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A Facile Synthesis of 4-Anilinomethylene-2-Phenyl-2-Oxazolin-5-one and its 1, 5-Bond Cleavage Products

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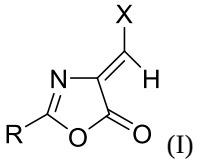
Abstract: 4-Anilinomethylene-2-phenyl-2-oxazolin-5-one (4) is an important compound in the class of 2-Substituted 4-heteromethylene-2-oxazolin-5-one (I). The classical Erlenmeyer Azlactone Synthesis is one of the most common process to synthesize Azlactones or 5(4*H*)-Oxazolones. The method employs the condensation of aromatic aldehydes with hippuric acid in acetic anhydride in the presence of fused sodium acetate, but it fails to produce 4-Anilinomethylene-2-phenyl-2-oxazolin-5-one (4) directly. In view to explore, attempts were made to synthesize 4-Anilinomethylene-2-phenyl-2-oxazolin-5-one (4) using five disciplined route and its solvolysis and aminolysis based products. 2-Phenyl-2-oxazolin-5-one (3) was generated by cyclizing hippuric acid (1) with either ethyl chloroformate (2a) or benzene sulphonyl chloride (2b) or *p*-toluene sulphonyl chloride (2c) in the presence of triethylamine base in dry benzene at room temperature, which declines the risk of high pressure development associated with solution phase reaction. The triethylamine salts produced were filtered under suction and the resultant intermediate (3) was allowed to condensed with N,N'-Diphenyl formamidine. On refluxing for 15 minutes, the resulting product 4-Anilinomethylene-2-phenyl-2-oxazolin-5-one (4) was obtained in good yield. Further, 4-Anilinomethylene-2-phenyl-2-oxazolin-5-one (4) was also prepared on treatment with aniline in one flask directly from 4-Ethoxymethylene-2-phenyl-2-oxazolin-5-one (5) which in turn was synthesized by heating hippuric acid (1) with ethyl orthoformate in presence of acetic anhydride. When a mixture of hippuric acid (1), ethyl orthoformate and phenyl isothiocyanate with the molar ratio of 1:1.1:1.2 was heated at 130°-140°C for 30 minutes in presence of pyridine as base, **4** was obtained directly along with hippuranilide (6) with 20% and 16% yields respectively.(SCHEME- 1) On solvolysis and aminolysis of 4-Anilinomethylene-2-phenyl-2-oxazolin-5-one (4) afford a variety of products either by the attack of nucleophiles through the cleavage of 1, 5-bond of the oxazolone ring or first by exchanging the anilino moiety followed by 1, 5-bond cleavage and subsequent recyclization. Accordingly, 3-Anilino-2-benzoylamino acrylic acid (7) by hydrolysis**,** Ethyl 3-anilino-2-benzoylamino acrylate (8) by ethanolysis, methyl 3-anilino-2-benzoylamino acrylate (9) by methanolysis, 4-benzoylamino-3-pyrazolin-5-one (11), and 4-benzamido-1-phenyl-3-pyrazolin-5-one (12) by hydrazinolysis with hydrazine and phenyl hydrazine respectively were synthesized using 4-Anilinomethylene-2-phenyl-2-oxazolin-5-one (4) as a synthon. (SCHEME-2)

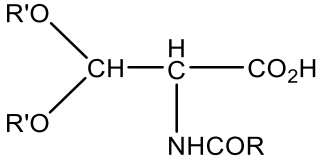
Key words: 4-Anilinomethylene-2-phenyl-2-oxazolin-5-one, Synthon, Solvolysis, Hydrazinolysis, 5(4*H*)-Oxazolone, 3-Pyrazolin-5-one.

I. INTRODUCTION

The exigencies of penicillin chemistry have led to the emergence of a new class of substances, which will be termed "4-heteromethylene-5-oxazolones." These are represented by the general formula (I), where the group X being attached through an oxygen, nitrogen, sulphur or halogen atom.



(I)



(II)

When the presence of an oxazolone ring in penicillin was first suspected the importance of the "2-alkyl-5-oxazolone-4-aldehydes", in connection with attempts at synthesis, was fully appreciated, and investigation led speedily to the discovery of two main methods which have served as the basis of further work.

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(i) The first method of preparing oxazolones of type 1 was called 'Orthoformate synthesis' as a special case of the Erlenmeyer azlactone synthesis where 4-Ethoxymethylene-2-phenyl-5-oxazolone (I; R= Ph, X= OEt) was prepared by heating hippuric acid with ethyl orthoformate and acetic anhydride.
(ii) The second method of preparing oxazolone called 'penaldate synthesis' as a special case of Carter's Oxazolone synthesis where 2-amyl-4-ethoxymethylene-5-oxazolones (I) R= C_5H_{11}, X= OEt) was obtained from a penaldic acid acetal of the general formula II[1]. Based on the above study, an attempt was made for the preparation of 4-Anilinomethylene-2-phenyl-2-oxazolin-5-one using a modified route and to study its solvolysis and aminolysis products.

2-Oxazolin-5-ones, also called 5(4*H*)-Oxazolones, continue to attract the attention of chemists because of their usefulness as synthons and their diverse bio-potentiality. The subject has been reviewed[1-9] from time to time.The objective of the present investigation was to develop a method for a facile and quick synthesis of 4-Heteromethylene-2-phenyl-2-oxazolin-5-one and its solvolysis and aminolysis products. In view of the above, an attempt was made to synthesize 4-Anilinomethylene-2-phenyl-2-oxazolin-5-one **(4)** using five disciplined route and its solvolysis and aminolysis based products. 2-Phenyl-2-oxazolin-5-one **(3)** was generated by cyclizing hippuric acid **(1)** with either ethyl chloroformate **(2a)** or benzene sulphonyl chloride **(2b)** or *p*-toluene sulphonyl chloride **(2c)** in the presence of triethylamine base in dry benzene at room temperature, which declines the risk of high pressure development associated with solution phase reaction. The triethylamine salts produced were filtered under suction and the resultant intermediate **(3)** was allowed to condensed with N,N'-Diphenyl formamidine. On refluxing for 15 minutes, the resulting product 4-Anilinomethylene-2-phenyl-2-oxazolin-5-one **(4)** was obtained in good yield. Further, 4-Anilinomethylene-2-phenyl-2-oxazolin-5-one (**4**) was also prepared on treatment with aniline in one flask directly from 4-Ethoxymethylene-2-phenyl-2-oxazolin-5-one (**5**) which in turn was synthesized by heating hippuric acid (**1**) with ethyl orthoformate in presence of acetic anhydride.

When a mixture of hippuric acid (**1**), ethyl orthoformate and phenyl isothiocyanate with the molar ratio of 1:1.1:1.2 was heated at 130°-140°C for 30 minutes in presence of pyridine as base, **4** was obtained directly along with hippuranilide (**6**) with 20% and 16% yields respectively.(SCHEME- 1)On solvolysis and aminolysis of 4-Anilinomethylene-2-phenyl-2-oxazolin-5-one **(4)** afford a variety of products either by the attack of nucleophiles through the cleavage of 1, 5-bond of the oxazolone ring or first by exchanging the anilino moiety followed by 1, 5-bond cleavage and subsequent recyclization.(SCHEME-2)

SCHEME-1

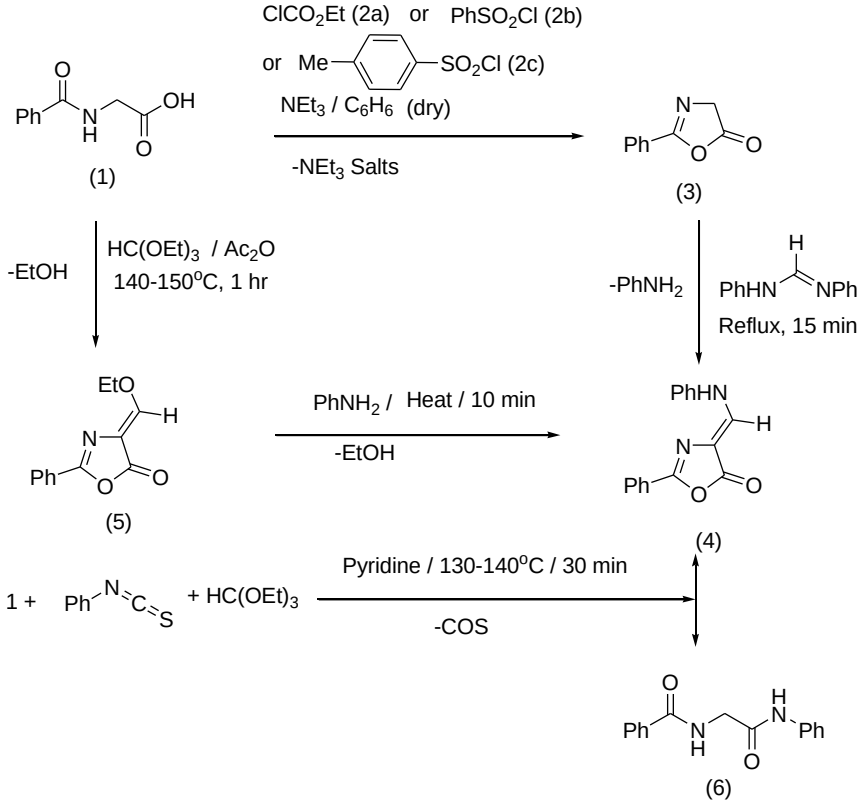

Figure-1: Five disciplined routes for the synthesis of 4-Anilinomethylene-2-phenyl-2-oxazolin-5-one

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SCHEME -2

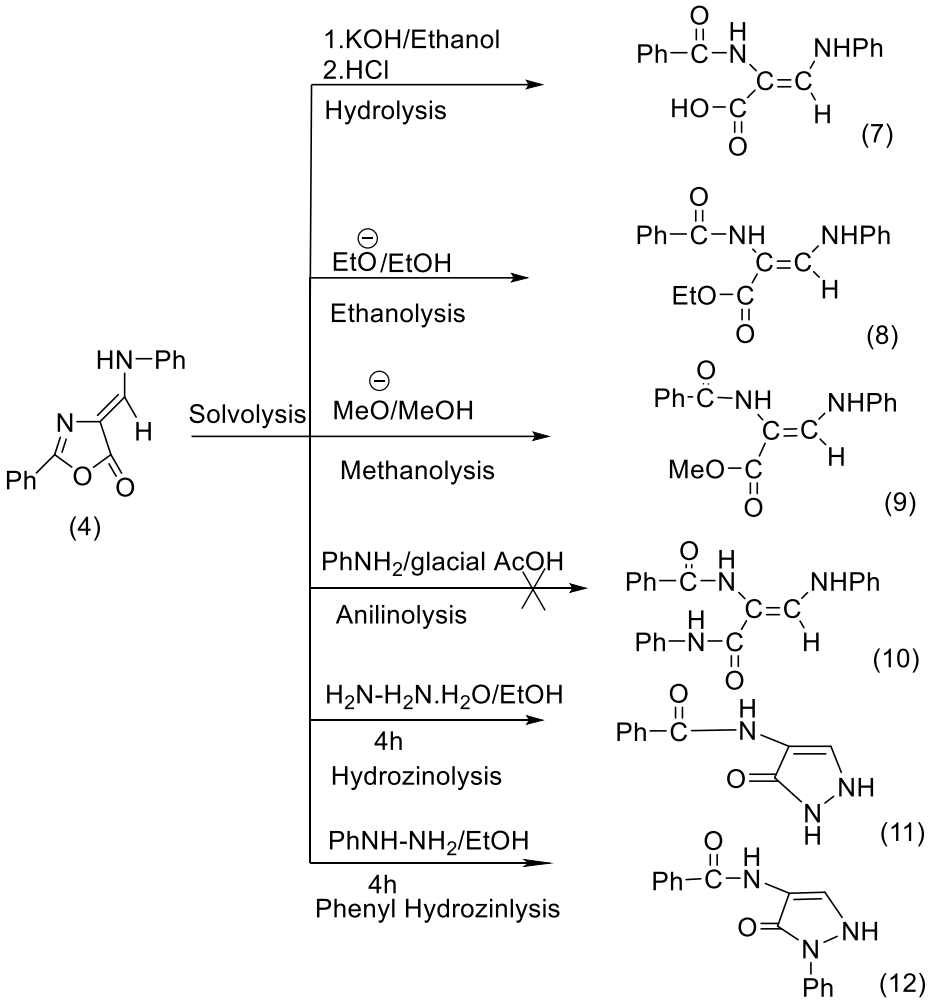

Figure-2: Solvolysis and aminolysis products from 4-Anilinomethylene-2-phenyl-2-oxazolin-5-one through 1, 5-bond cleavage

II. MATERIALS AND METHODS

All the prepared compounds are known in the literature[10,11]. The purity of the compounds were verified by TLC (silica gel based) and their melting points. Melting points were recorded by the metal block melting point apparatus and are uncorrected. The IR spectra of the compounds were recorded on IR Affinity-1, Shimadzu and Bruker, Alpha-II. PMR spectra were recorded on JEOL FX90Q spectrophotometer.

2.1 One flask synthesis of 4-Anilinomethylene-2-phenyl-2-oxazolin-5-one (4) using ethyl chloroformate (2a) as a cyclocondensing agent:

To a suspension of hippuric acid (0.90g; 0.005 mol) in dry benzene (25mL) containing triethylamine (0.91mL; 0.0065 mol), ethyl chloroformate (0.53mL ;0.0055mol) was added and the mixture shaken at room temperature until hippuric acid crystals dissolved and triethylamine hydrochloride separated out which was filtered off under suction and washed with dry benzene (2×3mL). The filtrate and washings were combined and to the benzene solution, N,N-diphenylformamidine (0.98g;0.005mol) was added. The mixture was heated under reflux for 15 minutes, the solvent was removed under reduced pressure and the residue was washed with petroleum ether (40-60^{o}C). On trituration with cold ethanol, a solid was obtained which was filtered and recrystallised from ethanol. Yield: 0.56g (42%), m.p.:160-162^{o}C (Reported[10]:160-162^{o}C), IR (KBr) ν_{max}: 3278 (NH), 1782 (C=O, oxazolone), 1738 (C=N), 1668 (C=C)[10] cm^{-1}, PMR ($CDCl_3$ / TMS) δ: 6.90- 7.84 (m, 11H, Ar-*H* and 4C=C*H*); 9.19 (s, 1H, exchangeable, -N*H*Ph) ppm.

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2.2 One flask synthesis of 4-Anilinomethylene-2-phenyl-2-oxazolin-5-one (4) using Benzene sulphonyl chloride (2b) as a cyclocondensing agent:

To a suspension of hippuric acid (0.90g; 0.005 mol) in dry benzene (30mL) containing triethylamine (1.30mL; 0.0125 mol), benzene sulphonyl chloride (0.89mL ;0.005mol) was added and the mixture shaken at room temperature until hippuric acid crystals dissolved and triethylamine salts separated out which was filtered off under suction and washed with dry benzene (2×3mL). The filtrate and washings were combined and to the benzene solution, N,N-diphenylformamidine (0.98g; 0.005mol) was added. The rest of the procedure is same as given in the method 2.1. Yield: 0.50g (37%), m.p.:160-162ºC (Reported[10]:160-162ºC).

2.3 One flask synthesis of 4-Anilinomethylene-2-phenyl-2-oxazolin-5-one (4) using *p*-toluene sulphonyl chloride (2c) as a cyclocondensing agent:

To a suspension of hippuric acid (0.90g; 0.005 mol) in dry benzene (30mL) containing triethylamine (1.30mL ; 0.0125 mol), *p*-toluene sulphonyl chloride (0.95g ; 0.005mol) was added and the mixture shaken at room temperature until hippuric acid crystals dissolved and triethylamine salts separated out which was filtered off under suction and washed with dry benzene (2×3mL). The filtrate and washings were combined and to the benzene solution, N,N-diphenylformamidine (0.98g; 0.005mol) was added. The rest of the procedure is same as given in the method 2.1. Yield: 0.45g, 34%), m.p.:160-162ºC (Reported[10]:160-162ºC).

2.4 One flask synthesis of 4-Anilinomethylene-2-phenyl-2-oxazolin-5-one (4) using modified Erlenmeyer azlactone synthesis:

Hippuric acid (7.2 g, 0.04 mol) and ethyl orthoformate (6.0g, 0.04mol) where heated for one hour under reflux with acetic anhydride (8.0g, 0.07mol) (bath temperature 140º-150ºC). Low boiling material was then removed (final bath temperature 135ºC) at 10 mm. The dark red residue (5) obtained was directly treated with aniline (4.0mL, 0.04mol). The solid obtained was washed with petroleum ether (40-60ºC) and it affords the product 4-Anilinomethylene-2-phenyl-2-oxazolin-5-one(4). Yield: (6.0g.), m.p.:160º-162ºC (reported[10]: 160º-162ºC).

2.5 Solvent free synthesis of 4-Anilinomethylene-2-phenyl-2-oxazolin-5-one (4) using phenyl isothiocyanate:

A mixture of hippuric acid (1), phenyl isothiocyanate and ethyl orthoformate in a molar ratio of 1:1.2:1.1 respectively with pyridine as a catalyst was thoroughly mixed and was heated in an oil bath for 30 minutes at 130º-140ºC in an open vessel. The residue was washed with light petroleum (60- 80ºC) to remove pyridine and the residue was treated with saturated solution of $NaHCO_3$ to remove unreacted hippuric acid (1) if any. Then it was taken up in hot benzene, from which the benzene soluble part was separated from the benzene insoluble part. Benzene insoluble part afforded hippuranilide (6), yield: 16%; m.p : 210º-212º C (reported[10]: 210º-212º C) IR (KBr) : ν_{max} 3300(NH),1690(CO),1650 (CO)cm^{-1}. Benzene soluble part afforded 4-Anilinomethylene-2-phenyl-2-oxazolin-5-one (4) after removing the solvent under reduced pressure and on trituration with chilled ethanol, yield: 20%; m.p. 160º-162º C (reported[10]: 160º-162º C).

2.6 1, 5-bond cleavage reaction of 4-Anilinomethylene-2-phenyl-2-oxazolin-5-one (4) with different nucleophiles

2.6.1 Hydrolysis by ethanolic KOH: Synthesis of 3-Anilino-2-benzoylamino acrylic acid (7)

A mixture of 4-Anilinomethylene-2-phenyl-2-oxazolin-5-one (0.13g; 0.0005mol), potassium hydroxide (0.03g, 0.0006 mol) and ethanol (10mL) was heated under reflux for 30 min. The solvent was completely removed under reduced pressure, the residue was dissolved in water (5mL) and filtered. The filtrate was acidified with conc. HCl (1mL) to give a solid (7) which was filtered, washed with water. It could not be recrystallized due to insufficient solubility in common solvents. Yield: 0.13g (46%) m.p.: 174-176º C (reported[11]: 176-178º C), IR (KBr): ν_{max} 3350 (NH), 3225(NH, amide), 1700 (C=O, carboxylic acid), 1660 (C=O, amide), 1620 (C=C)[11]cm^{-1}. PMR ($CDCl_3$ / TMS): Insoluble in $CDCl_3$.

2.6.2 Ethanolysis by ethanol and catalytic KOH: Synthesis of Ethyl 3-anilino-2-benzoylamino acrylate (8)

A solution of 4-Anilinomethylene-2-phenyl-2-oxazolin-5-one (0.26g, 0.001 mol) in ethanol (10mL) containing potassium hydroxide (0.01g) in catalytic amount, was heated under reflux for 30min and concentrated to dryness *in vacuo* and the residue treated with water (8mL) to afford a solid which was filtered, washed and recrystallized from aq. Ethanol to give Ethyl 3-anilino-2-benzoylamino acrylate **(8)**. Yield: 0.25g (80%), m.p.: 148-150º C (reported[11]: 148º-150º C), IR (KBr): ν_{max} 3375(NH), 3250 (NH, amide), 1720 (C=O, ester), 1660(C=O, amide), 1620 (C=C)[11]cm^{-1}. PMR ($CDCl_3$ / TMS) δ: 1.36 (t, 3H, CH_2-C*H*$_3$); 4.26 (q, 2H, -C*H*$_2$-CH_3); 7.00 (d, 1H, C=C*H*); 7.15- 7.90 (m, 10H, Ar-*H*); 8.29 (s, 1H, -CON*H*); 8.89 (d, 1H, -N*H*Ph) ppm.

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2.6.3 Methanolysis by methanol and catalytic sodium: Synthesis of methyl 3-anilino-2-benzoylamino acrylate (9)

A solution of 4-Anilinomethylene-2-phenyl-2-oxazolin-5-one (0.13g, 0.0005 mol) in methanol (10mL) containing sodium metal (0.03g) in catalytic amount was heated under reflux for 20 min and then concentrated to dryness *in vacuo*. The residue was treated with water (5mL) to afford a solid which was filtered, washed and recrystallized from aqueous methanol. The compound obtained was methyl 3-anilino-2-benzoylamino acrylate **(9)**. Yield: 0.14g (91%), m.p.: 176-178º C (reported[11]: 178-179º C), IR (KBr): ν_{max} 3350 (NH), 3250 (NH, amide), 1720 (C=O, ester), 1650(C=O, amide), 1620 (C=C)[11] cm^{-1} PMR ($CDCl_3$ / TMS) δ: 3.81 (s, 3H, -C*H*$_3$); 7.00 (d, 1H, C=C*H*); 7.15- 7.90 (m, 10H, Ar-*H*); 8.29 (s, 1H, -CON*H*); 8.88 (d, 1H, -N*H*Ph) ppm.

2.6.4 Aminolysis by aniline in glacial acetic acid: Expected synthesis of 3-Anilino-2-benzoylamino-N-phenyl acrylamide (10)

A mixture of 4-Anilinomethylene-2-phenyl-2-oxazolin-5-one and aniline taken in 1:1.1 molar ratio was heated under reflux in glacial acetic acid (10mL/g of **4**) for 4 hour. The solution was stripped of solvent *in vacuo*.The residue obtained was **4**and the titled compound i.e. 3-Anilino-2-benzoylamino-N-phenyl acrylamide **(10)** could not be achieved.

2.6.5 Hydrazinolysis by hydrazine hydrate: Synthesis of 4-benzoylamino-3-pyrazolin-5-one (11)

A mixture of 4-Anilinomethylene-2-phenyl-2-oxazolin-5-one (0.26g;0.001 mol) and hydrazine hydrate (0.055mL, 0.0011) taken in 1:1.1molar ratio was heated under reflux in ethanol (20mL) for 4 hour. The solution was stripped of solvent *in vacuo* and the residue washed with petroleum ether (60º-80ºC). The residue was triturated with water and only after seedling and long standing, the product 4-benzoylamino-3-pyrazolin-5-one (**11**) was obtained which was recrystallized from water. Yield: 0.14g (70%), m.p 205-206ºC (reported[11]: 205-206ºC), IR (KBr): ν_{max} 3384,3275,3203 (three N-H), 1684 (C=O, pyrazolone),1641(C=O, amide), 1604(C=C)[11] cm^{-1}. PMR ($CDCl_3$ / TMS) : Insufficiently soluble in $CDCl_3$.

2.6.6 Hydrazinolysis by phenyl hydrazine: Synthesis of 4-benzamido-1-phenyl-3-pyrazolin-5-one (12)

A mixture of 4-Anilinomethylene-2-phenyl-2-oxazolin-5-one (0.26g ; 0.001 mol) and phenyl hydrazine (0.12 mL, 0.0011) taken in 1:1.1molar ratio was heated under reflux in ethanol (20mL) for 4 hour. The solution was stripped of solvent *in vacuo* and the residue was washed with petroleum ether (60º-80º C). Then the residue was triturated with benzene and recrystallized from benzene. Yield: 0.23g (86%), m.p.: 198-199ºC. (reported[11]:198-199º C), IR (KBr): ν_{max} 3310, 3100 (two N-H), 1660 (C=O, pyrazlone), 1640(C=O, amide), 1600(C=C)[11] cm^{-1}. PMR ($CDCl_3$ / TMS) δ: 7.12-7.81 (m, 12H, one exchangeable, 3-C*H*, N*H* and Ar-*H*) 7.73 (s, 1H, exchangeable, -CON*H*) ppm.

III. RESULT AND DISCUSSION

4-Anilinomethylene-2-phenyl-2-oxazolin-5-one (**4**) was synthesized as a synthon to study its hydrolysis and aminolysis products by the cleavage of its 1, 5-bond using different nucleophiles. 2-Phenyl-2-oxazolin-5-one (**3**) was generated by cyclizing hippuric acid (**1**) with various cyclizing agents namely ethyl chloroformate (**2a**) or benzene sulphonyl chloride (**2b**) or *p*-toluene sulphonyl chloride (**2c**) in the presence of triethylamine base in dry benzene by shaking the mixture at room temperature till the complete dissolution of hippuric acid and the separation of triethylamine salts. In case of ethyl chloroformate (**2a**), the amount of triethylamine used was 1.3 mol whereas for arylsulphonyl chlorides (**2b** and **2c**) the amount taken was 2.5 mol. Carrying out the reaction at room temperature declines the risk of high pressure development associated with solution phase chemistry. The triethylamine salts obtained was filtered off under suction and was washed twice with dry benzene. The filtrate and washings were combined and N,N-diphenylformamidine was added into it with 1:1 molar ratio. The content was subjected to reflux for 15 minutes and the solvent was removed under reduced pressure. The residue was washed with petroleum ether (40-60ºC) and 4-Anilinomethylene-2-phenyl-2-oxazolin-5-one (**4**) was obtained on trituration with 95% ethanol. The product was recrystallized from ethanol.

4-Anilinomethylene-2-phenyl-2-oxazolin-5-one (**4**) was also synthesized as a synthon from 4-Ethoxymethylene-2-phenyl-2-oxazolin-5-one (**5**) in one flask using modified Erlenmeyer azlactone synthesis. Hippuric acid (**1**) and ethyl orthoformate were heated with acetic anhydride under reflux for one hour. The dark red residue obtained on cooling was washed with light petroleum and aniline was introduced in the same flask. On stirring, a dark yellow solid of the compound **4** was obtained in good yield. The compound **4** can also be prepared by heating a mixture of hippuric acid (**1**), ethyl orthoformate and phenyl isothiocyanate in presence of pyridine at 130º-140ºC for 30 min in an open vessel. Hippuranilide (**6**) was also formed with 16% yield as a by-product.

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Acetic anhydride mediated cyclization of hippuric acid (**1**) may lead to the formation of saturated azlactone (**3**) which on condensation with ethyl orthoformate at 4-position and subsequent β-elimination may lead to the formation of 4-ethoxymethylene-2-phenyl-2-oxazolin-5-one (**5**). On treatment of **5** with aniline, 4-Anilinomethylene-2-phenyl-2-oxazolin-5-one (**4**) was produced via the elimination of EtOH. The condensation of hippuric acid (**1**) with phenyl isothiocyanate proceeded through addition-elimination reactions to yield hippuranilide (**6**) and saturated azlactone (**3**). Pyridine as a catalyst/base facilitated the reaction. Apparently, this is owning to the fact that pyridine as a base enhance the concentration of the carboxylate ion which is the reactive species toward phenyl isothiocyanate.

4-Anilinomethylene-2-phenyl-2-oxazolin-5-one (**4**) as prepared was subjected to solvolysis and aminolysis through 1,5-bond cleavage. Hydrolysis was carried out by heating with ethanolic KOH, followed by acidification with conc. HCl which afford 3-Anilino-2-benzoylamino acrylic acid **(7)**. The result was obviously due to the generation of hydroxide ion as nucleophile which brought about the cleavage of the 1, 5-bond of compound **4**. When ethanolic KOH was used, a small amount of the corresponding ethyl ester (**8**) was also obtained. Ethyl 3-anilino-2-benzoylamino acrylate (**8**) may be obtained in much better yield by treating the compound **4** with ethanol in presence of the catalytic amount of KOH (ethanolysis). It was due to the generation of ethoxide ion as nucleophile by which the 1,5-bond was cleaved to yield the product (**8**). Methanolysis of the compound **4** was carried out in methanol in the presence of a catalytic amount of sodium metal in which methoxide ion as nucleophile cleaved the 1, 5-bond of the compound **4** and afforded methyl 3-anilino-2-benzoylamino acrylate (**9**). The compound **4** proceeded hydrolysis and base catalyzed alcoholysis of the 1, 5-bond, the hetero-methylene moiety remaining unaffected.Aminolysis of 4-Anilinomethylene-2-phenyl-2-oxazolin-5-one (**4**) gave different results, depending upon the type of reacting amines. 4-Anilinomethylene-2-phenyl-2-oxazolin-5-one (**4**) was found to be extremely resistant to aminolysis with aniline. The expected product 3-Anilino-2-benzoylamino-N-phenyl acrylamide **(10)** could not be achieved on anilinolysis of 1, 5-bond of the compound **(4).**4-Anilinomethylene-2-phenyl-2-oxazolin-5-one (**4**) was found to exhibit imine-enamine tautomerism. This was verified by its reaction with hydrazines which led to the exchange of the anilino moiety followed by the ring expansion of the resultant oxazolone ring (4) and was leading to the formation of 4-benzoylamino-3-pyrazolin-5-one (**11**) and 4-benzoylamino-1-phenyl-3-pyrazolin-5-one (**12**) with hydrazine hydrate and phenyl hydrazine respectively on refluxing in ethanol for 4 hour.

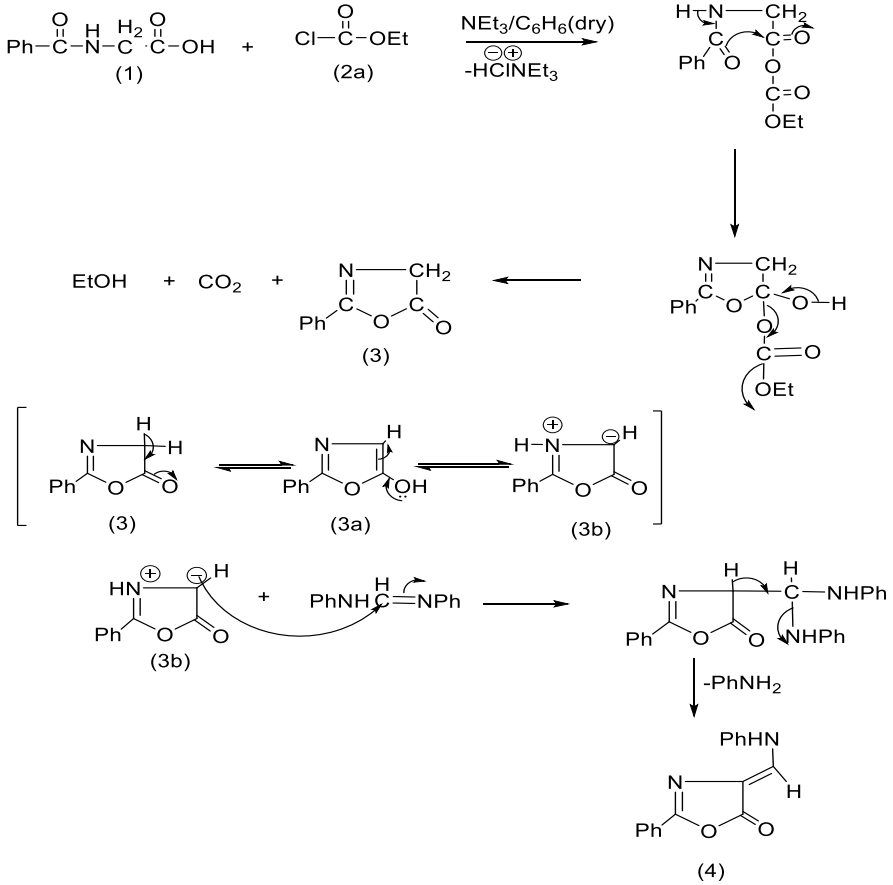

Figure-3: Mechanism for the formation of 4-Anilinomethylene-2-phenyl-2-oxazolin-5-one using ethyl chloroformate as cyclocondensing agent

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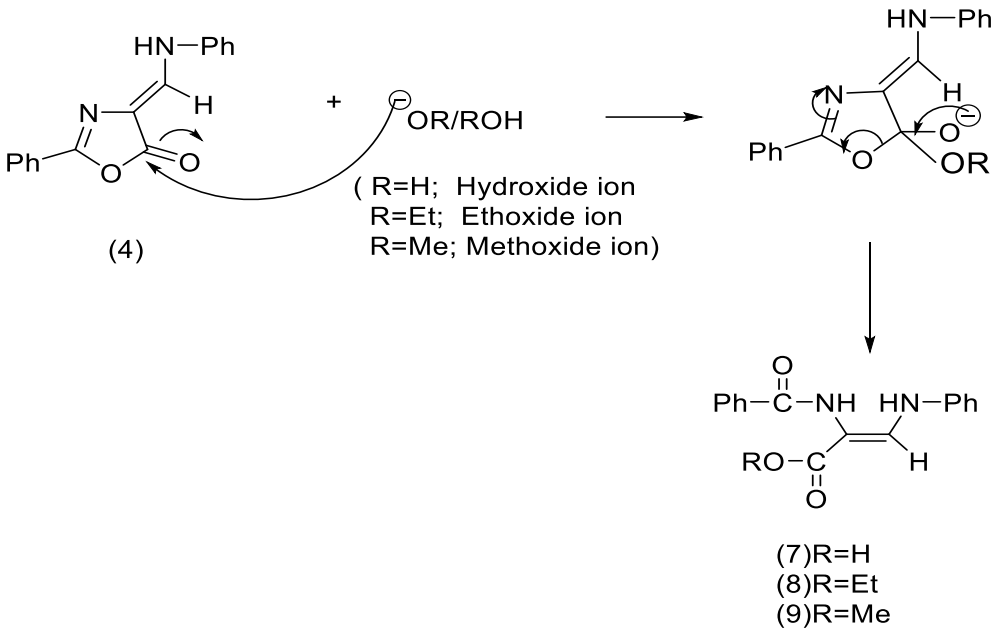

Figure-4: Mechanism for the formation solvolysis products through 1, 5-bond cleavage.

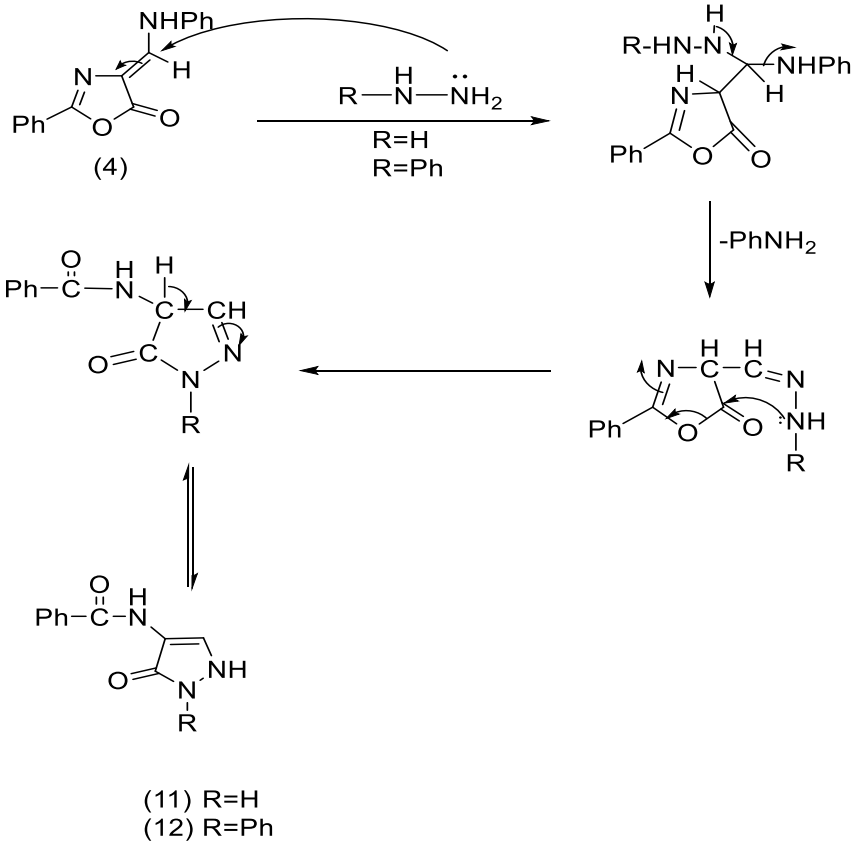

Figure-5: Mechanism for the formation Hydrazinolysis products through imine-enamine tautomerism followed by 1, 5-bond cleavage

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IV. CONCLUSION

Considering the easy availability of the starting materials, the speed of the reaction, the milder experimental conditions and simplicity of the work-up, the present eco-friendly method for the synthesis of 4-Anilinomethylene-2-phenyl-2-oxazolin-5-one (**4**) and its solvolysis and aminolysis products namely 3-Anilino-2-benzoylamino acrylic acid **(7),** Ethyl 3-anilino-2-benzoylamino acrylate **(8),** methyl 3-anilino-2-benzoylamino acrylate **(9),** 4-benzoylamino-3-pyrazolin-5-one **(11),** and 4-benzamido-1-phenyl-3-pyrazolin-5-one **(12)** appears to be useful in synthetic organic chemistry.

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