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Synthesis And Characterizations Of 2-(2-3"–Chlorophenyl-4-4'-Dimethylaminophenyl-1-3-Butadienyl)-3-Ethylbenzothiazoliium Iodide. [A Hemicyanine Dye]

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Abstract: Hemicyanine dyes are a sub class of polymethine colorants. At one end of their polymethine chain an unsaturated heterocyclic ring possessing a nitrogen atom as would be found in a cyanine dye. However, the other end is terminated by a nitrogen atom that does not form part of an unsaturated heterocycle. The name alludes to their half-cyanine substitution pattern. Later the scope of the term "hemicyanine" was extended to the phenylogous dyes where there is a phenyl group between the two terminal nitrogen atoms. The first main technical application of hemicyanine dyes was in textile coloration. Now a days hemicyanine dyes are used extensively as optical probes of cell membrane potential. The compound 3-ethyl-2-methylbenzothiazolium iodide and 3'-chlorophenyl-4-dimethylaminostyryl ketone were dissolved in absolute alcohol together with basic catalyst piperidine. The mixture was refluxed for about 6 hrs. Connected with $CaCl_2$ guard tube and subjected to overnight cooling. The dye obtained was recrystallised from methanol as dark brown sandy crystals.

Keywords: Cell membrane potential; Cyanine dyes; Franck–Condon principle; Hemicyanine dyes; Optical probes; Silver halide photographic materials; 3-ethyl-2-methylbenzothiazoliumiodide; 3'- chlorophenyl-4-dimethylaminostyryl ketone.

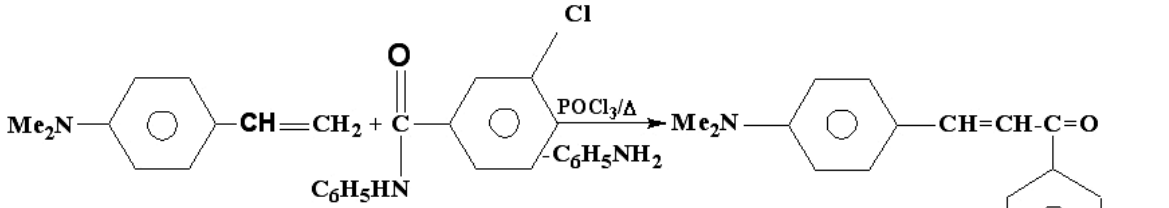
INTRODUCTION

The dye 2-(2-3"-chlorophenyl-4-4'-dimethylaminophenyl-1, 3-butadienyl) -3-ethylbenzothiazolium iodide has been prepared in following steps:-

Step–1:

Preparation of 3'-chlorophenyl-4-dimethylaminostyryl ketone.

The compound 3'-chlorophenyl-4-dimethylaminostyryl ketone has been prepared by heating a mixture of 4-dimthyl aminostyrene and 3-chlorobenzanilide in presence of $POCl_3$.



4-Dimethylamino Styrene | 3-Chloro benzanllide | 3-Chlorophenyl-4-dimethyl aminostyryl ketone

Procedure:

3-Chlorobenzanilide (IM) mixed with freshly distilled 4- dimethyl styrene. (2-2.Sm) in a flask and heated gently on a water bath till the mixture became viscous. Now the flask was immersed in a freezing mixture and phosphorus oxychloride ($POCl_3$) (1-2.Sm) was gradually added to the flask. Now the flask was heated on a water bath for four hours and then on an oil bath (110-115°c) for further two hours. Now the flask was cooled in an ice bath to solidify the offered ketone. The unreacted reactants were removed by addition of very dilute HCI followed by filtration. The crude solid ketone was dissolved into cone. HCI filtered off and then the filterate was neutralized by cold NaOH solution keeping the ph<7. The ketone was separated as solid which was recrystallized from ethanol. The compound was further analysed and found to contain C, H, N, Cl and O which corresponds to the molecular formula $C_{17}H_{16}CINO$.

Physical data:

Nature: sandy crystals, Colour: dirty yellow.

Yield	77%	M.P.	77°C	
Found:	C, 71.44	H, 5.64	N, 4.99	Cl, 12.38%

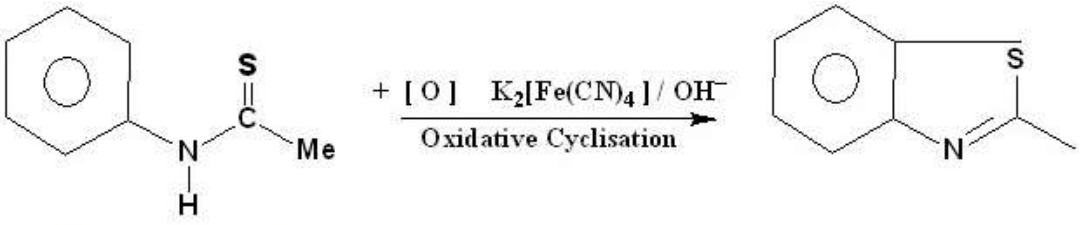
$C_{17}H_{16}CINO$ requires: C-71.47, H-5.64, N-4.90, Cl-12.41(%)

I.R. spectra (cm-1) :1626 (CH=CH), 1690(C=O), 1616(C=N), 710(Cl)

Step 2:

Preparation of 2- methyl benzothiazole.

2-Methyl benzothiazole was synthesised by treatment of thioacetanilide with alkaline. potassiumferricyanide using earlier adopted method (Jacobson, 1886, Mills, 1922 Beileson and Hamer, 1936). The alkaline potassium ferricyanide was used for oxidative cyclisat ion of the thioacetanilide which afforded crude product.



Thio acetanilide | 2-Methyl benzothiazole

The product was purified by steam distillation (Jacobson, 1886; Jacobson & Ney, 1889, Fries and Engelbertz, 1 915; Mills, 1992: Worall, 1924: Koning, 1928: Weilenson & Hamer, 1936) with some procedural alteration suggested by J.C. Banerji and others (Banerji and Doja, 1949, 1958).

Molecular formula C_8H_7NS

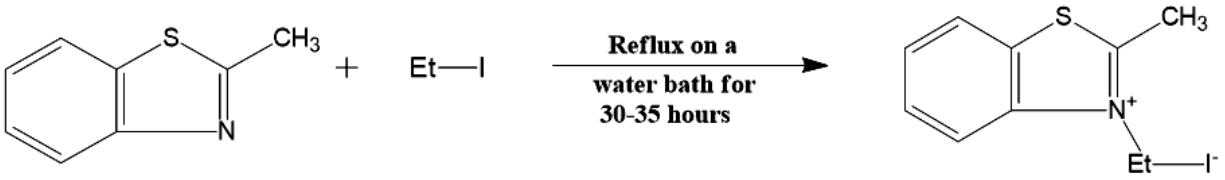
Physical data:

Nature	Obs: brown	viscous oil		
	Lit; dark	brown	viscous oil.	
Yield:	Observed	28%	Lit	30%
M. P.	Observed	240°C	Lit	240°C

Step 3:

Preparation of 3- Ethyl - 2 - meth. ylbenzot hiazoliumidide.

3-Ethyl-2-methylbenzothiazolium iodide was prepared by quaternisation of 2-methyl benzothiazole using the method of Johnson and Adams (1921) with slight procedural alteration made by Ansari et. al., (1994-1995). For quarternisation benzothiazole base was mixed with ethyl iodide (1:1.5M) in a pressure bottle and refluxed for 30-36 hours on water-bath. The resulting solid masses were recrystalised from hot water or aqueous ethanol as per requirement with a little bone charcoal.



2-methyl benzothiazole — Ethyl Iodide — 3-Ethyl-2-methyl benzothiazolium idodie

Molecular formula: $C_{10}H_{12}NSI$

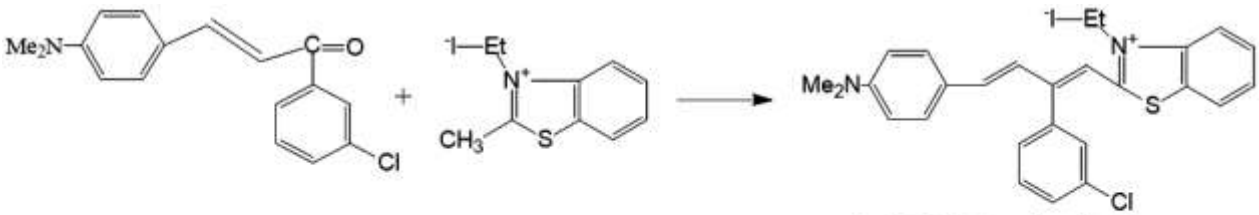
Physical data:

Nature:	Obs	brown plates	Lit	Colourless plates	
	Yield	Observed:	70%	Lit:	72%
	M.P.	Observed:	217°C	Lit:	219°C

Step 4:

Preparation of **2-(2-3"-chlorophenyl-4-4'-dimethylaminophenyl-1, 3-butadienyl)-3-ethylbenzothiazolium iodide.**

3-Ethyl-2-methylbenzothiazolium iodide (0.319 g) and 3'- chlorophenyl-4-dimethylaminostyryl ketone (0.285g) were dissolved in absolute alcohol together with basic catalyst piperidine 3 drops. The mixture was refluxed for about 6 hrs connected with $CaCl_2$ guard tube and subjected to overnight cooling. The dye obtained was recrestallised from methanol as dark brown sandy crystals.



3 - Chlorophenyl-4-dimethyl-aminostyryl ketone — 3-Ethyl-2-methyl benzothiazolium idodie — 2-(2-3"-Chlorophenyl-4-4-dimethylaminophenyl-1,3-butadienyl)-3-ethyl-benzothiazolium iodide

Molecular formula: $C_{27}H_2GNSCII$

Physical data:

Elements	Amount in Percentage (%)		
	Requires	Found	
Nitrogen	4.89	4.87	Yield – 29%
Chlorine + Iodine	28.38	28.36	M.P. – 205.8°C

I.R. Spectrum of 2-(2-3"-chlorophenyl-4-4'-dimethylaminophenyl-1, 3-butadienyl)-3-ethylbenzothiazolium iodide in KBr.

Absorption bands (cm^{-1})	Assignments.
2980-3050	C-H(Str.) (Aromatic)
2410-2450	C=N (Str.) Quaternary – N)
1400-1660	C=C(Str.) (Aromatic and conjugation) With C=N, Plane vibration)
720-880	C – H (Def.) (Aromatic nucleus)
500-750	C – X (Str.) X= -Cl

REFERENCES

[1] James TH, editor. The theory of the photographic process. 4th ed. New York: Macmillan, (1977).

[2] Tyutyulkov N, Fabian J, Mehlhorn A, Dietz F, Tadjer A. Polymethine dyes – structure and properties. Sofia: St. Kliment Ohridski University Press, (1991).

[3] Tolbert LM, Zhao X. Beyond the cyanine limit: Peierls distortion and symmetry collapse in a polymethine dye. J Am Chem Soc.; 119:3253(1997).

[4] Hunger K, editor. Industrial dyes, chemistry, properties, applications. Weinheim: Wiley-VCH, (2003).

[5] Fujita S. Organic chemistry in photography. Berlin: Springer, (2004).

[6] Deligeorgiev T, Gadjev N, Kaloyanova S, Lesev N, Vasilev A, Alexiev A. A novel general method for fast and easy preparation of cationic, neutral dimethinehemicyanine and dimethine dyes by uncatalysed Knoevenagel condensation. Color Technol.; 128:417(2012).

[7] Mustroph H, Ernst S, Senns B, Towns AD. Molecular electronic spectroscopy: from often neglected fundamental principles to limitations of state-of-the-art computational methods. Color Technol.; 131:9(2015).

[8] Mustroph H, Reiner K, Senns B. Bond length alternation in unsymmetrical cyanine dyes and its influence on the vibrational structure of their electronic absorption spectra. Color Technol.; 133:469(2017).

[9] Mustroph H, Towns A. Fine structure in electronic spectra of cyanine dyes: are sub-bands largely determined by a dominant vibration or a collection of singly-excited vibrations? Chem Phys Chem.; 19:1016(2018).

[10] Mustroph H. Cyanine dyes. Phys Sci Rev.; 5. DOI: 10.1515/psr-2020-0145(2020).