Effective synthesis of 1,2-di-, 1,2,3-tri-, 1,2,3,3-tetraalkyldiaziridines and 1,5-diazabicyclo[3.1.0]hexanes

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10.1070/MC2000v010n05ABEH001350

A versatile single-step procedure was proposed for the synthesis of the title compounds by the interaction of equimolar amounts of aliphatic carbonyl compounds, primary aliphatic amines and *N*-chloroalkylamines in an aprotic organic solvent in the presence of potassium carbonate.

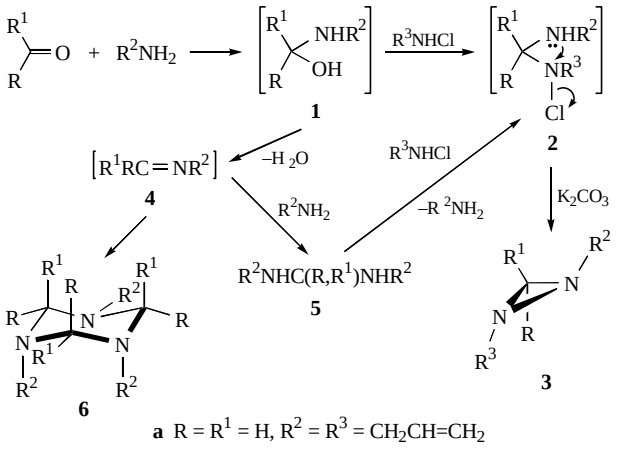
A number of methods for the synthesis of 1,2-dialkyldiaziridine derivatives are known,[1–5] depending on substituents at the 3-position of the ring. Thus, a synthesis of 1,2-dialkyl- and 1,2,3-trialkyldiaziridines is based on the interaction of 1 mol of an aldehyde and 2 mol of a primary aliphatic amine with NaOCl in an aqueous alkaline medium[1] under controlled pH.[2,3] However, methods based on reactions in water cannot be extended to the production of 1,2,3,3-tetraalkyldiaziridines and diaziridines from sterically hindered and water-insoluble amines. A few tetrasubstituted diaziridines were earlier prepared by transformations of 1-*H*- or 1,2-*H*-diaziridines.[6,7] At the same time, diaziridine derivatives are convenient compounds for studying the stereochemistry of nitrogen,[8] in particular, for spontaneous resolution into enantiomers.[9]

We synthesised[10] sterically hindered 1,2-di(1-adamantyl)diaziridine, which cannot be prepared using the above methods, by the interaction of 1 mol of Bu^{t}OCl with a mixture of 1 mol of formaldehyde and 2 mol of 1-aminoadamantane in $CHCl_3$ in the presence of K_2CO_3 as a base. On this basis, we hoped to develop a versatile single-step method for the preparation of 1,2-di-, 1,2,3-tri- and 1,2,3,3-tetraalkyldiaziridines. For this purpose, we examined the reaction of carbonyl compounds, primary aliphatic amines and *N*-chloroalkylamines in aprotic organic solvents in the presence of K_2CO_3.

It is well known[11] that, regardless of the synthetic procedure, the diaziridine ring is closed by intramolecular nucleophilic substitution in a methylenediamine intermediate **2**, which contains a readily leaving group (Hal, HSO_4 or OSO_2R) at a nitrogen atom. Intermediate **2** can be formed from an amine and a carbonyl compound *via* α-aminocarbinol **1** followed by the α-aminomethylation of an *N*-chloroalkylamine (Scheme 1). The cyclization of **2** to diaziridine **3** is rapid; because of this, the formation of **2** is the rate-limiting step in the synthesis of diaziridines. Successful formation of **2** in aqueous solution was optimised by adjusting the pH.[2,3] In an aprotic medium, the dehydration of **1** to form imines **4** and methylenebisamines **5** may be an alternative pathway of the reaction. In the case of aldehydes, and in particular, formaldehyde, trimerisation of **4** to hexahydro-1,3,5-triazines **6** can also occur. In principle, compounds **5**, as well as α-aminocarbinol **1**, can give diaziridines in the reaction with *N*-chloroalkylamines. However, it is likely that this reaction pathway is hindered in an aprotic medium (Scheme 1).

α-Aminocarbinols of aliphatic amines are unstable under ordinary conditions. In particular, *N*-piperidinocarbinol was isolated and characterised by spectroscopy at a low temperature; however, it transformed into methylenebispiperidine with increasing temperature.[12] Stable α-aminocarbinols were obtained from only amines or carbonyl compounds that bear electron-acceptor substituents.[13,14] Hydroxymethyl derivatives of diaziridines[15] and aziridines[16] were also described. There is no published data on the stability of α-aminocarbinols **1** in aprotic organic solvents over long time.

Thus, before attempting to synthesise diaziridines in the presence of K_2CO_3, we examined the behaviour of the reaction mixture (in both the absence and presence of K_2CO_3) obtained by passing gaseous formaldehyde into a solution of allylamine in CD_2Cl_2 at –30 °C by ^{1}H NMR spectroscopy. The ^{1}H NMR



Scheme 1

spectra† of parent allylamine and 1,3,5-triallylhexahydro-1,3,5-triazine **6a**[17] were measured under the same conditions. The spectrum measured immediately after mixing allylamine and formaldehyde at –30 °C exhibited the signals of allylamine† and two groups of signals with the 4:1 ratio between the integrated intensities, which can be attributed, by analogy with published data,[15,16] to a CH_2 group of α-aminocarbinol **1a** (s, 4.4 ppm) and an NCH_2N group (3.47 ppm) of methylenediamine **5a**. Next, the ampoule was heated to 20 °C and after holding for 1 min cooled again to –30 °C. In the ^{1}H NMR spectrum of this solution, the above signals were retained; however, the ratio between the integrated intensities was 1:1, and weak signals of hexahydrotriazine **6a** appeared. After holding this ampoule at 20 °C for 10 min, almost pure compound **6a** was detected in solution; that is, hexahydrotriazine **6a** is the end product of the reaction even after a short time under the conditions specified.

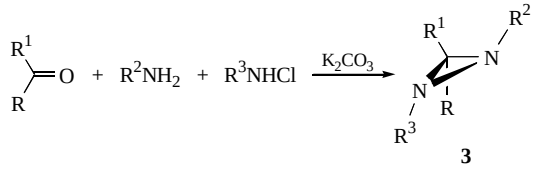
A completely different behaviour was observed when an equimolar amount of K_2CO_3 was added to an analogous reaction mixture prepared at –30 °C. After stirring at 20 °C for 10 min, the reaction mixture was cooled to –30 °C, potassium carbonate

† All new compounds exhibited satisfactory elemental analyses, and their structures were confirmed by IR, ^{1}H and ^{13}C NMR spectroscopy. The IR spectra were measured on an UR-20 spectrometer in thin films of pure substances; ^{1}H and ^{13}C NMR spectra were recorded on Bruker WM-250 (250 MHz) and Bruker AM-300 (75.5 MHz) spectrometers, respectively (TMS was used as an internal standard). 1,2-Dimethyl- (**3b**),[1] 1,2-bis(2-acetamidoethyl)- (**3c**),[2] 1,2,3-trimethyl- (**3f**)[2] and 1,2-dibutyl-3-methyl- (**3g**)[22] diaziridines as well as 1,5-diazabicyclo[3.1.0]hexane **7a**[18] and its 3-methyl (**7b**)[18] and 3,3-dimethyl (**7c**)[18] derivatives were described in the literature.

1,3,5-Triallylhexahydro-1,3,5-triazine **6a**: ^{1}H NMR (CD_2Cl_2, –30 °C) δ: 2.65, 3.65 (AB system, 2H, NCH_2N, ^2J 13 Hz), 2.95 (d, 2H, NCH_2, ^3J 8 Hz), 5.05 (m, 2H, $=CH_2$), 5.67 (m, 1H, =CH).

Allylamine: ^{1}H NMR (CD_2Cl_2, –30 °C) δ: 1.6 (br. s, 2H, NH_2), 3.15 (dq, 2H, NCH_2, ^3J 6 Hz and 2 Hz), 4.95 (m, 2H, $=CH_2$), 5.85 (m, 1H, =CH).

N-*Hydroxymethylallylamine* **1a**: ^{1}H NMR (CD_2Cl_2, –30 °C) δ: 3.5 (d, 2H, NCH_2C=), 4.4 (s, 2H, NCH_2O), 5.2 (m, 2H, CH_2=), 6.9 (m, 1H, CH=).



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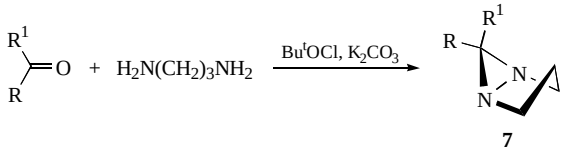
	R	R^1	R^2	R^3
a	H	H	$CH_2CH=CH_2$	$CH_2CH=CH_2$
b	H	H	Me	Me
c	H	H	$CH_2CH_2NHCOMe$	$CH_2CH_2NHCOMe$
d	H	H	Me	$CH_2CH_2NHCOMe$
e	H	H	Me	$CH_2CH_2NH_2$
f	H	Me	Me	Me
g	H	Me	Bu	Bu
h	Me	Me	Me	Me
i	Me	Me	CH_2CH_2OH	CH_2CH_2OH
j	Me	Me	$CH_2CH_2NHCOMe$	$CH_2CH_2NHCOMe$
k	Me	Me	Me	CH_2CH_2OH
l	Me	Me	Me	$CH_2CH_2NHCOMe$
m	Me	$CH_2NHCOMe$	Me	Me
n	Me	Et	Me	Me

Scheme 2

was filtered off, and the ^{1}H NMR spectrum of the resulting solution was measured. All operations were performed at –30 °C. α-Aminocarbinol **1a**† was found to be the main component of this reaction mixture. Moreover, after stirring at 20 °C with K_2CO_3 for 1 h followed by the removal of K_2CO_3, the shape of the ^{1}H NMR spectrum at –30 °C was changed only slightly. Although signals of **5a** appeared, **1a** was the major product. Hexahydrotriazine **6a** was almost completely absent from this mixture.

Thus, we found that the α-aminocarbinol prepared from a primary aliphatic amine and formaldehyde can be retained in an aprotic organic solvent containing K_2CO_3 for a reasonably long time without conversion into hexahydro-1,3,5-triazine. It is likely that potassium carbonate, which exhibits both basic and dehydrating properties, can remove trace water from an aprotic medium (under these conditions, water can play a role of a weak acid) and result in the stabilisation of the α-aminocarbinol. However, to perform the reaction successfully, the reaction mixture should be continuously efficiently stirred; when the stirring was stopped, a water layer appeared after several minutes, and hexahydrotriazine was formed.

Based on these results, we examined the synthesis of diaziridines from carbonyl compounds, primary aliphatic amines and *N*-chloroalkylamines in aprotic organic solvents in the presence of potassium carbonate.‡ Formaldehyde, acetaldehyde, acetone, methyl ethyl ketone and acetamidoacetone (a ketone with an electron-acceptor group) were taken as carbonyl compounds. Of primary amines, methylamine, allylamine, 2-hydroxyethylamine and 2-acetamidoethylamine (the two amines last named bear electron-acceptor substituents) were examined. For the reason of an amine and an *N*-chloroalkylamine with different alkyl groups, the *N*-chloroalkylamine was prepared by the reaction of the corresponding amine (as a rule, $MeNH_2$) with NaOCl followed by extraction with methylene chloride or chloroform, which were also used as the reaction solvent. In the case of an amine and an *N*-chloroalkylamine with identical alkyl groups, the *N*-chloroalkylamine was prepared by the reaction between 1 mol of BuOCl and 2 mol of the corresponding amine in the above solvents. The organic reactants were taken in equimolar amounts, and potassium carbonate was taken in a threefold amount (Scheme 2).§ The reaction was complete after 8–10 h in 30–70% yields. The optimum reaction temperature was 20–22 °C in the case of alkyl-substituted amines and carbonyl compounds or 24–26 °C for those bearing electron-acceptor substituents.



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a R = R^1 = H
b R = H, R^1 = Me
c R = R^1 = Me
d R = $CH_2NHCOMe$, R^1 = Me

Scheme 3

This procedure was extended to other compounds. Thus, a series of 1,5-diazabicyclo[3.1.0]hexanes† **7** was prepared in high yields from equimolar amounts of corresponding carbonyl compounds, 1,3-diaminopropane and Bu^{t}OCl in the presence of K_2CO_3 (Scheme 3).‡ § It was found previously[18-21] using ^{1}H and ^{13}C NMR spectroscopy and X-ray diffraction data that compounds **7a–c** predominantly occur in the boat conformation, and the introduction of an *endo*-Me group results in flattering the ring. A comparison of the chemical shifts of the carbon atoms and the spin–sp in coupling constants of the protons on the pyrazolidine ring of previously unknown compound **7d** with the corresponding values for **7b**,**c** suggests that it also contains a flattened boat conformation with methyl and acetamidomethyl groups in the *endo* and *exo* positions, respectively.

This work was supported by the Russian Foundation for Basic Research (grant no. 97-03-33021a) and INTAS (grant no. 99-0157).

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‡ *General procedure for the synthesis of 1,2-di-, 1,2,3-tri- and 1,2,3,3-tetraalkyldiaziridines with different 1,2-substituents*. A solution of 0.1 mol of NaOCl [prepared from 0.21 mol of NaOH and 7.1 g (0.1 mol) of Cl_2 in 30 ml of H_2O at –5–0 °C] was added dropwise to 0.1 mol 30% aqueous $MeNH_2$ solution at the specified temperature, and MeNHCl was extracted with two 50 ml portions of $CHCl_3$ or CH_2Cl_2. Then, 0.1 mol of a corresponding amine and 41.5 g (0.3 mol) of K_2CO_3 were added, the reaction mixture was cooled to –10 °C, and 0.1 mol of a carbonyl compound was added dropwise with stirring for 10–12 h at 20–22 °C (or 24–26 °C for amine or carbonyl compounds with electron-withdrawing substituents). The inorganic precipitate was filtered off and washed with $CHCl_3$ or CH_2Cl_2, the solvent was distilled off in a vacuum, and the final product was isolated by chromatography on SiO_2 L40/100 (eluent: $CHCl_3$, washed two times with equal volumes of 25% NH_3) followed by distillation.

General procedure for the synthesis of 1,2-di-, 1,2,3-tri- and 1,2,3,3-tetraalkyldiaziridines with identical 1,2-substituents. A solution of 0.1 mol of Bu^{t}OCl in 20 ml of $CHCl_3$ (CCl_4 or CH_2Cl_2) was added dropwise to a mixture of 0.2 mol of an amine and 41.5 g of K_2CO_3 in 100 ml of $CHCl_3$ at –5–0 °C with efficient stirring, and after 15 min 0.1 mol of a carbonyl compound was added. The temperature was increased to a required value, and the reaction was carried out as described above.

General procedure for the synthesis of 1,5-diazabicyclo[3.1.0]hexanes. The carbonyl compound (0.1 mol) was added to a mixture of 0.1 mol of 1,3-diaminopropane and 41.5 g (0.3 mol) of K_2CO_3 in 100 ml of $CHCl_3$ (CH_2Cl_2) at –5–0 °C, and a solution of 0.1 mol of Bu^{t}OCl in 20 ml of $CHCl_3$ (CH_2Cl_2 or CCl_4) was added dropwise. Next, the reaction was performed as described above.

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§ *1,2-Diallyldiaziridine* **3a**: yield 32%, bp 99 °C (170 Torr), n_D^{20} 1.4500. ^{1}H NMR ($CDCl_3$) δ: 2.3 (s, 2H, ring CH_2), 2.90 (dq, 2H, NCH_2, ^2J –6.0 Hz, ^3J 2.0 Hz), 5.0 (m, 2H, CH_2=, ^3J 9.0 Hz), 5.75 (m, 1H, CH=, ^3J 2.0 Hz, ^3J 9.0 Hz). IR (ν/cm^{-1}): 1650, 3040, 3080.

1-(2-Acetamidoethyl)-2-methyldiaziridine **3d**: yield 48%, bp 106–107 °C (1.5 Torr), n_D^{20} 1.4750. ^{1}H NMR ($CDCl_3$) δ: 1.95 (s, 3H, MeCO), 2.38 (s, 3H, MeN), 2.1, 2.58 (m, 2H, $N_{ring}CH_2$, ^2J –11.0 Hz, ^3J 5.5 Hz), 2.48 (q, 2H, ring CH_2, ^2J –6.0 Hz), 3.48 (m, 2H, CH_2NCO, ^3J 5.5 Hz), 6.3 (br. s, 1H, NH). IR (ν/cm^{-1}): 1660, 3050, 3300.

1-(2-Aminoethyl)-2-methyldiaziridine **3e**: yield 78%, bp 98 °C (13 Torr), n_D^{20} 1.4812. ^{1}H NMR ($CDCl_3$) δ: 2.3, 2.6 (m, 2H, CH_2N_{ring}, ^2J –11.5 Hz, ^3J 5.6 Hz), 2.63 (q, 2H, ring CH_2, ^2J –6.2 Hz), 2.77 (m, 2H, CH_2N, ^3J 5.5 Hz), 4.7 (s, 2H, NH_2). ^{13}C NMR ($CDCl_3$) δ: 41.9 (t, CH_2N_{ring}, ^1J 134.5 Hz), 48.4 (q, Me, ^1J 141 Hz), 59.4 (t, ring CH_2, ^1J 177 Hz), 64.0 (t, CH_2NH_2, ^1J 129 Hz). IR (ν/cm^{-1}): 875, 905, 1045, 1055, 1080, 3190, 3290, 3365.

1,2,3,3-Tetramethyldiaziridine **3h**: yield 51%, bp 76 °C (15 Torr), n_D^{20} 1.4370. ^{1}H NMR ($CDCl_3$) δ: 1.18 (s, 6H, CMe), 2.34 (s, 6H, NMe). ^{13}C NMR ($CDCl_3$) δ: 19.0 (CMe), 39.8 (NMe), 60.5 (diaziridine ring). IR (ν/cm^{-1}): 760, 1070, 1150, 1250, 1380, 1470, 1640, 2960.

1,2-Di-(2-hydroxyethyl)-3,3-dimethyldiaziridine **3i**: yield 33.7%, undistilled oil, n_D^{20} 1.4810. ^{1}H NMR ($CDCl_3$) δ: 1.34 (s, 6H, CMe), 2.50, 2.83 (dt, 4H, NCH_2, ^2J –13.4 Hz, ^3J 4.1 Hz), 3.85 (dt, 4H, OCH_2, ^3J 4.1 Hz), 4.75 (br. s, 1H, OH). ^{13}C NMR ($CDCl_3$) δ: 20.0 (q, Me, ^1J 126 Hz), 55.3 (t, NCH_2, ^1J 135 Hz), 59.2 (s, diaziridine ring), 61.8 (t, OCH_2, ^1J 142 Hz). IR (ν/cm^{-1}): 670, 760, 890, 1070, 1130, 1450, 1480, 1660, 2970, 3310.

1,2-Bis(2-acetamidoethyl)-3,3-dimethyldiaziridine **3j**: yield 32.5%, undistilled oil, n_D^{20} 1.4878. ^{1}H NMR ($CDCl_3$) δ: 1.26 (s, 6H, $C_{ring}Me$), 1.98 (s, 6H, MeCO), 2.37, 2.72 (dt, 4H, NCH_2, ^2J –12.0 Hz, ^3J 6.0 Hz), 3.29, 3.50 (dt, 4H, CH_2NH, ^2J –12.0 Hz, ^3J 6.0 Hz), 6.58 (br. s, NH). ^{13}C NMR ($CDCl_3$) δ: 19.8 (q, $C_{ring}Me$, ^1J 127 Hz), 23.1 (q, MeCO, ^1J 123 Hz), 39.3 (t, NCH_2, ^1J 139 Hz), 52.5 (t, CH_2NH, ^1J 136.0 Hz), 61.2 (s, diaziridine ring), 170.6 (s, CO). IR (ν/cm^{-1}): 884, 912, 1000, 1128, 1288, 1376, 1440, 1544, 1664, 2944, 3312.

2-(2-Hydroxyethyl)-1,3,3-trimethyldiaziridine **3k**: yield 35.8%, bp 97 °C (1 Torr), n_D^{20} 4.4623. ^{1}H NMR ($CDCl_3$) δ: 1.11 (br. s, 6H, CMe), 2.36 (s, 3H, NMe), 2.38, 2.71 (dt, 2H, NCH_2, ^2J –12.4 Hz, ^3J 5.8 Hz), 3.5 (br. s, 1H, OH), 3.67 (t, 2H, OCH_2, ^3J 5.8 Hz). ^{13}C NMR ($CDCl_3$) δ: 18.9, 19.5 (CMe_2), 40.0 (NMe), 54.6 (NMe), 60.7 (diaziridine ring), 61.0 (OCH_2).

2-(2-Acetamidoethyl)-1,3,3-trimethyldiaziridine **3l**: yield 37.6%, bp 102.5 °C (1 Torr), n_D^{20} 1.4650, ^{1}H NMR ($CDCl_3$) δ: 1.13 (s, 3H, CMe), 1.15 (s, 3H, CMe), 1.82 (s, 3H, COMe), 2.26 (s, 3H, NMe), 2.22, 2.58 (dt, 2H, NCH_2, ^2J –12.5 Hz, ^3J 5.8 Hz), 3.23, 3.28 (dt, 2H, $NHCH_2$, ^2J –12.0 Hz, ^3J 5.8 Hz), 6.50 (br. s, 1H, NH). ^{13}C NMR ($CDCl_3$) δ: 18.9, 19.2 (CMe_2), 22.7 (MeCO), 39.0 (NMe), 40.0 (NCH_2), 51.7 (CH_2NH), 60.5 (diaziridine ring), 169.7 (CO).

3-Acetamidomethyl-1,2,3-trimethyldiaziridine **3m**: yield 34.6%, bp 105 °C (1 Torr), n_D^{20} 1.4742. ^{1}H NMR ($CDCl_3$) δ: 1.28 (s, 3H, $C_{ring}Me$), 1.98 (s, MeCO), 2.43, 2.46 (2s, 6H, NMe), 3.43 (d, 2H, CH_2N, ^3J 5.3 Hz), 6.1 (br. s, 1H, NH). ^{13}C NMR ($CDCl_3$) δ: 16.0 (CMe), 23.0 (MeCO), 29.7, 41.4 (NMe), 62.1 (diaziridine ring), 170.1 (CO). IR (ν/cm^{-1}): 610, 690, 1000, 1140, 1270, 1380, 1560, 1660, 1888, 3080, 3290.

3-Ethyl-1,2,3-trimethyldiaziridine **3n**: yield 34%, bp 89 °C (15 Torr), n_D^{20} 1.4825. ^{1}H NMR ($CDCl_3$) δ: 0.85 (t, 3H, CH_2*Me*, ^3J 7.1 Hz), 1.07 (s, 3H, CMe), 1.38 (dq, 2H, CCH_2, ^3J 7.1 Hz), 2.25 (s, 3H, NMe), 2.29 (s, 3H, NMe). ^{13}C NMR ($CDCl_3$) δ: 9.5 ($MeCH_2$), 15.6 ($C_{ring}Me$), 25.8 ($C_{ring}CH_2$), 39.3, 39.9 (NMe), 64.0 (diaziridine ring). IR (ν/cm^{-1}): 970, 1410, 1460, 1640, 2990.

6-Acetamidomethyl-6-methyl-1,5-diazabicyclo[3.1.0]hexane **7d**: yield 52%, undistilled oil, n_D^{20} 1.4365. ^{1}H NMR ($CDCl_3$) δ: 0.90 (s, 3H, $C_{ring}Me$), 1.71 (s, 3H, MeCO), 1.68, 1.96 (m, 2H, ^2J –13.0 Hz, $^3J_{2a-3a}$ 11.5 Hz, $^3J_{2a-3e}$ 7.0 Hz, $^3J_{2e-3a}$ 10.1 Hz, $^3J_{2e-3e}$ 4.7 Hz), 2.60, 2.93 (m, 4H, NCH_2, ^2J –11.5 Hz, $^3J_{2a-3a}$ 11.5 Hz, $^3J_{2a-3e}$ 7.0 Hz, $^3J_{2e-3a}$ 10.1 Hz, $^3J_{2e-3e}$ 4.7 Hz), 3.0 (d, 2H, $C_{ring}CH_2$, ^3J 5.1 Hz), 6.60 (br. s, 1H, NH). ^{13}C NMR ($CDCl_3$) δ: 9.7 ($C_{ring}Me$), 22.5 (MeCO), 32.0 (CCC), 46.5 (CH_2NH), 47.2 (CH_2N), 61.6 (diaziridine ring), 170.0 (CO). IR (ν/cm^{-1}): 732, 1040, 1256, 1376, 1464, 1652, 2888, 2944, 3280.

Received: 26th June 2000; Com. 00/1676