International Journal of Engineering Science Invention (IJESI)
ISSN (Online): 2319-6734, ISSN (Print): 2319-6726
www.ijesi.org ||Volume 10 Issue 2 Series I || February 2021 || PP 12-20

Kinetic Studies on Heterocyclic Aldehyde (Ketone) Precursor's Material (1a) and Their Heterocyclic Schiff Bases Synthesis

For the firest time, the present invention pertains to an alternate synthetic route for heterocyclic carboxylic acids using Kinetic Base hydrolysis of heterocyclic aldehyde and heterocyclic quaternary salts or Keto methylene heterocyclic quaternary salts, insteade of traditional organic synthetic methods,meanwhile, the kinetic of formation pertains preparation of key mainintermediates entities suggesting of reaction mechanism. The present invention pertains to multi-step synthetic routes for dyes using heterocyclic amino carboxylic acid characterized with zwitter ions & heterocyclic metal enolate complexes as key intermediates insteade of heterocyclic quaternary salts for cyanine dyes synthesis.

Date of Submission: 30-01-2021 Date of Acceptance: 14-02-2021

Effect of Sodium Hydroxide Concentration.

Effect of (1a) Concentration:

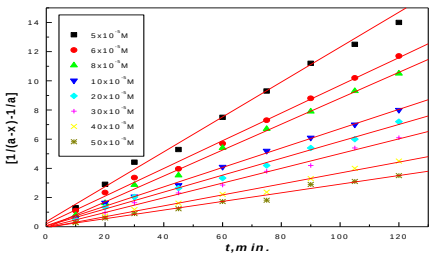


Fig. (35) : Second order rate plots for the hydrolysis of compound 1c in the presence of 20 % NaOH at 30 °C.

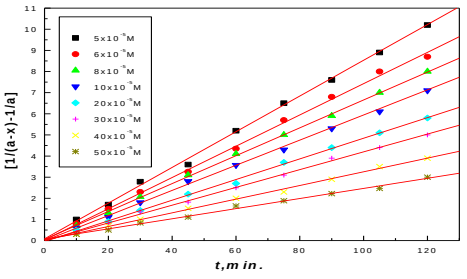


Fig. (34) : Second order rate plots for the hydrolysis of compound 1a in the presence of 20 % NaOH at 30 °C.

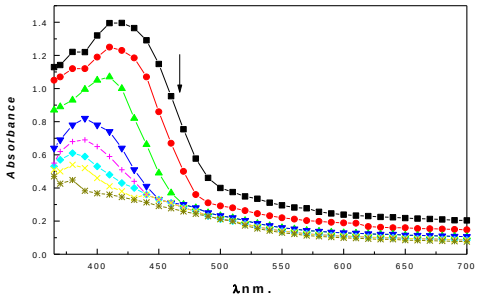


Fig. (36): Spectral scans as function of time (15-min intervals) for representative kinetic run for the base hydrolysis of $1x10^{-4}$ M of compound 1a

Effect of Molecular Structure on the Base Hydrolysis Rate:

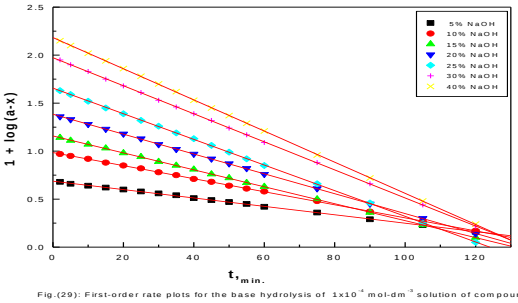


Fig.(29): First-order rate plots for the base hydrolysis of $1x10^{-4}$ mol-dm^{-3} solution of compound 1a in the presence of different concentrations of NaOH in aqueous media at 35°C and η 0.1 mol-dm^{-3}.

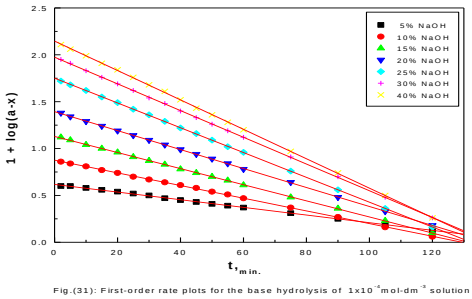


Fig.(31): First-order rate plots for the base hydrolysis of $1x10^{-4}$mol-dm^{-3} solution of compound 1b in the presence of different concentrations of NaOH in aqueous media at 35°C and η 0.1 mol-dm^{-3}

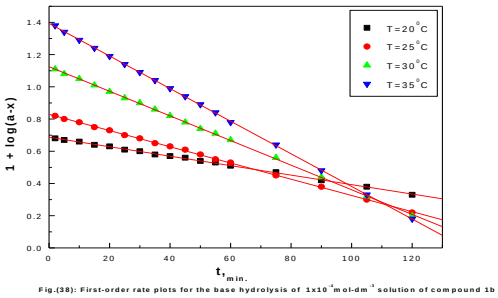


Fig.(38): First-order rate plots for the base hydrolysis of 1x10^{-4}mol-dm^{-3} solution of compound 1b in the presence of 20% solution of NaOH in aqueous media at different temperatures and ɳ 0.1 mol-dm^{-3}.

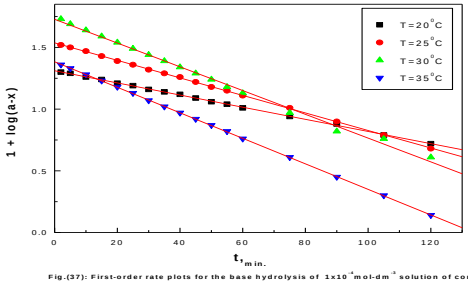


Fig.(37): First-order rate plots for the base hydrolysis of 1x10^{-4}mol-dm^{-3} solution of compound 1a in the presence of 20% solution of NaOH in aqueous media at different temperatures and ɳ 0.1 mol-dm^{-3}.

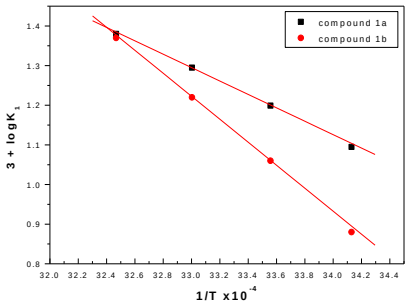
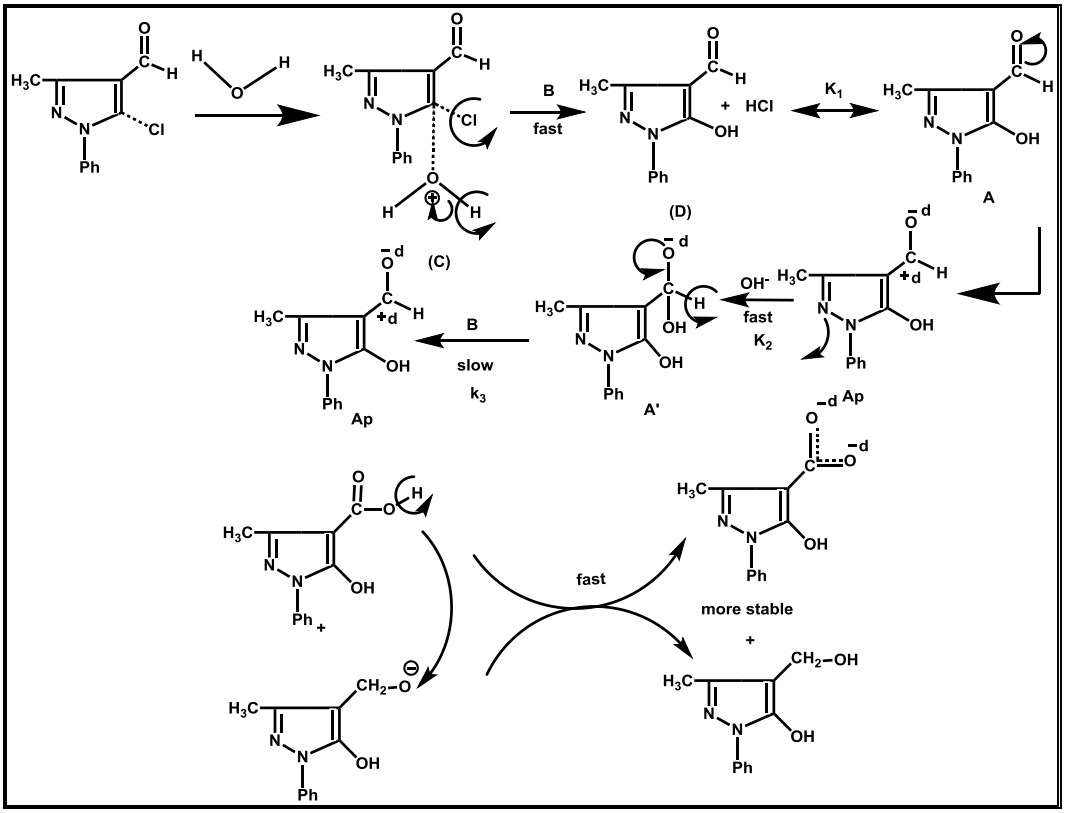


Fig.(39):Arrhenius plots for the base hydrolysis of 1x10^{-4} mol-dm^{-3} solution of compounds 1a and 1b in aqueous media in the presence of 20% NaOH.



Kinetics of Base Hydrolysis of Acyclic Heterocyclic Schiff Bases Quaternary Iodide Salts (2a,b): Effect of Molecular Structure of Acyclic Heterocyclic Schiff Base Quaternary Iodide Salt on the* hydrolysis *Rate:

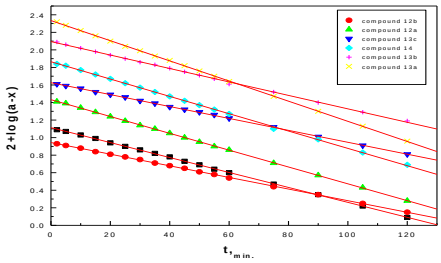


Fig.(77): First-order rate plots for the ring closure of $4x10^{-4}$ mol-dm^{-3} solution of compounds 12a,b,13a-c,14 in the presence of $4x10^{-3}$ mol-dm^{-3} solution of NaOH in aqueous media containing 20 % EtOH at 30 °C, and η 0.1 mol-dm^{-3}.

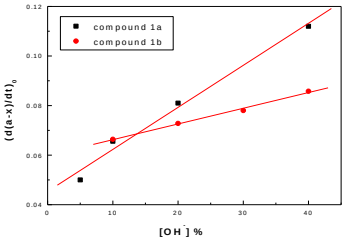


Fig.(33): Initial rate against [NaOH]% for the base hydrolysis of $1x10^{-4}$ mol-dm^{-3} solution of compounds 1a,b in aqueous media containing 20 % EtOH at 30 °C, and η 0.1 mol-dm^{-3}.

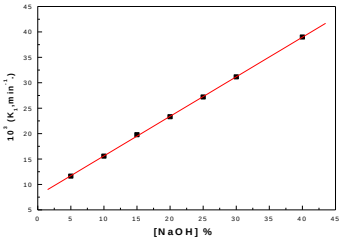


Fig.(32): First-order rate constant as function of sodium hydroxide concentration for the base hydrolysis of $1x10^{-4}$ mol-dm^{-3} solution of compound 1b in aquous medium at 35 °C, and η 0.1 mol-dm^{-3}.

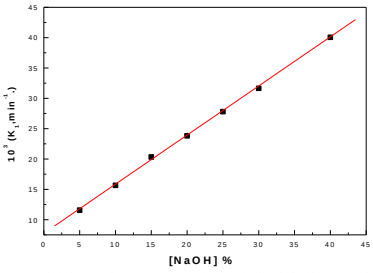


Fig.(30): First-order rate constant as a function of sodium hydroxide concentration for the base hydrolysis of $1x10^{-4}$ mol-dm^{-3} solution of compound 1a in aquous medium at 35 °C,and η 0.1 mol-dm^{-3}.

Kinetics Measurments of (5a-d):

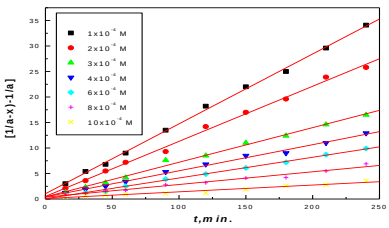


Fig. (96) : Second order rate plots for the formation of compound 19b using different concentrations of compound 18a and acetophenone in the presence of 0.15 M of NaOH in absolute EtOHat 30 °C.

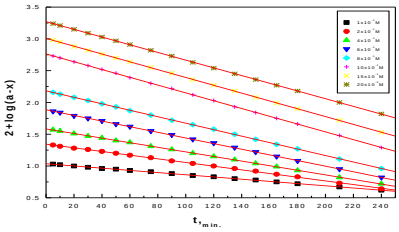


Fig. (95): First-order rate plots for the formation of compound 19b using $6x10^{-4}$ mol-dm^{-3} solution of both compounds 18a and of acetophenone in thepresence of different concentrations of NaOH in absolute EtOH at 30 °C.

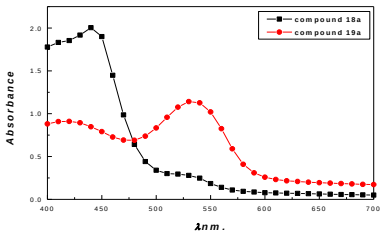


Fig. (97) : Absorption spectra for $6x10^{-4}$ mol-dm^{-3} solutions of compounds 18a and 19b in absolute EtOH.

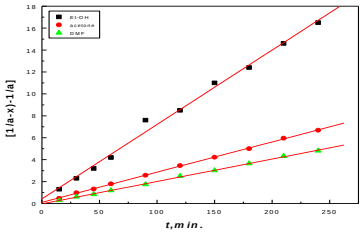


Fig. (99) : Second order rate plots for the formation of compound 19b using $6x10^{-4}$ mol-dm^{-3} solutions of both compound 18a and of acetophenone in the presence of 0.15 M of NaOH in different co-organic solvents at 30 °C.

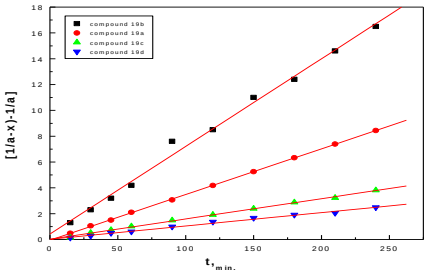


Fig. (98) : Second order rate plots for the formation of compounds 19a-d in the presence of 0.15 M of NaOH in absolute EtOHat 30 °C.

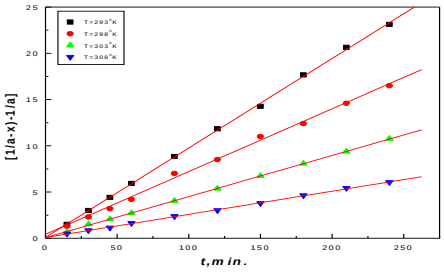


Fig. (100) : Second order rate plots for the formation of compound 19b using 6x10^{-4} mol-dm^{-3} solutions of both compound 18a and of acetophenone in the presence of 0.15 M of NaOH in absolute EtOH at different temperature.

Kinetics of Formation of 3-Methyl-1-Phenyl (5-Chloro-3-Methyl-1-Phenyl)-Pyrazol-5-One 4(1) [2(4)] Mero Cyanine Dyes (8a-d, 9a, b, 10 a, b):
Effectof Piperidine Concentration:

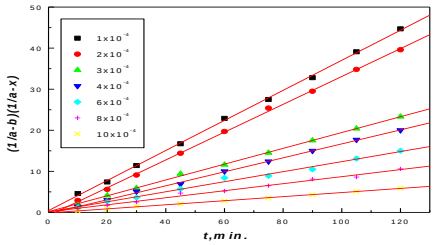


Fig. (64) : Second order rate plots for the formation of compound 8a using different concentrations of compound 4a and methylquinoline-2-ium salt in the presence of 0.2 M of pip. at 30 °C.

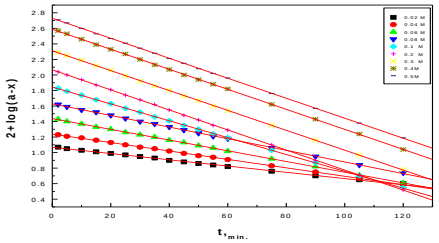
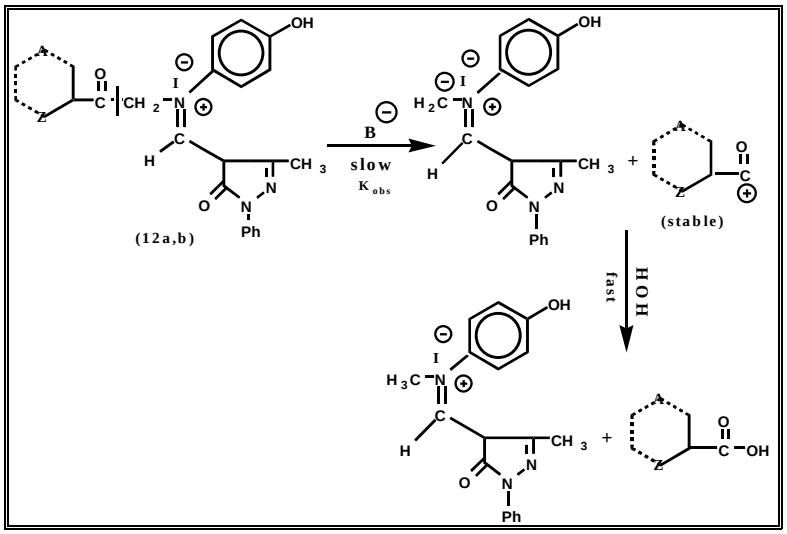
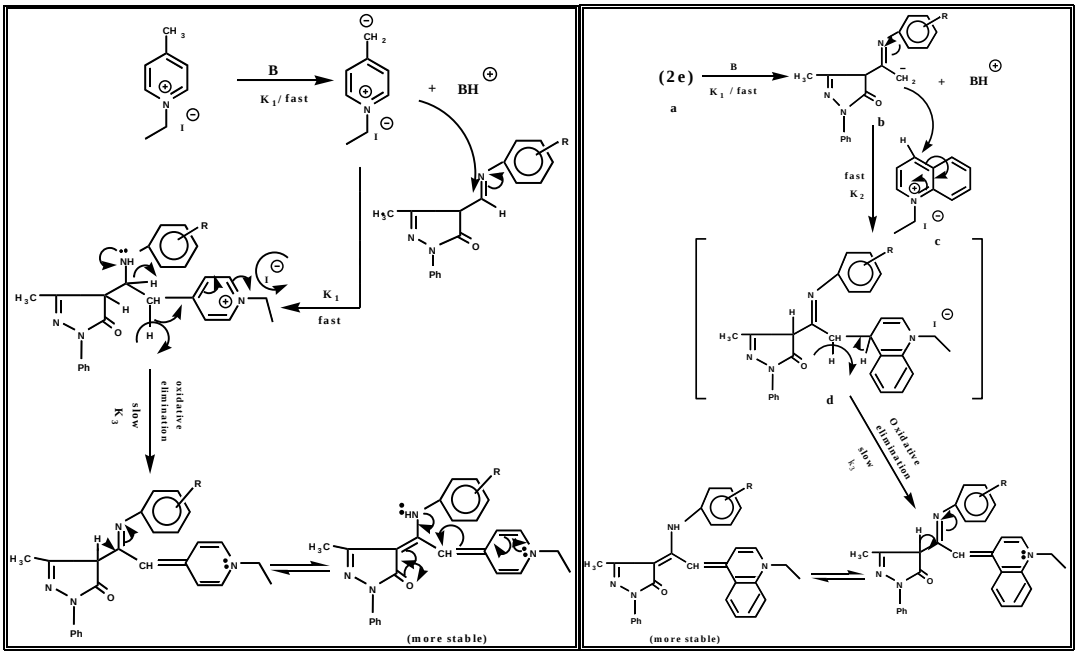


Fig.(63): First-order rate plots for the formation of compound 8a using 4x10^{-4} mol-dm^{-3} solution of compound 4a and of methylquinoline-2-ium salt the presence of different concentrations of pip. in absolute EtOH at 30°C.

FormationMechanism:

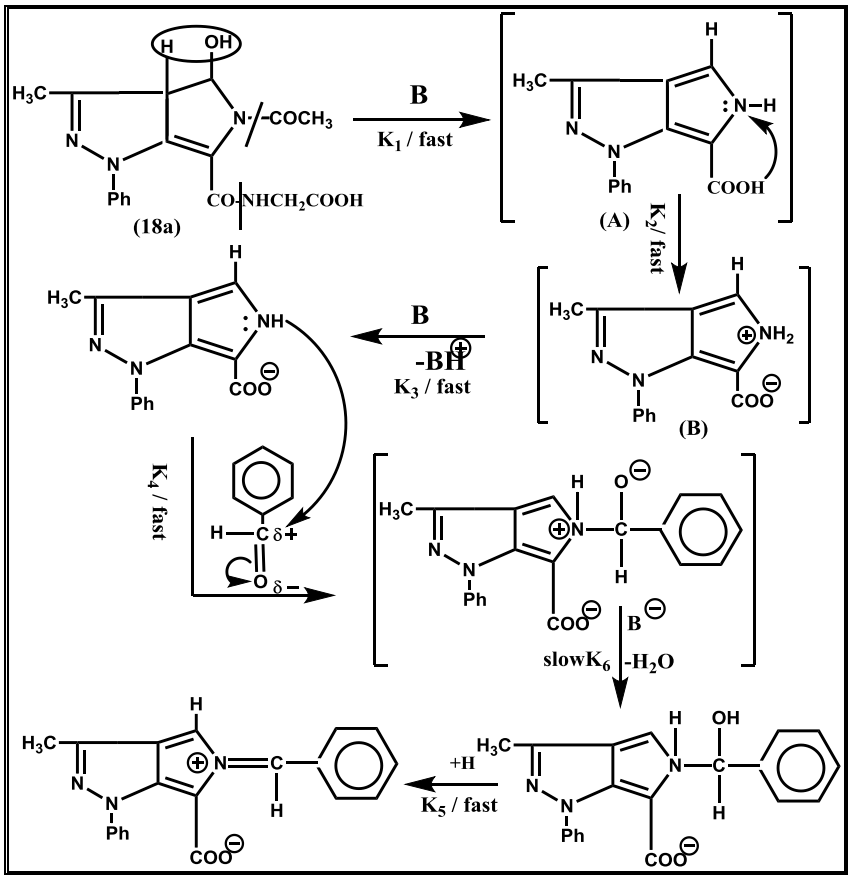


Equation (2).



Equation (5A)Equation (5B)

Effect of Heterocyclic Quaternary Salts Molecular Structure on the Formation Rate:



Equation (4)

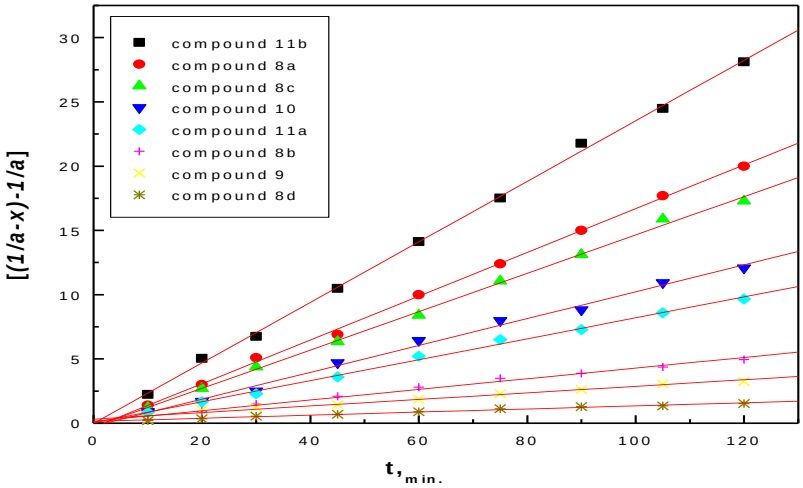


Fig. (66) : Second order rate plots for the formation of compounds 8a-d,9, 10, 11a,b in the presence of 0.2 M of pip. at 30 °C.

Effect of Medium on the Formation Rate:

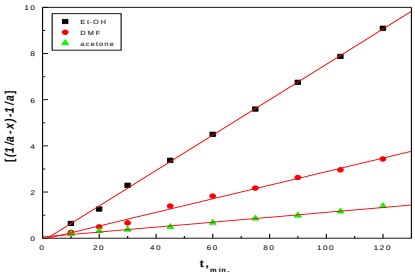


Fig. (67) : Second order rate plots for the formation of compound 8a using 4x10^{-4} M of compound 4a and methylquinoline-2-ium salt in the presence of 0.2 M of pip. in different co-organic solvents at 20 °C.

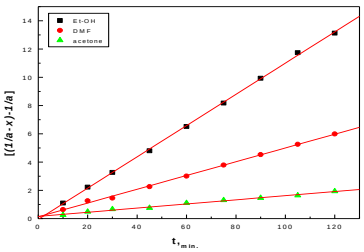


Fig. (68) : Second order rate plots for the formation of compound 8a using 4x10^{-4} M of compound 4a and methylquinoline-2-ium salt in the presence of 0.2 M of pip. in different co-organic solvents at 25 °C.

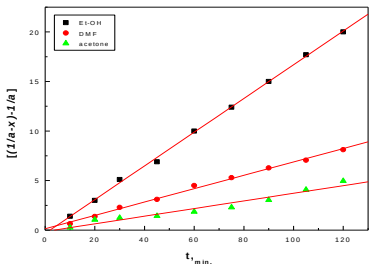


Fig. (69) : Second order rate plots for the formation of compound 8a using 4x10^{-4} M of compound 4a and methylquinoline-2-ium salt in the presence of 0.2 M of pip. in different co-organic solvents at 30 °C.

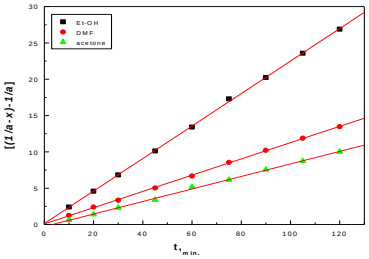


Fig. (70) : Second order rate plots for the formation of compound 8a using 4x10^{-4} M of compound 4a and methylquinoline-2-ium salt in the presence of 0.2 M of pip. in different co-organic solvents at 35 °C.

Effect of Temperature on Formation Rate:

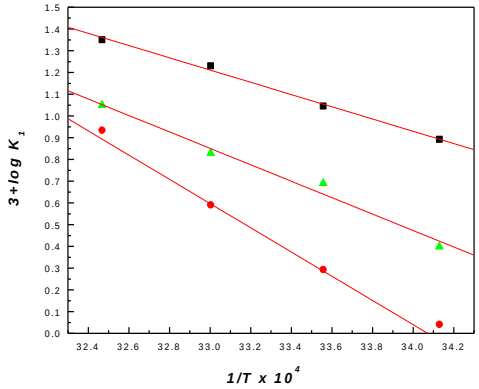


Fig.(71): Arrhenius plots for the formation of compound 8a in different solvents using 4x10^{-4} M of compound 4a and of methylquinoline-2-ium salt in the presence of 0.2 M of pip.

Kinetics of Formation of Pyrrolo [5, 4-d] Pyrazol-Zero-3[4(1)] Methine Cyanine Dyes (10a-c): Effect of Piperidine Concentration:

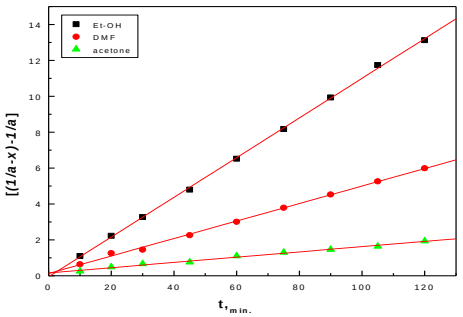


Fig. (68) : Second order rate plots for the formation of compound 8a using 4x10^{-4} M of compound 4a and methylquinoline-2-ium salt in the presence of 0.2 M of pip. in different co-organic solvents at 25 °C.

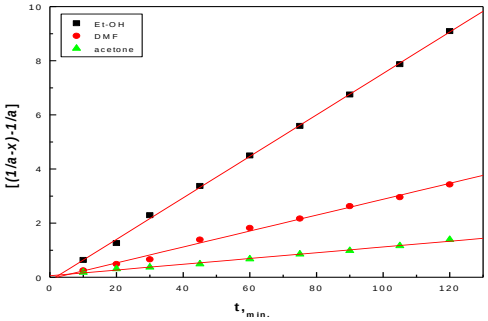
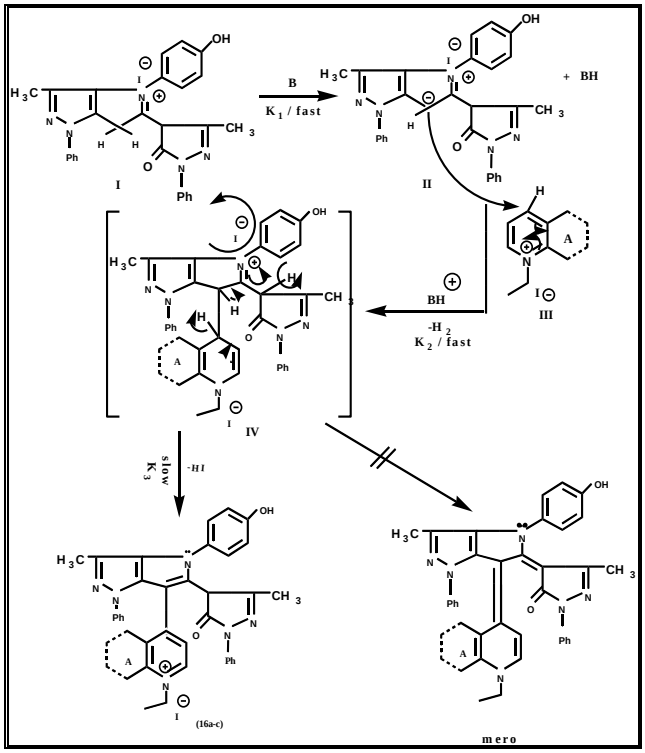


Fig. (67) : Second order rate plots for the formation of compound 8a using 4x10^{-4} M of compound 4a and methylquinoline-2-ium salt in the presence of 0.2 M of pip. in different co-organic solvents at 20 °C.

Formation Mechanism:



Equation (6)

Effect of Heterocyclic Quaternary Salts Molecular Structure on the Formation Rate:

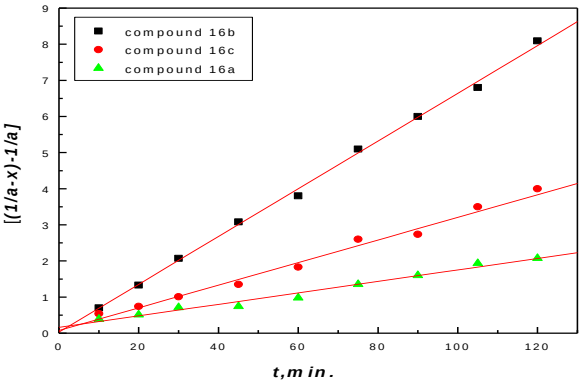


Fig. (89) : Second order rate plots for the formation of compounds 16a-c in the presence of 0.3 M of pip. at 30 °C.

Effect of Medium on the Formation Rate:

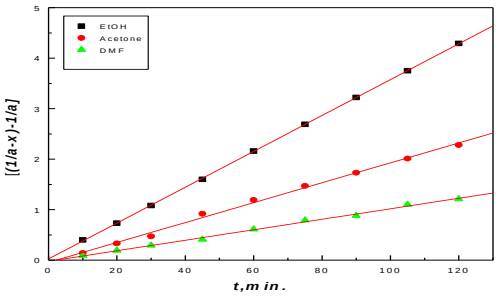


Fig. (90) : Second order rate plots for the formation of compound 16b using $7x10^{-4}$M of compound 15A and N-ethyl quinoline in the presence of 0.3 M of pip. at 20 °C.

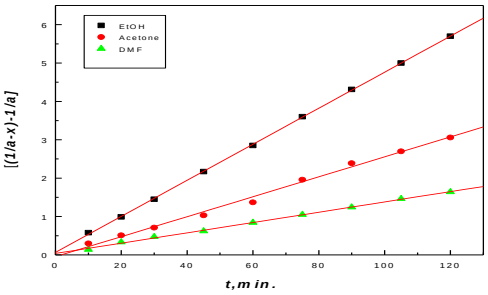


Fig. (91) : Second order rate plots for the formation of compound 16b using $7x10^{-4}$M of compound 15A and of N-ethyl quinoline in the presence of 0.3 M of pip. at 25 °C.

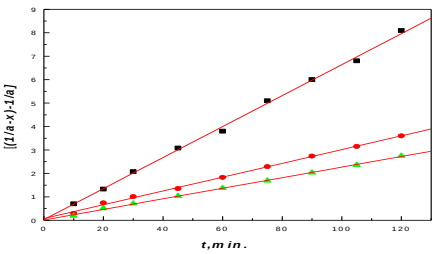


Fig. (92) : Second order rate plots for the formation of compound 16b using $7x10^{-4}$M of compound 15A and N-ethyl quinoline in the presence of 0.3 M of pip. at 30 °C.

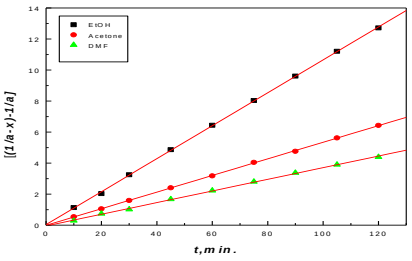


Fig. (93) : Second order rate plots for the formation of compound 16b using $7x10^{-4}$M of compound 15A and N-ethyl quinoline in the presence of 0.3 M of pip. at 35 °C.

Effect of Temperature on the Formation Rate:

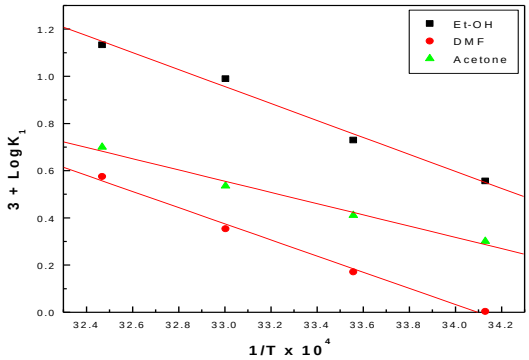


Fig.(94): Arrhenius plots for the formation of compound 16b in different co-organic solvents using $7x10^{-4}$ mol-dm^{-3} solution of 15A and of N-ethylquinoline in the presence of 0.3 mol-dm^{-3} solution of pip.

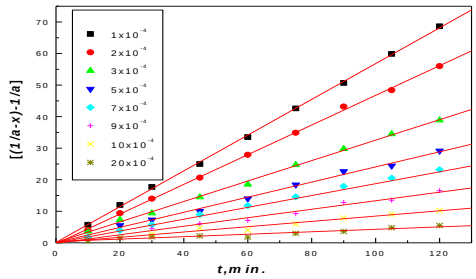


Fig. (102) : Second order rate plots for the formation of compound 28 using different concentrations of compound 24 and *p*-OH aniline at 30 °C.

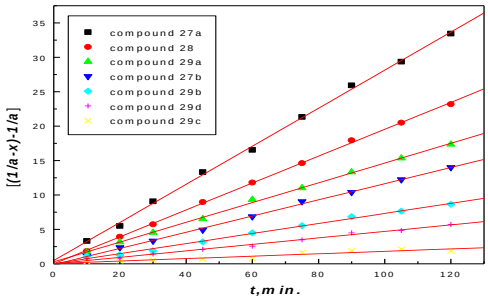


Fig. (104) : Second order rate plots for the formation of compounds 27aq,b, 28, 29a-d at 30 °C.

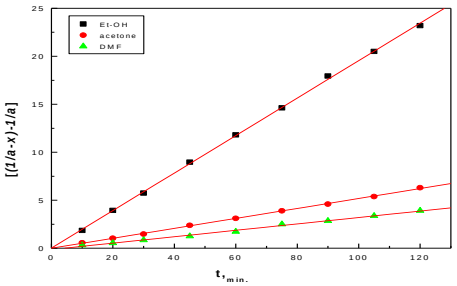


Fig. (105) : Second order rate plots for the formation of compound 28 using 7x10^{-4} mol-dm^{-3} solutions of compounds 24 and of *p*-OH aniline in different co-organic solvents at 30 °C.

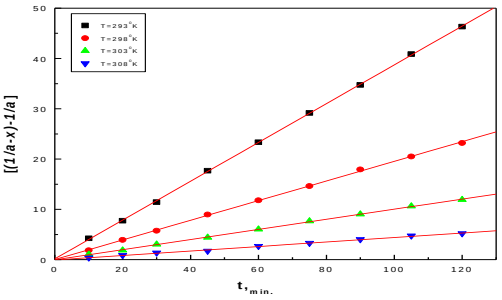


Fig. (106) : Second order rate plots for the formation of compound 28 using 7x10^{-4} mol-dm^{-3} solutions of compounds 24 and of *p*-OH aniline in absolute EtOH at different temperatures.

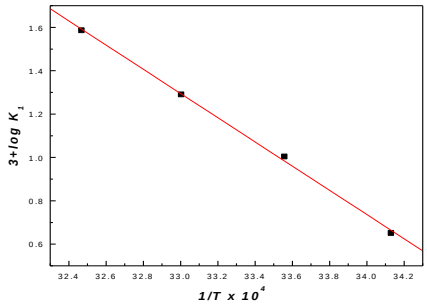


Fig.(107): Arrhenius plots for the formation of compound 28 in absolute EtOH using using 7x10^{-4} mol-dm^{-3} solutions of compounds 24 and of *p*-OH aniline in absolute EtOH.