



Ain Shams University
Faculty of Education
Department of Chemistry

Reactions of some substituted pyrano[3,2-c]quinolinediones

Thesis Submitted

By

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In

Partial Fulfillment

Of The Requirements of Master

For The Teacher's Preparation In Science

(Organic Chemistry)

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بِسْمِ اللَّهِ الرَّحْمَنِ الرَّحِيمِ



صدق الله العظيم

Dedication

To

my father,

my mother,

my sisters,

and my brothers

Theoretical courses which were studied by the student

1. General Diploma for The Teacher's Preparation in Science Courses (Chemistry)

Organic Chemistry 1:

- (A) Natural Products
- (B) Polymer Chemistry

Organic Chemistry 2:

- (A) Reaction Mechanism
- (B) Stereochemistry

Physical Chemistry 1:

- (A) Catalysis Chemistry
- (B) Electrochemistry

Physical Chemistry 2:

- Quantum Chemistry

Inorganic Chemistry 1:

- Polarography

Inorganic Chemistry 2:

- Organometallic Compounds

Inorganic Chemistry 3:

- Solutions

Inorganic Chemistry 4:

- Metal Chelates

Educational course 1

Educational course 2

English Language

2. Special Diploma for The teacher's Preparation in Science Courses (Organic Chemistry)

Organic Chemistry 1:

- Spectroscopy I: IR, UV and Mass Spectrometry

Organic Chemistry 2:

- Spectroscopy II: NMR Spectrometry

Organic Chemistry 3:

- Heterocyclic Chemistry

Organic Chemistry 4:

Selected Topics: Aromaticity, Delocalized Chemical bonding, and Aromatic Nucleophilic Substitution

Organic Chemistry 5:

Stereochemistry
Organic Chemistry 6:

Organic Reactions
Organic Chemistry 7:

Free Radicals Reactions
Organic Chemistry 8:

(A) Sulfur and Phosphorous

(B) Organic Analytical Chemistry

Organic Chemistry 9:

Review Article
Educational course 1
Educational course 2
English Language

3. Master for The Teacher's Preparation in Science Courses (Organic Chemistry)

Organic Chemistry 1:

Physico-organic Chemistry

Organic Chemistry 2:

(A) Microanalysis

(B) Modern Organic Synthesis

Organic Chemistry 3:

Advanced Organic Spectroscopy

Organic Chemistry 4:

Pericyclic Reactions
Educational course 1
Educational course 2
Language competence
English Language



Ain Shams University
Faculty of Education
Department of Chemistry

Approval Sheet

Reactions of some substituted pyrano[3,2-*c*]quinolinediones

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Higher studies:

The thesis was approved

Approval date / / 2013

Approved by Council of Faculty

Approved by Council of University

Date / / 2013

Date / / 2013

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Aim of the work

The present thesis aims to:

1. Synthesis of the novel 3-nitropyrano[3,2-*c*]quinoline-4,5-dione which will be used as the starting material.
2. Synthesis of pyrazolylquinolinones by treatment of 3-nitropyrano[3,2-*c*]quinoline-4,5-dione with some hydrazines.
3. Reaction of 3-nitropyrano[3,2-*c*]quinoline-4,5-dione with some 1,3-diaza-nucleophiles.
4. Preparation of diazepinyl and thiazepinylquinolinone derivatives by the reaction of 3-nitropyrano[3,2-*c*]quinoline-4,5-dione with *o*-phenylenediamine and *o*-aminothiophenol.
5. Study the chemical behaviour of 3-nitropyrano[3,2-*c*]quinoline-4,5-dione towards some C-nucleophiles.
6. Reaction of 3-nitropyrano[3,2-*c*]quinoline-2,5-dione with some 1,2-binucleophiles.
7. Study the chemical reactivity of 3-nitropyrano[3,2-*c*]quinoline-2,5-dione towards some 1,3-binucleophilic reagents.
8. Synthesis of diazepinyl and thiazepinylquinolinones by the reaction of 3-nitropyrano[3,2-*c*]quinoline-2,5-dione with some 1,4- binucleophiles.
9. Reaction of 3-nitropyrano[3,2-*c*]quinoline-2,5-dione with malononitrile and ethyl cyanoacetate, as C-nucleophiles.

Abstract

Reactions of Some Substituted Pyrano[3,2-*c*]quinolinediones

Dalia Abdel-Kader Abbass Elshobary

Department of Chemistry, Faculty of Education, Ain Shams University

6-Ethyl-3-nitropyrano[3,2-*c*]quinoline-4,5(6*H*)-dione (**4**) was synthesized and its reactivity towards some 1,2-, 1,3-, and 1,4-binucleophiles was investigated. Ring transformation via opening of the γ -pyrone ring and heterocyclizations throughout these reactions led to certain interesting five, six, and seven-membered heterocyclic substituents, viz. pyrazolyl, pyrimidyl, diazepinyl, and thiazepinyl at position-3 of quinolin-2-one moiety. Treatment of pyranoquinolinedione **4** with carbon nucleophiles, namely malononitrile and ethyl cyanoacetate, was also studied. Moreover nucleophilic reactions of 6-ethyl-3-nitropyrano[3,2-*c*]quinoline-2,5(6*H*)-dione (**2**) with some binucleophiles were described. These reactions led to several new quinolinones bearing pyrazole, pyrimidine, diazepine, and thiazepine. Furthermore, reactions of pyranoquinolinedione **2** with some carbon nucleophiles were investigated affording quinolinones bearing pyridine.

Keywords: Pyranoquinolinedione, pyrazole, ring-opening/ring-closure, benzodiazepines, pyridine, pyrimidine.

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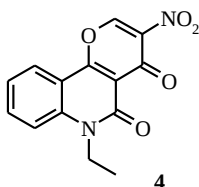
Prof. Dr. Mohamed Abass Mohamed Abdel-Rahman

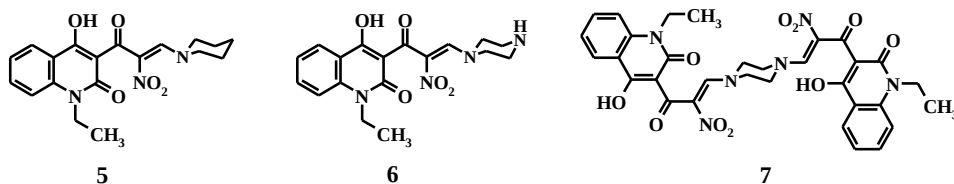
Professor of Organic Chemistry, Faculty of Education, Ain Shams University.

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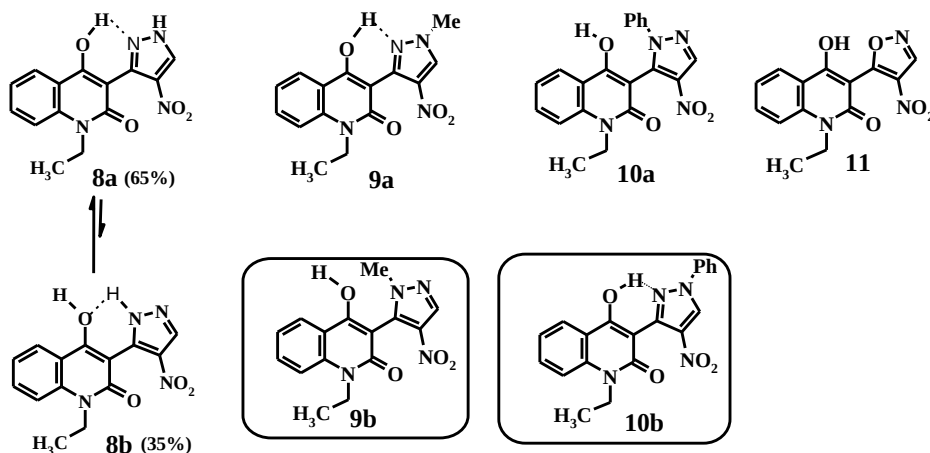
Lecturer of Organic Chemistry, Faculty of Education, Ain Shams University.

Summary of Original Work

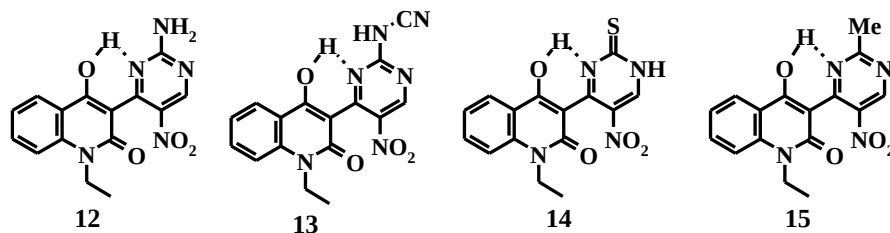




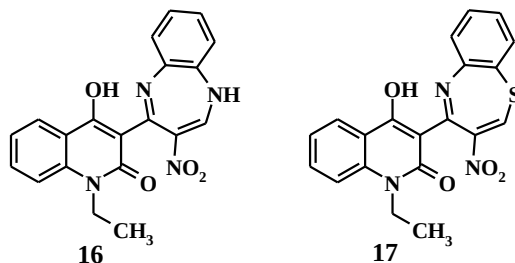
Compound **4** was subjected to react with 1,2-binucleophiles. Thus treatment of compound **4** with hydrazine hydrate, under reflux in DMF, afforded 3-nitropyrazolylquinolinone **8**. pyrazole **8** exists as a mixture of tautomers **8a** and **8b** (65:35). Reaction of compound **4** with methylhydrazine, in DMF, afforded 3-(1-methyl-4-nitropyrazol-3-yl)quinolinone **9**. Treatment of compound **4** with phenylhydrazine afforded the 3-(1-phenyl-4-nitropyrazol-5-yl)quinolinone **10**. Treatment of the 3-nitropyranquinoline-4,5-dione **4** with hydroxylamine hydrochloride, in pyridine, gave 3-(isoxazol-5-yl)quinolinone derivative **11**.



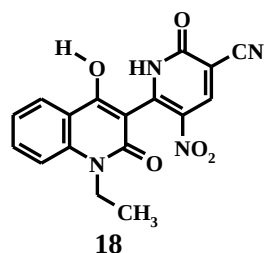
Also, the compound **4** was allowed to react with some 1,3-binucleophilic reagents in order to prepare 4-hydroxyquinolinones bearing pyrimidine moiety. Treatment of compound **4** with guanidine hydrochloride, in boiling DMF, caused γ -pyrone ring-opening followed by ring-closing (RORC) with loss of H₂O, to give the 3-(2-aminopyrimid-4-yl)quinolinone **12**. Reaction of compound **4** with cyanoguanidine afforded the 3-(2-cyanoaminopyrimid-4-yl)quinolinone **13**. The reaction of the compound **4** with thiourea, in DMF, afforded the 3-(2-thioxopyrimid-4-yl)quinolinone **14**. Treatment of the compound **4** with acetamidine, in DMF, afforded the 3-(2-methylpyrimid-4-yl)quinolinone derivative **15**.



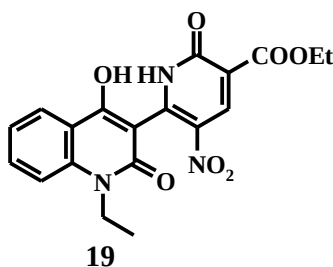
In continuation to this study, the reactivity of the compound **4** towards 1,4-binucleophiles, such as *o*-phenyldiamine and *o*-aminothiophenol was investigated. The reaction was carried out in boiling DMF giving rise to the corresponding 1,5-benzodiazepine **16** and 1,5-benzothiazepine **17**.



Reaction of the γ -pyrones with carbon nucleophiles was studied. Thus, treatment of the compound **4** with malononitrile, in DMF containing anhydrous potassium carbonate, gave 3-(pyrid-2-yl)quinolinone derivative **18**. Moreover, the compound **18** received chemical elucidation by reaction of 3-nitropyran[3,2-*c*]quinoline-4,5-dione **4** with cyanoacetamide.



Similarly, reaction of the compound **4** with ethylcyanoacetate, in DMF containing anhydrous potassium carbonate, afforded the ester derivative **19**.



Reaction of the compound **4** with cyanoacetohydrazide as a 1,4-C,N-dinucleophile was carried out, in refluxing DMF containing catalytic amount of triethylamine to give quinolinyl[1,2]diazepinone **21**.

