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New Access to Indenopyridine, Indenothiophene, Indenoisoxazole, Indenopyrazole, 2,2-Bis (2,5-dihydroxyphenyl)indane-1,3-dione and Indane-1-one Derivatives

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SEVERAL new indenopyridine, indenothiophene, indenoisoxazole , indenopyrazole, 2,2-bis (2,5-dihydroxyphenyl) indane-1,3-dione and indane-1-one derivatives which have a biological usage as potential biodegradable agrochemicals, and blood anticoagulants were prepared from cyclic ketones (1a-d) and active methylene nitriles (2a,b) as starting components.

Indane-1,3-dione and its derivatives are versatile reagents, which have been extensively utilized for synthesis of functionally substituted aromatic and heteroaromatic systems [1-5]. These aromatic and heteroaromatic systems are interesting as potential biodegradable agrochemical [4] , pharmaceuticals [3,4,6] , nonpeptide human deficiency virus (HIV) protease inhibitors [8,9] , rodenticides [4] , and blood anticoagulants [2,3,10].

Recently , we have puplished new methods for the preparation of polyfunctionally substituted aromatics and heteroaromatics [6-8]. In continuation to this effort , we report here new procedures for other derivatives of these ring systems using readily obtainable starting materials.

It has been found that the adducts 3 were prepared via reacting 1b,c with phenyl isothiocyanate in refluxing dry 1,4-dioxane containing equimolecular amounts of finely divided sodium metal. Thus, compounds 3a,b were condensed with malononitrile(2a) in refluxing glacial acetic acid in presence of ammonium acetate as catalyst to afford the indeno [2,1-*c*] pyridines 4a,b.These compounds can be also synthesized through reacting α,β-unsaturated nitriles 5a,b with phenyl isothiocyanate in sodium / 1,4-dioxane. Similar sequences have been previously reported in the literature for the formation of related systems [6] .

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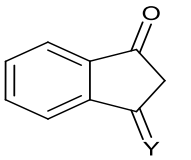
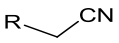


1 a,Y=O
b,Y=NOH
c,Y=NNHPh
d,Y=$NC_6H_4Cl(m)$



2 a,R= CN
b,R= $CO_2C_2H_5$

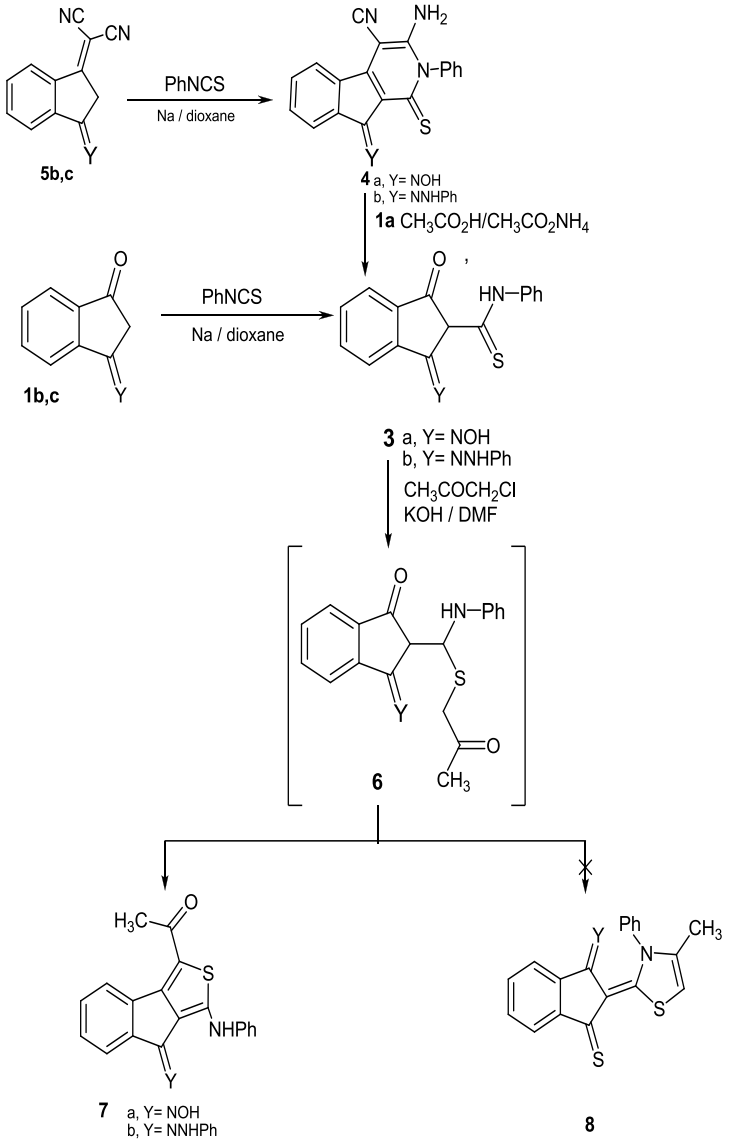
In addition, compounds 3a,b also reacted with chloroacetone in dimethylformamide containing the appropriate amounts of potassium hydroxide give-via water elimination products for which the structures of indeno[1,2-*c*]thiophenes 7 or thiazole derivatives 8 seemed *a priori* possible. Structures 8 were ruled out on the basis of the IR spectra which revealed the absence of carbonyl functions at $\tilde{\nu} \approx$ 1710-1718 cm^{-1} characteristic for carbonyl functions of indane-1,3-dione[6-8] . Also,the ^{1}H-NMR spectrum did not exhibit signals assignable to thiazole 5-H [11-13]. Thus, structures 7 were proposed for the reaction products (Scheme 1).

Attempts to form 1-substituted-3-phenyl-4-thioxo-2,3,4,4a-tetrahydr -1*H*-indeno[1,2-*d*]pyrimidin-5(9b*H*)-ones (9) or 2,4-diphenyl-5-thioxo-3,4,5,5a-tetrahydroindeno[2,1-*f*][1,2,4]triazepin-6(2*H*)-one(10)[14]via reacting the adducts 3a,b with paraformaldehyde in refluxing acetic acid through water elimination failed. However, the reaction resulted in the formation of a product via aniline elimination. 3-sulfanyl-*4H*-indeno[1,2-*c*]isoxazole-4-one(11) and 3-sulfanyl-2-phenylindeno[1,2-c]pyrazol-4(2H) -one(12) were supported as reaction products from their elemental analyses and spectral data. Products 11 and 12 were also obtained on boiling 3a,b in glacial acetic acid (Scheme 2). Elimination of aniline under the same conditions had been previously reported [15] .

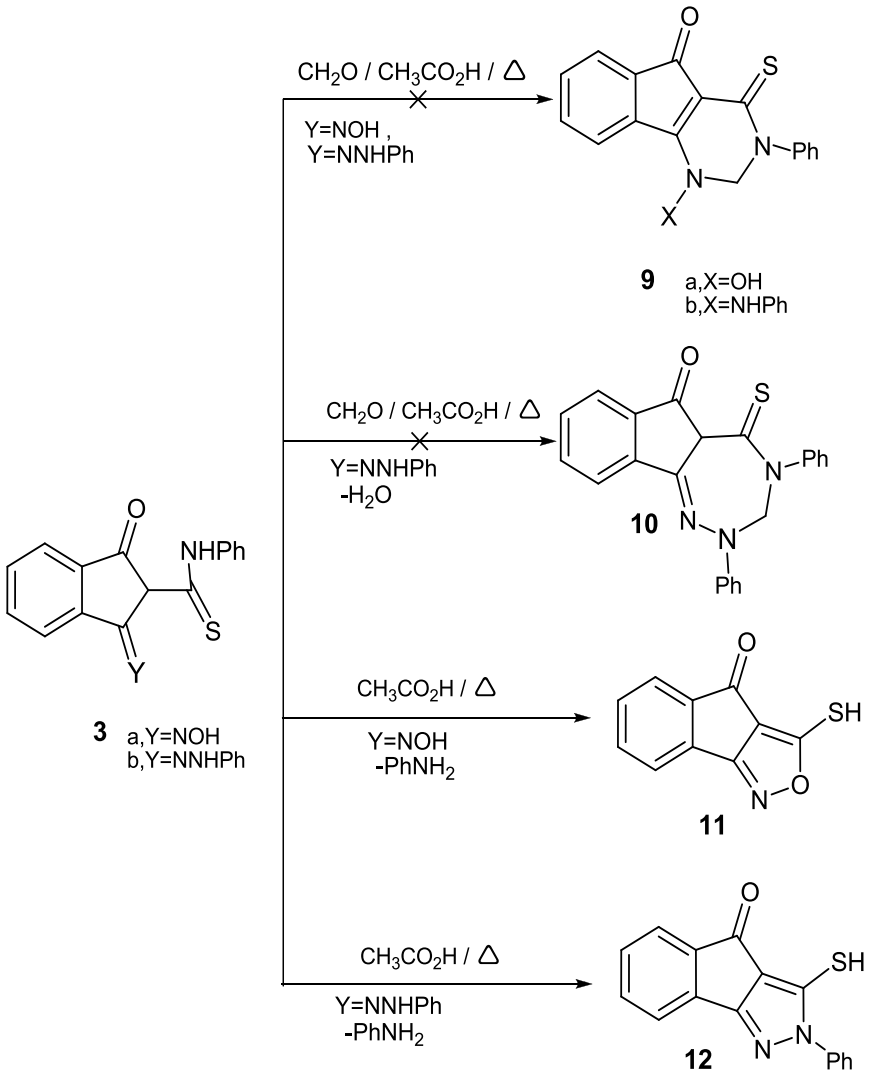
Compounds 1b,d reacted with malononitrile and sulfur in ethanol containing a catalytic amount of triethylamine, following Gewald's method, [6,8] to afford the indeno[2,1-*b*]thiophenes 14a,b. The same products were obtained by an independent synthesis by reacting 5 with elemental sulfur under the same reaction conditions. The indeno[2,1-*b*]thiophenes 14a,b or 14c,d were also obtained by heating a mixture of 1a,b with malononitrile or ethyl cyanoacetate and sulfur. Elemental analysis and spectral data are in good agreement with the proposed structures.

On the other hand, treatment of compound 5a with a mixture of formalin and primary aromatic amines in the molar ratio (1:1:1) resulted in the formation of dihydroindeno[2,1-*c*]pyridines 17. Elemental analysis and spectral data are in full agreement with the proposed structures 17.

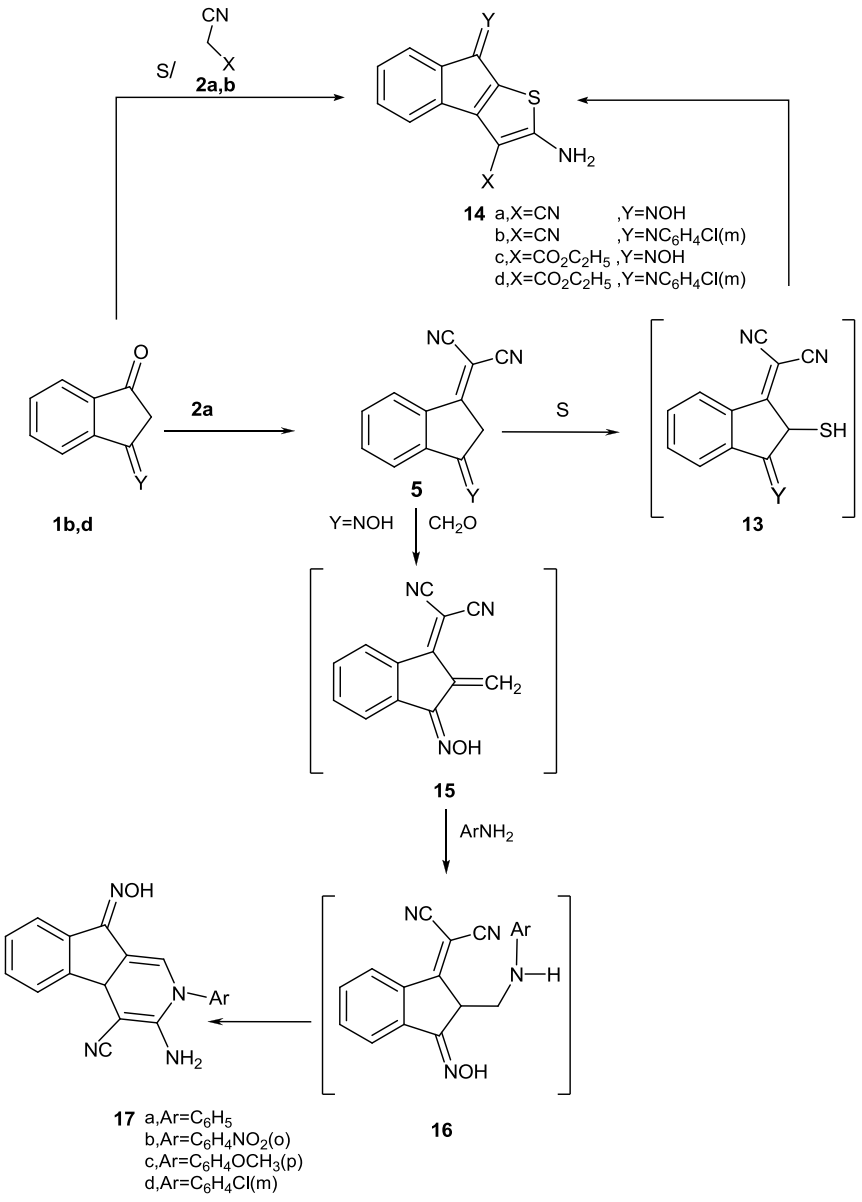
Compounds 17 were suggested to be formed via condensation of the active methylene in 5 with formaldehyde to give first the ylidene 15, which added one molecule of primary amine to give the adduct 16 and the latter readily cyclized to yield the isolable final products 17 (Scheme 3).


NC
CN
PhNCS
Na / dioxane
CN
NH2
N–Ph
S
Y
5b,c
4 a, Y= NOH
b, Y= NNHPh
1a CH3CO2H/CH3CO2NH4
O
PhNCS
Na / dioxane
HN–Ph
S
1b,c
3 a, Y= NOH
b, Y= NNHPh
CH3COCH2Cl
KOH / DMF
6
H3C
NHPh
7 a, Y= NOH
b, Y= NNHPh
Ph
N
CH3
8

Scheme 1.


CH2O / CH3CO2H / △
Y=NOH ,
Y=NNHPh
9
a,X=OH
b,X=NHPh
CH2O / CH3CO2H / △
Y=NNHPh
-H2O
10
CH3CO2H / △
Y=NOH
-PhNH2
11
CH3CO2H / △
Y=NNHPh
-PhNH2
12
3
a,Y=NOH
b,Y=NNHPh

Scheme 2.


CN
X
S/
2a,b
Y
S
NH2
X
14 a,X=CN ,Y=NOH
b,X=CN ,Y=NC6H4Cl(m)
c,X=CO2C2H5 ,Y=NOH
d,X=CO2C2H5 ,Y=NC6H4Cl(m)
O
Y
1b,d
2a
NC
CN
5
Y
S
NC
CN
SH
Y
13
Y=NOH
CH2O
NC
CN
CH2
NOH
15
ArNH2
NOH
N
Ar
NC
NH2
NC
CN
Ar
N
H
NOH
16
17 a,Ar=C6H5
b,Ar=C6H4NO2(o)
c,Ar=C6H4OCH3(p)
d,Ar=C6H4Cl(m)

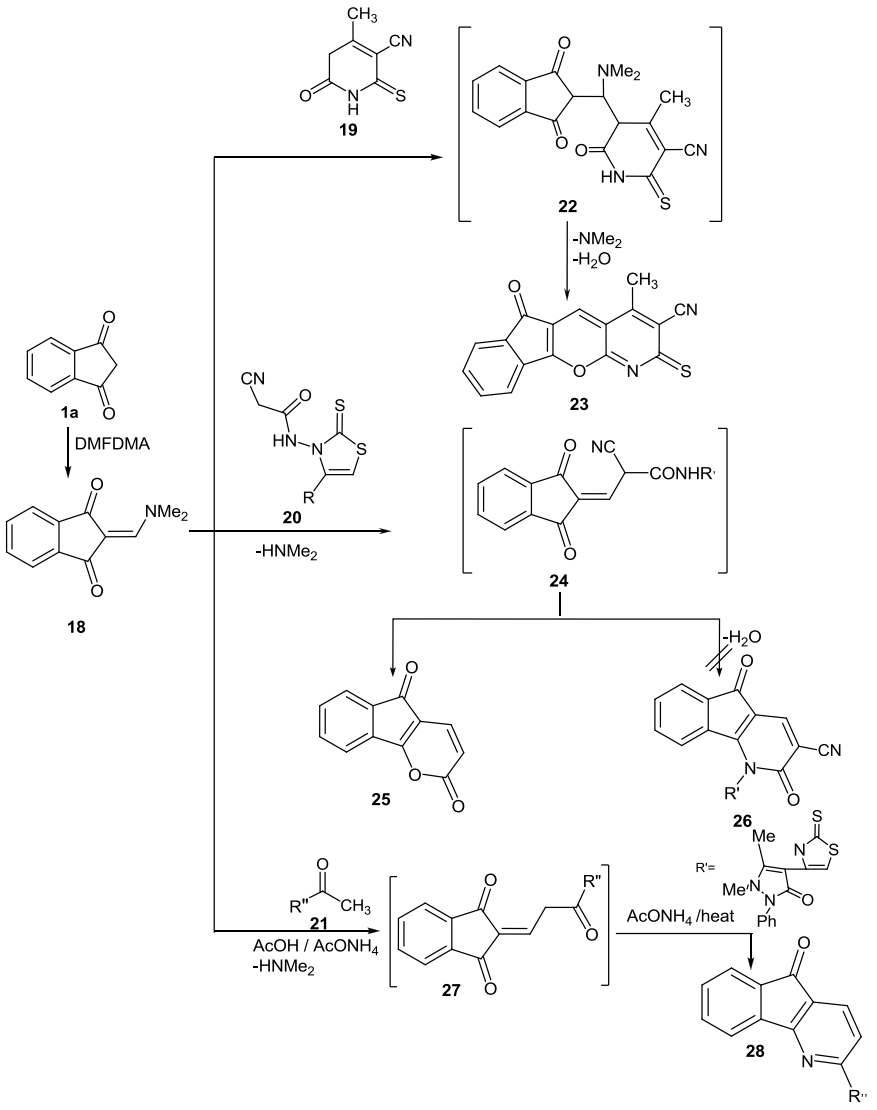
Scheme 3.

Recently, it has been reported that enaminones were extensively used as starting materials for the synthesis of aromatic and heteroaromati systems.[16, 18-24] In spite of the enormous amount of literature on the utility of acyclic enaminones in heterocyclic synthesis, to our knowledge little attention has been paid to the corresponding cyclic enaminones[16-19].

In continuation of our studies on the chemistry of cyclic ketones 1 and part of our program aimed at developing new synthetic procedures for various heterocycles fused to the indene ring for biological screening, we now report the utility of 2-dimethylaminomethyleneindane-1,3-dione (18)[16,18] as a building block for the synthesis of some new fused indene derivatives.Thus, treatment of indane-1,3-dione (1a) with dimethylformamide dimethylacetal (DMFDMA) in dry xylene at reflux temperature yielded 2-dimethylaminomethyleneindane-1,3-dione (18). We have investigated the reactivity of 18 towards methyleneactive reagents. For example,compound 18 reacted with 1,2,5,6-tetrahydro-6-oxo-2-thioxo-3-cyano-4-methylpyridine(19) in refluxing acetic acid to afford product-via dimethylamine and water-elimination, a single product identified as 4-methyl -6- oxo 2-thioxo -2,6-dihydroindeno [1,2-*b*]pyrano [2,3-*b*] pyridine-3-carbonitrile (23). This compound is suggested to be formed via initial addition of the active methylene in 19 to the activated double bond in 18 to give the adduct 18 which was readily cyclized to 23 via elimination of one molecule each of dimethylamine and water.

In a similar manner, compound 18 reacted with the 2-cyano-*N*-(4-(1,5-dimethyl-3-oxo-2-phenyl-2,3-dihydro-1*H*-pyrazol-4-yl)-2-thioxothiazol-3(2*H*)-yl)acetamide (20)[12] under the same reaction conditions to give a product for which indenopyran 25 or indenopyridine 26 were considered as possible structures. Structure 26 was ruled out for the reaction since IR spectrum clearly indicates the absence of a cyano group.

The reaction of the enaminone 18 with 3-acetylcoumarin (21) in refluxing acetic acid in the presence of ammonium acetate yielded a product that may be formulated as indeno[1,2-*b*]pyridine derivative 28. Compound 28 is proposed to be formed via initial Michael addition of the anionized methylketone in 21 across the double bond in 18 giving the intermediate 27, subsequent cyclization of which could lead to the formation of indeno[1,2-*b*]pyridine 28 (Scheme 4).

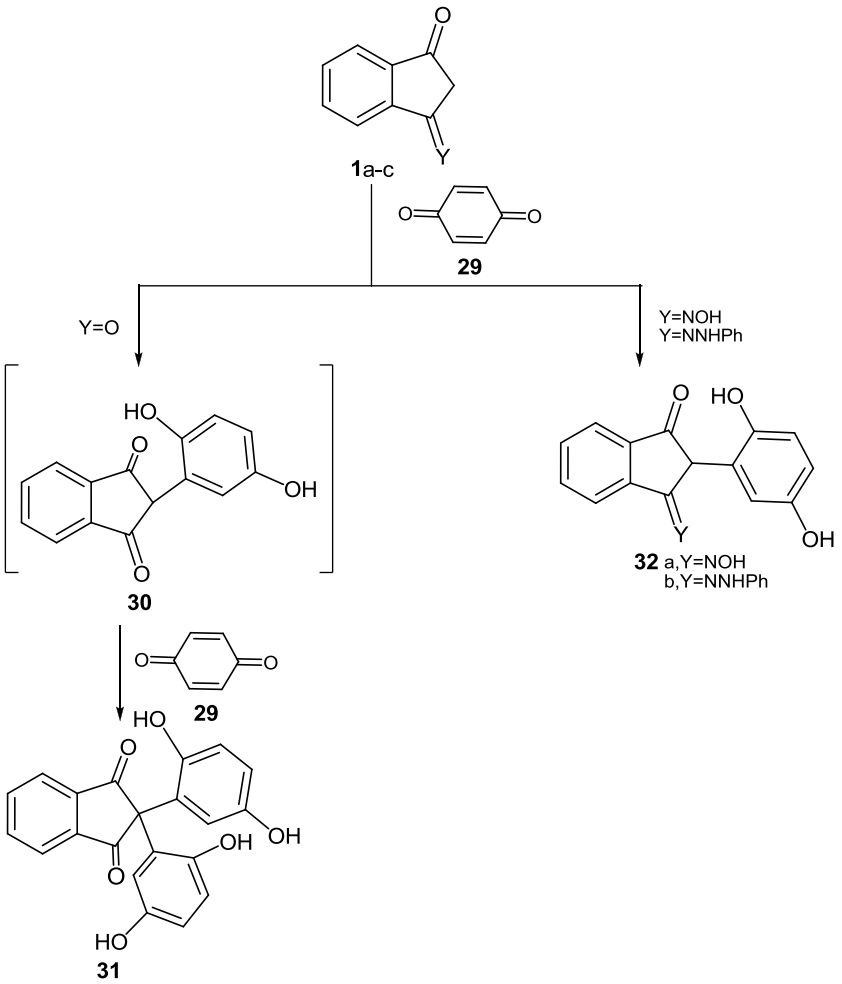


Scheme 4 .

Finally, we have studied the reactivity of cyclic ketones 1a-c towards *p*-benzoquinone (29). Therefore,treatment of indane-1,3-dione (1a) with *p*-benzoquinone in a molar ratio (1:1) or (1:2) in boiling acetic acid yield product with the gross formula $C_{21}H_{14}O_6$ .The structure 2,2-bis(2,5-dihydroxyphenyl)

indane-1,3-dione (31) was assigned for the reaction product from its elemental analysis and IR spectrum. Formation of 31 was assumed to proceed via the reaction pathway demonstrated in Scheme 5.

Cyclic ketones 1b,c also reacted with *p*-benzoquinone (29) in a molar ratio (1:1) or (1:2) to afford only the mono adduct 32 (Scheme 5).



Scheme 5 .

Experimental

All melting points are uncorrected and have been measured on a Griffin & George MBF010T (London) apparatus. Recorded yields correspond to pure products. IR (KBr) spectra were recorded on a Perkin Elmer SP-880 spectrometer and. From samples of sufficient solubility ^{1}H-NMR spectra were measured on a Varian 270 MHz spectrometer on DMSO-d_6 as solvent and 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 Units at Cairo and Mansoura Universities. Mass spectra were recorded on a MS 30(AEI) instrument at 70 eV ionization energy.

Formation of indane-1-one derivatives 3a,b

To a suspension of finely ground sodium metal (0.01mol) in dry 1,4-dioxan (50 ml) 1b,c (0.01mol) was added.The reaction mixture was refluxed for 3 hr, then left to cool and treated with dilute hydrochloric acid.The separated solid products were collected by filtration and crystallized from ethanol / DMF.

1-(Hydroxyimino)-3-oxo-N-phenylindane-2-carbothioamide (3a)

Brown crystals, m.p.112-114°C, yield 70% .-IR($\tilde{\nu}$/cm^{-1}) :3380, 3200 (NH,OH),1710(CO),1630(C=N).-$C_{16}H_{12}N_2O_2S$ (296.35) Calcd. C 64.85 , H 4.08, N 9.45. Found C 64.81 , H 4.12 , N 9.37. -Mol. mass 296 (MS).

1-Oxo-N-phenyl-3-(phenylhydrazono)indane-2-carbothioamide (3b)

Brown crystals , m.p. 240-242 °C , yield 67% .-IR($\tilde{\nu}$ /cm^{-1}) : 3410, 3380 (NH),1705(CO),1635(C=N).-$C_{22}H_{17}N_3OS$ (371.46) Calcd. C 71.14 ,H 4.61, N 11.31. Found C 71.28 , H 3.99 , N 11.42. Mol. mass 371 (MS).

Formation of indeno[2,1-c]pyridines 4a,b

Method A

A mixture of 3b,c (0.01mol) and malononitrile (0.01mol) in dry benzene (50ml) were refluxed for 6 hr in presence of acetic acid (1ml) and ammonium acetate (1g). The solvent was concentrated in vacuo and the solid precipitated was collected by filtration , crystallized from 1,4-dioxan and identified as 4a,b .

Method B

Compounds 4a,b were also prepared by reacting 5a,b with phenyl isothiocyanate in 1,4-dioxan containing finely divided sodium.

3-Amino -9- (hydroxyimino) -2- phenyl-1-thioxo-2,9-dihydro-1H-indeno [2,1-c] pyridine-4-carbonitrile (4a)

Brown crystals, no melt < 300°C, yield 65%.-IR($\tilde{\nu}$/cm^{-1}): 3320, 3194 (NH_2,OH),2015(conjugated CN),1650(C=N).-^{1}HNMR(DMSO-d_6)(δ ,ppm) :7.14-7.72(m, 9H, aryl H), 9.8(s, 2H, NH_2), 11.2(s, 1H,OH).- $C_{19}H_{12}N_4OS$ (344.39)

Calcd. C 66.26 , H 3.51, N 16.27. Found C 66.32 , H 3.60 , N 16.40. Mol. mass 344 (MS).

3-Amino -2- phenyl -9- (phenylhydrazono) -1- thioxo-2,9-dihydro-1H-indeno [2,1-c] pyridine-4-carbonitrile (4b)

Brown crystals, no melt < 300°C, yield 70%.-IR($\tilde{\nu}$/cm^{-1}) :3315, 3215(NH_2,NH),2194(conjugatedCN)1629(C=N).-$C_{25}H_{17}N_5S$(419.50) Calcd .C 71.58 ,H 4.08, N 16.69 .Found C 71.43, H 4.11, N 16.73. Mol. mass 419 (MS).

Preparation of indeno[1,2-c]thiophenes 7a,b

A solution of 3 a,b (0.01 mol) in dimethylformamide (50 ml) and (0.01 mol) of finely ground potassium hydroxide was stirred for 6hr. To this solution (0.01 mol) of chloroacetone was added, then the mixture was stirred again overnight. The solution was poured on ice and acidified with dilute hydrochloric acid. The solids obtained were filtered off, crystallized from ethanol / DMF and identified as 7a,b.

1-Acetyl-3-anilino-4H-indeno[1,2-c]thiophen-4-one oxime (7a)

Brown crystals, no melt < 300°C, yield 62%.-IR($\tilde{\nu}$/cm^{-1}) :3562, 3448,3336(NH,OH) ,1710 (CO), 1647(C=N).-$C_{19}H_{14}N_2O_2S$ (334.39) Calcd. C 68.24, H 4.22, N 8.38 . Found C 68.17, H 4.18, N 8.31. Mol. mass 344 (MS).

1-Acetyl-3-anilino-4H-indeno[1,2-c]thiophen-4-one phenylhydrazone (7b)

Brown crystals, m.p.252-254 °C, yield 68%.-IR($\tilde{\nu}$/cm^{-1}):3425(NH) ,1712 (CO), 1635(C=N) .-^{1}H-NMR(DMSO-d_6)(δ ,ppm): 3.28 (s,3H, CH3), 7.47-8.2 (m, 16H, 14 H aryl H and 2H, 2NH).-$C_{25}H_{19}N_3OS$ (409.50) Calcd. C 73.32 , H 4.68 , N 10.26 . Found C 73.17, H 4.82, N 10.54. Mol. mass 409 (MS).

Formation of 3-sulfanyl-4H-indeno[1,2-c]isoxazole-4-one(11) and 3- sulfany -2-phenylindeno[1,2-c]pyrazol-4(2H)-one(12)

A solution of 3a or 3b (0.01mol) in glacial acetic acid (50ml) was refluxed for 10 hr. The solvent evaporated in vacuo, then the remainder solution was triturated with ethanol, filtered off, crystallized from ethanol / DMF and identified as 11 and 12, respectively.

3-Sulfanyl-4H-indeno[1,2-c]isoxazole-4-one (11)

Deep brown crystals, m.p.220-222 °C, yield 60%.-IR($\tilde{\nu}$/cm^{-1}) :3449 (SH) , 1710 (CO), 1639(C=N) .-^{1}H-NMR(DMSO-d_6)(δ,ppm):7.33-7.74(m, 6H,5H, aryl H and 1H,SH).-$C_{10}H_5NO_2S$ (203.21) Calcd. C 59.10, H 2.48, N 6.89 .Found C 59.42, H 3.11, N 6.78. Mol. mass 203 (MS).

3-Sulfanyl -2-phenylindeno[1,2-c]pyrazol-4(2H)-one(12)

Brown crystals, m.p. 216-218 °C, yield 62%.-IR($\tilde{\nu}$/cm^{-1}) : 3421 (SH) , 1711(CO),1669(C=N).-^{1}H-NMR(DMSO-d_6)(δ,ppm):7.33-7.74(m, 6H,5H, aryl H

and 1H, SH).-$C_{16}H_{10}N_2OS$ (278.33) Calcd. C 69.05, H 3.62, N10.07 . Found C 69.42, H 3.74 , N10.11. Mol. mass 278 (MS).

Formation of indeno[2,1-b]thiophene derivatives 14a-d

Method A

A suspension of equivalent amounts of 1b,d (0.01mol), malononitrile or ethyl cyanoacetate (0.01mol) and elemental sulphur in ethanol (50ml) and triethylamine (0.5 ml) were heated under reflux for 3 hr. The solids deposited were collected by filtration,crystallized from ethanol/1,4-dioxan and identified as 14a-d.

Method B

Compounds 14a,b were also prepared by reacting 2a,b with sulphur under the same condition used in the above procedure.

2-Amino-8-(hydroxyimimo)-8H-indeno[2,1-b]thiophene-3-carbonitrile (14a)

Grey crystals, no melt < 300°C, yield 63% .-IR($\tilde{\nu}$/cm^{-1}): 3333, 3225 (NH_2.OH),2206(conjugatedCN),1650(C=N).-$C_{12}H_7N_3SO$ (241.27) Calcd. C 59.74, H 2.92, N 17.42. Found C 59.40 , H 2,71 , N 17.22 . Mol. mass 241 (MS).

2-Amino-8-[(3-chlorophenyl)imino]-8H-indeno [2,1-b] thiophene-3-carbonitrile (14b)

Brown crystals, no melt < 300C, yield 64% .-IR($\tilde{\nu}$/cm^{-1}): 3446, 3321 , 3186(NH_2), 2210(conjugatedCN), 1657(C=N).-^{1}H-NMR (DMSO-d_6) (δ,ppm): 7.12 -7.71 (m, 8H, aryl H), 8.62(s, 2H, NH_2).-$C_{18}H_{10}ClN_3S$ (335.82) Calcd. C 64.38, H 3.00 , N 12.51. Found C 64.54 ,H 3.23, N 12.45.Mol. mass 335 (MS).

Ethyl 2-amino-8-(hydroxyimino)-8H-indeno[2,1-b]thiophene-3-carboxylate (14c)

Pale yellow crystals, no melt < 300ºC, yield 70% .-IR($\tilde{\nu}$ /cm^{-1}):3517 , 3430,3387(NH_2,OH), 1699(CO ester), 1622(C=N).-$C_{14}H_{12}N_2O_3S$ (288.33) Calcd. C 58.32, H 4.20, N 9.72. Found C 58,12, H 4.16, N 9.66. Mol. mass 288 (MS).

Ethyl 2-amino -8- [(3'-chlorophenyl)imino] -8H-indeno [2,1-b] thiophene-3-carboxylate (14d)

Red crystals, no melt < 300ºC, yield 68% .-IR($\tilde{\nu}$/cm^{-1}) 3516, 3446, 3386(NH_2,OH),1707(COester),1650(C=N).-$C_{20}H_{15}ClN_2O_2S$(382.87) Calcd. C 62.74 ,H 3.95, N 7.32 .Found C 62.65, H 3.78, N 7.30. Mol. Mass 382 (MS).

Preparation of 3-amino-2-aryl-4a,9-dihydro-9-hydroxyimino-2H-indeno [2,1-c]pyridine-4-carbonitriles (17a-d)

A suspension of 5a(0.01mol) in ethanol (50ml) containing formaldehyde (0.01mol) and primary aromatic amine (0.01mol) was refluxed for 3 hr. The precipitates formed were filtered off, then crystallized from ethanol/DMF and identified as 17a-d.

3-Amino-9-(hydroxyimino)-2-phenyl-4a,9-dihydro-2H-indeno[2,1-c] pyridine-4-carbonitrile (17a)

Deep brown crystals, no melt < 300°C, yield 70% .-IR($\tilde{\nu}$ /cm^{-1}): 3395, 3240(NH_2,OH), 2191(conjugated CN), 1650(C=N).-$C_{19}H_{14}N_4O$ (314.35) Calcd. C 72.60 H ,4.49 ,N 17.82 . Found C 72.40 , H 4.60 , N 17.75. Mol. mass 314 (MS).

3-Amino -9- (hydroxyimino) -2- (2-nitrophenyl) -4a, 9-dihydro-2H-indeno [2,1-c]pyridine-4-carbonitrile (17b)

Brown crystals, no melt < 300ºC, yield 65% .-IR($\tilde{\nu}$/cm^{-1}):3486, 3450, 3382(NH_2,OH), 2200 (conjugated CN), 1658(C=N).- $C_{19}H_{13}N_5O_3$ (359.35) Calcd. C 63.51, H 3.65, N 19.49. Found C 63.20, H 3.92, N 19.34. Mol. mass 359 (MS).

3-Amino-9-(hydroxyimino)-2-(4-methoxyphenyl)-4a,9-dihydro-2H-indeno[2,1-c]pyridine-4-carbonitrile (17c)

Faint brown crystals, no melt < 300ºC, yield 68% .-IR($\tilde{\nu}$/cm^{-1}):3324 , 3191(NH_2,OH),2196 (conjugatedCN),1655(C=N).-^{1}H-NMR(DMSO-d_6) (δ,ppm): 3.81(s, 3H, OCH3), 7.11(s, 2H, NH_2), 7.54-7.97 (m, 10H, 9H aryl H and 1H, CH), 9.87(s, 1H, OH).-$C_{20}H_{16}N_4O_2$ (344.38) Calcd. C 69.76, H 4.68, N 16.27. Found C 69.63 , H 4.71, N 16.13. Mol. mass 344 (MS).

3-Amino -2- (3-chlorophenyl) -9- (hydroxyimino) -4a,9- dihydro-2H-indeno [2,1-c]pyridine-4-carbonitrile (17d)

Red crystals, m.p.>300 ºC, yield 73% .-IR($\tilde{\nu}$ /cm^{-1}):3322, 3197 (NH_2,OH),2194 (conjugatedCN),1660(C=N).-$C_{19}H_{13}ClN_4O$(348.79) Calcd. C 65.43, H 3.76 ,N 16.06 . Found C 65.23, H 3.65, N16.01. Mol. mass 348 (MS).

Preparation of compounds 23 and 25

Compound 18 (0.01mol) in glacial acetic acid (30ml) was treated with (0.01mol) of the pyridine 19 or 1,3-thiazoline 20.The reaction mixture was refluxed for 6 hr. Then left to cool to room temperature.The precipitated materials upon cooling were isolated by filtration and crystallized from the proper solvent to give 23 and 25, respectively.

4-Methyl -6-oxo2- thioxo -2,6- dihydroindeno [1,2-b]pyrano[2,3-b] pyridine -3-carbonitrile (23)

Yellow crystals from acetic acid, no melt < 300 ºC, yield 62% .-IR($\tilde{\nu}$ /cm^{-1}): 2209 (conjugatedCN),1706(CO),1650(C=N),1255(C=S).-$C_{17}H_8N_2O_2S$ (304.33) Calcd. C 67.09, H 2.65, N 9.20. Found C 67.12, H 2.92, N 9.13. Mol. mass 304 (MS).

N-[(1,5-dimethyl-2-phenyl-3-oxo-2,3-dihydro- 1H-pyrazol-4-yl)-2-thioxothiazol-3-yl]-2,5-dihydroindeno[1,2-b]pyran-3-carboxamide (25)

Buff crystals from ethanol, m.p.170-172 ºC, yield 60% .-IR($\tilde{\nu}$ /cm^{-1}) : 3423(NH), 1705(CO),1680(CO), 1660(CO antipyrinyl), 1240(C=S).-$C_{27}H_{18}N_4O_5S_2$ (542.58) Calcd. C 59.76 , H 3.34 , N 10.32. Found C 59.68 , H 3.23, N 10.22. Mol. mass 542 (MS).

Synthesis of 2-(3'-coumarinyl)indeno[1,2-b]pyridine-5-one (28)

A mixture of 18(0.01mol) and (0.01mol) of 3-acetylcoumarin (21) in glacial acetic acid (30ml) and (0.01 mol) of ammonium acetate was refluxed for 1hr. The precipitated material was isolated by filtration and crystallized from ethanol/1,4-dioxan to give 28 as buff crystals, m.p.280-282 ºC, yield 70%.-IR($\tilde{\nu}$ /cm^{-1}):1730 (CO coumarinyl),1712(CO indanone), 1630(C=N).-$C_{21}H_{11}NO_3$ (325.32) Calcd. C 77.53, H 3.41, N 4.31. Found C 77.62, H 3.53, N 4.45. Mol. mass 325 (MS).

Preparation of 2,2-bis(2,5-dihydroxyphenyl) indane-1,3-dione (31) and indane-1-one derivatives 32a,b

General procedure

A solution of 1a-c (0.01 mol) and *p*-benzoquinone (0.01 mol) or (0.02 mol) in glacial acetic acid (30ml) were refluxed for 7 hr. It was evaporated in vacuo, and then treated with methanol. The solid products obtained were collected by filtration, crystallized from acetic acid then identified as 31 and 32a,b, respectively.

2,2-Bis-(2,5-dihydroxyphenyl)indane-1,3-dione(31)

Deep brown crystals, no melt < 300ºC, yield, 64%.-IR($\tilde{\nu}$cm^{-1}) :3568, 3446,3429(OH), 1705,1680(CO).-$C_{21}H_{14}O_6$ (362.34) Calcd. C 69.61 , H 3.89, Found C 69.55 H 3.78 . Mol. mass 362 (MS).

2-(2,5-Dihydroxyphenyl)-3-hydroxyiminoindane-1-one (32a)

Deep brown crystals, no melt < 300ºC, yield, 62%.-IR($\tilde{\nu}$ /cm^{-1}) :3518, 3445,3386(OH),1714(CO),1657(C=N)-$C_{15}H_{11}NO$(269.26) Calcd. C 66.91, H 4.12 , N 5.20 .Found C 66.87 H, 4.09 , N 5.17. Mol. mass 269 (MS).

2-(2,5-Dihydroxyphenyl)-3 - phenylhydrazonoindane-1one (32b)

Brown crystals, no melt < 300ºC,yield,60%.–IR($\tilde{\nu}$cm^{-1}):3568, 3446, 3422(OH,NH),1716(CO),1661(C=N).-^{1}H-NMR(DMSO-d_6)(δ,ppm):6.55 (s, 1H, CH), 7.41-7.99(m, 12H, aryl H),8.4(s, 1H, OH),9.25,9.8(2s, 2H, 2OH).-$C_{21}H_{16}N_2O_3$ (344.37) Calcd. C 73.24, H 4.68, N 8.13. Found C 73.13, H 4.56 , N 8.11. Mol. mass 344 (MS).

References

1. **Wang, S., Ma, N., Zhang, G., Shi, F., Jiang , B., Lu,H., Gao,Y. and Tu, S.,** An efficient and clean synthesis of inedno [1,2-b]pyrazolo 4,3-e] pyridine-5 (1*H*)-one derivatives under microwave irradiation in water. *J.Heterocycl. Chem.* **47**, 1283 (2010)

2. **Ghahremanzadeh, R., Fereshtehnejad, F. and Bozgir, A.,** One – pot synthesis of spiro[diindeno[1,2-b:2',1'-e]pyridine-11,3'-indoline]-triones. *J. Heterocycl. Chem.* **47**, 1031 (2010)

3. **Boominathan, M., Nagaraj, M., Muthusubramanian, S. and Krishnakumar, R.V.,** Efficient atom economical one-pot multicomponent synthesis of densely functionalized 4*H*-chromene derivatives. *Tetrahedron*, **67**, 6057 (2011)

4. **Verma, R.V., Ila, H. and Singh, M.S.,** Heteroaromatic annulations studies 2-[bis(methylthio)methylene]-1,3-indanedione : Efficient routes to indenofused heterocycles. *Tetrahedron*, **66**, 7389 (2010)

5. **El-Zohry, M.F., Elossaily, Y.A., Mohamed, T. A. and Hussein, E.M.,** Synthesis and reactions of some new spiroindeno[1,2-b]pyran-4,3'-indolines. *Heterocycles*, **75**(4), 955 (2008)

6. **El-Taweel, F. M., Osman, A. I., El-Awad, S. M. H. and Elagamey, A. A**., New routes for the synthesis of indene derivatives using 1,3-indanedione. *Alex. J. Pharm. Sci.* **12**(1), 44 (1998)

7. **El-Taweel, F. M., Sofan, M. A., Ayaad, S. N., Abu El-Maati, T. M. and El-Agamey, A. A.,** Synthetic routes to indenothiophene, indenopyran , and fluorenone derivatives. *Bull. Chem. Farm.* **137**, 448 (1998)

8. **El-Taweel, F.M., Sofan, M.A., Abu El-Maati, T.M. and El-Agamey, A.A.,** Synthetic routes to fluorenone , indenopyridine ,4H-naphtho [2,1-b] pyrans and pyridine derivatives. *Bull. Chem. Farm.* **140**, 306 (2001)

9. **Afsa, E.M., H.W.S.. and Ahmed, A.F.S.,** Behaviour of 2-substituted 1,3-indanediones towards aldimines. *Bull.Chem.Farm.* **140**, 46 (2001)

10. **Ziehe, H., Wartchow, R. and Butenschon, H.,** Diastereoselective ring expansion rearrangement of (benzocyclobutenone) and (benzocyclobutenedione) chromium complexes: Synthesis of substituted 1-indanone and 1,3-indanedione complexes. *Eur. J. Org. Chem.* 832 (1999)

11. **El-Taweel, F.M.A.,** Novel and facile synthesis of thiophene , thiazole , 2*H*-pyran-2-one , benzimidazo[1,2-a]pyridine and pyridine derivatives containging antipyrine moiety. *Phosphorus Sulphur and Silicon* , **179**, 1277 (2004)

12. **El-Taweel, F.M., Elagamey, A.A., Kenawy, A.A. and Waly, M. A.,** Novel synthesis of thiazole ,coumarin,pyridine,thiophene and thieno [2,3-b]pyridine derivatives. *Phosphorus. Sulphur and Silicon* , **176**, 215 (2001)

13. **Farag, A.M., Dawood, K.M. and Kandeel, Z.E.,** Facile synthesis of novel polysubstituted thiophene and 1,3,4-thiadiazole derivatives . *Tetrahedron*, **53**, 161 (1997)

14. **Afsah, E.M., Hammouda, M., Zoorob, H., Khalifa, M.M. and Zimaity, M.,** Mannichreaction with 1,3-indanedione phenylhydrazones. *Z. Naturforsch.* **45**, 80 (1990)

15. **Osman, A. I., El-Taweel, F. M. A., El-Awaad, S. M. H. and Elagamey, A. A.,** Synthesis of functionally substituted pyridine and thiophene derivatives. *Indian J. Chem.* **37B,** 399 (1998)

16. **Afsah, E.M., Hammouda, M. and Khalifa, M. M.,** A study on the Mannich reaction with 1,3-indanedione. *Z. Naturforsch.,* **45**, 1055 (1990)

17. **Abu El Maati, T. M., Said, S. B., Abu Elenein, N. S., Khodier, M. N. and Sofan, M.A.,** 3-(Phenylhydrazono)-indan-1-one and 2-dimethylaminomethylene-3-(phenylhydrazono)-indan-1-one as useful synthons for the constraction of new heterocyclic systems . *J. Heterocycl . Chem.* **40**, 481 (2003)

18. **Oliveira-Campos, Ana M.F., Salaheldin, A.M., Almeida Paz, F.A. and Rodrigues, L.M.,** Synthesis of 3-indolylazoles and meridianin derivatives from inolylenaminonitriles. *Arkivoc*, (xi),121 (2011)

19. **Mabkhot, Y.N., Al-Majid, A.S. and Alamary, A.S.,** Synthesis and chemical characterization of some new diheteroaryl thienothiophene derivatives . *Molecules* , **16**, 7706 (2011)

20. **Abu-Shanab, F.A., Sherif, M.S. and Mousa, S.A.S.,** Dimethylformamid edimethylacetal as a building block in heterocyclic systems. *J. Heterocycl . Chem* . **46**, 801 (2009)

21. **El-Taweel, F. M. and Elnagdi, M. H.,** Studies with enaminones : Synthesis of new coumarin-3-ylazoles,coumarin-3-ylazines,coumarin-3-ylazoloazines,coumarin-3-ylpyron and coumarin-2-ylbenzo[b] furans. *J. Heterocycl. Chem.* **38**, 981 (2001)

22. **Abdel-Rahman, A. H., Keshk, E. M. and El-Telbani, E. M.,** Linearly fued furochromones by intramolecular enaminone reactions. *Z. Naturforsch*. **57b,** 557 (2002)

23. **Abu-Elmaati, T. M. and El-Taweel, F. M.,** Studies with alkylheterocycles:Novel synthesis of functionally substituted isoquinoline and pyridopyridine derivatives. *J. Chin. Chem. Soc.* **49**, 1045 (2002)

24. **Abdel-Khalik, M. M. and Elnagdi, M. H.,** Enaminones in organic synthesis: A novel synthesis of 1,3,5-trisubstituted benzene derivatives and of 2-substituted 5-aroylpyridines. *Synth. Commun.* **32**, 159 . (2002)

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طرق لتحضير مشتقات جديدة من إندينوبيريدين ، إندينوثيوفين ، ثنائي فينيل إندين دايون و إندن-١- أون

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في هذا البحث إخترنا الكيتونات الحلقية رقم ١ و النيتريلات ذات مجموعات الميثيلين النشيطة كمواد أولية بسيطة لتحضير مشتقات جديدة من إندينوبيريدين ، إندينوثيوفين ثنائي فينيل إندين دايون و إندن-١- أون ، حيث أن مشتقات الإندين ذات أهمية حيوية فمثلا تستخدم كمضادات للفئران ، تمنع تجلط الدم و كمنظمات لنمو النباتات .

تم إثبات التركيب البنائي للمركبات الجديدة بإستخدام طرق التحليل الطيفي و العنصري و كذلك الطرق الكيميائية .