Ain Shams University
Faculty of Education
Department of Chemistry

Using Pyranoquinoline in Synthesis of Some Novel Quinoline Derivatives

A Thesis Submitted
By

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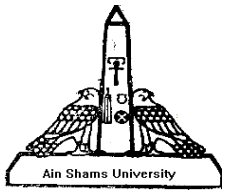

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Approval Sheet

Using Pyranoquinoline in Synthesis of Some Novel Quinoline Derivatives

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first of all, gratituted and
thanks come from all
my deep heart to
Allah
This work is dedicated to
my lovely father,
my lovely mother,
my lovely husband,
my pretty sister,
my lovely brother,
my lovely smart kid
(nour el-din)

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Al-Shimaa Badran Abdel-Monem

Contents

Table of Abbreviations

Abbreviation	*Expression*
Ar	*Aromatic or aryl group*
Ac_2O	*Acetic anhydride*
AIBN	*2,2-diazobisisobutyronitrile*
aq.	*Aqueous*
^oC	*Celsius*
^{13}C NMR	*Carbon-13 nuclear magnetic resonance*
D_2O	*Deuterated* water
DMF	*Dimethylformamide*
DMF-DMA	*Dimethylformamide-dimethylacetal*
DMSO	*Dimethylsulfoxide*
DMSO-d_6	*Hexadeuteriodimethylsulfoxide*
en gl	*Ethylene glycol*
eV	*electron Volt*
G	*gram (mass unit = 0.001 Kg)*
^1H NMR	*Proton nuclear magnetic resonance*
h	*Hour*
IR	*Infrared spectrum*
I_r %	*Intensity ratio (relative to base peak ion)*
$Yb(OTF)_3$	Ytterbium trifloromethanesulfonate
TBAB	Tetrabutylammonium bromide
DBU	1,8-Diazabicyclo[5.4.0]undec-7-ene
J	*Coupling constant (Hz) in NMR measurements*
L-proline	*Pyrrolidine-3-carboxylic acid*
M	*Molar (Molarity)*

Abbreviation	*Expression*
m.p. (T_m)	*Melting Point*
MW	*Microwave assisted process*
M.Wt.	*Molecular weight*
m/z	*Mass to electron charge ratio*
mL	*Milli-liter*
MHz	*Mega Hertz*
□	Gama
MS	*Mass spectrum*
α	Alpha
PPA	*Polyphosphoric acid*
PTC	*Phase transfer catalysis*
rt	Room temperature
TBAB	*Tetrabutylammonium bromide*
TEA	*Triethylamine*
Triflate	*Trifluoromethanesulfonate*
TMS	*Tetramethylsilane*
p-TsOH	*p-Toluenesulfoni*c acid
Δ	*Heat*
δ	*Chemical shift*

Aim of the work

The present work aims to:

1. Synthesize 6-ethyl-4,5-dioxo-5,6-dihydro-4*H*-pyrano[3,2-*c*]quinoline-3-carboxaldehyde (**4**) and utilize this compound as the starating material.
2. Prepare some new pyrazolylquinlinone derivatives *via* treatment of aldehyde **4** with some hydrazine derivatives.
3. Investigate the chemical reactivity of aldehyde **4** towards different nucleophilic reagents.
4. Synthesize new heterocyclic compounds, containing both quinolinone and other heterocycles in one molecular frame, of expected biological activity.
5. Study of spectral properties of different newly prepared quinolinone products.

Abstract

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6-Ethyl-4,5-dioxo-5,6-dihydro-4*H*-pyrano[3,2-*c*]quinoline-3-carboxaldehyde (**4**) was synthesized and efficiently utilized as a good precursor to obtain variety of novel pyrano[3,2-*c*]quinolinediones and 4-hydroxyquinolin-2(1*H*)-ones bearing variable heterocyclic systems. The chemical behavior of aldehyde **4** was studied towards some carbon nucleophiles, namely cyanoacetic acid, malonic acid, malononitrile, ethyl cyanoacetate, cyanoacetamide, malononitrile dimer, 3-methyl-1-phenyl-2-pyrazolin-5-one, 1,3-thiazolidine-2,4-dione, thiobarbituric acid, cyclohexane-1,3-dione and dimedone. The reactivity of aldehyde **4** towards some amines and hydrazine derivatives was studied. The reaction of aldehyde **4** with hydroxylamine hydrochloride was carried out, under different conditions, leading to different product. Treatment of aldehyde **4** with some 1,2-, 1,3-, and 1,4-binucleophiles led to certain interesting five, six, and seven-membered heterocyclic substituents, viz. pyrazole, pyrimidine and diazepine. Structures of the synthesized products have been deduced on the basis of thier elemental and spectral analyses.

Keywords: pyrano[3,2-*c*]quinoline, Vilsmeier-Haack reaction, , ring-opening/ring-closure, nucleophilic reaction, heterocyclization.

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