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# Synthesis and [4+2] Cycloaddition Reactions of 4-(*N*-Allyl-*N*-Aryl)amino-1,3-Diaza-1,3-Butadienes with Vinyl-, Isopropenyl- and Chloroketenes : Entry to Novel Pyrimidinone/Fused Pyrimidinone Derivatives

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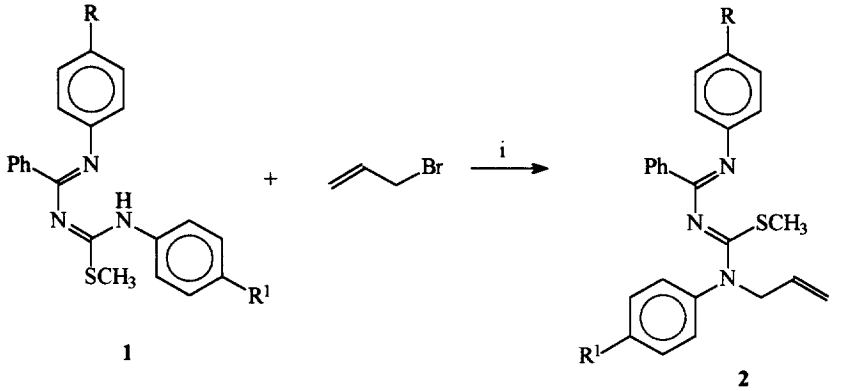
***Abstract:*** 4-(*N*-Allyl-*N*-aryl)amino-1,3-diaza-1,3-butadienes **2**, prepared by the treatment of *N*-arylamino-1,3-diaza-1,3-butadienes **1** with allyl bromide, underwent [4+2] cycloadditions with vinyl/isopropenyl- and accompanied by rearrangements in case of chloroketenes, to yield 5-vinyl/isopropenyl pyrimidinones **5** and 5-methylthio pyrimidinones **19**, respectively. The pyrimidinones **5** on refluxing in xylene gave pyrimidoazepines **6**, underwent annelation reaction, in refluxing benzene in presence of $AlCl_3$, to yield pyrimidoquinolines **7** and on treatment with DMAD in refluxing toluene, underwent [4+2] cycloaddition accompanied by the elimination of *N*-allylarylamine functionality to yield quinazolinone **9**. Further, the reactions of **5** with PhSH in the presence of AIBN in refluxing benzene followed unusual radical cyclisation involving *N*-aryl group leading to pyrimidoquinolines **10**. The iodocyclisation of pyrimidinones **19** yielded pyrimidothiazines **20**. © 1997 Elsevier Science Ltd.

Pyrimidine derivatives are attracting the increasing attention of synthetic community because of the important role played by such systems in many natural products,[1] antibiotics[2] and drugs.[3] A large variety of substituted pyrimidinones have been synthesised in our laboratories following extensive studies on [4+2] cycloaddition reactions of 1,3-diaza-1,3-butadienes[4] with a variety of ketenes.[5-7] It was thought worthwhile to utilise this azadiene-ketene cycloaddition pathway for the synthesis of fused pyrimidinone derivatives which over the years have shown to exhibit significant biological activity and are of potential medicinal value.[8]

In continuation of our pursuits towards synthesis of newer 1,3-diaza-1,3-butadienes, we have reported recently the synthesis of various 1-aryl-4-(*N*-arylamino)-2-phenyl-1,3-diaza-1,3-butadienes **1** which underwent nucleophilic/cycloaddition reactions with phenyl-, chloro-, bromo- and iodoketenes accompanied at times by interesting rearrangements to yield novel pyrimidinone derivatives.[9] It was felt that the synthesis of targeted benzo/heterocyclic ring fused pyrimidinones could be best realised by the initial [4+2] cycloaddition of 1-aryl-4-(*N*-allyl-*N*-aryl)amino-4-methylthio-2-phenyl-1,3-diaza-1,3-butadienes **2** with various ketenes. The 1,3-diazabutadiens **2**, so desired, were synthesised by the treatment of **1** with allyl bromide in acetone in the presence of potassium carbonate (Scheme 1). Thus, the reactions of **2** with isopropenyl/vinylketenes **3**, generated *in situ* from 3,3-dimethylacryloyl chloride/crotonyl chloride and triethylamine, resulted in very good yields of 3-aryl-6-(*N*-allyl-*N*-aryl)amino-5-isopropenyl/ethenyl-2-phenylpyrimidin-4(3*H*)-ones **5** (Scheme 2).



1

2

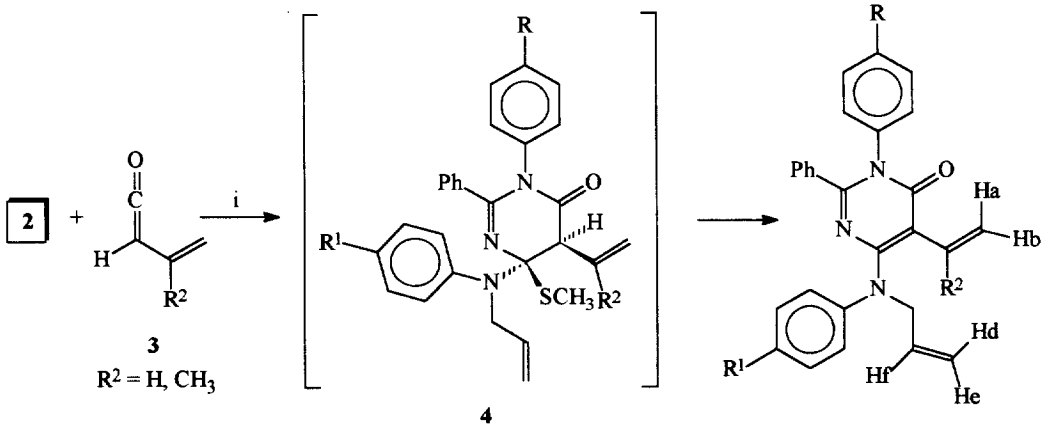
**1,2** **a.** $R = R^1 = H$ **d.** $R = CH_3$, $R^1 = H$

**b.** $R = H$, $R^1 = CH_3$ **e.** $R = R^1 = CH_3$

**c.** $R = H$, $R^1 = OCH_3$ **f.** $R = CH_3$, $R^1 = OCH_3$

**Scheme 1** *Reagents and conditions:* i, $K_2CO_3$, $Me_2CO$

The formation of pyrimidinones **5**, in this case, is in accordance with the [4+2] cycloaddition reactions reported recently in which vinyl/isopropenylketene participated as $2\pi$ component.[7] The pyrimidinones **5** are presumably formed *via* the elimination of HSMe from the initially formed [4+2] cycloadducts **4**, as intermediate. The structure **5** was assigned to these products on the basis of analytical and spectral data. The reactions of (*N*-allyl-*N*-aryl)amino-1,3-diaza-1,3-butadienes **2** with isopropenylketene were found to be quite efficient



3

$R^2 = H, CH_3$

4

5

**5** **a.** $R = R^1 = H$, $R^2 = CH_3$ **d.** $R = R^1 = R^2 = CH_3$

**b.** $R = H$, $R^1 = R^2 = CH_3$ **e.** $R = R^2 = CH_3$, $R^1 = OCH_3$

**c.** $R = H$, $R^1 = OCH_3$, $R^2 = CH_3$ **f.** $R = H$, $R^2 = Hc$, $R^1 = OCH_3$

**Scheme 2** *Reagents and conditions:* i, $Et_3N$, $CH_2Cl_2$, rt, 2 h

and pyrimidinones (**5a-e**) were isolated in very good yields. However, in reactions of **2** with vinylketene, though the tlc of the reaction mixture showed complete disappearance of the starting materials, the pure products could usually not be isolated, except pyrimidinone **5f**.

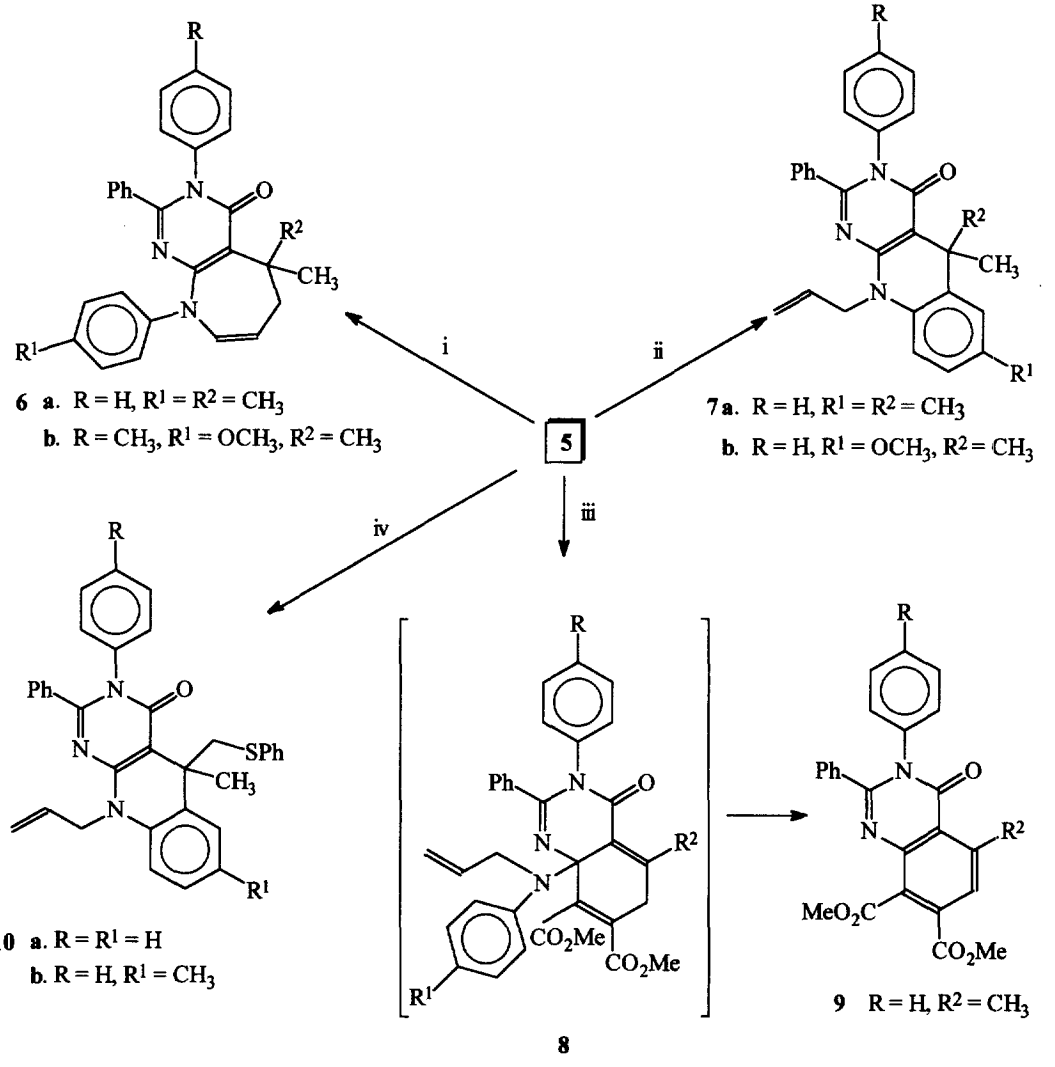
The pyrimidinones **5** having vinyl/isopropenyl function at C-5 and (*N*-allyl-*N*-aryl)amino function at C-6 appeared to be potent auxiliaries for the synthesis of various 5,6-fused pyrimidinones. Accordingly, the thermolysis of pyrimidinones **5** in refluxing xylene resulted in the formation of 3,9-diaryl-3,5,6,9-tetrahydro-5,5-dimethyl-2-phenyl-4*H*-pyrimido[4,5-*b*]azepin-4-ones **6**, which were isolated in good yields as colourless crystals after purification by silica gel column chromatography. The pyrimido[4,5-*b*]azepin-4-ones **6** are presumably the result of an intramolecular ene reaction between *N*-aryl group and isopropenyl group as enophile (Scheme 3). The IR, $^1$H NMR, $^{13}$C NMR and mass spectral data clearly established the assigned structure **6**. The detailed spectral features are given in the experimental section, however, the characteristic features are mentioned in the text. The compound **6a**, for example, analysed for $C_{29}H_{27}N_3O$, showed a molecular ion peak at *m/z* 433 in its mass spectrum and its IR spectrum (KBr) showed a strong peak at 1645 cm$^{-1}$ due to α,β-unsaturated carbonyl group. Its $^1$H NMR spectrum (300 MHz) showed the presence of three methyl groups (δ 1.59, s, 6H, 2 x -$CH_3$ and δ 2.37, s, 3H, -$CH_3$), a methylene group (δ 2.43, d, $J$ = 7.2 Hz) and olefinic protons (δ 5.54, ddd, $J$ = 7.4, 7.4, 7.4 Hz and 6.23, d, $J$ = 7.4 Hz). Its $^{13}$C NMR spectrum exhibited apart from other carbons, the signals for three methyl carbons ($\delta_C$ 21.1, -$CH_3$ and $\delta_C$ 29.2, 2 x -$CH_3$) which attest well to the assigned structure **6a**.

The treatment of 5-isopropenyl-6-(*N*-allyl-*N*-aryl)aminopyrimidinones **5** with aluminium chloride in refluxing benzene for about 30 minutes resulted in annelation reaction to yield novel pyrimidinone derivatives **7** (Scheme 3). The products were characterised as 10-allyl-3-aryl-5,5-dimethyl-2-phenyl-5,10-dihydro-pyrimido[4,5-*b*]quinolin-4(3*H*)-ones **7** on the basis of their analytical and spectral data. Their $^1$H NMR spectra exhibited the presence of aromatic protons with expected splittings. $^1$H NMR spectrum of **7a**, for example, showed the presence of three methyl groups (δ 1.87, 2 x -$CH_3$ and δ 2.30, Ar$CH_3$) and *N*-allyl protons. Presence of a molecular ion peak at *m/z* 433 in its mass spectrum and three methyl carbons ($\delta_C$ 20.7, 2 x -$CH_3$ and $\delta_C$ 30.3, -$CH_3$) along with quaternary carbons in its $^{13}$C NMR spectrum further supported the assigned structure **7a**.

It was felt that the reaction of pyrimidinones **5** with dimethyl acetylenedicarboxylate (DMAD) can, in principle, follow a number of different paths leading to the formation of fused pyrimidinones and this reaction was investigated in order to ascertain the reaction pathway followed and nature of the products formed in these cases. Thus, the treatment of **5** with DMAD in refluxing toluene for 17-18 h resulted in a product which was characterised as dimethyl 3,4-dihydro-5-methyl-4-oxo-2,3-diphenylquinazoline-7,8-dicarboxylate **9**. The quinazolinone **9** is presumably formed *via* the elimination of *N*-allylarylamine group from the initially formed [4+2] cycloadduct **8** as intermediate. The structure **9** could easily be assigned on the basis of analytical data and spectral evidences. The assigned structure **9** was further confirmed by cycloadditions of DMAD with pyrimidinones **5**, by varying $R^1$ ($R^1$= H, $CH_3$, $OCH_3$), all of which led interestingly to the same product **9**.

Radicals have recently attracted the attention of synthetic chemists due to high stereo and regioselectivity in radical cyclisations and because of their potentiality in the synthesis of both carbocyclic and heterocyclic compounds.[10] In continuation of our studies directed towards the synthesis of fused pyrimidinones, we have examined the use of sulfenyl radical in the cyclisation of pyrimidinones **5** having two different double bonds. Thus, the treatment of **5** with thiophenol in the presence of α,α′-azoisobutyronitrile

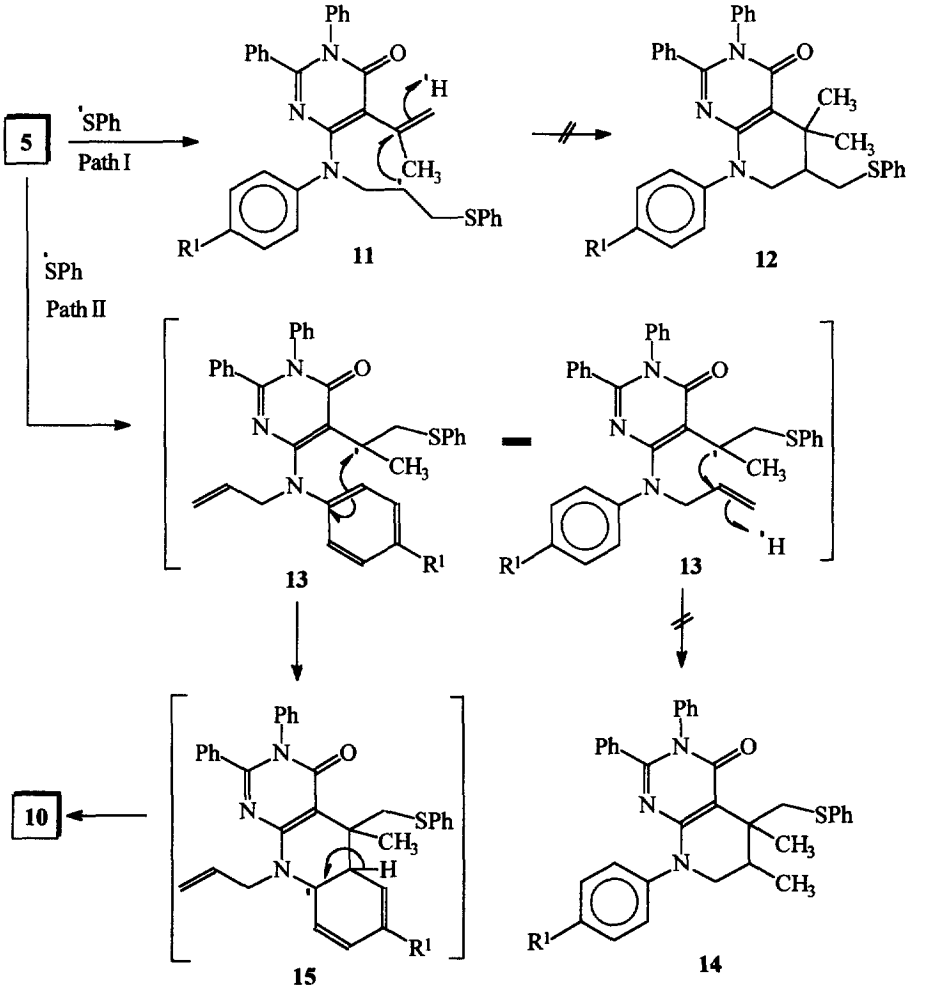
(AIBN) resulted in the formation of products which were characterised as 10-allyl-2,3-diphenyl-5-methyl-5-phenylthiomethyl-5,10-dihydropyrimido[4,5-*b*]quinolin-4(3*H*)-ones **10** (Scheme 3). The plausible mechanistic pathways, explaining the preferential formation of quinolinones **10**, are outlined in Scheme-4. In this scheme, it




**Scheme 3** *Reagents and conditions:* i, Xylene, reflux, 15 h; ii, $AlCl_3$, $C_6H_6$, reflux, 30 min; iii, DMAD, $PhCH_3$, reflux, 17-18 h; iv, PhSH, AIBN, $C_6H_6$, $N_2$-atmosphere, reflux, 7-8 h.

is assumed that the addition of sulfenyl radical to the *N*-allyl double bond may result in the radical intermediate **11** which on cyclisation as shown may yield pyridopyrimidinones **12** (Path I). It is also possible that the sulfenyl radical may add initially to the isopropenyl function leading to an intermediate **13** (Path II), which can cyclise either involving the carbon-carbon double bond of *N*-allyl leading to pyridopyrimidinones **14** or involving *N*-

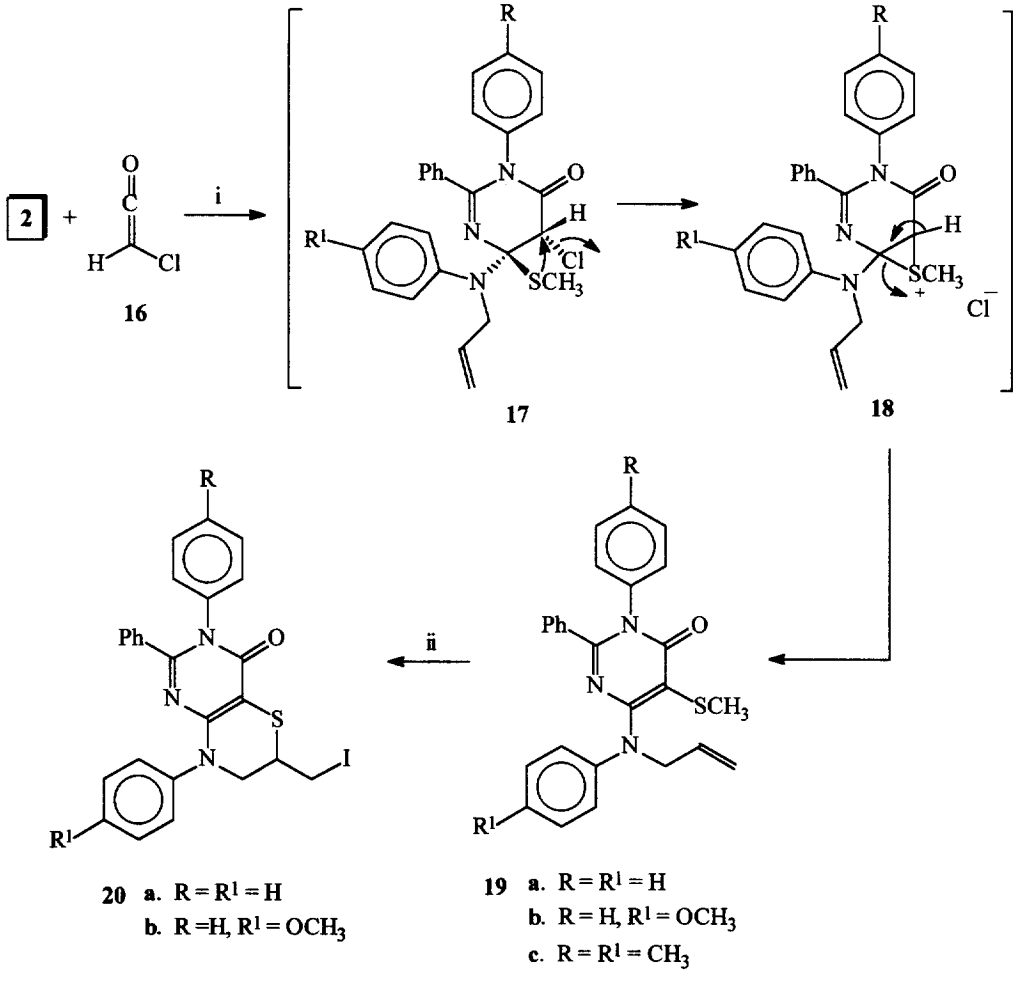
aryl function to yield products **10** *via* intermediate **15**. However, Path-I leading to pyridopyrimidinones **12** may be discriminated due to the preferential formation of more stable radical intermediate **13** as compared to **11**. The assignment of the structure **10** to the products, in preference to **14**, is based on analytical data and spectral evidences. The $^1$H NMR spectrum of **10a** exhibited two well separated doublets for -$CH_2$-SPh methylene protons at δ 3.24 and 4.64 ($J$ = 13.2 Hz each). The surprisingly large chemical shift difference between the two methylene protons is in accordance with the literature values[10] for such methylene protons. It also showed the presence of free *N*-allyl group with its terminal olefinic protons as doublets (δ 5.22, $J$ = 10.5 Hz and δ 5.36, $J$ = 17.3 Hz), and another olefinic proton as multiplet (δ 4.83). The *N*-aryl involvement in the cyclisation was also indicated by the appearance of two doublets (δ 6.92, $J$ = 8.3 Hz and δ 7.00, $J$ = 8.3 Hz) for two *ortho* protons of the fused aryl ring. Further evidence for the assigned structure **10** was drawn from the $^1$H NMR spectrum of




**Scheme 4**

**10b** which exhibited, in addition to other protons, a doublet (δ 6.82, $J$ = 8.4) for H-9, a doublet of doublet (δ 6.96, $J$ = 8.4 and 1.5 Hz) for H-8 and another doublet (δ 7.08, $J$ = 1.5) for H-6.

In continuation of our pursuits towards the construction of functionalised fused pyrimidinones, we have carried out the reactions of various (*N*-allyl-*N*-aryl)amino-1,3-diaza-1,3-butadienes **2** with chloroketene **16**. Thus, the reaction of **2** with chloroketene, generated *in situ* from chloroacetyl chloride and triethylamine in methylene chloride, resulted in various 3-aryl-6-(*N*-allyl-*N*-aryl)amino-5-methylthio-2-phenylpyrimidin-4(3*H*)-ones **19** (Scheme 5). The formation of pyrimidinones **19** was assumed to follow an identical pathway, *via* intermediates **17** and **18**, as observed in the reactions of 1-aryl-4-methylthio-2-phenyl-4-secondaryamino-1,3-diazabutadienes with chloroketene.[6]




**Scheme 5** *Reagents and conditions:* i, $CH_2Cl_2$, $NEt_3$, 2 h; ii, $I_2$, $CH_2Cl_2$, 15 h.

It was thought that the halocyclisation of pyrimidinones **19** might lead to fused 1,4-thiazines which over the years have shown to be of significant biological interest.[11] Thus, stirring a solution of **19** in methylene chloride with iodine resulted in the formation of desired pyrimidinone fused 1,4-thiazines **20** (Scheme 5). The products were characterised as 3,8-diaryl-7,8-dihydro-6-iodomethyl-2-phenyl-6*H*-pyrimido[5,4-*b*][1,4]-thiazin-4(3*H*)-ones **20** on the basis of their mass, IR, $^1$H NMR and $^{13}$C NMR spectral data. The IR spectrum of **20b**, for example, exhibited a strong peak as 1649 cm$^{-1}$ due to α,β-unsaturated carbonyl group and its $^1$H NMR spectrum showed, in addition to aromatic proton signals, a singlet (δ 3.82) for methoxy protons, a multiplet (δ 3.53-3.75) comprising of a methine and -$CH_2$-I, and a multiplet (δ 4.30-4.34) for -N-$CH_2$- protons. Its $^{13}$C NMR spectrum exhibited in addition to other carbon signals, a signal at $\delta_C$ 7.1 characteristic of methylene carbon attached to iodo group which further supported the assigned structure **20b**.

In conclusion, the reactions of (*N*-allyl-*N*-aryl)amino-1,3-diaza-1,3-butadienes **2** and their reactions with vinyl-, isopropenyl-and chloroketenes offer an easy access to various functionalised pyrimidinones. Careful manipulation of the functionalities present in these pyrimidinones led to the development of convenient routes for the synthesis of possibly biologically and medicinally important, heterocycle/benzo-fused pyrimidinones.

## Experimental

Melting points were determined with a Toshniwal melting point apparatus and are uncorrected. IR spectra were recorded on a Perkin-Elmer 983 Infrared spectrophotometer. $^1$H NMR spectra were recorded in deuteriochloroform, with a Varian 390 (90 MHz) and Bruker AC-F 300 (300 MHz) spectrometer using TMS as internal standard. Chemical shifts are expressed as δ ppm downfield from TMS and *J* values are in Hz. Splitting patterns are indicated as s: singlet, d: doublet, t: triplet, m: multiplet, q: quartet and br: broad peak. $^{13}$C NMR spectra were also recorded in Bruker AC-F 300 spectrometer in deuteriochloroform using TMS as internal standard. Mass spectra were obtained by electron impact at 70 eV. Column chromatography was performed on 60-120 mesh silica gel.

**General procedure for the preparation of 4-(*N*-allyl-*N*-aryl)amino-1-aryl-4-methylthio-2-phenyl-1,3-diaza-1,3-butadienes 2**: To a solution 1-aryl-4-(*N*-aryl)amino-4-methylthio-2-phenyl-1,3-diaza-1,3-butadienes[9] (5.0 mmol) in acetone (25 ml) was added potassium carbonate (1.0 g, 10.1 mmol). The mixture was refluxed for 2h and then allowed to reach rt. Allyl bromide (0.91 g, 7.5 mmol) was then added and the reaction mixture stirred at rt for 7-9 h. It was then filtered and the residue washed with acetone (10 ml). The combined filtrate was concentrated under reduced pressure, diluted with $CH_2Cl_2$ and washed with water (2 x 100 ml). The organic layer was dried ($Na_2SO_4$) and evaporated under reduced pressure to give the crude product which was purified by column chromatography on silica gel (Eluent: a mixture of EtOAc/hexane in a 1:10 ratio).

**4-Methylthio-1,2-diphenyl-4-(*N*-allyl-*N*-phenyl)amino-1,3-diaza-1,3-butadiene (2a).** Yield 83%; viscous liquid; IR ($CCl_4$) ν 1603, 1590, 1567, 1490 cm$^{-1}$; $^1$H NMR (90 MHz) δ 1.97 ( s, 3H, -$SCH_3$), 4.30 (d, *J* = 6.0, 2H, -$CH_2$-), 5.07 (pair of merged d, *J* = 17.0 and 9.2, 2H, =$CH_2$), 5.63-6.03 (m, 1H, -CH=), 6.83-7.63

(m, 13H, ArH), 8.10-8.33 (m, 2H, ArH); *m/z* 385 ($M^+$). Anal. Calcd for $C_{24}H_{23}N_3S$: C, 74.77; H, 6.01; N, 10.90. Found: C, 74.70; H, 6.06; N, 11.01.

**4-Methylthio-1,2-diphenyl-4-[*N*-allyl-*N*-(*p*-methylphenyl)]amino-1,3-diaza-1,3-butadiene (2b).** Yield 79%; viscous liquid; IR ($CCl_4$) ν 1608, 1596, 1566, 1507; $^1H$ NMR (90 MHz) δ 2.00 (s, 3H, $-SCH_3$), 2.30 (s, 3H, $-CH_3$), 4.30 (d, $J$ = 6.0, 2H, $-CH_2-$), 5.08 (pair of merged d, $J$ = 16.5 and 9.0, 2H, $=CH_2$), 5.70-6.15 (m, 1H, -CH=), 6.85 (d, $J$ = 8.5, 2H, ArH), 7.03-7.67 (m, 10H, ArH), 8.10-8.43 (m, 2H, ArH); *m/z* 399 ($M^+$). Anal Calcd for $C_{25}H_{25}N_3S$: C, 75.15; H, 6.30; N, 10.52. Found: C, 75.32; H, 6.34; N, 10.42.

**4-Methylthio-1,2-diphenyl-4-[*N*-allyl-*N*-(*p*-methoxyphenyl)]amino-1,3-diaza-1,3-butadiene (2c).** Yield 83%; viscous liquid; IR ($CCl_4$) ν 1601, 1594, 1561, 1498; $^1H$ NMR (90 MHz) δ 2.00 (s, 3H, $-SCH_3$), 3.73 (s, 3H, $-OCH_3$), 4.30 (d, $J$ = 6.0, 2H, $-CH_2-$), 5.07 (pair of merged d, $J$ = 17.5 and 9.0, 2H, $=CH_2$), 5.67-6.08 (m, 1H, -CH=), 6.77-6.97 (m, 4H, ArH), 7.20 (d, $J$ = 7.5, 2H, ArH), 7.33-7.70 (m, 6H, ArH), 8.08-8.40 (m, 2H, ArH); *m/z* 415 ($M^+$). Anal. Calcd for $C_{25}H_{25}N_3OS$: C, 72.26; H, 6.06; N, 10.11. Found: C, 72.48; H, 6.15; N, 10.27.

**1-(*p*-Methylphenyl)-4-methylthio-2-phenyl-4-(*N*-allyl-*N*-phenyl)amino-1,3-diaza-1,3-butadiene (2d).** Yield 79%' viscous liquid; IR ($CCl_4$) ν 1608, 1568, 1490 $cm^{-1}$; $^1H$ NMR (90 MHz) δ 1.90 (s, 3H, $-SCH_3$), 2.33 (s, 3H, $-CH_3$), 4.33 (d, $J$ = 6.0, 2H, $-CH_2-$), 5.00 (pair of merged d, $J$ = 17.5 and 9.0, 2H, $=CH_2$), 5.63-6.17 (m, 1H, -CH=), 6.80-7.53 (m, 12H, ArH), 8.07-8.33 (m, 2H, ArH); *m/z* 399 ($M^+$). Anal. Calcd for $C_{25}H_{25}N_3S$: C, 75.15; H, 6.30; N, 10.52. Found: C, 74.98; H, 6.26; N, 10.44.

**1-(*p*-Methylphenyl)-4-methylthio-2-phenyl-4-[*N*-allyl-*N*-(*p*-methylphenyl)]amino-1,3-diaza-1,3-butadiene (2e).** Yield 89%; viscous liquid; IR ($CCl_4$) ν 1609, 1556, 1506 $cm^{-1}$; $^1H$ NMR (90 MHz) δ 2.16 (s, 3H, $-SCH_3$), 2.31 (s, 3H, $-CH_3$), 2.36 (s, 3H, $-CH_3$), 4.28 (d, $J$ = 6.0, 2H, $-CH_2-$), 5.15 (pair of merged d, $J$ = 17.2 and 9.4, 1H, $=CH_2$), 5.69-6.11 (m, 1H, -CH=), 6.92 (d, $J$ = 7.8, 2H, ArH), 7.10-7.53 (m, 9H, ArH), 7.64 (d, $J$ = 7.8, 2H, ArH); *m/z* 413 ($M^+$). Anal. Calcd for $C_{26}H_{27}N_3S$: C, 75.51, H, 6.58; N, 10.16. Found: C, 75.75; H, 6.66; N, 10.11.

**1-(*p*-Methylphenyl)-4-methylthio-2-phenyl-4-[*N*-allyl-*N*-(*p*-methoxyphenyl)amino-1,3-diaza-1,3-butadiene (2f).** Yield 81%; viscous liquid; IR ($CCl_4$) ν 1608, 1596, 1558, 1506 $cm^{-1}$; $^1H$ NMR (90 MHz) δ 2.00 (s, 3H, $-SCH_3$), 2.37 (s, 3H, $-CH_3$), 3.76 (s, 3H, $-OCH_3$), 4.28 (d, $J$ = 5.5, 2H, $-CH_2-$), 5.23 (pair of merged d, $J$ = 17.5 and 9.0, 2H, $=CH_2$), 5.67-6.10 (m, 1H, -CH=), 6.80-7.73 (m, 11H, ArH), 8.10-8.46 (m, 2H, ArH); *m/z* 429 ($M^+$). Anal. Calcd for $C_{26}H_{27}N_3OS$: C, 72.69; H, 6.33; N, 9.78. Found: C, 72.55; H, 6.30; N, 9.86.

**Reactions of (*N*-allyl-*N*-aryl)amino-1,3-diaza-1,3-butadienes 2 with vinyl/isopropenylketenes 3; *General procedure for the pyrimidinones* 5:** To a well stirred solution of 1,3-diaza-1,3-butadiene 2 (4 mmol) and triethylamine (1 g, 10 mmol) in dry methylene chloride (30 ml), was added dropwise, a solution of crotonyl chloride/3,3-dimethylacroyl chloride (6 mmol) in dry methylene chloride (30 ml) over a period of 1.5-2 h at rt. After the completion of the reaction (tlc), the reaction mixture was washed several times with water (5 x 50 ml)

and the organic layer dried over anhydrous sodium sulfate. Removal of solvent under reduced pressure yielded the crude product, which was purified by silica gel column chromatography using (1:10) ethyl acetate:hexane mixture.

**5-Isopropenyl-2,3-diphenyl-6-(*N*-allyl-*N*-phenyl)aminopyrimidin-4(3*H*)-one (5a).** Yield 91%; mp 162-163 °C; IR (KBr) ν 1651 (C=O), 1552, 1517, 1490 $cm^{-1}$; $^1H$ NMR (300 MHz) δ 1.64 (s, 3H, $-CH_3$), 4.61 (d, *J* = 5.8, 2H, $-CH_2-$), 4.79 (br s, 1H, Ha), 4.85 (br s, 1H, Hb), 5.15 (pair of merged d, *J* = 17.3 and 10.3, 2H, Hd and He), 6.05 (dddd, *J* = 17.3, 10.3, 5.8 and 5.8, 1H, Hf), 7.04-7.33 (m, 15H, ArH); $^{13}C$ NMR (75.5 MHz) 21.1 ($-CH_3$), 55.1 ($-CH_2-$), 106.4 (C-5), 116.9 (C-8), 118.4 (C-11), 124.3, 125.3, 127.7, 128.0, 128.6, 128.7, 129.0, 129.2, 129.4 (C-10), 135.0, 135.1, 137.6 (C-7), 138.0, 146.1, 155.2 (C-6), 157.1 (C-2), 162.7 (C-4); *m/z* 419 ($M^+$). Anal. Calcd for $C_{28}H_{25}N_3O$: C, 80.16; H, 6.00; N, 10.02. Found: C, 80.36; H, 6.07; N, 10.17.

**5-Isopropenyl-2,3-diphenyl-6-[*N*-allyl-*N*-(*p*-methylphenyl)]aminopyrimidin-4(3*H*)-one (5b).** Yield 93%; mp 174-175 °C; IR (KBr) ν 1658 (C=O), 1554, 1507, 1485 $cm^{-1}$; $^1H$ NMR (300 MHz) δ 1.62 (s, 3H, $-CH_3$), 2.32 (s, 3H, $-CH_3$), 4.58 (d, *J* = 5.8, 2H, $-CH_2-$), 4.77 (br s, with fine splitting, 1H, Ha), 4.85-4.86 (m, 1H, Hb), 5.11 (dd, J = 10.0 and 1.5, 1H, Hd), 5.16 (dd, J = 16.9 and 1.5, 1H, He), 6.05 (dddd, J = 16.9, 10.0, 5.8 and 5.8, 1H, Hf), 6.99 (d, *J* = 8.5, with fine splitting, 2H, ArH), 7.07 (d, *J* = 8.3, 2H, ArH), 7.15-7.34 (m, 10H, ArH); $^{13}C$ NMR (75.5 MHz) δ 20.9 ($-CH_3$), 21.2 ($-CH_3$), 55.4 ($-CH_2-$), 105.8 (C-5), 116.8 (C-8), 118.4 (C-11), 125.6, 127.7, 128.0, 128.6, 129.1, 129.3, 129.4 (C-10), 134.1, 135.1, 135.3, 137.8 (C-7), 138.2, 143.5, 155.1 (C-6), 157.4 (C-2), 162.8 (C-4); *m/z* 433 ($M^+$). Anal. Calcd for $C_{29}H_{27}N_3O$: C, 80.34; H, 6.27; N, 9.69. Found: C, 80.53; H, 6.18; N, 9.74.

**5-Isopropenyl-2,3-diphenyl-6-[*N*-allyl-*N*-(*p*-methoxyphenyl)]aminopyrimidin-4(3*H*)-one (5c).** Yield 87%; mp 179.5-180.5 °C; IR (KBr) ν 1655 (C=O), 1556, 1508 $cm^{-1}$; $^1H$ NMR (300 MHz) δ 1.59 (s, 3H, $-CH_3$), 3.78 (s, 3H, $-OCH_3$), 4.54 (d, *J* = 5.9, 2H, $-CH_2-$), 4.71-4.72 (m, 1H, Ha), 4.85-4.86 (m, 1H, Hb), 5.12 (pair of merged d, *J* = 17.4 and 10.1, 2H, Hd and He), 6.04 (dddd, *J* = 17.4, 10.1, 5.9 and 5.9, 1H, Hf), 6.78 (d, *J* = 8.9, with fine splitting, 2H, ArH), 7.03 (d, *J* = 8.9, with fine splitting, 2H, ArH), 7.14-7.32 (m, 10H, ArH); $^{13}C$ NMR (75.5 MHz) δ 21.3 ($-CH_3$), 55.2 ($-OCH_3$), 55.7 ($-CH_2-$), 104.7 (C-5), 113.8, 116.9 (C-8), 118.2 (C-11), 127.6, 127.8, 127.9, 128.5, 129.1, 129.2, 129.3 (C-10), 135.1, 137.7 (C-7), 138.3, 138.9, 154.9 (C-6), 156.7, 157.3 (C-2), 162.5 (C-4); *m/z* 449 ($M^+$). Anal. Calcd for $C_{29}H_{27}N_3O_2$: C, 77.48; H, 6.05; N, 9.35. Found: C, 77.61; H, 6.05; N, 9.44.

**5-Isopropenyl-3-(*p*-methylphenyl)-2-phenyl-6-[*N*-allyl-*N*-(*p*-methylphenyl)]aminopyrimidin-4(3*H*)-one (5d).** Yield 83%; mp 183-184 °C; IR (KBr) ν 1657 (C=O), 1558, 1528, 1508 $cm^{-1}$; $^1H$ NMR (300 MHz) δ 1.62 (s, 3H, $-CH_3$), 2.27 (s, 3H, $-CH_3$), 2.30 (s, 3H, $-CH_3$), 4.57 (d, *J* = 4.7, 2H, $-CH_2-$), 4.77 (s, 1H, Ha), 4.84 (s, 1H, Hb), 5.14 (pair of merged d, *J* = 16.9 and 10.1, Hd and He), 6.04 (dddd, *J* = 16.9, 10.1, 5.8 and 5.8, 1H, Hf), 6.98 (d, *J* = 8.4, 2H, ArH), 7.02-7.08 (m, 6H, ArH), 7.15-7.24 (m, 3H, ArH), 7.34 (d, *J* = 8.2, with fine splitting, 2H, ArH); $^{13}C$ NMR (75.5 MHz) δ 20.9 ($-CH_3$), 21.1 ($-CH_3$), 21.2 ($-CH_3$), 55.3 ($-CH_2-$), 105.9 (C-5), 116.8 (C-8), 118.3 (C-11), 125.6, 127.8, 128.8, 129.3 (C-10 and one ArC), 134.0,

135.1, 135.3, 135.4, 137.9 (C-7), 138.3, 143.6, 155.2 (C-6), 157.3 (C-2), 163.0 (C-2); *m/z* 447 ($M^+$). Anal. Calcd for $C_{30}H_{29}N_3O$: C, 80.50; H, 6.53; N, 9.38. Found: C, 80.62; H, 6.43; N, 9.46.

**5-Isopropenyl-3-(*p*-methylphenyl)-2-phenyl-6-[*N*-allyl-*N*-(*p*-methoxyphenyl)]aminopyrimidin-4(3*H*)-one (5e).** Yield 91%; mp 180-181 °C; IR (KBr) ν 1652 (C=O), 1556, 1521, 1506 $cm^{-1}$; $^1H$ NMR (300 MHz) δ 1.60 (s, 3H, $-CH_3$), 2.28 (s, 3H, $-CH_3$), 3.79 (s, 3H, $-OCH_3$), 4.55 (d, *J* = 5.9, 2H, $-CH_2-$), 4.73 (br s, 1H, Ha), 4.85 (br s, 1H, Hb), 5.12 (pair of merged d, *J* = 17.2 aand 9.7, Hd and He), 6.05 (dddd, *J* = 17.2, 9.7, 5.9 and 5.9, 1H, Hf), 6.80 (d, *J* = 8.9, with fine splitting, 2H, ArH), 7.02-7.09 (m, 5H, ArH), 7.17-7.27 (m, 4H, ArH), 7.33-7.36 (m, 2H, ArH); $^{13}C$ NMR (75.5 MHz) δ 21.1 ($-CH_3$), 21.3 ($-CH_3$), 55.4 ($-OCH_3$), 55.8 ($-CH_2-$), 106.2 (C-5), 113.9, 116.9 (C-8), 118.2 (C-11), 127.7, 127.8, 128.8, 129.3 (C-7), 129.4 (C-10), 135.3, 137.8, 138.5, 139.2, 155.1 (C-6), 156.7, 157.4 (C-2), 162.9 (C-4); *m/z* 463 ($M^+$). Anal. Calcd for $C_{30}H_{29}N_3O_2$: C, 77.72; H, 6.30; N, 9.06. Found: C, 77.90; H, 6.26; N, 8.98.

**5-Ethenyl-2,3-diphenyl-6-[*N*-allyl-*N*-(*p*-methoxyphenyl)]aminopyrimidin-4(3*H*)-one (5f).** Yield 63%; mp 66-67 °C; IR (KBr) ν 1638 (C=O), 1548, 1497, 1485 $cm^{-1}$; $^1H$ NMR (300 MHz) δ 3.78 (s, 3H, $-OCH_3$), 4.67 (d, *J* = 5.5, 2H, $-CH_2-$), 4.85 (d, *J* = 9.8, 1H, Ha), 5.05 (d, *J* = 16.5, 1H, Hb), 5.15 (d, *J* = 10.3, 1H, He), 5.19 (d, *J* = 17.3, 1H, Hd), 5.86-6.03 (m, 2H, Hc and Hf), 6.82 (d, *J* = 8.9, 2H, ArH), 7.09 (d, *J* = 8.9, 2H, ArH), 7.16-7.37 (m, 10H, ArH); $^{13}C$ NMR (75.5 MHz) δ 55.5 ($-OCH_3$), 55.6 ($-CH_2-$), 106.5 (C-5), 114.3, 115.7 (C-11), 116.7 (C-8), 125.4, 125.9, 127.8, 128.3, 128.8, 129.1, 129.4, 129.5, 132.0, 135.2, 137.8, 139.1, 139.8, 155.1 (C-6), 156.3, 157.2 (C-2), 162.6 (C-4); *m/z* 435 ($M^+$). Anal. Calcd for $C_{28}H_{25}N_3O_2$: C, 77.22; H, 5.79; N, 9.65. Found: C, 77.34; H, 5.86; N, 9.60.

**3,5,6,9-Tetrahydro-5,5-dimethyl-2,3-diphenyl-9-(*p*-methylphenyl)-4*H*-pyrimido[4,5-*b*]azepin-4-one (6a).** A solution of **5b** (0.50 g, 1.08 mmol) in xylene (6 ml) was refluxed for 1.5 h. The solvent was concentrated under *vacuo* and the residue thus obtained was purified by column chromatography (silica gel, EtOAc/hexane, 1:9) to give 0.38 g (76%) of **6a**; mp 182-183 °C; IR (KBr) ν 1645 (C=O), 1560, 1507, 1360 $cm^{-1}$; $^1H$ NMR (300 MHz) δ 1.59 (s, 6H, 2 x $-CH_3$), 2.37 (s, 3H, $-CH_3$), 2.43 (d, *J* = 7.2, 2H, $-CH_2-$), 5.54 (ddd, *J* = 7.4, 7.4 and 7.4, 1H, H-7), 6.23 (d, *J* = 7.4, 1H, H-8), 6.99-7.02 (m, 4H, ArH), 7.09-7.12 (m, 3H, ArH), 7.19-7.28 (m, 7H, ArH); $^{13}C$ NMR (75.5 MHz) δ 21.1 ($-CH_3$), 29.2 (2 x $-CH_3$), 41.1 (C-6), 42.3 (C-5), 108.8 (C-4a), 117.0 (C-7), 127.5, 127.9, 128.0, 128.7 (C-8), 129.1, 129.3, 129.4, 129.5, 133.5, 134.3, 136.0, 138.1, 143.1, 151.6 (C-9a), 155.2 (C-2), 163.3 (C-4); *m/z* 433 ($M^+$). Anal. Calcd for $C_{29}H_{27}N_3O$: C, 80.34; H, 6.27; N, 9.69. Found: C, 80.25; H, 6.27; N, 9.79.

**3,5,6,9-Tetrahydro-5,5-dimethyl-9-(*p*-methoxyphenyl)-3-(*p*-methylphenyl)-2-phenyl-4*H*-pyrimido[4,5-*b*]azepin-4-one (6b).** A solution of **5e** (0.50 g, 1.08 mmol) in xylene (6 ml) was refluxed for 1.5 h. A similar work up, as employed for **6a**, yielded 0.42 g (82%) of **6b**; mp 185-187 °C; IR (KBr) ν 1645 (C=O), 1558, 1506, 1360 $cm^{-1}$; $^1H$ NMR (300 MHz) δ 1.58 (s, 6H, 2 x $-CH_3$), 2.26 (s, 3H, $-CH_3$), 2.42 (d, *J* = 7.3, 2H, $-CH_2-$), 3.80 (s, 3H, $-OCH_3$), 5.52 (ddd, *J* = 7.4, 7.3 and 7.3, 1H, H-7), 6.18 (d, *J* = 7.3, 1H, H-8), 6.91 (d, *J* = 8.8, with fine splitting, 2H, ArH), 6.97-7.11 (m, 9H, ArH), 7.21 (d, *J* = 8.7, with fine splitting, 2H, ArH); $^{13}C$ NMR (75.5 MHz) δ 21.1 ($-CH_3$), 29.2 (2 x $-CH_3$), 41.0 (C-6), 42.5 (C-5), 55.4 ($-OCH_3$), 108.5 (C-4a), 113.9, 116.7 (C-7), 127.5, 128.7 (C-8), 129.2, 129.3, 129.5, 133.7, 134.4, 135.3, 137.7, 138.6, 151.6 (C-

9a), 155.1 (C-2), 157.8, 163.3 (C-4); *m/z* 463 ($M^+$). Anal. Calcd for $C_{30}H_{29}N_3O_2$: C, 77.73; H, 6.30; N, 9.06. Found: C,77.61; H, 6.27; N, 9.11.

**10-Allyl-2,3-diphenyl-5,5,7-trimethyl-5,10-dihydropyrimido[4,5-*b*]quinolin-4(3*H*)-one (7a).** To a solution of **5b** (0.50 g, 1.16 mmol) in benzene (10ml) was added catalytic amount of $AlCl_3$. The mixture was refluxed for 30 min, cooled to rt and diluted with benzene (10 ml). The organic phase was then washed with saturated $NaHCO_3$ and water and dried over anhydrous $MgSO_4$. The solvent was removed under reduced pressure and the residue purified by column chromatography on silica gel (eluent: a mixture of EtOAc/hexane in 1:9 ratio) to give 0.47 g (94%) of **7a**; mp 216-217 °C; IR (KBr) ν 1652 (C=O), 1595, 1558, 1525, 1496, 1443 $cm^{-1}$; $^1H$ NMR (300 MHz) δ 1.87 (s, 6H, 2 x $-CH_3$), 2.30 (s, 3H, $-CH_3$), 4.83-4.85 (br s, with fine splittimg, 2H, $-CH_2-$), 5.18 (d, $J$ = 10.2, with fine splitting, 1H, $=CH_2$), 5.23 (d, $J$ = 17.3, with fine splitting, 1H, $=CH_2$), 5.96 (dddd, $J$ = 17.3, 10.2, 4.5 and 4.5, 1H, -CH=), 6.79 (d, $J$ = 8.4, 1H, H-9), 6.94 (dd, $J$ = 8.4 and 1.8, 1H, ArH, H-8), 7.12-7.30 (m, 11H, ArH); $^{13}C$ NMR (75.5 MHz) δ 20.7 ($-CH_3$), 30.3 (2 x $-CH_3$), 35.4 (C-5), 45.6 ($-CH_2-$), 101.6 (C-4a), 113.9, 116.0 (C-13), 127.4, 127.7, 127.8, 128.1, 128.7, 129.2, 129.3, 129.4 (C-12), 131.7, 133.3, 133.5, 134.2, 137.9, 152.0 (C-10a), 156.2 (C-2), 161.5 (C-4); *m/z* 433 ($M^+$). Anal. Calcd for $C_{29}H_{27}N_3O$: C, 80.34; H, 6.27; N, 9.69. Found: C, 80.57; H, 6.33; N, 9.85.

**10-Allyl-5,5-dimethyl-2,3-diphenyl-7-methoxy-5,10-dihydropyrimido[4,5-*b*]quinolin-4(3*H*)-one (7b).** To a solution of **5c** (0.50 g, 1.12 mmol) in benzene (10 ml) was added catalytic amount of $AlCl_3$. An identical procedure, as employed for **7a**, resulted in the isolation of 0.45 g (90%) of **7b**; mp 205-207; IR (KBr) ν 1650 (C=O), 1603, 1562, 1528, 1494, 1438 $cm^{-1}$; $^1H$ NMR (300 MHz) δ 1.88 (s, 6H, 2 x $-CH_3$), 3.80 (s, 3H, $-OCH_3$), 4.84-4.85 (br s, with fine splitting, 2H, $-CH_2-$), 5.19 (d, $J$ = 10.3, with fine splitting, 1H, $=CH_2$), 5.23 (d, J = 17.4, with fine splitting, 1H, $=CH_2$), 5.96 (dddd, $J$ = 17.4, 10.3, 4.5 and 4.4, 1H, -CH=), 6.71 (dd, $J$ = 8.9 and 2.9, with fine splitting, 1H ArH, H-8), 6.84 (d, $J$ = 8.9, 1H, H-9), 7.00 (d, $J$ = 2.9, 1H ArH, H-6), 7.12-7.30 (m, 10H, ArH); $^{13}C$ NMR (75.5 MHz) δ 30.2 (2 x $-CH_3$), 35.8 (C-5), 45.7 ($-CH_2-$), 55.4 ($-OCH_3$), 100.5 (C-4a), 111.7, 113.3, 114.8, 116.1 (C-13), 127.7, 128.1, 128.7, 129.2, 129.3, 129.4 (C-12), 130.4, 133.6, 135.0, 135.2, 137.9, 152.0 (C-10a), 155.2, 156.2 (C-2), 161.5 (C-4); *m/z* 449 ($M^+$). Anal. Calcd for $C_{29}H_{27}N_3O_2$: C, 77.48; H, 6.05; N, 9.35. Found: C, 77.69; H, 5.99; N, 9.45.

**Dimethyl 3,4-dihydro-5-methyl-4-oxo-2,3-diphenylquinazoline-7,8-dicarboxylate (9).** Equivalent amounts of **5a/5b/5c** and DMAD were refluxed in dry toluene for 17-18 h. The solvent was removed under reduced pressure and the crude product thus obtained was purified by comlumn chromatography on silica gel (eluent: a mixture of EtOAc/hexane in a 1:6 ratio) to give 90-95% of **9a**; mp 192-193 °C; IR (KBr) ν 1733 (2 x $-CO_2Me$), 1674 (C=O), 1588, 1559 $cm^{-1}$; $^1H$ NMR (300 MHz) δ 2.91 (s, 3H, $-CH_3$), 3.97 (s, 3H, $-CO_2CH_3$), 3.99 (s, 3H, $-CO_2CH_3$), 7.13-7.35 (m, 10H, ArH), 7.87 (s, 1H, H-6); $^{13}C$ NMR (75.5 MHz) δ 23.2 ($-CH_3$), 52.8 ($-OCH_3$), 52.9 ($-OCH_3$), 122.2, 127.7, 128.6, 129.0, 129.1, 129.5, 129.6, 129.7, 138.8, 132.7, 134.7, 137.5, 143.2, 146.6, 155.5 (C-2), 162.1 (C-4), 165.1 ($-CO_2Me$), 168.3 ($-CO_2Me$); *m/z* 428 ($M^+$). Anal. Calcd for $C_{25}H_{20}N_2O_5$: C, 70.08; H, 4.70; N, 6.54. Found: C, 70.15; H, 4.76; N, 6.50.

***General procedure for pyrimidoquinolines* (10).** A solution of thiophenol (0.30 g, 2.74 mmol) and AIBN (0.23 g, 1.40 mmol) in dry benzene was added dropwise, over a period of 2 h, to a solution of **5**

(2.5 mmol) in boiling benzene while stirring under nitrogen. The solution was further refluxed for 5-6 h and the solvent removed under *vacuo*. The resulting residue was purified by column chromatography on silica gel (eluent: a mixture of EtOAc/hexane in a 1:9 ratio).

**10-Allyl-5-methyl-2,3-diphenyl-5-phenylthiomethyl-5,10-dihydropyrimido[4,5-*b*]quinolin-4(3*H*)-one (10a).** Yield 61%; mp 161-162 °C; IR (KBr) ν 1655 (C=O), 1598, 1563, 1560, 1525 $cm^{-1}$; $^1H$ NMR (300 MHz) δ 1.99 (s, 3H, $-CH_3$), 3.24 (d, $J$ = 13.2, 1H, $-CH_2$-SPh), 4.64 (d, $J$ = 13.2, 1H, $-CH_2$-SPh), 4.83-4.95 (m, 2H, -N-$CH_2$-), 5.22 (d, $J$ = 10.5, 1H, $=CH_2$), 5.36 (d, $J$ = 17.3, 1H, $=CH_2$), 5.98 (dddd, $J$ = 17.3, 10.5, 4.4 and 4.4, 1H, -CH=), 6.92 (d, $J$ = 8.3, 1H, H-9), 7.00 (d, $J$ = 8.3, 1H, H-6), 7.09-7.32 (m, 17H, ArH); $^{13}C$ NMR (75.5 MHz) δ 29.3 ($-CH_3$), 41.6 (C-5), 45.5 ($-CH_2$-SPh), 47.0 (-N-$CH_2$-), 98.5 (C-4a), 114.1, 116.1 (C-13), 119.1, 125.7, 126.9, 127.4, 127.6, 128.1, 128.4, 128.6, 128.7, 129.0, 129.1, 129.3, 129.4 (C-12), 130.9, 133.1, 134.9, 137.5, 138.0, 153.2 (C-10a), 156.3 (C-2), 161.1 (C-4); *m/z* 527 ($M^+$). Anal. Calcd for $C_{34}H_{29}N_3OS$: C, 77.39; H, 5.54; N, 7.96. Found: C, 77.52; H, 5.55; N, 8.07.

**10-Allyl-5,7-dimethyl-2,3-diphenyl-5-phenylthiomethyl-5,10-dihydropyrimido[4,5-*b*]quinolin-4(3*H*)-one (10b).** Yield 73%; mp 181-183 °C; IR (KBr) ν 1652 (C=O), 1598, 1561, 1557, 1530, 1497 $cm^{-1}$; $^1H$ NMR (300 MHz) δ 1.98 (s, 3H, $-CH_3$), 2.26 (s, 3H, $-CH_3$), 3.24 (d, $J$ = 13.1, 1H, $-CH_2$-SPh), 4.64 (d, $J$ = 13.1, 1H, $-CH_2$-SPh), 4.79-4.97 (m, 2H, -N-$CH_2$-), 5.22 (d, $J$ = 10.4, with fine splitting, 1H, $=CH_2$), 5.35 (d, $J$ = 17.3, with fine splitting, 1H, $=CH_2$), 5.97 (dddd, $J$ = 17.3, 10.4, 4.3 and 4.3, 1H, -CH=), 6.82 (d, $J$ = 8.4, 1H, H-9), 6.96 ( dd, $J$ = 8.4 and 1.5, 1H, H-8), 7.08 (d, $J$ = 1.5, 1H, H-6), 7.11-7.29 (m, 15H, ArH); $^{13}C$ NMR (75.5 MHz) δ 20.8 ($-CH_3$), 29.3 ($-CH_3$), 41.7 (C-5), 45.4 ($-CH_2$-SPh), 47.0 (-N-$CH_2$-), 98.2 (C-4a), 114.1, 116.1 (C-13), 125.6, 127.5, 127.6, 128.0, 128.1, 128.3, 128.6, 128.8, 129.2, 129.4, 129.7 (C-12), 130.9, 131.9, 133.3, 135.0, 135.7, 137.5, 137.6, 153.2 (C-10a), 156.3 (C-2), 161.1 (C-4); *m/z* 541 ($M^+$). Anal. Calcd for $C_{34}H_{31}N_3OS$: C, 77.60; H, 5.77; N, 7.76. Found: C, 77.52; H, 5.65; N, 7.67.

***Reactions of (N-allyl-N-aryl)amino-1,3-diaza-1,3-butadienes* 2 *with chloroketene* 16; General procedure for pyrimidinones (19).** To a well stirred solution of **2** (4.0 mmol) and triethylamine (1 g, 10 mmol) in dry methylene chloride (30 ml), was added dropwise, a solution of chloroacetyl chloride (0.68 g, 6.0 mmol) in dry methylene chloride (30 ml) over a period of 1.5-2 h at rt. A similar work up, as employed for pyrimidinones **5**, yielded the crude products **19** which were purified by column chromatography on silica gel (eluent: a mixture of EtOAc/hexane in a 1:10 ratio).

**5-Methylthio-2,3-diphenyl-6-(*N*-allyl-*N*-phenyl)aminopyrimidin-4(3*H*)-one (19a).** Yield 89%; mp 125-126 °C; IR (KBr) ν 1657 (C=O), 1549, 1484 $cm^{-1}$; $^1H$ NMR (300 MHz) δ 2.15 (s, 3H, $-SCH_3$), 4.73 (d, $J$ = 5.1, with fine splitting, 2H, $-CH_2$-), 5.16 (dd, $J$ = 10.3 and 1.6, with fine splitting, 1H, $=CH_2$), 5.28 (dd, $J$ = 17.2 and 1.6, with fine splitting, 1H, $=CH_2$), 6.05 (dddd, $J$ = 17.2, 10.3, 5.1 and 5.1, 1H, -CH=), 7.03-7.34 (m, 15H, ArH); $^{13}C$ NMR (75.5 MHz) δ 16.3 ($-SCH_3$), 55.1 ($-CH_2$-), 100.8 (C-5), 116.5 (C-9), 123.1, 123.9, 127.8, 128.3, 128.8, 129.0, 129.1, 129.3, 129.4, 129.6 (C-8), 134.7, 134.9, 137.7, 146.6, 155.6 (C-6), 160.1 (C-2), 162.6 (C-4); *m/z* 425 ($M^+$), 378 ($M^+$ - $SCH_3$). Anal. Calcd for $C_{26}H_{23}N_3OS$: C, 73.38; H, 5.45; N, 9.87. Found: C, 73.21; H, 5.54; N, 9.83.

**5-Methylthio-2,3-diphenyl-6-[*N*-allyl-*N*-(*p*-methoxyphenyl)]aminopyrimidin-4(3*H*)-one (19b).** Yield 91%; mp 158.159 °C; IR (KBr) ν 1661 (C=O), 1540, 1482 $cm^{-1}$; $^1H$ NMR (300 MHz) δ 2.11 (s, 3H, $-SCH_3$), 3.79 (s, 3H, $-OCH_3$), 4.65 (d, $J$ = 5.4, 2H, $-CH_2-$), 5.14 (dd, $J$ = 10.3 and 1.3, 1H, $=CH_2$), 5.20 (dd, $J$ = 17.2 and 1.3, 1H, $=CH_2$), 6.04 (dddd, $J$ = 17.2, 10.3, 5.5 and 5.5, 1H, -CH=), 6.85 (d, $J$ = 8.9, with fine splitting, 2H, ArH), 7.08-7.32 (m, 12H, ArH); $^{13}C$ NMR (75.5 MHz) δ 16.5 ($-SCH_3$), 55.4 ($-OCH_3$), 55.8 ($-CH_2-$), 98.2 (C-5), 114.2, 116.8 (C-9), 125.7, 127.8, 128.2, 128.7, 129.0, 129.3, 129.6 (C-8), 134.8, 134.9, 137.8, 139.6, 155.5 (C-6), 156.6, 160.4 (C-2), 162.7 (C-4); *m/z* 455 ($M^+$), 408 ($M^+$ - $SCH_3$). Anal. Calcd for $C_{27}H_{25}N_3O_2S$: C, 71.18; H, 5.53; N, 9.22. Found: C, 71.26; H, 5.54; N, 9.33.

**3-(*p*-Methylphenyl)-5-methylthio-6-[*N*-allyl-*N*-(*p*-methylphenyl)]amino-2-phenylpyrimidin-4(3*H*)-one (19c).** Yield 86%; mp 154.155 °C; IR (KBr) ν 1652 (C=O), 1550, 1480 $cm^{-1}$; $^1H$ NMR (300 MHz) δ 2.14 (s, 3H, $-SCH_3$), 2.28 (s, 3H, $-CH_3$), 2.31 (s, 3H, $-CH_3$), 4.69 (d, $J$ = 5.1, 2H, $-CH_2-$), 5.14 (dd, $J$ = 10.3 and 1.1, 1H, $=CH_2$), 5.25 (dd, $J$ = 17.2 and 1.1, 1H, $=CH_2$), 6.03 (dddd, $J$ = 17.2, 10.3, 5.1 and 5.1, 1H, -CH=), 7.03 (d, $J$ = 8.4, 2H, ArH), 7.07-7.32 (m, 11H, ArH); $^{13}C$ NMR (75.5 MHz) δ 16.3 ($-SCH_3$), 20.9 ($-CH_3$), 21.1 ($-CH_3$), 55.2 ($-CH_2-$), 99.9 (C-5), 116.4 (C-9), 123.3, 124.6, 127.7, 127.8, 128.6, 128.7, 129.2, 129.3, 129.4, 129.5 (C-8), 129.6, 133.6, 134.6, 134.9, 135.0, 135.1, 138.2, 144.0, 155.6 (C-6), 160.1 (C-2), 162.7 (C-4); *m/z* 453 ($M^+$), 406 ($M^+$ - $SCH_3$). Anal. Calcd for $C_{28}H_{27}N_3OS$: C, 74.14; H, 5.99; N, 9.26. Found: C, 74.07; H, 5.97; N, 9.33.

***Representative procedure for pyrimidothiazines* 20.** To a solution of **19** (1.18 mmol) in methylene chloride at rt was added iodine (0.16 g, 1.27 mmol) and the mixture was allowed to stir for 15 h. The reaction mixture was washed with aqueous $NaHSO_3$ solution (50 ml) and then with water (3 x 50 ml). The organic layer was dried over anhydrous $MgSO_4$, evaporated under *vacuo* and the resulting residue purified by column chromatography on silica gel (eluent: a mixture of EtOAc/hexane in 1:7 ratio).

**7,8-Dihydro-6-iodomethyl-2,3,8-triphenyl-6*H*-pyrimido[5,4-*b*][1,4]thiazin-4(3*H*)-one (20a).** Yield 0.48 g (76%) from 0.50 g of **19a**; mp 184-186 °C; IR (KBr) ν 1652 (C=O), 1554, 1499, 1246 $cm^{-1}$; $^1H$ NMR (300 MHz) δ 3.49-3.71 (m, 3H; 2H, $-CH_2-I$ and 1H, methine), 4.28-4.32 (m, 2H, $-N-CH_2-$), 7.05-7.34 (m, 15H, ArH); *m/z* 537 ($M^+$), 410 ($M^+$ - I). Anal. Calcd for $C_{25}H_{20}N_3OSI$: C, 55.87; H, 3.75; N, 7.82. Found: C, 56.01; H, 3.79; N, 7.92.

**7,8-Dihydro-6-iodomethyl-8-(*p*-methoxyphenyl)-2,3-diphenyl-6*H*-pyrimido[5,4-*b*][1,4]thiazin-4(3*H*)-one (20b).** Yield 0.51 g (81%) from 0.54 g of **19b**; mp 219-221 °C; IR (KBr) ν 1649 (C=O), 1559, 1507, 1249 $cm^{-1}$; $^1H$ NMR (300 MHz) δ 3.53-3.75 (m, 3H; 2H, $-CH_2-I$ and 1H, methine), 3.82 (s, 3H, $-OCH_3$), 4.30-4.34 (m, 2H, $-N-CH_2-$), 6.92 (d, $J$ = 8.9, with fine splitting, 2H, ArH), 7.04-7.08 (m, 5H, ArH), 7.12-7.17 (m, 2H, ArH), 7.26-7.31 (m, 5H, ArH); $^{13}C$ NMR (75.5 MHz) δ 7.1 ($-CH_2-I$), 37.8 (methine C), 54.7 ($-N-CH_2-$), 55.4 ($-OCH_3$), 92.2 (C-4a), 114.1, 127.6, 128.2, 128.4, 128.8, 129.4, 134.2, 137.3, 152.6, 153.3, 157.7, 159.8; *m/z* 567 ($M^+$), 440 ($M^+$ - I). Anal. Calcd for $C_{26}H_{22}IN_3O_2S$: C, 55.03; H, 3.91; N, 7.40. Found: C, 54.89; H, 4.01; N, 7.36.

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