TRIETHYLAMINE, ETHANOL - MEDIATED DISCIPLINED REACTIONS OF S-BENZYLISOTHIOURONIUM CHLORIDE WITH UNSATURATED 2-OXAZOLIN-5-ONES: SYNTHESIS OF (Z)-2-AMINO-4-ARYLMETHYLENE-2-IMIDAZOLIN-5-ONES, 5-BENZOYLAMINO-2-BENZYLTHIO-6-OXO-4,4-SPIROCYCLOHEXYL-1,4,5,6-TETRAHYDROPYRIMIDINE, AND THEIR STRUCTURE

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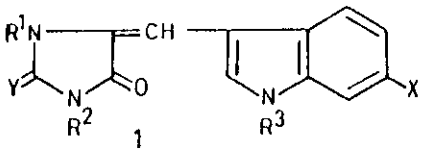
Abstract - Triethylamine-mediated condensation of S-benzylisothiouronium chloride with (Z)-4-arylmethylene-2-phenyl-2-oxazolin-5-ones (4) in ethanol gives (Z)-2-amino-4-arylmethylene-2-imidazolin-5-ones (7), whereas the similar reaction with 4-cyclohexylidene-2-phenyl-2-oxazolin-5-one(5) produces 5-benzoylamino-2-benzylthio-6-oxo-4,4-spirocyclohexyl-1,4,5,6-tetrahydropyrimidine (15) which on aminolyses with arylamines affords the corresponding 2-arylamino derivatives(16).

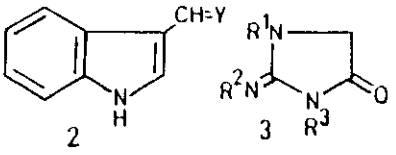
Counter-attack reagents[1] are of considerable importance in synthetic organic chemistry, but their scope in many reactions does not seem to have been properly explored. With an appropriate choice of the substrates, reagents, and the reaction conditions, it may be possible to carry out many multi-step syntheses in the same flask involving highly ordered conversions, resembling biochemical changes, following definite protocols. We propose to call such transformations as "disciplined reactions" and in this article present a novel one-pot synthesis of the title compounds(7) and (15), using the reactions of 4-arylmethylene-2-phenyl-2-oxazolin-5-ones(4) and 4-cyclohexylidene-2-phenyl-2-oxazolin-5-one(5), respectively, with S-benzylisothiouronium chloride(6) in ethanol containing triethylamine.

It should be noted that several 2-aminoimidazole alkaloids have been isolated from marine sponges.[2-5] Some of these, for example aplysinopsin-type alkaloids (1),[4,5] which contain a 3-indolylmethylene group at the 4(5)-position of the imidazole ring, have generated interest because of their reported cytotoxicity against cancer and for affecting neurotransmission. These compounds are related to creatinine, an important end product of nitrogen metabolism in human beings, which belongs to a class of heterocycles called glycocyamidines.[6,7]

The stereochemistry of aplysinopsin-type alkaloids (1) has been investigated and it has been found that the configuration at the olefinic centre depends on the substituent present in the molecule.[4,5] The stable isomers were amenable to photoisomerisation to the less stable isomers which in turn were thermolabile. Synthesis of 1 was carried out by the condensation of indole-3-carboxaldehyde (2,Y=O) with the corresponding 2-iminoimidazolidin-5-ones(3).[5] In our approach, (Z)-4-(3-indolylmethylene)-2-phenyl-2-oxazolin-5-one (4a) was used as a substrate and when heated with 6 in ethanol in the presence of triethylamine furnished a sulphur-free compound which has been characterised as 2-amino-4-(3-indolylmethylene)-2-imidazolin-5-one (7a) on the basis of its spectral data and chemical reactions.



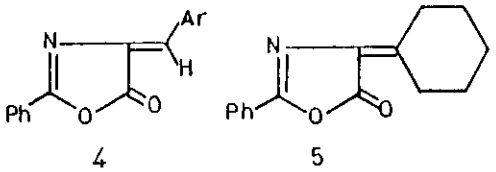
1



2 3

$R^1 = R^2 = H$ or Me ; $R^3 = H$;
X = H or Br ; Y = NH or NMe

Y = O or PhN $R^1 = R^2 = R^3 = H$ or Me



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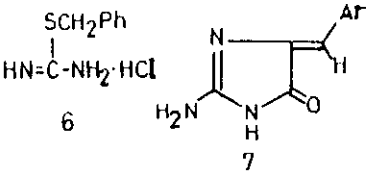
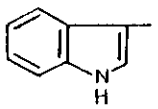
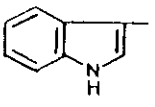


6 7

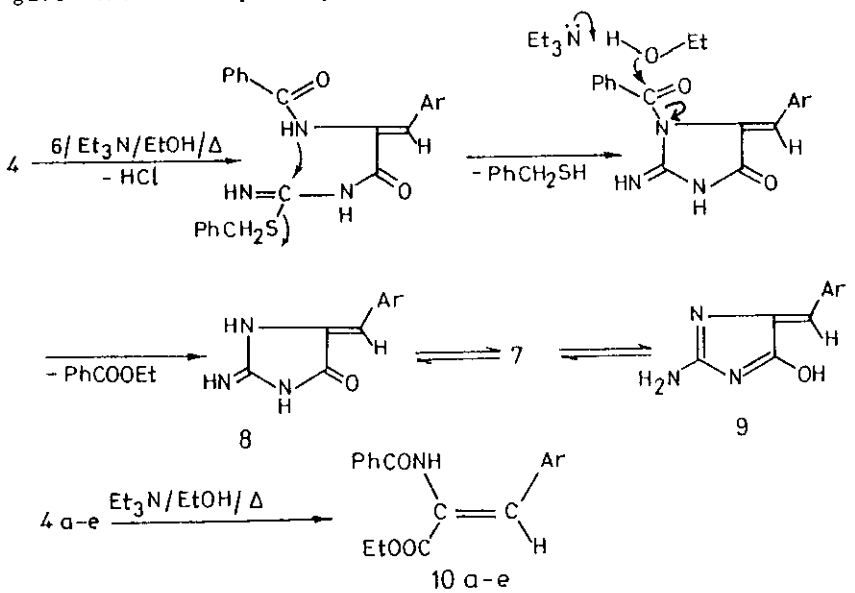
a, Ar = 

b, Ar = 2-$NO_2C_6H_4$
c, Ar = 3-$NO_2C_6H_4$
d, Ar = 4-$NO_2C_6H_4$
e, Ar = 

a, Ar = 

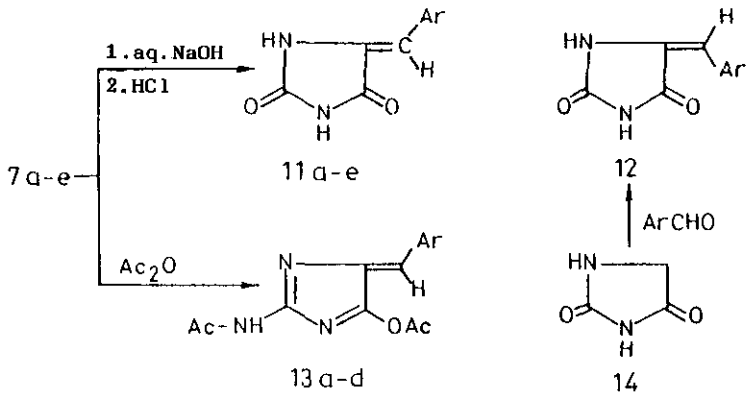
b, Ar = 2-$NO_2C_6H_4$
c, Ar = 3-$NO_2C_6H_4$
d, Ar = 4-$NO_2C_6H_4$
e, Ar = 

The similar condensation of other (Z)-4-arylmethylene-2-phenyl-2-oxazolin-5-ones (4b-e) gave the corresponding 4-arylmethylene-2-amino-2-imidazolin-5-ones (7b-e).



Scheme 1

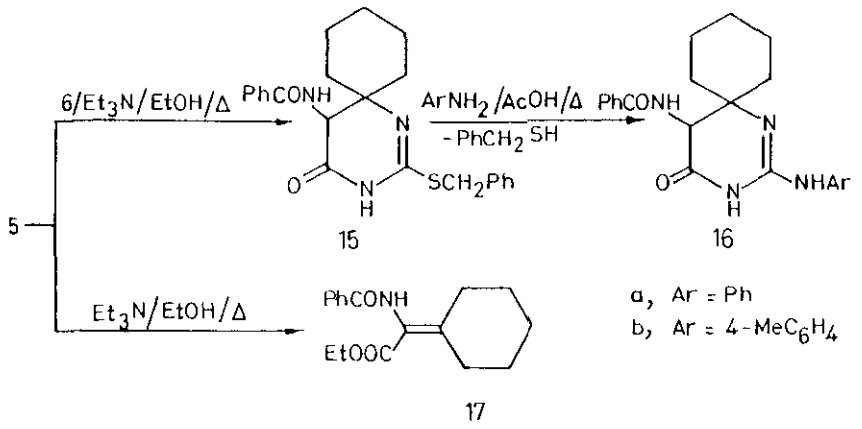
Compounds(7) were found to exist as 8 and 9 (Scheme 1), as would be evident from the chemical reactions. For example, hydrolysis of 7 by warming with dilute sodium hydroxide and/or with hydrochloric acid gave the corresponding hydantoins (11) which supported structure (8). On the other hand acetylation of 7a-d with acetic anhydride furnished the acetyl derivatives (13), except for that from 7e, which could arise only from 9. Compound (7a) gave triacetyl derivative (13a) (Ar=1-acetyl-3-indolyl) (Scheme 2).



Scheme 2

The configuration of 7 was based on the fact that these were derived from the corresponding (Z)-isomers of the unsaturated oxazolones (4). Compounds (4) are known to be more stable than their (E)-counterparts which have been well documented in a recent review.[8] The cleavage of the 1,5-bond of 4 did not affect the configuration of the olefinic centre. Besides, the ^{1}Hnmr spectrum of the unsaturated hydantoins (11), obtained by the hydrolysis of 7, shows deshielded olefinic proton, whereas the corresponding isomeric compounds (12), prepared by the condensation of aromatic aldehydes with 4-unsubstituted hydantoin (14),[9] had a shielded olefinic proton.[10] This observation indicated the (E)- and (Z)-configurations of 12 and 11, respectively, which in turn confirmed the assigned (Z)-stereochemistry of 7. Based on the molecular niceties of 7, the acetyl derivatives (13) were given (Z)-configuration which was supported by their ^{1}Hnmr spectrum.

The triethylamine-aided condensation of 6 with 4-cyclohexylidene-2-phenyl-2-oxazolin-5-one (5) under the similar reaction conditions gave a different result and led to the formation of 5-benzoylamino-2-benzylthio-6-oxo-4,4-spirocyclohexyl-1,4,5,6-tetrahydropyrimidine (15) which on aminolysis with arylamines afforded 2-arylamino-5-benzoylamino-6-oxo-4,4-spirocyclohexyl-1,4,5,6-tetrahydropyrimidine (16) (Scheme 3).



Scheme 3

Besides the main product, a compound in trace amount was detected in the reaction mixture by tlc, and it appeared to be the result of partial alcoholysis of the unsaturated oxazolones. This was verified by heating 4 and 5 in ethanol in the presence of triethylamine alone, when 3-substituted ethyl 2-benzoylaminoacrylates (10) and (17) were obtained, respectively, which were identical with the corresponding minor products detected and identified by tlc. These minor products could not be isolated and therefore their melting points and ir spectra could not be compared with those of the authentic samples.

The formation of 7 can be rationalised by an initial 1,5-bond cleavage of 4, followed by cyclisation based on the counter-attack principle. Once the imidazolinone ring had been formed, the N-debenzoylation followed under the triethylamine-aided generation of ethoxide ions (Scheme 1). On the other hand, the formation of the spiropyrimidine derivative (15) was due to the participation of 5 as a Michael acceptor in the reaction. The regioselective nature of these transformations is quite apparent. It is noteworthy that the conversion of 4 into 7 did not alter the stereochemistry of the olefinic centre. As mentioned, the formation of ethyl esters (10) was due to cleavage of the 1,5-bond of 4 by the ethoxide ions generated in situ.

Results of the present investigation revealed that the formation of 7 as well as 15 had precedence over ethanolysis of the substrates. The conversion of 4 into 7 involved ordered reactions following definite protocols. These transformations are very much within the premise of our definition of a "disciplined reaction". It should be emphasised that the products (7) are potentially useful because of their resemblance with the aplysinopsin-type alkaloids and also due to their facile stereospecific conversion to unsaturated (Z)-hydantoins (11) and into the (4H)-imidazole dervatives (13) which would be less easily available by any other route. Also, in view of the importance of pyrimidines, the spiro compounds (15) and (16) appear to be of considerable interest. Compounds reported in this

article were characterised by spectral data and elemental analyses.

EXPERIMENTAL

Melting points were determined on a Toshniwal melting point apparatus and are uncorrected. Ir spectra were recorded by a Perkin-Elmer 783 spectrophotometer. ^{1}HNmr and mass spectra were taken by JEOL FX90Q and VG micromass 70-70H and/or Finnigan-Mat 1020, using direct inlet system at 70 ev, spectrometers, respectively. Ir spectra were taken in Nujol, and for ^{1}Hnmr spectra TMS was used as an internal reference.

(Z)-2-Amino-4-(3-indolylmethylene)-2-imidazolin-5-one (7a)[11] :

A typical example for compounds (7) : To a suspension of (Z)-4-(3-indolylmethylene)-2-phenyl-2-oxazolin-5-one[12] (4a, 0.6 g; 0.0021 mol) and S-benzylisothiouronium chloride (6, 0.422 g; 0.0021 mol) in 95% ethanol (50 ml), triethylamine (0.632 g; 0.0063 mol) was added and the mixture was heated under reflux for 3.5 h. It was concentrated under reduced pressure, filtered under suction and repeatedly washed with ethanol. The crude product was recrystallised from ethanol; yield, 0.24 g (51%); mp 328-329°C (decomp.); M^+ : 226 (mol. mass 226). Ir : 3400, 3240, 1710, 1695, 1665, 1630 cm^{-1}; ^{1}Hnmr (DMSO-d_6), δ: 6.71 (s, 1H, = CH), 7.04-7.92 (m, 6H, two exchangeable, NH_2 and Ar-H), 8.16 (s, 1H, α-CH of indole), 10.42 (s, 1H, exchangeable, NH), 11.64 (br s, 1H, exchangeable, NH of indole) ppm. Microanalytical data could not be obtained within the permissible limit, though the compound was sufficiently pure (tlc and spectral data). However, products derived from it gave analytically pure samples (see below).

Compounds 7b-d were recrystallised from glacial acetic acid, however, 7e could not be properly recrystallised. These compounds failed to give proper elemental analyses though they were sufficiently pure (tlc and spectral data). However, their acetyl derivatives gave satisfactory elemental analyses.

Compound 7b : Yield, 66%, mp 278°C (decomp.); M^+ : 232 (mol. mass 232). Ir : 3320, 1710, 1640 cm^{-1}; ^{1}Hnmr (DMSO-d_6), δ : 6.52 (s, 1H, = CH), 7.38-8.85 (m, 6H, two exchangeable, NH_2 and Ar-H), 10.95 (br s, 1H, exchangeable, NH) ppm.

Compound 7c : Yield, 69%; mp 280°C (decomp.); M^+ : 232 (mol. mass 232). Ir : 3360, 1710, 1680, 1650 cm^{-1}; ^{1}Hnmr (DMSO-d_6), δ : 6.86 (s, 1H, = CH), 7.42-8.23 (m, 5H, two exchangeable, NH_2 and Ar-H), 8.75 (s, 1H, Ar-H), 10.10 (br s, exchangeable, NH) ppm.

Compound 7d : Yield, 83%; mp 285-287°C (decomp.); M^+ : 232 (mol. mass 232). Ir : 3340, 1710, 1680, 1645 cm^{-1}; ^{1}Hnmr (DMSO-d_6), δ : 6.37 (s, 1H, = CH), 7.59 - 8.35 (m, 6H, two exchangeable, NH_2 and Ar-H), 10.97 (s, 1H, exchangeable, NH) ppm.

Compound 7e : Yield, 70%; mp 308-310°C (decomp.); M^+ : 177 (mol. mass 177). Ir : 3340, 1710, 1680, 1645 cm^{-1}; ^{1}Hnmr (DMSO-d_6), δ : 6.34 (s, 1H, = CH), 6.77-7.96 (m, 5H, two exchangeable, NH_2 and furyl-H), 10.00 (s, 1H, exchangeable, NH) ppm.

Ethyl (Z)-3-aryl-2-benzoylaminoacrylates (10a-e) : General Procedure :
Compound (4) and triethylamine, taken in the molar ratio of 1 : 1.5, were heated

under reflux in ethanol for 2-3 h. Ethanol was removed under reduced pressure and the crude product was recrystallised from aqueous ethanol.

Compound 10a : Yield, 80%; mp 199-202°C (decomp.). Found : C, 72.01; H, 5.52; N, 8.29. Calcd for $C_{20}H_{18}N_2O_3$: C, 71.85; H, 5.38; N, 8.38. Ir : 3380, 3300, 1685, 1655, 1635 cm^{-1}; ^{1}Hnmr (DMSO-d_6), δ : 1.26 (t, J=6.0 Hz, 3H, CH_3CH_2), 4.26 (q, J=6.0 Hz, 2H, CH_3CH_2), 7.19-8.26 (m, 11H, = CH and Ar-H), 10.04 (s, 1H, exchangeable, NH), 11.90 (s, 1H, exchangeable, NH) ppm.

Compound 10b : Yield, 96%; mp 160°C. Found : C, 63.93; H, 4.57; N, 8.17. Calcd for $C_{18}H_{16}N_2O_5$: C, 63.52; H, 4.70; N, 8.23. Ir : 3220, 1730, 1640, 1630 cm^{-1}; ^{1}Hnmr ($CDCl_3$), δ : 1.34 (t, J=7.0 Hz, 3H, CH_3CH_2), 4.28 (q, J=7.0 Hz, 2H, CH_3CH_2), 7.14 (s, 1H, = CH), 7.25-8.04 (m, 10H, one exchangeable, NH and Ar-H) ppm.

Compound 10c : Yield, 77%; mp 160°C. Found : C, 63.73; H, 4.81; N, 8.10. Calcd for $C_{18}H_{16}N_2O_5$: C, 63.52; H, 4.70; N, 8.23. Ir : 3220, 1710, 1640 cm^{-1}; ^{1}Hnmr ($CDCl_3$), δ : 1.39 (t, J=7.0 Hz, 3H, CH_3CH_2), 4.32 (q, J=7.0 Hz, 2H, CH_3CH_2), 7.17-8.25 (m, 11H, one exchangeable, = CH, NH and Ar-H) ppm.

Compound 10d : Yield, 74%; mp 168°C. Found : C, 63.59; H, 4.48; N, 8.13. Calcd for $C_{18}H_{16}N_2O_5$: C, 63.52; H, 4.70; N, 8.23. Ir : 3220, 1720, 1650 cm^{-1}; ^{1}Hnmr ($CDCl_3$), δ : 1.35 (t, J=7.0 Hz, 3H, CH_3CH_2), 4.28 (q, J=7.0 Hz, 2H, CH_3CH_2), 7.13 (s, 1H, = CH), 7.26 - 8.06 (m, 10H, one exchangeable, NH and Ar-H) ppm.

Compound 10e : Yield, 89%; mp 127°C. Found : C, 66.30; H, 5.01; N, 4.85. Calcd for $C_{16}H_{15}NO_4.\frac{1}{3}H_2O$: C, 65.97; H, 5.38; N, 4.81. Ir : 3250, 1715, 1645, 1635 cm^{-1}; ^{1}Hnmr ($CDCl_3$), δ : 1.29 (t, J=7.0 Hz, 3H, CH_3CH_2), 4.23 (q, J=7.0 Hz, 2H, CH_3CH_2), 6.31-6.46 (m, 2H, β, β'-furyl-H), 6.96 (s, 1H, = CH), 7.28-7.85 (m, 6H, Ar-H and α-furyl-H), 8.09 (s, 1H, exchangeable, NH) ppm.

(Z)-4-Arylmethylenehydantoins (11a-e) : General Procedure : Compound (7) was warmed with aqueous sodium hydroxide (10%) for 3 min over a water bath when a homogeneous solution was obtained. It was cooled and acidified with conc. HCl, filtered under suction, washed with water and the crude product was recrystallised from ethanol or glacial acetic acid. Alternatively, compound (7) was treated with dil.HCl at room temperature when a clear solution was obtained which on standing for 3 min gave a solid which was worked up as before.

Compound 11a : Yield, 97%; mp 306-307°C (decomp.), lit.,[4] mp 300°C (decomp.). M^+ : 227 (mol. mass 227). Ir : 3320, 1735, 1705, 1660, 1630 cm^{-1}; ^{1}Hnmr (DMSO-d_6), δ : 7.10-7.90 (m, 6H, one exchangeable, = CH, NH and Ar-H), 8.42 (br s, 1H, α-CH of indole), 8.95 (br s, 1H, exchangeable, NH), 12.35 (s, 1H, exchangeable, NH of indole) ppm.

Compound 11b : Yield, 42%; mp 238-240°C. Found : C, 45.92; H, 4.16; N, 16.33. Calcd for $C_{10}H_7N_3O_4.1\frac{1}{2}H_2O$: C, 46.15; H, 3.84; N, 16.15. Ir : 3400, 3300, 1770, 1730, 1700, 1670, 1625 cm^{-1}; ^{1}Hnmr (DMSO-d_6), δ : 6.53 (s, 1H, = CH), 7.29-7.92 (m, 4H, Ar-H), 8.42 (s, 1H, exchangeable, NH), 8.50 (s, 1H, exchangeable, NH) ppm.

Compound 11c : Yield, 83%; mp 278°C. Found : C, 51.40; H, 3.40; N, 17.84. Calcd for $C_{10}H_7N_3O_4$: C, 51.50; H, 3.00; N, 18.02. Ir : 3360, 1770, 1730, 1710, 1670, 1640, 1630 cm^{-1}; ^{1}Hnmr (DMSO-d_6), δ : 6.49 (s, 1H, = CH), 7.47-8.78 (m, 6H, two exchangeable, NH and Ar-H) ppm.

Compound 11d : Yield, 87%; mp 295°C (decomp.). Found : C, 51.05; H, 3.38; N, 18.19. Calcd for $C_{10}H_7N_3O_4$: C, 51.50; H, 3.00; N, 18.02. Ir : 3340, 1780, 1710, 1670, 1640 cm^{-1}; ^{1}Hnmr (DMSO-d_6), δ : 6.83 (s, 1H, = CH), 7.90-8.32 (dd, J=8.6 and 8.6 Hz, 5H, one exchangeable, NH and Ar-H), 9.21 (br s, 1H, exchangeable, NH) ppm.

Compound 11e : Yield 69%; mp 255-257°C. Found : C, 43.17; H, 4.82; N, 12.89. Calcd for $C_8H_6N_2O_3.2\frac{1}{2}H_2O$: C, 43.05; H, 4.93; N, 12.55. Ir : 3400, 3310, 1740, 1710, 1690, 1660, 1620 cm^{-1}; ^{1}Hnmr (DMSO-d_6), δ : 6.47 (s, 1H, = CH), 6.61-6.95 (m, 3H, one exchangeable, NH and β,β'-furyl-H), 7.84 (d, J=2.0 Hz, 2H, one exchangeable, NH and α-furyl-H) ppm.

(Z)-5-Acetoxy-2-acetylamino-4-arylmethylene-4H-imidazoles (13a-d) : General Procedure : A mixture of compound (7) and acetic anhydride, taken in the molar ratio of 1 : 4, was heated under reflux for 30-40 min, cooled when a solid separated which was filtered, washed with benzene and recrystallized from benzene or ethanol.[15] In the acetylation of 7a, the use of the sodium acetate gave better results and in this case the reaction was worked up by treating the mixture with cold water.

Compound 13a (Ar = 1-acetyl-3-indolyl) : Yield, 70%; mp 254-257°C (decomp.). Found : C, 61.13; H, 4.47; N, 15.91. Calcd for $C_{18}H_{16}N_4O_4$: C, 61.36; H, 4.54; N, 15.90. Ir : 3280, 1750, 1705, 1640 cm^{-1}; ^{1}Hnmr (DMSO-d_6), δ : 2.52 (s, 3H, CH_3CO), 2.61 (s, 3H, CH_3CO), 2.71 (s, 3H, CH_3CO), 7.04 (s, 1H, = CH), 7.20-8.50 (m, 4H, Ar-H), 8.76 (s, 1H, α-CH of indole), 10.61 (br s, 1H, exchangeable, NH) ppm.

Compound 13b (Ar = 2-$NO_2C_6H_4$) : Yield, 73%; mp 260°C (decomp.) Found : C, 51.35; H, 4.23; N, 17.60. Calcd for $C_{14}H_{12}N_4O_5.\frac{1}{2}H_2O$: C, 51.69; H, 4.00; N, 17.23. Ir : 3320, 1730, 1690, 1640 cm^{-1}; ^{1}Hnmr ($CDCl_3$), δ: 2.57 (s, 3H, CH_3CO), 2.76 (s, 3H, CH_3CO), 7.28 (s, 1H, = CH), 7.40-8.57 (m, 4H, Ar-H), 10.52 (s, 1H, exchangeable, NH) ppm.

Compound 13c (Ar = 3-$NO_2C_6H_4$) : Yield, 80%; mp 194°C. Found : C, 51.86; H, 3.70; N, 17.18. Calcd for $C_{14}H_{12}N_4O_5.\frac{1}{2}H_2O$: C, 51.69; H, 4.00; N, 17.23. Ir : 3240, 1750, 1710, 1650 cm^{-1}, ^{1}Hnmr ($CDCl_3$), δ : 2.78 (s, 6H, two CH_3CO), 7.06 (s, 1H, = CH), 7.28-8.28 (m, 3H, Ar-H), 9.26 (s, 1H, Ar-H), 10.50 (s, 1H, exchangeable, NH) ppm.

Compound 13d (Ar = 4-$NO_2C_6H_4$) : Yield, 86%; mp 230°C. Found : C, 53.18; H, 4.16; N, 17.49. Calcd for $C_{14}H_{12}N_4O_5$: C, 53.16; H, 3.79; N, 17.72. Ir : 3220, 1760, 1690, 1650 cm^{-1}; ^{1}Hnmr ($CDCl_3$), δ : 2.61 (s, 3H, CH_3CO), 2.71 (s, 3H, CH_3CO), 7.03 (s, 1H, = CH), 7.24 (s, 1H, Ar-H), 8.23 (s, 3H, Ar-H), 10.53 (s, 1H, exchangeable, NH) ppm.

5-Benzoylamino-2-benzylthio-6-oxo-4,4-spirocyclohexyl-1,4,5,6-tetrahydropyrimidine (15) : It was prepared by the interaction of 5 and 6 following the procedure given

for compound (7a). The crude product was recrystallised from ethanol. Yield, 84%; mp 170°C. Found : C, 67.5; H, 6.47; N, 10.29. Calcd for $C_{23}H_{25}N_3O_2S$: C, 67.81; H, 6.14; N, 10.32. Ir : 3280, 3200, 1705, 1645, 1630 cm^{-1}; ^{1}Hnmr ($CDCl_3$), δ: 1.20-1.80 (m, 10H, C_6H_{10}<), 4.39 (s, 2H, $pHCH_2S$), 4.88 (d, J=8.0 Hz, 1H, 5-CH), 6.79 (d, J=8.0 Hz, 1H, exchangeable, PhCONH), 7.24-7.92 (m, 11H, one exchangeable, 1-NH and Ar-H) ppm.

2-Arylamino-5-benzoylamino-6-oxo-4,4-spirocyclohexyl-1,4,5,6-tetrahydropyrimidines (16) : General Procedure : A mixture of compounds (15) and aniline or 4-toluidine, taken in the molar ratio of 1 : 2, was heated under reflux in glacial acetic acid for 4 h. The solvent was removed over a steam bath and the crude product was recrystallised from ethanol.

Compound 16a : Yield, 84%; mp 248°C. Found : C, 70.38; H, 6.19; N, 14.65. Calcd for $C_{22}H_{24}N_4O_2$: C, 70.21; H, 6.38; N, 14.89. Ir : 3600, 3360, 3200, 1680, 1640, 1630 cm^{-1}; ^{1}Hnmr (DMSO-d_6), δ : 1.30-1.70 (m, 10H, C_6H_{10}<), 4.79 (d, J=8.4 Hz, 1H, 5-CH), 7.07-8.06 (m, 11H, one exchangeable, NH and Ar-H), 8.38 (d, J=8.4 Hz, 1H, exchangeable, PhCONH), 8.89 (s, 1H, exchangeable, 1-NH) ppm.

Compound 16b : Yield, 69%; mp 270-272°C. Found : C, 70.99; H, 6.59; N, 14.48. Calcd for $C_{23}H_{26}N_4O_2$: C, 70.76; H, 6.66; N, 14.35. Ir : 3420, 3280, 3220, 1685, 1640, 1630 cm^{-1}; ^{1}Hnmr (DMSO-d_6), δ: 1.37-1.73 (m, 10H, C_6H_{10}<), 2.29 (s, 3H, $Ar\text{-}CH_3$), 4.74 (d, J=8.4 Hz, 1H, 5-CH) 7.10-8.07 (m, 10H, one exchangeable, NH and Ar-H), 8.35 (d, J=8.4 Hz, 1H, exchangeable, PhCONH), 8.80 (s, 1H, exchangeable, 1-NH) ppm.

Compound 17[16] : It was prepared by the procedure given for compound (10); Yield, 86%; mp 126-127°C. Found : C, 71.12; H, 7.06; N, 4.84. Calcd for $C_{17}H_{21}NO_3$: C, 71.08; H, 7.31; N, 4.87. Ir : 3260, 1715, 1645, 1640 cm^{-1}; ^{1}Hnmr ($CDCl_3$), δ: 1.28 (t, J=7.7 Hz, 3H, CH_3CH_2), 1.66-2.76 (m, 10H, = C_6H_{10}<), 4.25 (q, J=7.7 Hz, 2H, CH_3CH_2), 7.19-8.00 (m, 6H, one exchangeable, NH and Ar-H) ppm.

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