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Synthesis and Regioselective [4+2] Cycloaddition/Nucleophilic Reactions of N-Arylamino-1,3-Diaza-1,3-Butadienes with Ketenes and accompanying Rearrangements

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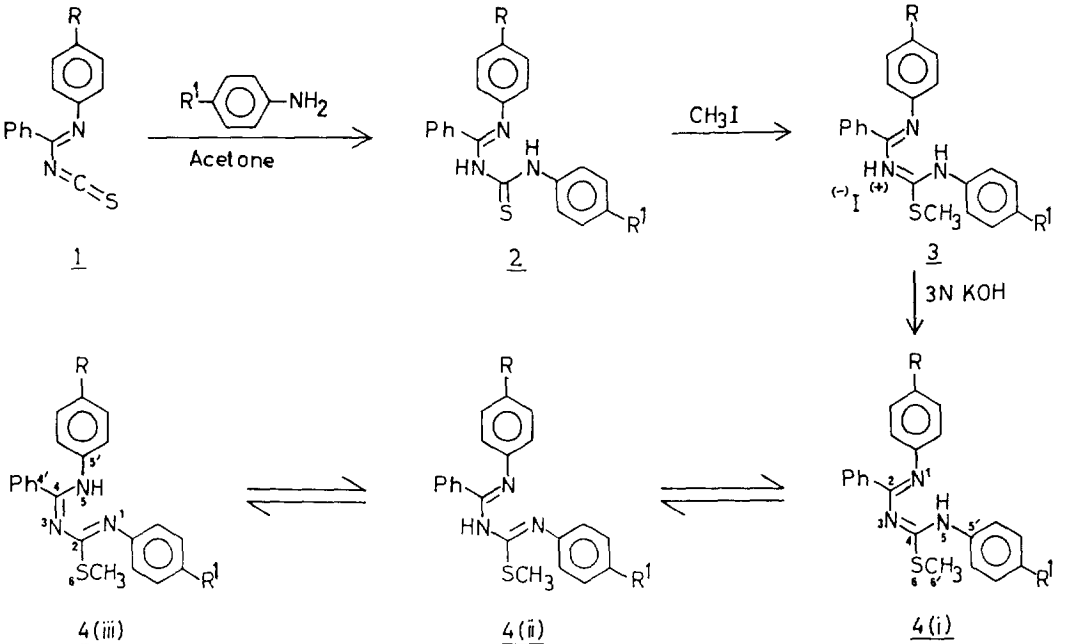
Abstract : *N-Arylamino-1,3-diaza-1,3-butadienes **4** are shown to undergo regioselective reactions with phenyl- and chloroketenes resulting in high yields of 3-aryl-2-methylthio-6-phenyl-4(3H)-pyrimidinones **7**. Similar reactions with bromo- and iodoketenes, resulted, via aziridinium intermediates **12**, in good yields of 3-aryl-5-(N-arylamino)-2-methylthio-6-phenyl-4(3H)-pyrimidinones **13**. The mechanistic aspects of cycloadditions and semi-empirical AM1 calculations for these diazabutadienes are also reported.*

The lack of extensive efforts with acyclic 1,3-diaza-1,3-butadienes were attributed partly to the non-availability of suitable methods for the preparation of such dienes.[1,2] Keeping this in view, we have recently reported simple methods for the preparation of various functionally substituted acyclic 1,3-diaza-1,3-butadienes[3] and utilised these successfully in [4+2] cycloaddition reactions with phenyl-, chloro-, bromo-, iodo-, chloromethyl-, dichloro-, vinyl-, isopropenyl- and various other ketenes.[4-6] In continuation of our pursuits in this direction, various *N*-arylamino-1,3-diaza-1,3-butadienes **4** have been synthesised by the reaction of *N*-arylbenzimidoyl isothiocyanates[7] **1** with primary aromatic amines followed by S-methylation of the resultant thioureas **2** (Scheme-1). It was felt that 1,3-diazabutadienes **4** can possibly exist in a number of tautomeric forms viz. 1-aryl-4-(*N*-arylamino)-4-methylthio-2-phenyl-1,3-diaza-1,3-butadienes form **4i**, *N*-imidoyl thioimidate form **4ii** and 1-aryl-4-(*N*-arylamino)-2-methylthio-4-phenyl-1,3-diaza-1,3-butadiene form **4iii**. In order to investigate the regiochemical aspects and to understand the nature of the reaction pathway followed, we have examined the reactions of such systems with various ketenes. Further, it was felt that the comparison of the dienic properties of tautomeric forms **4i** and **4iii** could be an interesting scientific enquiry, which in case of heterodienes in general and azadienes in particular have not been well attended to.

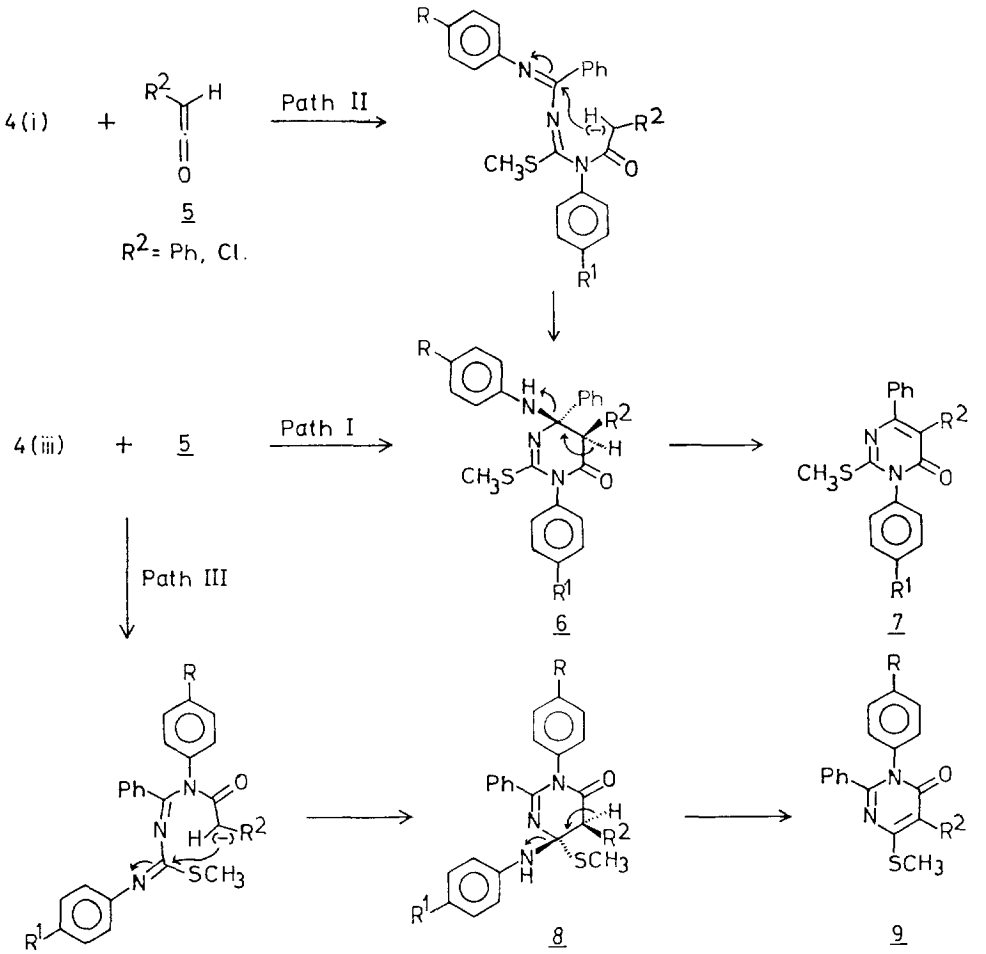
Thus, the reactions of **4** with monosubstituted ketenes **5** viz. phenyl- and chloroketenes, generated *in situ* from phenyl acetyl chloride/chloroacetyl chloride and triethylamine in methylene chloride, resulted



4. a. R = H, R^1 = H.
b. R = H, R^1 = Cl.
c. R = H, R^1 = CH_3.
d. R = H, R^1 = OCH_3
e. R = Cl, R^1 = H
f. R = CH_3, R^1 = H.
g. R = CH_3, R^1 = Cl.
h. R = CH_3, R^1 = OCH_3.

Scheme - 1

in very good yields (75-95%) of products which were characterised as pyrimidinones **7** on the basis of analytical and spectral evidence. In the IR spectra (KBr) of these adducts, strong absorption peak around 1680 cm^{-1} indicated the presence of an α,ß-unsaturated carbonyl group and the absence of any peak around 1730 cm^{-1} clearly ruled out the formation of any ß-lactam. Their ^1H NMR spectra showed the presence of methylthio protons and the loss of the proton signals from one *N*-arylamino function. On the basis of these data the products could be characterised either as 3-aryl-2-methylthio-6-phenyl-4(3 *H*)-pyrimidinones **7** or 3-aryl-6-methylthio-2-phenyl-4(3 *H*)-pyrimidinones **9**. However, the absence of protons due to *N*-arylamino function next to the carbon bearing the phenyl group in the ^1H NMR spectra of all these products indicated a preference for pyrimidinones **7** over pyrimidinones **9**. The compound **7a** for example analysed for $C_{24}H_{20}N_2O_2S$ and its mass spectrum showed in addition to the molecular ion peak at 400 (58.7%), peaks at 353 (30.1%,M^+-SCH_3), 192 (37.1%), 175 (60.0%), 163 (94.5%), 147 (30.2%),



7. a. R^2= Ph, R^1= OCH_3.
b. R^2= Ph, R^1= H.
c. R^2= Cl, R^1= OCH_3
d. R^2= Cl, R^1 = CH_3.
e. R^2= R^1 = Cl.

Scheme - 2

121 (99.3%) and 77 (18.5%). The probable mechanism leading to the formation of pyrimidinones **7** is outlined in Scheme-2. In this scheme, it is assumed that the reaction of 1,3-diazabutadienes **4** with ketenes **5** can follow three different pathways. The pathway I, involving regioselective [4+2] cycloadditions of 1-aryl-4-(*N*-arylamino)-2-methylthio-4-phenyl-1,3-diaza-1,3-butadienes **4iii** with ketenes **5** can yield the intermediate **6** which in the presence of excess of triethylamine undergoes elimination of aromatic amines resulting in pyrimidinones **7**. The pathway II assumes initial nucleophilic attack by

amino nitrogen of 1-aryl-4-(*N*-arylamino)-4-methylthio-2-phenyl-1,3-diazabutadienes **4i** at the ketene carbonyl followed by the cyclisation to give intermediate **6**, which as described above undergoes elimination of aromatic amines to give pyrimidinones **7**. According to pathway III, the nucleophilic attack by the arylamino nitrogen of **4iii** at the ketene carbonyl followed by cyclisation may result in an intermediate **8** which on elimination of aromatic amines yields pyrimidinones **9**, isomeric with pyrimidinones **7**. The formation of pyrimidinones **9** could be ruled out on the basis of earlier described ^{1}H NMR spectra. The formation of pyrimidinones **9** may further be ruled out since it has been reported that the intermediate of the type **8** prefer elimination of methylmercaptan over that of amines.[4b,6]

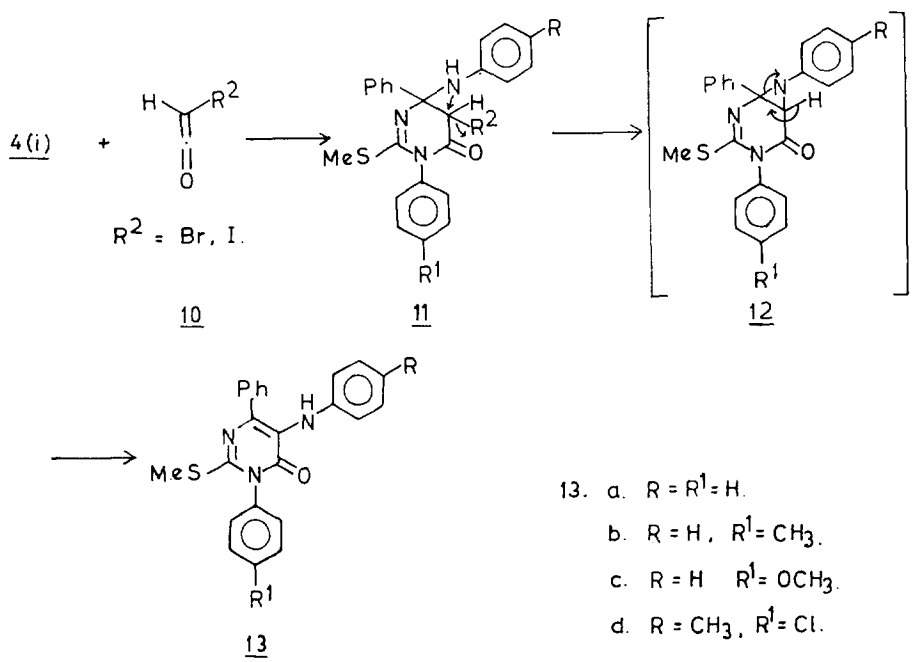
The pathway I and pathway II, assume initial attack by N-1 of structure **4iii** and N-5 of structure **4i**, respectively (Table-1). It was felt that the relative electron densities at these nitrogen atom may help in discriminating one mechanism over the other. Keeping this in view, we have carried out the semi-empirical AM1 calculations[8] for structure **4i** and **4iii**. The calculations were performed by using the MOPAC program package[9] without imposing any geometrical constraints. The results are presented for both structures in table-1 where charge on skeleton atoms are given from which it is evident that the N-atom (no. 5) in structure **4i**, having greater charge density as compared with the N-atom (no. 1) in structure **4iii**, is more nucleophilic.

Table-I

Structure 4i			Structure 4iii		
Atom no.	Chemical symbol	Charge	Atom no.	Chemical symbol	Charge
1	N	-0.3353	1	N	-0.2763
2	C	0.3331	2	C	0.2077
3	N	-0.3595	3	N	-0.3225
4	C	0.1860	4	C	0.2467
5	N	-0.3032	4′	C	-0.0628
5′	C	0.0651	5	N	-0.2466
6	S	-0.0549	5′	C	-0.0479
6′	C	0.0537	6	S	-0.0888

Based on these calculations it may be concluded that for the formation of pyrimidinones **7** in these reactions, the pathway II, involving initial nucleophilic attack of amino nitrogen of **4i** at the ketene carbonyl, may indeed be preferred over pathway I and pathway III. On the basis of above conclusion, it may also be inferred that 1,3-diazabutadienes **4** perhaps exist predominantly in tautomeric form **4i**.

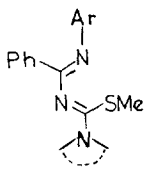
Further to our investigations, we have examined the reactions of 1,3-diazabutadienes **4** with bromo- and iodoketenes especially because it was felt that the intermediate **11**, because of better leaving group abilities of bromide and iodide, may undergo either elimination of aromatic amines or hydrobromic/ hydroiodic acid. Interestingly, the reactions of 1,3-diazabutadienes **4** with bromo- and iodoketenes, generated *in situ* from bromoacetyl bromide/triethylamine and iodoacetic acid/p-toluenesulfonyl chloride/triethylamine respectively, resulted in good yields of novel rearranged pyrimidinones **13**, which were characterised on the basis of analytical results and spectral data. The compound **13a**, for example, analysed for $C_{23}H_{19}N_3OS$ and its mass spectrum, in addition to the molecular ion peak at 385 (100%) showed peaks at 352 (22.9%), 294 (4.5%), 276 (5.4%), 207 (10.2%), 193 (10.7%), 150 (18%), 136 (15.2%), 104 (33.4%) and 77 (44.1%). Its ^1H NMR spectrum exhibited signals both for N-aryl and methylthio protons. The probable mechanism leading to the formation of rearranged pyrimidinones **13** is outlined in scheme-3. In this scheme it is assumed that the initial nucleophilic attack by the preferred



Scheme -3

tautomeric form **4i** at the ketene carbonyl followed by cyclisation leads to an intermediate **11**, which transforms into aziridinium intermediate **12** by the nucleophilic attack of N-aryl nitrogen at the C-5 bearing the bromide/iodide leaving group and finally rearranges to pyrimidinones **13**.

Although, we reported recently the 1,2-alkylthio shifts involving episulfonium intermediates in case of cycloaddition reactions of 1,3-diazabutadienes **14** with haloketenes [5], but the intermediacy of aziridinium ions could not be observed even in the reaction of 1,3-diazabutadienes **15** and **16** with bromo/iodoketenes. To our knowledge this may represent one of the rare examples of 1,2-amino shifts involving aziridinium intermediates in case of heterocyclic compounds.



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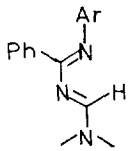

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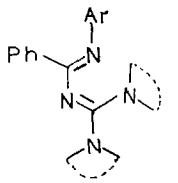

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Experimental

Melting points were determined on a Toshniwal melting point apparatus and are uncorrected. ^1H NMR spectra were recorded on a Varian EM 390 MHz spectrophotometer in $CDCl_3$ and the chemical shift values are expressed in δ ppm downfield from TMS as internal standard. IR spectra were recorded on Perkin-Elmer 983 spectrophotometer.

Preparation of 1-aryl-4-(N-arylamino)-4-methylthio-2-phenyl-1,3-diaza-1,3-butadienes 4i:
General procedure:

To a stirred solution of *N*-arylbenzimidoyl isothiocyanate **1** (2 mmol) in dry acetone (250 ml) was added dropwise a solution of primary amine (1 mmol) in dry acetone (30 ml) and stirring continued for 1 hr. To this solution, methyl iodide (1.2 mmol) was added dropwise and stirred for a further period of 3-4 hrs. The separated hydroiodide salt of **3** was filtered, basified with 3N aq. KOH (50ml) and extracted with chloroform (3x100 ml). The combined extract was washed with water (3x50 ml) and dried over anhydrous sodium sulfate. The removal of chloroform under reduced pressure afforded the products **4** which were recrystallised from a mixture (1:1) of benzene and hexane.

1,2-Diphenyl-4-methylthio-4-(N-phenylamino)-1,3-diaza-1,3-butadiene (4a): 90%, m.p. 142-144 °C. (Found: C, 73.01; H, 5.65; N,12.05. $C_{21}H_{19}N_3S$ requires C,73.04; H, 5.51; N, 12.17). ν_{max}: 1600 cm^{-1} (C=N). δ_H: 2.51 (s, 3H, $-SCH_3$); 7.08-7.80(m, 15H, arom) and 8.90-9.68(bs, 1H, -NH). M^+ 345.

1,2-Diphenyl-4-methylthio-4-{N-(p-chlorophenylamino)}-1,3-diaza-1,3-butadiene(4b): 92%, m.p. 140-142°C.(Found: C, 66.32; H, 4.77; N, 11.16. $C_{21}H_{18}ClN_3S$ requires C, 66.39; H, 4.76; N, 11.06). ν_{max}: 1592 cm^{-1} (C=N). δ_H: 2.53 (s, 3H, $-SCH_3$); 6.82- 7.71 (m, 14H, arom) and 8.88-9.80(bs, 1H, -NH). M^+ 379.

1,2-Diphenyl-4-methylthio-4-{N-(p-methylphenylamino)}-1,3-diaza-1,3-butadiene(4c): 90%, m.p. 135-137°C.(Found: C, 73.60; H, 5.80; N,11.70.$C_{22}H_{21}N_3S$ requires C, 73.50; H,5.89; N, 11.69). ν_{max}:1585 cm^{-1} (C=N). δ_H: 2.31 (s, 3H, $-CH_3$); 2.51 (s, 3H, $-SCH_3$); 6.80-7.48(m, 12H, arom); 7.54-7.70(m, 2H, arom) and 8.87-9.83(bs, 1H, -NH). M^+ 359.

1,2-Diphenyl-4-methylthio-4-{N-(p-methoxyphenylamino)}-1,3-diaza-1,3-butadiene (4d): 96%, m.p. 104-106 °C.(Found: C, 70.47; H, 5.55; N, 11.23. $C_{22}H_{21}N_3OS$ requires C, 70.37; H,5.64; N, 11.19). ν_{max}: 1600 cm^{-1} (C=N). δ_H: 2.51 (s, 3H, $-SCH_3$); 3.80 (s, 3H, - OCH_3); 6.80-7.46(m, 12H, arom); 7.51-7.74(m, 2H, arom) and 8.70-9.79(bs, 1H, -NH). M^+ 375.

1-(p-Chlorophenyl)-4-methylthio-4-(N-phenylamino)-2-phenyl-1,3-diaza-1,3-butadiene (4e): 90%, m.p. 138-140 °C.(Found: C, 66.35; H, 4.75; N, 11.16. $C_{21}H_{18}ClN_3S$ requires C, 66.39; H, 4.76; N, 11.06). ν_{max}: 1593 cm^{-1} (C=N). δ_H: 2.54 (s, 3H, $-SCH_3$); 6.82- 7.72 (m, 14H, arom) and 8.86-9.80(bs, 1H, -NH). M^+ 379.

1-(p-Methylphenyl)-4-methylthio-4-(N-phenylamino)-2-phenyl-1,3-diaza-1,3-butadiene (4f): 94%, m.p. 122-124 °C.(Found: C,73.50; H5.80; N,11.70.$C_{22}H_{23}N_3S$ requires C, 73.61; H,5.89; N,11.69). ν_{max}: 1585 cm^{-1} (C=N). δ_H: 2.31 (s, 3H, $-CH_3$); 2.53 (s, 3H, - SCH_3); 6.80-7.81(m, 15H, arom) and 8.90-9.82(bs, 1H, -NH). M^+ 359.

1-(p-Methylphenyl)-4-methylthio-4-{N-(p-chlorophenylamino)}-2-phenyl-1,3-diaza-1,3-butadiene (4g): 90%, m.p. 127-129 °C. (Found: C, 67.00; H,5.22; N, 10.62. $C_{22}H_{20}ClN_3S$ requires C, 67.08; H, 5.12; N,10.67). ν_{max}: 1599 cm^{-1} (C=N). δ_H: 2.30 (s, 3H, $-CH_3$); 2.53 (s, 3H, $-SCH_3$); 6.80-7.51(m, 13H, arom) and 8.89-9.97(bs, 1H, -NH). M^+ 393.

1-(p-Methylphenyl)-4-methylthio-4-{N-(p-methoxyphenylamino)}-2-phenyl-1,3-diaza-1,3-butadiene (4h): 91%, m.p. 133-135 °C.(Found: C, 70.82; H, 5.90; N, 10.82. $C_{23}H_{23}N_3OS$ requires C, 70.92; H, 5.95; N, 10.79). ν_{max}: 1590 cm^{-1} (C=N). δ_H: 2.30 (s, 3H, $-CH_3$); 2.51 (s, 3H, $-SCH_3$); 3.70 (s, 3H, $-OCH_3$);

6.80-7.12(m, 9H, arom); 7.28-7.54(m, 2H, arom); 7.60-7.90(m, 2H, arom) and 8.74-9.80(bs, 1H, -NH). M^+ 389.

Reactions of 1,3-Diaza-1,3-Butadienes with ketenes:

Method A: To a well stirred solution of 1,3-diaza-1,3-butadiene (4 mmol) and triethylamine (10 mmol) in dry chloroform (30 ml), was added gradually a solution of acid halide (6 mmol) in dry chloroform (30 ml) over a period of 1hr. at room temperature. After completion of the reaction (TLC), it was further diluted with chloroform and washed with water (5x50 ml), sodium hydrogen carbonate (2x30 ml), water (2x50 ml) and finally dried over anhydrous sodium sulfate. Removal of solvent under reduced pressure yielded the crude product, which was purified by silica gel column chromatography.

Method B: A solution of iodoacetic acid (6 mmol) and triethylamine (10 mmol) in dry chloroform (30 ml) was stirred for 10-15 mins. To this solution 1,3-diaza-1,3-butadiene (4 mmol) was added and stirring was continued. A solution of p-toluenesulfonyl chloride (6 mmol) in chloroform (30 ml) was added dropwise over a period of 1 hr. After the addition was over the reaction mixture was further stirred for 4-5 hrs. On completion of the reaction (TLC) it was successively washed with 5% sodium hydroxide solution (2x30 ml) and water (2x50 ml). The solution was dried over anhydrous sodium sulfate. The crude product obtained after removal of solvent under reduced pressure was purified by passing it through silica gel column.

5,6-Diphenyl-3-(p-methoxyphenyl)-2-methylthio-4(3H)-pyrimidinone (7a): 84%, m.p. 230-232 °C. (Found: C, 71.90; H, 5.06; N, 6.91. $C_{24}H_{20}N_2O_2S$ requires C,71.98; H, 5.03; N, 6.99). ν_{max}: 1680 cm^{-1} (C=O). δ_H: 2.54 (s, 3H, $-SCH_3$); 3.89 (s, 3H, $-OCH_3$) and 6.90-7.63 (m, 14H, arom). M^+ 400.

2-Methylthio-3,5,6-triphenyl-4(3H)-pyrimidinone (7b): 80%, m.p. 214-216 °C. (Found: C, 74.48; H, 4.93; N, 7.52. $C_{23}H_{18}N_2OS$ requires C, 74.47; H,4.90, N,7.56). ν_{max}: 1670 cm^{-1} (C=O). δ_H: 2.53 (s, 3H, $-SCH_3$) and 6.52-7.68 (m, 15H, arom). M^+ 370.

5-Chloro-3-(p-methoxyphenyl)-2-methylthio-6-phenyl-4(3H)-pyrimidinone (7c): 72%, m.p. 210-212 °C. (Found: C, 60.15; H, 4.30; N, 7.76. $C_{18}H_{15}ClN_2O_2S$ requires C, 60.25; H, 4.21; N, 7.81). ν_{max}: 1667 cm^{-1} (C=O). δ_H: 2.47 (s, 3H, $-SCH_3$); 3.88 (s, 3H, $-OCH_3$); 6.90-7.63 (m, 7H, arom) and 7.83-8.10 (m, 2H, arom). M^+ 358.

5-Chloro-3-(p-methylphenyl)-2-methylthio-6-phenyl-4(3H)-pyrimidinone (7d): 71%, m.p. 171-173 °C. (Found: C, 63.09; H, 4.41; N, 8.27. $C_{18}H_{15}ClN_2OS$ requires C, 63.06; H, 4.41; N, 8.17). ν_{max}: 1664 cm^{-1}

(C=O). δ_H: 2.45 (s, 3H, $-CH_3$); 2.55 (s, 3H, $-SCH_3$); 7.20-7.73 (m, 7H, arom) and 7.81-8.20 (m, 2H, arom). M^+ 342.

5-Chloro-3-(p-chlorophenyl)-2-methylthio-6-phenyl-4(3H)-pyrimidinone (7e): 72%, m.p. 222-224 °C. (Found: C, 60.15; H,4.30; N,7.80. $C_{18}H_{15}ClN_2O_2S$ requires C, 60.25; H, 4.21; N, 7.81). ν_{max}: 1640 cm^{-1} (C=O). δ_H: 2.49 (s, 3H, $-SCH_3$); 7.28-7.79 (m, 7H, arom) and 7.82-8.20 (m, 2H, arom). M^+ 363.

3,6-Diphenyl-2-methylthio-5-(N-phenylamino)-4(3H)-pyrimidinone(13a): 87%, m.p.209-211 °C.(Found: C, 71.60; H, 4.92; N, 10.90. $C_{23}H_{19}N_3OS$ requires C, 71.66; H, 4.97; N, 10.90). ν_{max}: 1675 cm^{-1} (C=O); 3300 cm^{-1} (-NH). δ_H: 2.53 (s, 3H, $-SCH_3$); 6.50- 6.79 (m, 3H, arom); 7.22-7.68(m, 10H, arom); 7.82-8.10 (m, 2H, arom) and 9.50-9.80 (bs, 1H, -NH). M^+ 385.

3-(p-Methylphenyl)-2-methylthio-5-(N-phenylamino)-6-phenyl-4(3H)-pyrimidinone (13b): 88%, m.p. 202-204 °C.(Found: C, 72.15; H, 5.30; N, 10.52. $C_{24}H_{12}N_3OS$ requires C, 72.25; H, 5.34; N, 10.59). ν_{max}: 1670 cm^{-1} (C=O) and 3300 cm^{-1} (-NH). δ_H: 2.33 (s, 3H, $-CH_3$); 2.50 (s, 3H, $-SCH_3$); 6.29-6.73 (m, 5H, arom); 6.80-7.30 (m, 19H, arom); 7.69-8.10 (m, 2H, arom) and 9.52-9.79 (bs, 1H, -NH). M^+ 399.

3-(p-Methoxyphenyl)-2-methylthio-5-(N-phenylamino)-6-phenyl- 4(3H)-pyrimidinone (13c): 82%, m.p. 189-191 °C.(Found: C, 69.35; H, 5.03; N, 10.11. $C_{24}H_{21}N_3O_2S$ requires C,69.37; H, 5.09; N, 10.05). ν_{max}: 1670 cm^{-1} (C=O). δ_H: 2.53 (s, 3H, $-SCH_3$); 3.90 (s, 3H, $-OCH_3$); 6.48-7.43(m, 12H, arom); 7.86-8.19(m, 2H, arom) and 9.51-9.78 (bs, 1H, -NH). M^+ 415.

3-(p-Chlorophenyl)2-methylthio-5-{N-(p-methylphenylamino)}-6-phenyl-4(3H)-pyrimidinone (13d): 78%, m.p. 200-202 °C. (Found: C, 65.43; H, 4.70; N, 9.99. $C_{23}H_{20}ClN_3OS$ requires C, 65.56; H, 4.75; N, 9.98). ν_{max}: 1680 cm^{-1} (C=O) and 3277 cm^{-1} (-NH). δ_H: 2.12 (s, 3H, $-CH_3$); 2.53 (s, 3H, $-SCH_3$); 6.53 (d, J=9Hz, 2H, arom); 6.87 (d, J=9Hz, arom); 7.22-7.78 (m, 7H, arom); 7.88-8.10 (m, 2H, arom) and 9.50-9.73 (bs, 1H, -NH). M^+ 421.

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