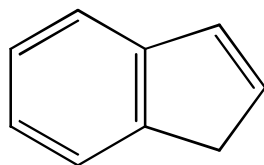
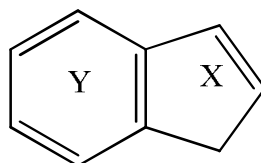


d) Azaindenes :



indene

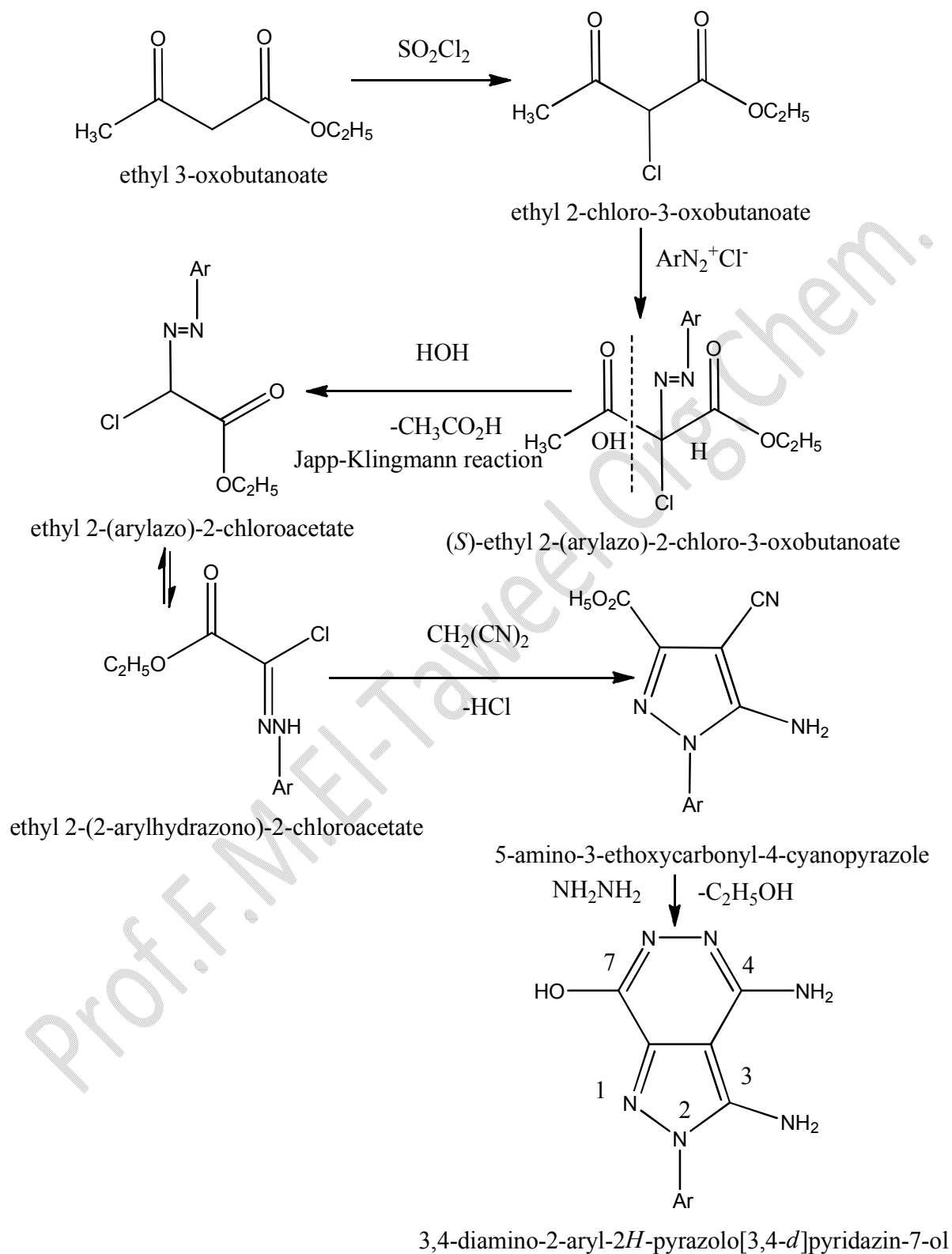


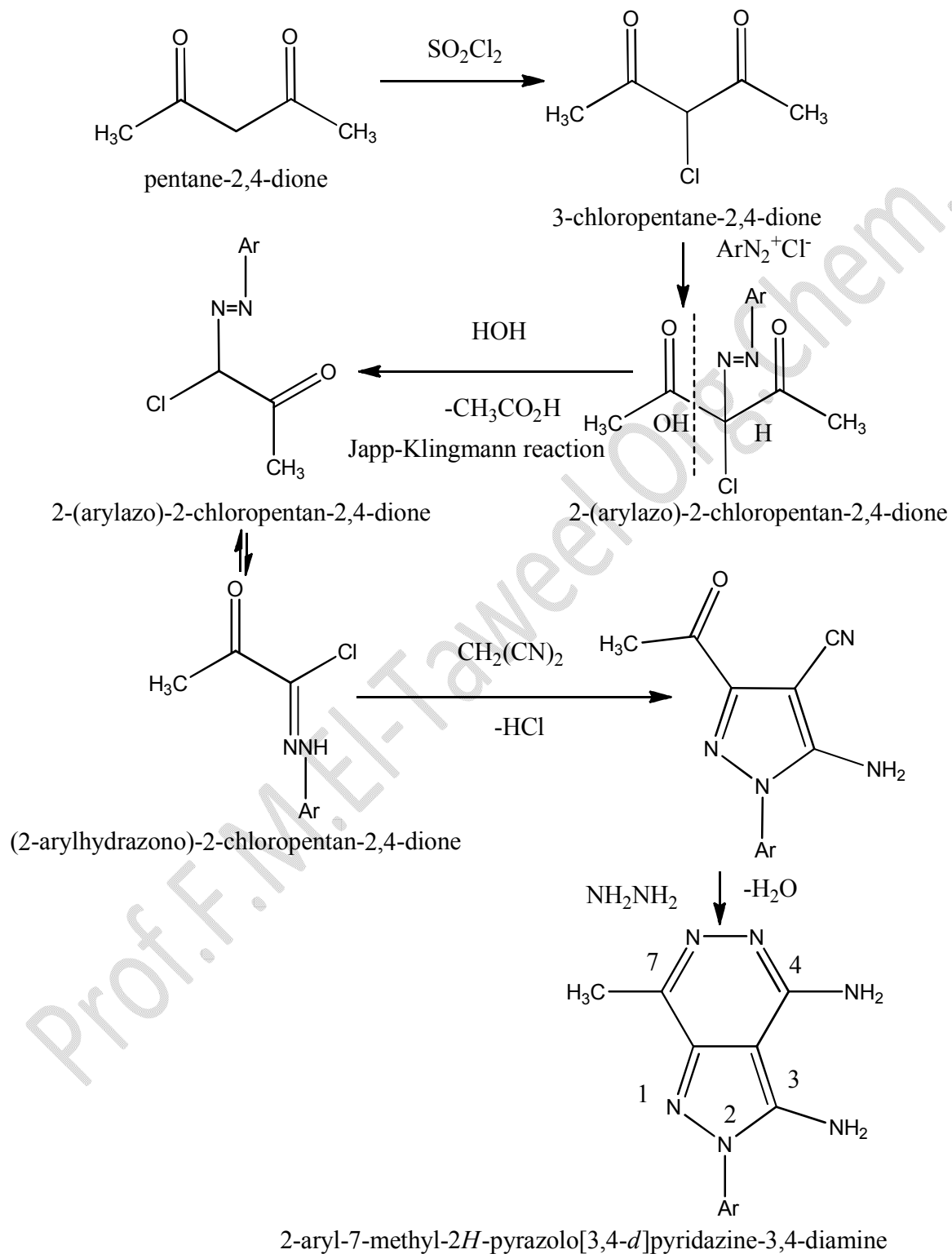
azaindenes where X, Y are heteroatoms N, O, S

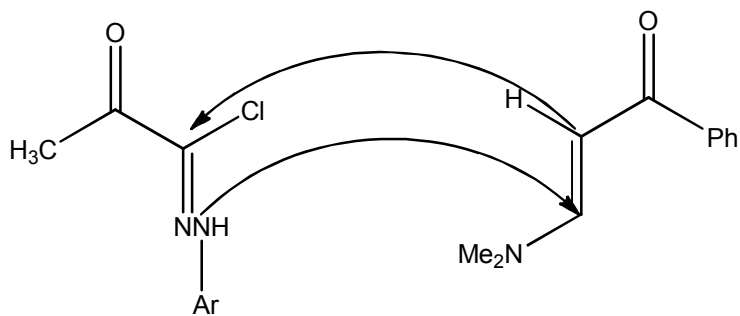
Synthesis and reactions of fused pyrazoles

Synthesis from 1,3-(β -)dicarbonyl compounds :

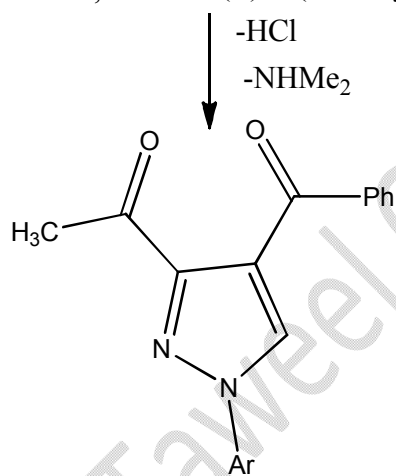
1-By formation of hydrazone halides from 1,3-(β -)dicarbonyl compounds (β -diketones or β -ketoesters) ,followed by condensation of hydrazone halides with active methylene reagents or enaminones.



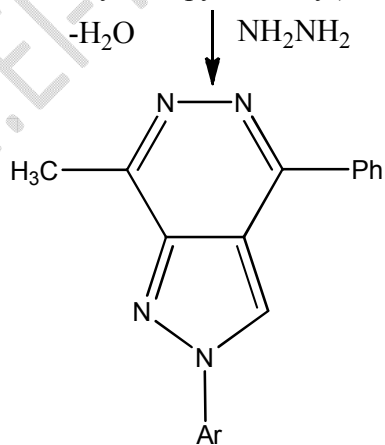




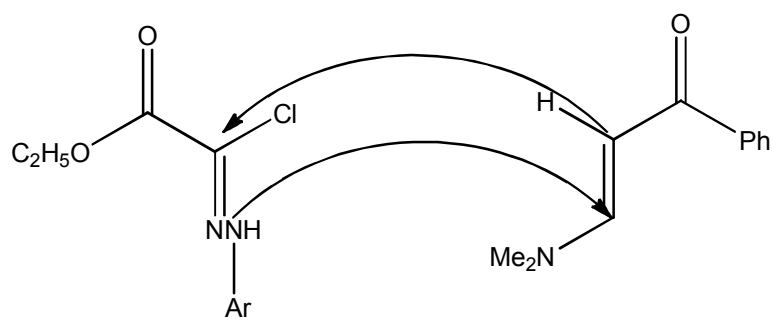
(2-arylhydrazono)-2-chloropentan-2,4-dione (*E*)-3-(dimethylamino)-1-phenylprop-2-en-1-one



1-(1-aryl-4-benzoyl-1*H*-pyrazol-3-yl)ethanone

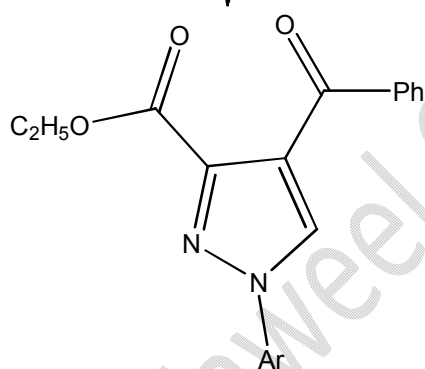
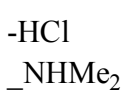


2-aryl-7-methyl-4-phenyl-2*H*-pyrazolo[3,4-*d*]pyridazine

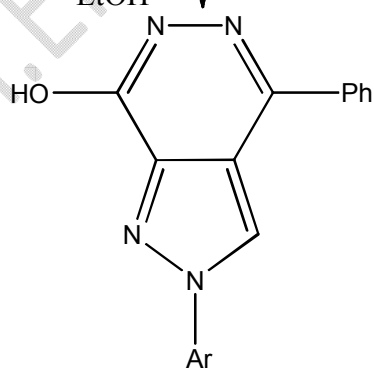
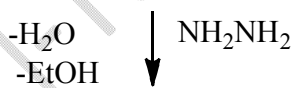


ethyl (2-aryldiazeno)-2-chloroacetate

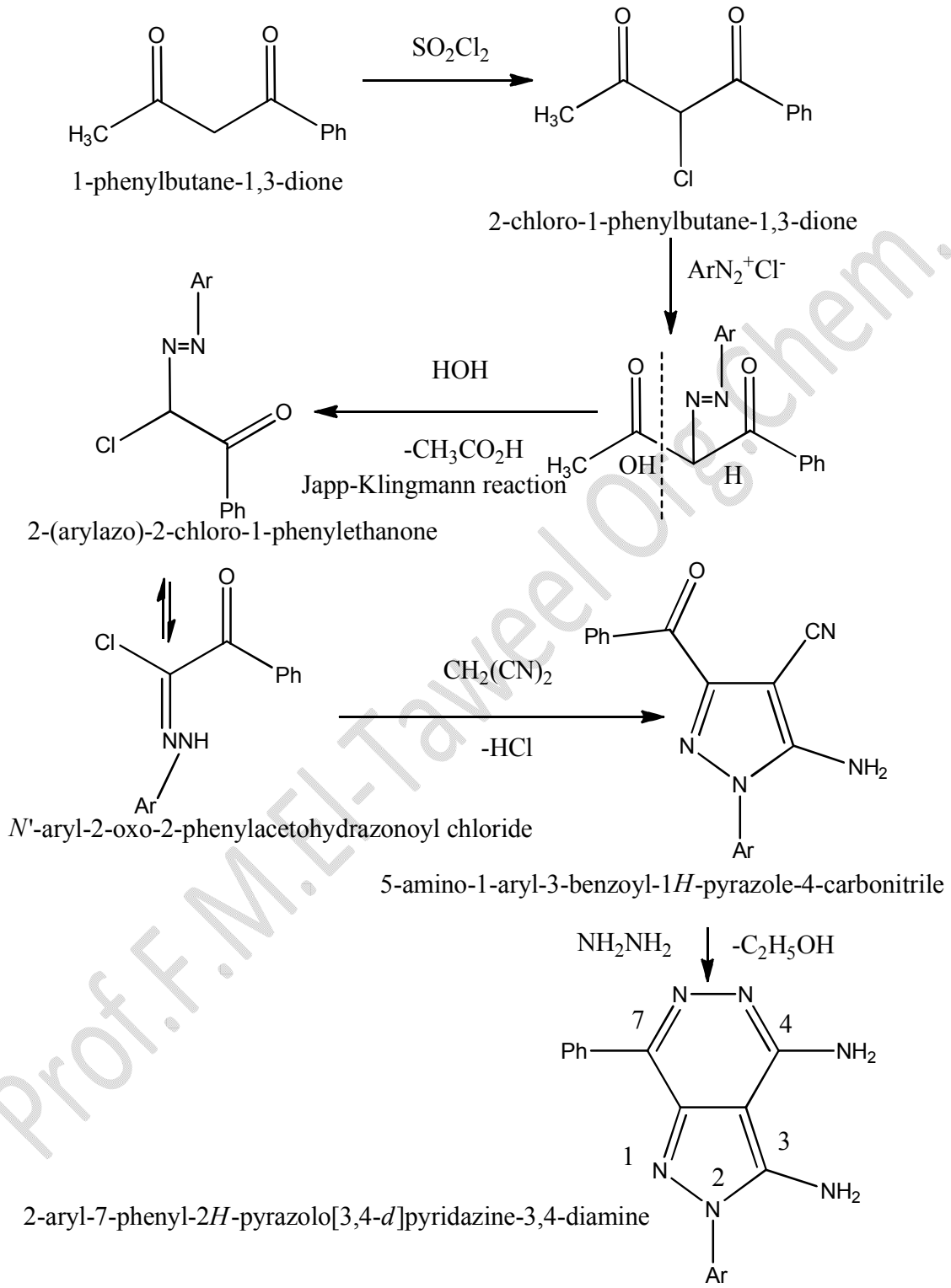
(*E*)-3-(dimethylamino)-1-phenylprop-2-en-1-one

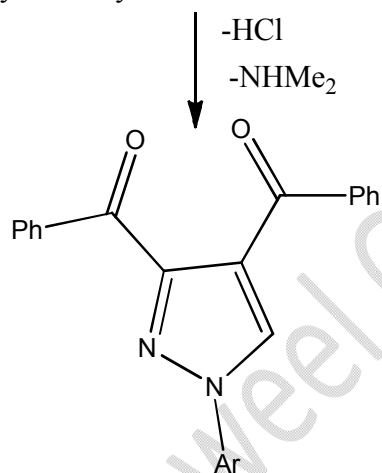
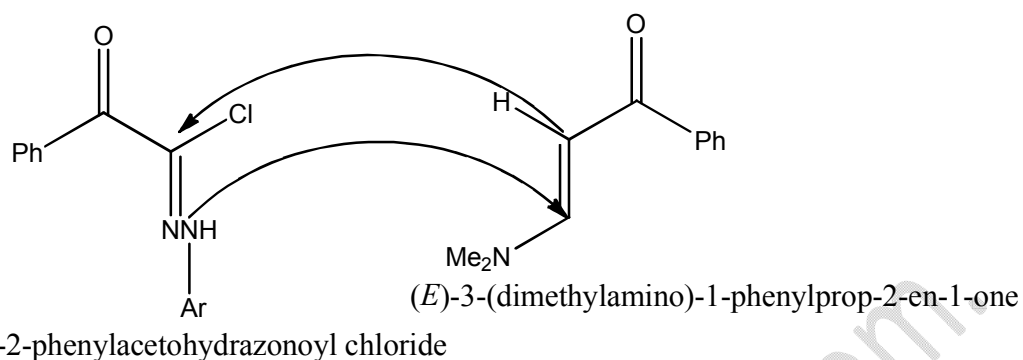


ethyl 1-aryl-4-benzoyl-1*H*-pyrazole-3-carboxylate

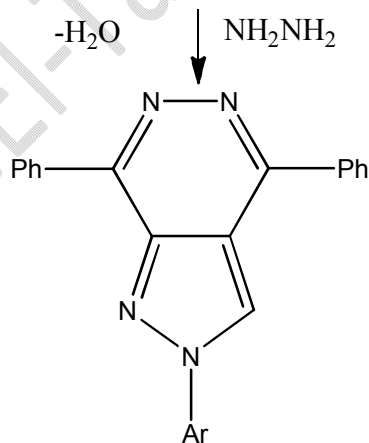


2-aryl-7-methyl-4-phenyl-2*H*-pyrazolo[3,4-*d*]pyridazine





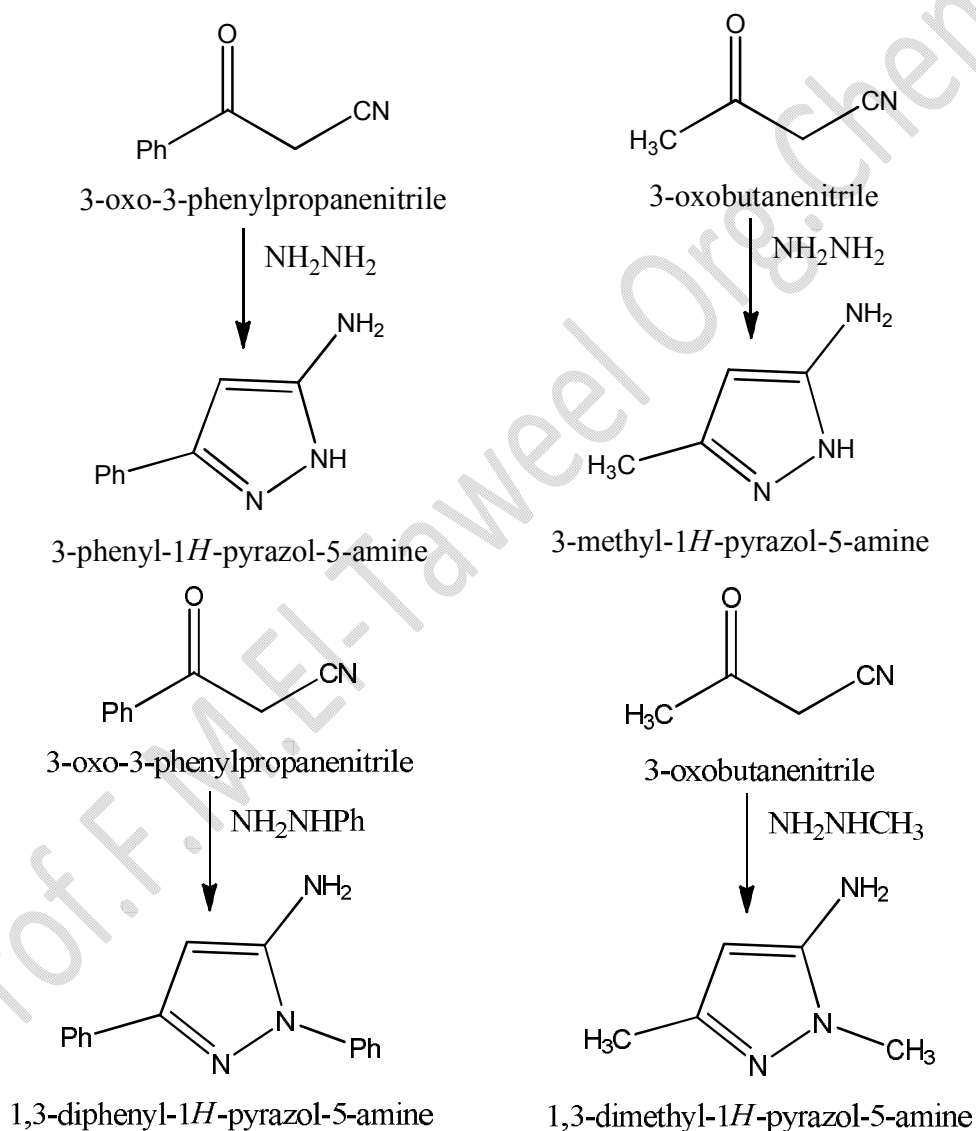
(1-aryl-1*H*-pyrazole-3,4-diyl)bis(phenylmethanone)

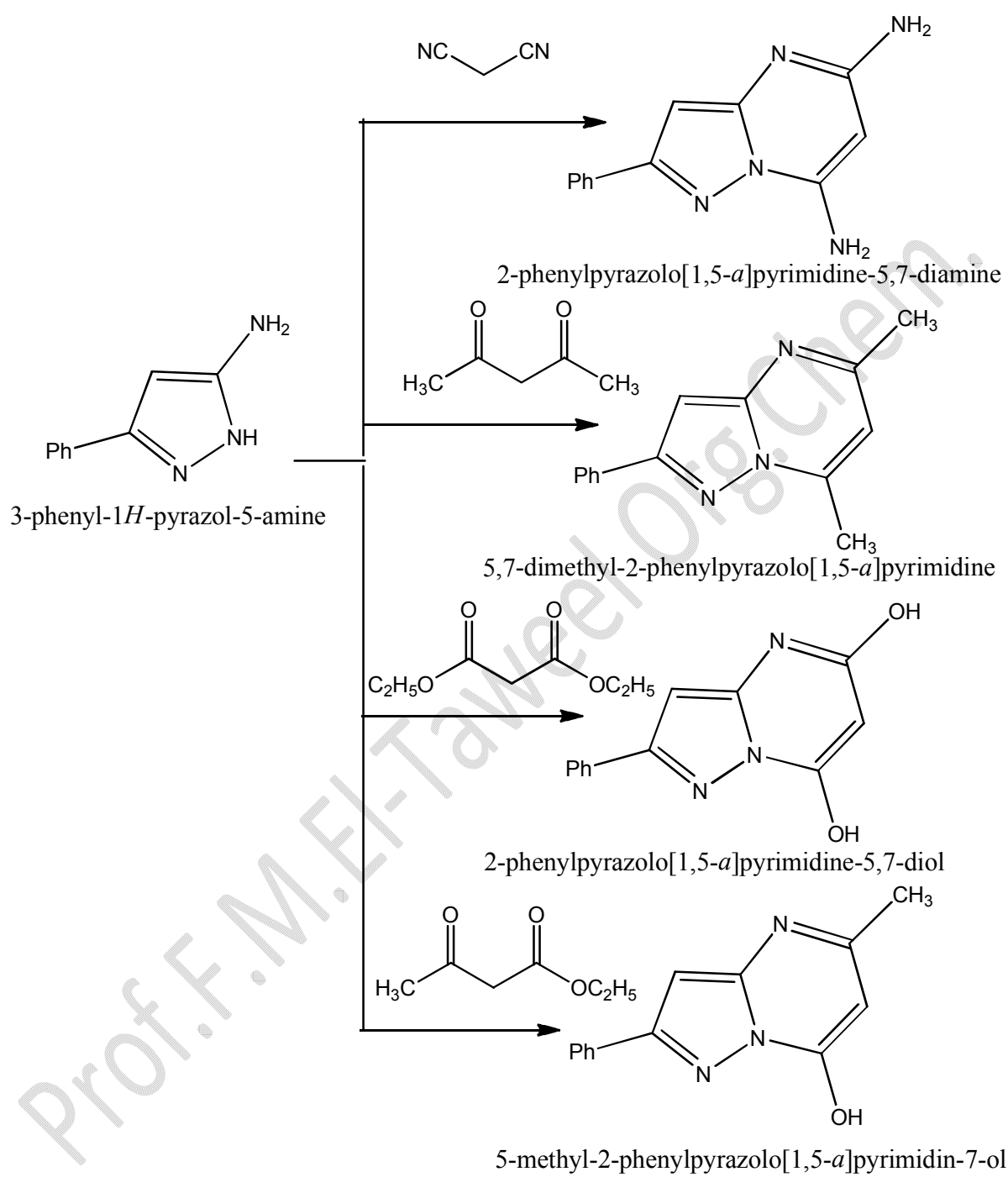


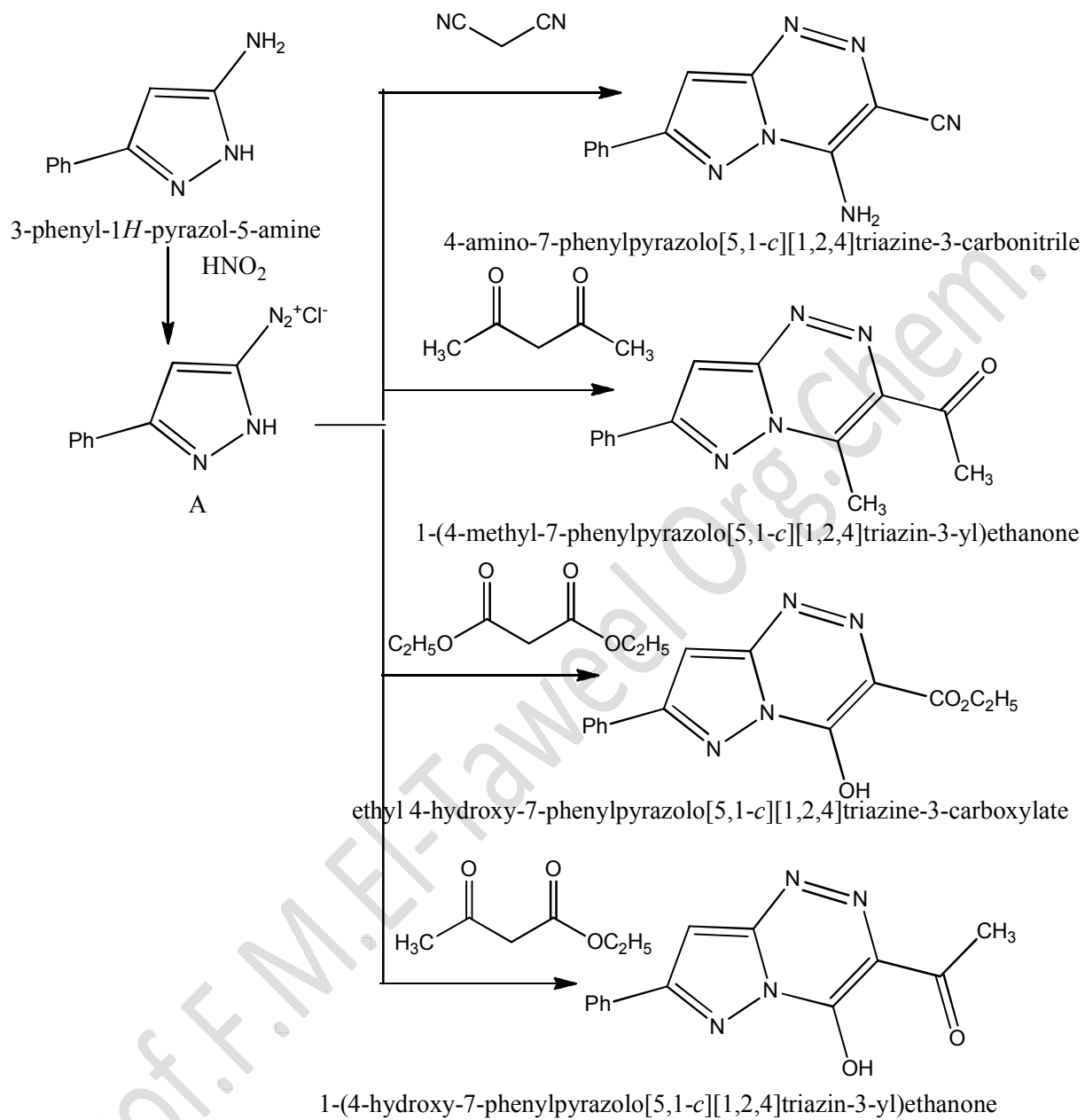
2-aryl-4,7-diphenyl-2*H*-pyrazolo[3,4-*d*]pyridazine

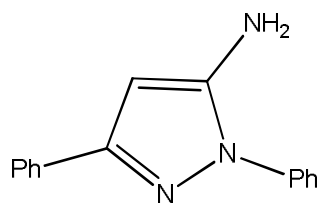
2-By condensation of β -ketonitriles with hydrazines to give 3(5)-aminopyrazoles (as heterocyclic amidines) followed by reaction of the latter with active methylene reagents such as reagents such as benzolacetonitrile, acetylacetonitrile, dicyanomethane, diethyl malonate, acetylacetone, dibenzoylmethane, benzoylacetone and

ethyl acetoacetate or ethyl benzoylacetate, to give pyrazol[1,5-c][1,2,4]triazines, or condensation of 3(5)-aminopyrazoles with active methylene reagents such as benzolacetonitrile, acetylacetonitrile, dicyanomethane, diethyl malonate, acetyl acetone, dibenzoylmethane, benzoylacetone and ethyl acetoacetate or ethyl benzoylacetate to give pyrazol[1,5-a]pyrimidines.

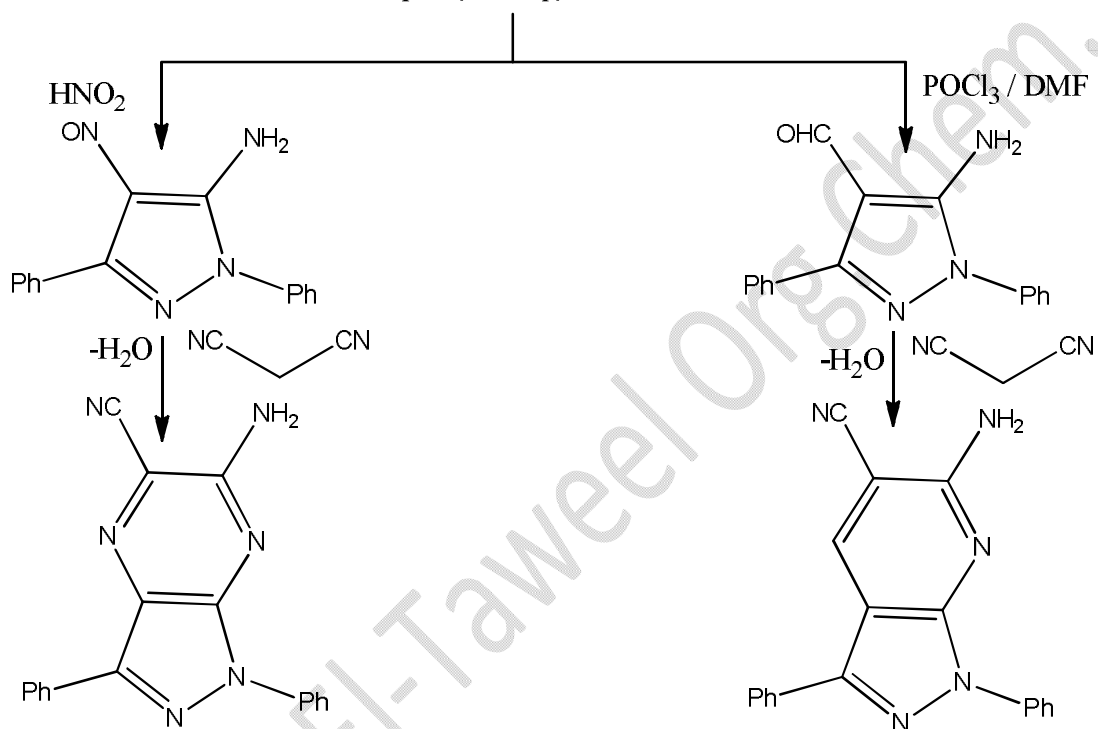






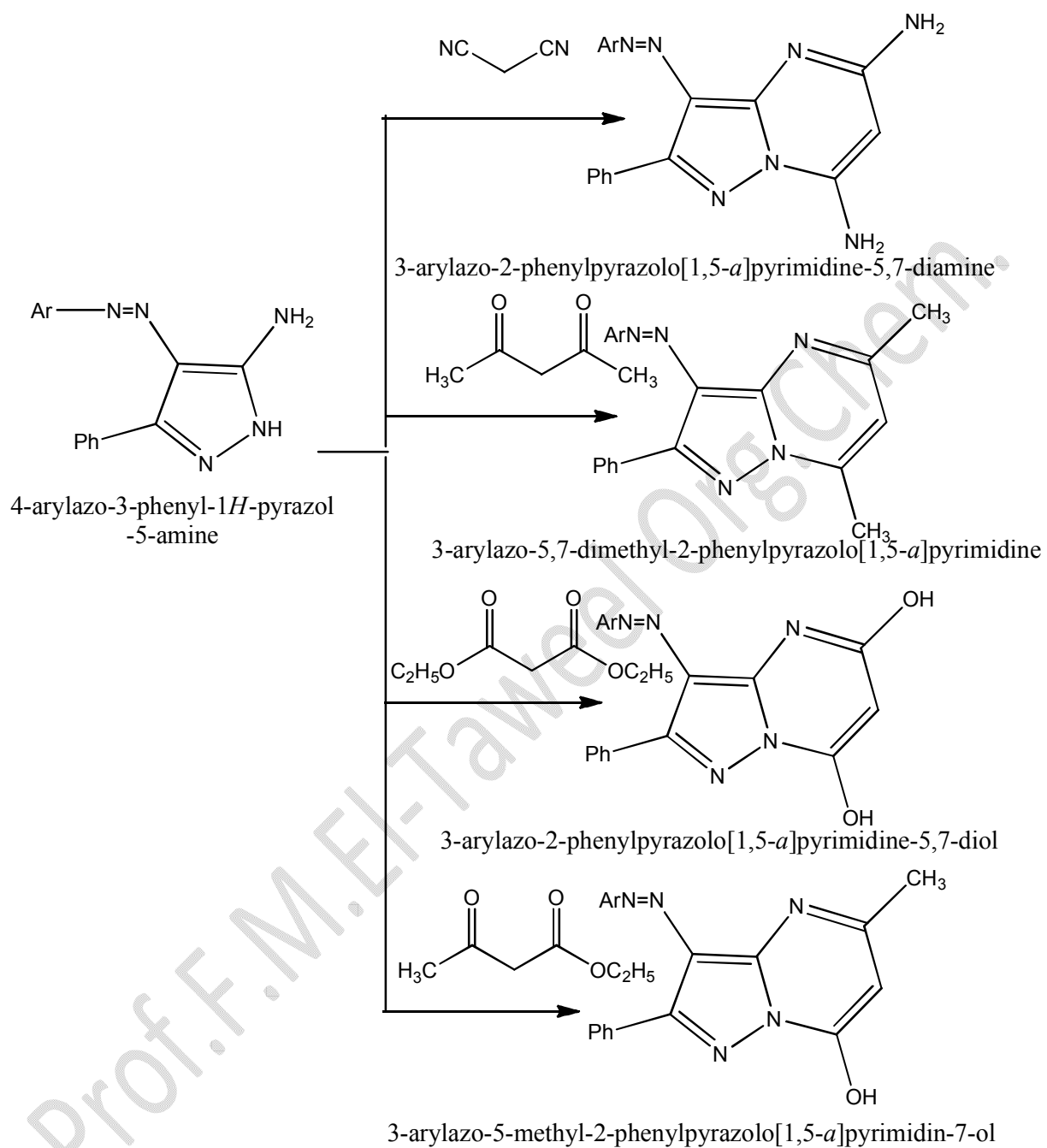


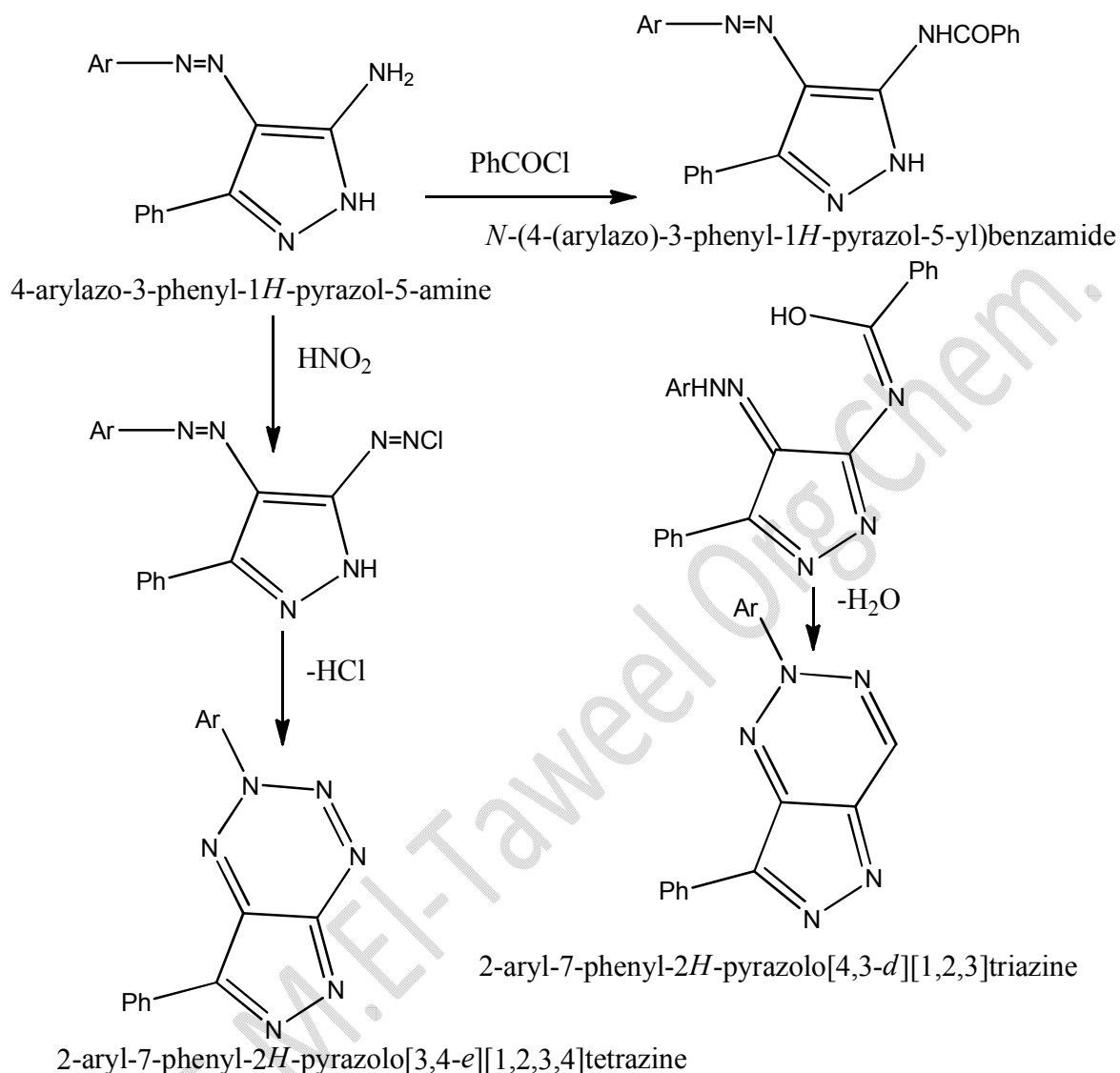
1,3-diphenyl-1*H*-pyrazol-5-amine



6-amino-1,3-diphenyl-1*H*-pyrazolo[3,4-*b*]pyrazine-5-carbonitrile

6-amino-1,3-diphenyl-1*H*-pyrazolo[3,4-*b*]pyridine-5-carbonitrile

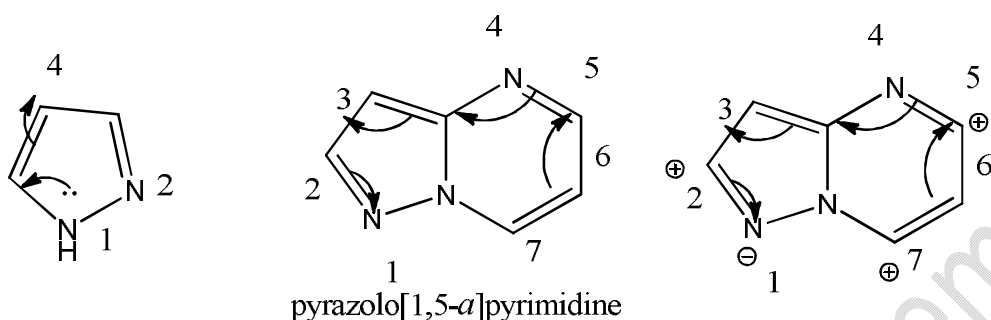




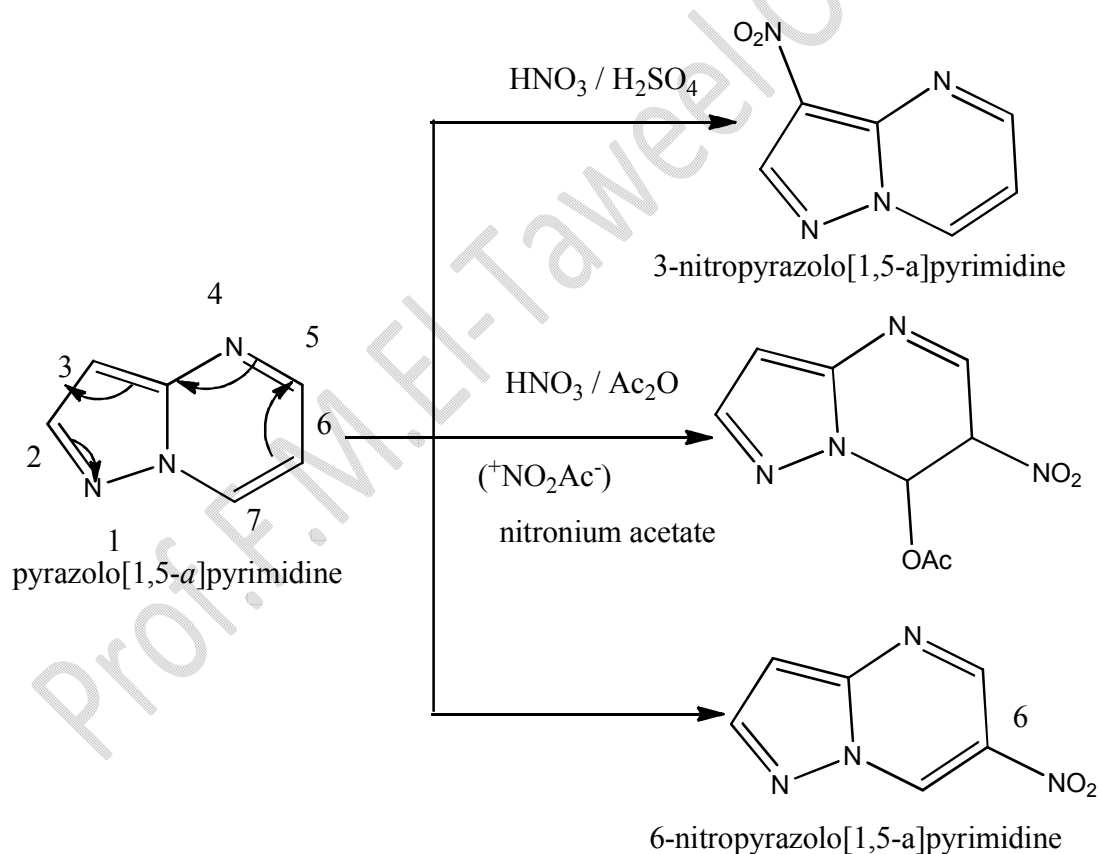
Chemical reactions of pyrazolo[1,5-*a*]pyrimidines:

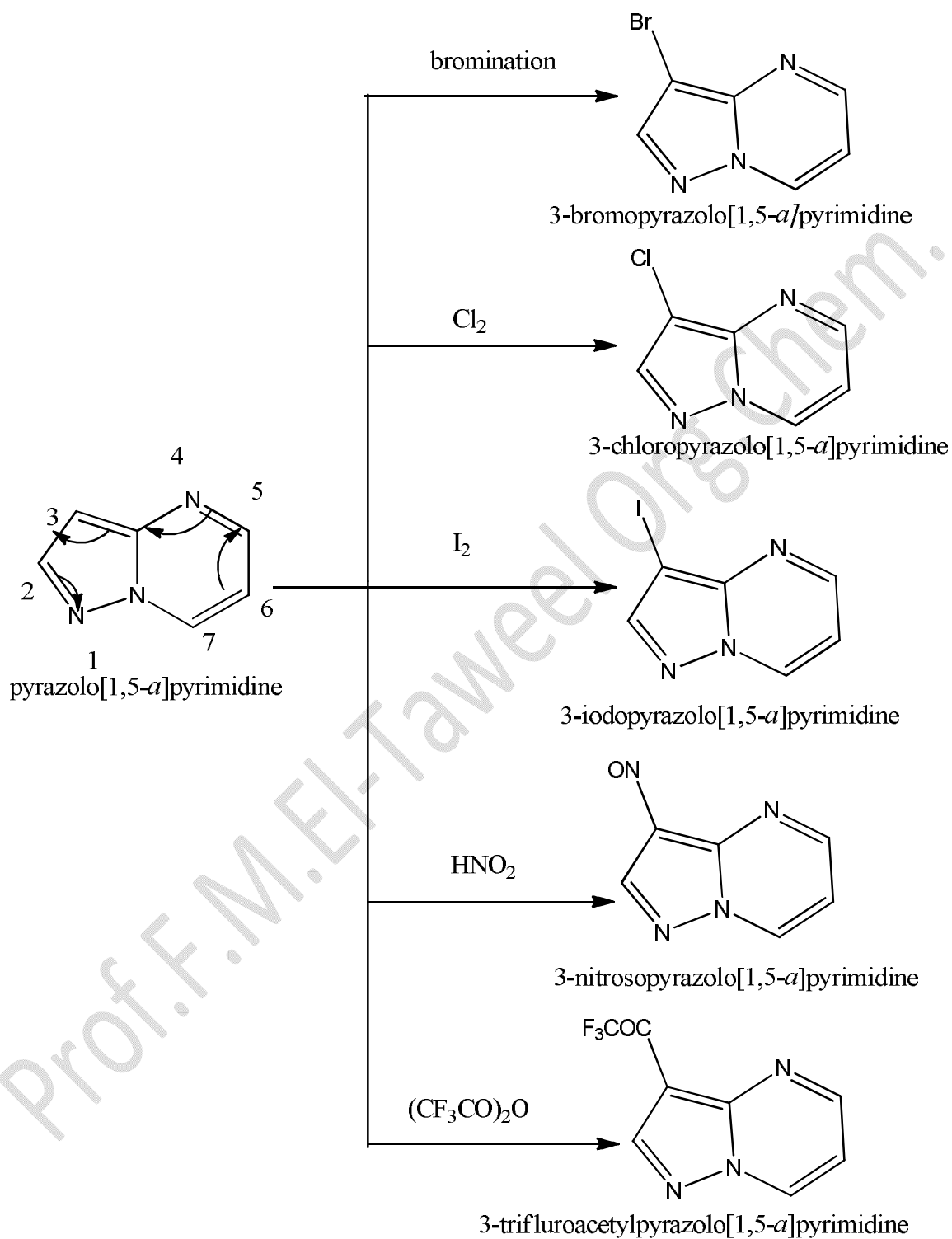
The chemistry of pyrazoles condensed to six membered rings can best be understood by assuming that this system consists of a five membered π -excessive heterocyclic ring that is fused to a six membered π -deficient ring. Thus, electrophilic reagents are expected to attack the pyrazole nitrogens or carbons.

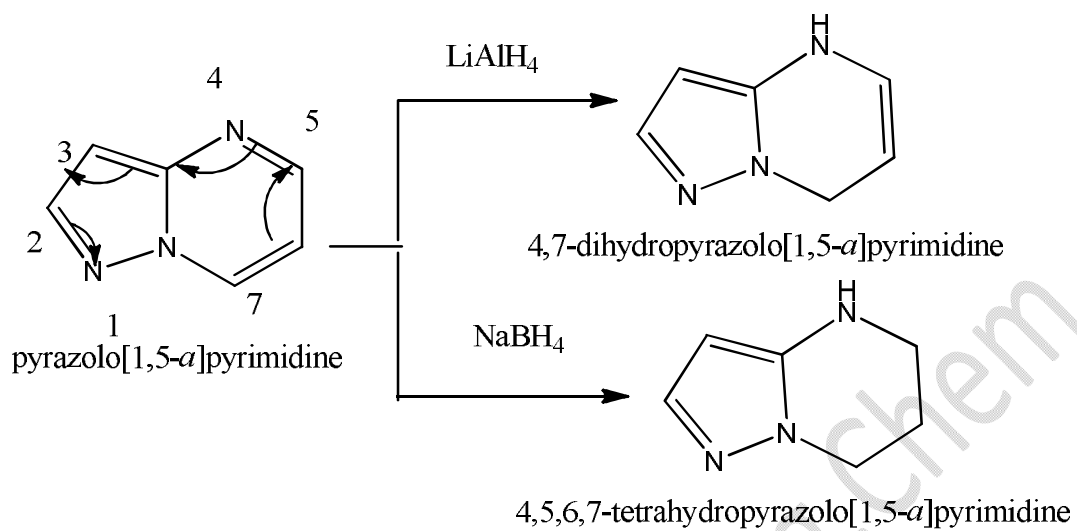
On the other hand, nucleophilic reagents are expected to attack the six membered. Also, little electrophilic substitutions at carbon atoms in these systems, because of their π -deficiency i.e. generally, azoloazines are expected to be relatively unreactive toward electrophiles. When electrophilic substitution normally takes place at carbons of the six membered ring. Thus, electrophilic substitution occurs at C-3 or may be at C-6 depends on the reagent.



It is clear that, the positive charges are localized at at C-2,5,7 and these positions for nucleophilic substitutions, and the negative charges are localized at at C-3,6 and it is better at C-3 (because the pyrazole ring is pi-excessive), these positions for electrophilic substitutions.







Mansoura University

2nd Semester Exam.2010/2011

Faculty of Science,Damietta Branch

Date : 5/6/2011

Chemistry Department

Students : 4th year

Examiner :*Prof.Fathy Eltaweel*

Chemistry Major

Subject: Organic Chemistry(409Chem.)

Time Allowed :3hrs.

Answer *all* questions:

90: Marks

1.Explain the following:(18 Marks)

- a.Oxidation of benzodiazines with KMnO_4 b.Nucleophilic addition to quinoxaline
c. Nucleophilic substitution in quinazoline
d.Reduction and electrophilic substitution of pyrazolo[1,5-a]pyrimidine

2. Write on : (18 Marks)

- a.Riehm reaction ;b.Gabriel-Colmann reaction, c.Richter reaction
d.Camps reaction

3.Prepare: (18 Marks)

- a.Phthalazine derivative from ethyl acetoacetate and quinazoline derivative from 3-aminocrotononitrile
b.Pyrazolo[3,4-e][1,2,3,4]tetrazine and pyrazolo[3,4-e]1,2,4]triazine from dicyanomethane
c.Pyrazolo[3,4-d]pyridazines from ethyl acetoacetate and acetylacetone

4.Convert :(18 Marks)

- a.2-Aminobezaldehyde to cinnoline derivatives, b.o-Nitroacetophone to 4-hydroxyquinoline, c.Acetylacetone to phthalazine derivative
d.Pyruvic acid to 2-phenylquinoline-4-carboxylic acid (atophan)

5. Write in equations: (18 Marks)

- a. Reaction of 2-aminobenzaldehyde with acetone / NaOH
bReaction of 2-aminoacetophenone with $\blacktriangleright \text{HNO}_2$

- c. Reaction of 3-aminocyclohexenone with ethyl propiolate
 d. Reaction of o-fluorocyanobenzene with guanidine, e. Nitration of quinazoline
 f. Oxidation of 2-methylquinazoline with SeO_2
 g. Reaction of o-phenylenediamine with diacetyl
 h. Reaction of 2-methylquinazoline with $\text{Br}_2/\text{CH}_3\text{CO}_2\text{H}$
 i. Reaction of o-diacetylbenzene with hydrazine



جامعة دمياط
 كلية العلوم
 قسم الكيمياء



تاريخ الإمتحان : ٤ يونيو ٢٠١٢

الفصل الدراسي : الثاني

إمتحان : كيمياء عضوية (حلقة غير متجانسة) (مقرر إختياري) (٤٠٩ ك)

الدرجة الكلية : ٩٠ درجة

الفرقة : الرابعة : شعبة كيمياء خاص

الإمتحان : ثلاث ورقات

الزمن : ٣ ساعات

Answer the following questions :

Time : 3hrs.

Question 1 : (18 Marks)

A) Give another name for **six** only of the following: (6x1.5=9 Marks)

- 1) Phthalazine; 2) Quinazoline; 3) Quinolizine; 4) Atophan; 5) Cinnoline;
 6) Indolizine; 7) Isoquinoline; 8) Quinoline.

B) Draw the chemical formula for **six** only of the following :

(6 x 1.5 = 9 Marks)

- [1,2,3]thiadiazolo[5,4-*d*]pyrimidine, pyridazino[1,2-*a*]pyridazine, pyrazolo[1,5-*d*]
 [1,2,4]triazine, imidazo[1,2-*a*]pyridine, imidazo[1,5-*a*]pyridine, pyrazino[2,3-*d*]
 pyrimidine, [1,2,3]thiadiazolo[2,3-*a*]pyridazine

Question 2 : (18 Marks)

A) Put (x) or (√) : (9x1=9 Marks)

- 1) Reduction of pyrazolo[1,5-*a*]pyrimidine with NaBH_4 give 4,7-dihydropyrazolo[1,5-*a*]pyrimidine **X**
 2) Oxidation of quinazoline with KMnO_4 give pyrimidine-1,3-dicarboxylic acid **X**
 3) Condensation of 2-aminobenzaldehyde with acetaldehyde give quinoline **√**

- 4) 2-Aminoacetophenone reacts with HNO_2 to give 4-hydroxy cinnoline \checkmark
 5) 2-Methylquinoxaline oxidized with SeO_2 to give quinoxaline-2-carboxylic acid
 6) Nucleophilic substitution of pyrazolo[1,5-a]pyrimidine occurs at C-3, C-6 **X**
 7) 1,2-Diaminobenzene reacts with dibenzoyl to give 2,3-diphenyl quinoxaline \checkmark
 8) 1,2-Diacetylbenzene reacts with hydrazine to give 1,2-dimethyl phthalazine **X**
 9) Reduction of pyrazolo[1,5-a]pyrimidine with LiAlH_4 give 1,2,3,4-dihydropyrazolo[1,5-a]pyrimidine **X**

B) Write in equations : (3 x 3 = 9 Marks):

- 1) Reaction of o-fluorocyanobenzene with guanidine
- 2) Reaction of 5-amino-3-phenylpyrazole with HNO_2 followed by coupling with acetylacetone
- 3) Reaction of 5-amino-1,3-dimethylpyrazole with $\text{POCl}_3 / \text{DMF}$ followed by condensation with dicyanomethane

Question 3: Explain : (18 Marks)

- b) Nucleophilic addition on quinoxaline (5 Marks)
- a) Electrophilic substitutions in pyrazolo[1,5-a]pyrimidine (8 Marks)
- c) Nucleophilic substitutions in quinazoline (5 Marks)

Question 4 : Write on : (3x6=18 Marks)

- a) Gabriel-Colmann reaction; b) Doebner reaction ; c) Richter reaction

Question 5 : Rewrite the following in equations : (3x6=18 Marks)

- a) Cyanoacetone + $\text{ArN}_2^+ \text{Cl}^-$; then ethyl cyanoacetate ; followed by arylidenemalononitriles
- b) Cyclization of 5-amino-4-arylo-3-methylpyrazole and 4,5-diamino-1,3-dimethylpyrazole with HNO_2
- c) Reaction of dicyanomethane ethyl 2-arylo-2-chloroacetate and 1-arylo-1-chloroacetone followed by condensation with hydrazine



جامعة دمياط
كلية العلوم
قسم الكيمياء



تاريخ الإمتحان : ٢٦ مايو ٢٠١٣

الفصل الدراسي : الثاني

إمتحان: كيمياء عضوية (حلقية غير متجانسة) (مقرر إختياري) (٤٠٩ ك)
الفرقة : الرابعة: شعبة كيمياء خاص
الزمن : ٣ ساعات
الدرجة الكلية : ٩٠ درجة
الإمتحان : ورقتان

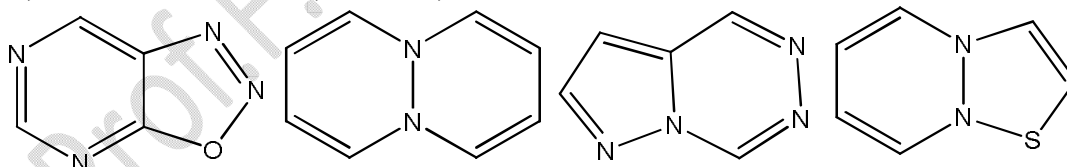
Answer the *following* questions : (18Marks for each question)

Question 1 :(18 Marks)

A) **Draw** and give another name for the following:(10 Marks)

1)Phthalazine; 2)Quinazoline; 3)Quinolizine; 4)Atophan; 5) Cinnoline;
6)Indolizine; 7)Isoquinoline ; 8)Quinoline; 9)Indazole;10)Benzimidazole

B) **Write** the names :(4 Marks)



c) **Draw** the chemical formula and then write the names (4 Marks)

imidazo[1,2-a]pyridine,imidazo[1,5-a]pyridine,benzo[c]isoxazole,
benzo[d]isoxazole

Question 2 :(18 Marks)

A) **Put** (x)for *incorrect* statements,making corrections and (✓) for *correct* statements
and write the equation in each case :(5 x 2 =10 Marks)

- 1) Reduction of pyrazolo[1,5-a]pyrimidine with NaBH_4 give 4,7-dihydropyrazolo[1,5-a] pyrimidine
- 2) 2-Methylquinoxaline oxidized with SeO_2 to give quinoxaline -2-carboxylic acid
- 3) 1,2-Diaminobenzene reacts diacetyl to give 2,3-dimethylquinoxaline
- 4) 1,2-Diacetylbenzene reacts with hydrazine to give 1,2-dimethylphthalazine
- 5) Reduction of pyrazolo[1,5-a]pyrimidine with LiAlH_4 give 1,2-dihydropyrazolo[1,5-a]pyrimidine

B) Write in equations : (4 x 2 = 8 Marks):

- 1) Nucleophilic substitutions in quinazoline
- 2) Reaction of 5-amino-3-methylpyrazole with HNO_2 followed by coupling with ethyl acetoacetate
- 3) Reaction of 5-amino-1,3-diphenylpyrazole with POCl_3 / DMF followed by condensation with dicyanomethane
- 4) Condensation of o-aminobenzaldehyde with acetaldehyde

Question 3 : Explain : (18 Marks)

- a) Nucleophilic addition on quinazoline (5 Marks)
- b) Electrophilic substitutions in pyrazolo[1,5-a]pyrimidine (7 Marks)
- c) Electrophilic substitutions in quinoline (6 Marks)

Question 4 : Write on : (4x4.5=18 Marks)

- | | |
|-----------------------------|------------------------|
| a) Gabriel-Colmann reaction | b) Pfitzinger reaction |
| c) Doebner reaction | d) Richter reaction |

Question 5 : Rewrite the following in equations : (3x6=18 Marks)

- a) Acetylacetone + $\text{ArN}_2^+\text{Cl}^-$; then ethyl cyanoacetate ; followed by arylidenemalononitriles
- b) Oxidation of benzodiazines with KMnO_4
- c) Reaction of dicyanomethane with ethyl 2-aryloxy-2-chloroacetate and 1-aryloxy-1-chloroacetone followed by condensation of the reaction products with hydrazine

Best regards

Examiner : Fathy Muhammad El-Taweel