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Synthesis Of 5-Imidazolones From 2-Methyl-4-(4-Substituted Benzylidene)-5-Oxazolones

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ABSTRACT

In the proposed work 2-methyl-4-(4-substituted benzylidene)-5-oxazolones were prepared as starting materials in the synthesis of 5-imidazolones. 5-Oxazolones were obtained from acetyl glycine and substituted aromatic aldehydes in acetic anhydride and anhydrous sodium acetate.

In the second step, each of above mentioned oxazolones was subjected to condensation reaction with variedly substituted aromatic amines in presence of Zeolite as a catalyst in ethanolic medium to form 1-(substituted phenyl)-2-phenyl-4-(substituted benzylidene)-5-imidazolones. The characterisation of synthesized compounds was made on the basis of chemical properties, elemental and spectral analysis. The use of Zeolite as a catalyst enabled us to reduce reflux time substantially and to improve percent yield of the products.

Keywords: N-Acetyl glycine, Aromatic aldehydes, acetic anhydride,5-oxazolones, aromatic amines Zeolite catalyst, 5-imidazolones.

I. INTRODUCTION

Imidazolones contained nitrogen atoms in 1 and 3position and C=O group in 5-position. However, imidazolones containing C=O group in 2 or 4 position are also reported Patel et al[1] reported synthesis of 4-benzylidene-1-(substitued-2benzothiazolyl)-2-methyl-1H-imidazol-5(4H)-one from N acetyl glycine as a starting material. These compounds were tested for their antibacterial and antifungal activities. Saxena et al[2] synthesized new imidazolinone derivatives by the reaction of hydrazide with azalactone in dry pyridine. Lokhandwala and Parekh[3] synthesized imidazolones based azetidinone analogues and examined them for antimicrobial activity. Osman and coworkers[4] reported synthetic approaches and biological evaluation of new sulfonate ester containing imidazolone derivatives. Solankee et al[5] synthesized a series of 1-(5'-bromofuran-2'-carboxamido)-2-phenyl-4-(benzylidene/substitutedbenzylidene)-5- imidazolones. The compounds were evaluated for antibacterial activity. Siamaki et al[6] studied the palladium-catalyzed coupling of imines, chloroformates, organotin reagents, and carbon monoxide which led to the one pot formation of keto carbamates in good yields. These products could further be converted to highly substituted imidazolones via a cyclo condensation reaction. Joo Hi Kang et al[7] reported some 2-arylsubstituted imidazolones via chemo selective addition of cabon nucleophile on variedly substituted carbodiimides prepared from natural L-amino acids. Jure Benzensek et al[8] studied transformations of enaminones, a simple one-pot synthesis of imidazolone derivatives. Ethyl (5-benzoyl-2-oxo-3-substituted-2,3dihydro-1H-imidazol-1-yl) carbamates were prepared by the Michael addition of diethyl azodicarboxylate to -3-(dimethylamino)-1-phenylprop-2-en-1-one followed by substitution of the dimethylamino group with primary amines. Jie-Fei Cheng et al[9] carried out a traceless solid phase synthesis of 2-imidazolones. Polymer-bound glycerol resin was reacted with bromo acetaldehyde diethyl acetal to give the cyclic acetal bromide on the solid support. Srivastava et al[10] synthesized a new series of biologically active analogues of 5-imidazolones by condensing equimolar amount of substituted 5-oxazolinones and hetero cyclic primary amines at 140^0C. Anitha sadula and Shubhashini[11] synthesized novel chalcone linked arylidene imidazolones and found

them as potential antimicrobial and antioxidant agents. Bishnoi et al[12] reported reaction of hippuric acid and cyclohexanone using acetic anhydride which gave 2-phenyl-4-cyclohexylidene-1,3-oxazolo-5-one, which on condensation with amine gave imidazolones. Greenshaw and George[13] reported some novel 1-substituted-2-aryloxymethyl-4- (p-bis-b-cyanoethyl amino benzilidine) 5-imidazolones and screened for their HIV activity. Some new 1-substituted phenyl-2- (2'-chloro-5'-nitrophenyl)-4-(p-N:N-bis cyanoethyl-amino benzilidine)-5-imidazolone derivatives were synthesized and tested for their anticancer, anti AIDS and antibacterial activities. Fozooni et al[14] reported Synthesis of oxazolone and imidazolone derivatives in Presence of H_2O_2 Promoted fly ash as a novel and efficient catalyst. Revanasiddappa and coworkers[15] reported synthesis and biological evaluation of novel imidazolinone derivatives. A new series of Oxazolones was prepared by reacting substituted aromatic aldehydes with N-acetyl glycine in presence of anhydrous sodium acetate and acetic anhydride as the solvent medium.

After review of the literature, it appeared that most of the methods either required longer reflux time of about 8-10 hours or isolation and purification of the products became tedious. It was therefore thought worthwhile to carried out synthesis of imidazolones in a such manner as to reduce the reflux time and improve the yield of the products.

II. EXPERIMENTAL

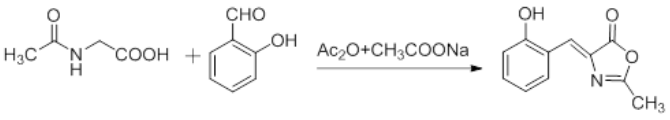
The work presented here involves preparation of 2-alkyl-4-(4-substituted arylidene)-5-oxazolones as a starting material. They were obtained from acetyl glycine by reaction with substituted aromatic aldehydes in acetic anhydride and anhydrous sodium acetate. In the second step, each of above mentioned oxazolones was subjected to condensation reaction with variedly substituted aromatic amines in presence of Zeolite as a catalyst in ethanolic medium to form 1-(substituted phenyl)-2-phenyl-4-(substituted benzylidene)-5-imidazolones. The characterisation of all the synthesized compounds was made on the basis of chemical properties, elemental and spectral analysis.

Scheme-1: Preparation of 2-methyl-4-(2-hydroxybenzylidene)-5-oxazolone.

2-Hydroxybenzaldehyde and acetylglycine was taken in equimolar (0.05mol) proportion and dissolved in acetic anhydride. To this solution, added 4.00gms of anhydrous sodium acetate. The reaction mixture was refluxed for two hours and kept overnight. The crystalline solid formed was washed with cold water-ethanol mixture and recrystallised from ethanol.

Yield :75% Melting point : 125^0C

REACTION :



(1a)

IR (KBr,cm-[1]) : 3379 (Ph-OH str); 3197 (Ar,C-H str); 2954 (Aliph,C-H str); 1751 (C=O str); 1658 (C=N str); 1523 (Ar,C=C str); 1248 (C-O str).

[1]H-NMR (DMSO, δ) : 2.50 (s,3H,-CH_3); 7.47-7.68 (m,4H,Ar-H); 8.57 (s,1H,Ph-CH); 9.79 (s,1H,Ph-OH).

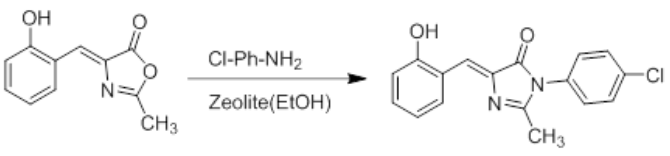
Table 1. Elemental Analysis for $C_{11}H_9NO_3$ (203.20)

Element(%)	C	H	N
Calculated	65.02	4.46	6.89
Found	65.00	4.42	6.85

Scheme 2 : Synthesis of 1-(4-chlorophenyl)-2-methyl-4-(2-hydroxybenzylidene)-5-imidazolone.

Equimolar mixture of 2-methyl-4-(2-hydroxybenzylidene)-5-oxazolone (0.005 mol) and 4-chloro aniline (0.005 mol) was dissolved in ethanol. One gram of Zeolite was added to this solution. The reaction mixture was refluxed for two and half hours. It was allowed to cool, acidified with dil HCl. An yellowish solid formed was washed 2-3 times with cold water and recrysatllised from etahnol.

Yield: 65% Melting point: 180^0C



(2a)

IR (KBr,cm-[1]) : 3332 (Ph, O-H str); 3074 (Ar, C-H str); 2927 (Aliph, C-H str); 1693 (C=O str); 1608(C=N str); 1535 (Ar,C=C str); 1246 (C-O str); 597 (C-Cl str)

^{1}H-NMR (DMSO) (δ) : 9.75 (s,1H,Ph-OH); 8.60 (s,1H,Ph-CH); 7.64-7.68 (t,2H,Ar-H); 7.28-7.51 (m,6H,Ar-H); 2.50 (s,3H,-CH_3)

Table 2. Elemental analysis for $C_{17}H_{13}ClN_2O_2$ (312.75)

Element(%)	C	H	N	Cl
Calculated	65.29	4.19	8.96	11.33
Found	65.20	4.16	8.92	11.30

III. RESULTS AND DISCUSSION

Thus eight variedly substituted 5-imidazolones were synthesized by the condensation of 2-methyl-4-(substituted benzylidene-5-oxazolones with 4-chloroaniline in presence of Zeolite as catalyst. The target compounds gave positive tests for Nitrogen, Chlorine and C=O group. The IR spectrum showed sharp bands at 3332 (Ph, O-H str); 3074 (Ar, C-H str); 1693 (C=O str); 1608 (C=N str) and 597 (C-Cl str). Similarly in ^{1}H-NMR spectrum, chemical shifts at 9.75 (s,1H,Ph-OH); 8.60 (s,1H,Ph-CH); 7.64-7.68 (t,2H,Ar-H); 7.28-7.51 (m,6H,Ar-H); 2.50 (s,3H,-CH_3) along with elemental analysis confirmed the formation of (2a). The synthesized compounds along with their percent yield and melting points are given in the following table.

Table 3. List of synthesized compounds along with their % yield and melting point

Sr. No	Compound	Percent Yield (%)	Melting point (°C)
1	1-(4-chlorophenyl)-2-methyl-4-(2-hydroxybenzylidene)-5-imidazolone	61	123
2	1-(4-chlorophenyl)-2-methyl-4-(4-nitrobenzylidene)-5-imidazolone	65	145
3	1-(4-chlorophenyl)-2-methyl-4-(4-hydroxybenzylidene)-5-imidazolone	68	105
4	1-(4-chlorophenyl)-2-methyl-4-(3,4,5-trimethoxybenzylidene)-5-imidazolone	58	118
5	1-(4-chlorophenyl)-2-methyl-4-(4-chlorobenzylidene)-5-imidazolone	63	155
6	1-(4-chlorophenyl)-2-methyl-4-(4-hydroxy-3-methoxybenzylidene)-5-imidazolone	69	150
7	1-(4-chlorophenyl)-2-methyl-4-(benzylidene)-5-imidazolone	70	148
8	1-(4-chlorophenyl)-2-methyl-4-(4-methoxybenzylidene)-5-imidazolone	66	160

IV. CONCLUSION

Hence the use of Zeolite as a catalyst in the synthesis of 5-imidazolones enabled us the rapid synthetic route. The products could be formed in as low as two and half hours. Moreover, the percent yield of the products was also increased . This could probably be attributed to the porous nature of Zeolite which causes rapid dehydration during the condensation reaction and consequent absorption of water in the pores of Zeolite catalyst. This results in the rapid conversion of reactants to products. Another advantage of it is that it is insoluble in solvent and does not interfere the reaction due to which isolation of the products became much easy.

V. REFERENCES

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