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BENZIMIDAZOLO-DIAZEPINES FROM 1,3-DIENES AND ARENEDIAZOCYANIDES THROUGH A 1,3,4-TRI-AZA-COPE REARRANGEMENT.

Daniel Rousselle, Thomas Ryckmans and Heinz G. Viehe*
Laboratoire de chimie organique,
Université Catholique de Louvain 1, Place Louis Pasteur, B-1348 Louvain-la-Neuve, Belgium

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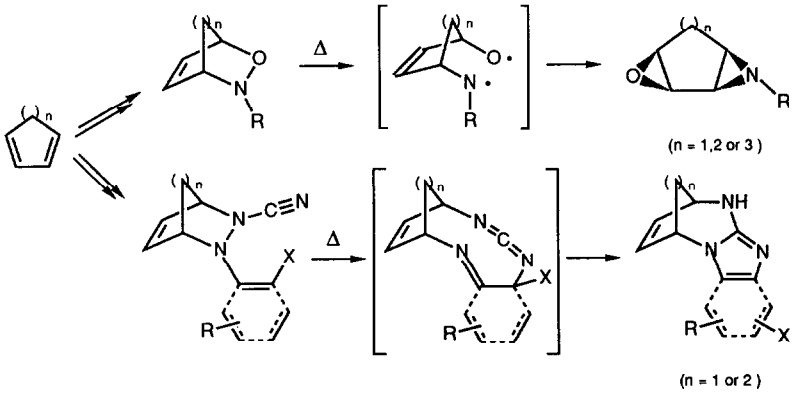
ABSTRACTS : Cyclic and bicyclic 1-cyano-2-arylhydrazines were prepared from arene diazocyanides and 1,3-dienes. Some of them rearrange at room temperature through a 1,3,4-tri-aza-Cope rearrangement, followed by an intramolecular cyclisation, to afford benzimidazolo-diazepines in moderate yields. When the competitive retro Diels-Alder reaction is made impossible by reduction of the cycloadducts, the rearrangement takes place at higher temperatures, with excellent yields, to previously unknown benzimidazolo-diazepines.

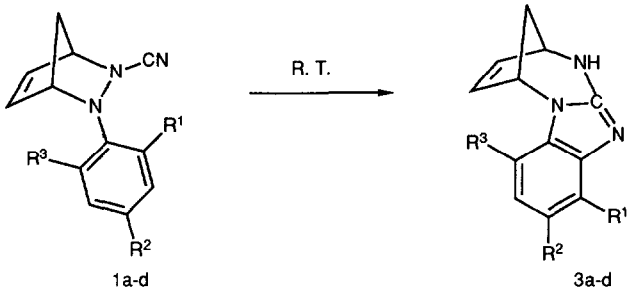
During our investigation of the Diels-Alder reaction between cyclic dienes and nitroso compounds, we found that cycloadducts were able to rearrange by "epoxy-epimination" if substituted adequately. This reaction permits the stereocontrolled functionalisation of all sp^2 carbon atoms of the conjugated diene[1-5]. We reported on the application of this reaction to the synthesis of streptamine derivatives[6]. In an attempt to extend the rearrangement of oxazines to aza-analogous N-cyanohydrazines, we found instead a different reaction leading to previously unknown imidazolo-diazepines [7].(Scheme 1).



Scheme 1

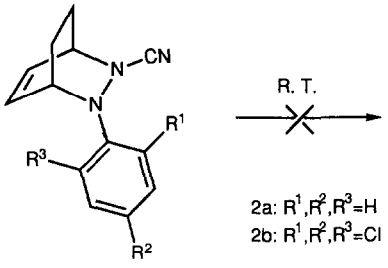
Whereas this unexpected reaction starting from dienes via [4+2] cycloaddition is new, the implied 1,3,4 tri-aza-Cope rearrangement ("nitrile-Cope") has precedence by the early work on cyanophenylhydrazines of Pellizari[8] and later by that of Bird[9] who has revealed the concerted nature of the rearrangement in the case of 4 or 5 membered cyclic cyanophenylhydrazines.

At room temperature and in various solvents such as dimethylsulfoxide, dichloromethane or ethanol, the 1-cyano-2-arylhydrazines 1 obtained by cycloaddition of cyclopentadiene on several arenediazocyanides rearrange slowly to the tetracyclic compounds 3. In contrast, the homologous and less strained hydrazines 2, prepared from 1,3-cyclohexadiene, are stable under such mild conditions (Scheme 2).



1a-d 3a-d

	R1	R2	R3	Reaction time	Yield of 3 (%)
a	H	H	H	5 weeks	35
b	H	F	H	7 days	15-20
c	H	Cl	H	15 days	50
d	Cl	Cl	Cl	8 days	68



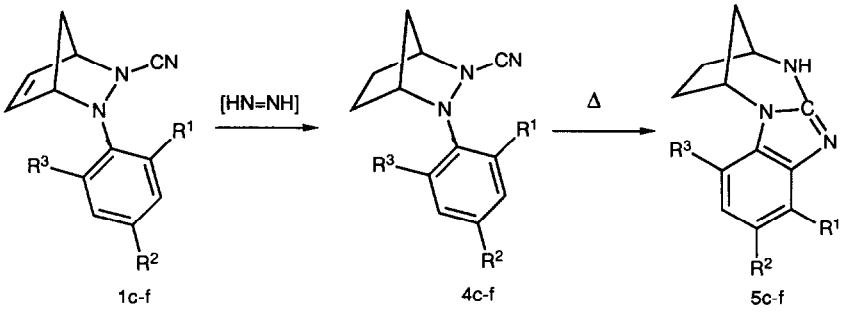
2a: R^1,R^2,R^3=H
2b: R^1,R^2,R^3=Cl

2a-b

Scheme 2

To avoid the competing retro-Diels-Alder decomposition of the adducts 1 and 2 upon heating, we hydrogenated the endocyclic double bond.

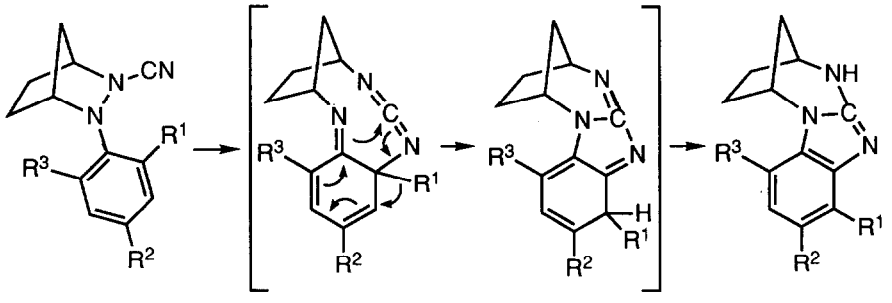
Reduction was best achieved with diimide, arising from acidification of potassium azodicarboxylate. After subsequent heating (110°C-150°C) the rearrangement was obtained; the reaction was clean and the yields were high (Scheme 3).



	R^1	R^2	R^3	Yield of 4 (%)	Reaction time	Temp. (°C)	Yield of 5 (%)
c	H	Cl	H	90	2 hours	110	90
d	Cl	Cl	Cl	95	1 hours	110	91
e	H	COPh	H	61	24 hours	110	94
f	H	NO_2	H	70	48 hours	150	92

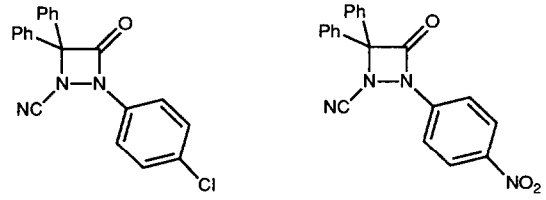
Scheme 3

The substituent effect merits further interest, but clearly para electronwithdrawing groups decrease the reaction rate. The rearrangement is accompanied by substituent displacement, formally depicted in scheme 4 as a concerted reaction. Other studies show[7b,9] that not only hydrogen and chlorine are able to migrate, but also bromine, alkylthio, cyano and methyl groups. (Scheme 4).



Scheme 4

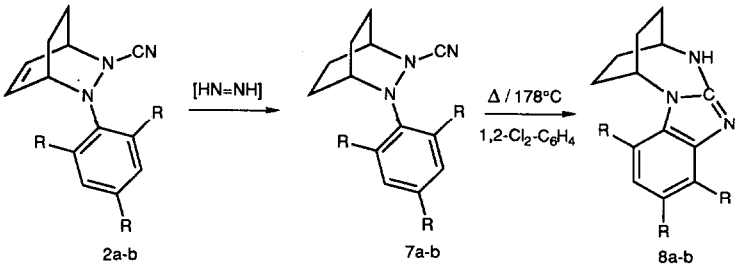
The activation energies of the rearrangements of hydrazines 5c and 5f have been measured as 29.8Kcal/mol and 31.3Kcal/mol, respectively . These figures can be compared to those reported by Bird[10] for the cyclic hydrazines 6a and 6b which bear the same substituents (24 and 30 kcal/mol.) (Scheme 5).



6a 6b

Scheme 5

It is of synthetic importance that we could generalise the reaction sequence to the arene diazocyanide adducts obtained from 1,3-cyclohexadiene and butadiene. As depicted in scheme 4, the diazabicyclo[2,2,2]octanes 7 rearrange slowly but in high yields when heated during 2 days in dichlorobenzene (Scheme 6).

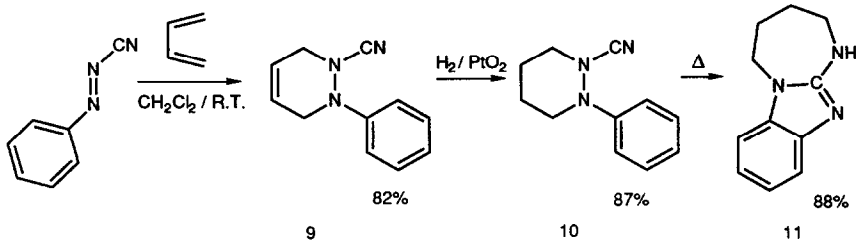


2a-b 7a-b 8a-b

	R	Yield of 7	Reaction time	Yield of 8
a	H	87%	2 days	78%
b	Cl	87%	2 days	81%

Scheme 6

The reaction starting from butadiene and benzenediazocyanide is of particular interest, because it involves a non-strained monocyclic hydrazine. After catalytic hydrogenation of the adduct, the rearrangement occurs in high yield although there is no strain assistance as in the cases mentioned before; however, the reaction requires five days heating in dichlorobenzene (Scheme 7).



Scheme 7

The benzimidazolo-diazepine structure 3e has been confirmed by X-ray analysis[7]. The benzimidazolo-diazepine structures 3, 5, 8 and 11 are deduced from the similarity of their NMR spectral characteristics to those of 3e.

In conclusion: The present report deals with a new functionalisation of 1,3-dienes leading to benzimidazolo-diazepine derivatives via a 1,3,4-tri-aza-Cope rerrangement. At least two factors influence this rearrangement: the nature of the aromatic substituents and the strain of the cyclic hydrazine. The generalisation of the rearrangement is now under investigation.

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EXPERIMENTAL SECTION

General

T.l.c. were carried out on silica gel plates (Merck $60F_{254}$) and visualised under U.V. light. Flash chromatographies were carried out with silica gel (Merck 60; 230-400 Mesh). Melting points were determined on a Buchi (Dr. Tottoli) apparatus, and are uncorrected. ^1H NMR were recorded in $CDCl_3$, DMSO-d6 or CD_3OD solution using TMS as internal reference at 200MHz on a Varian Gemini or XL 200 spectrometer. Mass spectra (MS) were recorded on a Varian AMT 44S spectrometer.

Benzenediazocyanide, 4-Chlorobenzenediazocyanide, 4-fluorobenzendiazocyanide and 4-nitrobenzenediazocyanide are known compounds; they were prepared according to the method described by G.W. Gokel [11]. The same methodology was used for the preparation of 4-benzoylbenzenediazocyanide

2,4,6-Trichlorobenzenediazocyanide. This known compound was prepared from 2,4,6-trichlorophenylhydrazine[12] via a new methodology: i) 2,4,6-trichlorophenylhydrazine was converted to 2,4,6-trichlorophenylsemicarbazide by Widman's[13] procedure modified as follows. Yield g (95%) as a white solid which was recrystallised from EtOH (m.p. 239-40°C). **^1H NMR** (DMSO) δ: 7.98 (s, NH); 7,49 (s, C-H); 7.13 (S,NH); 5,91 (s, NH_2). **^{13}C NMR** (DMSO) δ: 159.2 (S, CO); 141.6 (S, aromatic C-N); 128.72 (D, C-H); 125.1 (S, p-C-Cl); 124.6 (S, o-C-Cl).

ii) The 2,4,6-trichlorophenylsemicarbazide (40mmoles) in dichloromethane (200ml) was oxidized to 2,4,6-trichlorophenylazocarboxamide with lead tetraacetate (42mmoles). The solution was stirred at room temperature for 10 hours, after which insoluble salts were removed by filtration. The filtrate was washed with water and evaporated to give a red solid which was recrystallised from CCl_4 to yield 8.08g (80%) of pure 2,4,6-trichloropenylazocarboxamide. **^{1}H NMR** (DMSO) δ: 8.19 (s, NH_2); 7.90 (s, C-H). **^{13}C NMR** (DMSO) δ: 162.4 (S, CO); 145.6 (S, aromatic C-N); 134.5 (S, p-C-Cl); 129.7 (D, C-H); 126.8 (S, o-C-Cl). **IR** (KBr): 3510,3395 (NH_2 st); 1752 (CO st). **MS**: 253(M^+), 208, 143, 109, 79. Anal. Calcd. for $C_7H_4Cl_3N_3O$: C 32.27%, H 1.58%, N 16.63% found: C 32.95%, H 1.48%, N 16.44%.

iii) dehydration of the 2,4,6-trichlorophenylazocarboxamide give the 2,4,6-trichlorobenzenediazocyanide. Trifluoroacetic anhydride (3.06 ml, 22mmoles) was added to a stirred ice-cooled solution of the amide (20 mmoles) in anhydrous THF (30ml) and anhydrous pyridine (3,23 ml, 40 mmoles) at such a rate that the temperature was kept below 5°C. The reaction mixture was allowed to warm to room temperature and stirred for 3 hours and the solution was then evaporated to near dryness. The reaction product was isolated by flash chromatography (CH_2Cl_2). Yield 4.17g (89%) as a red solid which was recrystallised from Et_2O (m.p. 102°C). **^{13}C NMR** ($CDCl_3$) δ: 145.0 (S, aromatic C-N); 140.6 (S, p-C-Cl); 131.9 (S, o-C-Cl); 130.6 (D, C-H); 114,4 (S, CN).

Formation of 1,3-Diene-Arenediazocyanide adducts **1**, **2** and **8** -The adducts **1** and **2** were prepared by adding the calculated amount of 1,3-diene (150mmol) to a stirred solution of arenediazocyanide (15mmol) in CH_2Cl_2 (70ml). The reaction mixture, which usually rapidly became colourless, was set aside for several hours (1-12; the reaction course being monitored by t.l.c.). The solution was then evaporated to near dryness and the Diels-Alder adduct was separated by flash chromatography. The same procedure was used to prepare the adduct **8** except that the arenediazocyanide was added to a stirred solution of butadiene (freshly condensed; 40ml) in CH_2Cl_2.(40ml). In each case the solid adduct showed a characteristic band at 2205-2225 (CN) cm^{-1}.

1a Yield: 1.86g (63%) as a white solid (m.p. 74°C). **^{1}H NMR** ($CDCl_3$) δ: 7.27 (m, 2H); 7.00 (m, 3H); 6.46 (d, 1H); 6.36 (d, 1H); 4.93 (s, 1H); 4.77 (s, 1H); 2.15 (d, 1H); 1.82 (d, 1H). **^{13}C NMR** (CDCl3) δ: 149.4 (Sm, aromatic C-N); 137.8 (Dm, olefinic C-H); 134.3 (Dm, olefinic C-H); 129.0 (Dd, 3-aromatic C-H); 122.8 (Dm, 4-aromatic C-H); 117.9 (Dm, 2-aromatic C-H); 117.1 (S, CN); 69.6 (Dm, bridgehead CH), 69.1 (Dm, bridgehead CH); 46.8 (T, CH_2); **IR** (KBr): 3050, 2985 (=CH st),2210 (CN st), 1596 (C=C st).

1b was not isolated.

1c Yield 2.19g (63%) as a white solid (m.p. 101-103°C). **^{1}H NMR** ($CDCl_3$) δ: 7.2 (d, 9(J_{AB}), 2H), 6.9 (d, 9(J_{AB}), 2H), 6.5(m, 1H), 6.4(m, 1H), 4.9(s, 1H), 4.8(s, 1H), 2.2(d, 9(J_{AB}), 1H), 1.9(d, 9(J_{AB}), 1H). **^{13}C NMR** (CDCl3) δ: 147.9(Sm, 1-aromatic C-N), 137.6(Dm, 168($^1J_{CH}$), olefinic C-H), 134.3(Dm, 168($^1J_{CH}$), olefinic C-H), 129.0(Dd, 166($^1J_{CH}$), 6($^3J_{CH}$), 3-aromatic C-H), 128.0(Sm, 4-aromatic C-Cl), 119.2(Dd, 163($^1J_{CH}$), 6($^3J_{CH}$), 2-aromatic C-H), 116.7(S, CN), 70.0(Dm, 164($^1J_{CH}$), Bridgehead C-H), 69.3(Dm, 164($^1J_{CH}$), bridgehead C-H), 47.1(T, 141($^1J_{CH}$), -CH_2-). **MS**: 231(M^+), 190, 154, 139(Cl-C_6H_4-N_2), 111(Cl-C_6H_4), 66 (cyclopentadiene); **IR** (KBr): 2206 (CN st), 1591 (C=C st), 1092 (C-Cl). Anal. Calcd. for $C_{12}H_{10}ClN_3$: C 62.21%, H 4.35%, N 18.13%. found C 62.08%, H 4.34%, N 18.16%.

1d Yield: 3.83g (85%) as a white solid (m.p. 123°C). **^{1}H NMR** ($CDCl_3$) δ: 7.29 (s, 2H); 6.68 (sm, 2H); 4..88 (sm, 1H); 4.73 (sm, 1H); 2.24 (dm, 1H); 1.83 (dm, 1H). **^{13}C NMR** (CDCl3) δ: 139.2 (Sm, aromatic C-N); 137.9 (Dm, olefinic C-H); 136.8 (Dm, olefinic C-H); 130.5 (Sm, C-Cl); 130.3 (Dm, aromatic C-H); 116.6 (S, CN); 71.5 (Dm, bridgehead CH), 69.7 (Dm, bridgehead CH); 47.4 (Tm, CH_2). **MS**: 299 (M^+), 260, 207, 179, 158, 143, 66. **IR** (KBr): 3050, 2984 (=CH st), 2210 (CN st), 1450 (C=C st)

1e. Yield 4.2g(93%) as a white solid (m.p. 115-116°C). **^{1}H NMR** ($CDCl_3$) δ: 7.5-8 (m, 7H), 7.1(d, 8(J_{AB}), 2H), 6.5(s, 1H), 6.4(s, 1H), 5.1(s, 1H), 4.9(s, 1H), 2.1(dd, 9(J_{AB}), 2H). **^{13}C NMR** ($CDCl_3$) δ: 195.3(S, C=O), 153.0(S, aromatic C-N), 138.0(S, aromatic C-CO), 137.8(D, 180($^1J_{CH}$), olefinic C-H), 134.2(D, 180($^1J_{CH}$), olefinic C-H), 131.9(D, aromatic C-H), 131.6(D, aromatic C-H), 131.5(S, aromatic C-CO), 129.6(D, aromatic C-H), 128.1(D, aromatic C-H), 116.8(D, aromatic C-H), 116.4(S, CN), 70.1(Dm, 162($^1J_{CH}$), bridgehead C-H), 68.5(Dm, 163($^1J_{CH}$), bridgehead C-H), 47.5(T, 142($^1J_{CH}$), -CH_2-). **MS**: 301(M^+), 235(diazocyanide from retro Diels-Alder), 181($C_6H_5COC_6H_4$), 105(C_6H_5CO), 66(C5H6). IR (KBR):2207(CN st), 1649 (C=O st), 1578 (C=C st). Anal. Calcd. for $C_{19}H_{15}N_3O$: C 75.74%, H 5.02%, N 13.94%. found C 75.35%, H 4.86%, N 13.56%

1f Yield: 2.9g (80%) as a yellow solid (m.p. 108°C). **^{1}H NMR** ($CDCl_3$) δ: 8.14 (d, 9(J_{AB}), 2H); 7.12 (d, 9(J_{AB}), 2H), 6.53 (d, 5.5(J_{AB}), 1H); 6.42 (d, 5.5(J_{AB}), 1H); 5.17(s, 1H); 4.92 (s, 1H); 2.25 (d, 9.5(J_{AB}), 1H); 2.04 (d, 9.5(J_{AB}), 1H). **^{13}C NMR** ($CDCl_3$) δ: 154.6(Sm, 1-aromatic C-N), 142.3(Sm, 4-aromatic C-NO_2), 137.7(Dm, 177($^1J_{CH}$), olefinic C-H), 134.3 (Dm, 171($^1J_{CH}$), olefinic C-H), 125.1 (Dd, 173($^1J_{CH}$), 5($^3J_{CH}$), 3-aromatic CH); 117.0(Dd, 164($^1J_{CH}$), 6($^3J_{CH}$), 2-aromatic C-H); 115.9(S, CN); 70.5 (Dm, 164($^1J_{CH}$), bridgehead CH), 68.4 (Dm, 160($^1J_{CH}$), bridgehead C-H); 47.8 (DD, 142($^1J_{CH}$); 138 ($^1J_{CH}$), CH_2). **MS**: 242 (M^+), 201 (M-41), 176 (M-66, retro Diels-Alder), 154, 149(176 (diazocyanide)-26 (CN)), 122 (C_6H_4-NO_2). **IR** (CH_2Cl_2): 2212 (CN st), 1596 (C=C st), 1493 (NO_2 asym. st.), 1341 (NO_2 st.). Anal. Calcd. for $C_{12}H_{10}N_4O_2$: C 59.51%, H 4.16%, N 23.12%. found C 59.18%, H 3.92%, N 22.99%

2a Yield: 2.18g (69%) as a white solid (m.p. 73°C). **^{1}H NMR** ($CDCl_3$) δ: 7.27 (m, 2H); 7.03 (m, 3H); 6.56 (dd, 1H); 6.37 (dd, 1H); 4.53 (sm, 1H); 4.30 (sm, 1H); 2.31 (m, 2H); 1.47 (m, 2H). **^{13}C NMR** (CDCl3) δ: 149.6 (Sm, aromatic C-N); 133.5 (Dd, olefinic C-H); 130.8 (Dd, olefinic C-H); 128.9 (Dd, 3-aromatic C-H); 122.7 (Dm, 4-aromatic C-H); 117.9 (Dm, 2-aromatic C-H); 116.6 (S, CN); 54.8 (Dm, bridgehead CH), 53.7 (Dm, bridgehead CH); 23.1 (T, CH_2); 20.5 (T, CH_2). **MS:** 211 (M^+), 182, 172, 157, 133, 115, 80. **IR** (KBr): 3050, 2980 (=CH st), 2218 (CN st), 1600, 1580 (C=C st). Anal. Calcd. for $C_{12}H_{13}N_3$: C 73.93%, H 6.16%, N 19.90%. found C 74.06%, H 6.38%, N 19.96%

2b Yield: 3.67g (78%) as a white solid (m.p. 119°C). **^{1}H NMR** ($CDCl_3$) δ: 7.28 (s, 2H); 6.68 (ddd, 1H); 6.55 (dd, 1H); 4.40 (sm, 1H); 4.22 (sm, 1H); 2.60 (m, 1H); 2.42 (m, 1H); 1.51 (m, 2H). **^{13}C NMR** (CDCl3) δ: 139.1 (Sm, aromatic C-N); 133.5 (Dm, olefinic C-H); 133.3 (Dm, olefinic C-H); 130.7 (Sm, C-Cl); 130.4 (Sm, C-Cl); 130.0 (Dm, aromatic C-H); 116.0 (S, CN); 54.63(Dm, bridgehead CH), 54.56 (Dm, bridgehead CH); 21.9 (Tm, CH_2); 21.7 (Tm, CH_2). **MS** : 313 (M^+), 260, 221, 194, 181, 143, 80. **IR** (KBr): 3050, 2960 (=CH st), 2212 (CN st), 1570, 1550, 1450 (C=C st). Anal. Calcd. for $C_{13}H_{10}Cl_3N_3$: C 49.60%, H 3.18%, N 13.35%. found C 49.56%, H 3.10%, N 13.80%.

9 Yield: 2.27g (82%) as a white solid (m.p. 47.2°C). **^{1}H NMR** ($CDCl_3$) δ: 7.30 (dd, 2H); 7.00 (m, 3H); 5.96 (d, 1H); 5.84 (d, 1H); 3.83 (m, 4H). **^{13}C NMR** (CDCl3) δ: 146.0 (Sm, aromatic C-N); 129.1 (Dd, aromatic C-H); 123.9 (Dm, olefinic C-H); 122.7 (Dm, aromatic C-H); 122.0 (Dm, aromatic C-H); 115.0 (Dm, aromatic C-H); 115.0 (S, CN); 50.7 (Tm, CH_2); 45.0 (Tm, CH_2). **MS** : 185 (M^+), 170, 157, 143, 130, 93, 77. **IR** (KBr): 3060, 2940 (=CH st), 2220 (CN st), 1600, 1500 (C=C st). Anal. Calcd. for $C_{11}H_{11}N_3$: C 71.35%, H 5.95%, N 22.70% found: C 71.45%, H 6.10%, N 22.69%.

General Procedure for Dimide Reduction of 1,3-Diene-Arenediazocyanide adducts **1** and **2**.-A solution of acetic acid (200 mmol) in methanol (100 ml) was added dropwise to the yellow slurry formed by potassium azodicarboxylate (100mmol), methanol (100ml) and hydrazine derivative (10mmol); care was taken to keep vigorous gas evolution under control. After complete addition of the acid, the slurry was stirred until it became white and gas evolution stopped. Water (200ml) and methylene chloride (200 ml) were added to the residual mixture after removal of most of the methanol by vacuum distillation. The organic phase was washed with a saturated sodium bicarbonate solution (50ml) and then with water, dried over magnesium sulfate and the methylene chloride was evaporated under reduced pressure. The residue was purified by column chromatography yielding the corresponding saturated hydrazine.

Compound **4c** is prepared from hydrazine **1c** (2.31 g). Yield: 2.1 g (90%) as a light yellow solid (m.p. 100-101°C). **^{1}H NMR** (CDCl3) δ: 7.2(d, 9(J_{AB}), 2H), 6.95(d, 9(J_{AB}), 2H), 4.2(s, 1H), 4.18(s, 1H), 1.9(m, 6H). **^{13}C NMR** (CDCl3) δ:147.7(S, 1-aromatic C-N), 129.0(Dd, 165($^1J_{CH}$), 6($^3J_{CH}$), 3-aromatic C-H), 127.5(Sm, 4-aromatic C-Cl), 118.5(Dd, 162($^1J_{CH}$), 6($^3J_{CH}$), 2-aromatic C-H), 116.1(S, N-CN), 65.0(Dm, 157($^1J_{CH}$), bridgehead C-H), 64.0(Dm, 160($^1J_{CH}$), bridgehead C-H), 36.0(DDt, 139($^1J_{CH}$), 138($^1J_{CH}$), 6($^3J_{CH}$)), 27.5(Tm, 125($^1J_{CH}$), CH_2-CH_2), 26.7(Tm, 136($^1J_{CH}$), CH_2-CH_2). **MS**: 233(M^+), 204(M-29), 193(M-40), 179(M-54). **IR** (KBR): 2209 (st N-CN), 1095 (Ar-Cl). Anal. Calcd. for $C_{12}H_{12}ClN_3$: C 61.68%, H 5.18%, N 17.97%. found C 61.62%, H 5.02%, N 17.47%.

Compound **4d** is prepared from hydrazine **1d** (3g). Yield: 2,76g (92%) as a white solid (m.p. 153°C). **^{1}H NMR** (DMSO) δ:: 7.63 (s, 2H); 4.46 (sm, 1H); 4.04 (sm, 1H); 2.19 (m, 2H); 1.81 (m, 4H). **^{13}C NMR** (DMSO) δ: 139.6 (S, aromatic C-N); 130.0 (D, aromatic C-H); 129.5 (S, C-Cl); 129.3 (S, C-Cl); 116.0 (S, CN); 67.0 (D, C-H); 63.6 (D, C-H); 30.7 (T, CH_2); 27.6 (T, CH_2); 27.1 (T, CH_2). **MS**: 301 (M^+), 272, 249, 206, 179, 143, 67. **IR** (KBr): 3050, 2984 (=CH st), 2208 (CN st), 1450 (C=C st). Anal. Calcd. for $C_{12}H_{10}Cl_3N_3$: C 47.60%, H 3.31%, N 13.88% found: C 47.63%, H 3.32%, N 13.96%.

Compound **4e** is prepared from hydrazine **1e** (3g). Yield: 1.91g (61%) as a white solid (m.p. 109°C). **^{1}H NMR** ($CDCl_3$) δ: 7.5-8 (m, 7H), 7.05 (d, 9(J_{AB}), 2H), 4.42 (s, 1H), 4.26 (s, 1H), 1.9 (m, 6H). **^{13}C NMR** (CDCl3) δ: 194.8 (S,

C=O), 152.0(S, aromatic C-N), 137.6 (St, J($^3J_{CH}$), aromatic C-CO), 131.6 (D, 160($^1J_{CH}$), aromatic C-H), 131.4(D, 162($^1J_{CH}$), aromatic C-H), 130.6(S, C-C=O), 129.2(Dt, 161($^1J_{CH}$), 6 ($^3J_{CH}$), aromatic C-H), 127.8(Dd, 170 ($^1J_{CH}$), 7 ($^3J_{CH}$), aromatic C-H), 115.5(D, 162($^1J_{CH}$),5($^3J_{CH}$), aromatic C-H), 115.4 (S, CN), 64.0(D, 163($^1J_{CH}$), bridgehead C-H), 63.3(D, 161($^1J_{CH}$), bridgehead C-H), 36.5(T, 139($^1J_{CH}$), CH_2), 26.9(T, 138($^1J_{CH}$), CH_2-CH_2), 26.2(T, 132($^1J_{CH}$), CH_2-CH_2). **MS**: 303(M^+), 274(M-29), 263(M-40), 249(M-54), 105(C_6H_5CO). **IR**: 2209(N-CN st.), 1649(C=O st.). Anal. Calcd. for $C_{19}H_{17}N_3O$: C 75.23%, H 5.65%, N 13.85%. found C 75.31% H 5.63% N 13.82%.

Compound **4f** is prepared from hydrazine **1f** (2.42g). Yield:1.71g (70%) as a yellow solid (m.p. 96-98°C). **^{1}H NMR** (CDCl3) δ: 8.15(d, 9(J_{AB}), 2H), 7,0(d, 9(J_{AB}), 2H), 4.5 (d, 5(J_{AB}), 1H), 4.3(d, 5(J_{AB}), 1H), 1.9 (m, 6H). **^{13}C NMR** (CDCl3) δ:153.5(St, 9 ($^3J_{CH}$), 1-aromatic C-N), 143.0 (S, 4-aromatic C-NO_2), 125.2 (Dd, 168($^1J_{CH}$), 5($^3J_{CH}$), 3-aromatic C-H), 115.9 (Dd, 164($^1J_{CH}$), 6($^3J_{CH}$), 2-aromatic C-H), 115.1 (S, N-CN), 64.8(D, 159($^1J_{CH}$), bridgehead C-H), 63.5(D, 156($^1J_{CH}$), bridgehead C-H,), 37.3(T, 135($^1J_{CH}$), CH-CH_2-CH), 27(Tm, 131($^1J_{CH}$), CH_2-CH_2), 26.5(Tm, 136($^1J_{CH}$), CH_2-CH_2). **MS**: 244(M^+), 215(M-29), 204(M-40), 190(M-54), 122 (C_4H_6-NO_2). **IR**: 2206 (N-CN st), 1495 (NO_2, asym. st), 1338 (NO_2, st.). Anal. Calcd. for $C_{12}H_{12}N_4O_2$: C 59.02%, H 4.95%, N 22.93%. found C % 59.05, H 4.82%, N 22.94%.

Compound **7a** is prepared from hydrazine **2a** (2.1g). Yield: 1.84g (87%) as a white solid (m.p. 71°C). **^{1}H NMR** ($CDCl_3$) δ: 7.30 (dd, 2H); 7.08 (d, 2H); 6.95 (dd, 1H); 3.94 (s, 1H); 3.69 (s, 1H); 2.12 (sm, 4H); 1.72b (sm, 4H). **^{13}C NMR** ($CDCl_3$) δ: 149.2 (S, aromatic C-N); 129.0 (D, aromatic C-H); 121.3 (D, aromatic C-H); 115.6 (D, aromatic C-H); 114.0 (S, CN); 52.5 (D, C-H); 50.6 (D, C-H); 22.7 (T, CH_2); 22.0 (T, CH_2). **MS** : 213 (M^+), 158, 130, 119, 92, 76. **IR** (KBr): 3050, 2980 (=CH st), 2215 (CN st), 1600,1580 (C=C st).

Compound **7b** is prepared from hydrazine **2b** (3.2g). Yield: 2.8g (87%) as a white solid (m.p. 128°C). **^{1}H NMR** ($CDCl_3$) δ:7.34 (s, 2H); 3.71 (sm, 1H); 3.42 (sm, 1H); 2.63 (td, 2H); 2.29 (td, 2H); 1.79 (td, 2H); 1.73 (td, 2H). **^{13}C NMR** ($CDCl_3$) δ: 138.7 (S, aromatic C-N); 132.1 (S, C-Cl); 130.7 (S, C-Cl); 130.2 (D, aromatic C-H); 116.5 (S, CN); 54.1 (D, C-H); 53.3 (D, C-H); 24.0 (T, CH_2); 23.8 (T, CH_2). **IR** (KBr): 3050, 2960 (=CH st), 2210 (CN st), 1570,1550 (C=C st). **MS**: 315 (M^+), 280, 261, 206, 167, 149, 81. Anal. Calcd. for $C_{13}H_{12}Cl_3N_3$: C 49.45%, H 3.80%, N 13.31% found: C 49.25%, H 3.79%, N 13.08 %.

Catalytic Hydrogenation of the tetrahydropyridazine **9**.-The solution of the tetrahydropyridazine **9** (1,5g) in methanol (75ml) was shaken with PtO_2 (0,15g) in a 'Parr' Hydrogenator in hydrogen atmosphere (35Psi) for 48 hours. After filtration and removal of the solvent by vacuum distillation, the residue was purified by column chromatography (CH_2Cl_2) yielding 1.17g (78%) ofthe saturated pyridazine **10** as a yellow oil. **^{1}H NMR** ($CDCl_3$) δ::7.28 (m, 2H); 6.93 (m, 3H); 3.56 (sm, 2H); 3.32 (sm, 2H); 1.76 (m, 4H). **^{13}C NMR** ($CDCl_3$) δ: 145.7 (S, aromatic C-N); 129.2 (D, aromatic C-H); 121.1 (D, aromatic C-H); 114.8 (S, CN); 114.8 (D, aromatic C-H); 49.4 (T, CH_2); 46.4 (T, CH_2); 22.2 (T, CH_2); 21.1 (T, CH_2). **MS**: 187 (M^+), 161, 146, 132, 118, 104, 77. **IR** (KBr): 3058, 2960, 2810 (=CH st), 2220 (CN st), 1600, 1500 (C=C st).

Thermal Rearrangement of the 1-Cyano-2-Arylhydrazine Derivatives.-In each case the rearranged compound is a white solid which showed characteristic bands at 2500-3200 (NH) and 1640-1670 (C=N) cm^{-1}.

Compounds **3a-d** were obtained from hydrazines **1a-d** by stirring them several days in CH_2Cl_2. After removal of the solvent by vacuum distillation, the residue was recrystallised from $CHCl_3$, or purified by flash chromatography (Ethylacetate, ethylacetate/Ethanol 9:1 or Ethyl acetate/Ethanol 8:2).

3a (m.p. 242°C) Reaction time 5 weeks. Yield: 352mg (35%). **^{1}H NMR** (DMSO) δ: 7.50 (s broad, 1H); 7.30 (dd, 1H); 7.14 (dd, 1H); 6.88 (m, 2H); 6.25 (dd, 1H); 6.08 (dd, 1H); 5.26 (sm, 1H); 4.26 (sm, 1H); 2.16 (ddd, 1H); 1.91 (d, 1H). **^{13}C NMR** (DMSO) δ: 151.6 (S, NH-C=N); 142.1 (S, aromatic C-N=); 134.3 (Dm, olefinic C-H); 133.8 (S, aromatic C-N); 133.6 (Dm, olefinic C-H); 120.3 (Dd, aromatic C-H); 118.2 (Dd, aromatic C-H); 115.3 (Dd, aromatic C-H); 107.2 (Dd, aromatic C-H); 54.8 (Dd, C-H); 55.0 (D, C-H); 37.9 (T, CH_2). **MS**: 197 (M^+), 170, 132, 118, 90. **IR** (KBr): 3420 (NH, st), 3050, 2990 (=CH st), 1640 (C=N st), 1555, 1460 (C=C st). . Anal. Calcd. for $C_{12}H_{11}N_3$: C 73.10%, H 5.58 %, N 21.32% found: C 72.62%, H 5.48 %, N 21.33 %.

3b (m.p. 170°C (dec.)), Yield: 3.05 gr (20%). **^{1}H NMR** (CD_3OD) δ: 7.2 (dd, 9 (J_{AB}), 5 (^4J_F), 1H); 6.9 (dd, 10 (^3J_F), 2(^4J), 1H); 6.7(ddd,10 (^3J_F), 9 (J_{AB}), 2 (^4J), 1H); 6.2(d, 6 (J_{AB}), 1H), 6.1 (d,6(J_{AB}), 1H); 5,2 (m, 1H); 4.9 (s broad, 1H); 4.3 (m, 1H); 2.3 (d, 11(J_{AB}), 1H); 2.0 (d, 11(J_{AB}), 1H). **^{13}C NMR** (CD_3OD) δ: 160.3 (D, 233 ($^1J_{CF}$), 4-aromatic C-F); 153.6(S, NH-C=N); 143(D, 10 ($^3J_{CF}$), 2-aromatic C-N=); 134.3 (D, 171 ($^1J_{CH}$), C=C); 133.4 (D, 172($^1J_{CH}$), C=C),

130.3(S, 1-aromatic C-N); 108.0 (Dd, 164($^1J_{CH}$), 10 ($^3J_{CF}$), 6-aromatic C-H): 106.8 (Ddd, 163 ($^1J_{CH}$), 26 ($^2J_{CF}$), 4 ($^3J_{CH}$), 3-aromatic C-H); 102.4 (Ddd, 162($^1J_{CH}$), 26 ($^2J_{CF}$), 5 ($^3J_{CH}$) ,5-aromatic CH); 56.5 (D, 150 ($^1J_{CH}$), bridghead C-H); 55.3 (D, 148 ($^1J_{CH}$), bridgehead C-H); 38.6 (T, 137 ($^1J_{CH}$), CH_2). **MS** 215 (M^+), 214, 150 (M-65), 136. **IR** 1643(C=N st), 1575 (C=C st). Anal. Calcd. for $C_{12}H_{10}FN_3$: C 66.97%, H 4.68%, N 19.52% found: C 66.49%, H 4.54%, N 19.01%.

3c (m.p. 205°C (subl.)), Yield: 750 mg (50%). **^{1}H NMR** ($CDCl_3$) δ: 8.2 (s broad, 1H), 7.3 (m, 1H), 7 (m, 2H), 6.1 (s, 2H), 5(s, 1H), 4.4(s, 1H), 2.2 (d, 11(J_{AB}), 1H), 2.1 (d, 11(J_{AB}), 1H). **^{13}C NMR** ($CDCl_3$) δ: 152.2 (S, NH-C=N), 142.5(S, aromatic C-N=), 133.3(D, 178($^1J_{CH}$), olefinic C-H), 132.0 (D, 172($^1J_{CH}$), olefinic C-H), 131.1 (S, aromatic C-N), 126.1(S, aromatic C-Cl), 118.6(Dd, 159($^1J_{CH}$), 5($^3J_{CH}$), aromatic C-H), 115.5(Dd, 157($^1J_{CH}$), 5($^3J_{CH}$), aromatic C-H), 106.8(D, 162($^1J_{CH}$), aromatic C-H), 55.1(Dm, 152($^1J_{CH}$), bridgehead C-H), 53.9(Dm, 154($^1J_{CH}$), bridgehead C-H), 37.7(T, 140($^1J_{CH}$), CH_2 group). **MS** 231(M^+), 166(M-65). **IR** (KBR): 1640(C=N st), 1591(C=C st). Anal. Calcd. for $C_{12}H_{10}ClN_3$: C 62.21%, H 4.35%, N 18.13% found: C 61.65%, H 4.23%, N 17.82%.

3d (m.p. 252°C) Reaction time: 1 week. Yield: 906mg (91%). **^{1}H NMR** (DMSO) δ: 8.15 (s broad, 1H); 7.32 (s, 1H); 6.21 (dd, 1H); 6.12 (dd, 1H); 5.87 (sm, 1H); 4.27 (sm, 1H); 2.20 (ddd, 1H); 1.98 (d, 1H). **^{13}C NMR** (DMSO) δ: 152.0 (S, NH-C=N); 141.5 (S, aromatic C-N=); 132.8 (D, olefinic C-H); 131.4 (D, olefinic C-H); 128.6 (S, aromatic C-N); 123.3 (S, C-Cl); 118.7 (S, C-Cl); 115.0 (D, aromatic C-H); 111.4 (S, C-Cl); 57.1 (D, C-H); 52.9 (D, C-H); 36.9 (T, CH_2). **MS**: 299 (M^+) 274, 247, 233, 221, 131, 98. **IR** (KBr): 3430 (NH, st), 2990 (=CH st), 1660, 1630 (C=N st), 1560 (C=C st). Anal. Calcd. for $C_{12}H_8Cl_3N_3$: C 47.92%, H 2.66%, N 13.98% found: C 47.85%, H 2.56%, N 13.51%.

Compoud **5c** was obtained from hydrazine **4c** (1g), by warming in toluene (50 ml) for 2 hours. After removal of the solvent by vacuum distillation, the residue was purified by chromatography (Ethyl Acetate/Ethanol 8/2), affording **5c** as a white solid (m.p. 178-180°C) Yield: 900mg (90%). **^{1}H NMR** (CD_3OD) δ: 7.5(s, 1H), 7.03 (d, 8(J_{AB}), 1H), 6.9(d, 8(J_{AB}), 1H), 4.96(s, 1H), 4.7(s, 1H), 3.97(s, 1H), 2.0(m, 6H). **^{13}C NMR** (CD_3OD) δ: 154.7(Sm, N-C=N), 144.6(Sm, aromatic C-N=C), 132.5(Sm, aromatic C-N), 127.4(Sm, aromatic C-Cl), 119.9(Dd, 166($^1J_{CH}$), 5($^3J_{CH}$), aromatic C-H), 115.5(Dd, 164($^1J_{CH}$), 6($^3J_{CH}$), aromatic C-H), 108.3(D, 163($^1J_{CH}$), aromatic C-H), 54.7(D, 152($^1J_{CH}$), bridgehead C-H), 53.0(D, 153($^1J_{CH}$), bridgehead C-H), 35.3(T, 135($^1J_{CH}$)), 34.8(T, 134($^1J_{CH}$)), 34.6(T, 134($^1J_{CH}$)).**MS**: 233(M^+), 206, 203, 198, 167, 79. **IR**(KBR): 1639(C=N st.), 1052(C-Cl st). Anal. Calcd. for $C_{12}H_{12}ClN_3$: C 61.68%, H 5.18%, N 17.97%. found C 61.64%, H 5.10%, N 17.91%.

Compound **5d** was obtained from hydrazine **4d** (1g), by warming it in toluene (75ml) for 1 hour. After removal of the solvent by vacuum distillation, the residue was recrystallised from tetrahydrofuran to give **5d** (m.p. 292°C). Yield: 906mg (91%). **^{1}H NMR** (DMSO) δ: 7.99 (s broad, 1H); 7.27 (s, 1H); 5.46 (s, 1H); 3.89 (s, 1H); 2.10 (m, 6H). **^{13}C NMR** (DMSO) δ: 155.8 (S, NH-C=N); 144.1 (S, aromatic C-N); 132.3 (S, aromatic C-N); 129.2 (S, C-Cl); 127.1 (S, C-Cl); 114.8 (D, aromatic C-H); 109.9 (S, C-Cl); 55.0 (D, C-H); 50.4 (D, C-H); 34.3 (T, CH_2); 33.8 (T, CH_2); 33.5 (T, CH_2). **MS** : 302 (M^+) 273, 236, 202, 172, 121, 67. **IR** (KBr): 3450 (NH, st), 3050, 2990 (=CH st), 1635 (C=N st), 1550, 1425 (C=C st). Anal. Calcd. for $C_{12}H_{10}N_3Cl_3$: C 47.60%, H 3.31%, N 13.88% found: C 47.22%, H 2.89%, N 13.69%.

Compoud **5e** was obtained from hydrazine **4e** (1g), by warming in toluene (50 ml) for 24 hours. After removal of the solvent by vacuum distillation, the residue was purified by chromatography on silica gel (Ethyl Acetate/Ethanol 8/2), affording **5e** as a white solid (m.p. 218°C) Yield 940mg (94%). **^{1}H NMR** ($CDCl_3$) δ: 8.39 (br., 1H), 7.8(m, 3H), 7.5(m, 3H), 7.4(d, 8(J_{AB}), 2H), 4.7(s, 1H), 4.1(s, 1H), 2.0(m, 6H). **^{13}C NMR** ($CDCl_3$) δ: 196.9(S, C=O), 153.9(S, N-C=N), 142.6(S, aromatic C-N=C), 138.9(S), 136.3(S), 131.5(D, aromatic C-H), 130.5(D, aromatic C-H), 129.8(D, aromatic C-H), 127.9(D, aromatic C-H), 122.6(Dd, 162($^1J_{CH}$), 5($^3J_{CH}$), aromatic C-H), 117.7(Dd, 162($^1J_{CH}$), 6($^3J_{CH}$), aromatic C-H), 105.3(D, 160($^1J_{CH}$), aromatic C-H), 53.4(D, 153($^1J_{CH}$), bridgehead C-H), 51.5(D, 150($^1J_{CH}$), bridgehead C-H), 34.3(T, 134($^1J_{CH}$)), 34.2(T, 134($^1J_{CH}$)), 33.8(T, 134($^1J_{CH}$)). **MS**: 303(M^+), 274, 226, 198, 105. **IR**(KBR): 1640(C=O st). Anal. Calcd. for $C_{19}H_{17}N_3O$: C 75.23%, H 5.65%, N 13.85% found: C 74.67%, H 5.49%, N 13.89%.

Compoud **5f** was obtained from hydrazine **4f** (1g), by warming in xylene (50 ml) for 48 hours. After removal of the solvent by vacuum distillation, the residue was purified by chromatography on silica gel (Ethyl Acetate/Ethanol 8/2), affording **5f** as a yellow solid (m.p. 284-286°C) Yield 920mg (92%). **^{1}H NMR** (DMSO) δ: 8.0(m, 3H), 7.4(d, 8(J_{AB}), 1H), 5.0(s, 1H), 4.0(s, 1H), 2.0(m, 6h). **^{13}C NMR** (DMSO) δ: 154.8(S, N-C=N), 143.2(S,

aromatic C-N=C), 141.5(Sm, aromatic C-N), 138.0(Sm, aromatic C-N), 114.7(Dd, 167($^1J_{CH}$), 5($^3J_{CH}$), aromatic C-H), 109.4(Dd, 167($^1J_{CH}$), 5($^3J_{CH}$), aromatic C-H), 105.9(D, 170($^1J_{CH}$), aromatic C-H), 53.4(D, 148($^1J_{CH}$), bridgehead C-H), 50.9(D, 152($^1J_{CH}$), bridgehead C-H), 33.9(D, 132($^1J_{CH}$)), 33.5(D, 135($^1J_{CH}$), 33.3(D, 135($^1J_{CH}$)) **MS**: 244 (M^+), 215, 198, 169. **IR**(KBR): 1647(C=N st), 1490(NO_2 asym. st.), 1338(NO_2 st.). Anal. Calcd. for $C_{12}H_{12}N_4O_2$ C 59.02%, H 4.95%, N 22.93% found: C 58.66%, H 4.63%, N 22.67%.

Compounds **8a** and **b** were obtained from hydrazines **7a** and **b** respectively (1g), by warming them in 1,2-dichlorobenzene under reflux (75ml) for 2 days. After removal of the solvent by vacuum distillation, the resulting solid was purified by coluum chromatography (Ethylacetate/methanol 90/10 and Ethylacetate respectively) and recrystallised from tetrahydrofuran to give the corresponding benzimidazolo-diazepine. **8a** (m.p. 252°C) yield: 783mg (78%). **^{1}H NMR** (DMSO) δ: 7.31 (s broad, 1H); 7.06 (m, 2H); 6.82 (m, 2H); 5.73 (s, 1H); 4.46 (s, 1H); 2.03 (m, 4H); 1.92 (m, 4H). **^{13}C NMR** (DMSO) δ: 156.0 (S, NH-C=N); 143.2 (S, aromatic C-N); 132.4 (S, aromatic C-N); 119.9 (D, aromatic C-H); 117.6 (D, aromatic C-H); 114.2 (D, aromatic C-H); 106.5 (D, aromatic C-H); 46.9 (D, C-H); 45.3 (D, C-H); 27.4 (T, CH_2); 26.9 (T, CH_2). **IR** (KBr): 3430 (NH, st), 3030, 2980 (=CH st), 1620 (C=N st). Anal. Calcd. for $C_{13}H_{15}N_3$: C 73.24%, H 7.04%, N 19.72% found: C 73.08%, H 7.11%, N 19.65%.

8b (m.p. 261°C) yield: 794mg (79%). **^{1}H NMR** (DMSO) δ: 8.67 (s broad, 1H); 6.99 (s, 1H); 5.37 (s, 1H); 3.74 (s, 1H); 2.29 (m, 4H); 2.00 (m, 4H). **^{13}C NMR** (DMSO) δ: 158.9 (S, NH-C=N); 141.6 (S, aromatic C-N); 130.6 (S, aromatic C-N); 128.4 (S, C-Cl); 124.5 (S, C-Cl); 120.7 (D, aromatic C-H); 111.9 (S, C-Cl); 49.1 (D, C-H); 46.6 (D, C-H); 27.6 (T, CH_2); 27.2 (T, CH_2). **MS** : 315 (M^+), 286, 235, 207. **IR** (KBr): 3450 (NH, st), 3030, 2940 (=CH st), 1620 (C=N st). Anal. Calcd. for $C_{13}H_{12}N_3Cl_3$: C 49.29%, H 3.79%, N 13.27% found: C 49.78%, H 3.11%, N 13.30%.

Compound **11** was obtained from hydrazine **10** (1g), by warming it in 1,2-dichlorobenzene under reflux (75ml) for 5 days. After removal of the solvent by vacuum distillation, the residue was recrystallised from tetrahydrofuran to give **11** (m.p. 192°C). Yield: 880mg (88%). **^{1}H NMR** (DMSO) δ: 9.20 (s broad, 1H); 7.57 (d, 1H); 7.45 (d, 1H); 7.29 (m, 2H); 4.24 (s, 2H); 3.49 (s, 2H); 2.01 (m, 4H). **^{13}C NMR** (DMSO) δ: 151.0 (S, NH-C=N); 129.8 (S, aromatic C-N); 127.3.8 (S, aromatic C-N); 121.8 (D, aromatic C-H); 120.9 (D, aromatic C-H); 109.6 (D, aromatic C-H); 108.6 (D, aromatic C-H); 43.3 (T, CH_2); 41.5 (T, CH_2); 25.6 (T, CH_2); 23.6 (T, CH_2). **IR** (KBr): 3450 (NH, st), 3025, 2990 (=CH st), 1650 (C=N st), 1480, 1420 (C=C st). **MS** : 187 (M^+), 159, 132, 118, 90.

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