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Synthetic Exploitation of the Ring-Opening of 3,4-Dinitrothiophene. Access to 1,4-Disubstituted 2,3-Dinitro-1,3-butadienes and 2,3-Diaminobutanes[1]

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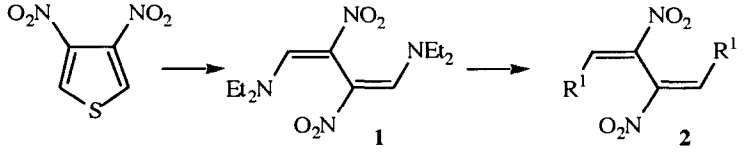
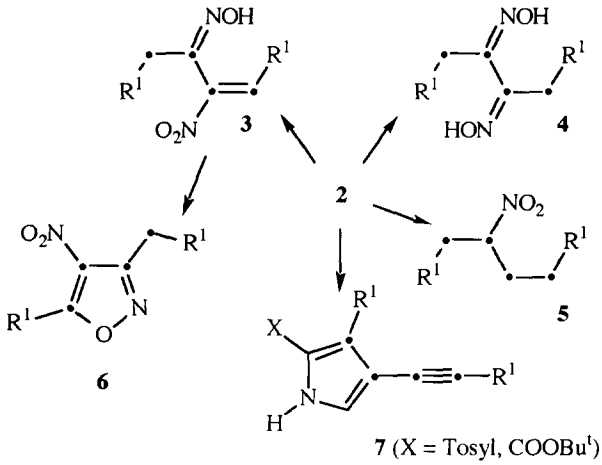
Abstract: The reactions of 1,4-bis(diethylamino)-2,3-dinitro-1,3-butadiene **1** (deriving from ring-opening of 3,4-dinitrothiophene with diethylamine) with one mole of Grignard reagents give, together with disubstituted products 1,4-dialkyl- and 1,4-diaryl-2,3-dinitro-1,3-butadienes **2**, the monosubstituted 1-alkyl-4-diethylamino- and 1-aryl-4-diethylamino-2,3-dinitro-1,3-butadienes **8** in yields dependent on the nature of the reagent employed. Aryl-substituted compounds **8** undergo a highly regioselective reaction with aryl Grignard reagents to furnish good yields of 1-Ar^1-4-Ar^2-2,3-dinitro-1,3-butadienes **9**. Preliminary results are also reported on the transformation of some dinitrobutadienes **2** and **9** into the corresponding 1,4-disubstituted 2,3-diaminobutanes **10**.

Utilization of the ring-opening of thiophene derivatives is representative of synthetically potent processes[2] exploiting both the benzenoid and the nonbenzenoid[3,4] behaviour of such heterocyclic system. This strategy allows the synthesis of various target molecules by further transformations of the relevant ring-opening products. In this subject the reactions of 3,4-dinitrothiophene with secondary amines[5,6] represent a pertinent example of application; thus, we have recently shown[6] (Scheme 1) that the reaction with Grignard reagents of the ring-opening product 1,4-bis(diethylamino)-2,3-dinitro-1,3-butadiene **1** easily provides 1,4-dialkyl- and 1,4-diaryl-2,3-dinitro-1,3-butadienes **2**. Such previously unknown compounds are amenable to further transformations to furnish derivatives whose skeleton is represented by the four carbons of the parent thiophene system. Consistently, our previous results have evidenced the easy accessibility from **2** of interesting target molecules (Scheme 2) such as 1,4-disubstituted 3-hydroximino-2-nitro-1-butenes **3**,[7a] 2,3-bis(hydroximino)-**4**[6b] and 2-nitro-butanes **5**[7b] as well as substituted 4-nitroisoxazoles **6**[7a] and 4-ethynylpyrroles **7**.[7c]

Scheme 1



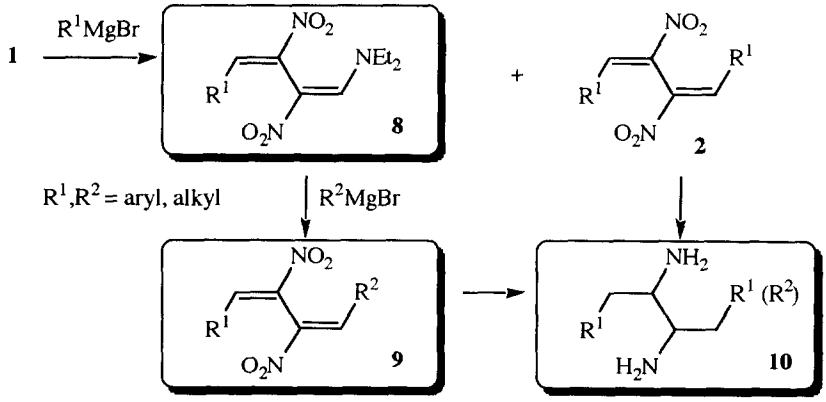
Scheme 2



The four carbons of the parent 3,4-dinitrothiophene are evidenced by dots

At this time, we report (Scheme 3) on the scope and limitation of the selective substitution of a single diethylamino group of **1** with aryl or alkyl groups by reaction with relevant Grignard reagents and on the possible transformation of the obtained 1-aryl-4-diethylamino-2,3-dinitro-1,3-butadienes **8** into 1,4-diaryl-2,3-dinitro-1,3-butadienes **9** with different aryl substituents in the 1,4-positions. A preliminary account on the transformation of some dinitrobutadienes **2** and **9** into the corresponding 1,4-disubstituted 2,3-diaminobutanes **10** is also given.

Scheme 3

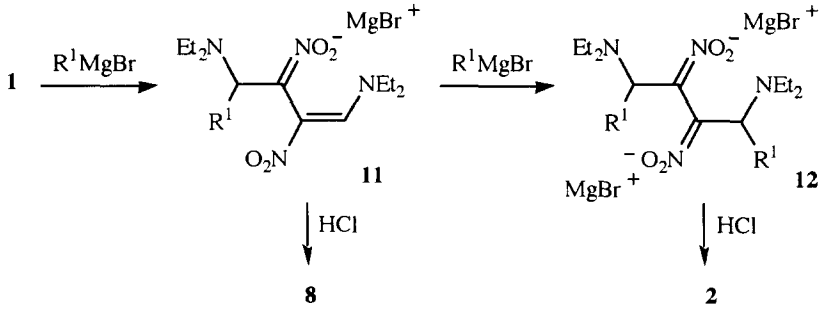


RESULTS AND DISCUSSION

Synthesis of asymmetrically 1,4-disubstituted 2,3-dinitro-1,3-butadienes 8 and 9

In agreement with the behaviour of monofunctional nitroenamines in the same kind of processes,[8,9,10a] it has been previously advanced[6b] (Scheme 4) that the transformation of **1** into dinitrobutadienes **2**, by action of 2 moles of Grignard reagent, could proceed through two successive 1,4-additions of the organometallic to the nitroalkene functions, followed by elimination of two diethylamine molecules after acidic quenching of the reaction. Accordingly, preliminary results[6b] have shown that when **1**, in THF at 0°, was reacted with 1.1 moles of phenylmagnesium bromide, besides unreacted **1** (30%) and the disubstituted dinitrobutadiene **2a** (R^1 = Ph, 38%), the monosubstituted product **8a** (R^1 = Ph) was also isolated in 31% yield. The latter evidently deriving from acidic quenching of the intermediate monoadduct **11**.

Scheme 4



The presence in compounds like **8a** of a nitroenaminic system coupled with a 1-nitroalkene functionality (the potentiality in synthesis of both systems being well known)[8,10-13] prompted us to investigate scope and limitation of similar monosubstitution processes on **1**.

Using the above mentioned reaction with phenylmagnesium bromide as a comparison standard, different reaction conditions were tested in order to improve absolute and relative yields of the monosubstitution product **8a**. For instance, we have observed that a decrease in the phenylmagnesium bromide to **1** molar ratio from 1.1 to 0.5 and to 0.1 caused, as expected, an increase in the relative yield of **8a** from 45 to 69 and to about 100%. In the last two conditions, however, because of the relatively low quantity of reacted **1**, the absolute yields of **8a** were not satisfactory on a pure preparative point of view as compared to those of the standard experiment. In spite of other attempts of modifying the reaction variables, the original conditions (employing 1.1 moles of Grignard reagent at 0° in THF) appeared to be preferable as the best compromise between absolute and relative yields of **8a**.

The results obtained from the analogous reactions of **1** with different Grignard reagents (Table 1) show that the formation of 4-substituted 1-diethylamino-2,3-dinitro-1,3-butadienes **8** occurs in yield which is dependent on the nature of the reagent employed. Even if, actually, entries 1, 4, 5 and 6 show no appreciable influence on the relative yield of **8** by 4-Me, 4-MeO or 3-Cl substituents in the benzene moiety of the Grignard reagent, a marked effect is observed when more sterically hindered reagents are used. Thus, on going

Table 1. Reactions of 1,4-bis(diethylamino)-2,3-dinitro-1,3-butadiene (**1**) with RMgBr in THF. [a]

Entry no.		R in RMgBr	Conversion (%) [b]	Monosubstituted products **8** yield (%) [c]	Disubstituted products **2** yield (%) [c]	Monosubstitution relative yield (%)
1	**a**	C_6H_5	70	44	54	45
2	**b**	1-Naphthyl	79	54	43	56
3	**c**	2-MeC_6H_4	72	66	32	67
4	**d**	4-MeC_6H_4	68	46	54	46
5	**e**	4-$MeOC_6H_4$	58	43	57	43
6	**f**	3-ClC_6H_4	65	40	48	45
7	**g**	2,4,6-$Me_3C_6H_2$	65	94	6	94
8	**h**	C_2H_5	66	13 [d]	68	16
9	**i**	*n*-C_4H_9	60	18 [d]	61	23
10	**j**	*sec*-C_4H_9	59	14	50	22
11	**k**	*cycl*-C_6H_{11}	56	20	60	25

a) [**1**] = 15.0 mM; [RMgX] = 16.5 mM; reaction time: 120 min a 0 °C. b) Based on the recovered unreacted **1**. c) Unless otherwise stated, yields are of products isolated by chromatography; the reported values are calculated on the basis of the reacted **1**. d) Yields estimated by ^1H NMR of the crude reaction mixture since products **8h** and **8i** could not be isolated in pure form by chromatography (see Experimental).

from phenyl-, to 1-naphthyl-, to 2-methylphenyl- and to 2,4,6-trimethylphenyl-magnesium bromide as reagent (entries 1, 2, 3 and 7) a significant increase in the monosubstitution relative yield is observed (from 45 up to 94%) which appears to parallel the increase in the steric demand of the Grignard reagent. At the light of the mechanism of Scheme 4, the above outcome interestingly discloses a higher sensitivity of the second addition step to steric effects. It is worth noting on this regard that under conditions favouring the formation of disubstituted products[6b] (treatment of a suspension of **1** in THF with 2.2 moles of Grignard reagent), whereas with 2-methylphenylmagnesium bromide only the disubstituted product **2c** is actually obtained (0% relative yield of **8c**), the analogous reaction with 2,4,6-trimethylphenylmagnesium bromide (non-tabulated result) still gives 54% relative yield of the monosubstituted product **8g**. As a final comment on the results collected in Table 1 it is noticeable that in the reactions with alkylmagnesium bromides (entries 8-11), because of their higher reactivity with respect to the aryl analogues, the selectivity of the process toward monosubstitution drops to very low values. This fact associated with the observed thermal instability of compounds substituted with primary alkyl groups (*e.g.* **8h** and **8i**, see Experimental) make the studied reactions generally unsatisfactory as far preparation of alkyl substituted dinitrobutadienes **8** is concerned.

Taking into account the importance of C-C bond forming reactions and in the framework of the possible synthetic utilization of the aryl-substituted dinitrobutadienes **8** we have successively investigated their behaviour with Grignard reagents under conditions similar to those previously employed.

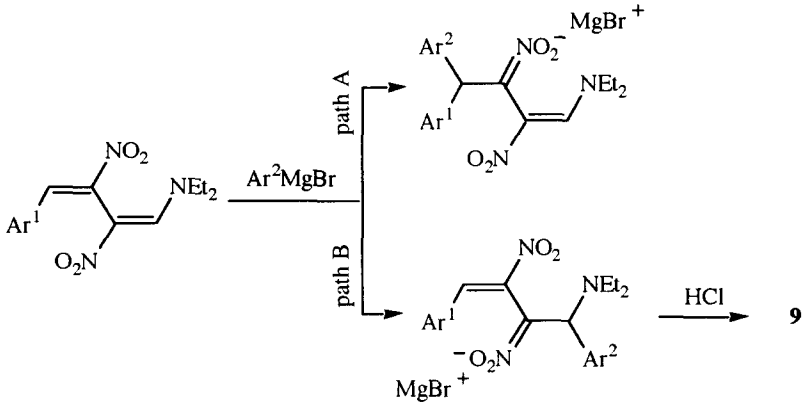
The results collected in Table 2 show that the treatment of some aryl-substituted diethylamino-dinitrobutadienes **8** with 1.1 moles of arylmagnesium bromide brings about an overall replacement of the diethylamino group by the aryl of the Grignard reagent in almost quantitative yields. The most striking feature of

Table 2. 1-Ar^1-4-Ar^2-2,3-dinitro-1,3-butadiene (**9**) by reaction of 1-Ar^1-4-diethylamino derivatives **8** with Ar^2MgBr in THF. [a]

Entry no.	Starting **8**	Ar^1 in **8**	Ar^2 in Ar^2MgBr	1-Ar^1-4-Ar^2-substituted product **9**	Yield (%) [b]
1	**8a**	C_6H_5	4-MeC_6H_4	**9ad**	90
2	**8b**	1-Naphthyl	C_6H_5	**9ba**	83
3	**8c**	2-MeC_6H_4	C_6H_5	**9ca**	90
4	**8c**	2-MeC_6H_4	3-ClC_6H_4	**9cf**	93
5	**8g**	2,4,6-$Me_3C_6H_2$	C_6H_5	**9ga**	80

a) **[8]** = 62.5 mM; $[Ar^2MgX]$ = 68.7 mM; reaction time: 45-60 min at 0 °C. b) Yields are of products isolated by chromatography.

Scheme 5



these findings is the high regioselectivity of the process: of the two parts of the molecule of **8** prone to undergo addition by the organometallic reagent, *viz.* the 1-nitroalkene[10,13,14] and the nitroenamine[8,9,10a] moieties (Scheme 5: path A and B, respectively), only the latter effectively reacts.

Thus, the high regioselectivity of the reaction makes available in good yields asymmetrically 1,4-disubstituted dinitrobutadienes **9**, a hitherto unknown class of compounds of possible interesting synthetic applications. It is necessary however to point out that a relevant preliminary screening of the behaviour of the same substrates **8** with alkyl Grignard reagents did not give encouraging results: under conditions similar to those employed with aryl Grignard reagents, complex mixtures, probably containing degradation and/or polymerization products, were actually obtained.

Anyway, in view of the predictable interest that the relevant products can have as synthetic intermediates, studies aimed at the improvement of the processes leading to compounds **8** from **1** and to compounds **9** from **8** also when using other alkyl organometallic reagents are under way. At the same time further insight is being pursued in order to provide full rationalization to some still open questions such as the influence of steric

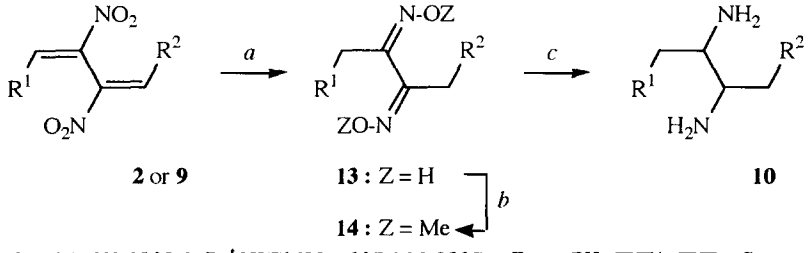
hindrance in the Grignard reagent on the relative yield of **8** from **1** and the just mentioned high regioselectivity implied by the **8** to **9** transformation.

*Synthesis of 1,4-disubstituted 2,3-diaminobutanes **10***

In view of the availability of the 1,4-disubstituted 2,3-dinitro-1,3-butadienes **2** and **9** and as a further step of a sequence aimed at exploiting the synthetic potentiality of our system, we have carried out a preliminary study on the reduction of some representative dinitrobutadienes **2** and **9** to the corresponding 1,4-disubstituted 2,3-diaminobutanes **10**.

Thus, using 2,3-dinitro-1,4-diphenyl-1,3-butadienes **2a** as a model substrate, various attempts to extend procedures, which have been successfully applied to monofunctional 1-nitroalkenes,[15] did not give results fully satisfactory as regards yield and purity of the isolated 2,3-diamino-1,4-diphenylbutane **10a**. At the moment, the

Scheme 6



a) Lead Powder/DMF-AcOH, 25 °C. *b*) Bu^{t}OK/DMSO, 15 °C; MeI, 25 °C. c) Excess BH_3•THF in THF, reflux; aq. NaOH, reflux.

Table 3. Results of the synthesis of some 1-R^1-4-R^2-2,3-diaminobutanes **10** from the corresponding dinitrobutadienes **2** or **9**.

Starting **2** or **9**	R^1 =	R^2 =	**2** (**9**) → **13** [a] Yield % [d]	**13** → **14** [b] Yield % [d]	**14** → **10** [c] Yield % [d,e]	Overall yield (%) of **10** from **2** (**9**)
2a	C_6H_5	C_6H_5	**13a** : 81 [f]	**14a** : 83	**10a** : 93	62
2b	1-Naphthyl	1-Naphthyl	**13b** : 72 [f]	**14b** : 77	**10b** : 69	38
2c	2-MeC_6H_4	2-MeC_6H_4	**13c** : 68 [f]	**14c** : 90	**10c** : 84	51
2d	4-MeC_6H_4	4-MeC_6H_4	**13d** : 75 [f]	**14d** : 83	**10d** : 93	58
2e	4-$MeOC_6H_4$	4-$MeOC_6H_4$	**13e** : 80 [f]	**14e** : 87	**10e** : 70	49
2f	3-ClC_6H_4	3-ClC_6H_4	**13f** : 83	**14f** : 96	**10f** : 80	64
2h	C_2H_5	C_2H_5	**13h** : 72 [f]	**14h** : 75	**10h** : 80	43
2i	*n*-C_4H_9	*n*-C_4H_9	**13i** : 85 [f]	**14i** : 84	**10i** : 77	55
2k	*cycl*-C_6H_{11}	*cycl*-C_6H_{11}	**13k** : 84 [f]	**14k** : 83	**10k** : 82	57
9cf	2-MeC_6H_4	3-ClC_6H_4	**13cf** : 85	**14cf** : 85	**10cf** : 73	53
9ga	2,4,6-$Me_3C_6H_2$	C_6H_5	**13ga** : 79	**14ga** : 76	**10ga** : 70	42

a) Reduction of **2** or **9** with lead powder in DMF/AcOH at 25 °C. b) Methylation to the hydroximino oxygens of **13** (Bu^{t}OK in DMSO and then MeI at 25 °C). c) Reduction of the bis(methoximino) derivatives **14** with borane-THF complex in THF at reflux temperature. d) Yields of isolated compounds. e) Yields of diamines **10** refer to an undetermined mixture of diastereomers. f) Data from ref. 6b.

method which appears to best couple high purity with satisfactory yields of the final product is the three-step procedure outlined in Scheme 6 which has been also applied to other dinitrobutadienes **2** and **9** (Table 3).

Following a previously established procedure[6b] 1,4-dialkyl- and 1,4-diaryl-2,3-dinitro-1,3-butadienes were first reduced to the corresponding 2,3-bis(hydroximino)butanes **13** with lead powder in a DMF-acetic acid mixture. The methylation at both oxygens of such dioximes **13** was then accomplished with methyl iodide on the corresponding non-isolated salts, prepared by action of two moles of potassium *tert*-butoxide in DMSO. The obtained 1,4-disubstituted 2,3-bis(methoximino)butanes **14** were eventually reduced[16] by excess borane-THF complex in refluxing THF to furnish the desired 1,4-disubstituted 2,3-diaminobutanes **10**, isolated as an essentially pure mixture of diastereomers.

As shown in Table 3 the overall yield of **10** from the three-step procedure is generally satisfactory and, in conclusion, the method herein represents a valid alternative access to variously substituted 1,2-diamines, a class of compounds of growing interest in synthesis[17,18] and a structural unit commonly present in various naturally occuring compounds and medicinal agents.[18,19]

EXPERIMENTAL

Melting points were determined on a Büchi 535 apparatus and are uncorrected. ^{1}H NMR spectra were taken on a Varian Gemini 200 spectrometer; TMS was used as internal standard and chemical shifts are reported as δ values (ppm).

Materials

Petroleum ether and light petroleum refer to the fractions with bp 40-60 °C and 80-100 °C respectively. Tetrahydrofuran (THF) was purified by standard methods and distilled over potassium benzophenone ketyl radical before use. Dimethylsulfoxide (Fluka) was stored over molecular sieves (4 Å) before use. Borane-THF complex 1M in THF and potassium *tert*-butoxide were commercial products (Aldrich) used as received. 3,4-Dinitrothiophene[20] and *(E,E)*-1,4-bis(diethylamino)-2,3-dinitro-1,3-butadiene[6b] **1** were synthesized as reported. THF solutions of Grignard reagents (0.8-1.0 M) were prepared from the corresponding bromoderivatives (commercial samples dried over 4 Å molecular sieves) using standard methods; such solutions were titrated just before use, using a reported procedure.[21]

Reactions of 1,4-Bis(diethylamino)-2,3-dinitro-1,3-butadiene 1 with Grignard Reagents

In a flame-dried flask, equipped with an argon inlet, a rubber septum and a magnetic stirring bar, **1** (2 mmol) was dissolved in 130 ml of THF and cooled to *ca.* 0 °C with an external ice bath. By means of a syringe, 2.2 mmol of the Grignard reagent (0.8-1.0 M in THF) was slowly added under magnetic stirring. The reaction mixture was routinely kept at the same temperature for 120 min and then poured into ice/3% HCl. After *ca.* 1 h at room temperature, the mixture was extracted with dichloromethane. The organic phase was dried over Na_2SO_4 and left overnight at room temperature.[22] Evaporation of the solvent under reduced pressure gave a residue which was chromatographed on a silica gel column using a gradient of dichloromethane and diethyl ether as eluant. The disubstituted **2a-k**, the monosubstituted **8a-k** and unreacted **1** were eluted in the order given with a good overall material balance (see also Table 1).

Samples of **2a-k** to be used for successive transformations were also prepared by reaction of **1** with 2 mol. equiv. of Grignard reagent as already reported.[6b] Under these conditions previously unknown compounds were isolated in the following yield: **2f** (95%), **2g** (35%), **2j** (51%).

1,4-Dialkyl- or 1,4-diaryl-2,3-dinitro-1,3-butadienes 2a-k

1,4-Diphenyl- **2a**,[6a] 1,4-bis(1-naphthyl)- **2b**,[6b] 1,4-bis(2-methylphenyl)- **2c**,[6b] 1,4-bis(4-methylphenyl)

2d,[6b] 1,4-bis(4-methoxyphenyl)- **2e**,[6b] 1,4-diethyl- **2h**,[6a] 1,4-dibutyl **2i**[6b] and 1,4-dicyclohexyl- **2k**[6a] derivatives [all isolated as *(E,E)*-stereoisomers] have already been described in our previous papers.

(E,E)-1,4-Bis(3-chlorophenyl)-2,3-dinitro-1,3-butadiene **2f**:[23] mp 124.9-126.7 °C (light petroleum -toluene) (Found: C, 52.4, H, 2.8; N, 7.5. $C_{16}H_{10}Cl_2N_2O_4$ requires: C, 52.6; H, 2.8; N, 7.7%); ^{1}H NMR ($CDCl_3$) δ 7.20 (4H, m), 7.27 (2H, t, *J* 7.7 Hz), 7.39 (2H, app. dt, *J* 1.6 and 8.3 Hz) and 8.36 (2H, s); ^{13}C NMR ($CDCl_3$) δ 127.65, 129.69, 130.58, 131.22, 132.08, 135.44, 139.81 and 141.03.

(E,E)-2,3-Dinitro-1,4-bis(2,4,6-trimethylphenyl)-1,3-butadiene **2g**:[23] mp 251.9-252.5 °C (light petroleum-toluene) (Found: C, 69.2, H, 6.3; N, 7.3. $C_{22}H_{24}N_2O_4$ requires: C, 69.5; H, 6.4; N, 7.4%); ^{1}H NMR ($CDCl_3$) δ 1.75 (12H, s), 2.24 (6H, s), 6.61 (4H, br s) and 8.31 (2H, s); ^{13}C NMR ($CDCl_3$) δ 19.48, 20.97, 126.12, 128.70, 136.53, 139.74, 141.05 and 142.47.

3,8-Dimethyl-5,6-dinitro-4,6-decadiene **2j**: pale yellow oil (Found: C, 55.9, H, 7.7; N, 10.6. $C_{12}H_{20}N_2O_4$ requires: C, 56.2; H, 7.9; N, 10.9%) which was also identified via transformation into the corresponding dioxime **13j** (see later). The ^{1}H NMR spectrum of the compound is consistent with the presence of four stereoisomers;[24] two diastereomers with configuration *(E,E)* were in *ca.* 1:1 ratio, whereas one of the diastereomers with *(E,Z)*-configuration was present in trace amount. Altogether a ratio between the *(E,E)*-**2j** and the *(E,Z)*-**2j** stereoisomers was found to be 51:49. ^{1}H NMR ($CDCl_3$) δ 0.83, 0.90 and 0.97 [6H of *(E,E)* + 6H of *(E,Z)* in all, three t partly overlapped (*J* 7.1, 7.4 and 6.7 Hz, respectively)], 1.07, 1.14 and 1.17 [6H of *(E,E)* + 6H of *(E,Z)* in all, three d partly overlapped (*J* 7.0, 7.0 and 7.7 Hz, respectively)], 1.50 [4H of *(E,E)* + 4H of *(E,Z)*, m], 2.19 and 2.35 [2H of *(E,E)* + 1H of *(E,Z)* in all, m and d of sext. (*J* 6.7 and 11.3 Hz) partly overlapped], 3.36 [1H of *(E,Z)*, d of sext., *J* 7.0 and 10.6 Hz], 6.03 [1H of *(E,Z)*, d, *J* 10.6 Hz], 7.33 [1H of *(E,Z)*, d, *J* 11.3 Hz], 7.45 [1H of *(E,E)*, d, *J* 11.1 Hz] and 7.50 [1H of *(E,E)*, d, *J* 11.7 Hz].

1-Alkyl-4-diethylamino- or 1-Aryl-4-diethylamino-2,3-dinitro-1,3-butadienes 8a-k

(E,E)-1-Diethylamino-4-phenyl-2,3-dinitro-1,3-butadiene **8a** has been described in a previous paper of ours.[6b]

(E,E)-1-Diethylamino-4-(1-naphthyl)-2,3-dinitro-1,3-butadiene **8b**: mp 162.0-163.0 °C (light petroleum-toluene) (Found: C, 63.1, H, 5.8; N, 12.2. $C_{18}H_{19}N_3O_4$ requires: C, 63.3; H, 5.6; N, 12.3%); ^{1}H NMR ($CDCl_3$) δ 0.75 and 0.88 (6H in all, two t partly overlapped, *J* 7.1 Hz in both), 2.78 (1H, A of ABX_3, J_{AX} = J_{BX} 7.1 Hz, J_{AB} 14.1 Hz), 3.24 (3H, m), 7.54 (4H, m), 7.95 (3H, m), 8.29 (1H, s) and 8.95 (1H, s); ^{13}C NMR ($CDCl_3$) δ 12.87, 14.27, 43.24, 52.41, 115.52, 122.90, 125.61, 126.73, 127.65, 127.75, 128.07, 129.18, 131.53, 131.75, 133.51, 135.04, 143.80 and 149.32.

(E,E)-1-Diethylamino-4-(2-methylphenyl)-2,3-dinitro-1,3-butadiene **8c**: mp 115.7-116.2 °C (light petroleum-toluene) (Found: C, 58.9, H, 6.1; N, 13.7. $C_{15}H_{19}N_3O_4$ requires: C, 59.0; H, 6.3; N, 13.8%); ^{1}H NMR ($CDCl_3$) δ 1.01 (6H, m), 2.44 (3H, s), 2.95 (1H, m), 3.27 (3H, m), 7.23 (4H, m), 8.42 (1H, s) and 8.50 (1H, s); ^{13}C NMR ($CDCl_3$) δ 13.06, 14.53, 20.06, 43.15, 52.47, 115.39, 126.79, 128.65, 130.01, 130.94, 131.29, 135.49, 139.04, 142.70 and 149.32.

(E,E)-1-Diethylamino-4-(4-methylphenyl)-2,3-dinitro-1,3-butadiene **8d**: mp 123.9-124.9 °C (light petroleum-toluene) (Found: C, 58.8, H, 6.3; N, 13.7. $C_{15}H_{19}N_3O_4$ requires: C, 59.0; H, 6.3; N, 13.8%); ^{1}H NMR ($CDCl_3$) δ 0.92 (3H, t, *J* 7.2 Hz), 1.23 (3H, t, *J* 7.2 Hz), 2.38 (3H, s), 3.00 and 3.20 (1H each, AB of ABX_3, J_{AX} = J_{BX} 7.2 Hz, J_{AB} 14.2 Hz), 3.42 (2H, q, *J* 7.2 Hz), 7.21 and 7.40 (2H each, AA'BB', *J* 8.2 Hz), 8.31 (1H, s) and 8.58 (1H, s); ^{13}C NMR ($CDCl_3$) δ 13.19, 14.85, 21.65, 43.29, 52.71, 114.90, 127.96, 130.17, 131.04, 138.25, 140.72, 142.88 and 149.33.

(E,E)-1-Diethylamino-4-(4-methoxyphenyl)-2,3-dinitro-1,3-butadiene **8e**: mp 115.0-116.0 °C (light petroleum-toluene) (Found: C, 55.9, H, 6.0; N, 13.0. $C_{15}H_{19}N_3O_5$ requires: C, 56.1; H, 6.0; N, 13.1%); ^{1}H NMR ($CDCl_3$) δ 0.92 (3H, t, *J* 7.3 Hz), 1.26 (3H, t, *J* 7.2 Hz), 3.03 and 3.21 (1H each, AB of ABX_3, J_{AX} = J_{BX} 7.2 Hz, J_{AB} 14.4 Hz), 3.43 (2H, q, *J* 7.3 Hz), 3.85 (3H, s), 6.92 and 7.49 (2H each, AA'BB', *J* 8.9 Hz), 8.32 (1H, s) and 8.61 (1H, s); ^{13}C NMR ($CDCl_3$) δ 13.24, 14.89, 43.27, 52.75, 55.54, 114.99, 123.14, 133.23, 138.22, 139.22, 149.34 and 162.68.

(E,E)-1-(3-Chlorophenyl)-4-diethylamino-2,3-dinitro-1,3-butadiene **8f**: mp 102.3-104.0 °C (light petroleum-toluene) (Found: C, 51.4, H, 5.0; N, 12.8. $C_{14}H_{16}ClN_3O_4$ requires: C, 51.6; H, 4.9; N, 12.9%); ^{1}H NMR ($CDCl_3$) δ 0.95 (3H, t, *J* 7.2 Hz), 1.23 (3H, t, *J* 7.2 Hz), 2.99 and 3.20 (1H each, AB of ABX_3, J_{AX} = J_{BX} 7.2 Hz, J_{AB} 14.4 Hz), 3.44 (2H, q, *J* 7.2 Hz), 7.39 and 7.46 (4H in all, two partly overlapped m),

8.28 (1H, s) and 8.57 (1H, s); ^{13}C NMR ($CDCl_3$) δ 13.08, 14.93, 43.40, 52.86, 114.26, 128.85, 130.24, 130.64, 131.61, 132.60, 135.40, 136.01, 142.84 and 149.51.

(E,E)-1-Diethylamino-2,3-dinitro-4-(2,4,6-trimethylphenyl)-1,3-butadiene **8g**: mp 170.0-170.8 °C (light petroleum-toluene) (Found: C, 61.2, H, 7.1; N, 12.6. $C_{17}H_{23}N_3O_4$ requires: C, 61.2; H, 7.0; N, 12.6%); ^1H NMR ($CDCl_3$) δ 0.76 (3H, m), 1.05 (3H, m), 2.18 (6H, s), 2.25 (3H, s), 2.74 (1H, m), 3.23 (3H, m), 6.87 (2H, s), 8.22 and 8.24 (2H in all, two partly overlapped s); ^{13}C NMR ($CDCl_3$) δ 12.77, 14.02, 20.03, 20.98, 42.89, 52.13, 115.73, 127.03, 129.37, 136.03, 137.04, 139.77, 144.56 and 149.50.

(E,E)-1-Diethylamino-2,3-dinitro-1,3-hexadiene **8h**: no pure analytical sample could be obtained of this compound which was identified only on the grounds of typical ^1H NMR absorptions of nitrovinyl protons [δ ($CDCl_3$): 8.54 (1H, s, Et_2N-C<u>H</u>=) and 7.51 (1H, t, *J* 7.8 Hz, CH_3-CH_2-C<u>H</u>=)] detected in the spectrum of the crude reaction mixture. In such spectrum the signals of the diethylamino and of the ethyl groups of **8h** were respectively hidden by the corresponding absorptions of the unreacted **1** and of the disubstituted product **2h**. Chromatography of the final reaction mixture allowed the isolation of **1** and **2h** as usually; on the contrary, as regards **8h**, the relevant chromatographic fractions gave, after evaporation of the solvent at reduced pressure, a yellow oil which quickly darkened and decomposed (^1H NMR check).

(E,E)-1-Diethylamino-2,3-dinitro-1,3-octadiene **8i**: no pure analytical sample of this compound could be obtained. The dinitrooctadiene **8i** was only identified on the grounds of the following typical absorptions in the ^1H NMR spectrum of the residue of chromatographic fractions containing also decomposition products of the same **8i**: δ ($CDCl_3$) 8.55 (1H, s, Et_2N-C<u>H</u>=), 7.54 (1H, t, *J* 7.7 Hz, CH_3-$(CH_2)_3$-C<u>H</u>=) and 2.15 (2H, app. q, *J* 7.7 Hz, CH_3-$(CH_2)_2$-C<u>H_2</u>-CH=).

(E,E)-1-Diethylamino-5-methyl-2,3-dinitro-1,3-heptadiene **8j**: mp 54.8-56.0 °C (petroleum ether) (Found: C, 52.9, H, 7.8; N, 15.4. $C_{12}H_{21}N_3O_4$ requires: C, 53.1; H, 7.8; N, 15.5%). The ^1H NMR analysis reveals that compound **8j**, most likely because of hindered rotation around the C(2)-C(3) bond, appears in solution as a mixture (*ca.* 56:44) of two conformers in the (*E,E*) configuration [small quantities of the (*E,Z*)-isomer are detected only in the crude product]. Consistently with the presence of two conformers, most of the ^1H NMR signals appears doubled: δ ($CDCl_3$) 0.86 and 0.90 (3H in all, two partly overlapped t, *J* 7.6 Hz), 1.07 and 1.08 [6H in all, two t (*J* 6.6 Hz) overlapped with a m], 1.40 [5H in all, one t (*J* 6.7 Hz) overlapped with a m], 2.20 (1H, d of sext., *J* 6.7 and 10.8 Hz), 3.08 (1H, m), 3.44 (3H, m), 7.34 and 7.41 (1H in all, two d, *J* 10.8 Hz in both), 8.52 and 8.53 (1H in all, two partly overlapped s). The high value (10.8 Hz) of the vicinal coupling constant between H(4) (doublets at δ 7.34 and 7.41) and H(5) (doublet of sextects at δ 2.20) is consistent[25] with a fixed conformation of the molecule owing to hindered rotation around the C(4)-C(5) bond.

(E,E)-1-Cyclohexyl-4-diethylamino-2,3-dinitro-1,3-butadiene **8k**: mp 140.5-141.6 °C (light petroleum-toluene) (Found: C, 56.3, H, 7.8; N, 14.0. $C_{14}H_{23}N_3O_4$ requires: C, 56.5; H, 7.8; N, 14.1%); ^1H NMR ($CDCl_3$) δ 1.22 (11H, m), 1.68 (5H, m), 2.10 (1H, m), 3.09 (1H, A of ABX_3, J_{AX} 7.2 Hz, J_{AB} 14.2 Hz), 3.41 (3H, m), 7.39 (1H, d, *J* 10.6 Hz) and 8.53 (1H, s); ^{13}C NMR ($CDCl_3$) δ 13.10, 14.79, 25.00, 25.08, 25.48, 30.87, 31.08, 39.07, 42.94, 52.17, 113.81, 142.30, 148.01 and 149.39.

Reactions of Some 1-Aryl-4-diethylamino-2,3-dinitro-1,3-butadienes with Grignard Reagents

Following the general procedure reported above for the reaction on **1**, 1 mmol of **8** in 15 ml of THF was treated (0 °C, 45-60 min reaction time) with 1.1 mmol of arylmagnesium bromide in THF. After the usual workup the residue obtained by evaporation of the dichloromethane extracts was either crystallized from the proper solvent or chromatographed on a silica gel column using a gradient of petroleum ether and dichloromethane. The asymmetrically 1,4-disubstituted 1,4-diaryl-2,3-dinitro-1,3-butadienes were obtained in very good yields (Table 2).

1-Ar^1-4-Ar^2-2,3-dinitro-1,3-butadienes

(E,E)-1-(4-Methylphenyl)-2,3-dinitro-4-phenyl-1,3-butadiene **9ad** (from **8a** and 4-methylphenylmagnesium bromide): mp 93.0-94.0 °C (light petroleum-toluene) (Found: C, 66.0, H, 4.5; N, 9.0. $C_{17}H_{14}N_2O_4$ requires: C, 65.8; H, 4.5; N, 9.0%); ^1H NMR ($CDCl_3$) δ 2.32 (3H, s), 7.13 (2H, AA' of AA'BB', *J* 8.1 Hz), 7.36 (7H in all, partly overlapped m and BB' of AA'BB'), 8.46 (1H, s) and 8.48 (1H, s); ^{13}C NMR ($CDCl_3$) δ 21.61, 126.93, 129.36, 129.86, 130.22, 130.46, 130.73, 132.27, 139.30, 140.63, 140.95, 141.34 and 143.69.

(E,E)-1-(1-Naphthyl)-2,3-dinitro-4-phenyl-1,3-butadiene **9ba** (from **8b** and phenylmagnesium bromide): mp 152.5-153.1 °C (light petroleum-toluene) (Found: C, 69.2, H, 4.2; N, 8.3. $C_{20}H_{14}N_2O_4$ requires: C, 69.4; H, 4.1; N, 8.1%); ^{1}H NMR ($CDCl_3$) δ 7.08 (5H, m), 7.28 (2H, m), 7.46 (2H, m), 7.59 (1H, m), 7.79 (2H, m), 8.22 (1H, s) and 9.01 (1H, s); ^{13}C NMR ($CDCl_3$) δ 123.10, 125.10, 126.72, 126.85, 127.32, 127.44, 128.75, 128.85, 129.39, 129.82, 130.82, 131.61, 131.96, 133.10, 139.71, 141.09, 141.29, 142.63.

(E,E)-1-(2-Methylphenyl)-2,3-dinitro-4-phenyl-1,3-butadiene **9ca** (from **8c** and phenylmagnesium bromide): mp 132.8-133.4 °C (light petroleum-toluene) (Found: C, 65.9, H, 4.3; N, 9.0. $C_{17}H_{14}N_2O_4$ requires: C, 65.8; H, 4.5; N, 9.0%); ^{1}H NMR ($CDCl_3$) δ 2.04 (3H, s), 7.22 (9H, m), 8.28 (1H, s) and 8.54 (1H, s); ^{13}C NMR ($CDCl_3$) δ 19.49, 126.39, 127.84, 129.04, 129.29, 129.62, 130.17, 130.53, 131.50, 131.73, 138.64, 140.16, 141.10, 141.18 and 141.70.

(E,E)-1-(3-Chlorophenyl)-4-(2-methylphenyl)-2,3-dinitro-1,3-butadiene **9cf** (from **8c** and 3-chlorophenylmagnesium bromide): mp 148.9-150.0 °C (light petroleum-toluene) (Found: C, 59.2, H, 3.9; N, 8.1. $C_{17}H_{13}ClN_2O_4$ requires: C, 59.2; H, 3.8; N, 8.1%); ^{1}H NMR ($CDCl_3$) δ 2.05 (3H, s), 7.05 and 7.27 (8H in all, two partly overlapped m), 8.17 (1H, s) and 8.53 (1H, s); ^{13}C NMR ($CDCl_3$) δ 19.47, 126.49, 127.40, 127.86, 128.76, 129.11, 130.24, 130.68, 131.30, 131.71, 131.96, 135.10, 138.67, 139.13, 140.52, 141.18 and 142.47.

(E,E)-2,3-Dinitro-1-phenyl-4-(2,4,6-trimethylphenyl)-1,3-butadiene **9ga** (from **8g** and phenylmagnesium bromide): mp 172.6-173.4 °C (light petroleum-toluene) (Found: C, 67.5, H, 3.5; N, 8.3. $C_{19}H_{18}N_2O_4$ requires: C, 67.4; H, 3.4; N, 8.3%); ^{1}H NMR ($CDCl_3$) δ 1.83 (6H, s), 2.18 (3H, s), 6.62 (2H, s), 6.96 (2H, app. q, *J* 7.2 Hz) 7.23 (2H, m), 7.35 (1H, m), 8.24 (1H, s) and 8.32 (1H, s); ^{13}C NMR ($CDCl_3$) δ 20.54, 125.96, 128.80, 130.53, 131.07, 136.35, 139.90, 140.62, 141.01, 141.60 and 142.99.

Preparation of Some 1,4-Disubstituted 2,3-Diaminobutanes

The title diamines were prepared as diastereomeric mixtures in three steps starting from dinitrobutadienes **2a-2f**, **2h-2k**, **9cf** and **9ga**. Yields of isolated products are reported in Table 3.

In the first step dinitrobutadienes were reduced with lead in DMF/AcOH to the corresponding 1,4-disubstituted 2,3-dihydroximinobutanes **13** following a procedure already reported.[6b] After usual workup crude dioximes **13** were generally purified by taking them up with a little dichloromethane, filtration and drying over P_2O_5 under reduced pressure.

In the second step dioximes **13** were *O*-methylated in DMSO as follows. To a solution of Bu^{t}OK (2.1 mmol) in 16 ml of dry DMSO, contained in a two-neck flask under argon, dioxime **13** (1 mmol) was slowly added under magnetic stirring and with cooling by an external water bath. After 30 min methyl iodide (2.1 mmol) was added and the reaction left 4-5 h at room temperature always under stirring.[26] The reaction mixture was poured into brine and extracted with Et_2O; the ether extracts were dried (Na_2SO_4) and the solvent removed under reduced pressure to give a residue which was chromatographed on a silica gel column using a 1:1 mixture of petroleum ether and dichloromethane as eluant. 1,4-Disubstituted 2,3-bis(methoximino)butanes **14** were obtained in good yields (see below) as single configurational isomers.

In the last step of the preparation of 1,4-disubstituted 2,3-diaminobutanes **10** compounds **14** were reduced as follows.[16] In a flame dried two-neck flask, equipped with a thermometer and a reflux condenser with an argon inlet and a rubber septum, a solution of **14** (1 mmol) in 2 ml of THF was deaerated using three freeze-pump-thaw cycles and cooled to *ca.* 0° with an external ice bath. Commercial borane-THF complex 1M in THF (6 mmol) was added to the reaction mixture by syringe maintaining the temperature below 10°. After addition of the borane reagent the reaction mixture was heated at reflux for 2-3 h, cooled again to 0°, cautiously added of 1 ml of water and then of 0.75 ml of 20% aqueous NaOH solution. The reaction mixture was heated 1 h at reflux, cooled to room temperature and exaustively extracted with ether. After washing of the ether extracts with brine, they were dried (Na_2SO_4) and evaporated at reduced pressure to furnish crude 1,4-disubstituted 2,3-diaminobutanes **10**. The crude material was routinely purified by dissolving it in excess dilute HCl; such solution was extracted with ether in order to remove some non-basic impurities, made basic with concentrated NaOH and the diamine extracted again into ether. Evaporation of the solvent under reduced pressure, after drying (Na_2SO_4), gave essentially pure diamine **10** (generally in good yields) which were stored under argon in the freezer.

1,4-Disubstituted 2,3-bis(hydroximino)butanes 13

1,4-Diphenyl- **13a**, 1,4-bis(1-naphthyl)- **13b**, 1,4-bis(2-methylphenyl)- **13c**, 1,4-bis(4-methylphenyl) **13d**, 1,4-bis(4-methoxyphenyl)- **13e**, 1,4-diethyl- **13h**, 1,4-dibutyl **13i** and 1,4-dicyclohexyl- **13k** derivatives have already been described in a previous paper.[6b] These dioximes together with the new ones described below (**13f**, **13cf** and **13ga**) were used for successive transformations (see Table 3 for the yields of **13** obtained). Dioxime **13j** was only prepared for the characterization of **2j**.

1,4-Bis(3-chlorophenyl)-2,3-bis(hydroximino)butane **13f**: mp 176.6-177.8 °C (light petroleum-toluene) (Found: C, 56.9, H, 4.4; N, 8.1. $C_{16}H_{14}Cl_2N_2O_2$ requires: C, 57.0; H, 4.2; N, 8.3%); ^{1}H NMR (CD_3COCD_3) δ 4.02 (4H, s), 7.20 (8H, m) and 11.00 (2H, s, exch. D_2O).

2,3-Bis(hydroximino)-3,8-dimethyldecane **13j** (obtained in 90% yield): mp 164.3-165.9 °C (light petroleum-toluene) (Found: C, 63.0, H, 10.8; N, 12.5. $C_{12}H_{24}N_2O_2$ requires: C, 63.1; H, 10.6; N, 12.3%); ^{1}H NMR (CD_3COCD_3) δ 0.84 and 0.87 [12H in all, partly overlapped d (*J* 6.8 Hz) and t (*J* 7.4 Hz)], 1.27 (4H, m), 1.83 (2H, m), 2.57 (4H, two AB parts of ABX, J_{AX} 6.8 Hz, J_{BX} 7.9 Hz, J_{AB} 11.9 Hz) and 10.38 (2H, s, exch. D_2O).

1-(3-Chlorophenyl)-2,3-bis(hydroximino)-4-(2-methylphenyl)butane **13cf**: mp 133.1-134.2 °C (light petroleum-toluene) (Found: C, 64.2, H, 5.6; N, 8.6. $C_{17}H_{17}ClN_2O_2$ requires: C, 64.5; H, 5.4; N, 8.8%); ^{1}H NMR (CD_3SOCD_3) δ 2.50 (3H, s), 3.84 (2H, s), 3.99 (2H, s), 6.72 (1H, d, *J* 7.0 Hz), 7.15 (7H, m) and 11.70 and 11.71 (2H in all, two partly overlapped s, exch. D_2O).

2,3-Bis(hydroximino)-1-phenyl-4-(2,4,6-trimethylphenyl)butane **13ga**: mp 118.9-119.8 °C (light petroleum-toluene) (Found: C, 73.3, H, 7.2; N, 8.9. $C_{19}H_{22}N_2O_2$ requires: C, 73.5; H, 7.1; N, 9.0%); ^{1}H NMR ($CDCl_3$) δ 2.11 (6H, s), 2.14 (3H, s), 3.81 (2H, s), 3.88 (2H, s), 6.67 (2H, s), 7.06 (2H, m), 7.15 (3H, m), 11.33 (1H, s, exch. D_2O) and 11.51 (1H, s, exch. D_2O).

1,4-Disubstituted 2,3-bis(methoximino)butanes 14

Yields of isolated **14** from *O*-methylation of **13** are reported in Table 3.

2,3-Bis(methoximino)-1,4-diphenylbutane **14a**: mp 83.2-84.4 °C (light petroleum) (Found: C, 73.0, H, 6.9; N, 9.5. $C_{18}H_{20}N_2O_2$ requires: C, 72.9; H, 6.8; N, 9.4%); ^{1}H NMR ($CDCl_3$) δ 3.95 (4H, s), 3.96 (6H, s) and 7.20 (10H, m).

2,3-Bis(methoximino)-1,4-bis(1-naphthyl)butane **14b**: mp 126.7-127.9 °C (light petroleum) (Found: C, 79.0, H, 6.0; N, 7.1. $C_{26}H_{24}N_2O_2$ requires: C, 78.8; H, 6.1; N, 7.1%); ^{1}H NMR ($CDCl_3$) δ 3.83 (6H, s), 4.47 (4H, s), 7.01 (2H, dd, *J* 0.9 and 7.2 Hz), 7.23 (2h, t, *J* 8.1 Hz), 7.47 (4H,m), 7.67 (2H, app. d, *J* 8.1 Hz), 7.83 (2H, m) and 8.14 (2H, m).

2,3-Bis(methoximino)-1,4-bis(2-methylphenyl)butane **14c**: mp 137.5-138.8 °C (light petroleum) (Found: C, 73.9, H, 7.6; N, 8.7. $C_{20}H_{24}N_2O_2$ requires: C, 74.0; H, 7.5; N, 8.6%); ^{1}H NMR ($CDCl_3$) δ 2.31 (6H, s), 3.87 (6H, s), 3.94 (4H, s), 6.87 (2H, app. d, *J* 7.0 Hz) and 7.04 (6H, m).

2,3-Bis(methoximino)-1,4-bis(4-methylphenyl)butane **14d**: mp 101.0-101.4 °C (light petroleum) (Found: C, 74.0, H, 7.6; N, 8.6. $C_{20}H_{24}N_2O_2$ requires: C, 74.0; H, 7.5; N, 8.6%); ^{1}H NMR ($CDCl_3$) δ 2.29 (6H, s), 3.90 (4H, s), 3.96 (6H, s), 7.01 and 7.11 (4H each, AA'BB', *J* 8.1 Hz).

2,3-Bis(methoximino)-1,4-bis(4-methoxyphenyl)butane **14e**: mp 144.3-144.7 °C (light petroleum) (Found: C, 67.4, H, 6.9; N, 8.0. $C_{20}H_{24}N_2O_4$ requires: C, 67.4; H, 6.8; N, 7.9%); ^{1}H NMR ($CDCl_3$) δ 3.77 (6H, s), 3.87 (4H, s), 3.97 (6H, s), 6.75 and 7.14 (4H each, AA'BB', *J* 8.7 Hz).

1,4-Bis(3-chlorophenyl)-2,3-bis(methoximino)butane **14f**: mp 86.9-87.8 °C (EtOH) (Found: C, 59.1, H, 5.2; N, 7.9. $C_{18}H_{18}Cl_2N_2O_2$ requires: C, 59.2; H, 5.0; N, 7.7%); ^{1}H NMR ($CDCl_3$) δ 3.91 (4H, s), 3.98 (6H, s), 7.10 (6H, m) and 7.19 (2H,s).

4,5-Bis(methoximino)octane **14h**: colorless oil (Found: C, 59.7, H, 10.0; N, 13.9. $C_{10}H_{20}N_2O_2$ requires: C, 60.0; H, 10.1; N, 14.0%); ^{1}H NMR ($CDCl_3$) δ 0.91 (6H, t, *J* 7.6 Hz), 1.48 (4H, sext, *J* 7.6 Hz), 2.53 (4H, app. t, *J* 7.7 Hz) and 3.91 (6H,s).

6,7-Bis(methoximino)dodecane **14i**: colorless oil (Found: C, 65.6, H, 11.2; N, 11.1. $C_{14}H_{28}N_2O_2$ requires: C, 65.6; H, 11.0; N, 10.9%); ^{1}H NMR ($CDCl_3$) δ 0.88 (6H, t, *J* 7.6 Hz), 1.31 and 1.45 (12H in all, two partly overlapped m), 2.53 (4H, app. t, *J* 7.6 Hz) and 3.91 (6H,s).

1,4-Dicyclohexyl-2,3-bis(methoximino)butane **14k**: mp 105.5-106.4 °C (light petroleum) (Found: C, 70.3, H, 10.6; N, 9.1. $C_{18}H_{32}N_2O_2$ requires: C, 70.1; H, 10.5; N, 9.1%); ^{1}H NMR ($CDCl_3$) δ 1.07 (10H,

m), 1.65 (12H, m), 2.48 (4H, d, *J* 6.8 Hz) and 3.90 (6H, s).

1-(3-Chlorophenyl)-2,3-bis(methoximino)-4-(2-methylphenyl)butane **14cf**: mp 69.8-70.7 °C (EtOH) (Found: C, 66.4, H, 6.3; N, 7.9. $C_{19}H_{21}ClN_2O_2$ requires: C, 66.2; H, 6.1; N, 8.1%); ^{1}H NMR ($CDCl_3$) δ 2.32 (3H, s), 3.88 and 3.90 (5H in all, two partly overlapped s), 3.95 and 3.97 (5H in all, two partly overlapped s), 6.82 (1H, d, *J* 7.0 Hz), 7.08 (6H, m) and 7.23 (1H, s).

2,3-Bis(methoximino)-1-phenyl-4-(2,4,6-trimethylphenyl)butane **14ga**: colorless oil (Found: C, 74.4, H, 7.8; N, 8.3. $C_{21}H_{26}N_2O_2$ requires: C, 74.5; H, 7.7; N, 8.3%); ^{1}H NMR ($CDCl_3$) δ 2.10 (6H, s), 2.22 (3H, s), 3.81 (3H, s), 3.85 (2H, s), 3.90 and 3.91 (5H in all, two partly overlapped s), 6.70 (2H, s) and 7.14 (5H, m).

1,4-Disubstituted 2,3-diaminobutanes 10.

Yields of isolated **10** from the reduction reaction of **14** are reported in Table 3. The data presented below are of mixtures of diastereomers whose ratio, only in some cases, is deducible by ^{1}H NMR analysis.

2,3-Diamino-1,4-diphenylbutane **10a**: waxy solid (Found: C, 79.7, H, 8.6; N, 11.5. $C_{16}H_{20}N_2$ requires: C, 80.0; H, 8.4; N, 11.7%); ^{1}H NMR ($CDCl_3$) δ 1.45 (4H, br s, exch D_2O), 2.58 (2H, m), 2.95 (4H, m) and 7.24 (10H, m).[27]

2,3-Diamino-1,4-bis(1-naphthyl)butane **10b**: waxy solid (Found: C, 84.5, H, 7.3; N, 8.1. $C_{24}H_{24}N_2$ requires: C, 84.7; H, 7.1; N, 8.2%); ^{1}H NMR ($CDCl_3$) δ 1.50 (4H of A + 4H of B, br s, exch D_2O), 3.02 (2H of A + 2H of B, m), 3.34 (2H of A + 2H of B, m), 3.55 (2H of A, m), 3.70 (2H of B, dd, *J* 2.6 and 13.0 Hz), 7.47 (8H of A + 8H of B, m), 7.78 (2H of A + 2H of B, m), 7.89 (2H of A + 2H of B, m), 8.03 and 8.12 (2H of A + 2H of B, two m slightly overlapped). The A to B ratio can be estimated as 56:44 by comparison of the integrated areas of the signals at δ 3.55 and 3.70 as well as of those of the two multiplets at δ 8.03 and 8.12. Pure diastereomer A showed ^{1}H NMR ($CDCl_3$) δ 1.41 (4H, br s, exch D_2O), 3.02 (2H, dd, *J* 9.9 and 13.3 Hz), 3.36 (2H, m), 3.70 (2H, dd, *J* 2.7 and 13.3 Hz), 7.49 (8H, m), 7.79 (2H, m), 7.89 (2H, m) and 8.12 (2H, m).

2,3-Diamino-1,4-bis(2-methylphenyl)butane **10c**: colorless oil (Found: C, 80.4, H, 9.2; N, 10.4. $C_{18}H_{24}N_2$ requires: C, 80.5; H, 9.0; N, 10.4%); ^{1}H NMR ($CDCl_3$) δ 1.33 (4H, br s, exch D_2O), 2.29 and 2.36 [6H in all, two s (ratio: 32/68)], 2.61 (2H, dd, *J* 9.9 and 13.5 Hz), 2.95 (2H, m), 3.09 (2H, m), 7.14 and 7.17 (8H in all, two partly overlapped m). The ratio between the integrated areas of the two methyl absorptions at δ 2.28 and 2.35 suggest a diastereomeric ratio of 32:68.

2,3-Diamino-1,4-bis(4-methylphenyl)butane **10d**: waxy solid (Found: C, 80.2, H, 9.1; N, 10.3. $C_{18}H_{24}N_2$ requires: C, 80.5; H, 9.0; N, 10.4%); ^{1}H NMR ($CDCl_3$) δ 1.30 (4H, br s, exch D_2O), 2.33 (6H, s), 2.52 (2H, m), 2.93 (4H, m), 7.10 and 7.12 (8H in all, two AA'BB', *J ca.* 8.0 Hz).

2,3-Diamino-1,4-bis(4-methoxyphenyl)butane **10e**: waxy solid (Found: C, 72.3, H, 8.1; N, 9.4. $C_{18}H_{24}N_2O_2$ requires: C, 72.0; H, 8.0; N, 9.3%); ^{1}H NMR ($CDCl_3$) δ 1.90 (4H, br s, exch D_2O), 2.50 (2H, m), 2.92 (4H, m), 3.80 (6H, s), 6.86 and 7.14 (4H each, AA'BB', *J* 8.6 Hz).

2,3-Diamino-1,4-bis(3-chlorophenyl)butane **10f**: colorless oil (Found: C, 62.1, H, 5.8; N, 9.3. $C_{16}H_{18}Cl_2N_2$ requires: C, 62.1; H, 5.9; N, 9.1%); ^{1}H NMR ($CDCl_3$) δ 1.50 (4H, br s, exch D_2O), 2.56 (2H, m), 2.92 (4H, m), 7.09 (2H, m) and 7.21 (6H, m).

4,5-Diaminooctane **10h**: colorless oil (Found: C, 66.8, H, 14.3; N, 19.5. $C_8H_{20}N_2$ requires: C, 66.6; H, 14.0; N, 19.4%); ^{1}H NMR ($CDCl_3$) δ 0.94 (6H, t, *J* 6.6 Hz), 1.37 (12H, m), 2.57 and 2.66 [2H in all, two partly overlapped m (ratio: 31/69)].[28]

6,7-Diaminododecane **10i**: colorless oil (Found: C, 72.1, H, 14.3; N, 14.0. $C_{12}H_{28}N_2$ requires: C, 71.9; H, 14.1; N, 14.0%); ^{1}H NMR ($CDCl_3$) δ 0.89 (6H, t, *J* 6.6 Hz), 1.32 (20H, m), 2.55 and 2.64 [2H in all, two partly overlapped m (ratio: 25/75)].

2,3-Diamino-1,4-dicyclohexylbutane **10k**: colorless oil (Found: C, 76.0, H, 12.9; N, 11.1. $C_{16}H_{32}N_2$ requires: C, 76.1; H, 12.8; N, 11.1%); ^{1}H NMR ($CDCl_3$) δ 1.17 (16H, m), 1.67 (14H, m), 2.65 and 2.79 [2H in all, two partly overlapped t (ratio: 25/75), *J* 5.6 Hz].

2,3-Diamino-1-(3-chlorophenyl)-4-(2-methylphenyl)butane **10cf**: waxy solid (Found: C, 71.0, H, 7.5; N, 9.9. $C_{17}H_{21}ClN_2$ requires: C, 70.7; H, 7.3; N, 9.7%); ^{1}H NMR ($CDCl_3$) δ 1.30 (4H, br s, exch D_2O), 2.29 and 2.34 [3H in all, two partly overlapped s (ratio: 42/58)], 2.58 (2H, m), 2.91 and 3.05 (4H in all, two partly overlapped m), 7.16 and 7.23 (8H in all, two partly overlapped m).

2,3-Diamino-1-phenyl-4-(2,4,6-trimethylphenyl)butane **10ga**: waxy solid (Found: C, 81.0, H, 9.6; N, 10.0. $C_{19}H_{26}N_2$ requires: C, 80.8; H, 9.3; N, 9.9%); ^1H NMR ($CDCl_3$) δ 1.35 (4H, br s, exch D_2O), 2.26, 2.28 and 2.33 (9H in all, three partly overlapped s), 2.61 (1H, m), 2.73-3.18 (5H, m), 6.85 and 6.86 [2H, two partly overlapped s (ratio: *ca.* 34/66)] and 7.28 (5H, m).

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23. Stereochemical assignments are based on ^1H NMR analogies with related compounds.[6]
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