SYNTHESIS OF 5-ISOPROPENYL/VINYL SUBSTITUTED PYRIMIDINONES *VIA* [4+2] CYCLOADDITION REACTIONS OF 1,3-DIAZA-1,3-BUTADIENES WITH ISOPROPENYL/VINYLKETENES AND THEIR FURTHER TRANSFORMATIONS: [4+2] AND UNUSUAL [3+2] CYCLOADDITIONS WITH α-NITROSOSTYRENES

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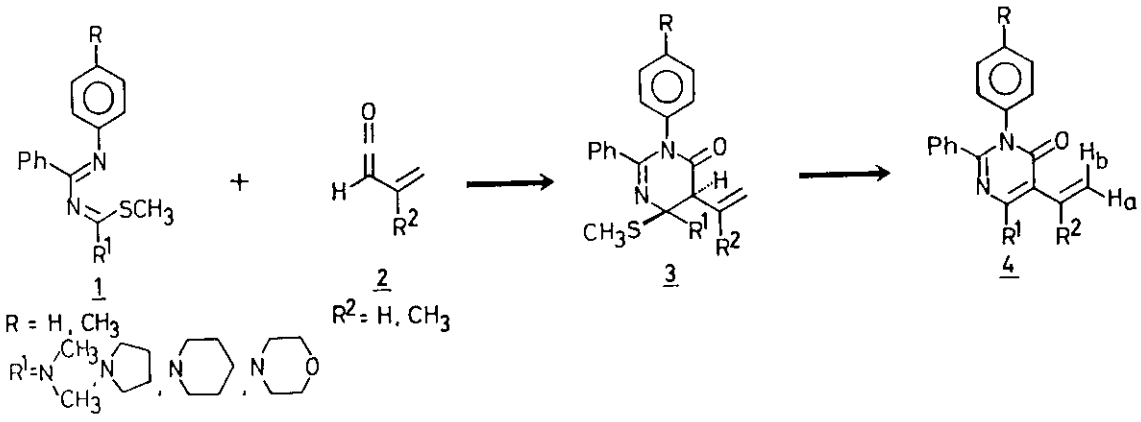
Abstract - 1,3-Diaza-1,3-butadienes (**1** and **5**) underwent [4+2] cycloaddition reactions with isopropenyl/vinylketenes (**2**), acting as 2π components, to result in pyrimidinones (**4** and **7**). The treatment of 5-isopropenyl substituted pyrimidinones with phosphorus pentasulfide in the presence of sodium carbonate in dry tetrahydrofuran gave pyrimidinones (**8**). The reactions of nitrosoalkenes with 5-vinyl substituted pyrimidinones resulted in [4+2] cycloadditions leading to 1,2-oxazines (**15**), whereas 5-isopropenyl substituted pyrimidinones resulted in unusual [3+2] cycloaddition reactions yielding the nitrones (**14**).

Ketene chemistry is dominated by [2+2] cycloaddition reactions and such reactions with carbon-nitrogen double bonds of imines, monoaza- and diazabutadienes have been shown to result in important ß-lactam derivatives.[1,2] We have recently reported the simple methods for the preparation of various acyclic 1,3-diaza-1,3-butadienes[3] and successfully utilised these in [4+2] cycloaddition reactions with phenyl-,

chloro-, bromo-, iodo-, chloromethyl-, dichloro- and various other ketenes.[4,5] It was further observed that the reactions of 4-alkylthio-1-aryl-4-dialkyl amino-2-phenyl-1,3-diazabutadienes (**1**) with various ketenes yielded [4+2] cycloadducts as intermediates, which underwent either elimination of alkylmercaptan [4] or 1,2-alkylthio shifts in case of halo ketenes,[5] yielding various substituted pyrimidinones. Also, there are reports of vinylketenes participating either as 2π component in [2+2] cycloadditions with imines/azadienes [6-8] or as 4π component in [4+2] cycloaddition reactions. It was thought that making a comparison of dienic properties between various dienes and/or heterodienes is an interesting scientific enquiry. However, little attention has been paid to such studies by carrying out cycloaddition reactions between such dienes. Accordingly, we got interested in investigating the cycloaddition reactions of 1,3-diazabutadienes with isopropenyl/vinylketenes and these were found to follow [4+2] cycloaddition pathway in which these ketenes behaved as 2π component. To our knowledge, this is the first report concerning the participation of such ketenes as 2π component in [4+2] cycloaddition reactions.

Thus, the reactions of 1-aryl-4-dialkyl amino-4-methylthio-2-phenyl-1,3-diaza-1,3-butadienes (**1**) with isopropenyl/vinylketenes (**2**), generated <u>in situ</u> from 3,3-dimethylacroyl chloride/crotonyl chloride and excess of triethylamine in dry methylene chloride, resulted in very high yields (89-95%) of 3-aryl-5-isopropenyl/vinyl-2-phenyl-6-dialkyl amino-4(3*H*)-pyrimidinones (**4**). (Scheme 1). The products were characterised on the basis of analytical and spectral evidences. Thus, compound (**4a**), for example, was analysed for $C_{21}H_{21}N_3O$ and its mass spectrum showed a molecular ion peak at m/z 331. Its ir spectrum (KBr) showed a strong absorption peak at 1654 cm^{-1} due to α,ß-unsaturated carbonyl group. The ^1H nmr spectrum of **4a** showed the absence of methylthio and the presence of dialkyl amino functions. It also exhibited the presence of $-CH_3$ proton at δ 2.13 and two protons as two broad singlets due to Ha at δ 5.03 and due to Hb at δ 5.33. The ^1H nmr spectrum of pyrimidinone (**4g**), in addition to aromatic and dialkyl amino protons showed the presence of three doublet of doublets due to vinylic protons. Ha proton appeared as a doublet of doublet at δ 5.40 (J_{HaH} = 11.4 Hz, J_{HaHb} = 2.5 Hz), Hb exhibited

another doublet of doublet at δ 6.00 (J_{HbH} = 17.5 Hz, J_{HbHa} = 2.5 Hz) and the proton H also appeared as a doublet of doublet at δ 6.67 (J_{HHb} = 17.5 Hz, J_{HHa} = 11.4 Hz). The downfield shift of proton Hb as compared to Ha in the pyrimidinones (**4**) may be due to the anisotropic deshielding of the carbonyl



4 a R = H, R^1 = N(CH3)2, R^2 = CH3

b R = H, R^1 = N, R^2 = CH3.

c. R = H, R^1 = N, R^2 = CH3.

d R = H, R^1 = N O, R^2 = CH3.

e R = R^2 = CH3, R^1 = N.

f. R = R^2 = CH3, R^1 = N O.

g. R = R^2 = H R^1 = N(CH3)2.

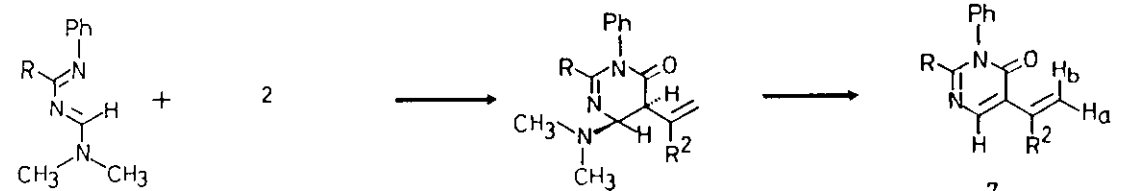
h. R = R^2 = H R^1 = N.

i. R = R^2 = H R^1 = N.

j. R = R^2 = H R^1 = N O

k. R = CH3, R^1 = N, R^2 = H

l. R = CH3, R^1 = N O, R^2 = H



7.a. R = Ph, R^2 = CH3

b R = Ph, R^2 = H

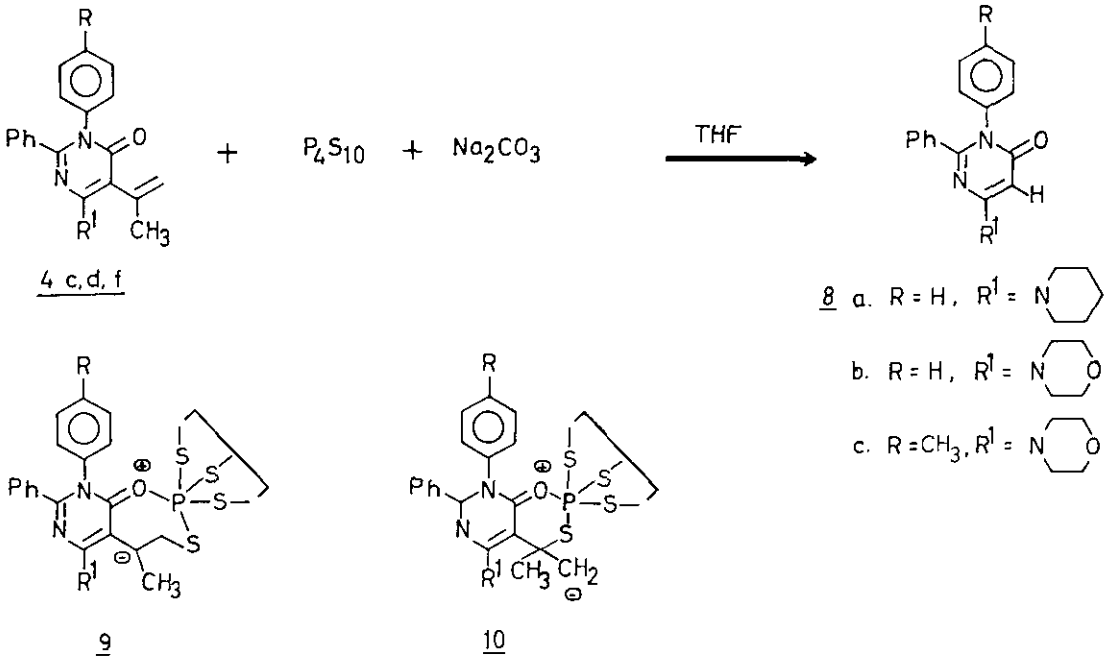
c R = SCH3 R^2 = CH3

Scheme 1

group. Similarly, the reactions of 4-dimethylamino-2-methylthio/phenyl-1-phenyl-1,3-diaza-1,3-butadienes (**5**) with vinylketenes resulted in the formation of pyrimidinones (**7**) by the elimination of dimethylamino function from the initially formed [4+2] cycloadducts (**6**) as intermediates. (Scheme 1). The pyrimidinones (**7**) were also analysed on the basis of their analytical and spectral data. Compound (**7a**), analysed for $C_{19}H_{16}N_2O$ showed the molecular ion peak at m/z 288 in its mass spectrum. Its ir spectrum exhibited a strong absorption band at 1668 cm^{-1} due to α,ß-unsaturated carbonyl group. The ^1H nmr spectrum showed, in addition to other protons, the presence of an olefinic proton at δ 8.21 and the absence of dimethylamine function. The formation of pyrimidinones (**4**) and (**7**) in these reactions requires the trans arrangement for H-5/methylthio functions and H- 5/dimethylamino functions in the intermediates (**3**) and (**6**), respectively. The intermediates (**3**) and (**6**) with the desired stereochemical arrangements may either be formed through highly stereoslective and concerted [4+2] cycloaddition or via the equilibration of the intermediates possibly through zwitterionic intermediate as reported earlier.[4b,5]

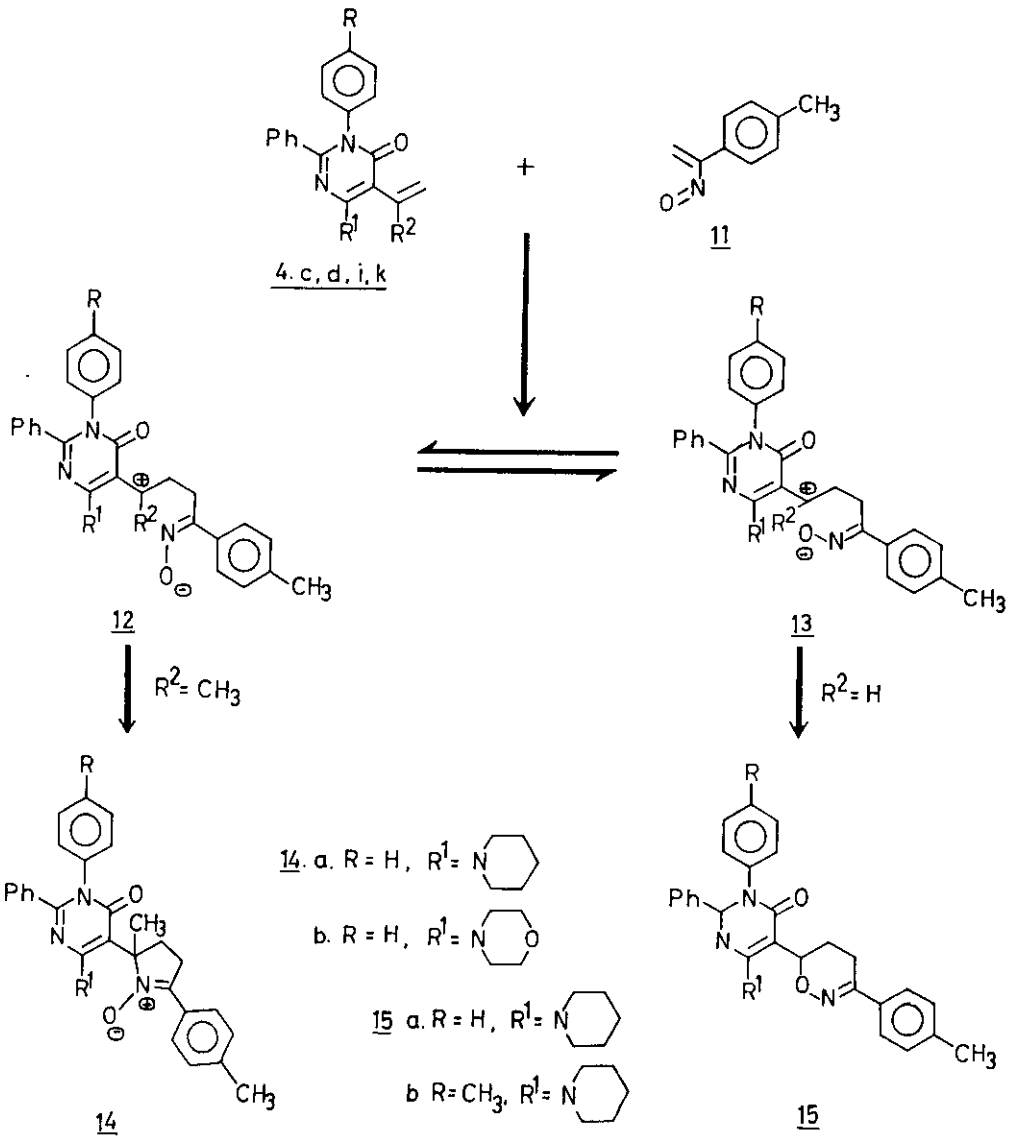
The 5-isopropenyl/vinylpyrimidinones so obtained were treated with phosphorus pentasulfide for their conversion into corresponding thiones. But these reactions resulted interestingly in the removal of isopropenyl functionality in case of 5-isopropenylpyrimidinones. Thus, the treatment of 5-isopropenyl -4(3*H*)-pyrimidinones (**4c,d,f**) with phosphorus pentasulfide in presence of sodium carbonate in dry tetrahydrofuran, followed by washing with aqueous sodium hydrogen phosphate resulted in very good yields (90-94%) of pyrimidinones (**8**) (Scheme 2). The pyrimidinones (**8**) were also characterised on the basis of analytical and spectral data. The compound (**8a**), for example, was analysed for $C_{21}H_{21}N_3O$ and showed the molecular ion peak at m/z 331. Its ir spectrum showed a sharp band at 1654 cm^{-1} due to α,ß-unsaturated carbonyl group and its ^1H nmr spectrum exhibited, in addition to other protons, the 5-H olefinic proton at δ 5.49. The possible mechanism leading to the formation of pyrimidinones (**8**) is not well understood but it is possible that the starting pyrimidinone first complexes with phosphorus pentasulfide to yield an intermediate (**9**) or (**10**), which then decomposes to give the pyrimidinones (**8**).

However, the reactions of 5-vinyl-4(3*H*)-pyrimidinones (**4g-l**) with phosphorus pentasulfide resulted in a mixture, from which no pure product could be isolated.



Scheme 2

It was thought that the 5-isopropenyl/vinylpyrimidinones (**4**) can be utilised for the synthesis of a large variety of 5-substituted pyrimidinones by carrying out their reactions with various dienes and 1,3-dipoles. Keeping this in view, we investigated the reactions of pyrimidinones (**4**) with α-nitrosostyrene (**11**), which have been reported to undergo [4+2] cycloadditions with carbon-carbon double bonds of alkenes, allenes, and dienes and unusual [3+2] cycloaddition with carbon-nitrogen double bonds.[9] Thus, the treatment of α-nitrosostyrene (**11**), generated in situ from α-chlorooximes and sodium carbonate, with 5-isopropenylpyrimidinones (**4c,d**) and 5-vinylpyrimidinones (**4i,k**) resulted in nitrones (**14**) and oxazines (**15**) arising from unusual [3+2] cycloadditions and [4+2] cycloadditions, respectively. To our knowledge, this is the first report of unusual [3+2] cycloaddition of α-nitrososty renes with carbon-carbon double



Scheme 3

bonds. The products were characterised as nitrones (**14**) and oxazine derivative (**15**) on the basis of their analytical and spectral evidences. The ir spectrum (KBr) for nitrone (**14a**), for example, showed strong absorption band around 1662 cm^{-1} due to α,ß-unsaturated carbonyl group and 1208 cm^{-1} for N-O of nitrone and its mass spectrum exhibited a weak molecular ion peak at m/z 518. The presence of two

downfield protons for the ortho protons of 4-methylphenyl group attached to nitrone ring in its ^{1}H nmr spectrum further supported the assigned structure.

Similarly, the products (**15**) were assigned the oxazine structure on the basis of their analytical and spectral evidences. The probable mechanism leading to the formation of these products is outlined in Scheme 3. In this scheme, it is assumed that the reactions of 5-isopropenyl/vinylpyrimidinones (**4**) with nitrosoalkene (**11**) yields interconvertible zwitterionic intermediates (**12**) and (**13**) and because of steric reasons, when $R^2 = CH_3$, the transiod form **12** leads to nitrones (**14**), whereas in case $R^2 = H$, the cisoid form (**13**) gives oxazines (**15**).

EXPERIMENTAL

Melting points were determined with a Toshniwal melting point apparatus and are uncorrected. Ir spectra were recorded in a Perkin-Elmer 983 Infrared Spectrophotometer using KBr disc. ^{1}H Nmr were recorded in deuteriochloroform, with a Varian 390 90 MHz and Burker AC-F 300 300 MHz using TMS as internal standard; J values are in Hz. ^{13}C Nmr spectra were also recorded in Bruker AC-F 300 in dueteriochloroform using TMS as internal standard. Mass spectra were obtained by electron impact at 70 eV.

Starting Materials:

1,3-Diaza-1,3-butadienes [3] and α-chlorooxime of p-methylacetophenone [10] were prepared by the reported procedures. Crotonyl chloride and 3,3-dimethylacroyl chloride were prepared form their corresponding acids as follows: An equimolar amount of thionyl chloride was added dropwise at room temperature to the crotonic acid / 3,3-dimethylacrylic acid. The acid immediately goes into solution accompanied by strong effervesce. After about 1.5-2 h, when the effervesce ceased, the reaction mixture was refluxed on water bath for 5-10 min to ensure complete elimination of HCl. The acid chloride thus obtained were used directly for these reactions.

Reactions of 1,3-Diaza-1,3-butadienes (1 and 5) with Ketenes (2):

To a well stirred solution of 1,3-diaza-1,3-butadiene (4 mmol) and triethylamine (1g, 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 room temperature. After 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.

6-Dimethylamino-2,3-diphenyl-5-isopropenyl-4(3 *H*)-pyrimidinone (4a): 94%; mp 196-197 °C (Anal. Calcd for $C_{21}H_{21}N_3O$: C, 76.11; H, 6.39; N, 12.68. Found: C, 76.05; H, 6.34; N, 12.60). ν_{max} : 1654 cm^{-1} (C=O). δ_H (90 MHz) : 2.13 (s, 3H, $-CH_3$); 3.13 (s, 6H, $-N(CH_3)_2$); 5.03 (br s, 1H, Ha); 5.33 (br s, 1H, Hb); 7.15-7.41 (m, 10H, arom). M^+ 331.

2,3-Diphenyl-5-isopropenyl-6-pyrrolidino-4(3 *H*)-pyrimidinone (4b): 93%; mp 221-222 °C. (Anal. Calcd for $C_{23}H_{23}N_3O$: C, 77.28; H, 6.49; N, 11.75. Found: C, 77.15; H, 6.48; N, 11.69). ν_{max} : 1652 cm^{-1} (C=O). δ_H (90 MHz): 1.85 -2.05 (m, 4H, $-CH_2-CH_2-$); 2.16 (s, 3H, $-CH_3$); 3.51-3.75 (m, 4H, $-CH_2-N-CH_2-$); 4.91 (br s, 1H, Ha); 5.39 (br s, 1H, Hb); 7.17-7.47 (m, 10H, arom). M^+ 357.

2,3-Diphenyl-5-isopropenyl-6-piperidino-4(3 *H*)-pyrimidinone (4c): 90%; mp 179-180 °C. (Anal. Calcd for $C_{24}H_{25}N_3O$: C, 77.60; H, 6.78; N, 11.31. Found: C, 77.56; H, 6.77; N, 11.22). ν_{max}: 1649 cm^{-1} (C=O). δ_H (300 MHz): 1.64 (br s, 6H, $-CH_2-CH_2-CH_2-$); 2.10 (s, 3H, $-CH_3$); 3.56 (br s, 4H, $-CH_2-N-CH_2-$); 5.07 (br s, 1H, Ha); 5.24 (br s, 1H, Hb); 7.10-7.26 (m, 10 H, arom). δ_C (75.46 MHz): 22.29 ($-CH_3$); 24.70 ($-CH_2-$); 25.88 (2 $-CH_2-$); 48.27 ($-CH_2-N-CH_2-$); 101.30 (C-5); 116.60 ($=CH_2$); 127.50, 127.65, 128.33, 129.12, 129.15, 135.34, 137.87 (aromatic); 140.02 ($-\underset{|}{C}=$); 154.42 (C- 6); 158.11 (C-2) and 162.35 (C-4). M^+ 371.

2,3-Diphenyl-5-isopropenyl-6-morpholino-4(3 *H*)-pyrimidinone (4d): 89%; mp 186-187 °C. (Anal. Calcd for $C_{23}H_{23}N_3O_2$: C, 73.97; H, 6.21; N, 11.25. Found : C, 73.83; H, 6.18; N, 11.23). ν_{max}: 1654 cm^{-1} (C=O). δ_H (90 MHz): 2.13 (s, 3H, $-CH_3$); 3.60-3.88 (br s, 8H, morpholine); 5.18 (br s, 1H, Ha); 5.33 (br s, 1H, Hb); 7.17-7.50 (m, 10H, arom). M^+ 373.

5-Isopropenyl-3-(4-methylphenyl)-2-phenyl-6-piperidino-4(3 *H*)-pyrimidinone (4e): 93%; 199-201 °C. (Anal. Calcd for $C_{25}H_{27}N_3O$: C, 77.89; H, 7.06; N, 10.90. Found: C, 77.85; H, 7.06; N, 10.80). ν_{max} : 1645 cm^{-1} (C=O). δ_H (90 MHz): 1.57-1.73 (br s, 6H, $-CH_2-CH_2-CH_2-$); 2.10 (s, 3H, $-CH_3$); 2.30 (s, 3H, $-CH_3$); 3.50-3.70 (br s, 4H, $-CH_2-N-CH_2-$); 5.13 (br s, 1H, Ha); 5.30 (br s, 1H, Hb); 7.09-7.47 (m, 9H, arom). M^+ 385.

5-Isopropenyl-3-(4-methylphenyl)-6-morpholino-2-phenyl-4(3 *H*)-pyrimidinone (4f): 91%; mp 198-199.5°C. (Anal. Calcd for $C_{24}H_{25}N_3O_2$: C, 74.39; H, 6.50; N, 10.84. Found: C, 74.31 H, 6.47; N, 10.71). ν_{max} : 1651 cm^{-1} (C=O). δ_H (90 MHz): 2.09 (s, 3H, $-CH_3$); 2.30 (s, 3H, $-CH_3$); 3.50-3.87 (br s, 8H, morpholine); 5.10 (br s, 1H, Ha); 5.30 (br s, 1H, Hb); 6.93-7.47 (m, 9H, arom). M^+ 387.

6-Dimethylamino-2,3-diphenyl-5-vinyl-4(3 *H*)-Pyrimidinone (4g): 90%; mp 156-157 °C. (Anal. Calcd for $C_{20}H_{19}N_3O$: C, 75.69; H, 6.03; N, 13.24. Found: C, 75.51; H, 6.02; N, 13.18). ν_{max} : 1658 cm^{-1} (C=O). δ_H (90 MHz): 3.17 (s, 6H, $-N(CH_3)_2$); 5.40 (dd, J 11.4 and 2.5, 1H, Ha); 6.00 (dd, J 17.5 and 2.5, 1H, Hb); 6.67 (dd, J 17.5 and 11.4, 1H, H); 7.13-7.47 (m, 10H, arom). M^+ 317.

2,3-Diphenyl-6-pyrrolidino-5-vinyl-4(3 *H*)-pyrimidinone (4h): 95%; mp 199-200 °C. (Anal. Calcd for $C_{22}H_{21}N_3O$: C, 76.94; H, 6.16; N, 12.24. Found: C, 76.77; H, 6.14; N, 12.24). ν_{max} : 1653 cm^{-1} (C=O). δ_H (90 MHz): 1.83-2.01 (m, 4H, $-CH_2-CH_2-$); 3.53-3.80 (m, 4H, $-CH_2-N-CH_2-$); 5.40 (dd, J 11.4 and 2.3, 1H, Ha); 5.73 (dd, J 17.5 and 2.3; 1H, Hb); 6.77 (dd, J 11.4 and 17.5, 1H, H); 7.12-7.49 (m, 10H, arom). M^+ 343.

2,3-Diphenyl-6-piperidino-5-vinyl-4(3 *H*)-pyrimidinone (4i): 88%; mp 163-164 °C. (Anal. Calcd for $C_{23}H_{23}N_3O$: C, 77.28; H, 6.49; N, 11.75. Found: C, 77.23; H, 6.47; N, 11.69). ν_{max} : 1650 cm^{-1} (C=O). δ_H (300 MHz): 1.75 (br s, 6H, $-CH_2-CH_2-CH_2-$); 3.55 (br s, 4H, $-CH_2-N-CH_2-$); 5.33 (dd, J 11.5 and 2.8, 1H, Ha); 6.21 (dd, J 17.6 and 2.8, 1H, Hb); 6.41 (dd, J 11.5 and 17.6, 1H, H); 7.10-7.23 (m, 10H, arom). δ_C (75.46 MHz): 24.65 ($-CH_2-$); 26.27 (2 $-CH_2-$); 49.99 ($-CH_2-N-CH_2-$); 98.62 (C-5); 115.41 ($=CH_2$); 127.57, 127.90, 128.55, 129.10, 129.17, 129.22, 129.58, 135.15, 137.83 (aromatic); 129.17 (-C=); 154.39 (C-6); 161.05 (C-2); 162.41 (C-4). M^+ 357.

2,3-Diphenyl-6-morpholino-5-vinyl-4(3 *H*)-pyrimidinone (4j): 90%; mp 180-182 °C. (Anal. Calcd for $C_{22}H_{21}N_3O_2$: C, 73.52; H, 5.89; N, 11.69. Found: C, 73.42; H, 5.87; N, 11.63). ν_{max} : 1651 cm^{-1} (C=O). δ_H (90 MHz): 3.53-3.90 (m, 8H, morpholine); 5.43 (dd, J 11.3 and 2.6, 1H, Ha); 6.23 (dd, J 17.6 and 2.6, 1H, Hb); 6.53 (dd, J 17.6 and 11.3, 1H, H) 7.13-7.47 (m, 10H, arom). M^+ 359.

3-(4-methylphenyl)-2-phenyl-6-piperidino-5-vinyl-4(3 *H*)-pyrimidinone (4k): 93%; mp 177-178 °C. (Anal. Calcd for $C_{24}H_{25}N_3O$: C, 77.60; H, 6.78; N, 11.31. Found: C, 77.49; H, 6.78; N, 11.23). ν_{max}: 1641 cm^{-1} (C=O). δ_H (90 MHz): 1.60-1.77 (br s, 6H, $-CH_2-CH_2-CH_2-$); 2.33 (s, 3H, $-CH_3$); 3.50-3.67 (br s, 4H, $-CH_2-N-CH_2-$); 5.38 (dd, J 11.6 and 2.5, 1H, Ha); 6.23 (dd, J 17.7 and 2.5, 1H, Hb); 6.60 (dd, J 17.7 and 11.6, 1H, H); 7.10-7.47 (m, 9H, arom). M^+ 371

3-(4-methylphenyl)-6-morpholino-2-phenyl-5-vinyl-4(3 *H*)-pyrimidinone (4l): 89%; mp 200-202 °C. (Anal. Calcd for $C_{23}H_{23}N_3O_2$: C, 73.97; H, 6.20; N, 11.25. Found: C, 73.88; H, 6.18; N, 11.23). ν_{max}: 1653 cm^{-1} (C=O). δ_H (300 MHz): 2.30 (s, 3H, $-CH_3$); 3.56-3.59 (br s, 4H, $-CH_2-N-CH_2-$); 3.76-3.79 (br s, 4H, $-CH_2-O-CH_2-$); 5.37 (dd, J 11.6 and 2.4, 1H, Ha); 6.21 (dd, J 17.5 and 2.4, 1H, Hb); 6.42 (dd, J 17.5 and 11.6, 1H, H); 6.99-7.27 (m, 9H, arom). δ_C (75.46 MHz): 21.08 (CH_3); 49.29 ($-CH_2-N-CH_2-$); 66.90 ($-CH_2-O-CH_2-$); 99.99 (C-5); 116.76 ($=CH_2$); 127.61, 128.66, 128.96, 129.12, 129.32, 134.95, 135.04; 137.84 (aromatic); 129.12 (-C=); 154.98 (C-6); 160.45 (C-2); 162.38 (C=O). M^+ 373.

2,3-Diphenyl-5-isopropenyl-4(3 *H*)-pyrimidinone (7a): 75%; mp 142-143 °C. (Anal. Calcd for $C_{19}H_{16}N_2O$: C, 79.14; H, 5.59; N, 9.72. Found: C, 79.04; H, 5.57; N, 9.69). ν_{max} : 1668 cm^{-1} (C=O). δ_H (90 MHz): 2.21 (s, 3H, $-CH_3$); 5.35 (br s, 1H, Ha); 6.05 (br s, 1H, Hb); 7.19-7.55 (m, 10H, arom); 8.21 (s, 1H, olefinic). M^+ 288.

2,3-Diphenyl-5-vinyl-4(3*H*)-pyrimidinone (7b): 78%; mp 137-139 °C. (Anal. Calcd for $C_{18}H_{14}N_2O$: C, 78.81; H, 5.14; N, 10.22. Found: C, 78.69; H, 5.14; N, 10.17). ν_{max} : 1661 cm^{-1} (C=O). δ_H (300 MHz) 5.45 (dd, J 11.4 and 1.7, 1H, Ha); 6.35 (dd, J 17.6 and 1.7, 1H, Hb); 6.66 (dd, J 17.6 and 11.4, 1H, H); 7.09-7.31 (m, 10H, arom); 8.10 (s, 1H, olefinic). M^+ 274.

5-Isopropenyl-2-methylthio-3-phenyl-4(3 *H*)-pyrimidinone (7c): 79%; mp 89-91 °C. (Anal. Calcd for

$C_{14}H_{14}N_2OS$: C, 65.09; H, 5.46; N, 10.84. Found: C, 64.98; H, 5.45; N, 10.83). ν_{max} : 1673 cm^{-1} (C=O). δ_H (*90 MHz*): 2.13 (s, 3H, $-CH_3$); 2.45 (s, 3H, $-SCH_3$); 5.29 (br s, 1H, Ha); 5.95 (br s, 1H, Hb); 7.30-7.50 (m, 2H, arom); 7.57-7.77 (m, 3H, arom); 8.05 (s, 1H, olefinic). M^+ 258.

Reactions of 3-Aryl-5-isopropenyl/vinyl-2-phenyl-6-dialkyl amino-4(3*H*)-pyrimidinone (4) with Phosphorus Pentasulfide:

General Procedure : Phosphorus pentasulfide (2.0 g, 4.5 mmol) and sodium carbonate (0.47 g, 4.5 mmol) are added to dry THF (30 ml) under dry conditions. The mixture is stirred vigorously for 15-25 min till the contents dissolve and then the pyrimidinone (**4**) (4 mmol) is added. After about 10 min, a 10% aqueous solution of disodium hydrogen phosphate (25 ml), ethyl acetate (20 ml) and hexane (20 ml) are respectively added. The aqueous layer is extracted with ethyl acetate (1x10 ml) and the organic layer is dried with magnesium sulfate. The removal of solvent under reduced pressure yielded the crude product, which was recrystallised form chloroform-hexane mixture.

2,3-Diphenyl-6-piperidino-4(3 *H*)-pyrimidinone (8a): 91%; mp 184-185 °C. (Anal. Calcd for $C_{21}H_{21}N_3O$: C, 76.11; H, 6.38; N, 12.68. Found: C, 75.97; H, 6.35; N,12.60). ν_{max} : 1654 cm^{-1} (C=O). δ_H (300 MHz): 1.66 (br s, 6H, $-CH_2-CH_2-CH_2-$); 3.61 (br s, 4H, $-CH_2-N-CH_2-$); 5.49 (s, 1H, olefinic); 7.08-7.25 (m, 10H, arom). δ_C (75.46 MHz): 24.56 ($-CH_2-$); 25.41 (2 $-CH_2-$); 45.45 ($-CH_2-N-CH_2-$); 84.02 (C-5); 127.49, 127.77, 128.46, 128.96, 129.06, 129.12, 135.47, 137.63 (aromatic); 157.66 (C-6); 160.17 (C-2); 163.25 (C-4). M^+ 331.

2,3-Diphenyl-6-morpholino-4(3 *H*)-pyrimidinone (8b): 94%; mp 189-191 °C (Anal. Calcd for $C_{20}H_{19}N_3O_2$: C, 72.05; H, 5.74; N, 12.60. Found: C, 72.00; H, 5.74; N, 12.56). ν_{max}: 1657 cm^{-1} (C=O). δ_H (90 MHz): 3.43-3.83 (m, 8H, morpholine); 5.49 (s, 1H, olefinic); 7.00-7.38 (m, 10H, arom). M^+ 333.

3-(4-Methylphenyl)-6-morpholino-2-phenyl-4(3 *H*)-pyrimidinone (8c): 93%; 212-214 °C (Anal. Calcd for $C_{21}H_{21}N_3O_2$: C, 72.60; H, 6.09; N, 12.09. Found: C, 72.47; H, 6.07; N; 11.99). ν_{max}: 1673 cm^{-1} (C=O). δ_H (90 MHz); 2.30 (s, 3H, $-CH_3$); 3.57-4.03 (m, 8H, morpholine); 5.57 (s, 1H, olefinic); 6.97-7.52 (m, 9H, arom). M^+ 347.

Reactions of 3-Aryl-5-isopropenyl/vinyl-2-phenyl-6-dialkyl amino-4(3*H*)-pyrimidinones (4) with α-Nitrososstyrene (11):

General Procedure : A solution of 3-aryl-5-isopropenyl/vinyl-2-phenyl-6-dialkyl amino-4(3 *H*)-pyrimidinone (**4**) (4 mmol) and α-chlorooxime (4.2 mmol) in dry methylene chloride (40 ml) was stired at room temperature in the presence of anhydrous sodium carbonate (0.64 g, 6 mmol) for 24-26 h. The separated salt and excess of sodium carbonate were removed by filtration and the residue was extracted with small portions (2 x 10 ml) of methylene chloride. The combined filtrate was washed with water (3 x 50 ml) dried over anhydrous sodium sulfate and freed from solvent under reduced pressure. The crude mixture was then chromatographed over silica gel. Elution with ethyl acetate: hexane (1:10) resulted in the isolation of unreacted starting pyrimidinones. Further elution with ethyl acetate : hexane (1.5:10) in case of 5-vinyl substituted and 2.5:10 in case of 5-isopropenyl substituted pyrimidinones resulted in the isolation of oxazine (**15**) and nitrone (**14**) derivatives, respectively.

3,4-Dihydro-5-methyl-2-(4-methylphenyl)-5-[2′,3′-diphenyl-6′-piperidino-4′(3′*H*)-pyrimidinonyl]-5*H*-pyrrole-1-oxide (14a): 21%; mp 210-212 °C. (Anal. Calcd for $C_{33}H_{34}N_4O_2$: C, 76.42; H, 6.60; N, 10.80. Found: C, 76.33; H, 6.54; N, 10.76). ν_{max}: 1662 (C=O), 1556, 1208 (N^+-O^-) and 1120 cm^{-1}. δ_H (300 MHz): 1.66 (br s, 6H, $-CH_2-CH_2-CH_2-$); 2.00 (s, 3H, $-CH_3$); 2.19-2.25 (m, 1H, 3-H); 2.36 (s, 3H, $-CH_3$); 2.71-2.81 (m, 1H, 3-H); 3.03-3.33 (m, 2H, 4-H); 3.40 (br s, 4H, $-CH_2-N-CH_2-$); 7.14-7.32 (m, 12H, arom); 8.22-8.25 (d, J 8.3, 2H, arom). M^+ 518.

3,4-Dihydro-5-methyl-2-(4-methylphenyl)-5-[2′,3′-diphenyl-6′-morpholino-4′(3′*H*)-pyrimidinonyl]-5*H*-pyrrole-1-oxide (14b): 23%; mp 205-207 °C. (Anal. Calcd for $C_{32}H_{32}N_4O_3$: C, 73.82; H, 6.19; N, 10.76. Found: C, 73.77; H, 6.17; N, 10.68). ν_{max}: 1654 (C=O), 1558, 1204 (N^+-O^-) and 1110 cm^{-1}. δ_H (300 MHz): 2.06 (s, 3H, $-CH_3$); 2.17-2.26 (m, 1H, 3-H); 2.35 (s, 3H, $-CH_3$); 2.71-2.79 (m, 1H, 3-H); 3.16-3.29 (m, 2H, 4-H); 3.54 (br s, 4H, $-CH_2-N-CH_2-$); 3.81 (br s, 4H, $-CH_2-O-CH_2-$); 7.14-7.35 (m, 12H, arom); 8.21-8.24 (d, J 8.3, 2H, arom). δ_C (75.46 MHz): 21.54 ($-CH_3$); 25.91 ($-CH_3$); 28.38 (C-3); 31.33 (C-4); 51.96 ($-CH_2-N-CH_2-$); 66.85 ($-CH_2-O-CH_2$); 80.43 (C-5); 108.15 (C-5′); 127.37, 127.70, 128.17,

128.25, 128.79, 129.31, 129.67, 134.42, 137.45, 138.05, 139.76 (aromatic); 154.95 (C-2′ and C-6′); 163.30 (C-2); 163.51 (C-4′). M^+ 520.

5,6-Dihydro-3-(4-methylphenyl)-6-[2′,3′-diphenyl-6′-piperidino-4′(3′*H*)-pyrimidinonyl]-4*H*-1,2-oxazine (15a): 30%; mp 209-211 °C (Anal. Calcd for $C_{32}H_{32}N_4O_2$: C, 76.16; H, 6.39; N, 11.10. Found: C, 76.08; H, 6.37; N, 11.07). ν_{max}: 1648 (C=O), 1510, 1407, 1006 and 892 cm^{-1}. δ_H (300 MHz): 1.67 (br s, 6H, $-CH_2-CH_2-CH_2-$); 1.98-2.05 (m, 1H, 4-H); 2.36 (s, 3H, $-CH_3$); 2.69-2.82 (m, 2H, 5-H); 3.33-3.41 (m, 1H, 4-H); 3.56-3.70 (m, 4H, $-CH_2-N-CH_2-$); 4.65-4.71 (m, 1H, 6-H); 7.14-7.30 (m, 12H, arom); 7.59-7.62 (d, J 8.3, 2H, arom). δ_C (75.46 MHz): 21.24 ($-CH_3$); 21.69 (C-4); 23.49 (C-5); 24.61 ($-CH_2-$); 26.40 (2 $-CH_2-$); 50.68 ($-CH_2-N-CH_2-$); 74.31 (C-6); 97.98 (C-5′) 125.35, 127.69, 127.95, 128.51, 128.97, 129.23, 129.47, 133.55, 135.14, 137.63, 139.03 (aromatic); 154.98 (C-6′); 156.06 (C-2′); 163.38 (C-3); 163.75 (C-4′). M^+ 504.

5,6-Dihydro-3-(4-methylphenyl)-6-[3′-(4′-methylphenyl)-2′-phenyl-6′-piperidino-4′(3′*H*)-pyrimidinonyl]-4*H*-1,2-oxazine (15b): 32%; mp 208-210 °C (Anal. Calcd for $C_{33}H_{34}N_4O_2$: C, 76.42; H, 6.60; N, 10.80. Found: C, 76.33; H, 6.59; N, 10.76). ν_{max}: 1654 (C=O), 1514, 1418, 1015 and 893 cm^{-1}. δ_H (300 MHz): 1.67 (br s, 6H, $-CH_2-CH_2-CH_2-$); 1.97-2.06 (m, 1H, 4-H); 2.28 (s, 3H, $-CH_3$); 2.36 (s, 3H, $-CH_3$); 2.69-2.83 (m, 2H, 5-H); 3.34-3.43 (m, 1H, 4-H); 3.55-3.69 (m, 4H, $-CH_2-N-CH_2-$); 4.65-4.71 (d, 1H, 6-H); 6.99-7.32 (m, 11H, arom); 7.59-7.62 (d, J 8.2, 2H, arom). δ_C (75.46 MHz): 21.10 ($-CH_3$); 21.15 ($-CH_3$); 21.67 (C-4); 23.50 (C-5); 24.62 ($-CH_2-$); 26.39 (2 $-CH_2-$); 50.69 ($-CH_2-N-CH_2-$); 74.35 (C-6); 98.12 (C-5′); 125.34, 127.68, 128.88, 128.96, 129.20, 129.24, 129.40, 133.56, 134.91, 135.27, 137.76, 139.01 (aromatic); 155.00 (C-6′); 156.17 (C-2′); 163.14 (C-3); 163.79 (C-4′) M^+ 518.

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