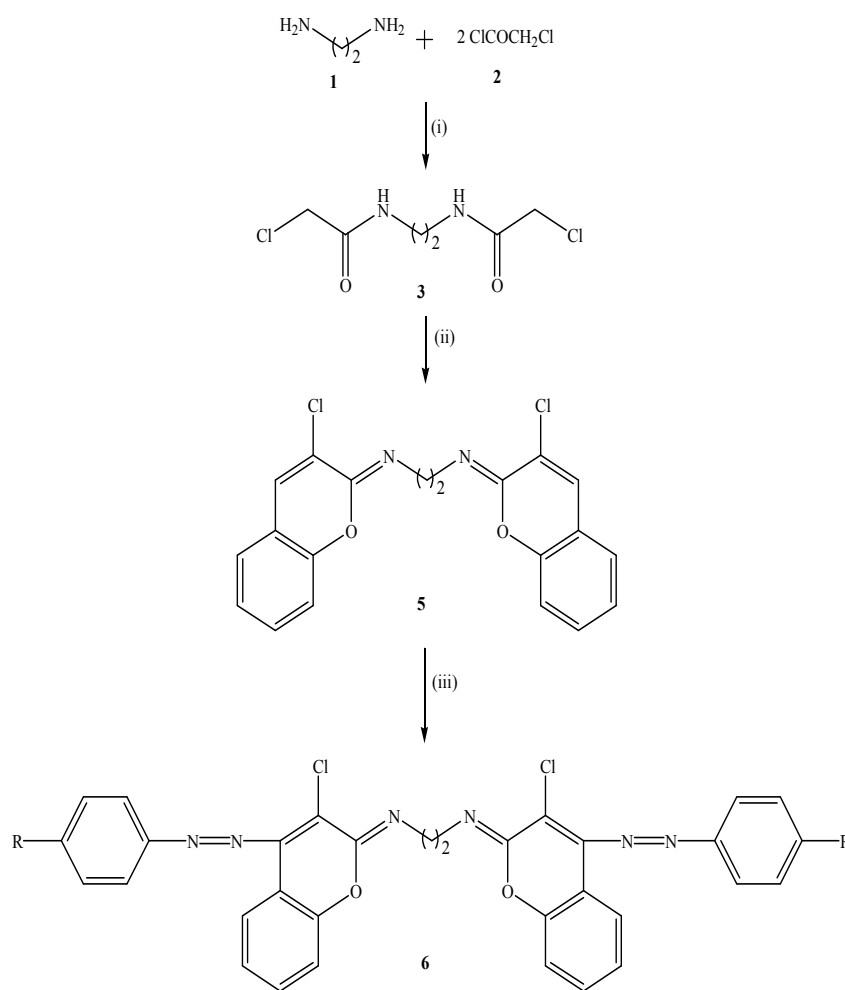
Many heterocyclic compounds are used extensively in disperse dye chemistry for textile or nontextile applications. These dyes are now marketed to produce a full range of dispersed dyestuffs without the use of colorants based on heteroaromatic diazo components. The azo dyes containing heterocyclic rings result in brighter and often deeper shades than their benzene analogs. On the other hand, they are very important in applications such as disperse dyes for polyester fibers, reprography, functional dye and nonlinear optical systems, photodynamic therapy and lasers¹⁻⁷. Chromenone derivatives are widely used for production of highly effective fluorescent dyes for synthetic fibres and daylight fluorescent pigments⁸⁻¹³. They also play a vital role in electrophotographic and electroluminiscent devices¹⁴⁻¹⁶. Synthesis and investigation of new heterocycles based on 2H-2-cromenone ring make possible new ways for scientific and technical usage. 2H-2-Chromenone (or coumarin) and its derivatives are known as bioactive compounds, many of them possess antibacterial and antifungal properties¹⁷. Coumarins are also of considerable biological and medical interest. Many derivatives of these products show

significant physiological effects: weakly toxic, anticarcinogenic, anticoagulant and antibiotic activities¹⁸⁻¹⁹.

Result and Discussion:

Compound **1** was prepared by the reaction of 1, 2-diaminoethane with chloroacetyl chloride in toluene at 0-5°C. Compound **3** was then allowed to react with salicyldehyde in refluxing ethanol containing a catalytic amount of potassium hydroxide to give bis[3-chloro-2H-chromene-2-iminyl]ethane **5**. The chromene derivatives was allowed to react with various diazonium salt of aromatic amines in the presence of sodium acetate and ethanol which yielded bis[3-chloro-4(substituted)phenylazo-2H-chromene-2-iminyl]ethane **6**. (**Scheme I**)

The structures of the compounds **5** and **6a-e** were confirmed by IR, ¹H and ¹³C NMR spectroscopy and elemental analysis.



Reaction conditions:

i) Toluene/ 0-5°C

ii) salicyldehyde (4)/ KOH/ ethanol, reflux temp

iii) diazonium salt/ 10% NaOAc solution / ethanol/ 0-5°C

Scheme-I: Synthetic route for the preparation of azo dyes

Experimental:

Melting points were determined using digital melting-point apparatus. FT-IR spectra were recorded as KBr pellets on a Jasco FT/IR-600 Plus spectrometer. ¹H-NMR and ¹³C-NMR spectra were recorded on JEOL NMR spectrometer (300 MHz) using CDCl₃ and DMSO-d₆ as a solvent and TMS as internal standard. The homogeneity of the compounds was checked on Aluminium backed silica gel coated TLC plates (Merck) as adsorbent and UV light was used for visualization.

Procedure for the synthesis of 3, 6-diaza -1, 8-dichloro-2, 7-dioxo octane 3

In a 4-necked 250 ml round bottom flask equipped with overhead stirrer, thermometer pocket, pressure equalising funnel-guard tube and N₂, 1, 2-diaminoethane **1** (0.1 mol, 6.0 gm) was taken in toluene (2 vol.). Chloroacetyl chloride **2** (0.24 mol, 19 ml) was dissolved in toluene (5 vol., 95 ml) and added drop wise with constant stirring at 0-5°C under nitrogen atmosphere to above solution. After complete addition of chloroacetyl chloride, stirring was continued for one hour. Thus Compound **3** obtained was filtered, washed with 30 ml of toluene followed by 30 ml of diethyl ether. Compound **3** was dried at room temperature under vacuum. m.p. 56-58°C, yield 89%.

Procedure for the synthesis of bis[3-chloro-2H-chromene-2-iminyl]ethane 5

In a 4-necked 100 ml round bottom flask equipped with overhead stirrer, thermometer pocket, a mixture of **3** (0.01 mol, 1.99), salicylaldehyde **4** (0.021 mol, 2.562 gm) and KOH (0.04 mol, 2.24 gm) in 30 ml ethanol was refluxed for 4-5 hr. The progress of reaction was monitored by TLC. Upon completion, the ethanol was evaporated under vacuum to dryness. Then residue was diluted with ice cold water. The Compound obtained was filtered, washed with ice water till neutral pH. Recrystallized by using aqueous alcohol to yield yellow shiny product **5**.

Representative procedure for the synthesis of bis[3-chloro-4(substituted)phenylazo-2H-chromene-2-iminyl]ethane 6.

To an ice cold solution of p-Toluidine (0.02 mol, 2.14 gm) in a mixture of conc. hydrochloric acid (8 ml), and water (11 ml), a cold aqueous solution of sodium nitrite (1.40 gm), was added portionwise at 0°C. The solution was stirred vigorously for 2 hrs to yield the diazonium salt solution at 0-2°C.

The diazonium salt solution was then added dropwise to pre-cooled (0°C) solution of **5** (0.01 mol, 3.87 gm in 10 ml ethanol) over the period of 1 hr with vigorous stirring at 0-3°C. The reaction mixture was further stirred for 2 hr at 0-5°C and then 10 % sodium acetate solution was added slowly until the pH became 4-5. After completion of the reaction (monitored by TLC), the product was filtered off, washed with water until free from acid, dried at 40°C in an oven to give **6b**, which was recrystallised from EtOH.

Spectral analysis:

bis[3-chloro-2H-chromene-2-iminyl]ethane (**5**)

M.F.: C₂₀H₁₆Cl₂N₂O₂; m.p. 162-164°C, yield 72%.

IR cm^{-1} : 1610 (C=N); 1210 (C-O).

^1H NMR: 2.56 (t, 4H, $2\times\text{CH}_2$), 6.54-7.28 (m, 10H, Ar-H & CH);

^{13}C NMR: 62.34 ($2\times\text{CH}_2$), 117.24-132.52 (Ar-C & C=C), 167.74 ($2\times\text{C}=\text{N}$);

Elemental analysis: Cal. C 62.35%; H 3.66%; N 7.27%; Found C 62.21%; H 3.47%; N 7.11%

bis[3-chloro-4-phenylazo-2H-chromene-2-iminyl]ethane (**6a**)

M.F.: $\text{C}_{32}\text{H}_{22}\text{Cl}_2\text{N}_6\text{O}_2$; m.p. 108-110, yield 89%

IR cm^{-1} : 1635 (C=N); 1216 (C-O),

^1H NMR: 3.10 (t, 4H, $2\times\text{CH}_2$), 6.68-7.75 (m, 18H, Ar-H);

^{13}C NMR: 56.32 ($2\times\text{CH}_2$), 115.01-139.88 (Ar-C), 164.07 ($2\times\text{C}=\text{N}$);

Elemental analysis: Cal. C 64.76%; H 3.74%; N 14.16%; Found C 64.58%; H 3.59%; N 13.92%

bis[3-chloro-4(4'-methyl)phenylazo-2H-chromene-2-iminyl]ethane (**6b**)

M.F.: $\text{C}_{34}\text{H}_{26}\text{Cl}_2\text{N}_6\text{O}_2$; m.p. 115-117, yield 85%

IR cm^{-1} : 1635 (C=N); 1218 (C-O),

^1H NMR: 2.18 (s, 6H, $2\times\text{CH}_3$), 3.06 (t, 4H, $2\times\text{CH}_2$), 6.73-7.81 (m, 16H, Ar-H);

^{13}C NMR: 22.12 ($2\times\text{CH}_3$), 53.24 ($2\times\text{CH}_2$), 117.24-135.10 (Ar-C), 162.83 ($2\times\text{C}=\text{N}$);

Elemental analysis: Cal. C 65.70%; H 4.22%; N 13.52%; Found C 65.55%, H 4.08%, N 13.39%

bis[3-chloro-4(4'-methoxy)phenylazo-2H-chromene-2-iminyl]ethane (**6c**)

M.F.: $\text{C}_{34}\text{H}_{26}\text{Cl}_2\text{N}_6\text{O}_4$; m.p. 121-125, yield 86%

IR cm^{-1} : 1634 (C=N); 1217 (C-O),

^1H NMR: 2.99 (t, 4H, $2\times\text{CH}_2$), 3.73 (s, 6H, $2\times\text{OCH}_3$), 6.69-7.83 (m, 16H, Ar-H);

^{13}C NMR: 52.91 ($2\times\text{CH}_2$), 55.97 ($2\times\text{OCH}_3$), 118.10-136.73 (Ar-C), 161.39 ($2\times\text{C}=\text{N}$);

Elemental analysis: Cal. C 62.49%; H 4.01%; N 12.86%; Found C 62.35%, H 3.85%, N 12.73%

bis[3-chloro-4(4'-chloro)phenylazo-2H-chromene-2-iminyl]ethane (**6d**)

M.F.: $\text{C}_{32}\text{H}_{20}\text{Cl}_4\text{N}_6\text{O}_2$; m.p. 112-115, yield 80%

IR cm^{-1} : 1628 (C=N); 1205 (C-O);

^1H NMR: 2.95 (t, 4H, $2\times\text{CH}_2$), 6.98-7.74 (m, 16H, Ar-H);

^{13}C NMR: 54.68 ($2\times\text{CH}_2$), 116.94-131.18 (Ar-C & C=C), 166.94 ($2\times\text{C}=\text{N}$);

Elemental analysis: Cal. C 58.03%; H 3.04%; N 12.69%; Found C 57.84%, H 2.84%, N 12.52%

bis[3-chloro-4(4'-bromo)phenylazo-2H-chromene-2-iminyl]ethane (**6e**)

M.F.: $\text{C}_{32}\text{H}_{20}\text{Br}_2\text{Cl}_2\text{N}_6\text{O}_2$; m.p. 116-119, yield 82%

IR cm^{-1} : 1628 (C=N); 1206 (C-O);

^1H NMR: 3.01 (t, 4H, $2\times\text{CH}_2$), 6.86-7.68 (m, 16H, Ar-H);

^{13}C NMR: 55.72 ($2\times\text{CH}_2$), 115.04-133.48 (Ar-C & C=C), 165.48 ($2\times\text{C}=\text{N}$);

Elemental analysis: Cal. C 51.16%; H 2.68%; N 11.19%; Found C 51.01%, H 2.54%, N 10.98%

Conclusion

3, 6-Diaza -1, 8-dichloro-2, 7-dioxo octane was successfully converted into bis-chromene moiety by the reaction with salicylaldehyde in presence of inorganic base such as potassium hydroxide. Further it was converted into azo dyes. A series of azo disperse dyes containing chromene moiety have been synthesised by conventional method and their structures were confirmed by spectral data.

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