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SYNTHESIS AND REACTION OF SOME INDENOPYRIDINE AND THIENO[2,3-*b*]INDENO[2,1-*e*]PYRIDINE DERIVATIVES

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Abstract. Synthesis of indenopyridine-2-thione derivatives **6a-e** *via* reaction of compound **1** with thioamides **2a-e** in good yields. Several thieno[2,3-*b*]indeno[2,1-*e*]pyridine **9a-e** have been synthesized. Some of them was used as a key intermediate in synthesis of **10-12**. On the other hand, compound **1** reacted with various reagents to yield **16, 19, 21-24**.

Indenopyridines exhibit potent antispermatogenic activity and are useful inhibitors of spermatogenesis in animals[1] and showed fungicidal activity.[2]

In continuation of our interest in exploring the utility of α,β-unsaturated nitriles as versatile precursors for the synthesis of substituted heterocycles[3-5] we report here the results of the reactivity of thioamides **2a-e** towards 1,3-indandione (**1**). Thus, refluxing of equimolar amounts of each **2a-e** and **1** in 1,4-dioxane in presence of catalytic amount of piperidine afforded indeno[1,2-*b*]pyridine-2-thione derivatives **6a-e**. Compound **6** is assumed to be formed *via* initial *Michael* adduct **3** followed by intramolecular cyclodehydration and spontaneous autoxidation under the

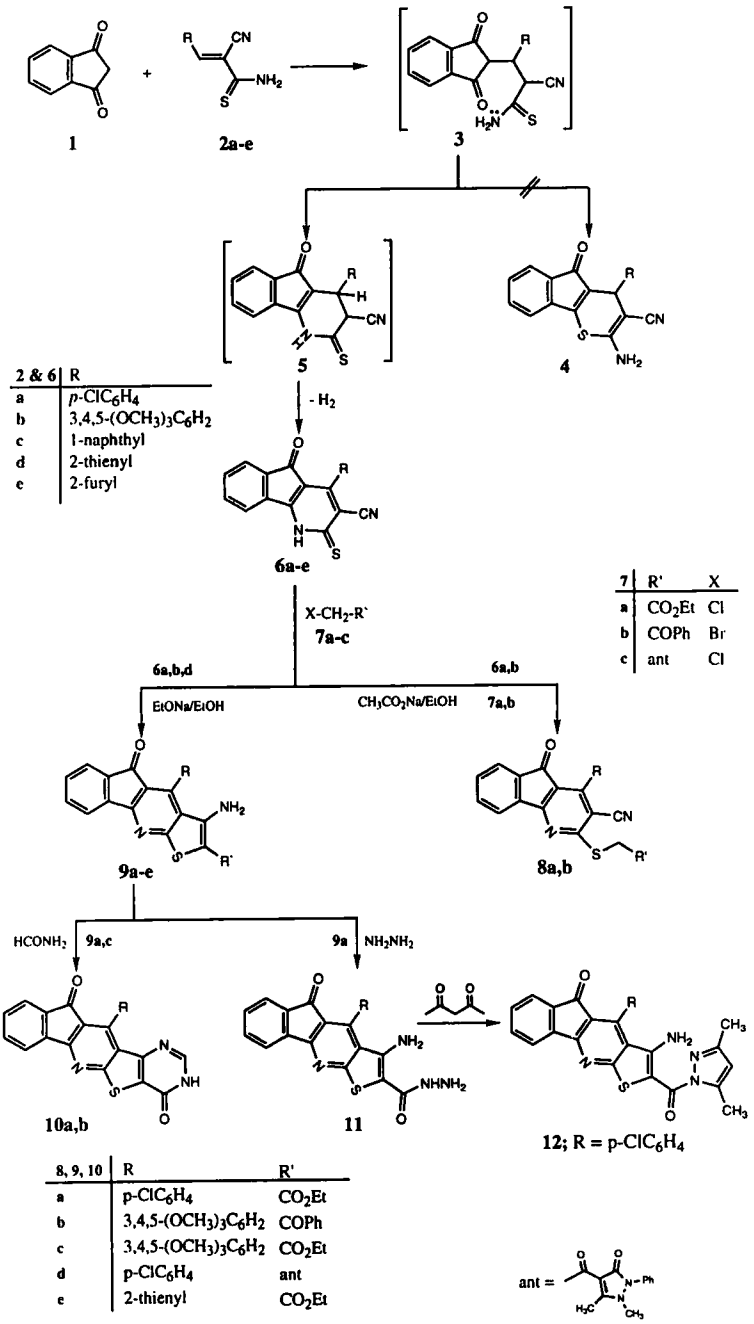
reaction condition.[6,7] Although cyclization of **3** to the aminobenzothiopyran **4** is also possible. Structure **6** was assigned to each of the isolated products on basis of their ^{1}H NMR spectra which revealed the absence of the 4-H in the thiopyran.

An approach to the synthesis of the thieno[2,3-*b*]indeno[2,1-*e*]pyridine derivatives **9**[8] involving the interaction of the thiolactam **6** with some active methylene chloro or bromo compounds **7a-c** in boiling ethanol in presence of sodium ethoxide is reported. Obviously, this reaction occurred through the intermediacy of **8** which could be obtained when less basic catalyst sodium acetate was used. The structures of compounds **8** and **9** were confirmed on basis of correct analysis as well as compatible spectral data. Thus, the IR spectra (KBr) of **9c** revealed the absence of C≡N function and the presence of amino group 3400, 3360 cm^{-1} and carbonyl group at 1714, 1685 cm^{-1}. Also, its ^{1}H NMR spectrum ($DCCl_3$) showed in addition to the expected signals singlet at δ 6.67 ppm (2H) assigned to the corresponding NH_2 protons. Its mass spectrum revealed a molecular ion peak at *m/z* 490 (100%) corresponding to the molecular formula $C_{26}H_{22}N_2O_6S$.

Condensation of **9a,c** with formamide afforded 12-arylindeno-[1",2":2',3']pyrido[5',6':4,5]thieno[3,2-*d*]pyrimidine-4,11-(3H)-dione (**10a,b**).

The aminohydrazide **11** was obtained upon treatment of the amino ester **9a** with hydrazine hydrate. Interaction of **11** with acetylacetone furnished the corresponding pyrazolyl derivatives **12** (Scheme 1).

We report here the reaction of compounds **14a-c** with appropriate β-aminocrotonitrile[9,10] **15a,b** in refluxing glacial acetic acid to yield the corresponding 4-aryl-2-methyl(phenyl)-5-oxo-1,4-dihydroindeno[1,2-*b*]-pyridine-3-carbonitrile (**16a-e**) in acceptable yields. Structure of compound **16** was established based on elemental analysis and spectroscopic studies. Thus, the mass spectrum of **16b** revealed molecular ion peak at m/z 388 (M^+, 38%) corresponding to the molecular formula $C_{23}H_{20}N_2O_4$. Also, its ^{1}H NMR spectrum (DMSO-d_6) showed a singlet signal at δ = 5.62 ppm (1H) attributed to 4-H pyridine beside the expected signals.



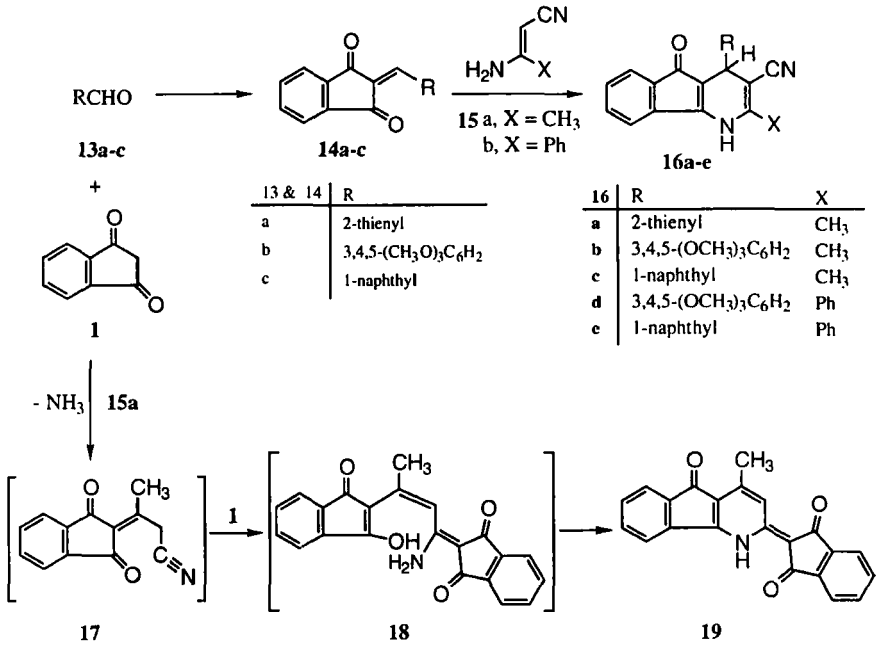
2 & 6	R
a	*p*-ClC_6H_4
b	3,4,5-$(OCH_3)_3C_6H_2$
c	1-naphthyl
d	2-thienyl
e	2-furyl

7	R'	X
a	CO_2Et	Cl
b	COPh	Br
c	ant	Cl

8, 9, 10	R	R'
a	p-ClC_6H_4	CO_2Et
b	3,4,5-$(OCH_3)_3C_6H_2$	COPh
c	3,4,5-$(OCH_3)_3C_6H_2$	CO_2Et
d	p-ClC_6H_4	ant
e	2-thienyl	CO_2Et

SCHEME 1

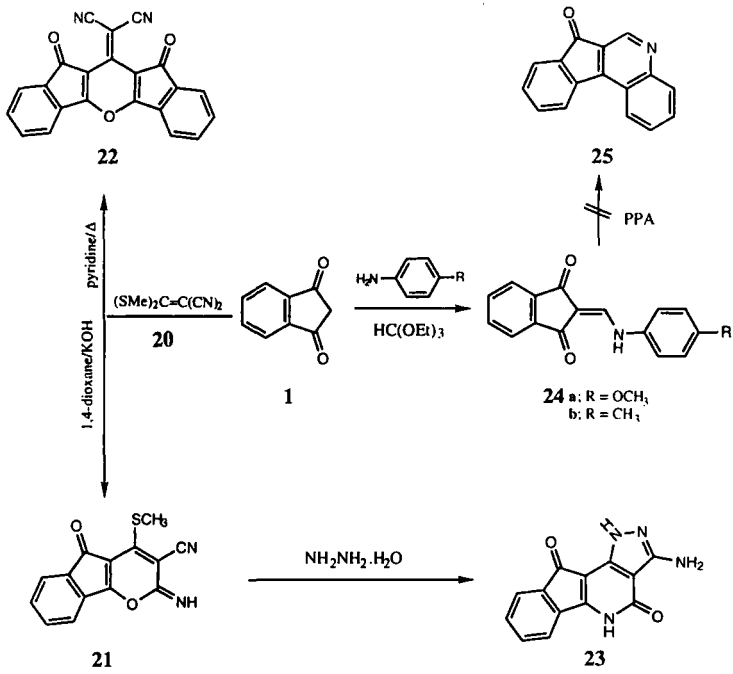
Reaction of compound **1** with β-aminocrotonitrile (**15a**) in 1,4-dioxane and a few drops of piperidine yielded 2-(2'-inden-1',3'-dione)-4-methyl-1H-5-oxoindeno[1,2-*b*]pyridine (**19**). Formation of **19** in this case was assumed to proceed *via* condensation and addition reactions to form intermediates[11] **17, 18** followed by intramolecular cyclization *via* loss water molecule. The validity of structure **19** was deduced from its correct elemental analysis and compatible spectral data (Scheme 2).



SCHEME 2

Similarly, the reaction of keten dithioacetal[12] **20** with compound **1** in 1,4-dioxane containing an equivalent amount of potassium hydroxide gave 2-imino-4-methylsulfanyl-2H-5-oxoindeno[1,2-*b*]pyran-3-carbonitrile (**21**). On the other hand, compound **22** was obtained by the reaction of **1** with **20** in refluxing pyridine.[13] The validity of structures **21** and **22** were deduced from their correct elemental analyses and compatible spectral data (*cf.* Experimental).

Compound **21** bearing latent functional substituent were found useful



SCHEME 3

for the synthesis of fused derivatives. It reacted with hydrazine in refluxing ethanol containing catalytic amount of piperidine to afford the corresponding 3-amino-1H-indeno[2,1-*e*]pyrazolo[4,5-*c*]pyridine-4,10-(5H)-dione (**23**). Both elemental analysis and spectral data of **23** are consistent with the assigned structure. Thus, the mass spectra revealed at m/z = 252 ((M^+, 100%) corresponding to the molecular formula $C_{13}H_8N_4O_2$. Its ^1H NMR spectrum (DMSO-d_6) showed a broad signal at 5.92 ppm (2H) attributed to NH_2 protons, a multiplet signal at 7.2-7.65 (4H) aromatic protons and two singlet signals at 11.21 and 12.4 corresponding to 2 NH protons (Scheme 3).

2-Arylaminomethyleneindene-1,3-dione (**24a,b**) were obtained *via* the reaction of compound **1** with arylamine and triethylorthoformate.[14] Cyclization attempts with polyphosphoric acid to obtain **25a,b** were unsucceful and get decomposition products instead.

Experimental

Melting points were recorded on a Gallenkamp melting point apparatus and are uncorrected. IR spectra were recorded as KBr pellets with a FTIR-8201 PC spectrophotometer (Shimadzu). ^{1}H NMR spectra were obtained on a Varian Gemini 200 MHz spectrometer in DMSO-d_6 or $CDCl_3$ as solvent and *TMS* as an internal reference. Mass spectra were performed on a Shimadzu GCMS-QP 1000 Ex at 70 ev. Microanalysis were performed by the Microanalytical center of Cairo University. 4-Chloroacetylantipyrine[15] was prepared according to reported literature.

4-Aryl-5-oxoindeno[1,2-b]pyridine-2-thione-3-carbonitrile* 6a-e. *General procedure. To a solution of **1** (1.46 g; 0.01 mol) in dioxane (20 ml) was added an equimolar amount (0.01 mol) of appropriate thioamide **2a-e** and few drops of piperidine. The reaction mixture was heated under reflux for 5 h. and then allowed to cool. The crystalline products thus formed were collected by filtration, washed with ethanol and then recrystallized from DMF to afford **6a-e**.

6a: Red crystals; yield (85%), mp > 295 °C; IR ν_{max}/cm^{-1} (KBr) 3221 (NH), 2216 (CN), 1706 (CO); δ_H (DMSO-d_6) 7.1-7.5 (m, 8H, H-arom), 12.3 (s, 1H, NH); *m/z*: 348 (M^+, 100%), 349 (49.2%), 350 (53.4), 313 (61.4), 284 (11.4). (Found: C, 65.40; H, 2.60; N, 8.10; S, 9.20; $C_{19}H_9N_2OSCl$ requires C, 65.42; H, 2.60; N, 8.03; S, 9.19%).

6b: Orange crystals; yield (82%); mp > 300 °C; IR ν_{max}/cm^{-1} (KBr) 2980 (CH-aliph), 2216 (CN), 1702 (CO), *m/z* 404 (M^+, 100%). (Found: C, 65.30; H, 3.90; N, 7.20; S, 8.10; $C_{22}H_{16}N_2O_4S$ requires C, 65.34; H, 3.96; N, 6.93; S, 7.92%).

6c: Deep brown; yield (75%); mp > 300°C; IR ν_{max}/cm^{-1} (KBr) 3220 (NH), 2217 (CN), 1700 (CO); *m/z* 364 (M^+, 100%). (Found: C, 75.90; H, 3.30; N, 7.70; S, 8.60 $C_{23}H_{12}N_2OS$ requires C, 75.82; H, 3.29; N, 7.69; S, 8.79%).

6d: Dark brown; yield (75%); mp 265°C; IR ν_{max}/cm^{-1} (KBr) 2216 (C≡N), 1709 (C=O); *m/z* 320 (M^+, 100%). (Found: C, 63.70; H, 2.50; N, 8.75; S, 20.10 $C_{17}H_8N_2OS_2$ requires C, 63.75; H, 2.50; N, 8.75; S, 20.00%).

6e: Deep dark brown; yield (65%); mp 252°C; IR ν_{max}/cm^{-1} (KBr) 3165 (NH), 2198 (C≡N), 1709 (C=O). (Found: C, 67.10; H, 2.60; N, 9.20; S, 10.5 $C_{17}H_8N_2O_2S$ requires C, 67.10; H, 2.63; N, 9.21; S, 10.52%).

Alkylation of 4-aryl-3-cyano-5-oxoindenopyridine-2-(1H)-thione **(8a,b).** *General procedure.* Compound **6** (0.005 mol) was dissolved in ethanolic solution of sodium acetate (20 ml, 20%). Then the alkylating agent (0.005 mol) was added and the mixture was heated under reflux for 30 min. After cooling, the reaction mixture was poured onto a cold water and the solid product formed was collected and crystallized from ethanol.

Ethyl [3-cyano-4-(p-chlorophenyl)5-oxoindeno[1,2-b]pyridinyl]thio-acetate **8a.** This compound was obtained from **6a** and ethyl bromoacetate as orange crystals; mp 280°C; yield 68%, IR ν_{max}/cm^{-1} (KBr) 2218 (CN), 1715 (CO) and 1695 (CO); δ_H (DMSO-d_6) 1.33-1.40 (t, 3H, CH_3, J = 7.2 Hz), 4.26-4.36 (q, 2H, CH_2, J = 7.2 Hz), 6.07 (s, 2H, CH_2), 7.56-7.65 (m, 8H, Ar-H). (Found: C, 63.50; H, 3.40; N, 6.30; S, 7.20 $C_{23}H_{15}N_2O_3SCl$ requires C, 63.52; H, 3.45; N, 6.44; S, 7.36%).

2-Benzoylmethylthio-4-(3',4',5'-trimethoxyphenyl)-5-oxoindeno[1,2-b]pyridine-3-carbonitrile **(8b).** This compound was obtained from **6b** and phenacyl bromide as orange crystals; mp 234°C; yield (65%); IR ν_{max}/cm^{-1} (KBr); 2218 (C≡N), 1708 (CO), 1680 (CO). (Found: C, 68.90; H, 4.20; N, 3.30; S, 6.10 $C_{30}H_{22}N_2O_5S$ requires C, 68.96; H, 4.20; N, 5.36; S, 6.13%).

3-Amino-2,4-disubstituted 5-oxothieno[2,3-b]indeno[1,2-e]pyridine **9a-e.** ***General procedure.*** To a solution of compound **6** (0.005 mol) in ethanolic sodium ethoxide solution (0.5 g of sodium in 25 ml of absolute ethanol) alkylating agent (0.005 mol) was added and the mixture was heated under reflux for 1 h. After cooling, the soild product was collected and crystallized from the proper solvent.

Ethyl 3-amino-4-(p-chorophenyl)-5-oxothieno[2,3-b]indeno[2,1-e]-pyridine-2-carboxylate **(9a).** This compound was obtained from **6a** and ethyl bromoacetate as yellowish brown crystals (ethanol); mp > 300 °C; yield 80%; IR ν_{max}/cm^{-1} (KBr) 3360, 3320 (NH_2), 1715 (CO-ester), 1695

(CO); δ_H (DMSO-d_6) 1.23-1.45 (t, 3H, CH_3, J = 7.0 Hz), 4.21-4.34 (q, 3H, CH_2, J = 7.2 Hz), 6.93 (br, 2H, NH_2), 7.45-7.89 (m, 8H, Ar-H); *m/z* 434.5 (M^+, 35%). (Found: C, 63.50; H, 3.40; N, 6.40; S, 8.10 $C_{23}H_{15}N_2O_3SCl$ requires C, 63.52; H, 3.45; N, 6.44; S, 7.36%).

3-Amino-2-benzoyl-4-(3',4',5'-trimethoxyphenyl)-5-oxothieno[2,3-b]-indeno[2,1-e]pyridine (**9b**). This compound was obtained from **6b** and phenacyl bromide as orange crystals (ethanol); mp 295°C; yield 75%; IR ν_{max}/cm^{-1} (KBr); 3410, 3330 (NH_2), 1702 (CO), 1680 (CO). *m/z* 522 (M^+, 38%). (Found: C, 68.90; H, 4.20; N, 3.30; S, 6.10 $C_{30}H_{22}N_2O_5S$ requires C, 68.96; H, 4.21; N, 5.36; S, 6.13%)

Ethyl 3-amino-4-(3',4',5'-trimethoxyphenyl)-5-oxothieno[2,3-b]indeno-[2,1-e]pyridine-2-carboxylate (**9c**). This compound was obtained from **6c** and ethyl bromoacetate as yellow crystals (ethanol); mp 270 °C; yield 85%; IR ν_{max}/cm^{-1} (KBr) 3400, 3360 (NH_2), 2995 (OCH_3), 1714 (CO ester), 1685 (CO); δ_H ($DCCl_3$) 1.33-1.40 (t, 3H, CH_3, J = 7.1 Hz), 3.88 (s, 6H, 2-OCH_3), 3.98 (s, 3H, OCH_3), 4.26-4.36 (q, 2H, CH_2, J = 7.1 Hz), 6.67 (s, 2H, NH_2), 7.26-7.95 (m, 6H, Ar-H); *m/z* 490 (M^+, 100%). (Found: C, 63.67, H, 4.30; N, 5.80; S, 6.60 $C_{26}H_{22}N_2O_6S$ requires C, 63.67; H, 4.48; N, 5.71; S, 6.53%).

3-Amino-2-(antipyrin-4'-yl)carbonyl-4-(p-chlorophenyl)-5-oxothieno-[2,3-b]indeno[2,1-e]pyridine (**9d**). This compound was obtained from **6a** and 4-chloroacetylantipyrine[15] as brown crystals (DMF); mp > 300 °C; yield 72%; IR ν_{max}/cm^{-1} (KBr) 3450, 3330 (NH_2), 1701 (CO), 1668 (CO); δ_H (DMSO-d_6) 2.25 (s, 3H, CH_3), 3.41 (s, 3H, N-CH_3), 7.49-7.99 (m, 15H, Ar-H + NH_2); *m/z* 576.5 (M^+, 35%). (Found: C, 66.60; H, 3.70; N, 9.90; S, 6.00 $C_{32}H_{21}N_4O_3SCl$ requires C, 66.60; H, 3.64; N, 9.71; S, 5.55%).

Ethyl 3-amino-4-(2-thienyl)-5-oxothieno[2,3-b]indeno[2,1-e]pyridine-2-carboxylate (**9e**). This compound was obtained from **6d** and ethyl bromoacetate as dark brown crystals (ethanol); mp 255°C; IR ν_{max}/cm^{-1} (KBr) 3420, 3380 (NH_2), 1710 (CO), 1702 (CO); *m/z* 406 (M^+, 33%). (Found: C, 62.00; H, 3.40; N, 6.80; S, 15.70 $C_{21}H_{14}N_2O_3S_2$ requires C, 62.06; H, 3.44; N, 6.89; S, 15.76%).

12-Arylindeno[1",2":2',3']pyrido[2',3':5,4]thieno[2,3-d]pyrimidine-4,11(3H)-dione **10a,b.** *General procedure.* Compound **9a** or **c** (0.005 mol) was refluxed in formamide (20 ml) for 6 h. The reaction mixture was cooled, dilute with water and the resulting precipitate was collected by filtration and recrystallized from DMF to give buff crystals.

10a: mp > 300 °C; yield (65%); IR ν_{max}/cm^{-1} (KBr) 3250 (NH), 1701 (CO), 1670 (CO); δ_H (DMSO-d_6) 7.51-8.42 (m, 9H, Ar-H); *m/z* 415 (M^+, 45%). (Found: C, 63.40; H, 2.40; N, 10.50; S, 7.80 $C_{22}H_{10}N_3O_2SCl$ requires C, 63.53; H, 2.40; N, 10.10; S, 7.70%).

10b: mp > 300 °C; yield (65%); IR ν_{max}/cm^{-1} (KBr) 3250 (NH), 1689 (CO), 1670 (CO). (Found: C, 63.60; H, 3.60; N, 8.90; S, 6.70 $C_{25}H_{17}N_3O_5S$ requires C, 63.69; H, 3.60; N, 8.91; S, 6.79%).

3-Amino-4-(p-chlorophenyl)-5-oxothieno[2,3-b]indeno[2,1-e]pyridine-2-carbo-hydrazide (**11**). A mixture of **9a** (0.01 mol) and hydrazine hydrate (0.1 mol) in ethanol (50 ml) was heated under reflux for 3 h. and was then allowed to cool. The soild precipitate was filtered, washed with water and crystallized from 1,4-dioxane as pale yellow crystals; mp 243-244 °C; yield (90%); IR ν_{max}/cm^{-1} (KBr) 3450, 3430 (NH-NH_2), 1692 (CO), 1670 (CO); δ_H (DMSO-d_6) 5.63 (br, 2H, NH_2), 6.92 (s, 2H, NH_2), 7.20-7.86 (m, 8H, Ar-H), 8.56 (s, 1H, NH); (Found: C, 60.10; H, 3.10; N, 13.30; S, 7.80 $C_{21}H_{13}N_4O_2SCl$ requires C, 59.92; H, 3.09; N, 13.31; S, 7.60%).

3-Amino-4-(p-chlorophenyl)-2-(3,5-dimethylpyrazol-1-yl)carbonyl-5-oxothieno-[2,3-b]indeno[2,1-e]pyridine **12**. A mixture of **11** (0.001 mol) and acetylacetone (0.001 mol) was heated under reflux in ethanol (20 ml) for 4 h. and was then allowed to cool. The solid formed was filtered and crystallized from ethanol to give reddish brown crystals; mp 211 °C; yield (45%); IR ν_{max}/cm^{-1} (KBr) 3464, 3373 (NH_2), 1702 (CO), 1668 (CO); *m/z* 484.5 (M^+, 38%). (Found: C, 64.80; H, 3.60; N, 11.60; S, 7.00 $C_{26}H_{17}N_4O_2SCl$ requires C, 64.39; H, 3.50; N, 11.55; S, 6.60%).

Preparations of compounds 14a-c (General procedure)

To a solution of **1** (0.01 mol) in ethanol (30 ml), the proper aldehyde (0.01

mol) and few drops drops of piperidine were, the reaction mixture was refluxed for 1 h. The soid formed was collected by filtration and crystallized from ethanol.

14a: This compound was obtained from **1** and 2-thiophenealdehyde as pale green crystals; mp 165-6°C, yield (80%); IR ν_{max}/cm^{-1} (KBr) 1710, 1692 (2CO). (Found: C, 70.10; H, 3.30, $C_{14}H_8O_2S$ requires C, 70.0; H, 3.31%)

14b: This compound was obtained from **1** and 3,4,5-trimethoxybenzaldehyde as deep yellow crystals; mp 177-8°C, yield (60%); IR ν_{max}/cm^{-1} (KBr) 2998 (CH-aliph.), 1703, 1675 (2CO). (Found: C, 70.50; H, 4.90 $C_{19}H_{16}O_5$ requires C, 70.38; H, 4.94%).

14c: This compound was obtained from **1** and 1-naphthaldehyde as yellow crystals; mp 170°C, yield (65%); IR ν_{max}/cm^{-1} (KBr) 1706, 1685 (2CO). (Found: C, 84.50; H, 4.22, $C_{20}H_{12}O_2$ requires C, 84.80; H,4.20%).

General procedure for preparation of compounds 16a-d. A solution of compounds **15a** or **b** (0.01 mol) and appropriate compound **14** (0.01 mol) in 50 ml glacial acetic acid was refluxed for 3h. The solid obtained was collected by filtration and recrystallized from the proper solvent.

2-Methyl-1,4-dihydro-4-(2-thienyl)-5-oxoindeno[1,2-b]pyridine-3-carbonitrile **(16a).** Compound **16a** was obtained from ethanol as brown crystals, yield (55%), mp 250°C; IR ν_{max}/cm^{-1} (KBr) 3300 (NH), 2216 (C≡N), 1709 (CO); *m/z* 304 (M^+, 38%). (Found: C, 71.10; H, 3.90; N, 9.20; S, 10.50 $C_{18}H_{12}N_2OS$ requires C, 71.05; H, 3.94; N, 9.21; S, 10.52%).

2-Methyl-1,4-dihydro-4-(3',4',5'-trimethoxyphenyl)-5-oxoindeno-[1,2-b]pyridine-3-carbonitrile **(16b).** Compound **16b** was obtained from ethanol as red crystals, mp 282°C; yield (85%); IR ν_{max}/cm^{-1} (KBr) 3317 (NH), 2997, 2945 (CH-aliph.), 2196 (C≡N), 1691 (CO); *m/z* 388 (M^+, 38%). δ_H (DMSO-d_6) 2.92 (s, 3H, CH_3), 3.90 (s, 6H, 2 OCH_3), 3.95 (s, 3H, OCH_3), 5.62 (s, 1H, H-4 pyridine), 6.77 (s, 2H, Ar-H), 7.5-7.98 (m, 4H, Ar-H), 11.2 (br, 1H, NH). (Found: C 71.10; H, 5.10; N, 7.20 $C_{23}H_{20}N_2O_4$ requires C, 71.13; H, 5.15; N, 7.21%).

2-Methyl-1,4-dihydro-4-(1'-naphthyl)-5-oxoindeno[1,2-b]pyridine (16c). Compound **16c** was obtained from acetic acid as deep red crystals; mp 291°C; yield (40%), IR ν_{max}/cm^{-1} (KBr) 3315 (NH), 2218 (C≡N), 1718 (CO); *m/z* 348 (M^+, 35%). (Found: C 82.70; H, 4.60; N, 8.10 $C_{24}H_{16}N_2O$ requires C, 82.72; H, 4.59; N, 8.04%).

2-Phenyl-1,4-dihydro-4-(3',4',5'-trimethoxyphenyl)-5-oxoindeno[1,2-b]-pyridine-3-carbonitrile (16d). Compound **16d** was obtained as deep yellow crystals, mp 265°C; yield (90%); IR ν_{max}/cm^{-1} (KBr) 3312 (NH), 2937 (CH-aliph), 2218 (C≡N), 1718 (CO); *m/z* 450 (M^+, 32%). (Found: C, 75.10; H, 4.90; N, 6.20 $C_{28}H_{22}N_2O_4$ requires C, 74.66; H, 4.88; N, 6.22%).

2-Phenyl-1,4-dihydro-4-(1'-naphthyl)-5-oxoindeno[1,2-b]pyridine-3-carbonitrile (16e). Compound **16e** was obtained from acetic acid as orange crystals; mp 272°C; yield (82%); IR ν_{max}/cm^{-1} (KBr) 3316 (NH), 2219 (C≡N), 1709 (CO). (Found: C 84.80; H, 4.50; N, 7.10 $C_{29}H_{18}N_2O$ requires C, 84.87; H, 4.39; N, 6.82%).

2-(2'-Inden-1',3'-dione)-4-methyl-1-hydro5-oxoindeno[1,2-b]pyridine (**19**). To a solution of **1** (0.01 mol) in 30 ml ethanol, β-aminocrotonitrile **15a** (0.012 mol) was added. The reaction mixture was treated with few drops of piperidine and refluxed for 1 h. The solid product was collected by filtration and recrystallized from ethanol as pale green crystals (65%); mp 262°C. IR ν_{max}/cm^{-1} (KBr) 3367 (NH), 1710, 1692, 1660 (3 CO); *m/z* 339 (M^+, 93.4%) and 340 (M^++1, 100%). (Found: C, 77.80; H, 3.800; N, 4.10 $C_{22}H_{13}NO_3$ require C, 77.87; H, 3.83; N, 4.12%).

2-Imino-4-methylsulfanyl-2H-5-oxoindeno[1,2-b]pyran-3-carbonitrile (**21**). To a solution of compound **1** (0.05 mol) and ketene dithioacetal **20** (0.05 mol) in 1,4-dioxane (50 ml), the equivalent amount of potassium hydroxide was added. The solution was then heated under reflux for 3h and after being allowed to cool, it was poured onto ice-water. The solution was then neutralized with HCl and the formed product was collected by filtration and recrystallized from DMF. Yellow crystals; mp > 300 °C; yield (63%); IR ν_{max}/cm^{-1} (KBr) 3210 (NH), 2220 (CN), 1715 (CO); δ_H (DMSO-d_6) 2.51 (s, 3H, SCH_3), 5.64 (br, 1H, NH), 7.38-7.53 (m, 4H, Ar-H); *m/z* 268

(M^+, 100%). (Found: C, 62.60; H, 3.00; N, 10.50; S, 12.30 $C_{14}H_8N_2O_2S$ requires C, 62.68; H, 2.98; N, 10.44; S, 11.94%).

Diindeno[1,2-b:2',1'-e]pyrano-4-ylidene)malononitrile **(22).** A solution of compound **1** (0.05) and ketene dithioacetal **20** (0.05 mol) in pyridine (20 ml) was heated under reflux for 4h. The solution was then poured onto ice-water and then neutralized with dilute HCl to precipitate the solid product which was separated by filtration and recrystallized from ethanol. Pale brown crystals; mp > 300 °C; yield (65%); IR ν_{max}/cm^{-1} (KBr) 2227, 2192 (2 CN), 1708 (CO); *m/z* 348 (M^+, 42%). (Found: C, 76.00; H, 2.50; N, 8.50; $C_{22}H_8N_2O_3$ requires C, 75.86; H, 2.24; N, 8.04%).

3-Amino-1H-10-oxoindeno[2,1-e]pyrazolo[4,5-c]pyridine-4(5H)one **(23).** A solution of equivalent amounts of **21** and hydrazine hydrate (0.01 mol) in ethanol (20 ml) was refluxed for 5 h. The solution was then concentrated and the solid precipitated was filtered off and recrystallized from DMF. Pale brown crystals; mp > 300 °C; yield (60%); IR ν_{max}/cm^{-1} (KBr) 3400, 3370, 3200 (NH_2, NH), 1701 (CO), 1682 (CO); δ_H (DMSO-d_6) 5.92 (br, 2H, NH_2), 7.2-7.62 (m, 4H, Ar-H), 11.21 (s, 1H, NH), 12.4 (s, 1H, NH); *m/z* 252 (M^+, 100%). (Found: C, 62.20; H, 3.20; N, 23.00 $C_{13}H_8N_4O_2$ requires C, 61.90; H, 3.17; N, 22.22%).

2-(Arylaminophenylmethylene)-1,3-indendione **(24a,b).** ***General procedure.*** A mixture of indan-1,3-dione (**1**) (0.005 mol), appropriate aromatic amine (0.005 mol) and triethylorthoformate (12 ml, 0.07 mol) was heated at 140 °C for 5 min. The mixture was cooled to room temperature, the precipitate filtered by suction and washed with ethanol to give **24a**: Yellowish green crystals; mp 196 °C; yield (80%); IR ν_{max}/cm^{-1} (KBr) 3250 (NH), 2980 (CH_3), 1702, 1685 (CO); *m/z* 279 (M^+, 100%). (Found: C, 73.10; H, 4.60; N, 5.20 $C_{17}H_{13}NO_3$ requires C, 73.11; H, 4.66; N, 5.02%). **24b**: Pale gray crystals; mp 205-208 °C; yield (90%); IR ν_{max}/cm^{-1} (KBr) 3200 (NH), 1700, 1685 (CO). (Found: C, 77.30; H, 4.90; N, 5.40 $C_{17}H_{13}NO_2$ requires C, 77.56; H, 4.94; N, 5.32%).

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