GLOBAL JOURNAL OF ENGINEERING SCIENCE AND RESEARCHES

ROUTES TO SYNTHESIZE SOME NEW AROMATICS AND HETEROAROMATICS: SYNTHESIS OF SOME NEW INDENOPYRIDINE, INDENOPYRAN, FLUORENEOXIME, PYRAZOLOINDENOTRIAZINE AND INDENOPYRIDAZINE DERIVATIVES

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ABSTRACT

Several new indenopyridine, indenopyran, fluorenoneoxime, indenopyridazine and pyroloindenotriazine derivatives were prepared using cyclic ketones **1,** arylmethylenenitriles **2** and active methylene nitriles **3** as starting materials.

Keywords: Fluoreneoxime, Pyrazoloindenotriazine, Aromatics.

I. INTRODUCTION

Indan-1,3-dione and its derivatives are versatile reagents, which have been extensively utilized for synthesis of functionally substituted aromatic and heteroaromatic systems [1-9]. These aromatic and heteroaromatic systems are interesting as potential biodegrable agrochemicals ,[1]pharmaceuticals,[3,4] rodenticides ,[10] and blood anticoagulants [5] The present work has resulted in the formation of several new indenopyridine, indenopyran, fluoreneoxime , indenopyridazine and pyrazolo [3,2-*c*]indeno[1,2-*e*] [1,2,4] triazine derivatives of potential biological importance using cyclic ketones **1**, arylmethylenenitriles **2** and active methylene nitriles **3** as starting materials.

It has been found that, cyclic ketones **1b,d** reacted readily with arylmethylenenitriles **2** in ethanol containing piperidine to yield (1:1) adducts.Thus, the indeno [1,2-*b*]pyrans **5** or the indeno[1,2-*b*] pyridines **7** can be considered as reaction products. Acyclic structures **4** were readily eliminated by^{1}H-NMR spectra which revealed signals at $\delta \approx 4.1–5.0$ ppm for one proton linked to sp^3 carbon. The indeno[1,2-*b*]pyridines **7 (**which can exist with their tautomeric structures **6** were established as reaction products based on IR spectra which revealed the presence of carbonyl groups at $\tilde{\nu}$ ≈1713-1717cm^{-1}.Signals at similar positions for similar systems was previously observed.**(4,5)** The formation of indeno[1,2-*b*] pyridines **7** were assumed to proceed via Michael type addition of the active methylene group in **1** to the activated double bond in **2** to give the Michael adducts **4**, which readily cyclized to yield **7** (*c.f.* Scheme 1).

Similarly, cyclic ketones **1** reacting with 2-(2-oxoindolin-3-ylidene)malononitrile **8a,** (Z)- ethyl 2-cyano-2-(2-oxoindolin-3-ylidene)acetate **8b** in ethanol containing piperidine as a catalyst afforded spiroanellated indeno [1,2-*b*]pyridines **10** rather than indeno[1,2-*b*] pyrans **11** as established by IR spectra which revealed carbonyl group at $\tilde{\nu} \approx 1700$- 1715 cm^{-1}.

Also, cyclic ketones **1** reacted with ethoxymethylenemalononitrile (**12**) using the same previous conditions to yield the indeno[1,2-*b*]pyridines **14**. Compounds **14** were most likely formed via the sequence demonstrated in scheme 2.

On the other hand, indane-1,3-dione **(1a)** underwent condensation with aromatic aldehydes to give 2-(arylmethylene)-1*H*-indene-1,3-(2*H*)-diones**(15).**[(11)]Michael condensation of compounds **15** with active methylene nitrile **3c**[12] in ethanol and in the presence of piperidine afforded indeno[1,2-*b*]pyrans **17**.The formation of **17** finds support from correct analytical, spectral data and independent synthesis through the Michael condensation of **1** with the arylmethylenenitriles**18**[12] in ethanol / piperidine (*c.f.* Scheme 3).

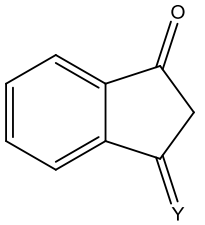
Indanylidenepropanedinitriles **19** were prepared by condensation of cyclic ketones **1** with malononitrile in dry benzene containing catalytic amount of ammonium acetate and glacial acetic acid using water separator, by refluxing for six hours. Compound **19a** reacted with arylmethylenenitriles **2** in refluxing ethanol / piperidine to yield the e fluoreneoximes **23** rather than indeno [1,2-*b*]pyridines **21**.Structurs **23** were established as reaction products based on their elemental analysis and spectral data. Compounds **23** were assumed to be formed via addition of acidic CH group in **19a** to the activated double bond in the arylmethylenenitriles **2** to give the intermediates **20**

which cyclized to **22** and finally aromatized to **23** via hydrogen cyanide or ethyl formate eliminationas has been recently reported for the formation of similar systems [3-5].

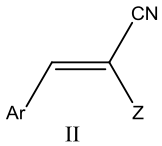
In a similar manner, the ylidenenitrile **19a** was subjected to react with1-phenyl-2-nitroethene **(24)** to give the fluoreneoxime derivative **26**. Formation of **26** was assumed to proceed via addition of acidic CH group in **19a** to the π-deficient double in **24** to give the intermediate **25** followed by cyclization and aromatization to yield **26** (*c.f.* Scheme 4).

The reactivity of cyclic ketones **1** towards aryl diazonium salts and heteroaryl diazonium salts was also studied. Thus, compound **1** was coupled with the aryl diazonium salt to give 1,5-dimethyl-4(2-(1-oxo-1*H*-inden-2(3*H*)-ylidene)hyrazinyl-2-phenyl-1*H*-pyrazol-3-(2*H*)-ones **27**. The later condensed with malononitrile in glacial acetic acid containing an equivalent amount of ammonium acetate under reflux to yield 2-(1,5-dimethyl-3-oxo-2-phenyl-2,3-dihydro-1H-pyrazol-4-yl)-3-oxo-3,9-dihydro-2*H*-indeno[2,1-c] pyridazine-4-carbonitriles **28**. Compounds **28** were also prepared via reacting the ylidenenitrile **19** with aryl diazonium salt to give **29**, followed by cyclization to 2-(1,5-dimethyl-3-oxo-2-phenyl-2,3-dihydro-1*H*-pyrazol-4-yl)-3-oxo-3,9-dihydro-2*H*-indeno[2,1-c]pyridazine-4-carbonitriles **28** by the effect of acetic acid.

The heterocyclic diazonium chlorides **30** coupled with cyclic ketones **1b,c** to afford 6*H*-indeno[1,2-*e*]pyrazolo[5,1-c][1,2,4] triazin-6-ones **32**.Compounds **32** were assumed to be formed via the intermediates **31** which readily underwent cyclization by the reaction of the highly nucleophilic pyrazole NH (*cf.* Scheme 5).

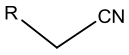


1a,Y= O
b,Y=NOH
c,Y=NNHPh
d,Y=NC$_6$H$_4$Cl(m)



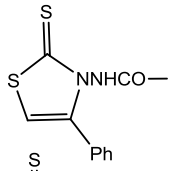
II

2	Z	Ar
a	CN	C_6H_5
b	CN	C_6H_4 Cl(p)
c	CN	C_6H_4 Br(p)
d	CN	C_6H_4 OH(p)
e	CO_2Et	C_6H_4 Cl(p)
f	CO_2Et	C_6H_4 OH(p)
g	CO_2Et	C_6H_4 OCH_3(p)

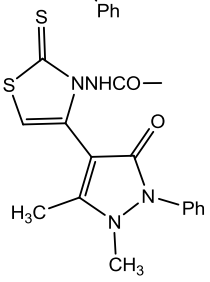


3a,R = CN
b,R = CO_2Et

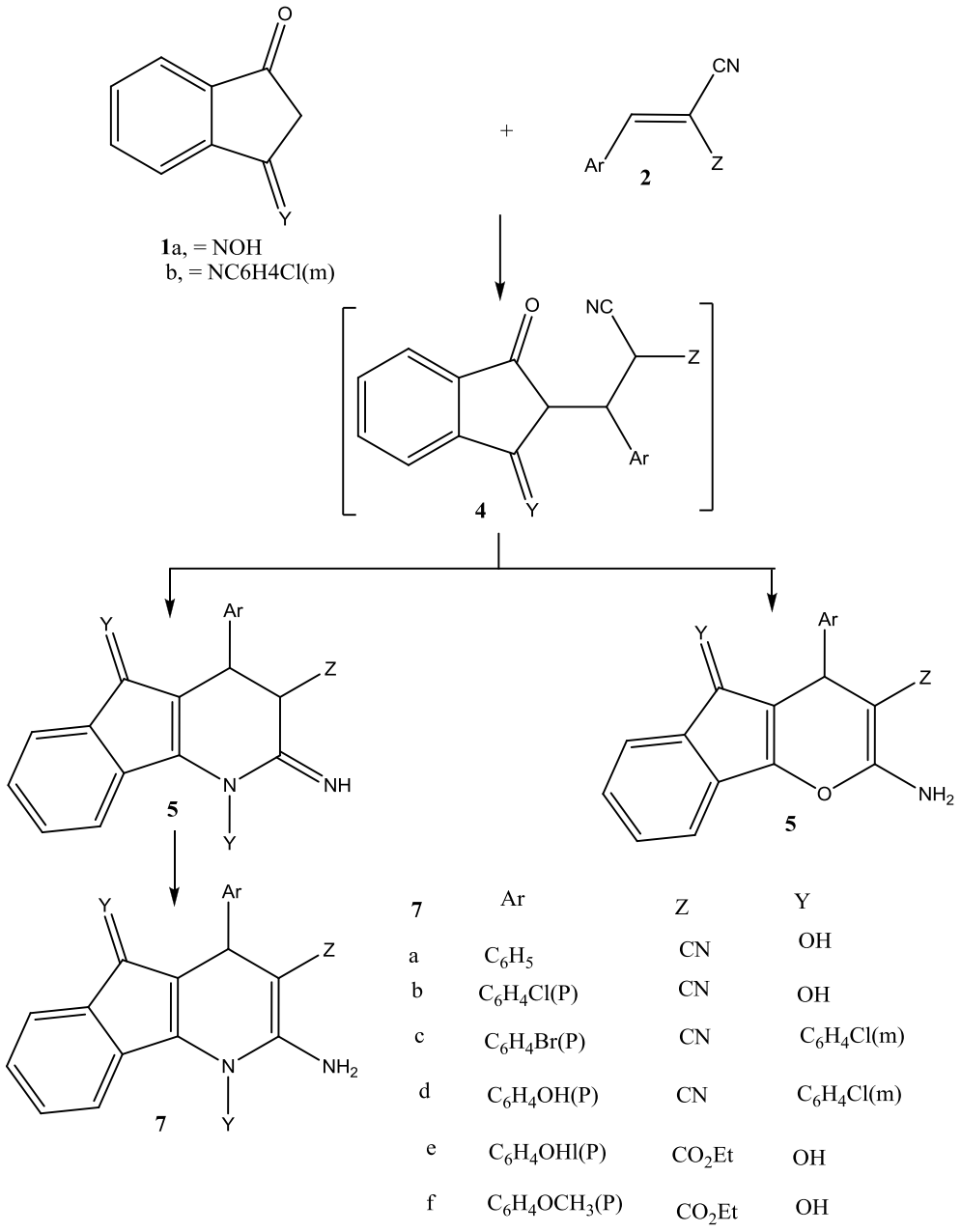
c, =



d, =



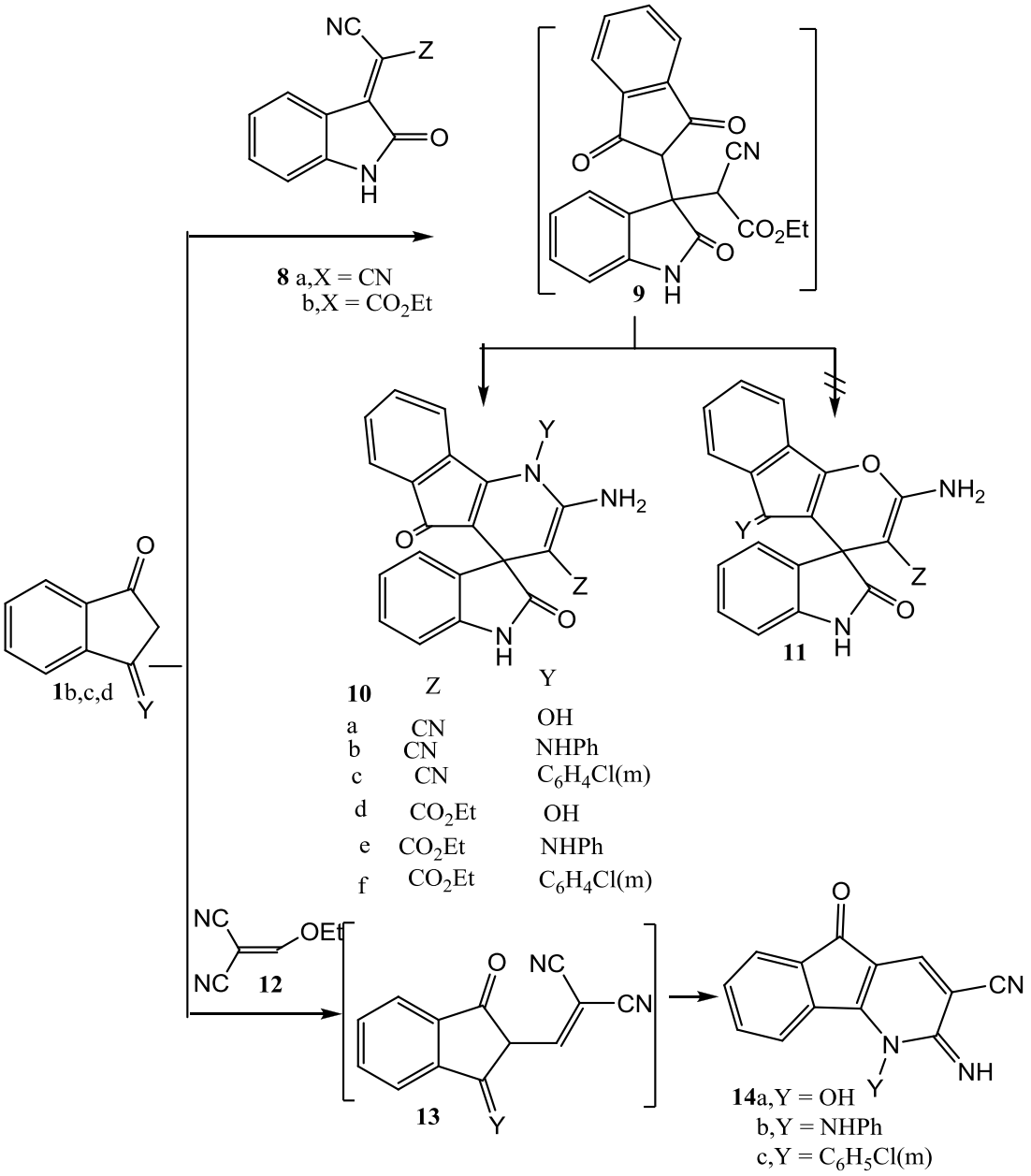
ISSN 2348 – 8034



7	Ar	Z	Y
a	C_6H_5	CN	OH
b	$C_6H_4Cl(P)$	CN	OH
c	$C_6H_4Br(P)$	CN	$C_6H_4Cl(m)$
d	$C_6H_4OH(P)$	CN	$C_6H_4Cl(m)$
e	$C_6H_4OHl(P)$	CO_2Et	OH
f	$C_6H_4OCH_3(P)$	CO_2Et	OH

Scheme 1

ISSN 2348 – 8034



Scheme 2

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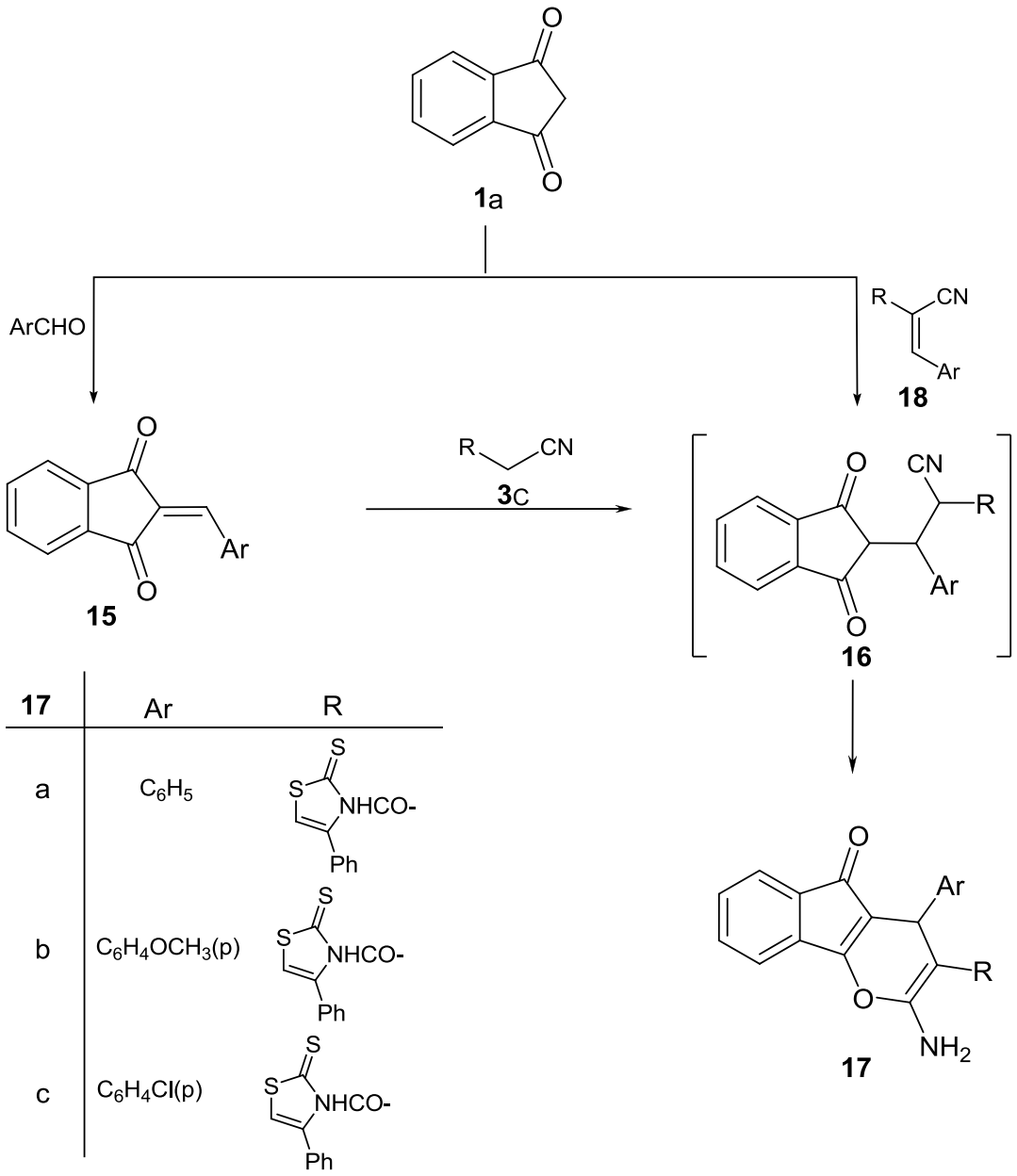
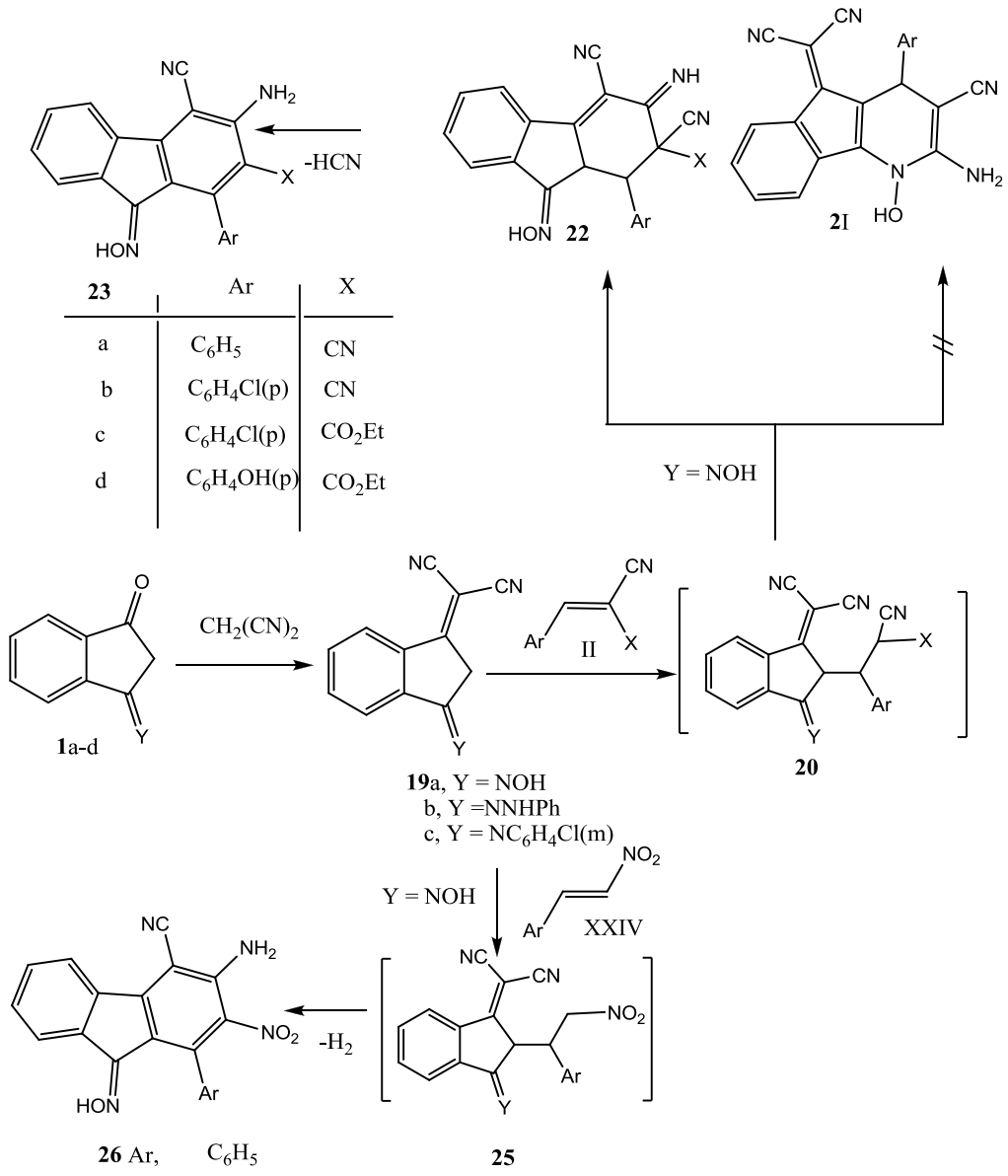


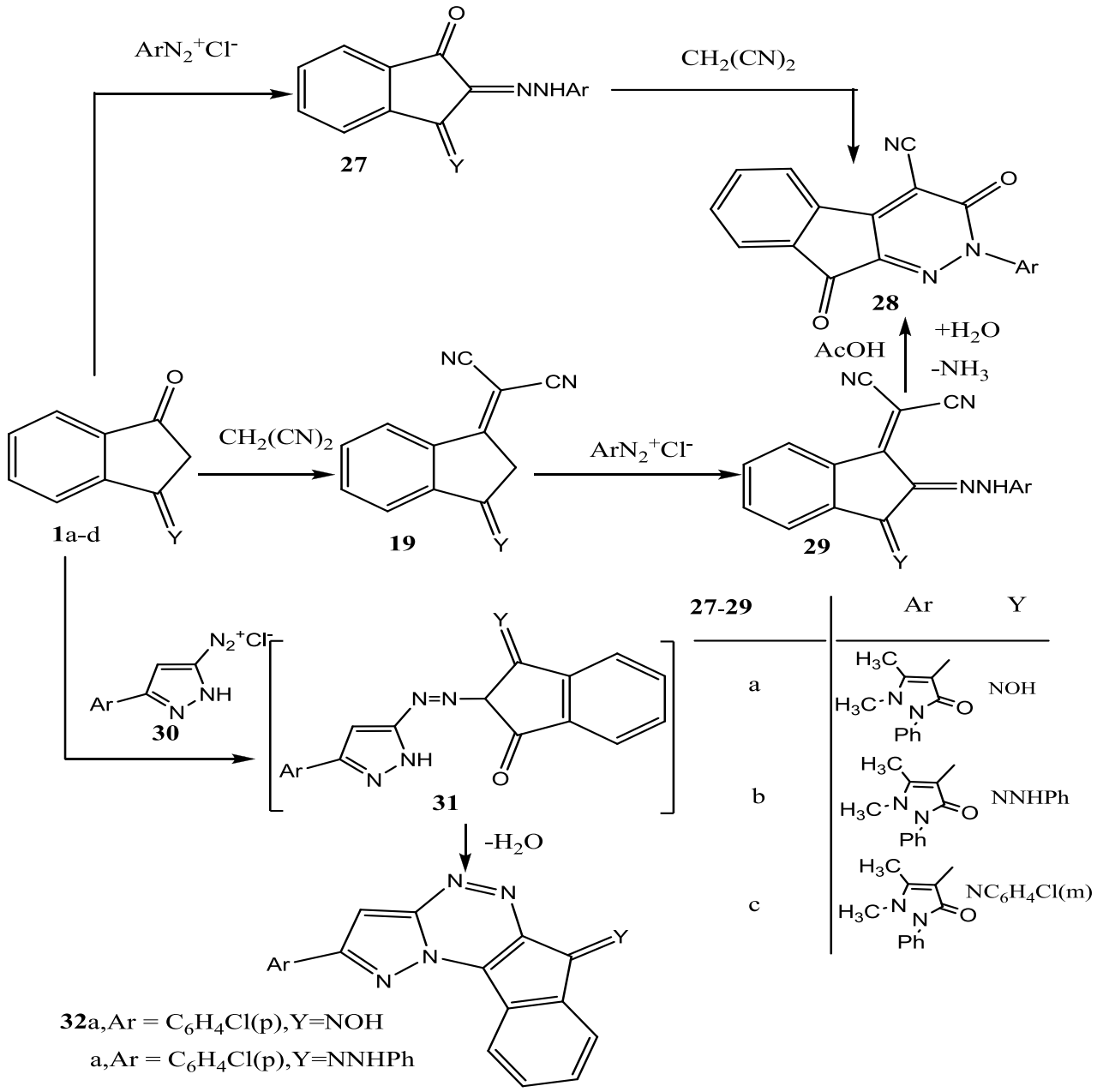
17	Ar	R
a	C_6H_5	
b	$C_6H_4OCH_3(p)$	
c	$C_6H_4Cl(p)$	

Scheme 3

ISSN 2348 – 8034



Scheme 4


ArN2+Cl-
NNHAr
27
Y
CH2(CN)2
NC
O
N
Ar
28
AcOH
+H2O
-NH3
1a-d
CH2(CN)2
NC
CN
19
ArN2+Cl-
29
27-29
Ar
Y
a
b
c
NOH
NNHPh
NC6H4Cl(m)
30
31
-H2O
32a,Ar = C6H4Cl(p),Y=NOH
a,Ar = C6H4Cl(p),Y=NNHPh

Scheme 5

II. EXPERIMENTAL

All melting points are uncorrected and have been measured on a Griffin&George MBF 010T (London) apparatus. Recorded yields correspond to the pure products. IR (KBr) spectra were recorded on a Perkin Elmer SP-880 spectrometer and ^{1}H-NMR spectra were measured on a Varian 270 MHz spectrometer in DMSO-d_6 as solvent and using TMS as an internal standard. Chemical shifts are reported in δ units (ppm). Microanalyses were performed on a LECO CHN-932 elemental analyzer and carried out in the Microanalytical Data Unit at Cairo and Mansoura Universities.Mass spectra were recorded on a MS 30(AEI) instrument at 70 eV ionization energy .

General procedure for preparation of indeno[1,2-*b*]pyridines 7a-f

A solution of 1b,d [9](0.01mol) in ethanol (50mL) was treated with the arylmethylenenitriles **2** (0.01mol) and few drops of piperidine .The reaction mixture was refluxed for 6 h , then left to cool at room temperature. The solids formed were collected by filtration , crystallized from the proper solvent and then identified as 7a-f .

2-Amino-1-hydroxy-5-oxo-4-phenyl-4,5-dihydro-1*H*-indeno [1,2-*b*] pyridine-3- carbonitrile (7a)

Brown crystals, from ethanol /1,4-dioxan, m.p. 240-242°C, yield 70%.-IR($\tilde{\nu}$/cm^{-1}):3240,3140(OH , NH_2) , 2220 (conjugated CN) , 1715 (CO) . –^{1}H-NMR (DMSO-d_6)(δ,ppm): 4.32 (s, 1H, 4-H),7.71-8.66(m ,9H, aryl H), 8.77 (s , 2 H,NH_2),11.99 (s, 1H, OH). - $C_{19}H_{13}N_3O_2$ (315.31) Calcd . C 72.37 H 4.15 N 13. Found C 72.24 H 4.43 N 13.56. MS : *m/z* = 315.

2-Amino-1-hydroxy-4-(4'-chlorophenyl)-5-oxo-4,5-dihydro-1*H*-indeno[1,2-*b*] pyridine-3-carbonitrile (7b)

Yellow crystals, from ethanol /DMF, m.p. 242-244°C, yield 65%.-IR($\tilde{\nu}$//cm^{-1}):3350,3263,3148 (OH,NH_2) , 2214 (conjugated CN) , 1713 (CO) . -^{1}H-NMR (DMSO-d_6)(δ,ppm): 4.28(s, 1H, 4-H), 7.71-8.66(m, 8H, aryl H), 8.88(s,2H,NH_2),11.99 (s, 1H, OH) **.-**$C_{19}H_{12}ClN_3O_2$ (349.77) Calcd. C 65.24 H 3.45 N 12.01 Found C 65.34 H 3.65 N 12.23. MS: *m/z* = 349 .

2-Amino-4-(4'-bromophenyl)-5-oxo-1-(3'-chlorophenyl)-4,5-dihydro-1*H*-indeno[1,2-*b*]pyridine-3-carbonitrile (**7c**)

Deep brown crystals, from ethanol /DMF, m.p.270-272°C, yield 80%.-IR($\tilde{\nu}$/cm^{-1}) : 3460,3311 (NH_2) , 2217 (conjugated CN) , 1717 (CO).-^{1}H-NMR (DMSO-d_6)(δ ,ppm): 4.93(s, 1H, 4-H), 5.96 (s, 2H, NH_2), 7.12-8.10(m, 12H, aryl H) .-$C_{25}H_{15}BrClN_3O$ (488.76) Calcd. C 61.43 H 3.09 N 8.60 Found C 61.75 H 3.94 N 8.73. MS : *m/z* = 488 .

2-Amino-4-(4'-hydroxyphenyl)-5-oxo-1-(3'-chlorophenyl)-4,5-dihydro-1*H*-indeno[1,2-*b*]pyridine-3-carbonitrile (7d*)*

Dark green crystals, from ethanol /1,4-dioxane, m.p.214-216°C, yield 70%.-IR($\tilde{\nu}$/cm^{-1}) : 3504,3363 (OH,NH_2) , 2211 (conjugated CN) , 1716 (CO)).-^{1}H-NMR (DMSO-d_6)(δ ,ppm): 4.93(s, 1H, 4-H), 5.88 (s, 2H, NH_2), 7.12-8.10(m, 12H, aryl H),10.35(s,1H,OH) .- $C_{25}H_{16}ClN_3O_2$ (425.86) Calcd. C 70.50 H 3.78 N 8.60 Found C 70.12 H, 4.66 N 8.73. MS :*m/z* = 425.

Ethyl 2-amino-1-hydroxy-5-oxo-4-(4'-hydroxyphenyl)-4,5-dihydro-1*H*-indeno[1,2-*b*]pyridine-3-caboxylate (7e)

Brown crystals, from ethanol /1,4-dioxan, m.p.294-296°C, yield 65%.-IR($\tilde{\nu}$/cm^{-1}) :3424,3312 (OH,NH_2), 1715 (CO) , 1684 (CO ester) .-^{1}H-NMR (DMSO-d_6)(δ ,ppm):1.25-131 (t,3H,CH_3) ,4.32-4.52(q,2H,CH_2),4.65(s,1H, 4-H), 6.64(s , 2H,NH_2) ,7.17-7.88(m,8H,aryl H),9.95(s,1H,OH).-$C_{21}H_{18}N_2O_5$ (378.37) Calcd. C 66.65 H 4.79 N 7.40 Found C 66.48 H 5.04 N 7.36. MS :*m/z* = 378.

Ethyl 2-amino-1-hydroxy-5-oxo-4-(4'-methoxyphenyl)-4,5-dihydro-1*H*-indeno[1,2-*b*]pyridine-3-caboxylate (7f*)*

Brown crystals, from ethanol / DMF, m.p. >300°C, yield 68%.-IR($\tilde{\nu}$/cm^{-1}) : 3524,3312(OH , NH_2), 1715 (CO), 1684(CO ester).-$C_{22}H_{18}N_2O_5$ (390.38) Calcd. C 67.68 H 4.64 N 7.18 Found C 67.72 H 4.46 N 7.24. MS : *m/z* = 390.

Preparation of spiro [(2-amino-1,3-disubstituted indeno[1,2-*b*] pyridine)-(5*H*),3'-[3*H*]indole]-2',5(1'*H*)diones (10a-f)

A mixture of 1b-d (0.01 mol) in ethanol (50 mL) were treated with (0.01 mol) of the ylidenenitriles 8a,b. The reaction mixture was stirred for 3 h at room temperature.The formed precipitates were collected by filtration, crystallized from the suitable solvent and then identified as 10a-f.

2-Amino-1-hydroxy-2'-,5-dioxo-1,5-dihydrospiro[indeno[1,2-b]pyridine-4,3-indoline--3-carbonitrile(10a)

***Red crystals, from DMF, no melt < 300°C, yield 60%.-IR ($\tilde{\nu}$/cm^{-1}) : 3450,3388,3329(OH,NH,NH_2),2208(conjugated CN) 1699 (CO) ,1625(CO amide). - $C_{20}H_{12}N_4O_3$ (356.33) Calcd. C 67.40 H 3.39 N 15.72 Found C 67.76 H 3.25 N 15.67. MS :* m/z = 356 .**

2-Amino-1-(phenylamino)-2'-,5-dioxo-1,5-dihydro spiro [indeno [1,2-b] pyridine-4,3-indoline]-3-carbonitrile (10b)

Orange crystals, from ethanol/ DMF, m.p.240-242 °C, yield 62%.- IR($\tilde{\nu}$/cm^{-1}) : 3490,3426,3348,3242 (NH_2, NH), 2186 (conjugated CN) 1704(CO) ,1638(CO amide).-^{1}H-NMR (DMSO-d_6)(δ,ppm): 6.58(s, 2H, NH_2), 7.01-7.67(m, 13H, aryl H),9.13,11.23(2s, 2H, 2NH) .-$C_{26}H_{17}N_5O_2$ (431.44) Calcd. C 72.37 H 3.97 N 16.23 Found C 72.70 H 4.23 N 16.43. MS: *m/z* = 431 .

2-Amino-1-(3-chloropheny)-2-,5-dioxo-1,5-dihydrospiro [indeno[1,2-b] pyridine-4,3-indoline]-3-carbonitrile (10c)

Faint brown crystals, from DMF, m.p.250-252°C, yield 70%. -IR($\tilde{\nu}$/cm^{-1}) : 3530, 3462 ,3358, 3302 (NH_2, NH), 2182 (conjugated CN) 1716 (CO) ,1641(CO amide).- $C_{26}H_{15}ClN_4O_2$ (450.87) Calcd . C 69.25 H 3.35 N 12.43 Found C 69.42 H 3.62 N 12.36. MS :*m/z* = 450.

Ethyl 2-amino-1-hydroxy-2-,5-dioxo-1,5-dihydrospiro [indeno [1,2-b]pyridine-4,3-indoline]-3-carboxylate (10d)

Orange crystals, from DMF, no melt < 300 °C, yield 65%.-IR ($\tilde{\nu}$/cm^{-1}) : 3449,3384,3271 (NH_2, NH,OH) , 1704 (CO), 1670 (CO ester) ,1646(CO amide).-^{1}H-NMR (DMSO-d_6)(δ,ppm): 1.32-1.39(t, 3H, CH_3), 4.38-4.45(q, 2H, CH_2), 7.15-7.81(m, 8H, aryl H), 8.76(s, 2H, NH_2), 9.15,10.04 (2s, 2H,NH and OH).-$C_{22}H_{17}N_3O_5$ (403.38) Calcd. C 65.50 H 4.24 N 10.42 Found C 65.65 H 4.21 N 10.33. MS :*m/z* = 403 .

Ethyl 2-amino-1-phenylamino-2-,5-dioxo-1,5-dihydrospiro [indeno[1,2-b]pyridine-4,3-indoline]-3-carboxylate (10e)

Yellow crystals, from ethanol/ DMF, no melt < 300°C, yield 60%.-IR ($\tilde{\nu}$/cm^{-1}) : 3515,3448,3394 (NH_2, NH) , 1710 (CO), 1675(CO ester) ,1651(CO amide).- $C_{28}H_{22}N_4O_4$ (478.49)Calcd. C 70.27 H 4.63 N 11.59 Found C 70.35 H 4.42 N 11.71. MS: m/z = 478 .

Ethyl 2-amino-1-(3-chloropheny)-2-,5-dioxo-1,5-dihydrospiro [indeno [1,2-*b*]pyridine-4,3-indoline]-3-carboxylate (10f)

Orange crystals, from DMF, m.p. 264-266 °C, yield 63%.-IR($\tilde{\nu}$/cm^{-1}) : 3468,3393(NH_2,NH), 1706 (CO), 1680(CO ester) ,1657(CO amide)..-$C_{28}H_{20}ClN_3O_4$ (497.92) Calcd. C 67.53 H 4.04 N 8.44 Found C 67.81 H 4.21 N 8.53. MS: *m/z* = 497 .

Synthesis of indeno[1,2-*b*]pyridine derivatives (14a-c)

A solution of 1b-d (0.01 mol) in ethanol (50 mL) containing (0.1 mL) piperidine, was treated with (0.01 mol) of ethoxymethylenemalononitrile (12). The reaction was heated under reflux for 6 h. The solvent was concentrated to its half volume then left to cool. The precipitates formed were collected by filtration, crystallized from the proper solvent and then identified as (14a-c).

1-Hydroxy-2-imino-5-oxo-2,5-dihydro-1*H*-indeno[1,2-*b*]pyridine-3-carbonitrile (14a)

Brown crystals from ethanol, m.p. 240-242ºC, yield 60%.-IR ($\tilde{\nu}$/cm^{-1}) : 3242 (NH), 2200(conjugated CN), 1701(CO), 1624 (C=N) .-$C_{13}H_7N_3O_2$ (237.22) Calcd. C 65.82 H 2.97 N 17.71 Found C 65.79 H 3.03 N 17.65. MS : *m/z* = 237 .

2-Imino-5-oxo-1-(phenylamnio)-2,5-dihydro-1*H*-indeno[1,2-*b*] pyridine-3-carbonitrile (14b)

Deep green crystals from 1,4-dioxane, m.p. 290-292ºC, yield 63% .-IR($\tilde{\nu}$/cm^1):3395(NH),2199(conjugatedCN),1697(CO).-^{1}H-NMR(DMSO-d_6)(δ,ppm):7.53-7.95(m,10H, aryl H), 8.4-8.8(2s, 2H, 2NH) .-$C_{19}H_{12}N_4O$ (312.32) Calcd. C 73.06 H 3.87 N 17.94 Found C 73.21 H 4.16 N 18.03. MS :*m/z* = 312 .

1-[(3'-Chlorophenyl)amino]-2-imino-5-oxo-2,5-dihydro-1*H*-indeno[1,2-*b*]pyridine-3-carbonitrile (14c)

Green crystals from ethanol/DMF, m.p.140-142ºC , yield 60%. – IR($\tilde{\nu}$/cm^{-1}) : 3450(NH), 2201(conjugated CN) , 1718(CO).-$C_{19}H_{10}ClN_3O$ (331.75) Calcd.C 68.78 H 3.03 N 12.67 Found C 68.53 H 3.91 N 12.56. MS :*m/z* = 331 .

Synthesis of 4*H*-indeno[1,2-*b*]pyrans 17a-c

Method A: A suspension of 2-(arylmethylene)indane-1,3-dione 15 (0.01mole) in ethanol (50 ml) containing piperidine (0.5 ml) was treated with 2-cyano-N-(4-phenyl-2-thioxo-3(2H)-thiazolyl)acetamide 3c (0.01 mole). The reaction mixture was refluxed for 6 h .The solid products obtained were crystallized and identified as 17a-c.

Method B:

Refluxing of indan-1,3-dione (1a)(0.01 mol) and 18 (0.01 mol) using the same previous procedure afforded 17a-c .

2-Amino-5-oxo-4-phenyl-*N*-(4-phenyl-2-thioxo-3(2*H*)-thiazolyl-4*H*-indeno[1,2-*b*]pyran-3-carboxamide (17a)

Red crystals from ethanol/DMF, m.p. >300 ºC, yield 60%.-IR($\tilde{\nu}$/cm^{-1}): 3450 ,3363(NH_2,NH), 1705(CO), 1679(CO amide).-$C_{28}H_{19}N_3O_3S_2$ (509.58) Calcd.C 66.00 H 3.75 N 8.25 Found C 66.11 H 4.03 N 8.13. MS : *m/z* = 509 .

2-Amino-5-oxo-4-(4-methoxyphenyl)-*N*-(4-phenyl-2-thioxo-3 (2*H*)-thiazolyl-4*H*-indeno[1,2-*b*]pyran-3-carboxamide (17b)

Deep red crystals from ethanol, m.p.175-177 ºC,yield 63%.-IR($\tilde{\nu}$/cm^{-1}):3500,3487,3380(NH_2,NH),1707(CO),1660 (COamide).-^{1}H-NMR (DMSO-d_6) (δ,ppm):3.83(s,3H,OCH_3), 5.23(s,1H,pyranH-4),7.26(s, 2H,

NH_2),6.62(s,1H,thiazole H-5),7.40-7.76(m,13H, aryl H), 9.86(s, 1H, NH) .-$C_{29}H_{21}N_3O_4S_2$ (539.61) Calcd.C 64.45 H 3.92 N 7.79 Found C 64.73 H 3.87 N 7.83. MS : *m/z* = 539 .

2-Amino4-(4-cholorophenyl)-5-oxo-*N*-(4-phenyl-2-thioxo-3 (2*H*)-thiazolyl-4*H*-indeno[1,2-*b*]pyran-3-carboxamide (17c)

Deep red crystals from ethanol, m.p. 290-292ºC, yield 70%.-IR (ṽ/cm^{-1}) :3484 ,3395(NH_2,NH),1712(CO), 1665(CO amide).- $C_{28}H_{18}ClN_3O_3S_2$ (544.03)Calcd.C 61.81 H 3.33 N 7.72 Found C 61.75 H 3.43 N 7.64. MS: *m/z* = 455

Formation of indanylidenepropanedinitriles (19a-c)

A suspension of 1b-d (0.01mol) and (0.01 mol) of malononitrile in dry benzene (50 mL) containing ammonium acetate (1 gm) and acetic acid (1 mL) were refluxed for 6 h using water separator .The solvent was concentrated in *vacuo* and the solid products were filtered off, crystallized from ethanol to give 19a-c.

3-Hydroxyiminoindanylidenepropanedinitrile (19a)

Brown crystals from ethanol / DMF, m.p.>300 ºC, yield 70%. -IR(ṽ/cm^{-1}): 3250 ,3160(OH), 2205(conjugated CN), 1630 (C=N)**.** - $C_{12}H_7N_3O$ (209.20) Calcd.C 68.89 H 3.37 N 20.09 Found C 68.74 H 3.50 N 20.05. MS : *m/z* = 209 .

3-Phenylhydrazonoindanylidenepropanedinitrile (19b)

Was prepared according to the procedure previously reported in the literature[4].

3-(3'-Chlorophenylimino)indanylidenepropanedinitriles (19c)

Violet crystals from ethanol, m.p. 206-208ºC,yield 75%.-IR (ṽ/cm^{-1}) :3450(NH),2200(conjugatedCN),1635(C=N).- $C_{18}H_{10}ClN_3$ (303.74) Calcd. C 71.18 H 3.32 N 13.83 Found C 71.12 H 3.21 N 13.67. MS : *m/z* = 303 .

Formation of fluoreneoximes 23a-d *and* 26

To a suspension of 19a (0.01 mol) in ethanol (50 mL) catalyzed by piperidine (0.1 mL) were added (0.01mol) of arylmethylenenitriles **2** or β-nitrostyrene 24.The reaction mixture was refluxed for 10 h. The crystalline solids, which separated out during reflux, were cooled, filtered, recrystallized from the proper solvent and identified as **23** and 26.

3-Amino-9-(hydroxyimino)-1-phenyl-9*H*-fluorene-2,4-dicarbonitrile (23a)

Brown crystals from DMF, m.p.280-282ºC, yield 63%.-IR(ṽ/cm^{-1}):3340,3209(NH_2,OH),2191(conjugatedCN),1620 (C=N) .-$C_{21}H_{12}N_4O$ (336.35) Calcd. C 74.99 H 3.60 N 16.66 Found C 75.12 H 3.52 N 16.72. MS : *m/z* = 336 .

3-Amino-1-(4'-chlorophenyl)-9-(hydroxyimino)-9*H*-fluorene-2,4-dicarbonitrile (23b)

Brown crystals ethanol/ DMF, m.p. >300 ºC, yield 66%.-IR(ν_{max},cm^{-1}):3460,3319(NH_2,OH),2193(conjugatedCN), 1660(C=N).-$C_{21}H_{11}ClN_4O$ (370.80) Calcd. C 68.02 H 2.99 N 15.11 Found C 68.11 H 3.12 N 15.08. MS : *m/z* = 370.

Ethyl 3-amino-1-(4'-chlorophenyl)-4-cyano-9-(hydroxyimino)-9*H*-fluorene-2-carboxylate (23c)

Deep brown crystals ethanol/ DMF, m.p. >300 ºC, yield 70% .-IR(ṽ/cm^{-1}):3337,3200(NH_2,OH),2203(conjugatedCN),1670 (CO), 1604(C=N).-$C_{23}H_{16}ClN_3O_3$ (417.85) Calcd. C 66.11 H 3.86 N 10.06 Found C 66.00 H 4.11 N 10.23. MS :*m/z* = 417 .

Ethyl 3-amino-4-cyano-9-(hydroxyimino)-1-(4-hydroxyphenyl)-9H-fluorene-2-carboxylate (23d*)*

Brown crystals ethanol / DMF, no melt < 300 ºC, yield 65%.-IR(ṽ/cm^{-1}): 3490,3378,3209(NH_2,OH), 2205(conjugated CN),

1660(CO),1610(C=N)).-^{1}H-NMR(DMSO-d_6)(δ,ppm):1.2-1.4(t, 3H, CH_3) , 4.2-4.4(q, 2H, CH_2), 6.8(s, 2H,NH_2), 7.2-7.95(m, 8H, aryl H), 8.8,9.6(2s, 2H, 2OH).$C_{23}H_{17}N_3O_4$ (399.41) Calcd.C 69.17 H 4.29 N 10.52 Found C 69.19 H 4.12 N 10.67. MS : *m/z* = 399 .

3-Amino-9-(hydroxyimino)-2-nitro-1-phenyl-9*H*-fluorene-4-carbonitrile (26)

Brown crystals ethanol, m.p. 278-279 ºC, yield 70%.-IR (ṽ/cm^{-1}):3333,3194,(NH_2,OH),2199(conjugatedCN),1630 (C=N)),1365(NO_2).-$C_{20}H_{12}N_4O_3$ (356.33) Calcd.C 67.41 H 3.39 N 15.72 Found C 67.33 H 3.52 N 15.68 . MS :*m/z* = 356 .

Preparation of 2-arylhydrazonoindan-1-one derivatives (27a-c)

A cold solution of 1b-d (0.01 mol) in ethanol (100 mL) was treated with a saturated sodium acetate solution (10 mL) and then with the aryldiazonium chloride .The mixture was left in the refrigerator for 24 h. the solid products were collected by filtration, crystallized from ethanol to give 27a-c.

*4-(2-(1-hydroxyimino)-3-1*H*-inden-2-(*3H*)-ylidene)hyrazinyl)-1,5-dimethyl-2-phenyl-1*H*-pyrazol-3(*2H*)-one(27a)*

Orange crystals, m.p. 180ºC, yield 70%. -IR(ṽ/cm^{-1}): 3490,3450,3370 (OH,NH), 1706(CO), 1655 (CO antipyrinyl), 1630(C=N).-C20H17N5O3 (375.39) Calcd. C 63.99 H 4.56 N 18.66 Found C 64.03 H 4.43 N 18.53. MS : m/z = *375* .

*1,5-Dimethyl-4(2-(1-oxo-3-(2-phenylhyrazono)-1*H*-inden-2(3*H*)-ylidene)hyrazinyl-2-phenyl-1*H*-pyrazol-3-(2*H*)-one (27b)*

Yellow crystals, m.p. 160-162ºC, yield 73%. - IR(ṽ/cm^{-1}): 3435,3340 (NH), 1714(CO), 1645(CO antipyrinyl), 1620 (C=N).-1H-NMR: Insoluble.-C26H22N6O2 (450.50)Calcd. C 69.32 H 4.92 N 18.65 Found C 69.43 H 4.85 N 18.73. MS : m/z *= 450 .*

*4-(2-((E)-1-(3-chlorophenylimino)-3-oxo-1*H*-inden-2(3*H*)-ylidene)hydrazinyl)-1,5-dimethyl-2-phenyl-1*H*-pyrazol-3(2*H*)-one(27c)*

Orange crystals, m.p. 169-170ºC, yield 63%.-IR(ṽ/cm^{-1}): 3485, (NH), 1716(CO),1647(CO antipyrinyl) , 1620(C=N).-C26H20ClN5O2 (469.93)Calcd. C 66.45 H 4.29 N 14.90 Found C 66.61 H 4.35 N 14.88. MS : m/z *= 469 .*

*Preparation of indeno[2,1-*c*]pyridazines (28a-c)*

Method A:

A mixture of 27 (0.01 mol) and malononitrile (0.01 mol) in dry benzene (100 mL) was refluxed for 3 h in presence of ammonium acetate (1gm) and acetic acid (1mL) using Dean- Stark trap.The solvent was concentrated to its half volume and left to cool. The solid deposited were collected by filtration, crystallized from ethanol/DMF to give 28a-c .

Method B:

Compounds 29 (0.01mol) in glacial acetic acid (30mL) were refluxed for five h. The solvent was removed in vacuo *and the formed solid products were crystallized and identified as 28.*

*2-(1,5-Dimethyl-3-oxo-2-phenyl-2,3-dihydro-1*H*-pyrazol-4-yl)-9-(hydroxyimino)-3-oxo-3,9-dihydro-2*H*-indeno[2,1-*c*] pyridazine-4-carbonitrile(28a)*

*Brown crystals, no melt < 300ºC, yield 62%.-IR(ṽ/cm^{-1}): 3440 (OH), 2203 (conjugated CN),1670(CO), 1645(CO antipyrinyl) .-1H-NMR(DMSO-d6)(δ,ppm):2.4(s, 3H, CH3), 3.3(s, 3H, N-CH3), 7.4-8.2(m, 10H, 9H, aryl H, 1H, OH).-C23H16N6O3 (424.42) Calcd.C 65.09 H 3.80 N 19.80 Found C 65.12 H 3.72 N 19.93 . MS :*m/z *= 424 .*

*2-(1,5-Dimethyl-3-oxo-2-phenyl-2,3-dihydro-1*H*-pyrazol-4-yl)-9-(phenylhydrazone)-3-oxo-3,9-dihydro-2*H*-indeno[2,1-*c*] pyridazine-4-carbonitrile(28b)*

Brown crystals, no melt < 300ºC, yield 63%.-IR(ṽ/cm^{-1}): 3444 (NH), 2209 (conjugated CN),1667(CO), 1647(CO antipyrinyl) ,1627(C=N).-C29H21N7O2 (499.54) Calcd. C 69.73 H 4.24 N 19.63 Found C 69.65 H 4.31 N 19.56. MS :*m/z* = 499 .

2-(1,5-Dimethyl-3-oxo-2-phenyl-2,3-dihydro-1*H*-pyrazol-4-yl)-9-(*N*-3-chlorophenyl)-3-oxo-3,9-dihydro-2*H*-indeno[2,1-*c*] pyridazine-4-carbonitrile(28c)

Deep brown crystals, no melt < 300ºC, yield 60%.-IR (ṽ/cm^{-1}) :2197 (conjugated CN),1668(CO), 1650(CO antipyrinyl) ,1620 (C=N) .-C29H19ClN6O2 (518.97) Calcd.C 67.12 H 3.69 N 16.19 Found C 67.45 H 3.77 N 16.24 . MS: *m/z* = 518 .

Formation of arylhydraz*ones* (29)

Reaction of aryldiazonium chloride with 19a-c using the procedure for preparation of 27 yielded 29 after crystallization from ethanol/DMF .

2-(2-(2- (1,5-Dimethyl-3-oxo-2-phenyl-2,3-dihydro-1*H*-pyrazol-4-yl) hydrazono)-3-(hydrpxyimino)-2,3-dihydro-1*H*-indene-1-ylidene)malononitrile (29a)

Brown crystals, m.p. <300ºC, yield 70%.-IR(ν_{max},cm^{-1}): 3323,3201, (NH,OH),2218, 2189 (two conjugated CN), 1646(CO phenazonyl).- $C_{23}H_{17}N_7O_2$ (423.44)Calcd.C 65.24 H 4.05 N 23.16 Found C 65.33 H 4.12 N 23.24. MS: *m/z* = 423 .

2-(2-(2-(1,5-Dimethyl-3-oxo-2-phenyl-2,3-dihydro-1*H*-pyrazol-4-yl)hydrazono)-3-(2-phenylhydrazono)-2,3-dihydro-1*H*-indene-1-ylidene)malononitrile 29b

Deep brown crystals ,m.p. 208-210ºC, yield 75%.-IR(ṽ/cm^{-1}): 3447,3298, (NH), 2222, 2188(two conjugated CN), 1643(CO phenazonyl), 1630(C=N).-$C_{29}H_{22}N_8O$ (498.55) Calcd. C 69.87 H 4.45 N 22.48 Found C 69.76 H 4.11 N 22.34. MS: *m/z* = 498.

2-((3*E*)-3-(3-chlorophenylimino)-2-(2-(1,5-dimethyl-3-oxo-2-phenyl-2,3-dihydro-1*H*-pyrazol-4-yl)hydrazono)-2,3-dihydro-1*H*-indene-1-ylidene)malononitrile 29c.

Dark brown crystals, m.p. 160-162ºC(, yield 60%.-IR(ṽ/cm^{-1}): 3443, (NH), 2220, 2213(two conjugated CN), 1647(CO phenazonyl).-$C_{29}H_{20}ClN_7O$ (517.98) Calcd. C 67.25 H 3.89 N 18.93 Found C 67.13 H 4.12 N 18.86. MS :*m/z* = 517.

Formation of 2-[4'-chlorophenyl]pyrazolo[3,2-*c*]indeno[1,2-*e*] [1,2,4] triazine derivatives (32a,b)

To a cold solution of 1b,c (0.01mol) in ethanol (50mL) containing saturated sodium acetate solution (10mL), the diazonium salt 30 prepared from the amine hydrochloride (0.01mol) and the equivalent amount of sodium nitrite was added dropwise with stirring. The reaction mixture was left in the refrigerator overnight .The resulting solids were collected by filtration, crystallized from ethanol to give 32a,b .

2-(4'-Chlorophenyl)-6*H*-indeno[1,2-*e*]pyrazolo[5,1-c][1,2,4] triazin-6-one oxime (32a)

Orange crystals ,m.p. 280-282ºC, yield 86%.-IR($\tilde{\nu}$/cm^{-1}) : 3300 , 3132 (OH) ,1630(C=N).- $C_{18}H_{10}ClN_5O$ (347.77) Calcd. C 62.17 H 2.90 N 20.14 Found C 62.33 H 3.03 N 20.21. MS: *m/z* = 347 .

2-(4'-Chlorophenyl)-6*H*-indeno[1,2-*e*]pyrazolo[5,1-c][1,2,4] triazin-6-one phenylhydrazone (32b)

Red crystals, m.p. 160-162ºC, yield 75%.-IR($\tilde{\nu}$/cm^{-1}): 3249 (NH),1673 (C=N).- $C_{24}H_{15}ClN_6$ (422.88) Calcd. C 68.17 H 3.58 N 19.87 Found C 68.34 H 3.43 N 19.67. MS : *m/z* = 422 .

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