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Reactions of 1,3-Diaza-1,3-Butadienes with Haloketenes - Rearrangements accompanying [4+2] Cycloaddition Reactions.

Sujit N. Mazumdar, Sucharita Mukherjee, Arun K. Sharma, Devashish Sengupta and Mohinder P. Mahajan*

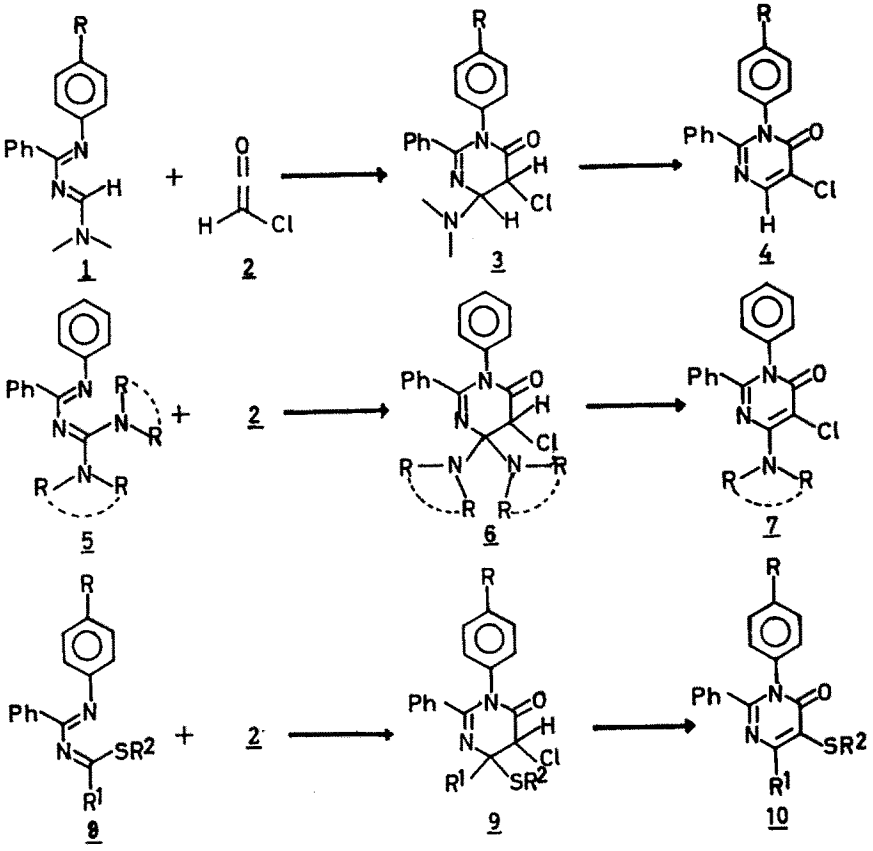
Department of Chemistry, North-Eastern Hill University,
Shillong - 793 003, Meghalaya, India

Abstract: *1-Aryl-2-phenyl-4-thioalkyl-4-secondaryamino-1,3-diaza-1,3-butadienes* **8** *yielded interesting pyrimidones* **10, 22** *and* **7** *with chloroketenes* **2, 11** *and* **12** *through their episulfonium intermediates, whereas 1-aryl-2-phenyl-(methylthio)-4-dimethylamino-1,3-diaza-1,3-butadienes* **1** *give different pyrimidones with different haloketenes (chloro, bromo and iodo).*

Because of their synthetic potential and interesting mechanistic features, the cycloaddition reactions of ketenes continue to be an important area of scientific quest[1]. Ketene chemistry is dominated by [2+2] cycloaddition reactions and such cycloadditions with carbon-nitrogen double bonds of imines, monoaza- and diazabutadienes have been successfully exploited for the synthesis of important ß-lactam derivatives[2,3]. The cycloaddition reactions of heterodienes have gained additional significance because of their utility in natural product synthesis. Although there are numerous reports concerning [4+2] cycloaddition reactions of 1,2- and 1,4-diaza-1,3-butadienes, such reports concerning 2,3- and 1,3-diaza-1,3-butadienes are very rare. Also, there are very few reports concerning the cycloaddition of azadienes with reactive ketenes like haloketenes, either due to their fast polymerisation or the lack of reactivity of azadienes. Keeping these observations in view, we have recently reported the simple methods for the preparation of various reactive acyclic 1,3-diaza-1,3-butadienes[4] which were successfully utilised in [4+2] cycloaddition with phenylketene[5] and sulfene[6]. It was also observed that the reactions of 1,3-diazabutadienes **1** and **5** with chloroketene resulted in pyrimidones **4** and **7** , which were supposedly formed by the elimination of secondary amines from initially formed [4+2] cycloadduct intermediates **3** and **6**, respectively. On further exploring, it was observed that the cycloaddition of 1,3-diaza-1,3-butadienes **8** with chloroketene resulted interestingly in pyrimidones which contained both alkylthio and secondary amino functions. In order to understand the mechanistic aspects and to generalise such cycloaddition reactions, it was thought worthwhile to carry out detailed investigations regarding reactions of various 1,3-diaza-1,3-butadienes with chloro-, bromo-, iodo-, chloromethyl- and dichloroketenes.

Thus, the reactions of 1,3-diaza-1,3-butadienes **8** with monochloroketene, generated *in situ* at 0-5°C from chloroacetyl chloride and excess of triethylamine resulted in excellent yields (73-90%) of

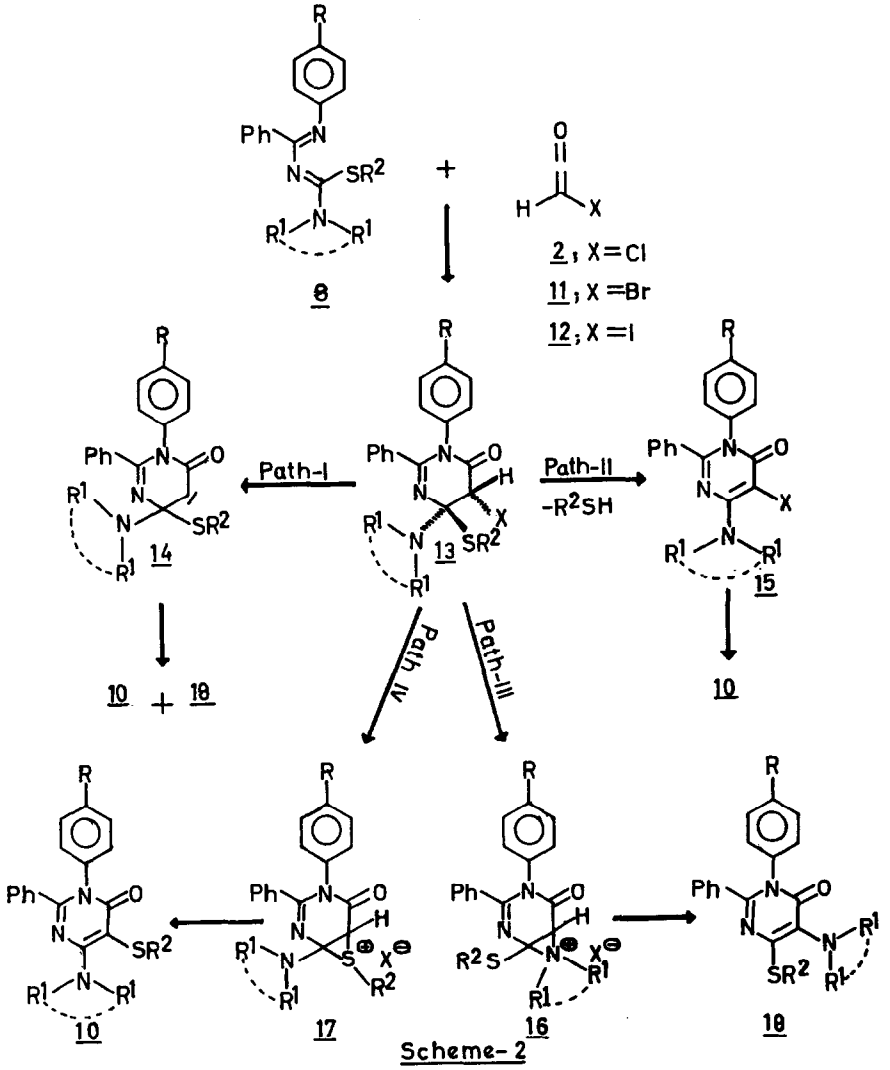
previously unknown 5-alkylthio-3-aryl-6-dialkylamino-2-phenyl-4(3H)-pyrimidones **10**. The products were characterised on the basis of analytical and spectral evidences. Thus, compound **10a**, for example, was analysed for $C_{19}H_{19}N_3OS$ and its mass spectrum showed a molecular ion peak at m/z 337. Its IR spectrum showed an α,β-unsaturated carbonyl peak at 1670 cm^{-1}. The ^1H and ^{13}C NMR spectra showed signals both for dimethylamino and methylthio groups. On the basis of above analytical and spectral data the products could be assigned the structure **10** or **18**. The probable mechanistic pathways leading



8,10 a: R=H, R^1=N(CH3)2, R^2=CH3
b: R=H, R^1=morpholino, R^2=CH3
c: R=H, R^1=piperidino, R^2=CH3
d: R=H, R^1=pyrrolidino, R^2=CH3
e: R=H, R^1=N(CH3)2, R^2=CH2CH3
f: R=H, R^1=morpholino, R^2=CH2CH3
g: R=H, R^1=piperidino, R^2=CH2CH3
h: R=H, R^1=pyrrolidino, R^2=CH2CH3
i: R=CH3, R^1=N(CH3)2, R^2=CH3
j: R=CH3, R^1=morpholino, R^2=CH3
k: R=CH3, R^1=piperidino, R^2=CH3
l: R=CH3, R^1=pyrrolidino, R^2=CH3
m: R=Cl, R^1=N(CH3)2, R^2=CH3
n: R=Cl, R^1=morpholino, R^2=CH3
o: R=Cl, R^1=piperidino, R^2=CH3
p: R=Cl, R^1=pyrrolidino, R^2=CH3

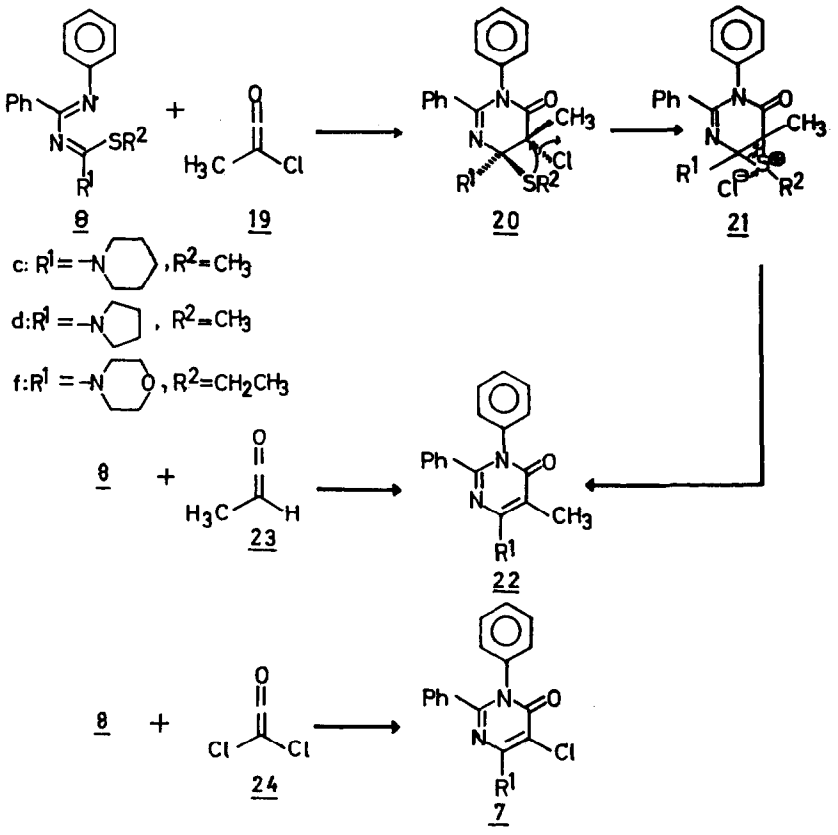
Scheme-1

to the formation of these pyrimidones are outlined in scheme-2. In this scheme it is proposed that 1,3-diaza-1,3-butadienes **8** undergo [4+2] cycloaddition with chloroketene, resulting in an intermediate **13**. This intermediate may then follow four different pathways. The pathway I assumes that the intermediate **13**, in presence of excess of triethylamine, may result in a carbene intermediate **14** leading to the products. This pathway may be ruled out since such an intermediate should have resulted in a mixture of pyrimidones **10** and **18** , containing at least a small proportion of **18** due to lower nucleophilicity of nitrogen as compared to that of sulfur. The formation of carbene intermediate may further be ruled out since no such rearranged pyrimidone was observed in the reactions of 1,3-diazabutadienes **1** and **5** with chloroketene. The pathway II assumes that the intermediate **13** may undergo base assisted elimination of alkylmercaptan yielding pyrimidone **15** which then reacts with the



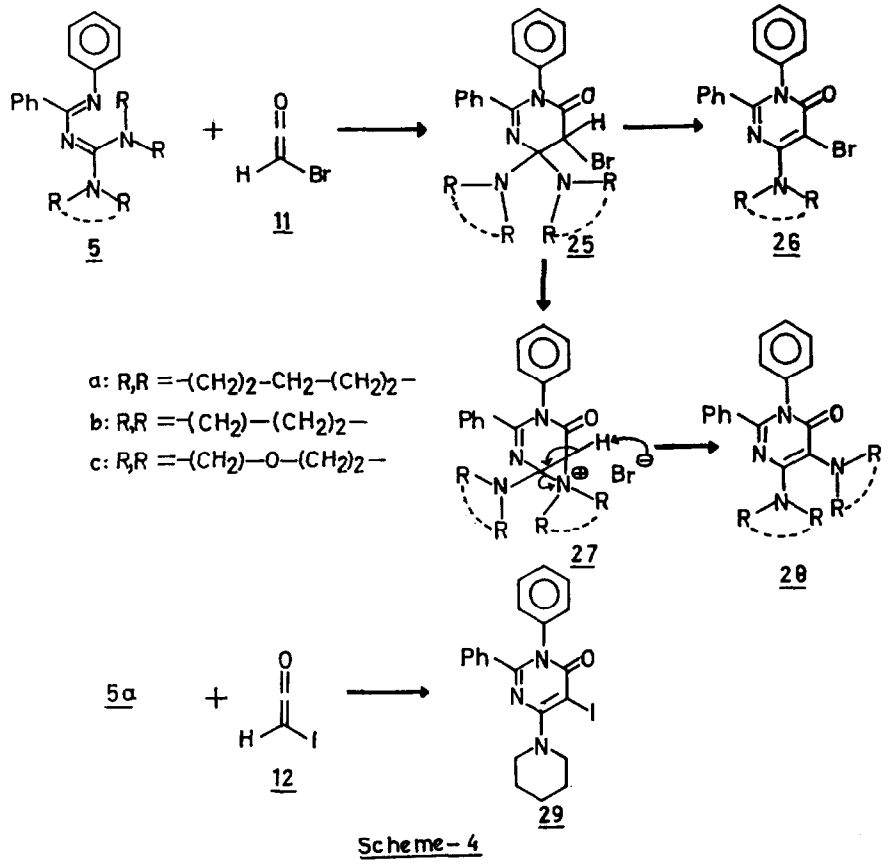
Scheme-2

eliminated alkylmercaptan to give pyrimidone **10**. This mechanism is also ruled out since the reaction of ethylmercaptan with 5-chloropyrimidone **7** obtained by the reaction of 1,3-diazabutadiene **5** with chloroketene, under identical reaction conditions did not result in the displacement of chloride[5] by alkylthio and the starting pyrimidone was recovered unchanged. The pathway III leading to the formation of pyrimidone **18** via aziridinium intermediate **16** could also be ruled out since it involves the attack of lesser nucleophilic nitrogen at C-5 bearing a leaving group. Also no such rearrangements was observed in cycloadditions of chloroketene with 1,3-diazabutadienes **1** and **5** . The most likely pathway IV involves the transformation of intermediate **13** into an episulfonium intermediate **17** by the attack of more nucleophilic sulfur at C-5 bearing the halide. The intermediate **17** then rearranges by the loss of a proton and migration of an alkylthio function to give pyrimidones **10**. The preferential migration of alkylthio group requires a trans rearrangement of chloro and alkylthio groups in the intermediate **20**. This intermediate with the desired stereochemical arrangement of alkylthio and chloro is obtained either through highly stereoselective [4+2] cycloaddition or *via* the equilibration of the intermediate possibly through a zwitterionic intermediate. Similarly the reactions of 1,3-diazabutadienes **8** with monobromo- and iodoketenes, generated *in situ* from bromoacetyl bromide and triethylamine, and iodoacetic acid in presence of p-toluenesulfonyl chloride and triethylamine, respectively, resulted in good yields of identical pyrimidones **10**.



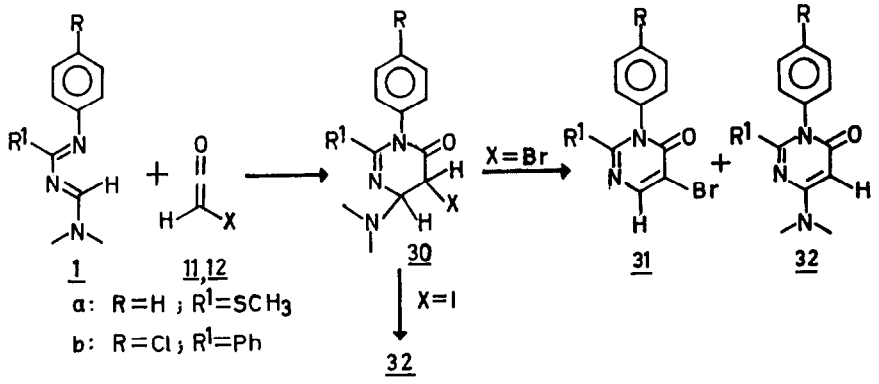
Scheme-3

In scheme-2, it is assumed that the presence of a hydrogen atom at C-5 in intermediate **17** is perhaps essential for the formation of rearranged pyrimidones **10**. In order to investigate this, it was thought worthwhile to undertake the reactions of 1,3-diazabutadienes **8** with substituted chloroketenes viz., chloromethylketene and dichloroketene. Thus, the treatment of 1,3-diazabutadienes **8** with chloromethylketene **19**, generated *in situ* form α-chloropropionic acid in presence of p-toluenesulfonyl chloride and triethylamine, resulted interestingly in another set of rearranged pyrimidones **22**. The ^{1}H NMR spectra of these pyrimidones showed the presence of secondary amino and methyl protons, and the absence of alkylthio protons. Further information for the structure **22c** was derived from the superimposable IR spectra and undepressed mixed melting point with a sample prepared by the reaction of **8c** with methylketene **23**, generated *in situ* from propionic acid in presence of p-toluenesulfonyl chloride and triethylamine. The probable mechanism leading to the formation of pyrimidones **22** is outlined in scheme-3. Here again, it is assumed that the initial [4+2] cycloadduct **20** leads to the formation of episulfonium intermediate **21**, which as depicted then undergoes elimination of alkylsulfenyl chloride to yield pyrimidones **22**. Similarly, the treatment of 1,3-diazabutadienes **8** with dichloroketene, generated from trichloroacetyl chloride and zinc, resulted in the formation of 5-chloro-6-dialkylamino-2,3-diphenyl-4(3H)-pyrimidone **7** arising *via* the loss of methylsulfenyl chloride from an intermediate of type **21**.



Scheme-4

It was thought that the intermediate [4+2] cycloadduct **25**, formed by the reaction of 1,3-diazabutadienes **5** with bromoketene,having a better leaving group bromide at C-5, may result in an aziridinium intermediate **27** leading ultimately to rearranged pyrimidones **28**. However, the intermediate **25** also underwent the usual elimination of secondary amines resulting in pyrimidones **26**. (Scheme-4). Similar reactions of **5** with monoiodoketene led to 2,3-diphenyl-5-iodo-6-piperidino-4(3H)-pyrimidone **29**. It has been reported earlier that intermediate **3** formed in the case of reactions of 1,3-diazabutadienes **1** with chloroketene underwent exclusive elimination of



Scheme-5

dimethylamine, yielding pyrimidones **4**. On the contrary, the intermediate **30** (X = I) underwent exclusive elimination of hydroiodic acid resulting in pyrimidones **32**. In case of bromoketene cycloaddition this intermediate underwent loss, both of dimethylamine and hydrobromic acid resulting in pyrimidones **31** and **32** respectively (scheme-5). This mixture of pyrimidones was separated with the help of silica gel column chromatography, using a mixture (1:10) of ethyl acetate-hexane,as eluent. The pyrimidones **31** (**a**,36%; **b**,32%) and **32** (**a**,42%; **b**,38%) were isolated, and indicates the formation of pyrimidones in almost equal yields.The ^{1}H NMR spectra exhibited vinylic protons at ca. δ 8.00 and δ 5.20 assigned to vinylic protons of the pyrimidones **31** and **32** respectively.

Experimental

Melting points were determined with a Toshniwal melting point apparatus and are uncorrected. IR spectra were recorded on a Perkin-Elmer 297 spectrophotometer, using KBr disc. ^{1}H NMR were recorded in $CDCl_3$, with a Varian 390 90 MHz spectrophotometer using TMS as the internal standard. Mass spectra were obtained by electron impact at 70 eV.

Reactions of 1,3-Diaza-1,3-Butadienes[4] 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 1.5-2 h at room temprature. After completion of the reaction (TLC), it was further diluted with chloroform and washed several times with water (5x50 ml), sodium hydrogen carbonate (2x30 ml), water (2x50 ml) and finally dried over anhydrous magnesium sulphate. Removal of solvent under reduced pressure yielded the crude product, which was purified by silica gel column chromatography.

Method B: A solution of acid (6 mmol) and triethylamine (10 mmol) in dry chloroform (30 ml) was stirred for half an hour. To this solution, 1,3-diaza-1,3-butadiene (4mmol) was added and stirring was continued. A solution of p-toluenesulfonylchloride (6 mmol) in chloroform (30 ml) was added dropwise over a period of 1 h and the reaction mixture was stirred at room temprature for a further period of 3-4 h. On completion of the reaction (TLC), it was diluted with chloroform, washed with water (5x50 ml), 5% sodium hydroxide solution (2x30 ml), brine (2x50 ml) and dried over anhydrous magnesium sulphate. The crude product obtained after removal of solvent under reduced pressure were purified by passing them through silica gel column.

5-Chloro-2,3-diphenyl-6-piperidino-4(3H)-pyrimidone (7c): 81%, m.p. 200-201°C. (Found: C,68.52; H,5.40; N,11.60. $C_{21}H_{20}ClN_3O$ requires C,68.95; H,5.47; N,11.49). ν_{max}: 1670 cm^{-1} (C=O). δ_H: 1.60-176 (m, 6H, $-CH_2-CH_2-CH_2-$); 3.65-3.82 (m, 4H, $-CH_2-N-CH_2-$) and 6.98-7.35 (m, 10H, arom). M^+ 365.

5-Chloro-2,3-diphenyl-6-pyrrolidino-4(3H)-pyrimidone (7d): 76%, m.p. 210-12°C. (Found: C,69.03; H,5.16; N,12.10. $C_{20}H_{18}ClN_3O$ requires C,68.28; H,5.12; N,11.95). ν_{max}: 1670 cm^{-1} (C=O). δ_H: 1.83-2,03 (m, 4H, $-CH_2-CH_2-$); 3.80-4.00 (m, 4H, $-CH_2-CH_2-$) and 6.93-7.42 (m, 10H, arom). M^+ 351.

5-Chloro-2,3-diphenyl-6-morpholino-4(3H)-pyrimidone(7f): 83%, m.p.222-3°C. (Found: C,66.02; H,4.88; N,11.40. $C_{20}H_{18}ClN_3O_2$ requires C,65.31; H,4.90; N,11.43). ν_{max}: 1680 cm^{-1} (C=O). δ_H: 3.66-3.94 (m, 8H, morpholine) and 7.15-7.50 (m, 10H, arom). M^+ 367.

6-Dimethylamino-2,3-diphenyl-5-methylthio-4(3H)-pyrimidone (10a): 90%, m.p. 128-30°C. (Found: C,67.50; H,5.68; N,12.40. $C_{19}H_{19}N_3OS$ requires C,67.66; H,5.64; 12.46). ν_{max}: 1670 cm^{-1} (C=O). δ_H: 2.28 (s, 3H, $-SCH_3$); 3.26 (s, 6H, $-N(CH_3)_2$) and 7.13-7.33 (m, 10H, arom). δ_C: 17.68 ($-SCH_3$); 41.10 ($-N(CH_3)_2$); 91.48 (C-5); 127.62, 128.48, 128.97, 129.11 (C-2′,3′,6′,7′); 127.87, 129.43 (C-4′,8′); 134.85, 137.75 (C-1′,5′); 164.87 (C-2); 163.52 (C-4,6). M^+ 363.

2,3-Diphenyl-5-methylthio-6-morpholino-4(3H)-pyrimidone (10b): 90%, m.p. 176°C. (Found: C,66.36; H,5.52; N,11.10. $C_{21}H_{21}N_3O_2S$ requires C,66.49; H,5.54; N,11.02). ν_{max}: 1670 cm^{-1} (C=O). δ_H: 2.36 (s, 3H, $-SCH_3$); 3.86-3.92 (m, 8H, morpholine) and 7.10-7.33 (m, 10H, arom). M^+ 379.

2,3-Diphenyl-5-methylthio-6-piperidino-4(3H)-pyrimidone (10c): 88%, m.p. 126-7°C. (Found: C,69.97; H,6.00; N,11.00. $C_{22}H_{23}N_3OS$ requires C,70.03; H,6.10; N,11.14). ν_{max}: 1670 cm^{-1} (C=O). δ_H: 1.63-1.80 (m, 6H, $-CH_2-CH_2-CH_2-$); 2.33 (s, 3H, $-SCH_3$); 3.66-3.86 (m, 4H, $-CH_2-N-CH_2-$) and 7.10-7.36 (m, 10H, arom). M^+ 377.

2,3-Diphenyl-5-methylthio-6-pyrrolidino-4(3H)-pyrimidone (10d): 88%, m.p. 152°C. (Found: C,69.43; H,5.85; N,11.50. $C_{21}H_{21}N_3OS$ requires C,69.47; H,5.79; N,11.57). ν_{max}: 1670 cm^{-1} (C=O). δ_H: 1.80-2.03 (m,

4H, $-CH_2-CH_2-$); 2.33 (s, 3H, SCH_3); 3.80-4.02 (m, 4H, $-CH_2-N-CH_2-$) and 7.10-7.30 (m, 10H, arom). M^+ 363.

6-Dimethylamino-2,3-diphenyl-5-ethylthio-4(3H)-pyrimidone (10e): 74%, m.p. 107-8°C (Found: C,68.01; H,6.11; N,11.90. $C_{20}H_{21}N_3OS$ requires C,68.38; H,5.98; N,11.97). ν_{max}: 1670 cm^{-1} (C=O). δ_H: 1.13-1.30 (t, 3H, $-CH_3$); 2.70-2.93 (q, 2H, $-SCH_2-$); 3.30 (s, 6H, $-N(CH_3)_2$); and 7.06-7.36 (m, 10H, arom). M^+ 351.

2,3-Diphenyl-5-ethylthio-6-morpholino-4(3H)-pyrimidone (10f): 80%, m.p. 183°C. (Found: C,67.00; H,5.74; N,10.62. $C_{22}H_{23}N_3O_2S$ requires C,67.18; H,5.85; N,10.69). ν_{max}: 1670 cm^{-1} (C=O). δ_H: 1.19-1.30 (t, 3H, $-CH_3$); 2.73-3.00 (q, 2H, $-SCH_2-$); 3.70-3.86 (m, 8H, morpholine) and 7.06-7.28 (m, 10H, arom). M^+ 393.

2,3-Diphenyl-5-ethylthio-6-piperidino-4(3H)-pyrimidone (10g): 80%, m.p. 137-8°C. (Found: C,70.40; H,6.30; N,10.70. $C_{23}H_{25}N_3OS$ requires C,70.59; H,6.39; N,10.74). ν_{max}: 1670 cm^{-1} (C=O). δ_H: 1.16-1.33 (t, 3H, $-CH_3$); 1.66-1.80 (m, 6H, $-CH_2-CH_2-CH_2-$); 2.80-3.95 (q, 2H, $-SCH_2-$); 3.73-3.90 (m, 4H, $-CH_2-N-CH_2-$) and 7.06-7.36 (m, 10H, arom). M^+ 391.

2,3-Diphenyl-5-ethylthio-6-pyrrolidino-4(3H)-pyrimidone (10h): 78%, m.p. 164°C. (Found: C,69.30; H,6.17; N,11.07. $C_{22}H_{23}N_3OS$ requires C,70.03; H,6.10; N,11.14). ν_{max}: 1670 cm^{-1} (C=O). δ_H: 1.16-1.33 (t, 3H, $-CH_3$); 1.83-2.00 (m, 4H, $-CH_2-CH_2-$); 2.68-2.93 (q, 2H, $-CH_2-$); 3.83-4.00 (m, 4H, $-CH_2-N-CH_2-$) and 7.06-7.36 (m, 10H, arom). M^+ 377.

6-Dimethylamino-3-(4-methylphenyl)-5-methylthio-2-phenyl-4(3H)-pyrimidone (10i): 87%, m.p. 129-30°C. (Found: C,66.58; H,5.98; N,11.88. $C_{20}H_{21}N_3OS$ requires C,66.38; H,5.98; N,11.97). ν_{max}: 1660 cm^{-1} (C=O). δ_H: 2.30 (s, 3H, $-CH_3$); 2.33 (s, 3H, $-SCH_3$); 3.30 (s, 6H, $-N(CH_3)_2$); 6.97-7.06 (m, 4H, arom) and 7.16-7.26 (m, 5H, arom). M^+ 351.

3-(4-Methylphenyl)-5-methylthio-6-morpholino-2-phenyl-4(3H)-pyrimidone (10j): 90%, m.p. 168-70°C. (Found: C,67.70; H,5.80; N,10.72. $C_{22}H_{23}N_3O_2S$ requires C,67.18; H,5.85; N,10.69). ν_{max}: 1660 cm^{-1} (C=O). δ_H: 2.22 (s, 3H, $-CH_3$); 2.35 (s, 3H, $-SCH_3$); 3.73-3.88 (m, 8H, morpholine); 7.00-7.10 (m,4H,arom) and 7.20-7.40 (m, 5H, arom). M^+ 393.

3-(4-Methylphenyl)-5-methylthio-2-phenyl-6-piperidino-4(3H)-pyrimidone (10k): 86%, m.p. 174-5°C. (Found: C,70.40; H,6.30; N,10.72. $C_{23}H_{25}N_3OS$ requires C,70.59; H,6.39; N,10.74). ν_{max}: 1660 cm^{-1} (C=O). δ_H: 1.66-1.82 (m, 6H, $-CH_2-CH_2-CH_2-$); 2.28 (s, 3H, CH_3); 2.33 (s, 3H, $-SCH_3$); 3.70-3.90 (m, 4H, $-CH_2-N-CH_2-$); 7.00-7.10 (m, 4H, arom) and 7.23-7.33 (m, 5H, arom). M^+ 391.

3-(4-Methylphenyl)-5-methylthio-2-phenyl-6-pyrrolidino-4(3H)-pyrimidone (10l): 81%, m.p. 164°C. (Found: C,69.70; H,6.08; N,11.08. $C_{22}H_{23}N_3OS$ requires C,70.03; H,6.10; N11.14). ν_{max}: 1660 cm^{-1} (C=O). δ_H: 1.83-2.03 (m, 4H, $-CH_2-CH_2-$); 2.33 (s, 6H, $-CH_3$ and $-SCH_3$); 3.80-3.98 (m, 4H, $-CH_2-N-CH_2-$); 7.00-7.08 (m, 4H, arom) and 7.13-7.33 (m, 5H, arom). M^+ 377.

3-(4-Chlorophenyl)-6-dimethylamino-5-methylthio-2-phenyl-4(3H)-pyrimidone (10m): 78%, m.p. 127°C. (Found: C,61.90; H,4.80; N,11.34. $C_{19}H_{18}ClN_3OS$ requires C,61.37; H,4.85; N,11.31). ν_{max}: 1670 cm^{-1} (C=O). δ_H: 2.32 (s, 3H, $-SCH_3$); 3.33 (s, 6H, $-N(CH_3)_2$) and 7.00-7.33 (m, 9H, arom). M^+ 371.

3-(4-Chlorophenyl)-5-methylthio-6-morpholino-2-phenyl-4(3H)-pyrimidone (10n): 73%, m.p. 233°C. (Found: C,60.50; H,4.74; N,10.12. $C_{21}H_{20}ClN_3OS$ requires C,60.94; H,4.84; N,10.16). ν_{max}: 1670 cm^{-1} (C=O). δ_H: 2.26 (s, 3H, $-SCH_3$); 3.68-3.90 (m, 8H, morpholine) and 7.00-7.36 (m, 9H, arom). M^+ 413.

3-(4-Chlorophenyl)-5-methylthio-2-phenyl-6-piperidino-4(3H)-pyrimidone (10o): 76%, m.p. 195°C. (Found: C,64.04; H,5.32; N,10.30. $C_{22}H_{22}ClN_3OS$ requires C,64.16; H,5.35; N,10.21). ν_{max}: 1670 cm^{-1} (C=O). δ_H: 1.60-1.76 (m, 6H, $-CH_2-CH_2-CH_2-$); 2.32 (s, 3H, $-SCH_3$); 3.70-3.86 (m, 4H, $-CH_2-N-CH_2-$) and 7.00-7.36 (m, 9H, arom). M^+ 411.

3-(4-Chlorophenyl)-5-methylthio-2-phenyl-6-pyrrolidino-4(3H)-pyrimidone (10p): 75%, m.p. 169-71°C. (Found: C,64.40; H,5.00; N,11.50. $C_{21}H_{20}ClN_3OS$ requires C,63.40; H,5.03; N,11.57). ν_{max}: 1660 cm^{-1} (C=O). δ_H: 1.83-2.00 (m, 4H, $-CH_2-CH_2-$); 2.30 (s, 3H, $-SCH_3$); 3.80-4.00 (m, 4H, $-CH_2-N-CH_2-$) and 7.00-7.33 (m, 9H, arom). M^+ 397.

2,3-Diphenyl-5-methyl-6-piperidino-4(3H)-pyrimidone (22c): 74%, m.p. 184-8°C. (Found: C,76.20; H,6.70; N,12.18. $C_{22}H_{23}N_3O$ requires C,76.36; H,6.75; N,12.23). ν_{max}: 1660 cm^{-1} (C=O). δ_H: 1.60-1.76 (m, 4H, $-CH_2-N-CH_2-$); 2.06 (s, 3H, $-CH_3$); 3.36-3.56 (m, 4H, $-CH_2-N-CH_2-$) and 7.10-7.40 (m, 10H, arom). M^+ 343.

2,3-Diphenyl-5-methyl-6-pyrrolidino-4(3H)-pyrimidone (22d): 84%, m.p. 234-6°C. (Found: C,75.86; H,6.35; N,12.60. $C_{21}H_{21}N_3O$ requires C,76.11; H,6.39; N,12.68). ν_{max}: 1660 cm^{-1} (C=O). δ_H: 1.76-2.00 (m, 4H, $-CH_2-CH_2-$); 2.23 (s, 3H, $-CH_3$); 3.66-3.93 (m, 4H, $-CH_2-N-CH_2-$) and 7.13-7.40 (m, 10H, arom). M^+ 331.

2,3-diphenyl-5-methyl-6-morpholino-4(3H)-pyrimidone (22f): 83%, m.p. 207-8°C. (Found: C,72.72; H,6.02; N,12.14. $C_{21}H_{21}N_3O_2$ requires C,72.60; H,6.09; N,12.10). ν_{max}: 1675 cm^{-1} (C=O). δ_H: 2.13 (s, 3H, $-CH_3$); 3.43-3.60 (m, 4H, $-CH_2-N-CH_2-$); 3.76-3.93 (m, 4H, $-CH_2-O-CH_2-$) and 7.13-7.40 (m, 10H, arom). M^+ 347.

5-Bromo-2,3-diphenyl-6-piperidino-4(3H)-pyrimidone (26a): 83%, m.p. 148-50°C. (Found: C,61.01; H,4.85; N,10.20. $C_{21}H_{20}BrN_3O$ requires C,61.47; H,4.91; N,10.24). ν_{max}: 1670 cm^{-1} (C=O). δ_H: 1.60-1.76 (m, 6H, $-CH_2-CH_2-CH_2-$); 3.60-3.83 (m, 4H, $-CH_2-N-CH_2-$) and 7.13-7.43 (m, 10H, arom). M^+ 410.

5-Bromo-2,3-diphenyl-6-pyrrolidino-4(3H)-pyrimidone (26b): 70%, m.p. 160-62°C. (Found: C,60.37; H,4.53; N,10.60. $C_{20}H_{18}BrN_3O$ requires C,60.62; H,4.58; N,10.60). ν_{max}: 1660 cm^{-1} (C=O). δ_H: 1.90-2.06 (m, 4H, $-CH_2-CH_2-$); 3.90-4.06 (m, 4H, $-CH_2-N-CH_2-$) and 7.23-7.46 (m, 10H, arom). M^+ 396.

5-Bromo-2,3-diphenyl-6-morpholino-4(3H)-pyrimidone (26c): 76%, m.p. 199-201°C. (Found: C,58.00; H,4.32; N,10.10. $C_{20}H_{18}BrN_3O_2$ requires C,58.26; H,4.40; N,10.19). ν_{max}: 1680 cm^{-1} (C=O). δ_H: 3.90 (s, 8H, morpholine) and 7.26-7.50 (m, 10H, arom). M^+ 412.

2,3-Diphenyl-5-Iodo-6-piperidino-4(3H)-pyrimidone (29): 66%, m.p. 157-59°C. (Found: C,55.10; H,4.38; N,9.10. $C_{21}H_{20}IN_3O$ requires C,55.16; H,4.41; N,9.19). ν_{max}: 1680 cm^{-1} (C=O). δ_H: 1.63-1.83(bs, 6H, $-CH_2-CH_2-CH_2-$); 3.70-3.90(bs, 4H, $-CH_2-N-CH_2-$) and 7.16-7.40(m, 16H, arom). M^+ 457.

5-Bromo-2-methylthio-3-phenyl-4(3H)-pyrimidone (31a): 36%, m.p. 178-9°C. (Found: C,43.43; H,3.00; N,9.41. $C_{11}H_9BrN_2O$ requires C44.46; H,3.05; N,9.43). ν_{max}: 1700 cm^{-1} (C=O). δ_H: 2.43 (s, 3H, $-SCH_3$); 7.30-7.43(m, 2H, arom); 7.56-7.73(m, 3H, arom) and 8.26 (s, 1H, olefinic). M^+ 297.

5-Bromo-3-(4-Chlorophenyl)-2-phenyl-4(3H)-pyrimidone (31b): 32%, m.p. 209-10°C. (Found: C,52.92; H,2.76; N,7.82. $C_{16}H_{10}BrClN_2O$ requires C,53.14; H,2.79; N,7.75). ν_{max}: 1690 cm^{-1} (C=O). δ_H: 7.27-7.40 (m, 4H, arom); 7.47-7.60(m, 5H, arom) and 8.18 (s, 1H, olefinic). M^+ 361.

6-Dimethylamino-2-methylthio-3-phenyl-4(3H)-pyrimidone (32a): 72% (Iodoketene), 42% (Bromoketene), m.p. 119-20°C. (Found: C,59.63; H,5.75; N,16.00. $C_{13}H_{15}N_3OS$ requires C,59.75; H,5.78; N,16.08). ν_{max}: 1645 cm^{-1} (C=O). δ_H: 2.43 (s, 3H, $-SCH_3$); 3.13 (s, 6H, $-N(CH_3)_2$); 5.26 (s, 1H, olefinic); 7.26-7.43(m, 2H, arom) and 7.53-7.63(m, 3H, arom). M^+ 261.

3-(4-Chlorophenyl)-6-dimethylamino-2-phenyl-4(3H)-pyrimidone (32b): 76% (Iodoketene), 38% (Bromoketene), m.p. 168-69°C. (Found: C,66.20; H,4.92; N,12.86. $C_{18}H_{16}ClN_3O$ requires C,66.36; H,4.95; N,12.90). ν_{max}: 1670 cm-1 (C=O). δ_H: 3.10 (s, 6H, $-N(CH_3)_2$); 5.40 (s, 1H, olefinic); 7.03-7.16(m, 2H, arom) and 7.26-7.40(m, 7H, arom). M^+ 325.

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