Synthesis and Visible Spectral Behaviour of Some New Photosensitizers: Monomethine, Dimethine, Trimethine, Styryl and Mixed Cyanine Dyes

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Hassan A. Shindy

Department of Chemistry, Aswan Faculty of Science, Aswan, Egypt

The new photosensitizers, monomethine, dimethine, trimethine, styryl and mixed cyanine dyes incorporating pyrazolo/oxazole(thiazole) nuclei are prepared; the visible absorption spectra for all the synthesized cyanines were examined in 95% ethanol; structural confirmation is carried out by elemental analysis, IR and ^{1}H NMR spectroscopy.

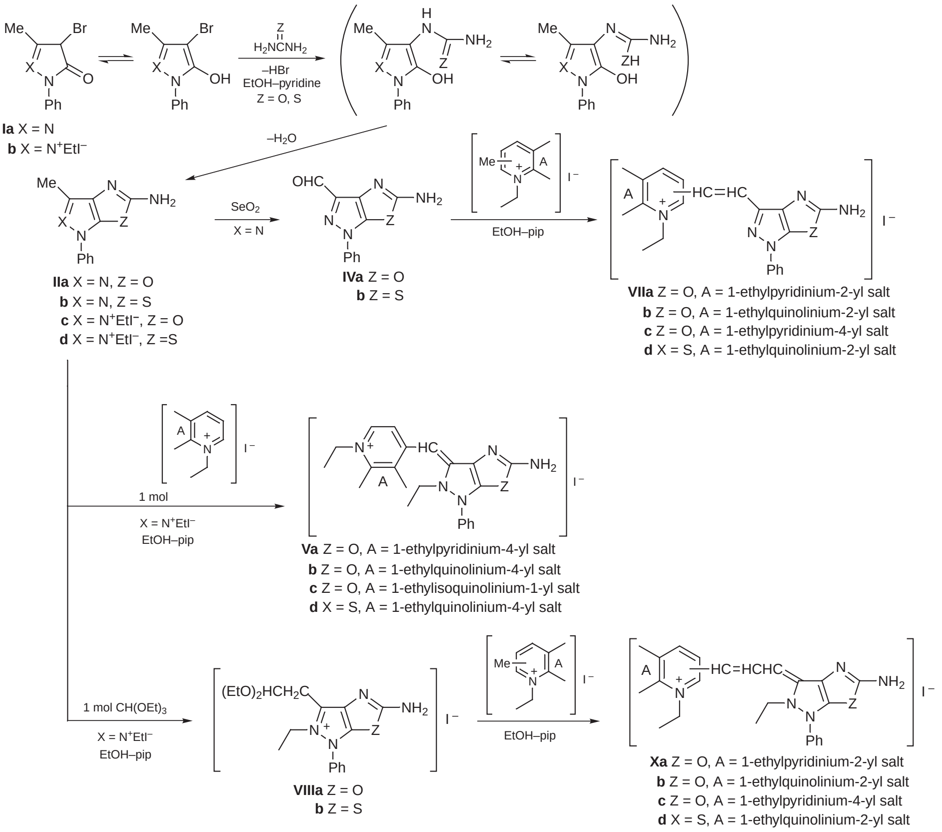
Extended to our previous publications[16] 4-bromo-3-methyl-1-phenyl-pyrazole-5-one **Ia** and its 2-ethyl iodide salt **Ib** were reacted with urea (thiourea) in ethanol–pyridine and afforded 5-amino-3-methyl-1-phenyl-1*H*-pyrazolo-[4,5-*d*][1,3]oxazole (thiazole) **IIa**,**b** and their 2-ethyl iodide salts **IIc**,**d** (Scheme 1).

Quaternization of the latter compounds using bimolar (equimolar) amounts of iodoethane afforded the diquaternized compounds **IIIa**,**b**. Oxidation of **IIa**,**b** using equimolar amounts of selenium dioxide afforded the 3-formyl compounds **IVa**,**b**.

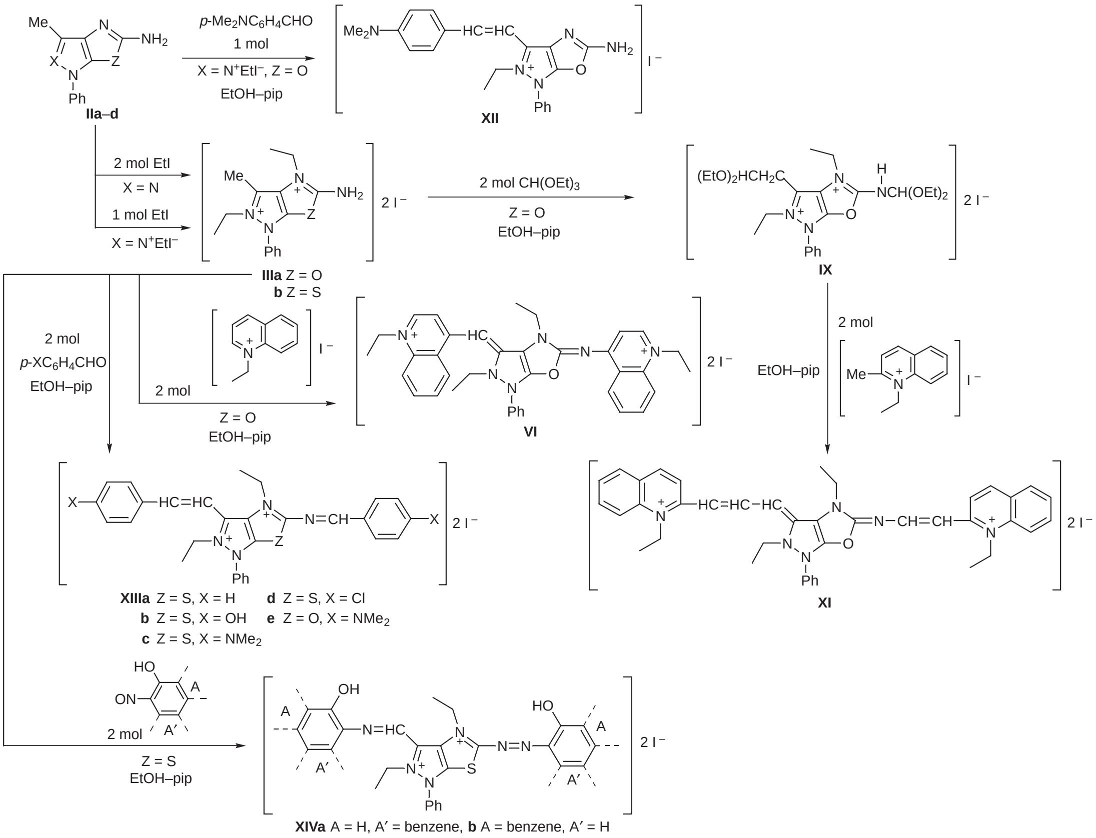
Interaction of **IIc**,**d** (**IIIa**) with equimolar (bimolar) ratios of *N*-ethyl (pyridinium, quinolinium, isoquinolinium) iodide in ethanol–piperidine afforded 3[4(1)]-monomethine cyanine dyes **Va**–**d** and 3(4)-mono-5(4)-azamonomethine mixed cyanine dye **VI**. Interaction of the 3-formyl compounds **IVa**,**b** in equimolar ratios with 2(4)-methyl quaternary salts of *N*-ethyl-2(4)-methyl (pyridinium, quinolinium) iodide in ethanol–piperidine afforded the 3[2(4)]-dimethine cyanine dyes **VIIa**–**d**. Additionally interaction of **IIc**,**d** (**IIIa**) with equimolar (bimolar) ratios of triethyl orthoformate in ethanol–piperidine resulted the intermediate compounds **VIIIa**,**b** (**IX**), which reacted with equimolar (bimolar) amounts of 1-ethyl (α-picolinium, quinaldinium, γ-picolinium) iodide in ethanol–piperidine to give 3[2(4)]-trimethine cyanine dyes **Xa**–**d** and 3(2)-tri-5(2)-azatrimethine mixed cyanine dye **XI**.

On the other hand, interaction of the diquaternized compounds **IIIa**,**b** with equimolar (bimolar) ratios of aromatic aldehydes in ethanol–piperidine resulted 3(1)-styryl cyanine dye **XII** and 3(1)-styryl-5(1)-azastyryl mixed cyanine dyes **XIIIa**–**c**. Interaction of the diquaternized compounds **IIIa**,**b** with nitroso compounds (α-nitroso-β-naphthol, β-nitroso-α-naphthol) in 1 : 2 molar ratios and in ethanol–piperidine afforded 3,5[2(1)]-bis(azadimethine)cyanine dyes **XIVa**,**b**.

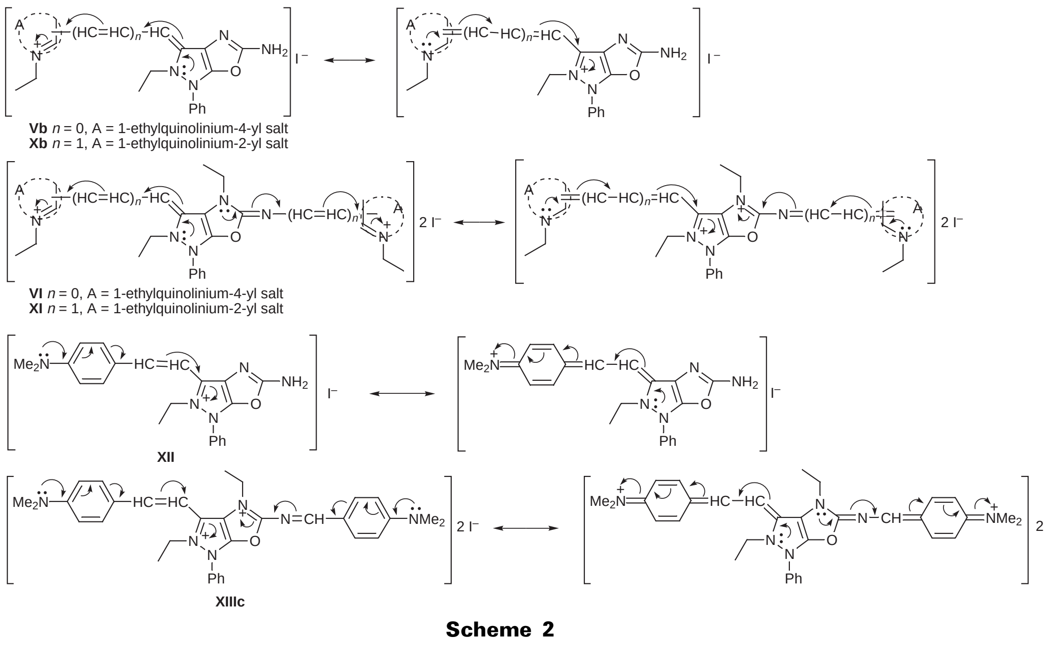
The structures of the compounds were confirmed by elemental analysis, IR and ^{1}H NMR spectral data. The electronic absorption spectra of the cyanine dyes in 95% ethanol were examined and it was observed that the photosensitization of the dyes increased (decreased) by



Scheme 1 (continued opposite)



Scheme 1 (continued)



Scheme 2

increasing (decreasing) conjugation, by the presence of thiazole (oxazole) ring, presence of electron donating (withdrawing) groups, presence of two (one) charge transfer and higher (lower) planarity of the dyes. Resonance structures of some dyes are shown in Scheme 2.

References: 18

Tables: 6 (mps, yields, molecular formulae, molecular mass, colour of crystals, CHN analysis, absorption spectra, IR spectra, ^{1}H NMR spectra).

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References cited in this synopsis

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