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SYNTHESIS OF DIFFERENT CLASSES OF SIX MEMBERED HETEROCYCLIC CYANINE DYES

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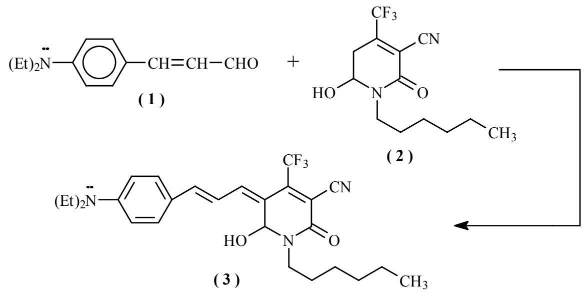
In this paper review, synthesis of different classes of some six membered heterocyclic cyanine dyes have been reviewed. Detailed synthesis steps were represented via equations. The synthesis covers styryl cyanine dyes (hemi cyanine dyes), bis styryl cyanine dyes (bis hemi cyanine dyes), cyclic mero cyanine dyes, trimethine cyanine dyes (carbocyanine dyes), pentamethine cyanine dyes (dicarbocyanine dyes), undecamethine cyanine dyes (pentacarbocyanine dyes), meso substituted methine cyanine dyes, bridged cyanine dyes and zwitterionic bridged cyanine dyes. In addition, some important uses, application and properties of cyanine dyes were given in the introduction section of this review paper. Reviewing some synthesis of different classes of only six membered heterocyclic cyanine dyes can be considered as a new and/or novel idea of reviewing which have not mentioned in the literature before.



INTRODUCTION

Cyanine dyes[1] are classes of organic heterocyclic functional dyes which have long held the interest of the scientific community. This is because their multi purposes applications in diverse areas of science, technology and engineering. Such as photographic sensitizers[2] in photographic industry, as non linear optical materials[3] and more recently as fluorescent probes for biomolecular labeling.[2-6] in particular, their use in genetic analysis, DNA sequencing,[7,8] in vivo imaging[9] and proteomics[10] is growing. The appeal to this class of fluorophores derives from their straightforward synthesis,[11,12] their high near-infrared (NIR) absorption and emission wavelength and moderate fluorescence quantum yields. Therefore, many different polymethine cyanine dyes have been synthesized in the last decade.[13]

The first cyanine dyes was discovered in 1856 by C. H. Greville Williams. Later in 1873, H. W. Vogel began to use cyanine dyes in photography. Since then, research on cyanine dyes developed rapidly due to their extra sensitizing power on silver halide in the region of spectra from visible to near infrared (IR) in photography. In the early days, efforts mainly focused on the synthesis of new cyanine dyes, the elucidation of their chemical structures and the examination of their photographic properties.[14] Cyanine dyes have relatively good stability, high molar absorption extinction coefficients (molar absorbitivity), medium fluorescent intensity, narrow spectrum width with the ability to form H- or J-aggregates. The maximum absorption wavelength of cyanine dyes can be tuned precisely from UV to near-IR by chemical structure modification. With these unique photophysical and photochemical properties, cyanine dyes are recently being used in many applications such as optical data storage, dye laser, photorefractive materials and photodynamic therapy.[14]

The large numerous number of scientific publications in the synthesis, characterization and applications of cyanine dyes chemistry in the present time[15-25] is strong evidence for the continuous

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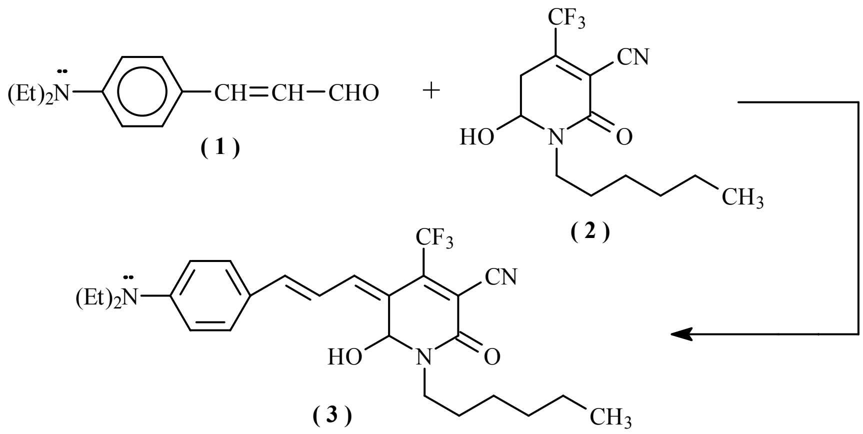
importance and positive future of these dyes in modern sciences and advanced technologies.

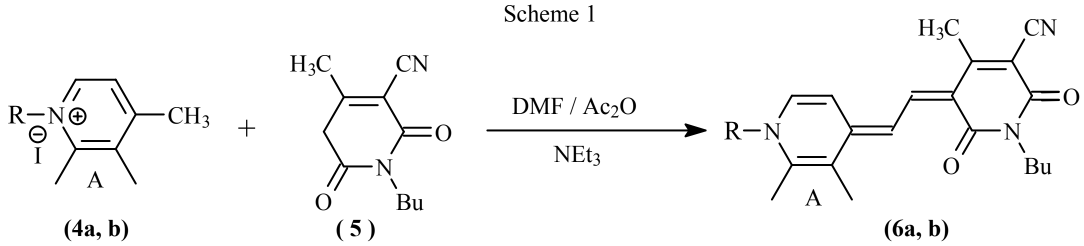
SYNTHESIS OF DIFFERENT CLASSES OF SIX MEMBERED HETEROCYCLIC CYANINE DYES:

Grund *et al.*[26] synthesized new styryl cyanine dye having pyridinone nucleus by condensation of ρ-(diethylamino)cinnamaldehyde with 3-cyano-1-hexyl-6-hydroxy-4-trifluoromethyl-2-pyridinone, Scheme 1.

New merocyanine dyes were synthesized by Frank Würthner via interaction of 1,4-dimethyl pyridinium iodide quaternary salt and/or 1-ethyl-4-methyl quinolinium iodide quaternary salt with 1,2,5,6-tetrahydro-2,6-dioxo-3-pyridine carbonitriles.[27] The reaction proceeded via formylation condensation system of DMF in acetic anhydride and subsequent rearrangement, Scheme 2.



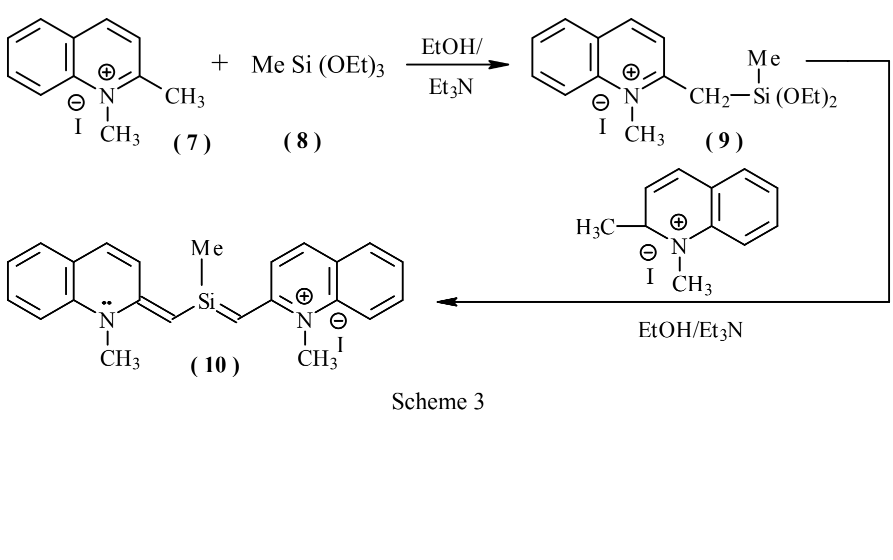
Scheme 1



Scheme 2

Substituents in Scheme 2:
(4a, b); (6a,b): R = CH_3, A = 2H (a); R = CH_3CH_2, A = C_4H_4 (b).

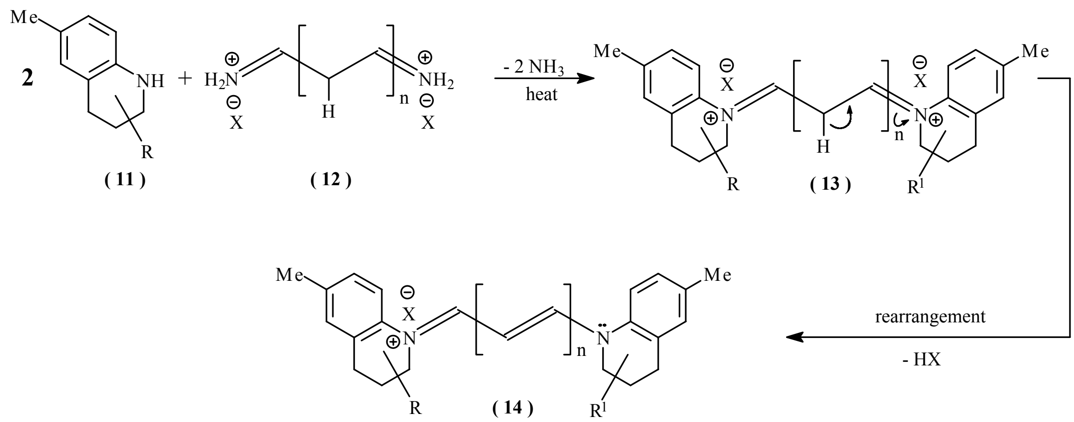
Zhang[28] prepared new silicon heterocyclic polymethine cyanine dyes for photographic sensitizers via interaction of 1,2-dimethyl quinolinium iodide salt with $MeSi(OEt)_3$ under basic conditions, Scheme 3.



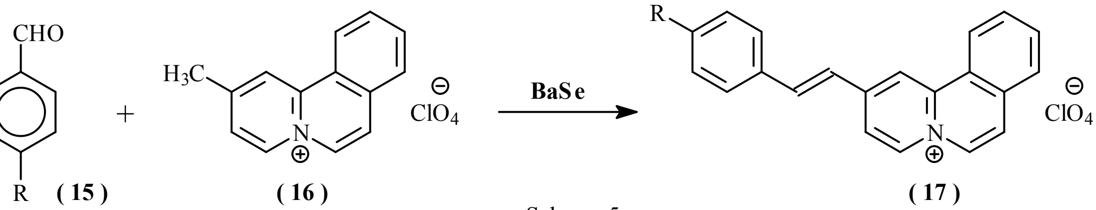
Scheme 3

Starting with 1,2,3,4-tetrahydro-3, 6-dimethylquinoline, Reichardt, *et al.*[29] have synthesized new symmetrical and unsymmetrical carbocyanine dyes including tri- and penta-methines (14, R = 2-Me, R^1 = H; R = 3-Me, R^1 = H; R = 3-Me, R^1 = 3-Me; R = 2-Me, R^1 = 3-Me; n = 1, 2; X = ClO_4, Br), Scheme 4.

Arai *et al.*[30] synthesized new styryl cyanine dyes having a benzo[a] quinolizinium ring by the base catalyzed aldol type condensation of 2-methyl-benzo[a] quinolizinium perchlorate with substituted benzaldehyde derivatives, Scheme 5.



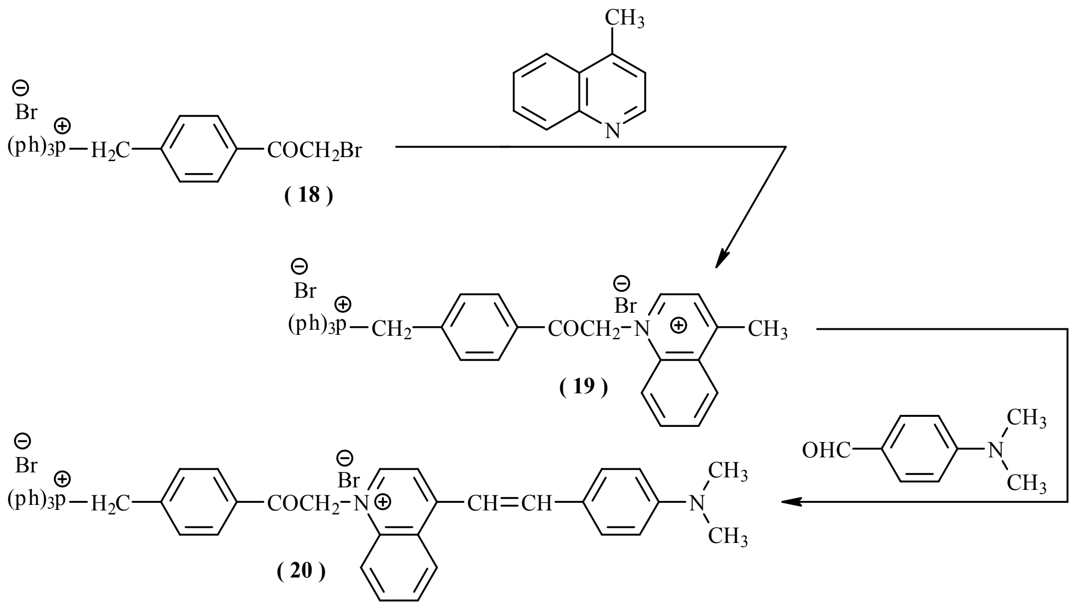
Scheme 4



Scheme 5

Substituents in Scheme 5:
(15, 17): R = H, Me, OH, OMe, NMe_2, NO_2, Br, -CH=CH_2.

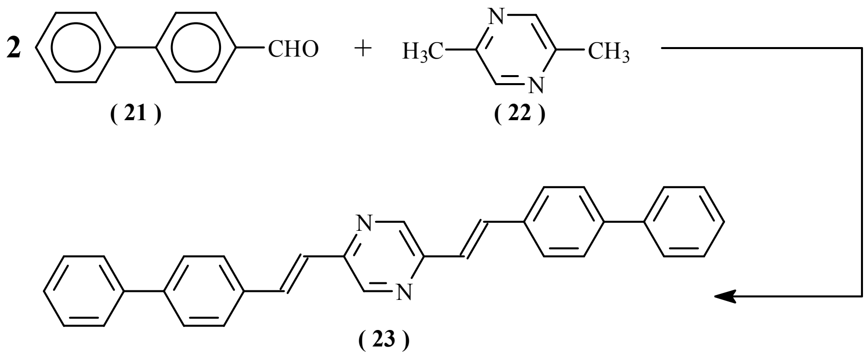
Yagodinets *et al.*[31] synthesized new phosphorus-containing quinostyryl cyanine dye via alkylation of 4-methylquinoline by bromoacetophenone-ρ-triphenylphosphonium bromide to give nitrogen substituted methylquinolinium salt and further reaction with ρ-dimethylaminobenzaldehyde, Scheme 6.



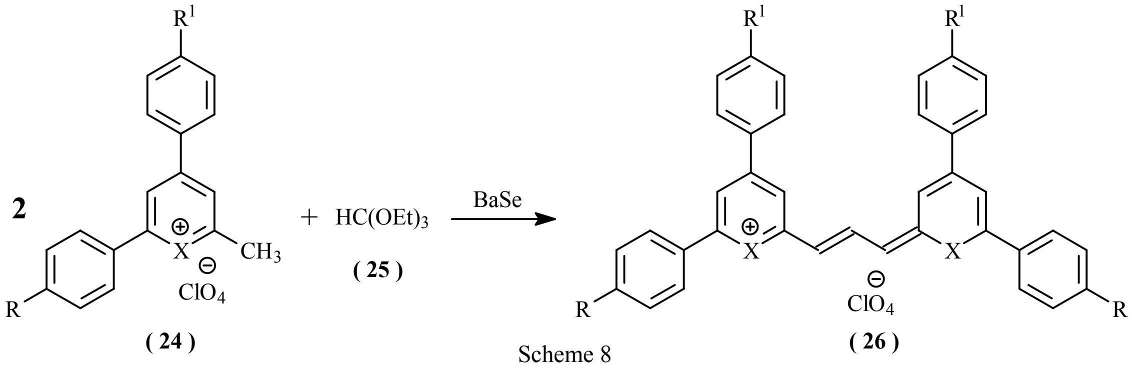
Scheme 6

Hasegawa *et al.*[32] synthesized bis styryl cyanine dye having pyrazine ring by condensation of ρ-phenylbenzaldehyde and 2, 5-dimethylpyrazine, Scheme 7.

Gavrilyuk *et al.*[33] synthesized new trimethine cyanine dyes containing pyrylium, thiopyrylium and pyridinium moeites via interaction of 2,4-diaryl-6-methylpyrylium or thiopyrylum salts with $HC(OEt)_3$. Substituting the oxygen atom in pyrylium dye by N-Me to give pyridinium dye is carried out by the reaction with $MeNH_2$, Scheme 8.



Scheme 7



Scheme 8

Substituents in Scheme 8:
(24, 26): R, R^1 = H, OMe; X = O, S, N-Me

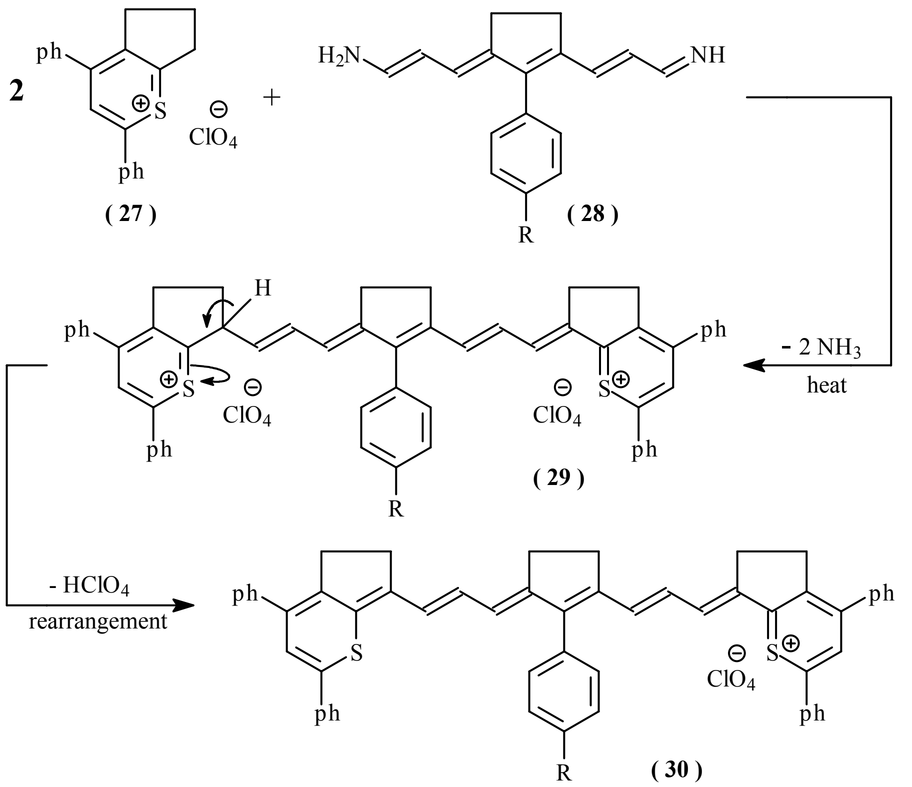
Kudinova *et al.*[34] synthesized new pentacarbocyanine dyes having thiopyrylium nucleus by the condensation of 6,7-dihydro-2,4-diphenyl-5H-cyclopenta[b]thiopyrylium perchlorate with the appropriate dianil derivatives, Scheme 9.

Substituents in Scheme 9:
(28, 29, 30): R = H, NMe_2.

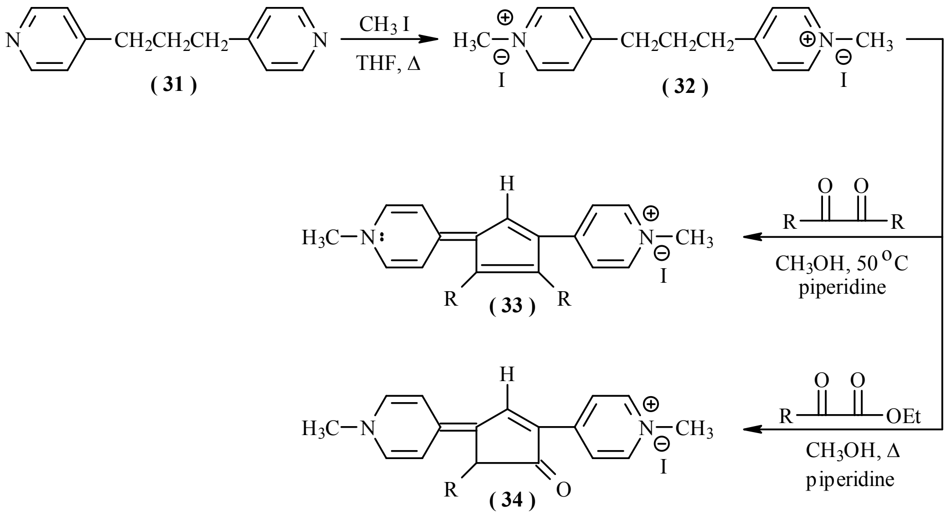
Katritzky *et al.*[35] synthesized novel classes of bridged cyanine dyes containing pyridine nucleus via quaternization of 1,3-di(4-pyridyl) propane to give 1,3-bis(N-methyl-4-pyridyl) propane diiodide salts and subsequent condensing with diverse α-diketones and α-ketoesters, Scheme 10.

Substituents in Scheme 10:
(33): R = ph (a); CH_3 (b); -CH_2CH_2- (c); 2-pyridyl (d); 2-furyl (e); m.Cl-C_6H_4 (f).
(34): R = ph (a); CH_3 (b).

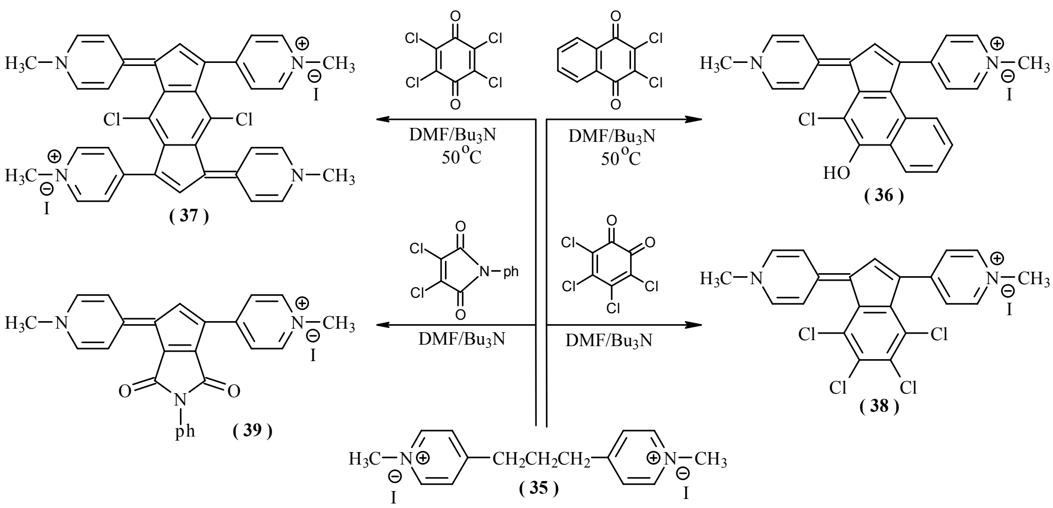
New fused ring bridged pyridyl cyanine dyes were synthesized by Katritzky *et al.*[36] via the reaction of 1,3-bis(N-methyl-4-pyridyl)-propane diiodide salts with 2,3-dichloro-1,4-naphthoquinone, tetrachloro-1,2- and –1,4-benzoquinone, 3,4-dichloro-N-phenyl-maleimide, 2,3-dichloroquinoxaline and phenanthrenquinone in dimethyl-formamide at 50 °C in presence of tributylamine, Scheme 11.



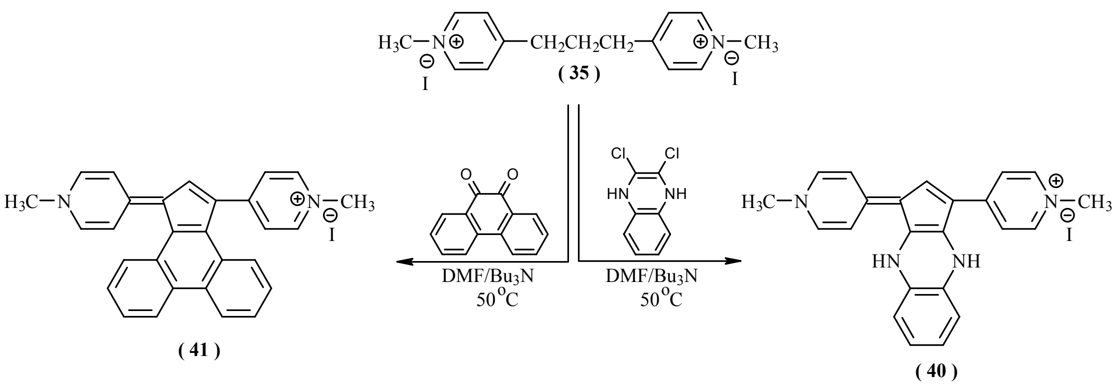
Scheme 9



Scheme 10

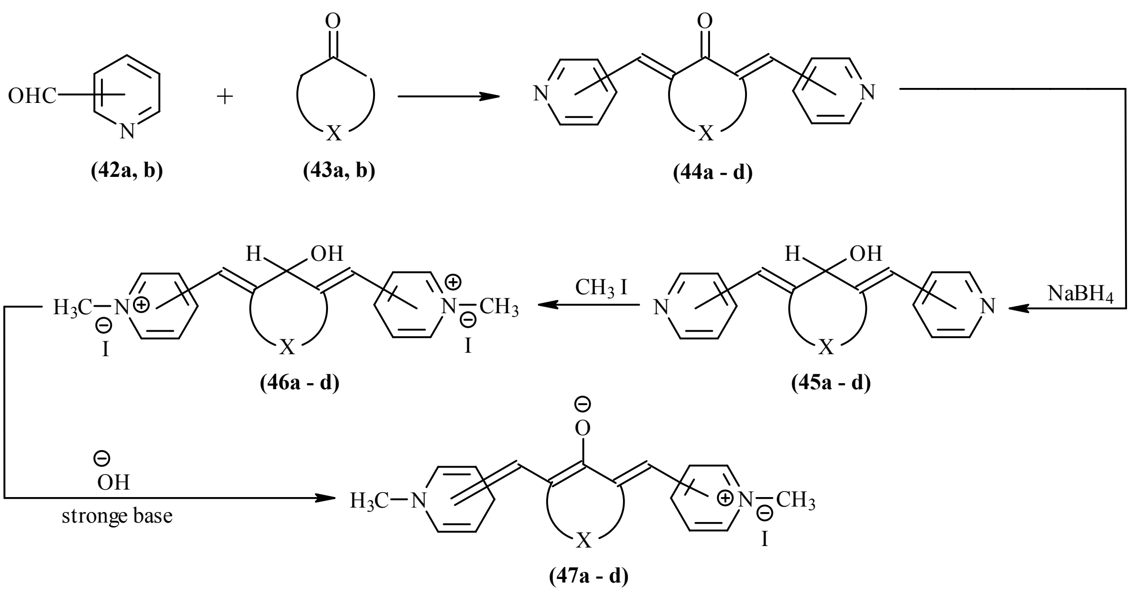


Scheme 11



Scheme 11 continued

Katritzky *et al.*[37] prepared new classes of pyridyl zwitterionic bridged cyanine dyes by treatment of 2, $\bar{2}$-bis (N-methyl-pyridino-4(2)-methylidene) cyclo-alkanols with strong base, Scheme 12.



Scheme 12

Substituents in Scheme 12:
(42a, b): 2-formyl pyridine (a); 4-formyl pyridine (b).
(43a, b): X = $(CH_2)_2$ (a); $(CH_2)_3$ (b).
(44a – d); (45a – d); (46a – d); (47a – d): 4-pyridyl, X = $(CH_2)_2$ (a);
4-pyridyl, X = $(CH_2)_3$ (b);
2-pyridyl, X = $(CH_2)_2$ (c);
2-pyridyl, X = $(CH_2)_3$ (d).

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