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An Efficient Synthesis of Nitrogen Heterocarbaldehydes Synthon by Remodel Reimer-Tiemann Reaction

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Abstract : A series of Nitrogen heterocarbaldehydes were synthesized from Nitrogen heterocycles by remodel Reimer-Tiemann reaction. The remarkable advantages of this method is, short time reaction, simple workup procedure, avoid steam distillation, and excellent yield of the products. All the synthesized Nitrogen heterocarbaldehydes were checked purity by TLC and spectral analysisIR, ^{1}H NMR& Mass.
Keywords : Nitrogen heterocycles, nitrogen heterocarbaldehydes, Remodel Reimer-Tiemann reaction.

Introduction:

An environmentally friendly chemical process is the vital part of the current chemical research and development[1].Syntheses of o-hydroxybenzaldehydes are made from corresponding phenol by Reimer–Tiemann Reaction[2-3]. A continuous part of our research work devoted to development of different methodologies in organic chemistry[4-7].Heterocycles form by far the largest of classical divisions of organic chemistry and are of immense importance biologically and industrially. The majority of pharmaceuticals and biologically active agrochemicals are heterocyclic while countless additives and modifiers used in industrial applications ranging from cosmetics, reprography, information storage and plastics are heterocyclic in nature[8]. Nitrogen and oxygen containing heterocycles are one of the most extensively synthesized and screened compounds as they show diverse pharmacological activities[9].

Especially, nitrogen containing heterocyclic moieties plays a vital role in discovering novel candidates having antimicrobial potentials[10].The quinoline ring system is an important structural unit in naturally occurring quinoline alkaloids, therapeutics and synthetic analogous with interesting biological activities[11].Quinoline family compounds are widely used as a parent compounds to make drugs especially antimalerial medicine, fungicides, biocides, alkaloids, dyes, rubber, chemicals, falvouring agents, antiseptic and antipyretic[12].Quinoline derivatives have also been reported as anti-inflammatoy[13], antiviral[14], antitumor[15].

Therefore we reported here a general and efficient protocol is described for the synthesis of nitrogen heterocarbaldehydes by formylation of heterocycles using chloroform, sodium hydroxide and aq. alcohol with very shorter reaction times and higher yields by remodel Reimer-Tiemann reaction.

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Experimental:

All chemicals that used in this work were of analytical reagent grade from Sdfine, Merck and Qualigens with high grade of purification.All the melting points were determined in open capillaries are uncorrected. The purity of compounds were checked by TLC on silica gel 'G' coated glass plates. IR spectra were recorded with KBr on a Schimdzu FT-IR 8300 spectrophotometer, ^{1}HNMR spectra in $CDCl_3$ on a Perkin Elmer R-32 using TMS as an internal standard.Mass Spectra was taken with Shimadzu GCMS-QP2010 Ultra (semi chemical ionization) with 5-20evionization energy.

General Procedure For 2-Methyl Indole 3- Carbaldehyde:

2-Methyl Indole [0.1mol, 15.9gm] and sodium hydroxide [7.8gm in 29ml water and 12ml ethyl alcohol v/v] was taken in 500 ml three-necked round bottom-flask. The flask was mounted over mercury sealed mechanical stirrer, fitted with reflux condenser and separating funnel. Then the flask was heated on water bath up to 60^{0}C. Chloroform [0.25mol,20.07ml] taken in a separating funnel was added within 45 minutes slowly in a way that refluxing continue. After completion of the addition of chloroform, reaction mixture was heated further for 1hour. At55-60^{0}C and then cooled to15-20^{0}c for 1hour. Solid separates outs,was washed with proper solvents and dissolved in minimum amount of water and acidified with very little amount of dil. HCl. The product separates out. Separated solid was recrystallized from methyl alcohol.

Other nitrogen heterocarbaldehydessynthon were prepared by the same method withphysical and analytical data was given in (Table-1)

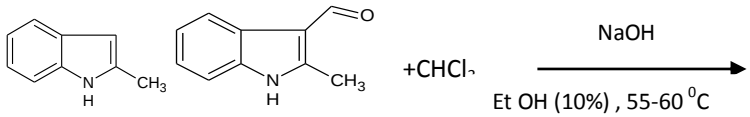
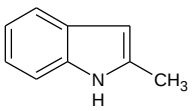
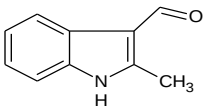
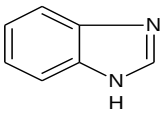
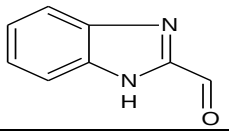
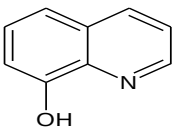
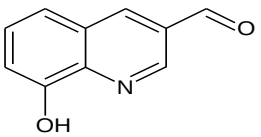
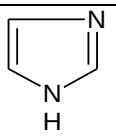
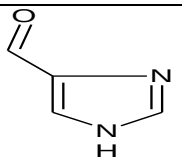
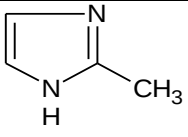
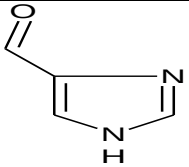
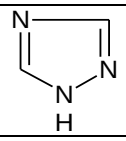
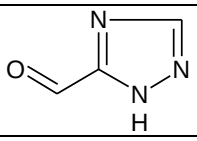
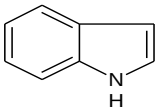
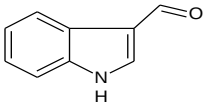
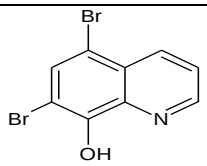
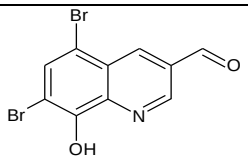
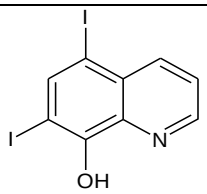
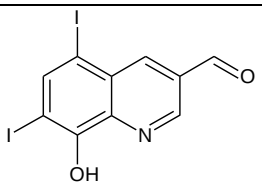


Table 1. Physical Data And Analytical Data:

Sr. No	Substrate	Product	M.P. (^{0}C)		Yield(%)
			Reported	Found	
1			200-201	205	58
2			224	219	51
3			210	207	54
4			174-177	171	54
5			165	162	58

6			—	169	47
7			193-198	193	62
8			—	189	55
9			—	194	52

Result and Discussion:

Synthesis of Heterocarbaldehyde was made from corresponding heterocycles by Remodel Reimer-Riemann reaction in solvent water:ethyl alcohol [90:10 v/v] instead of water dissolving hydroxide. After completion of the heating of the reaction as above reaction mixtures was cooled at 15-20^{0}C for 1hours, Solid Separates out. Separated solid was filtered and washed with proper solvent for 2-3times. Further solid was dissolved in minimum amount of water and resulting solution was acidified with very little amount of dil. acid. Nine heterocarbaldehydes were prepared by this procedure. The structure of the products was confirmed by IR, ^{1}HNMR, Mass and by comparing their melting points with those of samples prepared by known literature value.

The remodel procedure for synthesis of heterocarbaldehydes have remarkable advantages are, The procedure is very simple, isolation of products is very easy and gets 100% pure product, no need of further purification, Steam distillation is avoided, time as well as heat energy can be saved and obtained excellent yields.

Spectral Analysis:

1) **2-Methyl indole 3- Carbaldehyde:**
   IR (KBr): ν (cm-^{1}) 1765, 2620,3387;**^{1}H-NMR** δ=7.4-7.36(d, 1H),7.26-7.23(d, 1H),6.99-6.87(m, 2H),10.88(s, 1H, CHO), 12.48 (s,N-NH).2.36 (s,3H)
   Mass (m/z):299,287,274,257,250,249,234,180,145,78,44.
2) **Benzimidazole 2- Carbaldehyde :**
   IR (KBr): ν (cm-^{1}) 1770, 2620,3418 ;**^{1}H-NMR** δ=8.4(d, 1H),8.38(d, 1H),7.64-7.61(m, 1H),9.7(s, 1H, CHO), 13.08 (s,N-NH)
   Mass(m/z):192,193,186,160,148,146,147,78,44.
3) **8-hydroxy quinoline-3- Carbaldehyde :**
   IR (KBr): ν (cm-^{1}) 1658, 2620,3418 ;**^{1}H-NMR** δ=8.78(s, 1H),7.9(s, 1H),7.71(d, 1H),7.75(d, 1H), 7.53 (t,1H),10.23(s,CHO),4.4 (s,-OH)
   Mass (m/z):173,153,106,80,44
4) **Imidazole 4-Carbaldehyde:**
   IR (KBr): ν (cm-^{1}) 1759, 2731,3422; **^{1}H NMR** δ 8.0-7.9 (d ,2H), 13.0(s ,-NH) ,9.7(s, 1H,CHO) **Mass (m/z):**256,233,220,129,119,111,102,97,44.
5) **2-Methyl-1*H*-Imidazole 4-Carbaldehyde:**
   IR (KBr): ν (cm-^{1}) 1759, 2731,3422; **^{1}H NMR** δ 2.39 (s ,3H), 7.58 (s ,1H) ,9.5(s, 1H,CHO).**Mass (m/z):**110,102,79,44.

6) 1,2,4 Triazole -5-Carbaldehyde:
IR (KBr): ν (cm-^{1}) 1759, 2731,3422; **^{1}H NMR** δ 8.2 (s ,1H), 9.9 (s ,1H,CHO)
Mass(m/z):97,82,60,44.

7) **Indole 3-Carbaldehyde:**
IR (KBr): ν (cm-^{1}) 1707, 2729,2932,3422; **^{1}H NMR** δ 8.3 (s ,1H),8.21-8.14 (d ,1H),7.55-7.52,7.5-7.2 (m ,2H) ,13.0 (s ,-NH) ,9.6(s, 1H,CHO) **Mass(m/z):**145,102,98,57,44.

8) 5,7 dibromo 8-hydroxy quinoline-3-Carbaldehyde
IR (KBr): ν (cm-^{1}) 1707, 2729,2932,3422; **^{1}H NMR** δ 8.91 (s ,1H),7.8(s ,1H), 10.48 (s ,1H) ,7.7 (s ,1H) ,4.6(s,-OH)**Mass (m/z):**346,297,158,123,79,44.

9) 5,7 dibromo 8-hydroxy quinoline-3-Carbaldehyde
IR (KBr): ν (cm-^{1}) 1707, 2729,2932,3422; **^{1}H NMR** δ 8.9 (s ,1H),7.8 (s ,1H), 10.49 (s ,1H) ,7.7 (s ,1H) ,4.52(s,-OH)**Mass(m/z) :**440,396,346,297,158,123,79,44.

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