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Different methods in the synthesis of mono(Bi)-heterocyclic six membered cyanine dyes: a review

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ABSTRACT

This paper is reviews of different methods in the synthesis mono(bi)- heterocyclic six membered cyanine dyes. In this paper review detailed synthesis steps were represented via equations. The synthesis covers monomethine cyanine dyes (simple cyanine dyes), dimethine cyanine dyes, trimethine cyanine dyes (carbocyanine dyes), meso-substituted trimethine cyanine dyes, tetramethine cyanine dyes, bis tetramethine cyanine dyes, styryl cyanine dyes (hemi cyanine dyes), bis styryl cyanine dyes (bis hemi cyanine dyes), aza-styryl cyanine dyes (aza-cyanine dyes), bis aza-styryl cyanine dyes (bis aza-cyanine dyes), a cyclic mero cyanine dyes, cyclic mero cyanine dyes and mixed cyanine dyes. In addition, some significant uses, applications and properties of cyanine dyes were given in the introduction section of this paper review. Reviewing some of the different methods in the synthesis of only mono(bi)-heterocyclic six membered cyanine dyes can be considered as a new and/or a novel type of reviewing which have not mentioned in the literature before.

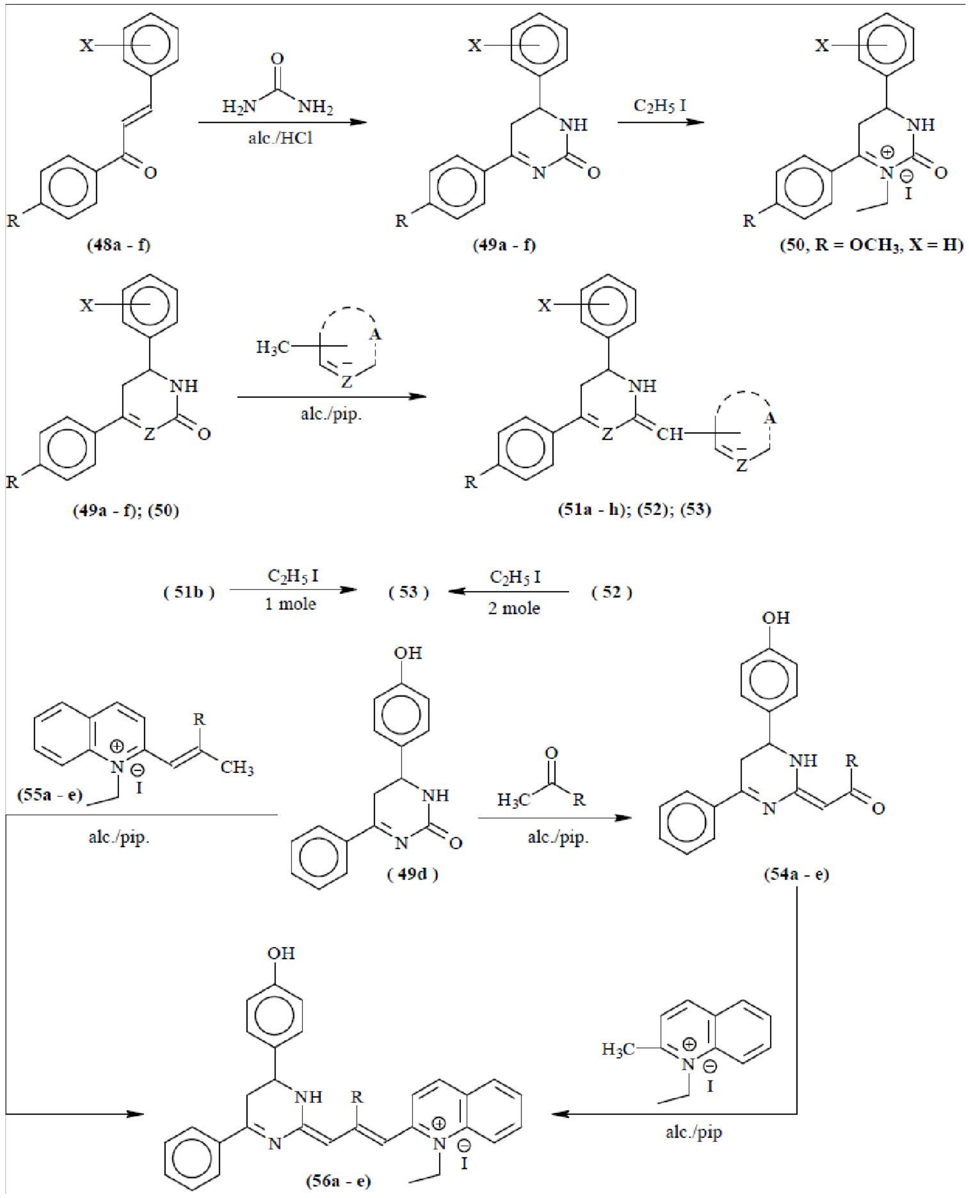
KEYWORDS

Cyanine dyes;
Synthesis;
Six membered cyanine dyes;
Methine cyanine dyes;
Hemi cyanine dyes;
Aza-cyanine dyes;
Mero cyanine dyes.

INTRODUCTION

Functional dyes play an important role in material science. Cyanine dyes [1-10] is one of the most important classes of organic heterocyclic functional dyes which have been studied for over 150 years old and still continue to be of interest in a broad area of science, technology, engineering, pharmacology and medicine. These dyes have tunable wavelengths across the visible spectrum and exhibit high molar extinction coefficients permitting the use of low concentrations. The developments of cyanine dyes have come into limelight both in experimental and theoretical aspects. They present favorable optical properties and have been explored as important organic functional dyes materials in many fields. Such as sensitizers for silver halide emulsion in photographic industry, as data storage materials, sensitizers in solar cells, in laser disks material, in analytical chemistry, in clinical and environmental analysis, sensitizer for photodynamic therapy, diagnostic by fluorescent detection, fluorescent labels in DNA, protein detection and nonlinear optical materials. In addition, this class of dyes possess versatile applications in inorganic large bandgab semiconductor materials, light harvesting systems of photosynthesis and photovoltaics, photoreflactive materials and as antitumor agents [11].

Cyanine dyes have unusual optical properties, and high fluorescent quantum yield of their aggregates, strongly absorbing in the visible region, highly fluorescent in monomers and aggregates both in solution and



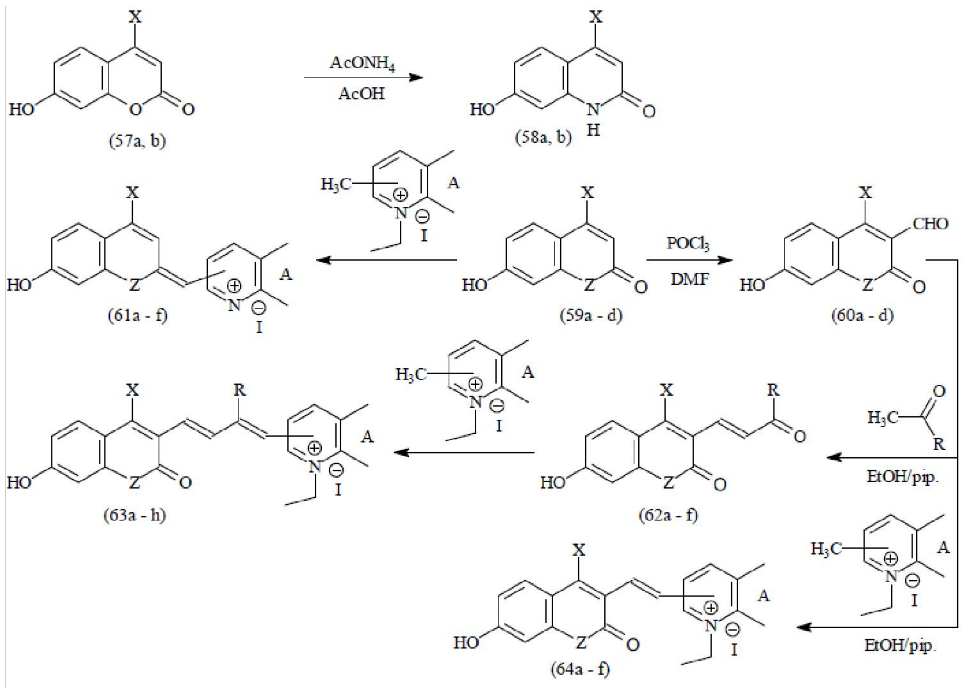
Scheme 1

organized media. The two types of aggregates that are known for cyanine dyes are H-aggregate recognized by their blue shifted broad absorption band and J-aggregate that exhibit a sharp red shifted absorbance with respect to the monomer absorption. The ease of formation of aggregates in conjunction with their potential applications in optical devices, photosensitizers, and fluorescent probes for bio-membrane fluidity made cyanine dyes particularly interesting [12]. The number of scientific publication in the synthesis, characterizations and applications of cyanine dyes in the recent years [13-21] is an strong evidence for the vital position of cyanine dyes in the chemistry of dyes and pigments, and for its continuous importance in modern sciences and advanced technology.

DIFFERENT METHODS IN THE SYNTHESIS OF MONO(BI)-HETEROCYCLIC SIX MEMBERED CYANINE DYES

Shindy, et al. [22] synthesized new photosensitizers unsymmetrical 2[2(4)]-mono- and tri- (substituted tri-) methine cyanine dyes incorporating 1,2,5,6,-tetrahydro-4,6-diaryl pyrimidine (pyrimidinium-1-yl salt)-2-one, Scheme (1).

Substituents in Scheme (1)



Scheme 2

(48a – f); (49a – f): R = OCH_3, X = H (a); R = NO_2, X = H (b); R = Cl, X = H (c); R = H, X =4.OH (d); R = NO_2, X = 4.OH (e); R = H, X = 2.NO_2 (f).

(50): R = OCH_3, X = H.

(51a – h): Z = N, $\bar{Z}$ = $\overset{\oplus}{N}$ $\ominus$ I ; R = OCH_3, X = H, A = 1-ethyl pyridinium-2-yl salt (a),

R = OCH_3, X = H, A = 1-ethyl quinolinium-2-yl salt (b),

R = OCH_3, X = H, A = 1-ethyl pyridinium-4-yl salt (c),

R = NO_2, X = H, A = 1-ethyl quinolinium-2-yl salt (d),

R = Cl, X = H, A = 1-ethyl quinolinium-2-yl salt (e);

R = H, X =4.OH, A = 1-ethyl quinolinium-2-yl salt (f),

R = NO_2, X =4.OH, A = 1-ethyl quinolinium-2-yl salt (g),

R = H, X = 2.NO_2, A = 1-ethyl quinolinium-2-yl salt (h).

(52): Z = = N, R = OCH_3, X = H, A = 2-quinoline.

(53) Z = =, R = OCH_3, X = H, A = 1-ethyl quinolinium-2-yl salt.

(54a – e); (55a – e); (56a – e): R = H (a); CH_3 (b), C_6H_5 (c); C_6H_4-ρ.OCH_3 (d); C_6H_4-ρ.NO_2 (e).

Abd El-Aal, et al. [23] prepared novel monomethine, dimethine and tetramethine cyanine dyes incorporating coumarin and /or quinoline derivatives, Scheme (2).

Substituents in Scheme (2)

(57a, b); (58a, b): X = H (a); CH_3 (b).

(59a – d); (60a – d): X = H, Z = O (a); X = CH_3, Z = O (b); X = H, Z = NH (c); X = CH_3, Z = NH (d).

(61a – f); (64a – f): X = H, Z = O, A = 2H-2-yl salt (a);

X = H, Z = O, A = C_4H_4-2-yl salt (b);

X = H, Z = O, A = 2H-4-yl salt (c);

X = CH_3, Z = O, A = C_4H_4-2-yl salt (d);

X = H, Z = NH, A = C_4H_4-2-yl salt (e);

X = CH_3, Z = NH, A = C_4H_4-2-yl salt (f).

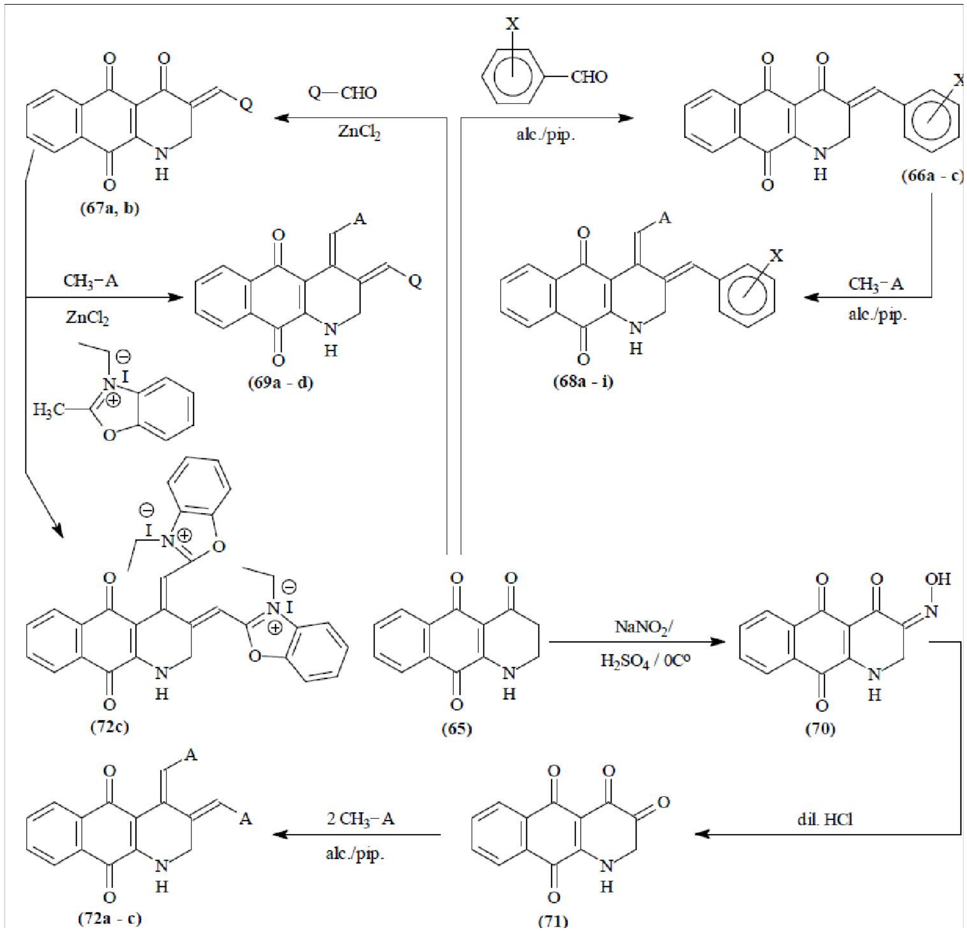
(62a – f): X = H, Z = O, R = H (a); X = H, Z = O, R = CH_3 (b);

X = H, Z = O, R = ph (c); X = CH_3, Z = O, R = H (d);

X = H, Z = NH, R = H (e); X = CH_3, Z = NH, R = H (f).

(63a – h): X = H, Z = O, R = H, A = 1-ethyl pyridine-2-ium salt (a);

X = H, Z = O, R = H, A = 1-quinoline-2-ium salt (b);



Scheme 3

X = H, Z = O, R = H, A = 1-ethyl pyridine-4-ium salt (c);

X = H, Z = O, R = CH_3, A = 1-ethyl quinoline-2-ium salt (d);

X = H, Z = O, R = ph, A = 1-ethyl quinoline-2-ium salt (e);

X = H, Z = NH, R = H, A = 1-ethyl quinoline-2-ium salt (f);

X = CH_3, Z = O, R = H, A = 1-ethyl quinoline-2-ium salt (g);

X = CH_3, Z = NH, R = H, A = 1-ethyl quinoline-2-ium salt (h).

El-Maghraby, et al.[24] synthesized new asymmetrical and symmetrical styryl cyanine dyes using 4,5,10-trioxo-1,2,3,4,5,10-hexahydro-benz [g]quinoline as starting material, Scheme (3).

Substituents in Scheme (3)

(66a – c): X = H (a); ρ.OCH_3 (b); ρ.NO_2 (c).

(67a, b): Q = 1-ethyl quinolinium-2-yl salt (a); 3-ethyl benzoxazolium-2-yl salt (b).

(68a – i): X = H, A = 1-ethyl pyridinium-2-yl salt (a);

X = H, A = 1-ethyl quinolinium-2-yl salt (b);

X = H, A = 3-ethyl benzoxazolium-2-yl salt (c);

X =ρ.OCH_3, A = 1-ethyl pyridinium-2-yl salt (d);

X =ρ.OCH_3, A = 1-ethyl qunolinium-2-yl salt (e);

X =ρ.OCH_3, A = 3-ethyl benzoxazolium-2-yl salt (f);

X =ρ.NO_2, A = 1-ethyl pyridinium-2-yl salt (g);

X =ρ.NO_2, A = 1-ethyl quinolinium-2-yl salt (h);

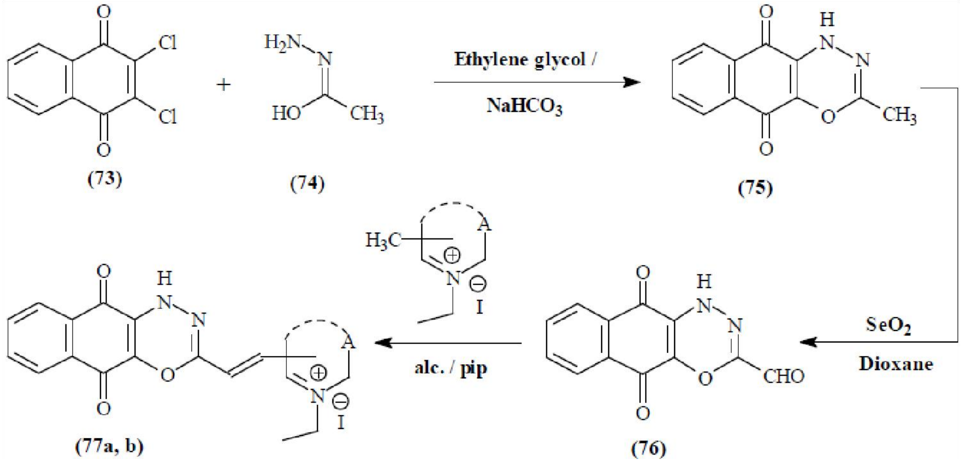
X =ρ.NO_2, A = 3-ethyl benzoxazolium-2-yl salt (i).

(69a – d): Q = 1-ethyl quinolinium-2-yl salt, A = 1-ethyl pyridinium-2-yl salt (a);

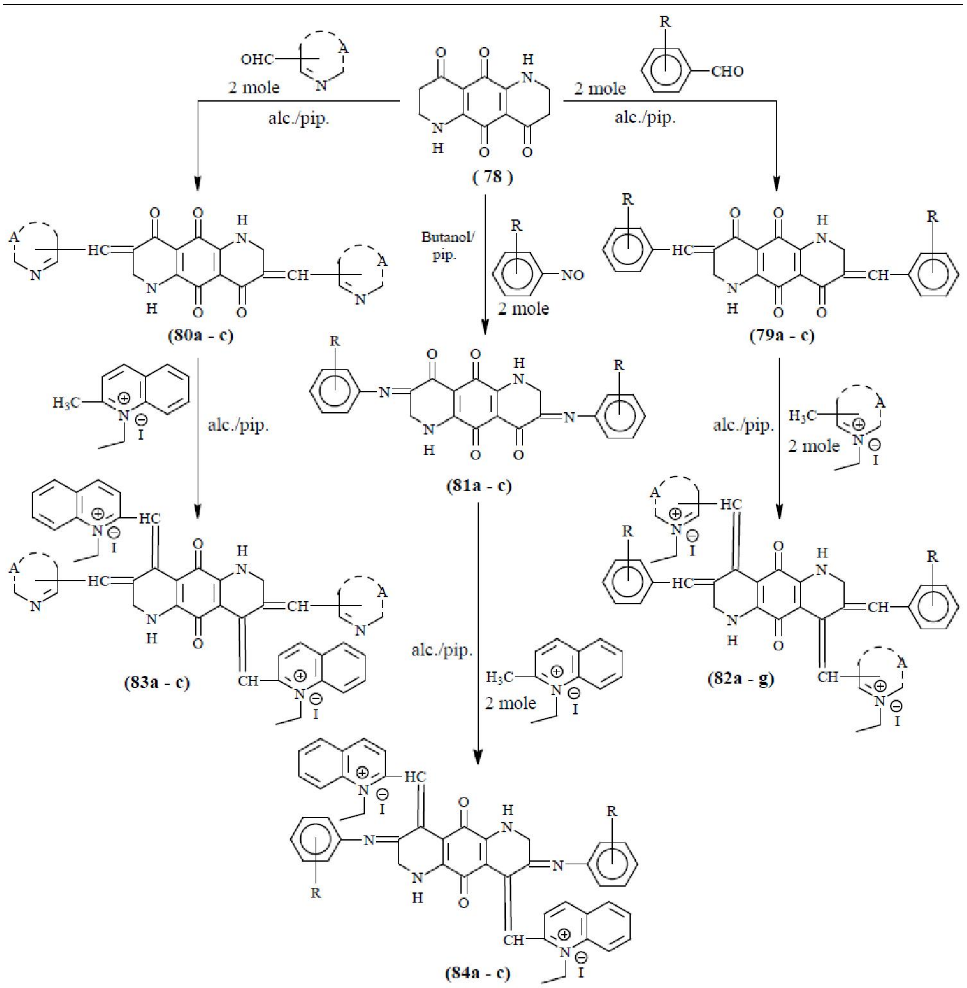
Q = 1-ethyl quinolinium-2-yl salt, A = 3-ethyl benzoxazolium-2-yl salt (b);

Q = 3-ethyl benzoxazolium-2-yl salt, A = 1-ethyl pyridinium-2-yl salt (c);

Q = 3-ethyl benzoxazolium-2-yl salt, A = 1-ethyl



Scheme 4



Scheme 5

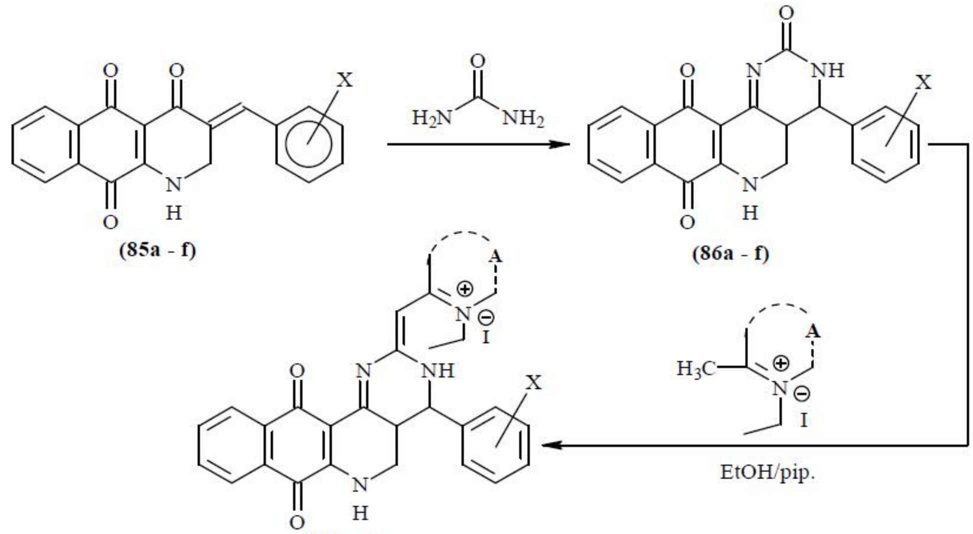
quinolinium-2-yl salt (d).

(72a – c): A = 1-ethyl pyridinium-2-yl salt (a); A = 1-ethyl quinolinium-2-yl salt (b); A = 3-ethyl benzoxazolium-2-yl salt (c).

Koraiem, et al.[25] synthesized new photosensitizers dimethine cyanine dyes having oxadiazine ring, Scheme (4).

Substituents in Scheme (4)

(77a, b): A = 1-ethyl pyridinium-2-yl salt (a); 1-



Scheme 6

ethyl quinolinium-2-yl salt (b).

Shindy, et al.[26] synthesized new symmetrical bis (styryl, tetramethine, aza-styryl) cyanine dyes derived from 4,9-dioxopiperidino[2,3-g]-1,2,3,4,6,7,8,9-octahydroquinolinoquinone, Scheme (5).

Substituents in Scheme (5)

(79a – e): R = H (a); 4-OCH_3 (b); 4-OH (c); 2-OH (d); 4-NO_2 (e).

(80a – c); (83a – c): A = 2-formyl pyridine (a); 2-formyl quinoline (b); 4-formyl pyridine (c).

(81a – c); (84a – c): R = 4-OH (a); 2-OH, 5, 6-benzo-substituent (b); 2-OH, 3, 4-benzo-substituent (c).

(82a – g): A = 1-ethyl quinolinium-2-yl salt, R = H (a);

A = 1-ethyl quinolinium-2-yl salt, R = 4-OCH_3 (b);

A = 1-ethyl quinolinium-2-yl salt, R = 4-OH (c);

A = 1-ethyl quinolinium-2-yl salt, R = 2.OH (d);

A = 1-ethyl quinolinium-2-yl salt, R = 4-NO_2 (e);

A = 1-ethyl pyridinium-2-yl salt, R = 4-NO_2 (f);

A = 1-ethyl pyridinium-4-yl salt, R = 4-NO_2 (g).

El-Maghraby, et al. [27] prepared new asymmetrical monomethine cyanine dyes incorporations pyrimidine nucleus, Scheme (6).

Substituents in Scheme (6)

(85a – f); (86a – f): X = H (a); ρ.OCH_3 (b); ρ.OH (c); ρ.$N(CH_3)_2$ (d); ρ.NO_2 (e); 2.OH (f).

(87a – f): A = 1-ethyl pyridinium-2-yl salt, 1-ethyl quinolinium-2-yl salt, and 3-ethyl benzoxazolium-2-yl salt.

X = H (a); ρ.OCH_3 (b); ρ.OH (c); ρ.$N(CH_3)_2$ (d); ρ.NO_2 (e); 2.OH (f).

Abd El-Aal, R.M. [28] synthesized a series of monomethine cyanine dyes containing oxazine, thiazine and pyrazine nucleus, Scheme (7).

Substituents in Scheme (7)

(91a – c); (93a – c); (94a – c): A = H-2-yl salt (a); C_6H_4-2-yl salt (b); H-4-yl salt (c).

(95a – c); (96a – c); (97a – c); (98a – c): R = H (a); NO_2 (b); OCH_3 (c).

(99a, b): X = NH (a); S (b).

(100a – e): R = H, X = O (a); R = OCH_3, X = O (b); R = NO_2, X = O (c); R = NO_2, X = NH (d); R = NO_2, X = S (e).

Koraiem et al. synthesized a series of monomethine cyanine dyes and trimethine cyanine dyes containing oxadiazine nucleus [29, 30], Scheme (8).

Substituents in Scheme (8)

(103a-c): A = 1-methyl pyridinium-4-yl salt (a),

A = 1-methyl quinolinium-4-yl salt (b),

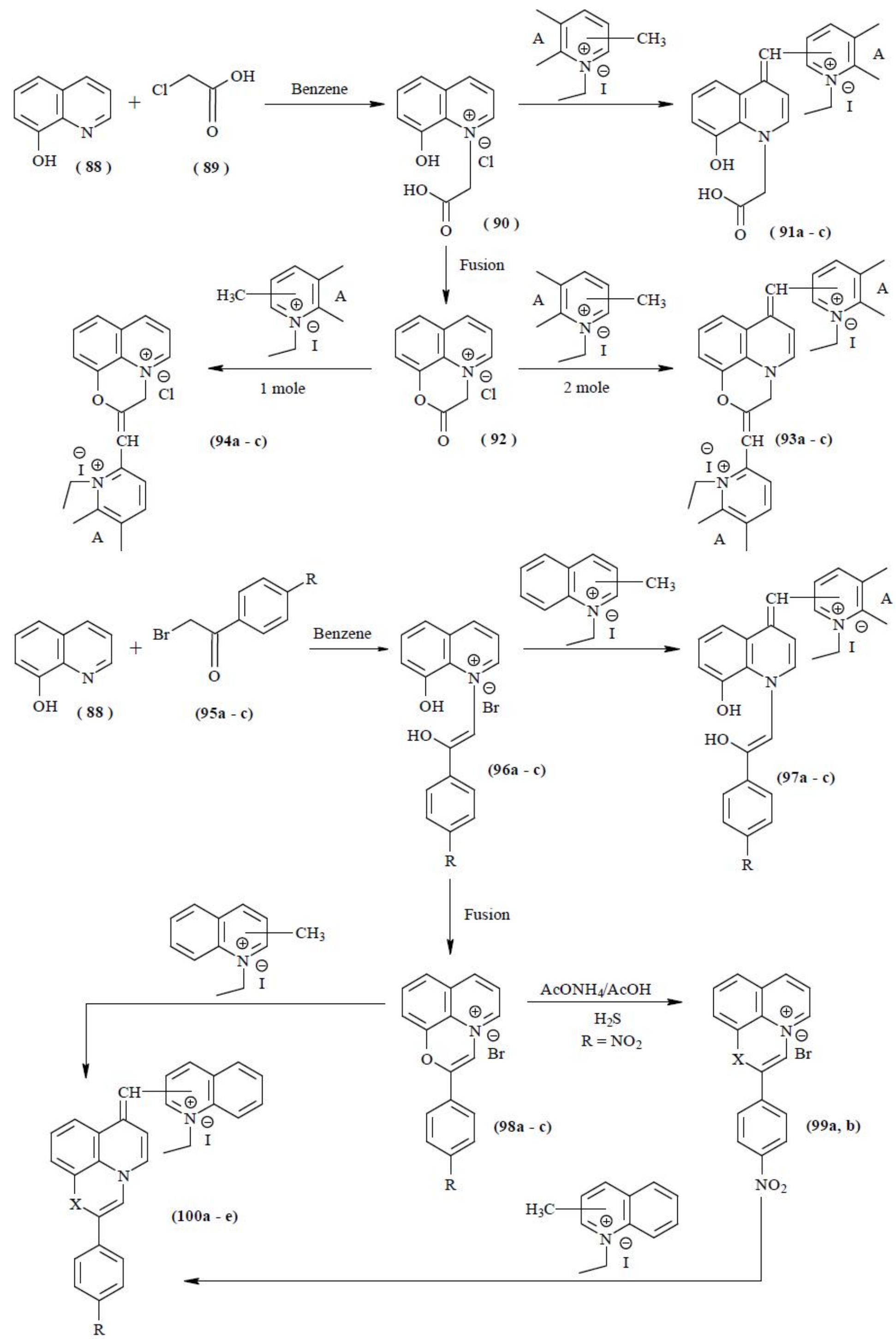
A = 2-methyl isoquinolinium-1-yl salt (c).

(105a-c): A = 1-methyl pyridinium-2-yl salt (a),

A = 1-methyl quinolinium-2-yl salt (b),

A = 1-methyl pyridinium-4-yl salt (c).

Shindy et al. prepared a number of monomethine cyanine dyes, trimethine cyanine dyes and meso-sub-



Scheme 7

stituted trimethine cyanine dyes having 1,3,4-oxadiazine nucleus [31], Scheme (9).

Substituents in Scheme (9)

(107a, b); (108a, b); (109a, b)(111a,b) & (113a, b): X = H (a), X = Ph (b).

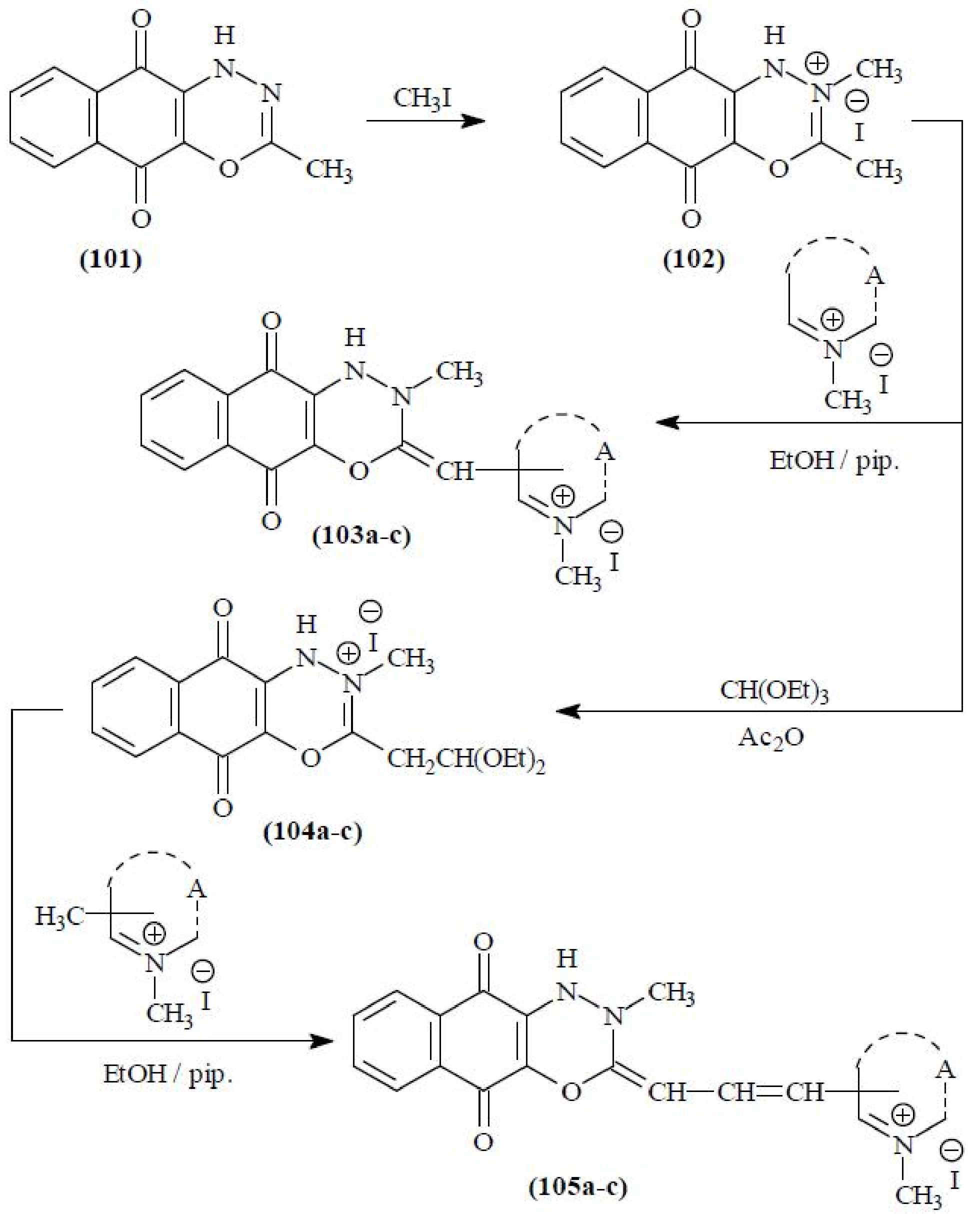
(110a – d): X = H, A = 1-ethyl pyridinium-4-yl salt (a),

X = H, A = 1-ethyl quinolinium-4-yl salt (b),

X = H, A = 2-ethyl isoquinolinium-1-yl salt (c),

X = Ph, A = 1-ethyl quinolinium-4-yl salt (d).

(114a – e): X = H, R = (H) (a), X=Ph, R= H (b), X=H, R= $-CH_3$ (c), X=H, R= $-C_6H_5$ (d) X=Ph, R= -



Scheme 8

CH_3 (e).

(112a-d), (l15a-d): X=H, A= l-ethyl pyridinium-2-yl salt (a), X=H, A= 1-ethyl quinolinium-2-yl salt (b), X=H, A= 1-ethyl pyridinium-4-yl salt (c), X=Ph, A= 1-ethyl quinolinium-2-yl salt (d).

(116a-c): X=H, R= $-CH_3$ (a), X=H, R= $-C_6H_5$ (b), X=Ph, R= $-CH_3$ (c).

A series of styryl, aza-styryl, acyclic mero, cyclic mero and mixed cyanine dyes with 1,3,4-oxadiazine nucleus were synthesized by Shindy, et al. [32], Scheme (10).

Substituents in Scheme (10)

(117a – d): X = Ph, Y = (a); X = H, Y = (b); X = Ph, Y = N (c);

X = H, Y = N (d).

(118a, b): X = Ph (a); H (b).

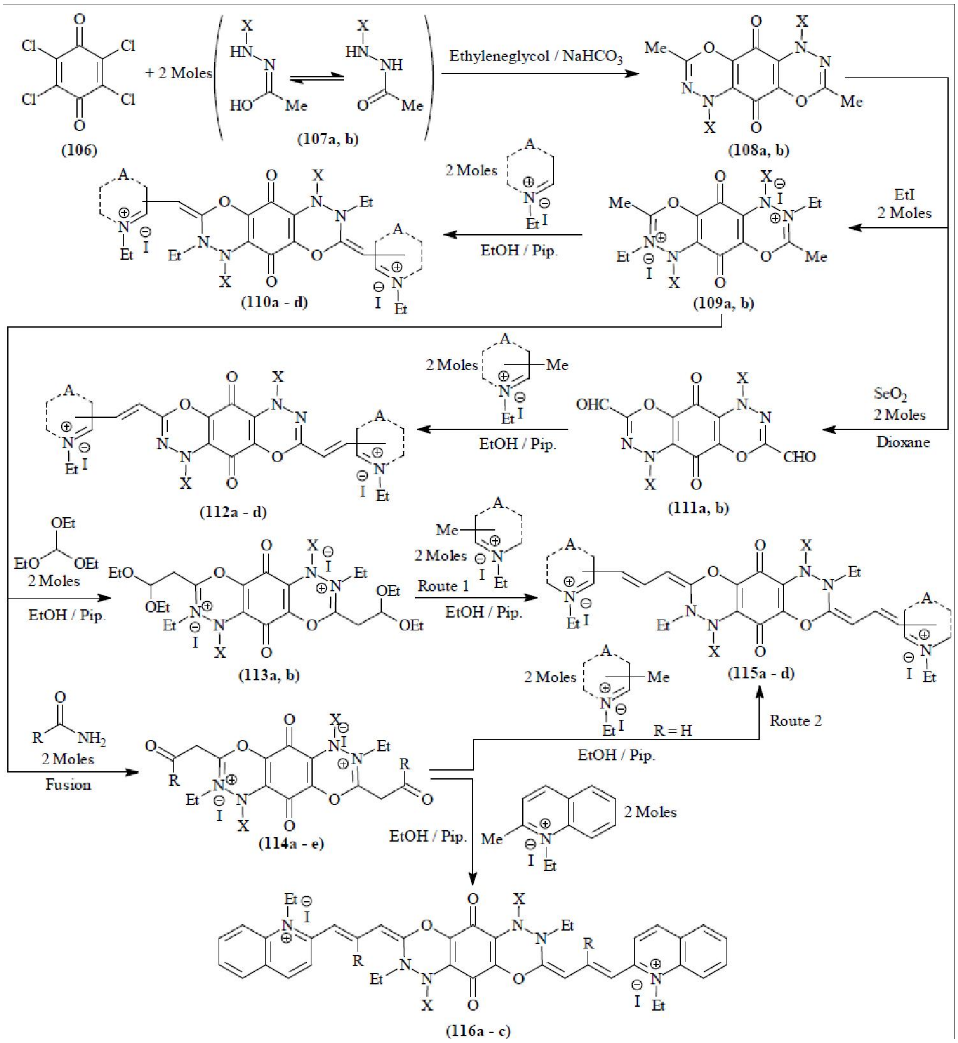
(119a – g): X = Ph, Y = H (a); X = Ph, Y = OH (b); X = Ph, Y = OMe (c);

X = Ph, Y = NMe_2 (d); X = Ph, Y = NO_2 (e); X = Ph, Y = Cl (f);

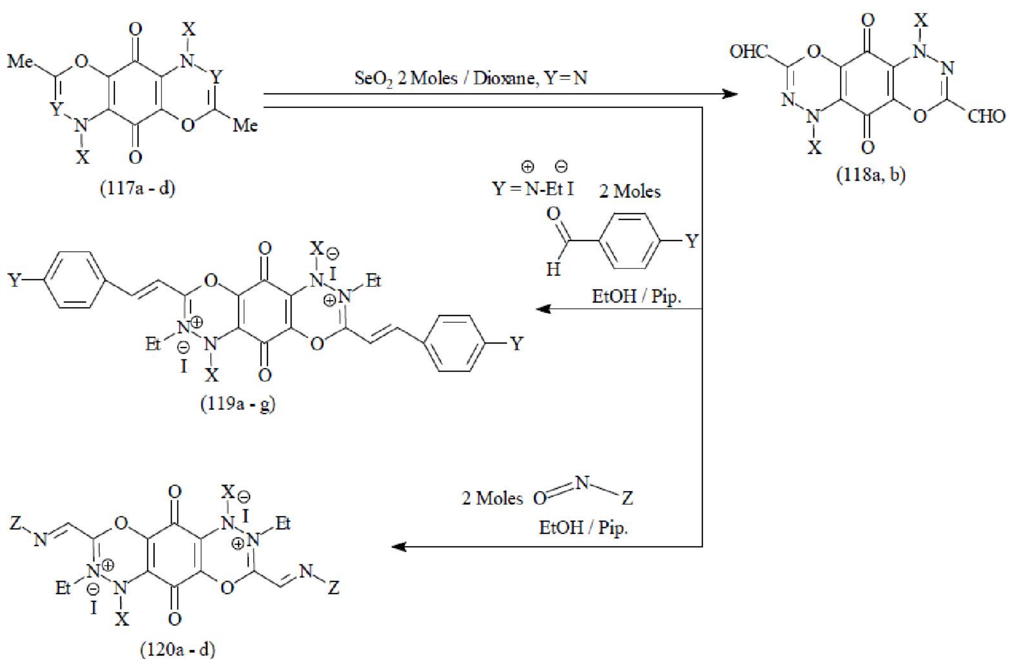
X = Ph, Y = NMe_2 (g).

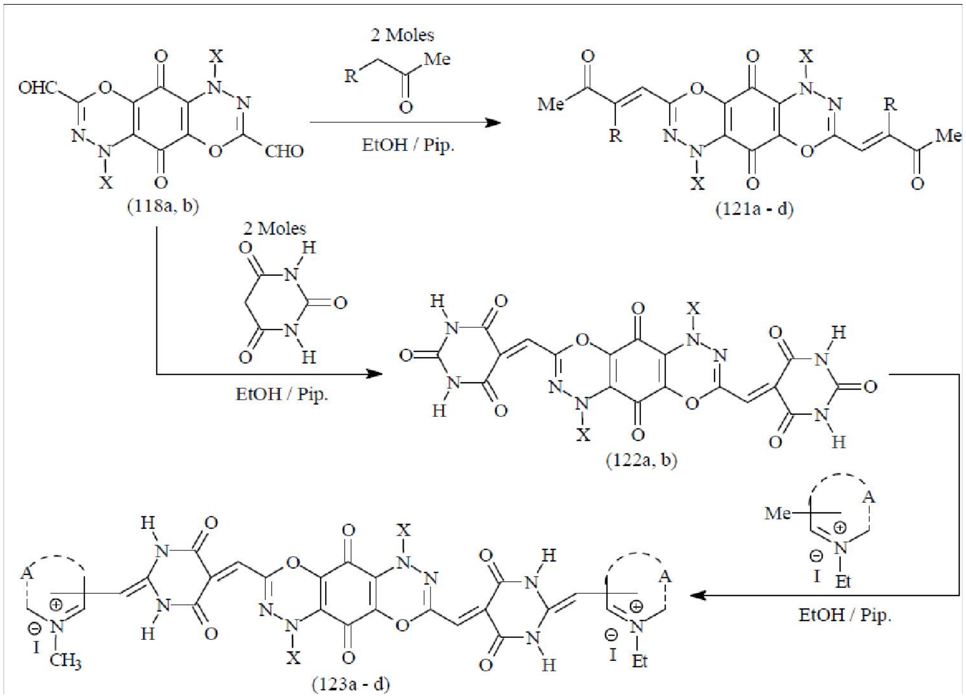
(120a – d): X = Ph, Z = 4-phenol (a); X = Ph, Z = 1(2-naphthol) (b); X = Ph, Z = 2(1-naphthol) (c); X = H, Z = 1(2-naphthol) (d).

(121a – d): X = Ph, R = H (a); X = Ph, R = COMe



Scheme 9





Scheme 10

(b); X = Ph, R = COOEt (c); X = H, R = COMe (d).

(122a, b): X = Ph (a); H (b).

(123a – d): X = Ph, A = 1-ethyl-pyridinium-2-yl salt (a);

X = Ph, A = 1-ethyl-quinolinium-2-yl salt (b);

X = Ph, A = 1-ethyl-pyridinium-4-yl salt (c);

X = H, A = 1-ethyl-quinolinium-2-yl salt (d).

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