[2+2] VERSUS [4+2] CYCLOADDITION REACTIONS OF 1,3-DIAZA-1,3-BUTADIENES WITH VARIOUS MONO- AND DISUBSTITUTED KETENES AND SUPPORTING MECHANISTIC CONSIDERATIONS

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Abstract - Reactions of 1,3-diaza-1,3-butadienes with various mono- and disubstituted ketenes alongwith the associated interesting mechanistic features involved are reported. Reactions of 1,3-diazabutadienes with monosubstituted ketenes *e.g.* cyano-, *p*-nitrophenyl-, succinimido-, phthalimido- and phenoxyketenes gave [4+2] cycloadducts irrespective of the nature of azadiene and/or ketene substituents. However, diphenylketene underwent [2+2] cycloaddition reactions with 1,3-diazabutadienes (**1a**) and gave [4+2] adducts with **1b**, having electron donating function at 2-position. Interestingly, the reactions of 4-(*N*-arylamino)-1,3-diaza-1,3-butadienes (**19**) with diphenylketene gave simple nucleophilic addition products (**22**), whereas, their reaction with dimethylketene, yielded [4+2] cycloadducts (**23**). The factors influencing [2+2] versus [4+2] and cyclic versus acyclic products are also discussed.

Ketenes have received significant attention owing to their ability to act as 2π component in cycloaddition reactions.[1] They are known to participate effectively as 2π component in the commonly encountered [2+2] cycloaddition reactions, which is a well documented route to the synthesis of four membered carbocyclic[2] and heterocyclic systems including valuable intermediates for various antibiotics and natural products.[3,4] Also, there are several literature reports[4a,5] concerning the participation of 1,2- and 1,4-diaza-1,3-butadienes as effective 4π components in Diels-Alder cycloadditions. However, such reports in case of

Dedicated to Professor Koji Nakanishi on his 75th birthday

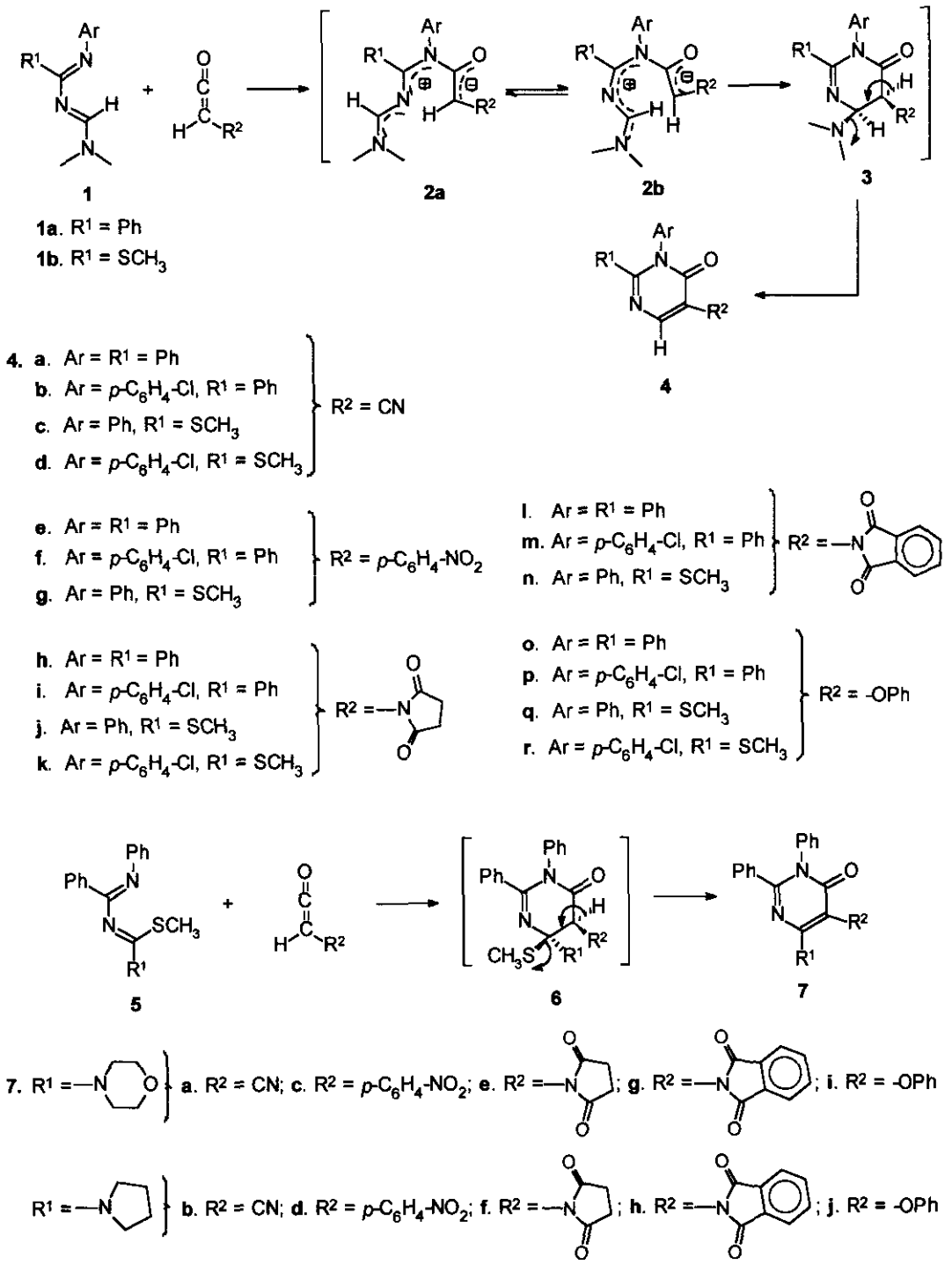
1,3-diaza-1,3-butadienes are much less common[4,5] and correspond mostly to heterocyclic 1,3-diaza-1,3-butadienes.[6] The reactions of acyclic 1,3-diaza-1,3-butadienes with diphenylketene were reported to yield exclusively [2+2] cycloadducts.[7] However, the reactions of recently synthesised and highly polarised 1,3-diaza-1,3-butadienes[8] with phenyl-, chloro-, bromo-, iodo-, chloromethyl-, dichloro-, vinyl- and isopropenylketenes have been shown to undergo [4+2] cycloadditons leading to very good yields of pyrimidinones .[9-11]

Since, ketene chemistry is dominated by [2+2] cycloadditions, the observed formation of [4+2] adducts in 1,3-diazabutadiene-ketene cycloadditions has led to a number of speculations concerning the mechanistic aspects of such cycloadditions and to establish the most probable mechanistic pathway was thought to be interesting scientific enquiry. In view of this, we have carried out the reactions of various mono- and disubstituted ketenes by selecting electron donating/withdrawing, bulky substituents on ketene and/or 1,3-diazabutadienes and the results of these investigations are presented herein.

The reactions of 1,3-diaza-1,3-butadienes (**1**) with cyanonketene, generated *in situ* from cyanoacetic acid/*p*-toluenesulphonyl chloride/triethylamine, where anionic component of the zwitterionic intermediate (**2**) could be stabilised by conjugatively electron withdrawing cyano group, followed the expected [4+2] cycloaddition pathway leading to good yields of previously unknown pyrimidinones (**4a-d**). These pyrimidinones arise presumably *via* the base induced elimination of dimethylamine from the initially formed [4+2] cycloadducts (**3a-d**) (Scheme 1). The intermediates (**3a-d**) with desired stereochemical arrangement of hydrogen (at C-5) and dimethylamino (at C-6) functions is obtained either through highly stereoselective [4+2] cycloaddition and/or *via* the equilibration of these intermediates involving either acidic hydrogen next to carbonyl or through zwitterionic intermediates (**2**).

The steric factors have been reported to alter the nature of the cycloaddition pathway, in case of the reactions of 1,3-diaza-1,3-butadienes with diphenylketene.[12] In order to ascertain the influence of steric factors on the nature of the zwitterionic intermediate and in turn on the nature of the cycloaddition pathway, the reactions of cyanoketene with 1-aryl-4-methylthio-2-phenyl-4-morpholino/pyrrolidino-1,3-diaza-1,3-butadienes (**5**), having bulkier secondary amino and methylthio functions at C-4, were investigated which were shown to result in very good yields of pyrimidinones (**7a,b**). The formation of pyrimidinones (**7a,b**) can again be best explained *via* the initial formation of [4+2] cycloadducts (**6a,b**), as intermediates, which then undergo the expected preferential elimination of methylmercaptan to yield the products. Similarly, the reactions of 1,3-diaza-1,3-butadienes (**1**) and (**5**) with *p*-nitrophenylketene, generated *in situ,* from *p*-nitrophenylacetic acid, *p*-toluenesulphonyl chloride and triethylamine, as expected, followed [4+2] cycloaddition path leading to good yields of novel pyrimidinones (**4e-g**) and (**7c,d**), respectively.

Further, it was thought worthwhile to examine the reactions of 1,3-diaza-1,3-butadienes (**1**) and (**5**) with ketenes bearing the substituents which are not that efficient stabilisers of the anionic component of the

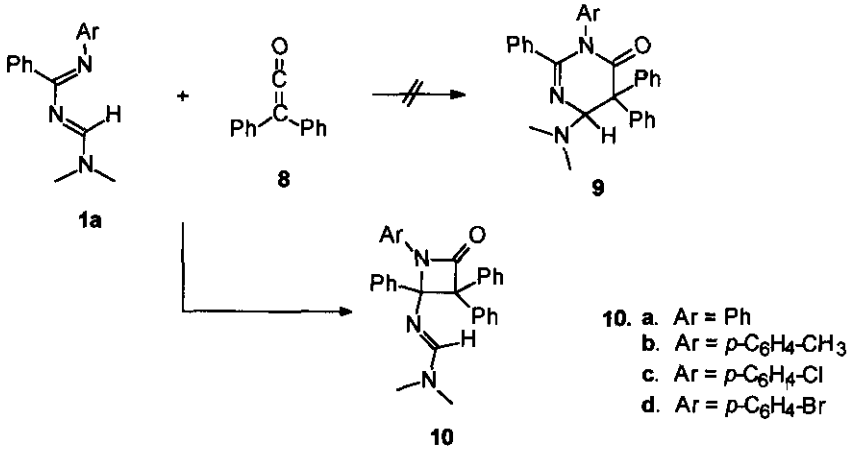


Scheme 1

zwitterion. The ketenes selected for this purpose were succinimido and phthalimidoketenes. Thus, the reactions of **1** with succinimido- and phthalimidoketenes, generated *in situ* from corresponding acetyl chlorides in the presence of triethylamine, were found to result in very good yields of 5-succinimidyl- and 5- phthalimidylpyrimidinone derivatives (**4h-k**) and (**4l-n**), respectively. Interestingly, even the reactions of 1,3-diazabutadienes (**5**), bearing two bulkier substituents at 4-position, with these ketenes having bulkier succinimidyl/phthalimidyl substituents, were also found to follow [4+2] cycloaddition pathway leading to pyrimidinones (**7e,f**) and (**7g,h**). Hence, it may be inferred that that the steric factors alone perhaps do not play much significant role in the predominance of one zwitterionic form over the other and are perhaps not so important in determining the nature of the cycloaddition pathway followed.

Further to these investigations, it was decided to investigate the reactions of 1,3-diaza-1,3-butadienes (**1**) and (**5**) with phenoxyketene, having, to a limited extent, electron donating phenoxy group which possibly may destabilise the anionic component of the zwitterionic intermediate. However, these reactions were also found to follow the [4+2] cycloaddition pathway yielding 5-phenoxypyrimidin-4(3*H*)-ones (**4o-r**) and (**7i,j**). Thus, it may be inferred that the stability of the anionic component of zwitterionic intermediate and steric factors alone perhaps do not influence much the reaction course in case of monosubstituted ketenes.

It was observed that the reactions of **1a** with diphenylketene (**8**) resulted in good yields of products, which were initially thought to be [4+2] cycloadducts (**9**)[9a] and later identified as azetidinones (**10**)[12] arising presumably *via* zwitterionic intermediate of the type (**2**) (Scheme 2). Wurthwein *et al.*[12] explained

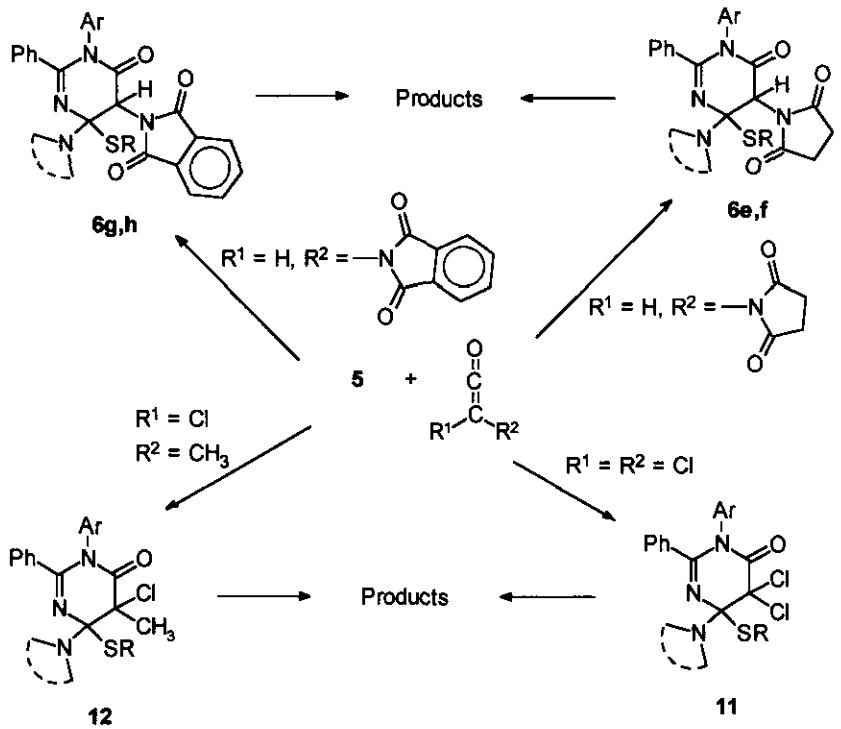


Scheme 2

the preferred formation of [2+2] cycloadducts (**10**) on the basis of steric reasons, since, it was felt that the formation of pyrimidinone (**9**) with one dimethylamino and two phenyl groups in vicinal positions suffers much more steric hindrance as compared to azetidinone (**10**) having three vicinal phenyl groups.

Thus, they confirmed the explanation proposed by Matsuda *et al.*[7] that the steric factors are decisive for the cycloaddition mode.

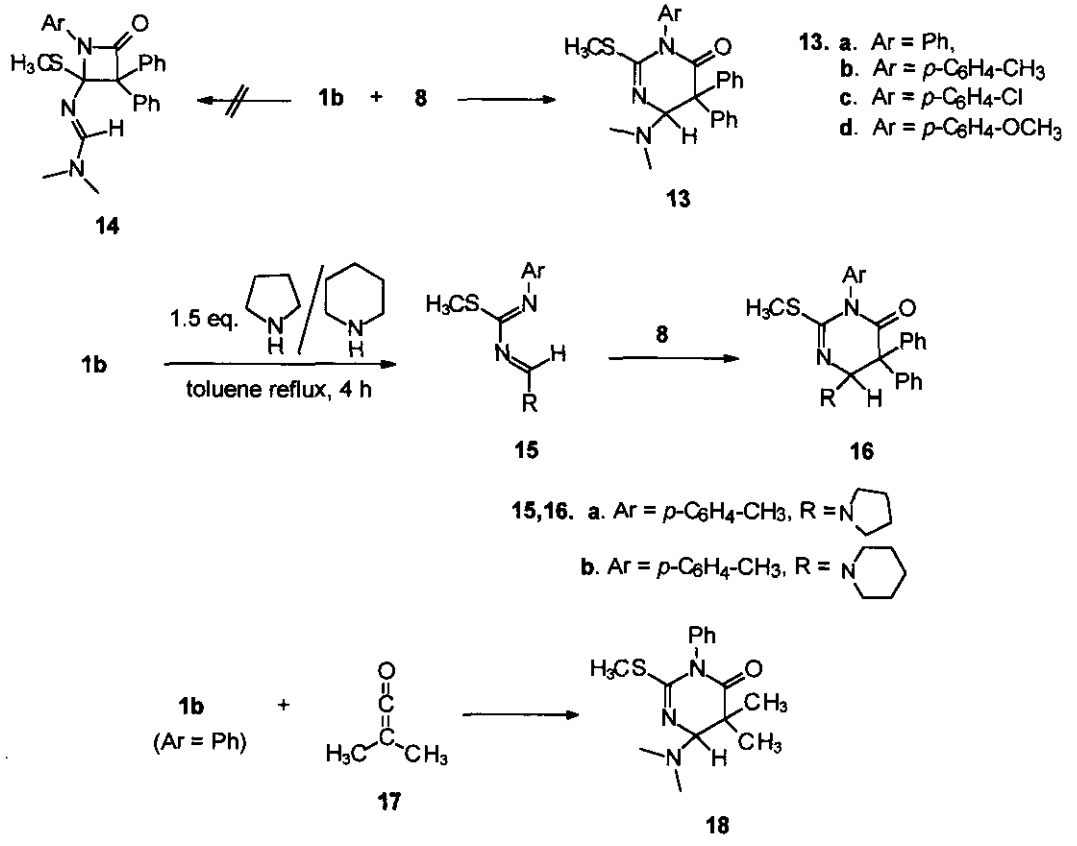
We felt that explaining the cycloaddition mode purely by steric reasons is perhaps oversimplification of the problem since the observed formation of [4+2] cycloadduct in case of 1,3-diazabutadiene-ketene reactions mentioned earlier cannot be explained in this manner. For example, the reactions of 1,3-diaza-1,3-butadienes (**5**), having bulkier secondary amino and methylthio functions at 4-position, with bulkier succinimidyl/phthalimidylketenes and dichloro/chloromethylketenes[10] were shown to follow [4+2] cycloaddition mode even though the intermediate [4+2] cycloadducts (**6 e,f,g,h**), (**11**) and (**12**) clearly suffer from severe steric hindrance as compared to that in alternative azetidinones (Scheme 3). Thus, in order to have a deeper insight into the factors influencing the mode *i.e.* [4+2] versus [2+2] cycloaddition and to firmly establish the mechanism, it was thought worthwhile to further investigate the reactions of 1,3-diaza-1,3-butadienes with disubstituted ketenes.



Scheme 3

Interestingly, the reactions 1,3-diaza-1,3-butadienes (**1b**), having polarising methylthio function at 2-position and dimethylamino function at 4-position, with diphenylketene resulted in very good yields of [4+2] cycloadducts which were characterised as 3-aryl-6-dimethylamino-5,5-diphenyl-2-methylthio-5*H*, 6*H*-pyrimidin-4(3*H*)-ones (**13**) on the basis of analytical data and spectral evidences. In order to generalise

this mode of cycloaddition, it was decided to investigate the reactions of diphenylketene with 4-pyrrolidino/piperidino-2-methylthio-1-aryl-1,3-diaza-1,3-butadienes (**15**), which were synthesised by the treatment of **1b** with pyrrolidine/piperdine. These reaction were also found to follow [4+2] cycloaddition mode resulting in good yields of 5,5-diphenyl-2-methylthio-6-pyrrolidino/piperidinio-5*H*,6*H*-pyrimidin-4(3*H*)-one (**16**) (Scheme 4). ^{1}H NMR spectrum of **16a** showed, apart from other protons, the signals for pyrrolidino protons at δ 1.59 (s, 4H, -CH_2-CH_2-), 2.46-2.49 (m, 2H, -N-CH_2) and 2.93-2.96 (m, 2H, -N-CH_2). The nonequivalence of -CH_2-N-CH_2- protons in cases of both **16a** and **16b** may be due to the restricted rotation of pyrrolidine/piperidine moiety due to the presence of bulkier phenyl groups at adjacent carbon. ^{13}C NMR spectra of **16a** and **16b** showed, in addition to other carbons, charactristic signals for C-2, C-4, C-5 and C-6.



14 **13** **15** **16** **17** **18**

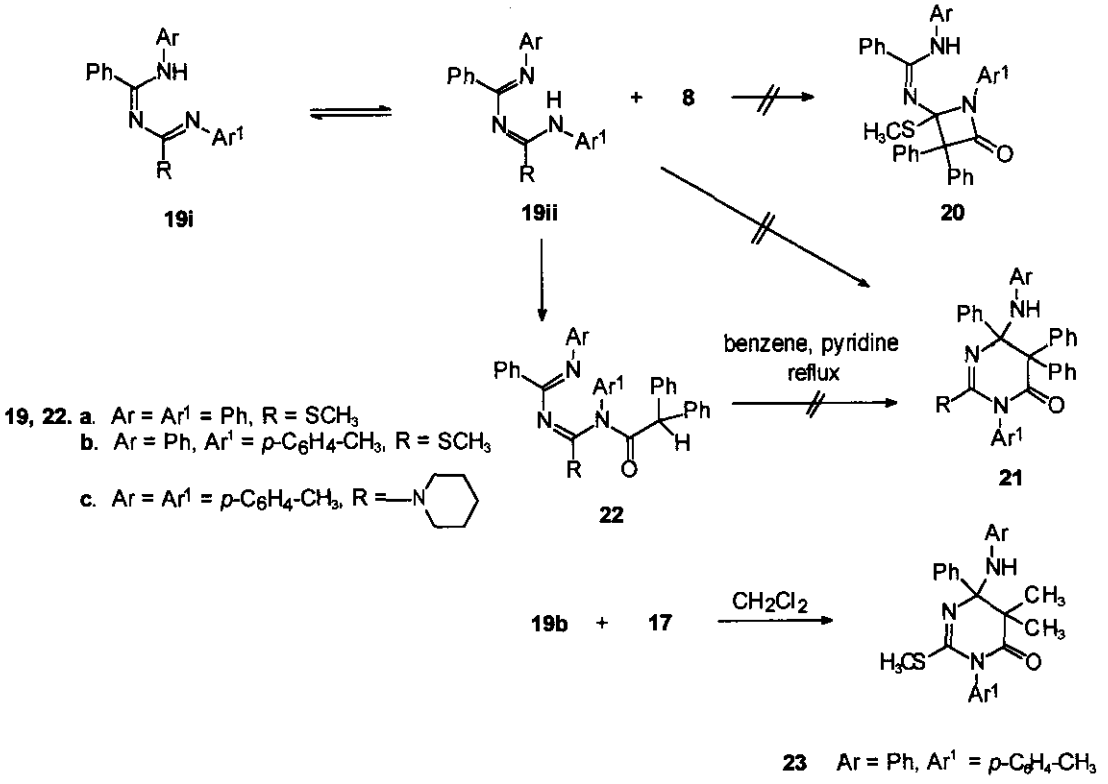
Scheme 4

In view of the lesser steric requirements of methyl group as compared to phenyl, the reactions of 4-dimethylamino-1-phenyl-2-methylthio-1,3-diaza-1,3-butadiene (**1b**) was carried out with dimethylketene (**17**). Thus, the treatment of **1b** (Ar = Ph) with **17**, generated *in situ* from isobutyryl chloride and triethylamine, resulted in a [4+2] cycloadduct characterised as 5,5-dimethyl-6-dimethylamino-3-phenyl-2-

methylthio-5*H*,6*H*-pyrimidin-4(3*H*)-one (**18**) (Scheme 4).

The observed [4+2] cycloaddition mode in reactions of 1,3-diazabutadienes (**1b** and **15**) with dimethyl- and diphenylketenes again indicates that steric factors alone perhaps do not determine the cycloaddition mode in such cases. since, on steric grounds, the formation of alternative azetidinone should perhaps be preferred. Thus, it may be proposed that in addition to steric factors, the electronic factors also play an important role in determining the mode of such cycloadditions. Further, it may be said that [4+2] cycloadducts may always be formed exclusively in reactions of dimethyl/diphenylketenes with 1,3-diaza-1,3-butadienes having conjugatively donating functions at 2-position.

In continuation of our investigations concerning the mechanistic aspects involved in the reactions of disubstituted ketenes with 1,3-diazabutadienes and to further substantiate the inference drawn above, we have investigated the reactions of various *N*-arylamino-1,3-diazabutadienes (**19**), which can exist in

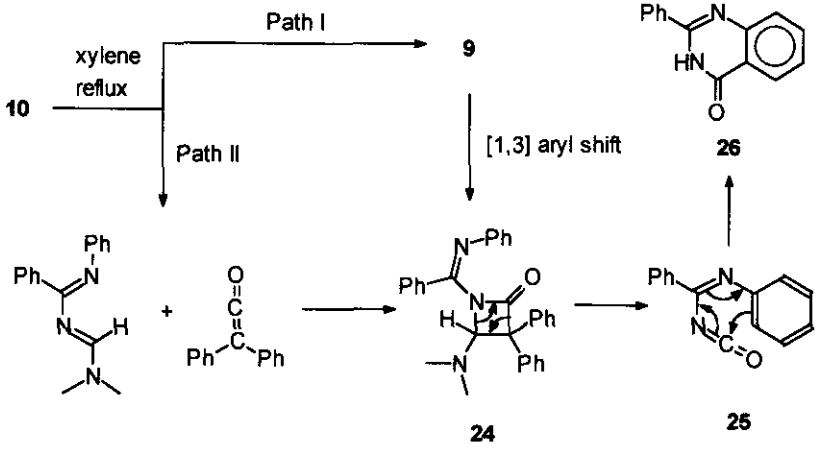


Scheme 5

tautomeric forms (**19i**) and (**19ii**). Among these two forms, the terminal nitrogen (NH-aryl) of the form (**19ii**) has been shown to be more nucleophilic and attack preferentiallly at ketene carbonyl.[11b] Interestingly, the reactions of **19** with diphenylketene did not yield any of the expected products *i.e.* azetidinones (**20**) or pyrimidinones (**21**), but resulted in the formation of substituted acyclic

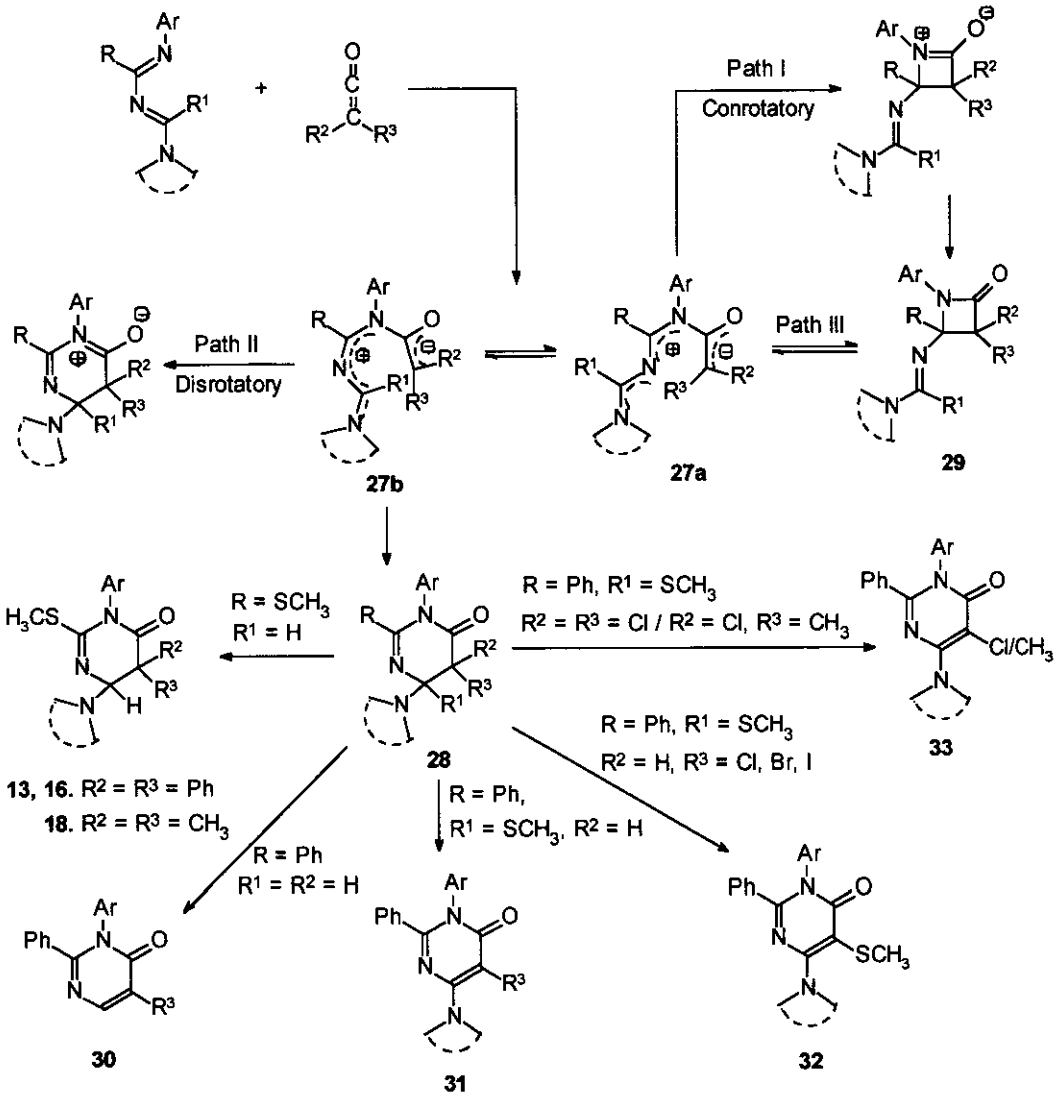
1,3-diazabutadienes (**22**). However, the reaction of **19b** with dimethylketene was found to result in [4+2] cycloadduct characterised as 5,5-dimethyl-2-methylthio-3-(*p*-methylphenyl)-6-phenyl-6-anilino-3,4,5,6-tetrahydropyrimidin-4-one (**23**) (Scheme 5). It may be mentioned here that acyclic 1,3-diazabutadiene derivatives (**22**) failed to cyclise to pyrimidinone even in refluxing benzene in presence of pyridine as a base.

Also, it was reported[12] that the formation of β-lactam in such cycloadditions is a kinetically governed process and the β-lactam was predicted to be *ca.* 32 kcal/mol higher in energy than the corresponding pyrimidinone system.[12] Thus, it was felt that the thermolysis of azetidinone (**10**), may probably yield pyrimidinone (**9**). Interestingly, refluxing a xylene solution of azetidinone (**10**) (Ar = Ph) for 2 h, yielded a product which was characterised as 2-phenylquinazolin-4-one (**26**) on the basis of analytical and spectral data and its comparable mp (235-236 °C) with the reported[13] mp (236 °C). Probable mechanistic pathways leading to the formation of **26** are outlined in Scheme 6. In this Scheme, it is assumed that β-lactam (**10**) may initially undergo rearrangement to pyrimidinone (**9**) (Path I) which by 1,3-aryl ahift may lead to another β-lactam (**24**) as intermediate. The intermediate (**24**) then by facile enamine elimination may yield iminoisocyanate intermediate (**25**), which then follows usual electrocyclic ring closure to yield **26**. It is also possible that β-lactam (**10**) reverts to 1,3-diazabutadiene and diphenylketene (Path II). The diphenylketene, so generated, then adds across 3,4-imino bond to yield β-lactam (**24**) as intermediate, which then follows the above mentioned route to yield **26**.



Scheme 6

Mechanistic considerations: The probable mechanistic pathways leading to the formation of [2+2] or [4+2] cycloadducts in case of reactions of 1,3-diazabutadienes with various ketenes are outlined in Scheme 7. In this scheme, it is assumed that the initial nucleophilc attack of N-1 of 1,3-diazabutadienes at



Scheme 7

ketene carbonyl results in the formation of stabilised zwitterionic intermediate of the type (**27**), which can exist in forms (**27a**) and (**27b**) due to smaller barrier to rotation across C-N bond. Some of the mechanistic possibilities *viz.* (i) the highly stabilised zwitterionic intermediate always prefer to give pyrimidinones, say (**28**) (ii) the conrotatory ring closure of zwitterionic form (**27a**) (path I) gives β-lactam (**29**) and (iii) the isrotatory ring closure of zwitterionic form (**27b**) (path II) leads to pyrimidinones (**28**), may be ruled out on the basis of observed variance in the products formed with different substituted diazabutadienes and ketenes. The most reasonable mechanism which better explains the formation of various products assumes that kinetic control leads to the ring closure of zwitterionic intermediate to give initially β-lactam (**29**)

(path III). But this path is reversible due to the presence of polar donating formamidine moiety. The reversal of β-lactam (**29**), even if allows for small satationary concentration of [4+2] cycloadduct (**28**), which may or may not be thermodyanamically more stable but, in any case, is removed from considration by (i) the elimination of secondary amine or CH_3SH, in reactions of monosubstituted ketenes, to give pyrimidinones (**30**) and (**31**)[9b] and (ii) by rearrangement, in reactions of monohalo- and chloromethyl-/dichloroketenes, to give pyrimidinones (**32**) and (**33**), respectively. In reactions of diphenylketene, where such elimination or rearrangement is not possible, intermediate (**28**) reverts *via* zwitterion (**27**) to β-lactam (**29**), as stable product. In case of 1,3-diazabutdienes having polar donating methylthio function at 2-position, the initially formed β-lactam becomes further unstable, then there is only small stationary concentration of β-lactam and hence, reverts faster to **28** *via* **27** and the observed products are [4+2] cycloadducts (**13**, **16** and **18**), provided it does not impose severe steric constraints. The reactions of *N*-arylamino substituted 1,3-diazabutadienes (**19**) with diphenylketene, neither assume β-lactam structure (**20**), because of its unstable nature due to the presence of amidine and methylthio functions nor pyrimidinone structure (**21**) due to severe steric constraints imposed by the vicinity of three phenyl and one arylamino functions (see Scheme 5). However, in reactions of **19** with dimethylketene [2+2] cycloadduct is not observed due to reasons discussed above and [4+2] cycloadduct, the pyrimidinone (**23**), was isolated due to lesser steric constraints of one phenyl, one arylamino and two methyl groups at vicinal positions as compared to the similar product with diphenylketene.

EXPERIMENTAL

Melting points were determined on a Toshniwal melting point apparatus and are uncorrected. IR spectra were recorded on a Perkin-Elmar 297 and 983 Infrared spectrophotometers using KBr disc. ^{1}H NMR spectra were recorded in deuteriochloroform, with Varian EM 390 (90 MHz) and Bruker ACF 300 (300 MHz) spectrometer using TMS as internal standard; *J* values are in Hz. ^{13}C NMR spectra were also recorded in Bruker AC-F 300 spectrometer in deuteriochloroform using TMS as internal standard. MS spectra were obtained by electron impact at 70eV. Column chromatography was performed on a 60-120 mesh silica gel.

Starting materials: 1,3-Diaza-1,3-butadienes were prepared by the procedures reported earlier.[8, 11a] The acid chlorides wherever used were prepared by treating acid with phosphorus pentachloride. *p*-Toluene-sulphonyl chloride was purified from a mixture of chloroform and hexane (1:5) and its further recrystallisation form hexane.

***Reactions of 1,3-diaza-1,3-butadienes with ketenes;* General Procedures:**

Method A: A solution of acid (cyanoacetic acid/*p*-nitrophenyl acetic acid) (4 mmol) and triethylamine (1.4 mL, 10 mmol) in dry benzene (30 mL) was stirred at rt for about 30 min. To this was added a solution of 1,3-diaza-1,3-butadienes (4 mmol) in dry benzene (10 mL). A solution of *p*-toluenesulphonyl chloride (1.14 g, 6 mmol) in benzene (30 mL) was then added dropwise over a period of 1 h. The reaction mixture was then diluted with benzene, washed with 5% sodium hydroxide (2 x 30 mL), water (3 x 50 mL) and finally dried over anhydrous magnesium sulphate. The crude products obtained by stripping of the solvents under reduced pressure were purified by recrystallisation from a mixture (2:1) of chloroform and hexane.

Method B: A solution of 1,3-diaza-1,3-butadienes (4 mmol) and dry triethylamine (1.4 mL, 10 mmol) in dry benzene (30 mL) was stirred at rt. To this was added a solution of acid chloride (6 mmol) in benzene (30 mL) over a period of 1 h. After the reaction was complete, it was washed with water (3 x 50 mL) and finally dried over anhydrous sodium sulphate. Removal of solvent under reduced pressure yielded crude products which were purified by recrystallisation from a mixture (2:1) of chloroform and hexane.

2,3-Diphenyl-5-cyanopyrimidin-4(3*H*)-one (4a): Yield 65%; mp 164-165 °C; IR ν 2250 (CN), 1700 (C=O) cm^{-1}; ^1H NMR (90 MHz) δ 7.20-7.53 (m, 10H, ArH), 8.56 (s, 1H, olefinic); MS *m/z* 273 (M^+). *Anal.* Calcd for $C_{17}H_{11}N_3O$: C, 74.71; H, 4.06; N, 15.38. Found: C, 74.88; H, 4.02; N, 15.30.

3-(*p*-Chlorophenyl)-5-cyano-2-methylthiopyrimidin-4(3*H*)-one (4d): Yield 70%; mp 203-204 °C; IR ν 2225 (CN), 1700 (C=O) cm^{-1}; ^1H NMR (90 MHz) δ 2.53 (s, 3H, $-SCH_3$), 7.16-7.33 (m, 2H, ArH), 7.50-7.70 (m, 2H, ArH), 8.36 (s, 1H, olefinic); MS *m/z* 277 (M^+).

2,3-Diphenyl-5-(*p*-nitrophenyl)pyrimidin-4(3*H*)-one (4e): Yield 69%; mp 206-207 °C; IR ν 1690 (C=O), 1510 (NO_2) cm^{-1}; ^1H NMR (90 MHz) δ 7.25-7.43 (m, 8H, ArH), 7.50-7.66 (m, 4H, ArH), 8.13 (s, 1H, olefinic), 8.30-8.46 (m, 2H, ArH); MS *m/z* 369 (M^+). *Anal.* Calcd for $C_{22}H_{15}N_3O_3$: C, 71.53; H, 4.09; N, 11.38. Found: C, 71.83; H, 4.02; N, 11.36.

2-Methylthio-5-(*p*-nitrophenyl)-3-phenylpyrimidin-4(3*H*)-one (4g): Yield 60%; mp 198 °C; IR ν 1690 (C=O), 1510 (NO_2) cm^{-1}; ^1H NMR (90 MHz) δ 2.00 (s, 3H, $-SCH_3$), 7.36-7.50 (m, 3H, ArH), 7.56-7.63 (m, 4H, ArH), 8.10 (s, 1H, olefinic), 8.26-8.43 (m, 2H, ArH); MS *m/z* 339 (M^+). *Anal.* Calcd for $C_{17}H_{13}N_3O_3S$: C, 60.17; H, 3.86; N, 12.38. Found: C, 59.89; H, 3.93; N, 12.52.

2,3-Diphenyl-5-succinimidylpyrimidin-4(3*H*)-one (4h): Yield 66%; mp 276 C; IR ν 1720, 1635 (C=O) cm^{-1}; ^1H NMR (90 MHz) δ 2.86-3.00 (br s, 4H, $-CH_2-CH_2-$), 7.26-7.50 (m, 10H, ArH), 8.20 (s, 1H,

olefinic); MS *m/z* 345 (M^+). *Anal.* Calcd for $C_{20}H_{15}N_3O_3$: C, 69.56; H, 4.38; N, 12.17. Found: C, 69.88; H, 4.40; N, 11.92.

3-(*p*-Chlorophenyl)-2-methylthio-5-succinimidylpyrimidin-4(3*H*)-one (4k): Yield 85%; mp 204 °C; IR ν 1720, 1640 (C=O) cm^{-1}; ^1H NMR (90 MHz) δ 2.60 (s, 3H, $-SCH_3$), 2.90-3.03 (m, 4H, $-CH_2-CH_2-$), 7.10-7.26 (m, 2H, ArH), 7.43-7.53 (m, 2H, ArH), 7.93 (s, 1H, olefinic); MS *m/z* 349 (M^+).

2,3-Diphenyl-5-phthalimidylpyrimidin-4(3*H*)-one (4l): Yield 70%; mp 207 °C; IR ν 1710, 1625 (C=O) cm^{-1}; ^1H NMR (90 MHz) δ 7.43-7.53 (m, 2H, ArH), 7.56-7.66 (m, 4H, ArH), 7.70-7.96 (m, 8H, ArH), 8.40 (s, 1H, olefinic); MS *m/z* 393 (M^+). *Anal.* Calcd for $C_{24}H_{15}N_3O_3$: C, 73.27; H, 3.84; N, 10.68. Found: C, 73.50; H, 3.72; N, 10.43.

2-Methylthio-3-phenyl-5-phthalimidylpyrimidin-4(3*H*)-one (4n): Yield 65%; mp 133-134 °C; IR ν 1720, 1620 (C=O) cm^{-1}; ^1H NMR (90 MHz) δ 2.43 (s, 3H, $-SCH_3$), 7.33-7.60 (m, 5H, ArH), 7.80-8.00 (m, 4H, ArH), 8.10 (s, 1H, olefinic); MS *m/z* 363 (M^+).

2,3-Diphenyl-5-phenoxypyrimidin-4(3*H*)-one (4o): Yield 76%; mp 165-166 °C; IR ν 1690 (C=O) cm^{-1}; ^1H NMR (90 MHz) δ 7.00-7.13 (m, 2H, ArH), 7.43-7.63 (m, 11H, ArH), 8.13-8.23 (m, 2H, ArH), 8.30 (s, 1H, olefinic); MS *m/z* 340 (M^+). *Anal.* Calcd for $C_{22}H_{16}N_2O_2$: C, 77.63; H, 4.74; N, 8.23. Found: C, 77.75; H, 4.72; N, 8.18.

3-(*p*-Chlorophenyl)-2-methylthio--5-phenoxypyrimidin-4(3*H*)-one (4r): Yield 66%; mp 170 °C; IR ν 1700 (C=O) cm^{-1}; ^1H NMR (90 MHz) δ 2.43 (s, 3H, $-SCH_3$), 7.03-7.16 (m, 2H, ArH), 7.20-7.33 (m, 5H, ArH), 7.46-7.63 (m, 2H, ArH), 7.76 (s, 1H, olefinic); MS *m/z* 344 (M^+).

2,3-Diphenyl-5-cyano-6-morpholinopyrimidin-4(3*H*)-one (7a): Yield 77%; mp 258-259 °C; IR ν 2225 (CN), 1680 (C=O) cm^{-1}; ^1H NMR (90 MHz) δ 3.76-3.93 (m, 4H, $-CH_2-N-CH_2-$), 4.10-4.26 (m, 4H, $-CH_2-O-CH_2-$), 7.20-7.50 (m, 10H, ArH); MS *m/z* 358 (M^+).

2,3-Diphenyl-6-pyrrolidino-5-(*p*-nitrophenyl)pyrimidin-4(3*H*)-one (7d): Yield 65%; mp 228-229 °C; IR ν 1680 (C=O), 1530 (NO_2) cm^{-1}; ^1H NMR (90 MHz) δ 1.76-2.13 (m, 4H, $-CH_2-CH_2-$), 3.20-3.40 (m, 4H, $-CH_2-N-CH_2-$), 7.16-7.40 (m, 10H, ArH), 7.60-7.73 (m, 2H, ArH), 8.20-8.33 (m, 2H, ArH); MS *m/z* 438 (M^+).

2,3-Diphenyl-6-morpholino-5-succinimidylpyrimidin-4(3*H*)-one (7e): Yield 80%; mp 242 °C; IR ν 1725, 1650 (C=O) cm^{-1}; ^1H NMR (90 MHz) δ 2.76-2.93 (m, 4H, $-CH_2-CH_2-$), 3.73 (br s, 8H,

morpholine), 7.20-7.40 (m, 8H, ArH), 7.86-8.06 (m, 2H, ArH); MS *m/z* 430 (M^+). *Anal.* Calcd for $C_{24}H_{22}N_4O_4$: C, 66.96; H, 5.15; N, 13.01. Found: C, 67.23; H, 4.99; N, 12.91.

2,3-Diphenyl-5-phthalimidyl-6-pyrrolidinopyrimidin-4(3*H*)-one (7h): Yield 80%; mp 255-256 °C; IR ν 1720, 1655 (C=O) cm^{-1}; ^1H NMR (90 MHz) δ 1.80-2.63 (m, 4H, $-CH_2-CH_2-$), 2.73-2.93 (br s, 4H, $-CH_2-N-CH_2-$), 7.30-7.36 (m, 12H, ArH), 7.80-8.15 (m, 2H, ArH); MS *m/z* 462 (M^+). *Anal.* Calcd for $C_{28}H_{22}N_4O_3$: C, 72.71; H, 4.79; N, 12.11. Found: C, 73.01; H, 4.85; N, 12.22.

2,3-Diphenyl-6-morpholino-5-phenoxypyrimidin-4(3*H*)-one (7i): Yield 65%; mp 204-205 °C; IR ν 1690 (C=O) cm^{-1}; ^1H NMR (90 MHz) δ 3.13-3.30 (m, 4H, $-CH_2-N-CH_2-$), 3.40-3.46 (m, 4H, $-CH_2-O-CH_2-$), 6.96-7.13 (m, 2H, ArH), 7.23-7.50 (m, 11H, ArH), 8.10-8.30 (m, 2H, ArH); MS *m/z* 425 (M^+).

All other derivatives of **4** and **7** not exemplified above, are listed below alongwith their melting points and yields.

Product	mp °C	Yield %	Product	mp °C	Yield %
4b	178	78	**4q**	141-142	64
4c	172	87	**7b**	266	85
4f	252	72	**7c**	234	80
4i	285-286	70	**7f**	228-229	85
4j	200-202	75	**7g**	159-160	74
4m	216	70	**7j**	243	65
4p	171	70			

4-(*N,N*-Dimethylformamidino)-1,3,3,4-tetraphenylazetidin-2-one (10a): Yield 81%; mp 164-165 °C; IR ν 1730 (C=O) cm^{-1}; ^1H NMR (90 MHz) δ 2.70 [s, 6H, $-N(CH_3)_2$], 6.83 (s, 1H, olefinic), 7.16-7.54 (m, 20H, ArH); MS *m/z* 445 (M^+). *Anal.* Calcd for $C_{30}H_{27}N_3O$: C, 80.87; H, 6.01; N, 9.43. Found: C, 81.15; H, 6.05; N, 9.53.

4-(*N,N*-Dimethylformamidino)-1-(*p*-methylphenyl)-3,3,4-triphenylazetidin-2-one (10b): Yield 83%; mp 148 °C; IR ν 1730 (C=O) cm^{-1}; ^1H NMR (90 MHz) δ 2.20 (s, 3H, $-CH_3$), 2.75 [s, 6H, $-N(CH_3)_2$], 6.90

(s, 1H, olefinic), 7.23-7.56 (m, 19H, ArH); MS *m/z* 459 (M^+). *Anal.* Calcd for $C_{31}H_{29}N_3O$: C, 81.02; H, 6.36; N, 9.14. Found: C, 81.31; H, 6.43; N, 9.01.

1-(*p*-Chlorophenyl)-4-(*N,N*-dimethylformamidino)-3,3,4-triphenylazetidin-2-one (10c): Yield 85%; mp 180-181 °C; IR 1730 (C=O) cm^{-1}; ^1H NMR (90 MHz) δ 2.70 [s, 6H, -N(CH_3)$_2$], 6.86 (s, 1H, olefinic), 7.15-7.55 (m, 19H, ArH); MS *m/z* 480 (M^+). *Anal.* Calcd for $C_{30}H_{26}N_3OCl$: C, 75.07; H, 5.46; N, 8.75. Found: C, 75.40; H, 5.49; N, 8.85.

1-(*p*-Bromophenyl)-4-(*N,N*-dimethylformamidino)-3,3,4-triphenylazetidin-2one (10d): Yield 86%; mp 174-175 °C; IR ν 1730 (C=O) cm^{-1}; ^1H NMR (90 MHz) δ 2.68 [s, 6H, -N(CH_3)$_2$], 6.83 (s, 1H, olefinic), 7.20-7.63 (m, 19H, ArH); MS *m/z* 524 (M^+). *Anal.* Calcd for $C_{30}H_{26}N_3OBr$: C, 68.70; H, 4.99; N, 8.01. Found: C, 68.80; H, 5.10; N, 7.89.

6-Dimethylamino-2-methylthio-3,5,5-triphenyl-5*H*,6*H*-pyrimidin-4(3*H*)-one (13a): Yield 84%; mp 122 °C; IR ν 1700 (C=O) cm^{-1}; ^1H NMR (90 MHz) δ 2.26 (s, 3H, -SCH_3), 2.34 [s, 6H, -N(CH_3)$_2$], 5.16 (s, 1H, methine), 7.06-7.60 (m, 15H, ArH); MS *m/z* 415 (M^+). *Anal.* Calcd for $C_{25}H_{25}N_3OS$: C, 72.26; H, 6.06; N, 10.11. Found: C, 74.43; H, 6.09; N, 10.21.

6-Dimethylamino-5,5-diphenyl-2-methylthio-3-(*p*-methylphenyl)-5*H*,6*H*-pyrimidin-4(3*H*)-one (13b): Yield 80%; mp 194-195 °C; IR ν 1700 (C=O) cm^{-1}; ^1H NMR (90 MHz) δ 2.26 (s, 3H, -SCH_3), 2.29 (s, 3H, -CH_3), 2.36 [s, 6H, -N(CH_3)$_2$], 6.16 (s, 1H, methine), 7.06-7.54 (m, 14H, ArH); MS *m/z* 429 (M^+). *Anal.* Calcd for $C_{26}H_{27}N_3OS$: C, 72.69; H, 6.33; N, 9.78. Found: C, 72.80; H, 6.15; N, 9.81.

3-(*p*-Chlorophenyl)-6-dimethylamino-5,5-diphenyl-2-methylthio-5*H*,6*H*-pyrimidin-4(3*H*)-one (13c): Yield 83%; mp 148 °C; IR ν 1700 (C=O) cm^{-1}; ^1H NMR (90 MHz) δ 2.28 (s, 3H, -SCH_3), 2.32 [s, 6H, -N(CH_3)$_2$], 5.16 (s, 1H, methine), 7.00-7.50 (m, 14H, ArH); MS *m/z* 449 (M^+). *Anal.* Calcd for $C_{25}H_{24}N_3OClS$: C, 66.72; H, 5.37; N, 9.34. Found: C, 67.00; H, 5.36; N, 9.39.

6-Dimethylamino-5,5-diphenyl-3-(*p*-methoxyphenyl)-2-methylthio-5*H*,6*H*-pyrimidin-4(3*H*)-one (13d): Yield 81%; mp 134-135 °C; IR ν 1700 (C=O) cm^{-1}; ^1H NMR (90 MHz) δ 2.26 (s, 3H, -SCH_3), 3.03 [s, 6H, -N(CH_3)$_2$], 3.73 (s, 3H, -OCH_3), 5.16 (s, 1H, methine), 6.76-6.96 (m, 2H, ArH), 7.16-7.60 (m, 12H, ArH); MS *m/z* 445 (M^+). *Anal.* Calcd for $C_{26}H_{27}N_3O_2S$: C, 70.08; H, 6.11; N, 9.43. Found: C, 71.20; H, 6.04; N, 9.35.

Preparation of 1-aryl-2-methylthio-4-pyrrolidino/piperidino-1,3-diaza-1,3-butadienes (15): **General Procedure:** A mixture of 1-aryl-2-methylthio-4-dimethylamino-1,3-diaza-1,3-butadiene (**1b**) (4 mmol) and

pyrrolidine/piperidine (6 mmol) was refluxed in dry toluene (12 mL) for 4 h. Removal of solvent under reduced pressure yielded the crude product, which was purified by passing through silica gel column using a mixture (*1:9*) of ethyl acetate and hexane.

1-(*p*-Methylphenyl)-2-methylthio-4-pyrrolidino-1,3-diaza-1,3-butadiene (15a): Yield 86%; viscous liquid; IR ν 1615, 1538, 1440, 1359 cm^{-1}; ^1H NMR (300 MHz) δ 1.91 (br s, 4H, $-CH_2-CH_2-$), 2.29 (s, 3H, $-CH_3$), 2.34 (s, 3H, $-SCH_3$), 3.48-3.54 (m, 4H, $-CH_2-N-CH_2-$), 6.70-7.18 (m, 4H, ArH), 8.38 (s, 1H, olefinic); MS *m/z* 261 (M^+). *Anal.* Calcd for $C_{14}H_{19}N_3S$: C, 64.33; H, 7.32; N, 16.08. Found: C, 64.70; H, 7.22; N, 16.18.

1-(*p*-Methylphenyl)-2-methylthio-4-piperidino-1,3-diaza-1,3-butadiene (15b): Yield 81%; viscous liquid; IR ν 1612, 1540, 1445, 1360 cm^{-1}; ^1H NMR (90 MHz) δ 1.67 (br s, 6H, $-CH_2-CH_2-CH_2-$), 2.33 (s, 3H, $-CH_3$), 2.40 (s, 3H, $-SCH_3$), 3.26-3.46 (br s, 2H, $-N-CH_2-$), 3.60-3.80 (br s, 2H, $-CH_2-N-$), 6.76-7.27 (m, 4H, ArH), 8.33 (s, 1H, olefinic); MS *m/z* 275 (M^+). *Anal.* Calcd for $C_{15}H_{21}N_3S$: C, 65.41; H, 7.68; N, 15.26. Found: C, 65.63; H, 7.58; N, 15.39.

5,5-Diphenyl-3-(*p*-methylphenyl)-2-methylthio-6-pyrrolidino-5*H*,6*H*-pyrimidin-4(3*H*)-one (16a): Yield 86%; mp 144-145 °C; IR ν 1689 (C=O), 1620, 1510, 1438 cm^{-1}; ^1H NMR (300 MHz) δ 1.59 (br s, 4H, $-CH_2-CH_2-$), 2.24 (s, 3H, $-CH_3$), 2.36 (s, 3H, $-SCH_3$), 2.46-2.49 (m, 2H, $-CH_2-N-$), 2.93-2.96 (m, 2H, $-CH_2-N-$), 5.34 (s, 1H, methine), 7.11-7.23 (m, 9H, ArH), 7.27-7.35 (m, 3H, ArH), 7.46 (d, J = 8.1, with fine splitting, 2H, ArH); ^{13}C NMR (75.5 MHz) δ 15.1 ($-SCH_3$), 21.3 ($-CH_3$), 23.7 ($-CH_2-CH_2-$), 48.8 ($-CH_2-N-$), 59.3 ($-N-CH_2-$), 96.1, 126.1, 126.9, 127.5, 128.1, 128.6, 128.9, 129.0, 129.1, 129.6, 129.7, 133.4, 139.3, 140.6, 153.6, 170.7 (C-4); MS *m/z* 455 (M^+). *Anal.* Calcd for $C_{28}H_{29}N_3OS$: C, 73.81; H, 6.41; N, 9.22. Found: C, 77.77; H, 6.43; N, 9.10.

5,5-Diphenyl-3-(*p*-methylphenyl)-2-methylthio-6-piperidino-5*H*,6*H*-pyrimidin-4(3*H*)-one (16b): Yield 89%; mp 158-159 °C; IR ν 1694 (C=O), 1622, 1505, 1444 cm^{-1}; ^1H NMR (300 MHz) δ 1.29 (br s, 6H, $-CH_2-CH_2-CH_2-$), 2.24 (s, 3H, $-CH_3$), 2.34 (s, 3H, $-SCH_3$), 2.41-2.45 (m, 2H, $-N-CH_2-$), 2.85-2.89 (m, 2H, $-CH_2-N-$), 4.98 (s, 1H, methine), 7.05-7.16 (m, 9H, ArH), 7.25-7.30 (m, 3H, ArH), 7.44 (d, J = 8.2, with fine splitting, 2H, ArH); ^{13}C NMR (75.5 MHz) δ 14.9 ($-SCH_3$), 21.2 ($-CH_3$), 24.0, 25.9, 50.1, 58.1, 82.8, 95.9, 125.5, 126.7, 127.4, 127.9, 128.5, 129.1, 129.3, 133.3, 138.5, 141.1, 141.3, 153.1, 169.6 (C-4); MS *m/z* 469 (M^+). *Anal.* Calcd for $C_{29}H_{31}N_3OS$: C, 74.16; H, 6.65; N, 8.95. Found: C, 74.39; H, 6.53; N, 9.06.

5,5-Dimethyl-6-dimethylamino-2-methylthio-3-phenyl-5*H*,6*H*-pyrimidin-4(3*H*)-one (18): Yield 45%;

mp 144-145 °C; IR ν 1700 (C=O), 1613 cm^{-1}; ^1H NMR (300 MHz) δ 1.28 (s, 3H, $-CH_3$), 1.36 (s, 3H, $-CH_3$), 2.29 (s, 3H, $-SCH_3$), 2.37 [s, 6H, $-N(CH_3)_2$], 4.27 (s, 1H, methine), 7.12-7.18 (m, 2H, ArH), 7.37-7.46 (m, 3H, ArH); ^{13}C NMR (75.5 MHz) δ 14.9, 19.3, 26.5, 40.8 (C-5), 40.9 [$-N(CH_3)_2$], 83.3 (C-6), 129.0, 129.2, 136.1, 153.1 (C-2), 175.1 (C-4); MS *m/z* 291 (M^+). *Anal.* Calcd for $C_{15}H_{21}N_3OS$: C, 61.82; H, 7.26; N, 14.42. Found: C, C, 62.07; H, 7.21; N, 14.36.

1,2-Diphenyl-4-methylthio-4-(*N*-phenyl-*N*-diphenylacetyl)-1,3-diaza-1,3-butadiene (22a): Yield 38%; mp 175 °C; IR ν 1687 (C=O), 1588, 1490 cm^{-1}; ^1H NMR (300 MHz) δ 2.09 (s, 3H, $-SCH_3$), 4.92 (s, 1H, methine), 6.66 (d, J = 7.5, 1H, ArH), 6.73 (d, J = 7.3, 1H, ArH), 6.83-7.51 (m, 22H, ArH), 8.02 (dd, J = 8.1 and 1.9, 1H, ArH); MS *m/z* 539 (M^+).

1,2-Diphenyl-4-methylthio-4-[*N*-(*p*-methylphenyl)-*N*-diphenylacetyl]-1,3-diaza-1,3-butadiene (22b): Yield 40%; mp 173 °C; IR ν 1683 (C=O), 1602, 1589 cm^{-1}; ^1H NMR (300 MHz) δ 2.10 (s, 3H, $-SCH_3$), 2.28 (s, 3H, $-CH_3$), 4.92 (s, 1H, methine), 6.51 (d, J = 7.8, 1H, ArH), 6.71 (d, J = 7.6, 1H, ArH), 6.85-7.43 (m, 21H, ArH), 8.03 (d, J = 8.2, 1H, ArH); ^{13}C NMR (75.5 MHz) δ 15.4 ($-SCH_3$), 21.1 ($-CH_3$), 54.9 (methine C), 121.2, 121.9, 123.0, 127.2, 127.3, 128.0, 128.2, 128.3, 128.4, 128.5, 128.6, 128.65, 128.7, 128.8, 128.9, 129.2, 129.9, 130.7, 134.2, 135.3, 138.6, 138.7, 148.8, 155.1 (C-2), 157.1 (C-4), 171.9 (C-4); MS *m/z* 553 (M^+). *Anal.* Calcd for $C_{36}H_{31}N_3OS$: C, 78.09; H, 5.64; N, 7.59. Found: C, 78.33; H, 5.53; N, 7.56.

1-(*p*-Methylphenyl)-4-piperidino-2-phenyl-4-[*N*-(*p*-methylphenyl)-*N*-diphenylacetyl]-1,3-diaza-1,3-butadiene (22c): Yield 35%; mp 124-125 °C; IR ν 1683 (C=O), 1621, 1598, 1577 cm^{-1}; ^1H NMR (300 MHz) δ 1.40-1.51 (m, 6H, $-CH_2-CH_2-CH_2-$), 2.23 (s, 3H, $-CH_3$), 2.32 (s, 3H, $-CH_3$), 3.18-3.25 (m, 4H, $-CH_2-N-CH_2-$), 4.93 (s, 1H, methine), 6.37 (d, J = 8.1, 2H, ArH), 6.70-6.82 (m, 8H, ArH), 6.95 (d, J = 8.0, 2H, ArH), 7.00-7.50 (m, 10H, ArH), 7.96 (d, J = 7.0, 1H, ArH); ^{13}C NMR (75.5 MHz) δ 20.9 ($-CH_3$), 21.1 ($-CH_3$), 24.3 ($-CH_2-CH_2-CH_2-$), 25.3 ($-CH_2-CH_2-CH_2-$), 46.7 ($-CH_2-N-CH_2-$), 53.7 (CH), 122.2, 127.0, 127.1, 127.9, 128.1, 128.3, 128.5, 128.8, 129.0, 129.7, 129.9, 131.6, 135.8, 138.0, 138.3, 138.6, 144.2, 146.7, 158.1 (C-2), 159.6 (C-4), 171.7 (C=O); MS *m/z* 604 (M^+). *Anal.* Calcd for $C_{41}H_{40}N_4O$: C, 81.42; H, 6.67; N, 9.26. Found: C, 81.83; H, 6.73; N, 9.40.

5,5-Dimethyl-2-methylthio-3-(*p*-methylphenyl)-6-phenyl-6-anilino-5*H*,6*H*-pyrimidin-4(3*H*)-one (23): Yield 41%; mp 181 °C; IR ν 1683 (C=O), 1608, 1507 cm^{-1}; ^1H NMR (90 MHz) δ 1.03 (s, 3H, $-CH_3$), 1.30 (s, 3H, $-CH_3$), 2.35 (s, 3H, $-CH_3$), 2.43 (s, 3H, $-SCH_3$), 7.10-7.51 (m, 12H, ArH), 7.62-7.80 (m, 2H, ArH); MS *m/z* 429 (M^+). *Anal.* Calcd for $C_{26}H_{27}N_3OS$: C, 72.69; H, 6.33; N, 9.78. Found: C, 72.96; H, 6.42; N, 9.91.

2-Phenylquinazolin-4-one (26): 1 g (2.25 mmol) of β-lactam (**10a**) was refluxed in dry xylene (8 mL) for 2 h. The solvent was removed under reduced pressure and the crude product was purified by passing through a silica gel column using a mixture (1:9) of ethyl acetate : hexane to yield quinazolinone (**26**) (0.35 g, 70.5%); mp 235-236 °C; IR ν 1666 (C=O), 1601, 1476, 1556 cm^{-1}; ^1H NMR (300 MHz) δ 7.49-7.54 (m, 1H, ArH), 7.56-7.64 (m, 3H, ArH), 7.78-7.86 (m, 2H, ArH), 8.25-8.28 (m, 2H, ArH), 8.33 (d, *J* = 7.6, with fine splitting, 1H, ArH), 11.72 (br s, 1H, exchangable with D_2O, -NH); ^{13}C NMR (75.5 MHz) δ 120.8, 126.4, 126.8, 127.4, 128.0, 129.1, 131.7, 132.8, 134.9, 149.3, 151.8, 163.9 (C=O); MS *m/z* 222. *Anal.* Calcd for $C_{14}H_{10}N_2O$: C, 75.66; H, 4.53; N, 12.60. Found: C, 75.54; H, 4.63; N, 12.63.

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