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[4+2] CYCLOADDITION REACTIONS OF VARIOUS 1,3-DIAZA-1,3-BUTADIENES WITH KETENES

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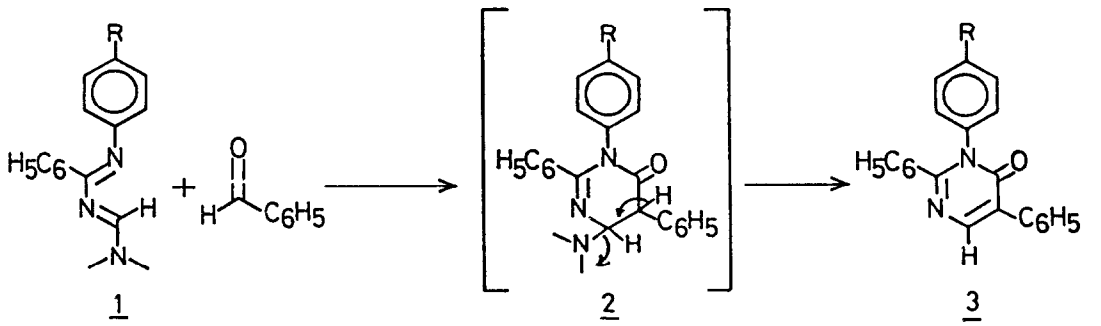
Abstract: *[4+2] cycloaddition reactions of 1-aryl-4-dimethylamino-1,3-diaza-1,3-butadienes (1),1-aryl-4-dimethylamino-2-methylthio-1,3-diaza-1,3-butadienes (5), 1-aryl-4-methylthio-2-phenyl-4-sec.amino-1,3-diaza-1,3-butadienes (9) and 4,4-bis(sec.amino)-1,2-diphenyl-1,3-diaza-1,3-butadienes (12) with monophenylketene and similar cycloaddition reactions of 1, 5 and 12 with monochloroketene are described.*

The hetero Diels-Alder reaction is perhaps the single most powerful tool for the preparation of six membered heterocyclic system[1-4]. Appropriate selection of heterodienes and dienophiles allow for a wide range of structural variations in the cycloadducts. Dienes containing two nitrogen atoms have attracted the attention of chemists in recent years because of their importance in natural product syntheses[3,5-7]. Although there are numerous reports concerning the [4+2] cycloaddition reactions of 1,2- and 1,4-diazabutadienes, such reports concerning 2,3- and 1,3-diaza-1,3-butadienes are very rare[1,2]. It may probably be due to lack of availability of good synthetic methods for stable yet reactive 1,3-diaza-1,3-butadienes[2]. The ketene chemistry is dominated by [2+2] cycloaddition reactions[8-10]. It has been reported that diphenylketene generally affords [2+2] cycloadducts with 1,3-diaza-1,3-butadienes[11,12].In case of reactions of 1,3-diaza-1,3-butadienes (1) with diphenylketene, the [4+2] cycloaddition pathway reported by us[13] was subsequently contradicted and these reactions were shown to follow [2+2] cycloaddition pathway[12]. We wish to report here successful [4+2] cycloaddition reactions of various 1,3-diaza-1,3-butadienes with monophenyl and monochloroketene.

In our preliminary communication[13], we reported that the treatment of 1-aryl-4-dimethylamino-2-phenyl-1,3-diaza-1,3-butadienes (1) with monophenylketene generated in situ at 0-5^{0}C,from phenylacetylchloride and excess of triethylamine,resulted in excellent yields (84-92%) of 1-aryl-2,5-diphenyl-1,6-dihydropyrimidin-6-ones (3) (Scheme-1). The products were characterised on the basis of analytical and spectral evidences. Thus, compound 3a, for example,was analysed for $C_{22}H_{16}N_2O$ and its mass spectrum showed the molecular ion peak at m/z 324. Its i.r. spectrum (KBr) showed a strong absorption peak at 1675 cm^{-1} due to α,β-unsaturated carbonyl group.The ^{1}H n.m.r.spectrum ($CDCl_3$) of 3 showed the absence of $-N(CH_3)_2$ protons and the presence of a singlet at δ 8.2 (1H) due to olefinic proton (=N-HC=C-).The reaction pro-

ceeds through the initial formation of [4+2] cycloadduct 2 as an intermediate, which undergoes very facile elimination of dimethylamine leading to the formation of 3.

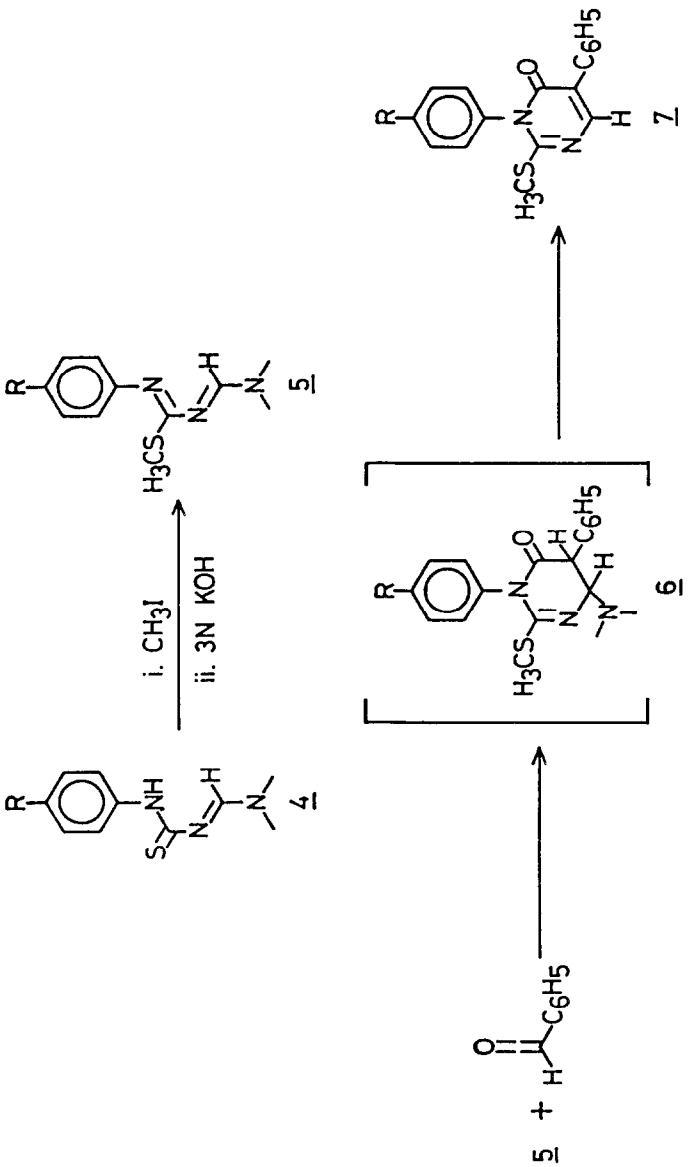


1-3, a: R=H; b: R=CH3; c: R=Cl; d: R=Br

Scheme 1

In continution of this work, we considered it worthwhile to investigate the reactions of monophenylketene with 1,3-diaza-1,3-butadienes having another polarising function at position 2, especially with a view to examine the nature of cycloaddition pathway followed in these cases. Thus, treatment of 1-aryl-4-dimethylamino-2-methylthio-1,3-diaza-1,3-butadienes (5) [prepared by thiomethylation of N,N-dimethyl-N'-(N-arylthiocarbamoyl)formamidines (4)], with monophenylketene resulted in very good yields (85-95%) of previously unknown 1-aryl-2-methylthio-1,6-dihydropyrimidin-6-ones (7). The formation of pyrimidones (7), in this case, resulted from base induced elimination of dimethylamine from intermediate cycloadduct, 6 (Scheme-2). The i.r. spectrum (KBr) of, 7 showed a strong absorption peak at ca. 1675 cm^{-1} due to α,β-unsaturated carbonyl group. The ^1H n.m.r. spectra ($CDCl_3$) of them exhibited singlets at ca.δ 2.40 (3H) and ca.δ 8.03 (1H), assigned to $-SCH_3$ protons and olefinic proton, respectively.

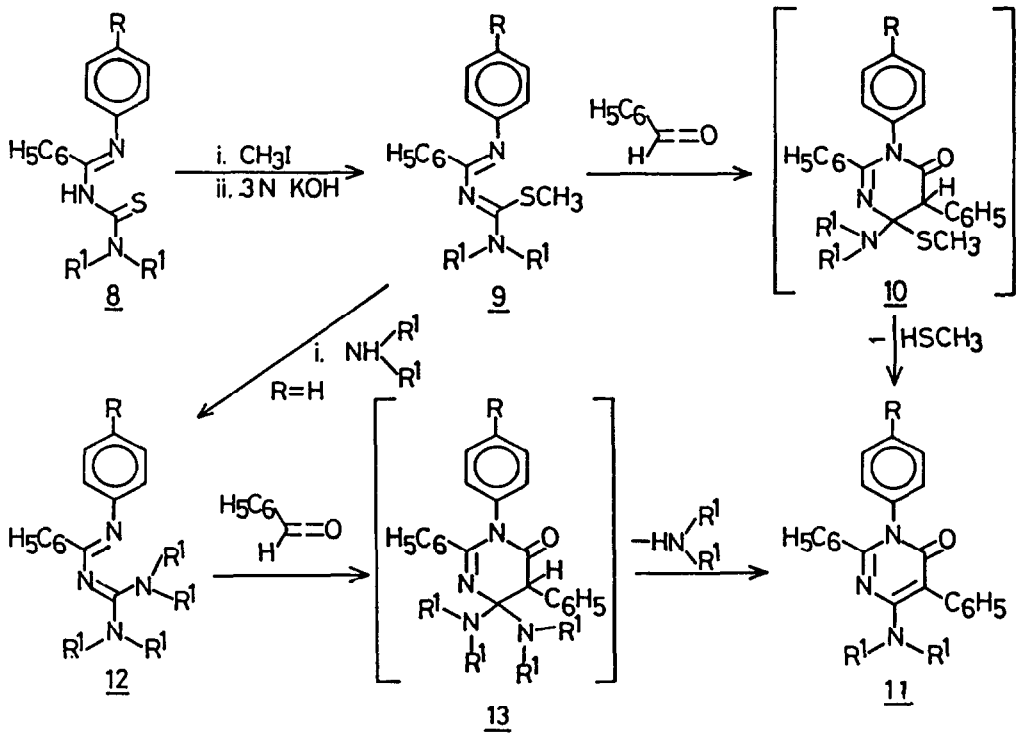
The steric factors have been shown to influence the nature of the cycloaddition pathway, in case of reactions of 1,3-diaza-1,3-butadienes with diphenylketene. Hence, in order to investigate the steric as well as the electronic effects of two polarising functions at position 4 of 1,3-diaza-1,3-butadienes, we have carried out the reactions of 1-aryl-4-methylthio-2-phenyl-4-sec.amino-1,3-diaza-1,3-butadienes (9) with monophenylketene



5-7, a:R=H; b:R=CH3; c:R=Cl; d:R=OCH3

Scheme 2

(Scheme-3). The 1,3-diaza-1,3-butadienes (9) were obtained by the methylation of 4-[(α-arylimino)benzylidenethiocarbamoyl]sec.amines (8)[14].The treatment of 9 with phenylacetylchloride in presence of excess of triethylamine, in chloroform gave almost quantitative yields of 1-aryl-2,5-diphenyl-4-sec. amino-1,6-dihydropyrimidin-6-ones (11). The reaction proceeds through the initial formation of [4+2] cycloadduct 10, as an intermediate, which as expected, undergoes preferential base assisted elimination of methylmercaptan leading to 11. The structure 11 was assigned to the products on the basis of elemental and spectral data. Thus, compound 11a,for example, was



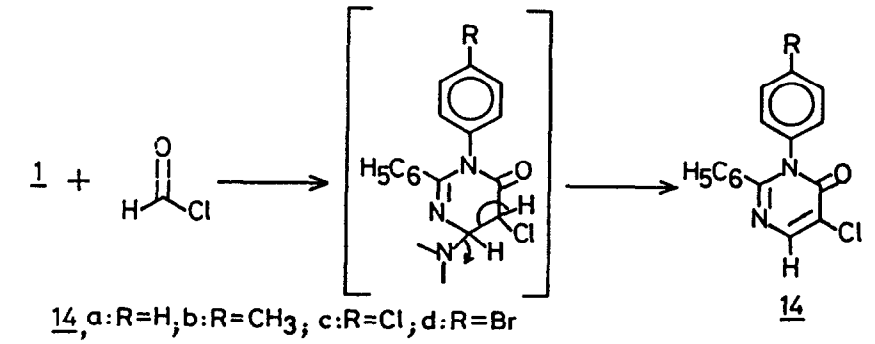
11 a : R=H ; R¹,R¹ = O
b : R=H ; R¹,R¹ =
c : R=H ; R¹,R¹ =
d : R=H ; R¹=R¹= CH3
e : R=CH3 ; R¹,R¹ = O
f : R=CH3 ; R¹,R¹ =
11 g : R=CH3 ; R¹,R¹ =
h : R=CH3 ; R¹=R¹= CH3
i : R=Cl ; R¹,R¹ = O
j : R=Cl ; R¹,R¹ =
k : R=Cl ; R¹,R¹ =
l : R=Cl ; R¹=R¹= CH3

Scheme 3

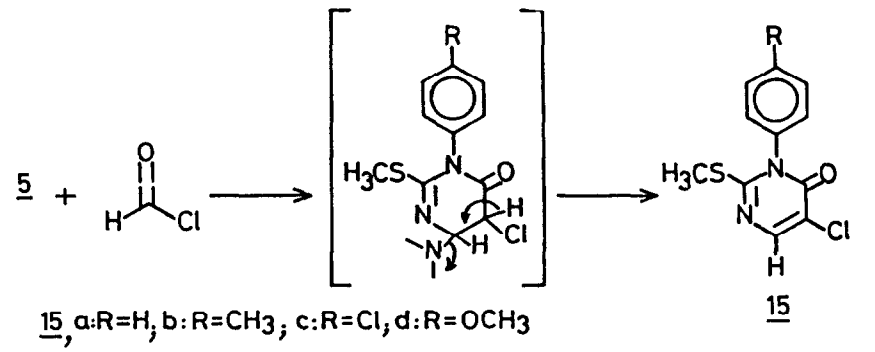
analysed for $C_{26}H_{23}N_3O_2$ and its mass spectrum exhibited the molecular ion peak at m/z 409. Its i.r. spectrum (KBr) showed the carbonyl stretching frequency at 1660 cm^{-1}. Its ^1H n.m.r. spectrum ($CDCl_3$) showed two triplets at δ3.30-3.43 (4H) and δ3.50-3.66 (4H), which were assigned to the $-CH_2-O-CH_2-$ and $-CH_2-N-CH_2-$ protons of morpholine, respectively. The aromatic protons appeared as a multiplet at around δ 7.13-7.60 (15H). The structures of 11 a, b, and c were further confirmed by the superimposable i.r., ^1H n.m.r. and undepressed m.p. with the samples prepared by the reactions of 12 a, b and c with monophenylketene. The 1,3-diaza-1,3-butadienes 12 used for this purpose, were prepared by refluxing 9 a, b, and c with morpholine, piperidine and pyrrolidine, in toluene, respectively. A number of futile attepmts were made to isolate the intermediate [4+2] cycloadducts 2, 6, 10 and 13. All these attempts, even in presence of one equivalent of triethylamine led invariably to the final products.

With a view to generalise the participation of these 1,3-diaza-1,3-butadienes as 4π components in Diels-Alder cycloaddition reactions with different substituted ketenes, we have investigated the reactions of 1,5 and 12 with monochloroketene. The recent reviews[1,2] concerning the Diels-Alder cycloadditions of heterodienes, revealed the rare use of monochloroketene in such cycloaddition reactions. It may probably be due to its fast polymerisation. However, the successful [4+2] cycloadditions of 1,3-diaza-1,3-butadienes, 1, 5 and 12, with monochloroketene, have been realised by very slow addition of methylenechloride solution of three equivalents of chloroacetylchloride. These reactions resulted in very good yields of heretofore unknown 1-aryl-5-chloro-2-phenyl-1,6-dihydropyrimidin-6-ones (14), 1-aryl-5-chloro-2-methylthio-1,6-dihydropyrimidin-6-ones (15) and 5-chloro-1,2-diphenyl-4-sec.amino-1,6-dihydropyrimidin-6-ones (16) (Scheme-4).

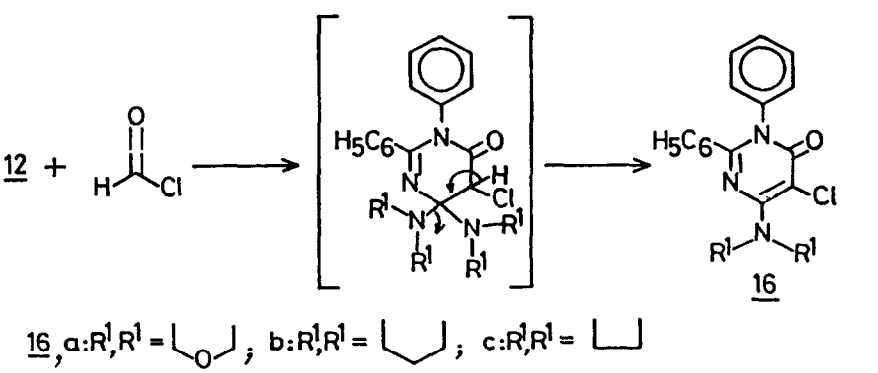
The probable mechanism for formation of pyrimidone derivatives 3,7,11,14,15 and 16 could be similar to the one reported for 1-aza-1,3-butadienes[15], and is outlined in Scheme-5. In this scheme it is presumed that the N-1 of polarised 1,3-diaza-1,3-butadienes attacks the carbonyl of ketene leading to the formation of the zwitterionic intermediate 17. The initial attack by N-1 is preferred over that of N-3, as the latter is placed in an unfavourable site of the butadiene system[9]. Also, because of the considerable differences in electronegativity of the reacting atoms, a stepwise mechanism leading to 17 is proposed[16]. The zwitterionic intermediate 17, can then follow four different pathways. The pathway I,leading to the formation of 18 and19, and pathway II, leading to oxadiazine derivatives (20) were ruled out, because these involve attack by less nucleophilic alkoxide anion. The pathway III results β-lactam derivatives through [2+2] cycloaddition and pathway IV, involving [4+2] can give the intermediate 22. The absence of characteristic β-lactam carbonyl absorption band at about 1720 cm^{-1} in i.r. spectra of the products clearly rules out the formation of any [2+2] cycloadducts in these reactions. The pathway IV is preferred, because the enhanced stability of the zwitterionic intermediate 17, which increases its tendency for ring closure to yield thermodynamically more stable cycloadducts.



14, a: R=H; b: R=CH3; c: R=Cl; d: R=Br



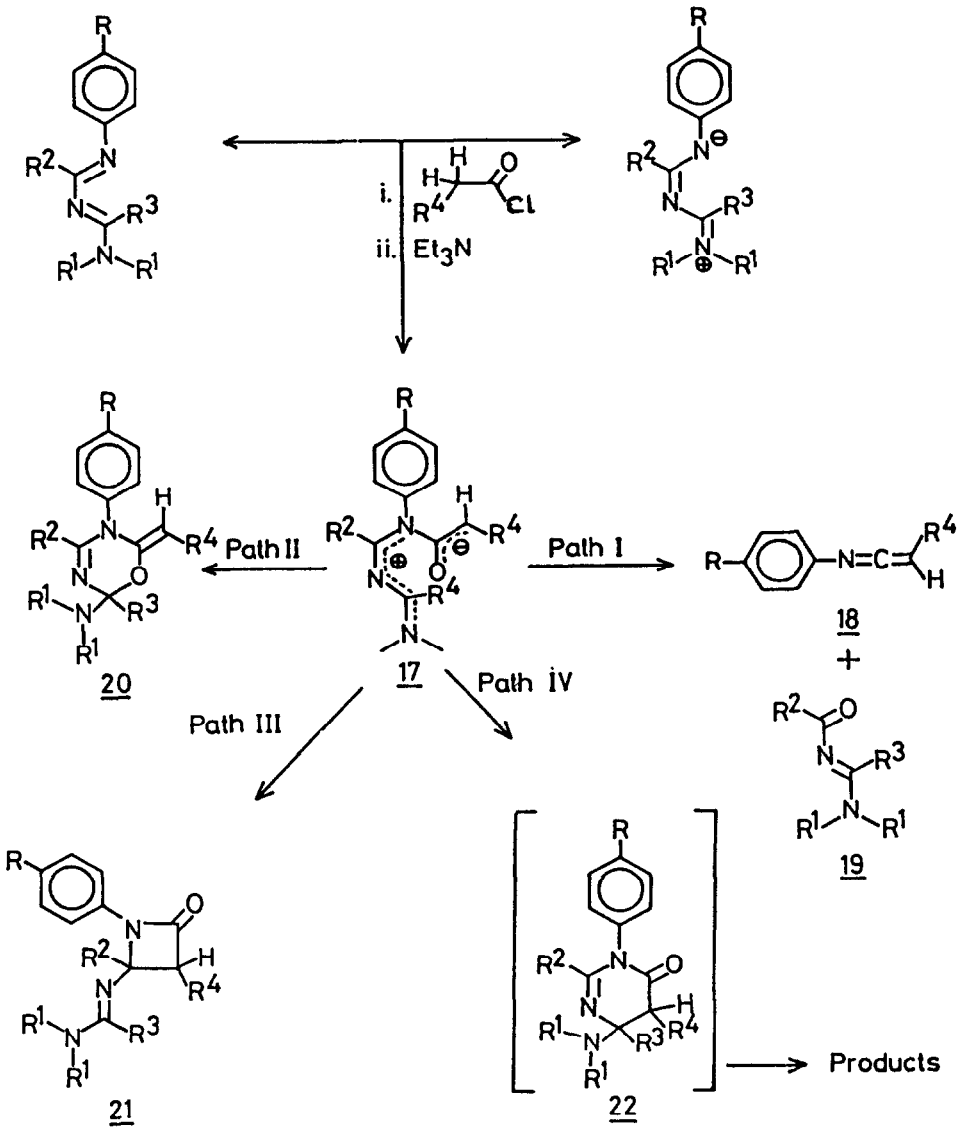
15, a: R=H; b: R=CH3; c: R=Cl; d: R=OCH3



16, a: R1,R1 = O; b: R1,R1 = CH2CH2; c: R1,R1 = CH2

Scheme 4

The intermediate 22, finally undergoes elimination of secondary amine or methylmercaptan leading to the formation of the desired products.The impet-



Scheme 5

us for [4+2] cycloaddition reactions in these cases probably stems from the presence of a polarising secondary amine function at position 4 of 1,3-diaza-1,3-butadienes. It is also possible that [2+2] cycloaddition pathway III is reversible and the formed ß-lactam (21) is unstable and exists on in a very small stationary concentration. The reversal (21) to 17 may

then lead to more stable [4+2] adducts. A detailed study concerning the reaction of various 1,3-diaza-1,3-butadienes with diphenylketene is underway and the results of these investigations will be reported shortly.

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Experimental

Melting points were determined with a Toshniwal melting point apparatus and are uncorrected. I.r. spetra were recorded on a Perkin-Elmer 297 spectrophotometer, using KBr disc. ^1H n.m.r. were recorded in $CDCl_3$, with a Varian 390 90MHz spectrometer using TMS as the internal standard. Mass spectra were recorded on Jeol D 300 Mass spectrometer.

Preparation of 1,3-Diaza-1,3-Butadienes[17] : 1-Aryl-4-dimethylamino-2-phenyl-1,3-diaza-1,3-butadienes (1) were prepared by the reported procedure[18]. 1-Aryl-4-dimethylamio-2-methylthio-1,3-diaza-1,3-butadienes (5) and 1-aryl-4-methylthio-2-phenyl-4-sec.amino-1,3-diaza-1,3-butadienes (9) were prepared by the thiomethylation of N,N-dimethylamino-N′-(N-arylthiocarbamoyl)formamidines and 4-[(α -arylamino)benzylidenethiocarbamoyl]secondary-amine (8) with methyliodide, respectively. 4,4-Bis(sec.amino)-1,2-diphenyl-1,3-diaza-1,3-butadienes (12) were prepared by refluxing 9 a, b and c with morpholine, pipreridine and pyrrolidine, respectively in dry toluene for 20-30 hours.

Reactions of 1,3-Diaza-1,3-Butadienes (1,5,9 and 12) with monophenylketene; General Procedure: A solution of phenylacetylchloride (2.2 mmole) in dry benzene (15 ml) (chloroform in case of 9 and 12) was added gradually over a period of 1h to an ice-water cooled solutior (5-10 °C) well stirred benzene solution (25 ml) (chloroform in case of 9 and 12) of 1,3-diaza-1,3-butadiene (2.0 mmol) and triethylamine (4.6 mmole). After complete addition of acidchloride,the reaction mixture was siterred for a further period of 30 min at the same temperature. It was then thoroughly washed with cold water (6X50 ml) and dried over anhydrous magnesium sulphate. The crude product so obtained after removal of solvent under reduced pressure was further purified by passing it through a silica gel column (1:4 :: ethylactate: hexane) and were recrystallised from a mixture of benzene and petroleum ether.

1,2,5-Triphenyl-1,6-dihydropyrimidin-6-one; (3a): white solid; yield,86%; mp. 166-7°C. (Found: C, 81.70; H, 4.90; N, 8.62. $C_{22}H_{16}N_2O$ requires C,81.48; H, 4.93, N, 8.64). ν max : 1675 cm^{-1} (C=O).δ_H : 7.01-7.63 (m, 15H, arom) and 8.10 (s, 1H, olefinic). M^+ 324.

2,5-Diphenyl-1-p-tolyl-1,6-dihydropyrimidin-6-one; (3b) : white solid; yield, 92%; mp. 196-7°C. (Found: C,81.93; H, 5.34; N, 8.30. $C_{23}H_{18}N_2O$ requires C, 81.65; H, 5.32; N,8.28). ν max: 1670 cm^{-1} (C=O).δ_H : 2.35 (s, 3H, CH_3);6.96-7.68 (m, 14H, arom) and 8.10 (s, 1H, olefinic). M^+ 338.

1-p-Chlorophenyl-2,5-diphenyl-1,6-dihydropyrimidin-6-one; (3c): white solid; yield, 86%;mp. 163-4°C. (Found: C, 74.00; H, 4.20; N, 7.81.

$C_{22}H_{15}ClN_2O$ requires C, 73.64, H, 4.18, N, 7.81). νmax: 1680 cm^{-1}. δ_H:7.02-7.70 (m, 14H, arom) and 8.03 (s, 1H, olefinic). M^+ 358.

1-p-Bromophenyl-2,5-diphenyl-1,6-dihydropyrimidin-6-one; (3d): white solid; yield, 84%; mp. 222-3°C. (Found: C, 66.03; H, 3.73; N, 6,93. $C_{22}H_{15}BrN_2O$ requires C, 65,50; H, 3.72, N, 6.94). νmax: 1680 cm^{-1} (C=O). δ_H: 7.00-7.68 (m, 14H, arom) and 8.03 (s, 1H, olefinic). M^+ 403.

1,5-Diphenyl-2-methylthio-1,6-dihydropyrimidin-6-one; (7a): white solid; yield, 95%; mp. 112°C. (Found: C,69.78; H, 4.78; N, 9.50. $C_{17}H_{14}N_2OS$ requires C, 69.38; H, 4.76; N, 9.52).νmax: 1675 cm^{-1} (C=O).δ_H: 2.40 (s, 3H,-SCH_3); 7.20-7.70 (m, 10H,arom) and 8.01 (s, 1H, olefinic). M^+ 294.

5-Phenyl-2-methylthio-1-p-tolyl-1,6-dihydropyrimidin-6-one; (7b):white solid; yield, 95%; mp. 168°C. (Found: C, 70.21; H, 5.22; N, 9.12. $C_{18}H_{16}N_2OS$ requires C, 70.12; H, 5.19; N, 9.09).νmax: 1680 cm^{-1} (C=O). δ_H: 2.40 (s, 3H, -SCH_3); 7.06-7.40 (m, 9H, arom) and 7.98 (s,1H, olefinic). M^+ 308.

1-p-Chlorophenyl-5-phenyl-2-methylthio-1,6-dihydropyrimidin-6-one; (7c): white solid; yield, 93%; mp. 194°C. (Found: C,62.98; H, 3.97; N, 8.57. $C_{17}H_{13}ClN_2OS$ requires C, 62.10; H, 3.95; N, 8.52).νmax: 1670 cm^{-1} (C=O). δ_H: 2.42 (s, 3H, -SCH_3); 7.16-7.63 (m, 9H, arom) and 8.03 (s,1H, olefinic). M^+ 328.

1-p-Methoxyphenyl-2-methylthio-5-phenyl-1,6-dihydropyrimidin-6-one; (7d): white solid; yield, 90%; mp. 207°C. (Found: C, 66.60; H, 4.92; N, 8.64. $C_{18}H_{16}N_2O_2S$ requires C, 66.66; H,,4.93; N,8.64). νmax: 1660 cm^{-1} (C=O). δ_H: 2.43 (s, 3H, -SCH_3); 3.83 (s, 3H, -OCH_3); 6.96-7.30 (m,9H,arom) and 8.01 (s, 1H, olefinic). M^+ 324.

4-Morpholino-1,2,5-triphenyl-1,6-dihydropyrimidin-6-one; (11a): white solid; yield, 90%; mp. 199-200°C. (Found: C, 76.40; H, 5.65; N, 10.26. $C_{26}H_{23}N_3O_2$ requires C, 76.28; H, 5.62; N, 10.27). νmax: 1660 cm^{-1} (C=O). δ_H: 3.30-3.43 (t, 4H, -CH_2-N-CH_2-); 3.50-3.66 (t, 4H, -CH_2-O-CH_2-) and 7.13-7.60 (m, 15H, arom). M^+ 409.

4-Piperidino-1,2,5-triphenyl-1,6-dihydropyrimidin-6-one; (11b): white solid, yield, 90%; mp. 191°C. (Found: C, 79.31; H, 6.11; N, 10.34. $C_{27}H_{25}N_3O$ requires C,79.61; H, 6.14; N, 10.32). νmax: 1660 cm^{-1} (C=O). δ_H: 1.33-1.56 (m, 6H, -CH_2-CH_2-CH_2-); 3.20-3.43 (m, 4H, -CH_2-N-CH_2-) and 7.13-7.53 (m, 15H, arom). M^+ 407.

4-Pyrrolidino-1,2,5-triphenyl-1,6-dihydropyrimidin-6-one; (11c): white solid; yield, 90%; mp. 211°C. (Found: C, 80.04; H, 5.88; N, 10.72. $C_{26}H_{23}N_3O$ requires C, 79.39; H, 5.85; N, 10.69). νmax: 1670 cm^{-1} (C=O). δ_H: 1.60-1.80 (m, 4H, -CH_2-CH_2-); 3.16-3.30 (m, 4H, -CH_2-N-CH_2) and 7.13-7.43 (m, 15H, arom). M^+ 393.

4-Dimethylamino-1,2,5-triphenyl-1,6-dihydropyrimidin-6-one; (11d): white solid; yield, 92%; mp. 174-5°C. (Found: C, 78.51; H, 5.73; N, 11.46. $C_{24}H_{21}N_3O$ requires C, 78.47; H, 5.72; N, 11.47). νmax: 1660 cm^{-1} (C=O). δ_H: 2.85 (s, 3H, -$N(CH_3)_2$) and 7.10-7.50 (m, 15H, arom). M^+ 367.

2,5-Diphenyl-4-morpholino-1-p-tolyl-1,6-dihydropyrimidin-6-one; (11e): pale yellow solid; yield, 90%; mp. 214-5°C. (Found: C, 76.85; H, 5.94; N,9.94. $C_{27}H_{25}N_3O_2$ requires C, 76.60; H, 5.91; N, 9.93). νmax: 1660 cm^{-1} (C=O).δ_H:2.25 (s, 3H, $-CH_3$); 3.25-3.40 (t, 4H, $-CH_2-N-CH_2-$); 3.50-3.63 (t, 4H, $-CH_2-O-CH_2-$); 6.90-7.06 (m, 2H, arom) and 7.16-7.60 (m, 12H, arom). M^+ 423.

2,5-Diphenyl-4-piperidino-1-p-tolyl-1,6-dihydropyrimidin-6-one; (11f): white soid; yield, 92%; mp. 212-3°C. (Found: C, 79.46; H, 6.43; N, 9.98. $C_{28}H_{27}N_3O$ requires C, 79.81; H, 6.41; N, 9.98). νmax: 1660 cm^{-1} (C=O). δ_H: 1.40-1.60 (m, 6H, $-CH_2-CH_2-CH_2-$); 2.26 (s, 3H. $-CH_3$); 3.26-3.40 (m, 4H, $-CH_2-N-CH_2-$); 6.90-7.08 (m, 2H, arom) and 7.17-7.60 (m, 12H, arom). M^+ 421.

2,5-Diphenyl-4-pyrrolidino-1-p-tolyl-1,6-dihydropyrimidin-6-one; (11g): white solid; yield, 85%; mp. 208-10°C. (Found: C, 80.32; H,6.20; N, 10.33. $C_{27}H_{25}N_3O$ requires C, 79.61; H, 6.14; N, 10.32). νmax: 1660 cm^{-1} (C=O). δ_H: 1.60-1.80 (m, 4H, $-CH_2-CH_2-$); 2.23 (s, 3H, CH_{32}); 3.03-3.26 (m, 4H, $-CH_2-N-CH_2-$); 6.90-7.10 (m, 2H, arom) and 7.16-7.60 (m, 12H, arom) M^+ 407.

4-Dimethylamino-2,5-diphenyl-1-p-tolyl-1,6-dihydropyrimidin-6-one; (11h): white solid; yield, 91%; mp. 228°C. (Found: C,78.61; H, 6,06; N, 11.06. $C_{25}H_{23}N_3O$ reqires C, 78.74; H, 6.04; N, 11.02). νmax: 1660 cm^{-1} (C=O). δ_H: 2.23 (s, 3H, $-CH_3$); 2.85 (s, 6H, $-N(CH_3)_2$); 6.90-7.06 (m, 2H, arom) and 7.16-7.50 (m, 12H, arom). M^+ 381.

1-p-Chlorophenyl-2,5-diphenyl-4-morpholino-1,6-dihydropyrimidin-6-one;(11i) : white solid; yield, 92%; mp. 234°C. (Found: C, 70.00; H, 4.96; N, 9.49. $C_{26}H_{22}ClN_3O_2$ requires C, 70.35; H, 4.96; N, 9.47).νmax: 1670 cm^{-1} (C=O). δ_H: 3.23-3.36 (t, 4H, $-CH_2-N-CH_2-$); 3.46-3.60 (t,4H,$-CH_2-O-CH_2-$) and 6.96-7.50 (m, 14H, arom). M^+ 443.

1-p-Chlorophenyl-2,5-diphenyl-4-piperidino-1,6-dihydropyrimidine-6-one; (11j): white solid; yield, 90%; mp. 195°C. (Found: C, 73.81; H, 5.47; N,9.54. $C_{27}H_{24}ClN_3O$ requires C, 73.39; H,5.44; N, 9.51). νmax: 1660 cm^{-1} (C=O).δ_H: 1.36-1.56 (m, 6H, $-CH_2-CH_2-CH_2-$); 3.20-3.40 (m, 4H, $-CH_2-N-CH_2-$) and 7.00-7.53 (m, 14H, arom). M^+ 441.

1-p-Chlorophenyl-2,5-diphenyl-4-pyrrolidino-1,6-dihydropyrimidin-6-one; 11k): white solid; yield, 90%; mp. 218-20°C. (Found: C, 72.68; H, 5.17; N, 9.84. $C_{26}H_{22}ClN_3O$ requires C, 72.98; H, 5.15; N, 9.82). νmax: 1660 cm^{-1} (C=O).δ_H: 1.63-1.83 (m, 4H, $-CH_2-CH_2-$); 3.13-3.43 (m, 4H,$-CH_2-N-CH_2-$) and 7.00-7.50 (m, 14H, arom). M^+ 427.

1-p-Chlorophenyl-4-dimethylamino-2,5-diphenyl-1,6-dihydropyrimidin-6-one; 11l): white solid; yield, 92%; mp. 225°. (Found: C, 71.43; H, 4.98; N,10.44. $C_{24}H_{20}ClN_3O$ requires C, 71.73; H, 4.98; N, 10.46). νmax: 1660 cm^{-1}.δ_H: 2.86 (s, 6H, $-N(CH_3)_2$) and 7.06-7.50 (m, 14H, arom). M^+ 401.

Reactions of 1,3-Diaza-1,3-Butadienes (1, 5 and 12) with monochloroketene; General Procedure: A solution of chloroacetylchloride (6 mmole)

in dry methylenechloride (15 ml) was added dropwise over a period of 1h to an ice-water cooled solution of 1,3-diaza-1,3-butadiene (2 mmole) and triethylamime (6 mmole) in methylenechloride (25 ml).After the complete addition of acidchloride, the reaction mixture was stirred for a further period of 30 min at the same temperature. The workup of the reaction mixture,as described for monophenylketene, yielded the crude product which were purified by passing it through a silica gel column (1:4, ethylacetate:hexane).

5-Chloro-1,2-diphenyl-1,6-dihydropyrimidin-6-one; (**14a**): white solid; yield, 97%; mp. 227°. (C, 68.26; H, 3.90; N, 9.93. $C_{16}H_{11}ClN_2O$ requires C, 67.96; H,3.89; N, 9.91). ν max: 1670 cm^{-1} (C=O).δ_H: 7.23-7.60 (m, 8H, arom); 7.83-7.93 (m, 2H, arom) and 8.13 (s, 1H, olefinic). M^+ 282.

5-Chloro-2-phenyl-1-p-tolyl-1,6-dihydropyrimidin-6-one; (**14b**): white solid; yield, 97%; mp. 156-7°C. (Found: C, 69.02; H, 4.39; N, 9.41. $C_{17}H_{13}ClN_2O$ requires C, 68.80; H, 4.38; N, 9.44).ν max: 1670 cm^{-1} (C=O). δ_H: 2.43 (s, 3H, CH_3); 7.20-7.53 (m, 7H, arom); 7.80-7.93 (m, 2H, arom) and 8.18 (s, 1H, olefinic). M^+ 296.

5-Chloro-1-p-chlorophenyl-2-phenyl-1,6-dihydropyrimidin-6-one; (**14c**): grey white solid; yield, 96%; mp. 125°C. (Found: C, 60.59; H, 3.17; N, 8.83. $C_{16}H_{10}Cl_2N_2O$ requires C, 60.56; H, 3.15; N, 8.83).νmax: 1680 cm^{-1} (C=O ,).δ_H: 7.26-7.53 (m, 7H, arom); 7.70-7.90 (m, 2H, arom) and 8.10 (s, 1H, olefinic). M^+ 317.

1-p-Bromophenyl-5-chloro-2-phenyl-1,6-dihydropyrimidin-6-one; (**14d**):white solid; yield, 96%; mp. 125°C. (Found: C, 53.32; H, 2.80; N.7.76. $C_{16}H_{10}BrClN_2O$ requires C, 53.18; H, 2.77; N, 7.74).νmax: 1670 cm^{-1} (C=O) δ_H: 7.20-7.53 (m, 7H, arom); 7.70-7.90 (m, 2H, arom) and 8.12 (s,1H, olefinic). M^+ 361.

5-Chloro-2-methylthio-1-phenyl-1,6-dihydropyrimidin-6-one; (**15a**):white solid; yield, 98%; mp. 147-8°C. (Found: C, 52.39; H, 3.54; N, 11.08. $C_{11}H_9ClN_2OS$ requires C, 52.27; H, 3.56; N, 11.08).νmax: 1680 cm^{-1} (C=O). δ_H: 2.43 (s, 3H, SCH_3); 7.20-7.36 (m, 3H, arom); 7.50-7.60 (m, 2H, arom) and 8.03 (s, 1H, olefinic). M^+ 252.

5-Chloro-2-methylthio-1-p-tolyl-1,6-dihydropyrimidin; (**15b**):white solid; yield, 97%; mp. 174-5°C. (Found: C, 54.11; H, 4.16; N, 10.56.$C_{12}H_{11}ClN_2OS$ requires C, 54.03; H, 4.13; N, 10.56).ν max: 1685 cm^{-1} (C=O).δ_H: 2.40 (s, 3H, $-CH_3$); 2.45 (s, 3H,- SCH_3); 7.08-7.18 (m, 2H, arom); 7.36-7.43 (m, 2H, arom) and 8.03 (s, 1H, olefinic). M^+ 266.

5-Chloro-1-p-chlorophenyl-2-methylthio-1,6-dihydropyrimidin-6-one; (**15c**): white solid; yield, 93%; mp. 187°C. (Found: C,46.23; H, 2.78; N, 9.76. $C_{11}H_8Cl_2N_2OS$ requires C,45.99; H, 2.79; N, 9.75).ν max: 1680 cm^{-1} (C=O) δ_H: 2.33 (s, 3H, SCH_3); 7.03-7.16 (m, 2H, arom); 7.33-7.50 (m, 2H, arom) and 7.93 (s, 1H, olefinic). M^+ 287.

5-Chloro-2-methylthio-1-p-methoxyphenyl-1,6-dihydropyrimidin-6-one; (**15d**): white solid; yield, 96%; mp. 164-5°C. (Found: C, 50.95; H, 3.85; N, 9.92. $C_{12}H_{11}ClN_2O_2S$ requires C, 50.97; H,3.89; N, 9.91).ν max: 1680 cm^{-1} (C=O).

δ_H: 2.40 (s, 3H,-SCH_3); 3.86 (s, 3H,-OCH_3); 6.96-7.08 (m, 2H, arom); 7.13-7.30 (m, 2H, arom) and 8.01 (s, 1H, olefinic). M^+ 282.

5-Chloro-1,2-diphenyl-4-morpholino-1,6-dihydropyrimidin-6-one; (**16a**): white solid; yield, 93%; mp. 222-3°C. (Found: C, 65.42; H, 4.94; N, 11.43. $C_{20}H_{18}ClN_3O_2$ requires C, 65.31; H, 4.90; N, 11.43). ν_{max}: 1680 cm^{-1} (C=O). δ_H: 3.66-3.92 (m, 8H, CH_2, morpholine) and 7.15-7.50 (m, 10H, arom). M^+ 367.

5-Chloro-1,2-diphenyl-4-piperidino-1,6-dihydropyrimidin-6-one; (**16b**): grey white solid; yield, 93%; mp. 200-201°C. (Found: C, 69.02; H, 5.49; N, 11.50. $C_{21}H_{20}ClN_3O$ requires C, 68.95; H, 5.47; N, 11.49). ν_{max}: 1670 cm^{-1} (C=O). δ_H: 1.60-1.76 (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-1,2-diphenyl-4-pyrrolidino-1,6-dihydropyrimidin-6-one; (**16c**): white solid; yield, 86%; mp. 210-12°C. (Found: C, 68.43; H, 5.16; N, 11.93. $C_{20}H_{18}ClN_3O$ reqiures 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-N-CH_2-) and 6.93-7.42 (m, 10H, arom). M^+ 351.

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