Available online at www.sciencedirect.com
SCIENCE DIRECT®
Tetrahedron 60 (2004) 4315–4324
Tetrahedron

Synthesis of novel heterocyclic fused 1,3-diazabuta-1,3-dienes and accompanying rearrangements in their cycloaddition reactions with ketenes: synthesis of heterocyclic fused pyrimidinone derivatives

S. Jayakumar, Parvesh Singh and Mohinder P. Mahajan*

Department of Applied Chemistry, Guru Nanak Dev University, Amritsar 143005, India

Received 17 April 2003; revised 19 January 2004; accepted 12 February 2004

Abstract—The reactions of 1,3-diazabuta-1,3-dienes **1** with 2-aminothiophenol have been shown to result in excellent yields of *N*-benzothiazol-2-yl-*N'*-aryl benzamidines **2**. Their regioselective [4+2] cycloadditions with various ketenes are shown to yield novel benzothiazolo pyrimidinones **4**. A similar and convenient protocol for the synthesis of bisthiosubstituted 1,3-diazabuta-1,3-dienes **8** and **9** and interesting rearrangements accompanying their [4+2] cycloadditions with a number of ketenes are described.

1. Introduction

Nitrogen-containing compounds are widely distributed in nature and include many biologically important molecules. The synthesis of nitrogen-containing heterocycles has attracted considerable attention due largely to their importance as building blocks for many therapeutically useful materials and the wide range of potential biological activity of both synthetic and naturally occurring derivatives. The hetero-Diels–Alder methodology employing azadienes represents a straightforward and an efficient approach to nitrogen-containing six membered heterocycles. Extensive studies have been carried out on this [4+2] cycloaddition process and the rapid and rigorous development in this area has led to several reviews highlighting the utility of azadienes as readily available templates in the synthesis of novel heterocycles and complex natural products.[1] Dienes containing two nitrogen atoms have attracted attention of chemists in recent years because of their importance in natural product synthesis.[1] In the last decade there have been numerous reports concerning the participation of 1,3-diazabuta-1,3-dienes as 4π components in cycloaddition reactions with isocyanides,[2] oxazolines,[3] enamines,[4] alkynes[5] etc. On the other hand the reactions of ketenes with 1,3-diaza-1,3-butadienes are reported to undergo [4+2] as well [2+2] cycloadditions. A vast prevalence of such reported cycloadditions correspond to [4+2] cycloaddition type in which 1,3-diazabuta-1,3-dienes add as 4π components across C=C bond of the ketenes.[6] Over the years, we have been actively involved in the synthesis and cycloaddition reactions of various functionalized 1,3-diazabuta-1,3-dienes and have developed a simple protocol for the synthesis of stable acyclic 1,3-diazadienes.[7] It is noticed that rearrangements accompany the [4+2] cycloaddition reactions of 4-tertiaryamino-4-methylthio-1,3-diazabuta-1,3-dienes, 4-(*N*-arylamino)-4-methylthio-1,3-diazabuta-1,3-dienes and 4-(*N*-arylamino)-4-tertiaryamino-1,3-diazabuta-1,3-dienes with various ketenes.[8] In view of these observations and our interest in the synthesis of new diazadienes, it was considered worthwhile to synthesise and examine the reactions of heterocyclic fused 1,3-diazabuta-1,3-dienes with various ketenes.

2. Results and discussion

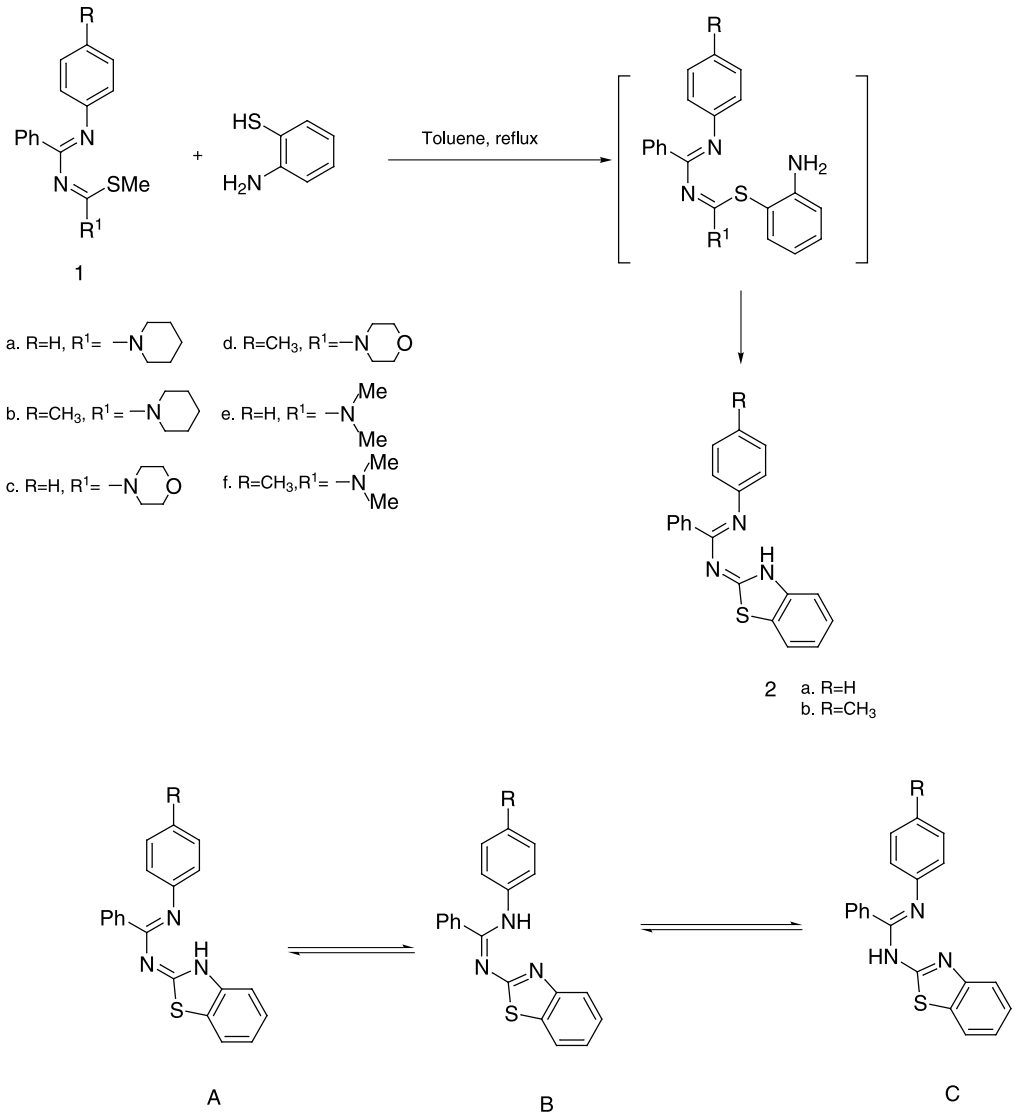
Thus, the treatment of 4-tertiaryamino-4-methylthio-1,3-diazabuta-1,3-dienes **1** with 2-aminothiophenol, in refluxing toluene resulted in good yields of the desired benzothiazolo fused 1,3-diazabuta-1,3-dienes **2**. The structural assignments to the diazadienes **2** were based on spectral and analytical evidence. The detailed spectral features of the 1,3-dienes **2** are described in the experimental section, however; only the salient features are mentioned here. The 1,3-diene **2b**, for example, characterized as *N*-benzothiazol-2-yl-*N'*-*p*-tolyl-benzamidine, was analysed for $C_{21}H_{17}N_3S$ and showed a molecular ion peak at *m*/*z* 343. Its ^{1}H NMR spectrum showed the absence of the protons corresponding

Keywords: 1,3-Diazabuta-1,3-dienes; Pyrimidinones; Ketenes.
* Corresponding author. Tel.: +91-183-2258802-09x3320; fax: +91-183-2258819-20; e-mail address: mohinderpmahajan@angelfire.com

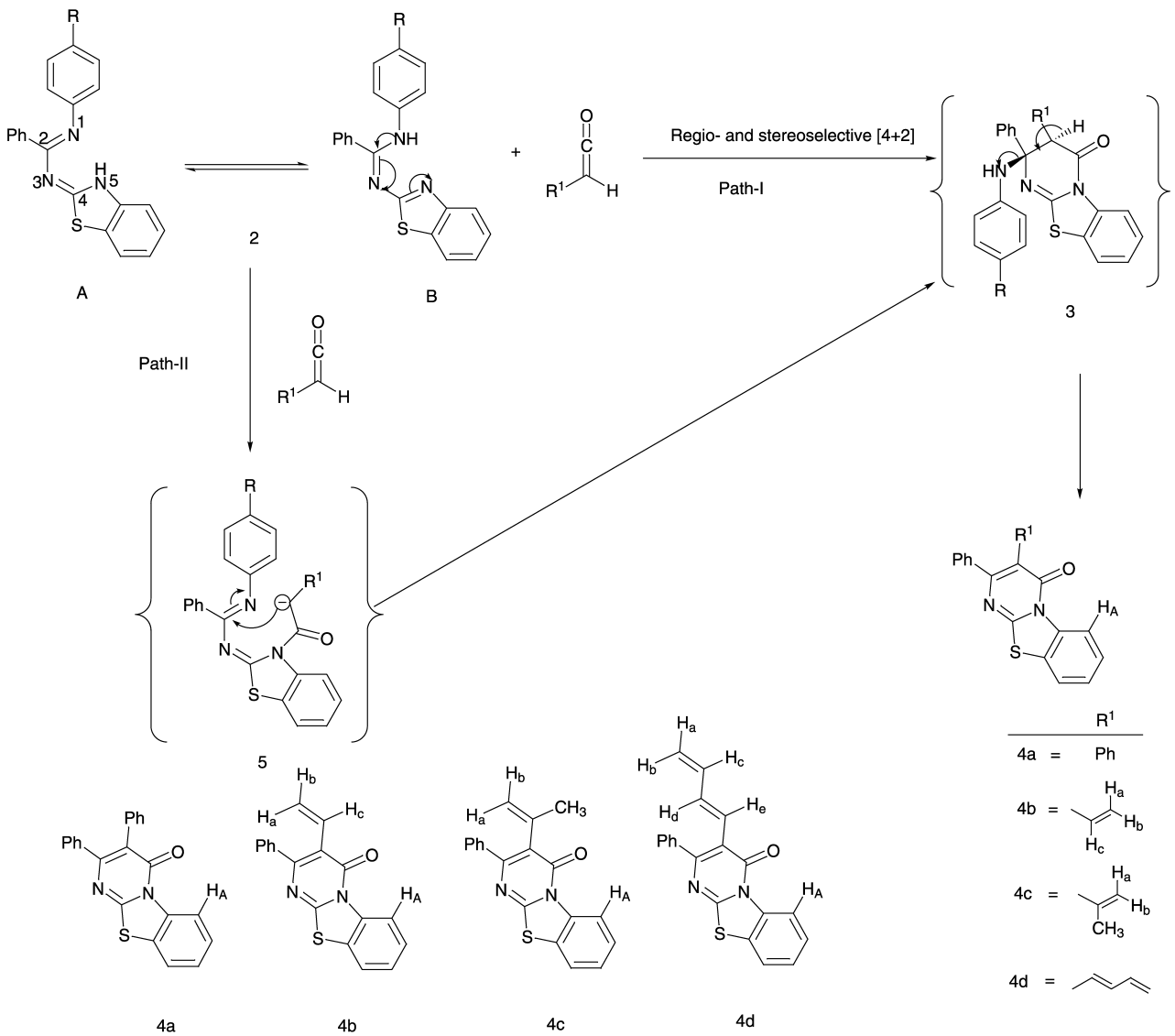
0040–4020/$ - see front matter © 2004 Published by Elsevier Ltd.
doi:10.1016/j.tet.2004.02.023

to the secondary amine and the methylthio functions and the presence of a singlet at δ 2.29 for a methyl group attached to an aromatic ring and a broad singlet appeared at δ 12.62 for an exchangeable N–H proton. The signals in its ^{13}C NMR spectrum are also in agreement with the assigned structure. The formation of *N*-aryl-*N*′-(2-benzothiazolyl)-benzamidines **2** in these reactions may be explained by the initial displacement of methylmercaptan, by attack of the sulphur of aminothiophenol on C-4 of 1,3-diazabutadiene, followed by the displacement of secondary amine by the nitrogen of aromatic amine group via an addition–elimination mechanism (Scheme 1).

1,3-Diazabutadienes **2** probably exist in a number of tautomeric forms (**A**, **B** and **C**). In order to have an idea about the predominant tautomeric form in this mixture and to examine the regiochemical aspects of their cycloadditions, we have examined their reactions with ketenes. Thus, the reactions of 1,3-diazabutadienes **2** with monophenyl, vinyl-, and isopropenyl ketenes, generated in situ from phenylacetyl chloride, crotonyl chloride, and 3,3-dimethylacryloyl chloride, respectively, in the presence of triethylamine in methylene chloride, resulted in good yields of the products which were characterized as novel benzothiazolo fused pyrimidinones **4**. The detailed spectral features of these pyrimidinones are discussed in the experimental section while the salient features are mentioned here. For example, pyrimidinone **4b**, analyzed for $C_{18}H_{12}N_2OS$ showed a molecular ion peak at *m*/*z* 304 in its mass spectrum. ^{1}H NMR spectrum attests to the presence of vinylic protons and loss of the aryl amine attached to the phenyl-bearing carbon. The aromatic proton H_A in pyrimidinones **4** appeared unexpectedly downfield, around δ 9.12–9.15 as doublet of a doublet, probably due to the deshielding effect of the carbonyl group. The signals in the ^{13}C NMR spectrum were also in agreement with the assigned structure. The probable mechanisms for the formation of pyrimidinones **4** are depicted in Scheme 2. It is assumed that the stereoselective [4+2] cycloaddition of tautomer **2B** with ketene forms an intermediate **3**, which on elimination of the aromatic amine leads to the desired benzothiazolopyrimidinone **4** (Path I). The formation of **4** may also be explained by an initial nucleophilic attack of the N-5 of **2A** on ketene carbonyl to form an intermediate **5**, its



Scheme 1.



Scheme 2.

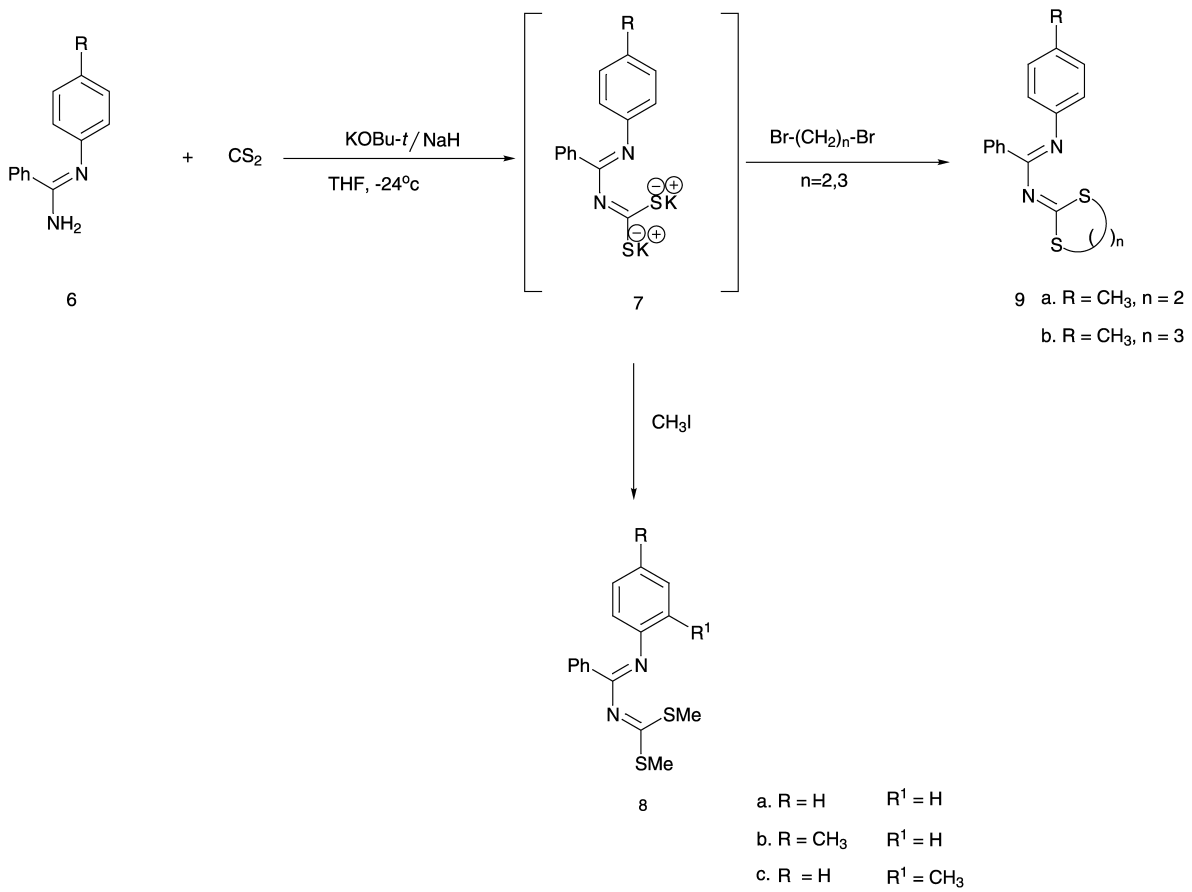
cyclisation to **3** and usual elimination of aromatic amine (Path II). The tautomeric form **2B** appears to be more stable and hence preferred over the form **2A** due to the higher stabilization imparted by its aromatic benzothiazole component. Thus, the regioselective and stereoselective [4+2] cycloaddition (Path I) similar to one reported earlier,[8e] appears to be a preferred route for the formation of fused pyrimidinones **4** (Scheme 2).

Recent disclosure from our laboratory has shown remarkable substituent dependent tandem [1,5]H, [1,3]NHPh and [1,5]NHPh sigmatropic shifts accompanying [4+2] cycloaddition reactions of 4-N-arylamino substituted 1,3-diazabuta-1,3-dienes with butadienylketene.[9] In continuation of these studies, we have examined the reactions of benzothiazole-incorporated 1,3-diazabuta-1,3-dienes **2** with butadienylketene. The treatment of benzothiazolyl incorporated 1,3-diazabuta-1,3-dienes **2** with butadienylketene, generated in situ, was found to result in the exclusive formation of 5-butadienyl pyrimidinone **4d**, while no product corresponding to the rearrangement observed earlier could be isolated. The pyrimidinone **4d** was characterized on the basis of analytical data and spectral evidence. It appears that the more stable tautomeric form **2B** of 1,3-diazabuta-1,3-dienes **2**, undergoes regio/stereoselective [4+2] cycloaddition reaction with butadienylketene to form an intermediate **3** which on elimination of aromatic amine results in the formation of pyrimidinone **4d**. The alternative mechanistic possibility (Path II) involving initial nucleophilic attack, followed by cyclisation and elimination of aromatic amine, is less likely as this would have resulted in rearranged pyrimidinone derivatives as observed in reactions of *N*-arylamino-1,3-diazabuta-1,3-diene with butadienylketene.[9b] A simpler and more acceptable explanation for the exclusive formation of pyrimidinones **4d** in these reactions assumes an additional nucleophilic push from sulfur in intermediate **3**, which shortens its life time and favours the elimination of arylamine over rearrangement involving [1,5]H sigmatropic shift followed by a [1,5]NH-Ph shift.

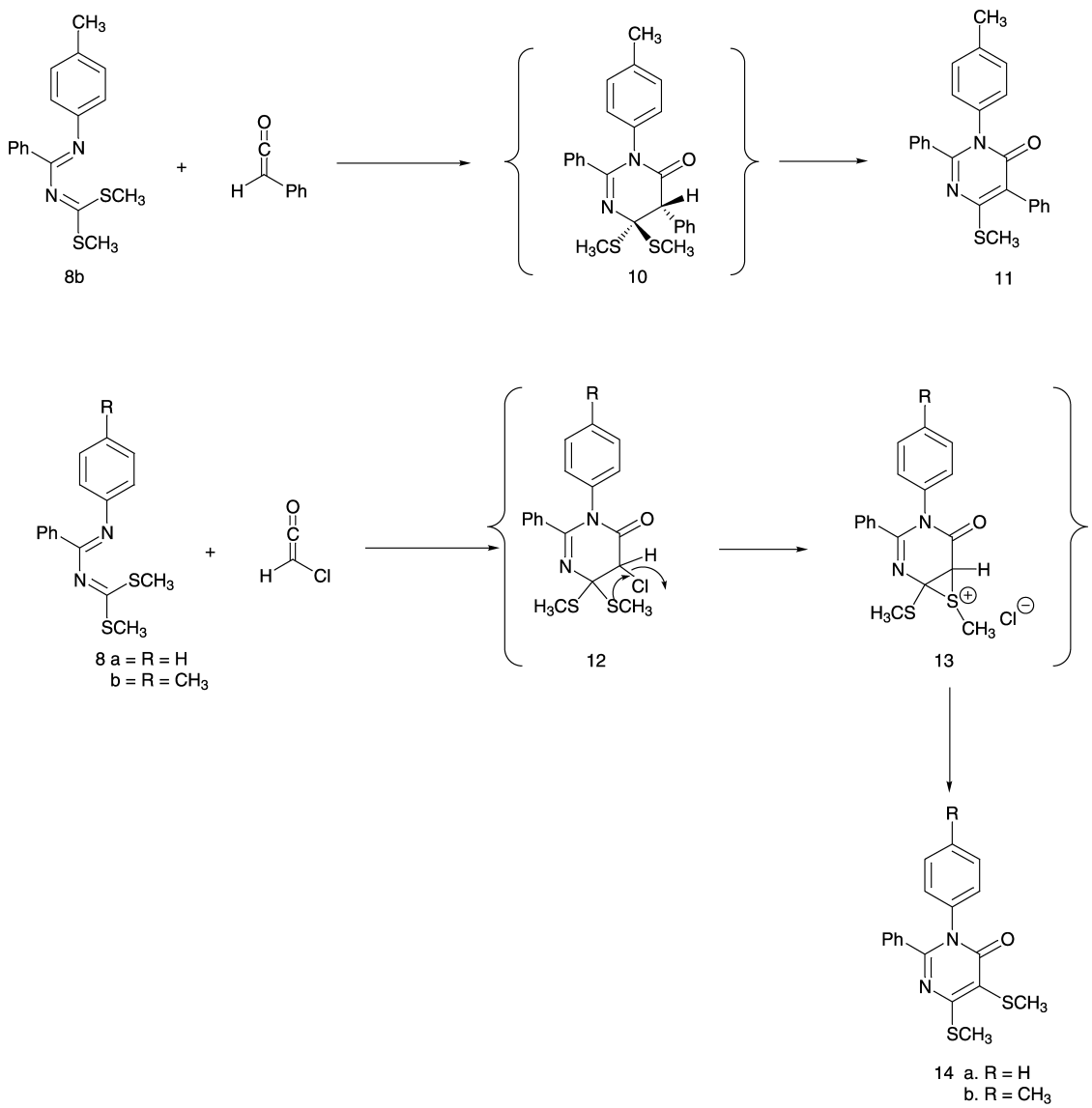
Inspired by the highly stereo- and regioselective cycloadditions observed in these reactions, it was considered worthwhile to extend these studies to other similar

heterocyclic fused 1,3-diazabuta-1,3-dienes. Thus, simple and elegant protocols for the synthesis of 4,4-bisthioalkyl substituted 1,3-diazabuta-1,3-dienes have been developed (Scheme 3). The treatment of benzamidines **6** with carbon disulfide in the presence of potassium-*tert*-butoxide/sodium hydride and subsequent treatment of resulting intermediate **7** with methyl iodide, 1,3-dibromopropane and 1,2-dibromoethane resulted in good yields of 4,4-bismethylthio-1,3-diazabuta-1,3-dienes **8a**–**c**, 1-aryl-2-phenyl-4[2-(1,3-dithiolanyl)]-1,3-diazabuta-1,3-diene **9a** and 1-aryl-2-phenyl-4[2-(1,3-dithianyl)]-1,3-diazabuta-1,3-diene **9b** derivatives, respectively. The structural assignments to the product **8** and **9** were based on analytical data and spectral evidences. The compound **9b**, for example, exhibited a molecular ion peak at *m*/*z* 326. Its ^{1}H NMR spectrum exhibited a multiplet at δ 2.03 (2H) for $-CH_2-$ group, a singlet at δ 2.31 for $-CH_3$ and a multiplet at δ 2.91 for four methylene protons attached to sulfur, in addition to the aromatic protons. The assigned structure was further corroborated by its ^{13}C spectrum which showed a peak at δ 20.8 for $-CH_2-$, a peak at δ 21.6 for $-CH_3$ and a peak at δ 29.7 corresponding to two $-SCH_2$ carbons.

The 1,3-diazabuta-1,3-dienes, **8**, **9a** and **9b** (Schemes 4 and 5) obtained were treated with various ketenes, generated in situ from the corresponding acid chlorides. The treatment of **8b** with phenylacetyl chloride in presence of dry triethylamine resulted in the isolation of 2,5-diphenyl-6-methylthio-3-(*p*-tolyl)-pyrimidin-4(3*H*)-one **11** presumably via the initial formation of pyrimidinone **10** as an intermediate. However, [1,2]-methylthio shift, similar to the one reported earlier,[8c] have been shown to accompany the [4+2] cycloadditions in reactions of **8** with chloroketene. These reactions resulted in the formation of 2-phenyl-3-aryl-5,6-bismethylthio-pyrimidin-4(3*H*)-one **14** and probably involve an initial formation of an intermediate **12**, its subsequent transformation to episulfonium intermediate **13** before rearrangement to **14** (Scheme 4). On the other hand, the reactions of 1,3-diazabuta-1,3-dienes **9** with chloroketene resulted in a mixture (≈1:1) of pyrimidinones **19** and **20** (Scheme 5). The separation of this mixture of **19** and **20** with very close R_f values was accomplished by careful silica gel column chromatography with natural loss of yields. The pyrimidinones **19** and **20** were characterized on the basis of their analytical and spectral data. Compound **19b** (Scheme 5), for example, analyzed for $C_{22}H_{20}N_2S_2O_2Cl_2$ exhibited in its mass spectrum a molecular ion peak at *m*/*z* 479 (M^+). Its IR spectrum showed a sharp peak at 1678 cm^{-1}, assigned to the α,β-unsaturated carbonyl group. Its ^{1}H NMR spectrum exhibited a multiplet at δ 2.07 (2H) for the $-CH_2-$ group, singlet at δ 2.31 (3H) for the aromatic substituted methyl group, a triplet (J=7.0 Hz) at δ 3.06 for the methylene protons attached to sulfur, a triplet (J=7.0 Hz) at δ 3.26 for methylene attached to another sulfur and a singlet at δ 4.12 for the methylene attached to chlorine, in addition to the aromatic protons. Its ^{13}C NMR spectrum was also in agreement with the assigned structure. The pyrimidinone **20b** on the other hand was analyzed for $C_{20}H_{18}N_2OS_2$ and exhibited in its mass spectrum a molecular ion peak at *m*/*z* 366 (M^+). Its IR spectrum



Scheme 3.

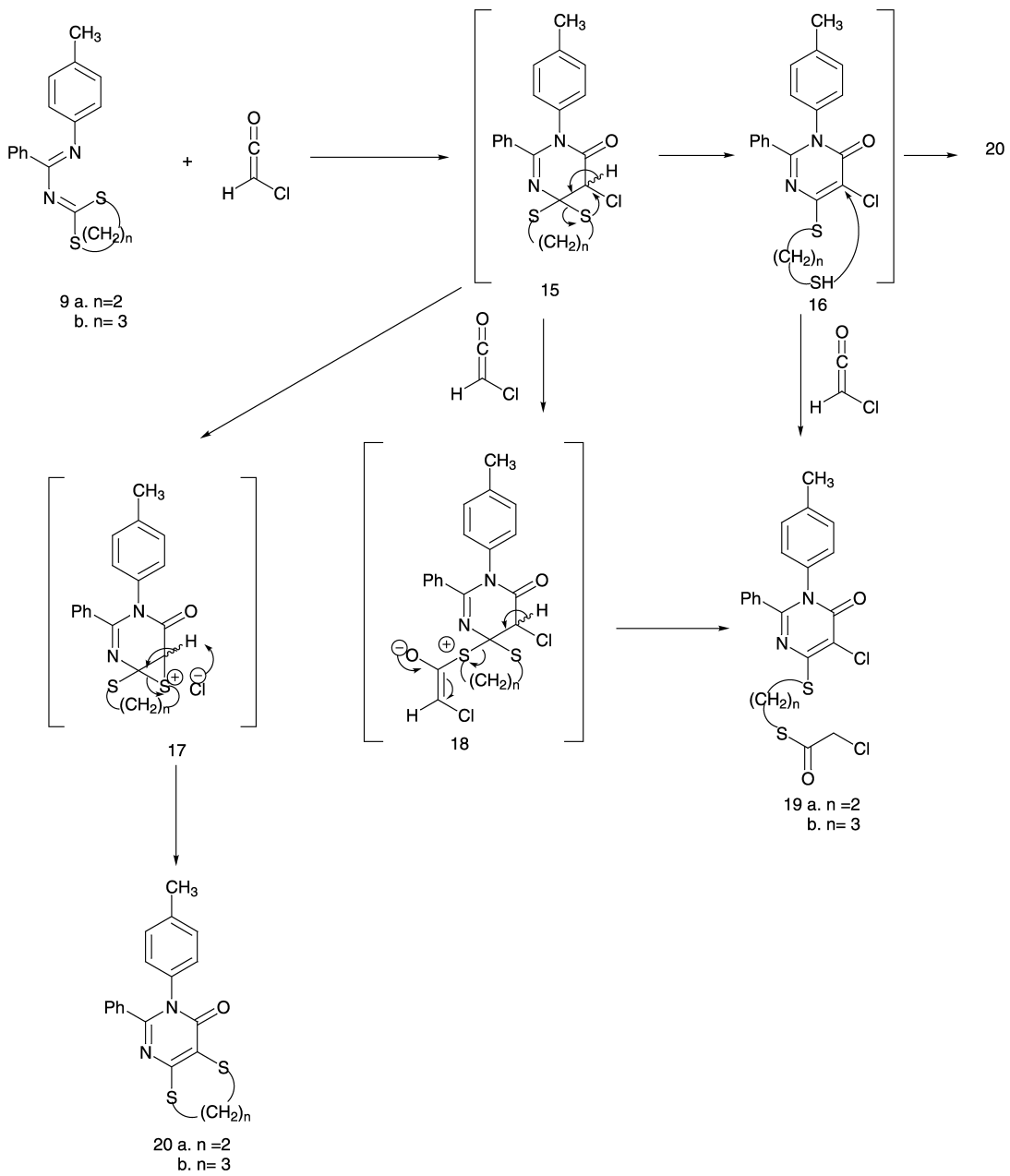


Scheme 4.

showed intense absorption at 1672 cm^{-1} due to the α,β-unsaturated carbonyl group. Its ^1H NMR spectrum exhibited a multiplet at δ 2.14–2.22 (2H) corresponding to the methylene, a singlet at δ 2.28 (3H) corresponding to the aromatic substituted $-CH_3$ group, a triplet (J=6.0 Hz) at δ 3.59 for the methylene attached to sulfur, another triplet (J=6.0 Hz) at δ 3.69 for the for the second $-S-CH_2-$ group, in addition to the aromatic protons. The assigned structure was further corroborated by signals present in its ^{13}C NMR spectrum which showed a signal at δ 159.7 indicating the presence of a carbonyl carbon and two signals at δ 27.6 and 30.1 corresponding to two methylene carbons.

The plausible mechanism for the formation of pyrimidinones **19** and **20** is depicted in Scheme 5. In this scheme it is believed that 1,3-diazabuta-1,3-diene **9** undergoes [4+2] cycloaddition reaction with chloroketene resulting in initial formation of intermediate **15** which leads to intermediate **16**. The nucleophilic reaction of the thiol of intermediate **16** with either chloroketene or chloroaceteyl chloride results in the formation of pyrimidinones **19**. The pyrimidinones **19** may also be the result of proton assisted sulfur ring opening of intermediate **18**, which in turn is obtained by the reaction of the second molecule of ketene at the sulfur of intermediate **15**. The formation of pyrimidinones **20** from intermediate **15** probably proceeds through a rearrangement involving an episulfonium intermediate **17**, wherein dehydrohalogenation is accompanied by a 1,2-alkylthio shift. The formation of pyrimidinones **20** by dehydrohalogenation of intermediate **16** may be ruled out on the basis of arguments eluded to, earlier reported similar reactions.[8c]

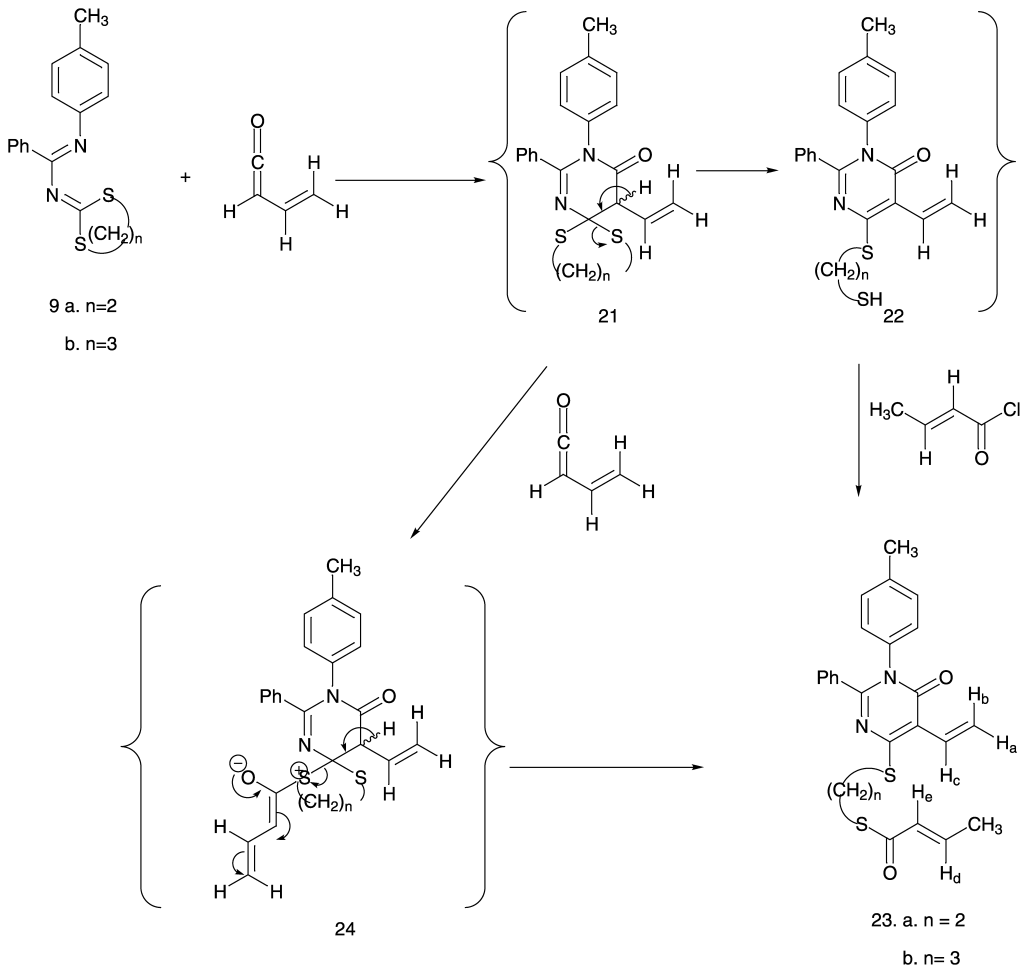
Similarly, the reactions of 1-(*p*-tolyl)-2-phenyl-4-[2-(1,3-dithiolanyl)]-1,3-diazabuta-1,3-diene **9a** and 1-(*p*-tolyl)-2-phenyl-4-[2-(1,3-dithianyl)]-1,3-diazabuta-1,3-diene **9b** with vinyl ketene, generated in situ from crotonyl chloride and triethylamine in dry methylene chloride, resulted in the isolation of products which were characterized as pyrimidinones **23** on the basis of analytical data and spectral evidence. For example, 2-phenyl-3-(*p*-tolyl)-5-vinyl-6-{8-[(*E*)-5,8-dithiaoct-2-ene-4-one]}-pyrimidin-4(3*H*)-one **23a** (Scheme 6) analyzed for $C_{25}H_{24}N_2O_2S_2$ showed by EIMS a



Scheme 5.

molecular ion peak at *m/z* 448. Its IR spectrum showed a strong absorption at 1669 cm^{-1} due to α,β-unsaturated carbonyl group. Its ^1H NMR spectrum showed a doublet of doublet (J=6.8, 1.6 Hz) at δ 1.68 for the isopropenyl $-CH_3$ group, a singlet at δ 2.30 for the aromatic substituted $-CH_3$ group, two multiplets at δ 3.26–3.34 (2H) and δ 3.40–3.47 (2H) for the protons of two methylene groups attached to sulfur, a doublet of doublet (J=11.4, 2.6 Hz) at δ 5.56 (H_a), a doublet of a doublet with fine splitting (J=15.3, 1.6 Hz) at δ 6.12 (H_e), a doublet of a doublet (J=17.6, 2.6 Hz) at δ 6.54 (H_b), a doublet of doublet (J=17.6, 11.4 Hz) at δ 6.73 (H_c), a doublet of a quartet (J=15.4, 6.9 Hz) at δ 6.90 (H_d) in addition to the aromatic protons. The assigned structure was further corroborated by its ^{13}C NMR spectrum. The plausible mechanism for the formation of pyrimidinones **23** is depicted in Scheme 6 and is similar to the one proposed for the formation of pyrimidinones **19**. It is believed that 1,3-diazabuta-1,3-diene **9** undergoes an initial [4+2] cycloaddition reaction with vinyl ketene leading to the formation of an intermediate **21**, which isomerises to pyrimidinones **22** and its reactions with crotonyl chloride results in the formation of desired pyrimidinones **23**. It is also possible that the sulfur of intermediate **21** attacks the carbonyl carbon of another molecule of ketene to form an intermediate **24** which undergoes proton assisted ring opening to form the pyrimidinones **23** (Scheme 6).

Thus, a conceptually attractive strategy has been developed for the synthesis of novel heterocyclic fused 1,3-diazabuta-1,3-dienes, which have been shown to undergo interesting cycloaddition with various ketenes. Additionally, bisthio substituted 1,3-diazabuta-1,3-dienes have also been formed. Depending on the ketene used, this class of dienes leads to a series of structurally distinct



Scheme 6.

pyrimidinones, some of which are the result of an interesting rearrangement.

3. Experimental

3.1. General

Melting points were determined by open capillary using Veego Precision Digital Melting Point apparatus (MP-D) and are uncorrected. IR spectra were recorded on a Shimadzu D-8001 spectrophotometer. ^{1}H NMR spectra were recorded in deuterochloroform with Bruker AC-E 200 (200 MHz) and AC-E 300 (300 MHz) spectrometers using TMS as internal standard. Chemical shift values are expressed as ppm downfield from TMS and *J* values are in Hz. Splitting patterns are indicated as s: singlet, d: doublet, t: triplet, m: multiplet, q: quartet and br: broad peak. ^{13}C NMR spectra were also recorded on a Bruker AC-200E (50.4 MHz) or Bruker AC-300E (75.0 MHz) spectrometers in deuterochloroform using TMS as internal standard. Mass spectra were recorded on Shimadzu GCMS-QP-2000 mass spectrometer. Elemental analyses were performed on Heraus CHN-O-Rapid Elemental Analyzer. Column chromatography was performed on a silica gel (60–120) mesh or Harrison Research Chromatotron using 2 mm plates (Silica gel 60 PF_{254}). THF/Diethyl ether were dried over sodium benzophenone ketyl and distilled under nitrogen. Dichloromethane dried over di-phosphorous pentoxide and stored over molecular sieves (4A).

3.2. Starting materials

Benzamidines,[10] 1-aryl-2-phenyl-4-thiomethyl-4-tertiary-amino-1,3-diazabuta-1,3-dienes **1**[7] were prepared by reported methods. Phenyl-, propenyl-, crotonoyl-, 3,3-dimethylacryl-, chlorides and sorbyl chloride[11] where prepared from the corresponding acid and thionyl chloride.

3.3. General method for the preparation of *N*-aryl-*N*′-(2-benzothiazol)-benzamidine 2

A solution of 1-aryl-2-phenyl-4-thiomethyl-4-tertiary amino-1,3-diazabuta-1,3-diene **1** (10 mmol) and 2-amino-thiophenol (12 mmol) in dry toluene (30 mL) was refluxed for a period of 6–7 h. After the completion of reaction (tlc), solvent was removed under reduced pressure and the crude product was purified through silica gel column chromatography and recrystallized using hexane–chloroform mixture (5:1).

3.3.1. *N*-Benzothiazol-2-yl-*N*′-phenyl-benzamidine 2a. Yellow crystalline solid, yield: 82%; mp 134–135 °C. Anal. Calcd for $C_{20}H_{15}N_3S$: C, 79.92; H, 4.59; N, 12.76.

Found: C, 80.05; H, 4.57; N, 12.80%. IR (KBr) ν_{max}: 1651, 1589 cm^{-1}. δ_H (200 MHz, $CDCl_3$): 6.96 (d, J=7.7 Hz, 2H, ArH); 7.05–7.42 (m, 8H, ArH); 7.58 (d, J=7.9 Hz, 2H, ArH); 7.76 (dd, J=7.9, 3.7 Hz, 2H, ArH); 12.87 (s, 1H, NH, D_2O exchangeable). δ_C (50.4 MHz, $CDCl_3$): 121.0, 121.2, 123.8, 124.2, 125.2, 125.8, 128.2, 129.0, 129.7, 130.3, 132.7, 134.8, 139.2, 151.0, 159.8, 173.2. m/z: 329 (M^+).

3.3.2. *N*-Benzothiazol-2-yl-*N'*-*p*-tolyl-benzamidine 2b. Pale yellow crystalline solid, yield: 79%; mp 97–98 °C. Anal. Calcd for $C_{21}H_{17}N_3S$: C, 73.44; H, 4.99; N, 12.23. Found: C, 73.45; H, 4.97; N, 12.20%. IR (KBr) ν_{max}: 1652, 1589, 1437, 1385 cm^{-1}. δ_H (200 MHz, $CDCl_3$): 2.29 (s, 3H, $-CH_3$); 6.84 (d, J=8.1 Hz, 2H, ArH); 7.00 (d, J=8.1 Hz, 2H, ArH); 7.23–7.33 (m, 5H, ArH); 7.55 (dd, J=7.5, 1.4 Hz, 2H, ArH); 7.71–7.76 (m, 2H, ArH); 12.62 (br, 1H, NH, D_2O exchangeable). δ_C (50.4 MHz, $CDCl_3$): 20.9 ($-CH_3$) 121.0, 121.1, 123.7, 124.1, 125.7, 128.1, 129.5, 129.6, 130.1, 132.8, 134.8, 137.0, 151.0, 159.8, 173.2. m/z: 343 (M^+).

3.4. Reactions of 1,3-diazabutadienes 2 with phenyl-/vinyl-/isopropenyl-/butadienyl-ketenes

General procedure. To a well stirred solution of 1,3-diazabuta-1,3-diene **2** (10 mmol) and triethylamine (40 mmol) in dry methylene chloride (30 mL) was added dropwise a solution of phenylacetyl chloride/crotonyl chloride/3,3-dimethylacryloyl chloride/sorbyl chloride (20 mmol) in dry methylene chloride (30 mL) over a period of 1 h at 0 °C. After completion of the reaction (tlc), the reaction mixture was first washed with saturated sodium bicarbonate solution (2×25 mL) and water (5×50 mL) and the organic layer dried over anhydrous sodium sulfate. Removal of solvent under reduced pressure yielded the crude product, which was purified by silica gel column chromatography using a mixture of ethyl acetate and hexane (1:10, V/V).

3.4.1. 2,3-Diphenyl-9-thia-1,4a-diaza-fluoren-4-one 4a. White crystalline solid, yield: 73%; mp 132–133 °C. Anal. Calcd for $C_{22}H_{14}N_2OS$: C, 74.51; H, 3.91; N, 7.91. Found: C, 74.45; H, 3.91; N, 7.90%. IR (KBr) ν_{max}: 1662, 1526, 1454, 1861 cm^{-1}. δ_H (300 MHz): 7.19–7.41 (m, 8H, ArH); 7.48–7.56 (m, 2H, ArH); 7.70–7.73 (m, 3H, ArH); 9.12–9.15 (dd, J=9.2, 1.8 Hz, 1H, H_A). δ_C (50.4 MHz, $CDCl_3$): 119.5, 120.2, 121.9, 124.7, 127.0, 127.1, 127.6, 127.9, 128.3, 129.0, 129.7, 131.3, 133.7, 136.4, 137.9, 156.3, 159.6, 161.6. m/z: 354 (M^+).

3.4.2. 2-Phenyl-3-vinyl-9-thia-1,4a-diaza-fluoren-4-one 4b. Colourless solid, yield: 78%; mp 141–142 °C. Anal. Calcd for $C_{18}H_{12}N_2OS$: C, 71.12; H, 3.94; N, 9.21. Found: C, 71.10; H, 3.95; N, 9.17%. IR (KBr) ν_{max}: 1679, 1549, 1504 cm^{-1}. δ_H (300 MHz, $CDCl_3$): 5.48 (dd, J=11.0, 4.4 Hz, 1H, H_b); 6.52 (dd. J=18.0, 4.4 Hz, 1H, H_a); 6.59 (dd, J=18.0, 11.0 Hz, 1H, H_c); 7.45–7.70 (m, 8H, ArH); 9.12–9.15 (dd, J=8.2, 1.2 Hz, 1H, H_A). δ_C (50.4 MHz, $CDCl_3$): 114.2, 120.1, 121.7, 124.5, 126.8, 126.9, 127.0, 129.3, 129.4, 129.5, 136.1, 137.6, 159.4, 160.4. m/z: 304 (M^+).

3.4.3. 3-Isopropenyl-2-phenyl-9-thia-1,4a-diaza-fluoren-4-one 4c. Colourless solid, yield: 72%; mp 132–133 °C. Anal. Calcd for $C_{19}H_{14}N_2OS$: C, 71.67; H, 4.43; N, 8.80. Found: C, 71.68; H, 4.45; N, 8.81%; IR (KBr) ν_{max}: 1662, 1526, 1454, 1861 cm^{-1}. δ_H (300 MHz, $CDCl_3$): 2.04 (s, 3H, $-CH_3$); 4.96 (s, 1H, H_a); 5.30 (s, 1H, H_b); 7.38–7.71 (m, 8H, ArH); 9.12–9.15 (dd, J=9.2, 1.8 Hz, 1H, H_A). δ_C (50 MHz): 119.5, 120.2, 121.9, 124.7, 127.0, 127.1, 127.6, 127.9, 128.3, 129.0, 129.7, 131.3, 133.7, 136.4, 137.9, 156.3, 159.6, 161.6. m/z=318 (M^+).

3.4.4. 3-Buta-1,3-dienyl-2-phenyl-9-thia-1,4a-diaza-fluoren-4-one 4d. White crystalline solid, yield: 62%; mp 174–175 °C. Anal. Calcd for $C_{20}H_{14}N_2SO$: C, 72.70; H, 4.27; N, 8.48. Found: C, 72.68; H, 4.27; N, 8.50%. IR (KBr) ν_{max}: 1682, 1662, 1552 cm^{-1}. δ_H (300 MHz, $CDCl_3$): 5.15 (d, J=10.2 Hz, 1H, H_a); 5.38 (d, J=16.8 Hz, 1H, H_b); 6.35 (ddd, J=10.2, 10.2, 16.9 Hz, 1H, H_c); 6.47 (d, J=15.5 Hz, 1H, H_e); 7.46–7.77 (m, 8H, ArH and H_d); 9.18–9.20 (dd, J=9.1, 1.8 Hz, 1H, H_A). δ_C (50 MHz, $CDCl_3$): 114.4, 116.1, 120.2, 121.7, 124.7, 125.9, 127.0, 127.1, 128.4, 129.4, 129.6, 135.0, 136.2, 137.3, 138.7, 159.6 and 161.6. m/z: 330 (M^+).

3.5. General method for the preparation of 1-aryl-2-phenyl-4,4-bismethylthio-1,3-diazabuta-1,3-dienes 8, 1-(*p*-tolyl)-2-phenyl-4[2-(1,3-dithianyl)]-1,3-diazabuta-1,3-diene 9a and 1-(*p*-tolyl)-2-phenyl-4[2-(1,3-dithiolanyl)]-1,3-diazabuta-1,3-dienes 9

To a well stirred suspension of potassium *t*-butoxide/sodium hydride (22 mmol) in dry THF (30 mL) was added a solution of benzamidine (20 mmol) in dry THF at −20 °C under an atmosphere of nitrogen and stirring continued for about 5–10 min. To this a solution of carbon disulphide (22 mmol) in dry THF (10 mL) was added and the reaction mixture allowed to stir for further 10–15 min and added a solution of 1,3-dibromopropane/1,2-dibromoethane (22 mmol) or methyl iodide (45 mmol) in dry THF (10 mL). The reaction mixture was further stirred for a period of 2–3 h. After the completion of the reaction (tlc), solvent was evaporated under reduced pressure, the crude product was washed with water (2×50 mL) and the organic layer dried over anhydrous sodium sulfate. Removal of solvent under reduced pressure yielded the crude product, which was purified by silica gel column chromatography using a mixture of ethyl acetate and hexane (1:10,V/V).

3.5.1. 1,2-Diphenyl-4,4-bis(thiomethyl)-1,3-diazabuta-1,3-diene 8a. Pale yellow crystalline solid, yield: 72%; mp 93–94 °C. Anal. Calcd for $C_{16}H_{16}N_2S_2$: C, 63.96; H, 5.37; N, 9.32; Found: C, 63.98; H, 5.36; N, 9.34%. IR (KBr) ν_{max}: 1609, 1579, 1503 cm^{-1}. δ_H (200 MHz, $CDCl_3$): 2.40 (s, 6H, 2×$-SCH_3$); 6.95–6.99 (m, 3H, ArH); 7.21–7.26 (m, 2H, ArH); 7.39–7.46 (m, 3H, ArH); 7.86–7.91 (m, 2H, ArH). δ_C (50.4 MHz, $CDCl_3$): 15.0 (2×$-SCH_3$), 121.2, 123.2, 127.9, 128.2, 128.2, 128.8, 130.7, 134.3, 149.3, 159.0, 163.1. m/z: 300 (M^+, 5%), 287 (15%), 286 (20%).

3.5.2. 1-(*p*-Tolyl)-2-phenyl-4,4-bis(thiomethyl)-1,3-diazabuta-1,3-diene 8b. Yellow crystalline solid, yield: 78%; mp 98–100 °C. Anal. Calcd for $C_{17}H_{18}N_2S_2$: C, 64.93; H, 5.77; N, 8.9; Found: C, 64.94; H, 5.79; N, 9.0%. IR (KBr) ν_{max}: 1609, 1579, 1503 cm^{-1}, δ_H (200 MHz, $CDCl_3$): 2.33 (s, 3H, $-CH_3$); 2.40 (s, 6H, 2×$-SCH_3$); 6.90

(d, J=8.2 Hz, 2H, ArH); 7.05 (d, J=8.2 Hz, 2H, ArH); 7.40–7.43 (m, 3H, ArH); 7.85–7.89 (m, 2H, ArH). δ_C (50.4 MHz, $CDCl_3$): 15.0 (2×$-SCH_3$), 21.1 (q, $-CH_3$), 121.4 (d), 127.9 (d), 128.2 (d), 128.9 (d), 130.5 (d), 132.2 (s), 134.8 (s), 148.8 (s), 158.1 (s), 162.5 (s). m/z: 315 (M^++1, 5%), 314 (M^+, 6%), 300 (16%), 299 (80%).

3.5.3. 1-(*o*-Tolyl)-2-phenyl-4,4-bis(thiomethyl)-1,3-diazabuta-1,3-diene 8c. Yield: 69%; viscous oil. Anal. Calcd for $C_{17}H_{18}N_2S_2$: C, 64.93; H, 5.77; N, 8.9; Found: C, 64.92; H, 5.76; N, 9.1%. IR (KBr) ν_{max}: 1609, 1579, 1503 cm^{-1}. δ_H (200 MHz, $CDCl_3$): 2.14 (s, 3H, $-CH_3$); 2.37 (s, 6H, 2×$-SCH_3$); 6.86 (d, J=7.8 Hz, 1H, ArH); 6.90 (dd, J=7.2, 7.4 Hz, 1H, ArH); 7.06 (dd, J=7.2, 7.4 Hz, 1H, ArH); 7.12 (d, J=7.8 Hz, 1H, ArH); 7.38–7.47 (m, 3H, ArH); 7.90–7.94 (m, 2H, ArH). m/z: 314 (M^+).

3.5.4. *N*-[1,3]Dithian-2-ylidene-*N'*-*p*-tolyl-benzamidine 9a. Yellow crystalline solid, yield: 61%; mp 130–132 °C. Anal. Calcd for $C_{17}H_{16}N_2S_2$: C, 65.35; H, 5.16; N, 8.97. Found: C, 65.37; H, 5.14; N, 8.99%. IR (KBr) ν_{max}: 1609, 1579, 1503 cm^{-1}. δ_H (300 MHz, $CDCl_3$): 2.32 (s, 3H, $-CH_3$); 3.44 (m, 4H, 2×$-CH_2-$); 6.68 (d, J=7.9 Hz, 2H, ArH); 6.99 (d, J=8.3 Hz, 2H, ArH); 7.38–7.46 (m, 3H, ArH); 7.92–7.94 (m, 2H, ArH). m/z: 312 (M^+).

3.5.5. *N*-[1,3]Dithiolan-2-ylidene-*N'*-*p*-tolyl-benzamidine 9b. Colourless crystalline solid, yield: 58%; mp 90–91 °C. Anal. Calcd for $C_{18}H_{18}N_2S_2$: C, 66.22; H, 5.56; N, 8.58. Found: C, 66.26; H, 5.58; N, 8.56%. IR (KBr) ν_{max}: 1609, 1579, 1503 cm^{-1}. δ_H (300 MHz, $CDCl_3$): 2.03 (m, 2H, $-CH_2-$); 2.31 (s, 3H, $-CH_3$); 2.91 (m, 4H, 2×$-SCH_2-$); 6.97 (d, J=8.0 Hz, 2H, ArH); 7.09 (d, J=7.9 Hz, 2H, ArH); 7.38–7.46 (m, 3H, ArH); 7.90 (m, 2H, ArH). δ_C (75 MHz, $CDCl_3$): 20.8 ($-CH_2-$), 21.6 ($-CH_3$), 29.7 (2×$-SCH_2$), 121.4, 127.6, 128.8, 129.1, 130.5, 132.5, 134.4, 146.0, 150.9, 165.3. m/z: 328 (M^++2), 327 (M^++1), 326 (M^+).

3.6. General procedure for the reactions of 1,3-diazabutadienes 8 with phenyl-/chloroketenes

To a well stirred solution of 1,3-diazabuta-1,3-diene **8** (10 mmol) and triethylamine (40 mmol) in dry methylene chloride (30 mL) was added dropwise a solution of phenylacetyl chloride/chloroacetyl chloride (20 mmol) in dry methylene chloride (30 mL) over a period of 1 h at 0 °C. After completion of the reaction (tlc), the reaction mixture was first washed with saturated sodium bicarbonate solution (2×25 mL) and water (5×50 mL) and the organic layer dried over anhydrous sodium sulfate. Removal of solvent under reduced pressure yielded the crude product, which was purified by silica gel column chromatography using a mixture of ethyl acetate and hexane mixture (1:10, V/V).

3.6.1. 2,5-Diphenyl-3-(*p*-tolyl)-6-methylthio-pyrimidine-4(3*H*)-one 11. White crystalline solid, yield: 82%; mp 185–186 °C. Anal. Calcd for $C_{24}H_{20}N_2OS$: C, 75.00; H, 5.21; N, 7.29. Found: C, 74.75; H, 5.34; N, 6.99%. IR (KBr) ν_{max}: 1671 cm^{-1}. δ_H (200 MHz, $CDCl_3$): 2.32 (s, 3H, $-CH_3$); 2.49 (s, 3H, $-SCH_3$); 6.98–7.41 (m, 14H, ArH). δ_C (50.4 MHz, $CDCl_3$): 15.0 ($-SCH_3$), 21.0 ($-CH_3$), 121.3, 127.9, 128.1, 128.6, 130.5, 132.2, 134.6, 146.6, 158.1, 162.5. m/z: 384 (M^+).

3.6.2. 2,3-Diphenyl-5,6-bis(methylthio)-pyrimidine-4(3*H*)-one 14a. White crystalline solid, yield: 71%; mp 221–222 °C. Anal. Calcd for $C_{18}H_{16}N_2OS_2$. C, 63.50; H, 4.74; N, 8.23. Found: C, 63.52; H, 4.75; N, 8.25%. IR (KBr) ν_{max}: 1668, 1550 cm^{-1}. δ_H (200 MHz, $CDCl_3$): 2.58 (s, 6H, 2×$-SCH_3$); 7.06–7.32 (m, 10H, ArH). m/z: 340 (M^+).

3.6.3. 2-Phenyl-3-(*p*-tolyl)-5,6-bis(methylthio)-pyrimidine-4(3*H*)-one 14b. Colourless solid, yield: 67%; mp 190–192 °C. Anal. Calcd for $C_{19}H_{18}N_2OS_2$. C, 64.40; H, 5.08; N, 7.91. Found: C, 64.53; H, 4.98; N, 8.08%. IR (KBr) ν_{max}: 1669, 1548 cm^{-1}. δ_H (300 MHz, $CDCl_3$): 2.31 (s, 3H, $-CH_3$); 2.47 (s, 3H, $-SCH_3$); 2.59 (s, 3H, $-SCH_3$); 6.98 (d, J=8.2 Hz, 2H, ArH); 7.11 (d, J=8.2 Hz, 2H, ArH); 7.18–7.32 (m, 5H, ArH). m/z: 354 (M^+).

3.7. General procedure for the reactions of 1,3-diazabutadienes 9 with vinyl-/chloro ketene

To a well stirred solution of 1,3-diazabuta-1,3-diene **9** (10 mmol) and triethylamine (40 mmol) in dry methylene chloride (30 mL) was added dropwise a solution of crotonylchloride/chloroacetyl chloride (25 mmol) in dry methylene chloride (30 mL) over a period of one hour at 0 °C After completion of the reaction (tlc), the reaction mixture was first washed with saturated sodium bicarbonate solution (2×25 mL) and water (5×50 mL) and the organic layer dried over anhydrous sodium sulfate. Removal of solvent under reduced pressure yielded the crude product, which was purified by silica gel column chromatography using a mixture of ethyl acetate and hexane (1:10,V/V).

3.7.1. 2-Phenyl-3-(*p*-tolyl)-5-chloro-6-{6-[3,6-dithiahex-1-chloro-2-one]}-pyrimidine-4(3*H*)-one 19a. Pale white solid, yield: 37%; mp 140–142 °C. Anal. Calcd for $C_{21}H_{18}N_2O_2S_2Cl_2$: C, 54.19; H, 3.87; N, 6.02. Found: C, 53.94; H, 4.02; N, 5.88%. IR (KBr) ν_{max}: 1672 cm^{-1}. δ_H (300 MHz, $CDCl_3$): 2.31 (s, 3H, $-CH_3$); 3.29–3.35 (m, 2H, $-CH_2-$); 3.39–3.45 (m, 2H, $-CH_2-$); 4.14 (s, 2H, $-CH_2-$); 6.99 (d, J=8.2 Hz, 2H, ArH); 7.11 (d, J=8.2 Hz, 2H, ArH); 7.19–7.31 (m, 5H, ArH). δ_C (75 MHz, $CDCl_3$): 21.1 ($-CH_3$), 29.6 ($-CH_2-$), 29.9 ($-CH_2-$), 47.8 ($-CH_2-$), 114.7, 127.8, 128.1, 129.1, 129.6, 129.9, 133.8, 134.1, 138.8, 156.2, 156.9, 160.8, 193.3. m/z: 465 (M^+).

3.7.2. 2-Phenyl-3-(*p*-tolyl)-5-chloro-6-{7-[3,7-dithiahept-1-chloro-2-one]}-pyrimidine-4(3*H*)-one 19b. Colourless crystalline solid, yield: 33%; mp 94–95 °C. Anal. Calcd for $C_{22}H_{20}N_2O_2S_2Cl_2$: C, 55.11; H, 4.17; N, 5.84 Found: C, 54.90; H, 3.86; N, 5.56%. IR (KBr) ν_{max}: 1678 cm^{-1}. δ_H (300 MHz, $CDCl_3$): 2.07 (m, 2H, $-CH_2-$); 2.31(s, 3H, $-CH_3$); 3.06 (t, J=7.0 Hz, 2H, $-S-CH_2-$); 3.26 (t, J=7.0 Hz, 2H, $-S-CH_2-$); 4.12 (s, 2H, $-CH_2-$); 6.99 (d, J=8.2 Hz, 2H, ArH); 7.11 (d, J=8.2 Hz, 2H, ArH); 7.20–7.33 (m, 5H, ArH). δ_C (50.4 MHz, $CDCl_3$): 21.1 ($-CH_3$), 28.2 ($-CH_2-$), 29.0 ($-CH_2-$), 29.6 ($-CH_2-$), 47.8 ($-CH_2-$), 114.7, 127.9, 128.1, 129.1, 129.6, 129.8, 134.1, 134.2, 138.9, 156.0, 157.1, 161.5 (C-4), 193.7 (C=O). m/z: 479 (M^+).

3.7.3. 2-Phenyl-(*p*-tolyl)-3,6,7-trihydro-pyrimidino-[4,5,*b*]-dithiane-4-one 20a. White crystalline solid, yield: 36%; mp 158–160 °C. Anal. Calcd for $C_{19}H_{16}N_2OS_2$: C,

64.77; H, 4.54; N, 7.95. Found: C, 63.97; H, 4.32; N, 7.74%. IR (KBr) ν_{max}: 1682 cm^{-1}. δ_H (200 MHz, $CDCl_3$): 2.23 (s, 3H, $-CH_3$); 3.42–3.48 (m, 2H, $-CH_2-$); 3.64–3.66 (m, 2H, $-CH_2-$); 7.00 (d, J=8.3 Hz, 2H, ArH); 7.26 ((d, J=8.3 Hz, 2H, ArH); 7.24–7.51 (m, 5H, ArH). δ_C (50.4 MHz, $CDCl_3$): 20.9 ($-CH_3$), 34.1 ($-CH_2-$), 40.4 ($-CH_2-$), 118.1, 128.2, 129.0, 129.2, 129.4, 133.6, 134.5, 160.2. *m/z*: 352 (M^+).

3.7.4. 2-Phenyl-3-(*p*-tolyl)-3,6,7,8-tetrahydro-pyrimido-[4,5,*b*]-1,4-dithiapene-4-one 20b. White crystalline solid, yield: 36%; mp 273–274 °C. Anal. Calcd for $C_{20}H_{18}N_2OS_2$ C, 65.57; H, 4.91; N, 7.65. Found: C, 64.64; H, 5.53; N, 7.54%. IR (KBr) ν_{max}: 1672 cm^{-1}. δ_H (300 MHz, $CDCl_3$): 2.14–2.22 (m, 2H, $-CH_2-$); 2.28 (s, 3H, $-CH_3$); 3.59 (t, J=6 Hz, 2H, $-S-CH_2-$); 3.69 (t, J=6 Hz, 2H, $-S-CH_2-$); 6.96 (d, J=8.3 Hz, 2H, ArH); 7. 08 (d, J=8.3 Hz, 2H, ArH); 7.13–7.26 (m, 5H, ArH). δ_C (50.4 MHz, $CDCl_3$): 21.1 ($-CH_3$), 27.6 ($-CH_2-$), 30.1 ($-CH_2-$), 30.6 ($-CH_2-$), 119.7, 127.8, 128.2, 129.1, 129.5, 133.8, 134.1, 136.5, 153.6, 159.7. *m/z*: 366 (M^+).

3.7.5. 2-Phenyl-3-(*p*-tolyl)-5-vinyl-6-{8-[(*E*)-5,8-dithiaoct-2-ene-4-one]}-pyrimidine-4(3*H*)-one 23a. Colourless crystalline solid, yield: 69%; mp 157–158 °C. Anal. Calcd for $C_{25}H_{24}N_2O_2S_2$: C, 66.93; H, 5.39; N, 6.24. Found: C, 66.95; H, 5.38; N, 6.26%. IR (KBr) ν_{max}: 1669 cm^{-1}. δ_H (200 MHz, $CDCl_3$): 1.68 (dd, J=6.8, 1.6 Hz, 3H, $-CH_3$); 2.30 (s, 3H, $-CH_3$); 3.26–3.34 (m, 2H, $-S-CH_2-$); 3.40–3.47 (m, 2H, $-S-CH_2-$); 5.56 (dd, J=11.4, 2.6 Hz, 1H, H_a); 6.12 (dd, J=15.3, 1.6 Hz, 1H, H_e); 6.54 (dd, J=17.6, 2.6 Hz, 1H, H_b); 6.73 (dd, J=17.6, 11.4 Hz, 1H, H_c); 6.90 (dq, J=15.4, 6.9 Hz, 1H, H_d); 6.99 (d, J=8.2 Hz, 2H, ArH); 7.12 (d, J=8.2 Hz, 2H, ArH); 7.16–7.32 (m, 5H, ArH). δ_C (50.4 MHz, $CDCl_3$): 18.0 ($-CH_3$), 21.1 ($-CH_3$), 29.3 ($-CH_2-$), 30.2 ($-CH_2-$), 116.0, 121.0, 127.0, 127.4, 127.8, 128.4, 129.3, 129.6, 129.7, 129.9, 134.5. 134.6, 141.3, 142.1, 155.4, 159.5, 116.1 (C-4), 189.0 (C=O). *m/z*: 448 (M^+).

3.7.6. 2-Phenyl-3-(*p*-tolyl)-5-vinyl-6-{9-[(*E*)-5,9-dithianon-2-ene-4-one]}-pyrimidine-4(3*H*)-one 23b. White crystalline solid, yield: 72%; mp 98–100 °C. Anal. Calcd for $C_{26}H_{26}N_2O_2S_2$: C, 67.53; H, 5.62; N, 6.06. Found: C, 67.28; H, 5.86; N, 5.93%. IR (KBr) ν_{max}: 1672 cm^{-1}. δ_H (300 MHz, $CDCl_3$): 1.88 (dd, J=7.1, 1.5 Hz, 3H, $-CH_3$); 2.00–2.12 (m, 2H, $-CH_2-$); 2.31 (s, 3H, $-CH_3$); 3.05 (t, J=7.1 Hz, 2H, $-S-CH_2-$); 3.29 (t, J=7.1 Hz, 2H, $-S-CH_2-$); 5.56 (dd, J=11.7, 2.2 Hz, 1H, H_a); 6.11 (dd, J=15.4, 1.8 Hz, 1H, H_e); 6.54 (dd, J=17.1, 2.2 Hz, 1H, H_b); 6.75 (dd, J=17.1, 11.7 Hz, 1H, H_c); 6.90 (dq, J=15.4, 7.1 Hz, 1H, H_d); 7.00 (d, J=8.3 Hz, 2H, ArH); 7.12 (d, J=8.3 Hz, 2H, ArH); 7.18–7.32 (m, 5H, ArH). δ_C (75 MHz, $CDCl_3$): 17.9 ($-CH_3$), 21.1 ($-CH_3$), 27.4 ($-CH_2-$), 29.2 ($-CH_2-$), 30.2 ($-CH_2-$), 115.8, 120.8, 127.5, 127.8, 128.5, 129.3, 129.6, 130.1, 134.6. 138.5, 140.8, 155.2, 159.5, 161.7 (C-4), 189.4 (C=O). *m/z*: 462 (M^+).

Acknowledgements

S.J. is grateful to CSIR, New Delhi for a Senior Research Fellowship and the financial assistance by CSIR, New Delhi, is gratefully acknowledged.

References and notes

1. For recent reviews on azadienes see: (a) Boger, D. L. *Tetrahedron* **1983**, *39*, 2869. (b) Boger, D. L. *Chem. Tract-Org. Chem.* **1996**, *9*, 149. (c) Barluenga, J.; Tomas, M. *Adv. Heterocycl. Chem.* **1993**, *57*, 1. (d) Boger, D. L. *Comprehensive organic synthesis*; Trost, B. M., Fleming, I., Eds.; Pergamon: Oxford, 1991; Vol. 5. Chapter 4.3. (e) Ghosez, L. *Stereocontrolled organic synthesis*; Blackwell: London, 1994; p 193. (f) Boger, D. L.; Weinreb, S. M. *Hetero Diels–Alder methodology in organic synthesis*; Academic: San Diego, 1987.
2. Gorel, G.; Marchand, E.; Toupet, L.; Foucaud, A. *J. Org. Chem.* **1989**, *54*, 1185.
3. (a) Sain, B.; Singh, S. P.; Sandhu, J. S. *Tetrahedron Lett.* **1991**, *32*, 5151. (b) Sain, B.; Singh, S. P.; Sandhu, J. S. *Tetrahedron* **1992**, *48*, 4567.
4. (a) Barluenga, J.; Tomas, M.; Bellestros, A.; Lopez, L. A. *Heterocycles* **1994**, *37*, 1109. (b) Gilchrist, T. L.; Gonsalves, A. M. R.; Teresa, M. D. V. P. *Tetrahedron Lett.* **1993**, 4097. (c) Molina, P.; Aller, E.; Lopez-Lazaro, A.; Alajarin, M.; Lorenzo, A. *Tetrahedron Lett.* **1994**, *35*, 3817.
5. Ibnusaud, I.; Malar, E. P. J.; Sundaram, N. *Tetrahedron Lett.* **1990**, *47*, 1473.
6. (a) Crooks, S.; Sykes, P. *J. Chem. Soc., Perkin Trans. 1* **1977**, 1791. (b) Mazumdar, S. N.; Sharma, M.; Mahajan, M. P. *Tetrahedron Lett.* **1987**, *28*, 2641. (c) Mazumdar, S. N.; Ibnusaud, I.; Mahajan, M. P. *Tetrahedron Lett.* **1986**, *27*, 5875. (d) Barluenga, J.; Tomas, M.; Bellestros, A.; Lopez, L. A. *Tetrahedron Lett.* **1989**, *30*, 4573. (e) Rossi, E.; Celentano, G.; Stradi, R.; Strada, R. *Tetrahedron Lett.* **1990**, *31*, 903. (f) Wurthwein, E. U.; Luthadart, P. *Tetrahedron Lett.* **1988**, *29*, 921. (g) Mastuda, I.; Yamamoto, S.; Ishii, Y. *J. Chem. Soc., Perkin Trans. 1* **1976**, 1528. (h) Bhartam, P. V.; Kumar, R. S.; Mahajan, M. P. *Org. Lett.* **2000**, *2*, 2725.
7. (a) Mazumdar, S. N.; Mahajan, M. P. *Synthesis* **1990**, 417. (b) Dey, P. D.; Sharma, A. K.; Rai, S. N.; Mahajan, M. P. *Tetrahedron* **1995**, *51*, 7459. (c) Sharma, A. K.; Mahajan, M. P. *Tetrahedron* **1997**, *53*, 13841.
8. (a) Mukherjee, S.; Mazumdar, S. N.; Sharma, A. K.; Mahajan, M. P. *Heterocycles* **1998**, *47*, 933. (b) Mazumdar, S. N.; Mahajan, M. P. *Tetrahedron* **1991**, *47*, 1473. (c) Mazumdar, S. N.; Sharma, A. K.; Mukherjee, S.; Sengupta, D.; Mahajan, M. P. *Tetrahedron* **1994**, *50*, 7579. (d) Sharma, A. K.; Mahajan, M. P. *Heterocycles* **1995**, *40*, 787. (e) Dey, P. D.; Sharma, A. K.; Mahajan, M. P. *Tetrahedron* **1995**, *51*, 7459. (f) Dey, P. D.; Sharma, A. K.; Bhartam, P. V.; Mahajan, M. P. *Tetrahedron* **1997**, *53*, 13829.
9. (a) Sharma, A. K.; Jayakumar, S.; Mahajan, M. P. *Tetrahedron Lett.* **1998**, *39*, 7205. (b) Sharma, A. K.; Jayakumar, S.; Hundal, M. S.; Mahajan, M. P. *J. Chem. Soc., Perkin Trans. 1* **2002**, 774–778.
10. Chaudhary, S.; Debroy, A.; Mahajan, M. P. *Can. J. Chem.* **1982**, *60*, 1122.
11. Sharma, A. K.; Mazumdar, S. N.; Mahajan, M. P. *J. Org. Chem.* **1996**, *61*, 5506.