Tetrahedron Vol. 48, No. 21, pp. 4407-4418, 1992
Printed in Great Britain

0040-4020/92 $5.00+.00

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

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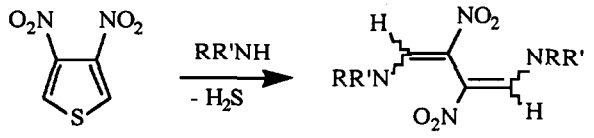
(*Received in UK* 30 *March* 1992)

Abstract *: The optimized ring-opening reaction of 3,4-dinitrothiophene* ***1*** *with either primary or secondary amines leads to 1,4-bis(alkylamino)- and 1,4-bis(arylamino)-* ***2*** *or 1,4-bis(dialkylamino)-2,3-dinitro-1,3-butadienes* ***3*** *in satisfactory to excellent yields. While compounds* ***2*** *in solution appear to be mixtures of (Z,Z), (Z,E) and (E,E) stereoisomers, whose composition is influenced by the nature of the solvent, compounds* ***3*** *appear as single (E,E) isomers. The reaction of* ***3*** *with various organometals in THF represents a novel access to unknown (E,E)-1,4-dialkyl- and (E,E)-1,4-diaryl-2,3-dinitro-1,3-butadienes* ***4****. Finally, Pb-reduction of the two nitrovinylic functionalities of* ***4*** *effectively leads to the corresponding symmetrically 1,4-disubstituted 2,3-butanedione dioximes* ***5****.*

In the field of nucleophilic substitutions on thiophene derivatives,[1] the non-benzenoid behaviour of 3,4-dinitrothiophene **1** is well evidenced, *inter alia*, by the ring-opening reactions that it undergoes by treatment with primary and secondary amines. On this regard, two short communications from our laboratories[2,3] reported on the unexpected isolation of some 1,4-bis(alkylamino)- and 1,4-bis(arylamino)- (**2**) or 1,4-bis(dialkylamino)-2,3-dinitro-1,3-butadienes (**3**) in the attempted nucleophilic substitution of a nitro group of **1** by action of amines [equation (1)].



(1)

1

2 : R = alkyl, aryl; R' = H

3 : R = R' = alkyl

An extremely interesting aspect of compounds **2** and **3** is the presence of two conjugated nitroenaminic

functionalities. The chemistry of nitroenamines has been extensively investigated and their utility in organic synthesis is well established.[4,5] Particularly remarkable is, *e.g.*, the reactivity of tertiary nitroenamines towards carbon nucleophiles which leads to elongation of the carbon skeleton *via* an overall substitution of the dialkylamino group. Significant examples are represented by: *a*) the formation of synthetically useful nitroolefins by reaction with alkyl metals,[6] indole[7] and enolates of active methine carbonyl compounds;[8,9] *b*) the syntheses of α,β-unsaturated ketones, oximes, nitriles and several other interesting derivatives, *via* reaction with carbonyl compounds containing a methyl or methylene group at the α-position.[10]

As anticipated in a preliminary account of the present work,[11] we are presently investigating the properties of compounds **2** and **3** in order to ascertain, in particular, whether and to what extent the latter would display the typical reactivity of simple 2-nitroenamines, an outcome which would open up new applications of them as synthetic fragments. As a first obvious stage of this research, we have more deeply investigated the reaction of equation 1 in order to extend its scope, simplify experimental procedures and optimize yields of the diaminobutadienes **2** and **3**. Accordingly, we report herein on the preparation and characterization of some **2** and **3**, on the transformation of the latter derivatives into 1,4-dialkyl- and 1,4-diaryl-2,3-dinitro-1,3-butadienes **4** and, finally, on the reduction of **4** to the corresponding 1,4-disubstituted 2,3-butanedione dioximes **5**.

RESULTS AND DISCUSSION

Synthesis of 1,4-Diaminobutadienes 2 and 3.

The reaction of **1** with primary or secondary amines in various experimental conditions leads to variable yields of 1,4-bis(alkylamino)- and 1,4-bis(arylamino)- (**2**) or 1,4-bis(dialkylamino)-2,3-dinitro-1,3-butadienes (**3**) *via* opening of the heterocyclic ring and elimination of hydrogen sulfide [equation (1)]. This peculiar reactivity of an *ortho* -like aromatic dinitro derivative is probably linked to some α,β-double-bond localization in **1**, as suggested by the results we obtained from studies on the behaviour of **1** itself and of other structurally related thiophene derivatives with different nucleophiles.[1]

The mechanism of the aminolysis leading to **2** or **3** is not yet completely clear, but it is envisaged that it involves two successive Michael additions of the amine to the nitro-activated double bonds of **1**, with the eventual elimination of hydrogen sulfide; such process can be formally related to the facile substitution[12] of the phenylthio group in 1-nitro-2-phenylthioalkenes by treatment with either aliphatic or aromatic amines[13] in conditions similar to those employed herein.

As concerns the experimental conditions of the reaction of equation (1), a preliminary screening showed that the yields of **2** and especially of **3** are markedly dependent on the reaction variables: a number of solvents (toluene, acetonitrile, Et_2O, MeOH, EtOH), different molar ratios or concentrations of reagents and temperatures (0°, 25° or reflux) were tried and darkening with formation of significant amounts of tarry material was often observed. The most convenient conditions eventually resulted to be the treatment of a suspension of **1** in EtOH with 4 molar equivalents of amine at 0°C. After completion of the reaction, the precipitated **2** or **3** were simply isolated by filtration in good yields (Table 1);[14] the only exceptions were represented by the reactions with the six-membered cyclic amines piperidine and morpholine, where the yields of **3** fell to low values (35% and 47% respectively).

A ^1H NMR study of compounds **2** and **3** was carried out in order to investigate on the existence of tautomeric forms of **2** as well as on the configuration of both classes of compounds. It was first of all

Table 1. Ring-opening of 3,4-dinitrothiophene **1** with primary and secondary amines: reaction conditions and yields of isolated diaminodinitrobutadienes **2** and **3.**

Compd.	R	R'	yield (%) [a]	temp. (°C) [b]	time (h)
2a	Et	H	89	0-20	2.0
2b	Bu^n	H	81	0-20	2.0
2c	Bu^t	H	65	0-20	2.0
2d	c-C_6H_{11}	H	97	0-20	2.4
2e	$PhCH_2$	H	80	20	2.5
2f	Ph	H	89	20	7.0
2g	3-MeC_6H_4	H	87	20	7.0
2h	4-MeC_6H_4	H	90	20	3.5
3a	Me	Me	60	0	1.5
3b	Et	Et	75	0-20	22.0
3c	Pr^n	Pr^n	74	0-20	72.0
3d	—$(CH_2)_4$—		90	0	2.5
3e	—$(CH_2)_5$—		35	0-20	0.8
3f	—$(CH_2)_2$–O–$(CH_2)_2$—		47	0	2.5

a) Yields of isolated products; by ^1H NMR compounds **2a-h** appeared as mixtures of (*E,E*), (*E,Z*) and (*Z,Z*) stereoisomers while **3a-f** showed to be pure (*E,E*)-forms (see text). b) The amine was added to a suspension of **1** in EtOH cooled at 0 °C with an ice bath; cooling of the reaction mixture was maintained (0°) or, alternatively, the bath was either left to slowly reach room temperature (0-20°) or removed after addition of the amine (20°).

Table 2. Relative concentrations[a] of some diastereomeric diaminodinitrobutadienes **2** in $CDCl_3$ and CD_3SOCD_3.[b]

Compd. (solvent)	(*Z,Z*) %	(*E,Z*) %	(*E,E*) %
2a ($CDCl_3$)	77	21	2
2a (DMSO)	11	28	61
2b ($CDCl_3$)	80	20	*c*
2b (DMSO)	11	34	55
2c ($CDCl_3$)	71	21	8
2c (DMSO)	4	33	63
2f (DMSO)[d]	2	17	81

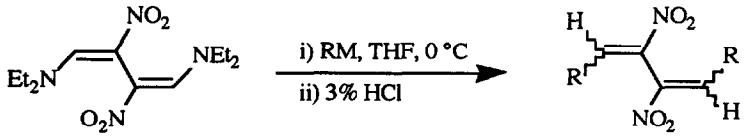
a) Relative concentrations were generally calculated from normalized integrals of signals of nitrovinylic protons belonging to (*E,E*), (*E,Z*) and (*Z,Z*) stereoisomers; whenever this was not possible the NH signals were used. b) ^1H NMR spectra were recorded of solutions at the same concentrations: 18 mM in $CDCl_3$ and 37 mM in DMSO.c) Undetectable at the concentration employed. d) A satisfactory spectrum of **2f** in $CDCl_3$ could not be obtained because of the too low solubility of the compound.

ascertained that diaminodinitrobutadienes **2** follow the general rule of simple nitroenamines[4,15] in being true enamines in solution, as no signals attributable to tautomers[4, 16] with a 2-nitroiminic structure [-N=CH-CH(NO_2)-] were detected.[17]

As far as configuration is concerned, in agreement with previous reports[4, 15, 18-20] on structurally related nitroenamines, ^{1}H NMR data[21] showed that while **3** invariably have the less hindered and more stable (*E,E*) configuration, compounds **2** exist in solution as mixtures of the three possible configurational isomers (*E,E*), (*E,Z*) and (*Z,Z*), the composition depending on the nature of the solvent. The data collected in Table 2 for some significative compounds show that (*Z,Z*)-**2** isomers predominate in $CDCl_3$ because of the stabilisation provided by an intramolecular hydrogen bond between NH and the nitro group (as revealed, *inter alia*, by the deshielding of the NH protons); conversely, in the more polar and hydrogen-bond-accepting DMSO the (*E,E*) isomer results to be the favoured one.

Synthesis of 1,4-Diaryl- and 1,4-Dialkyl-2,3-dinitro-1,3-butadienes 4.

As previously mentioned, one of the most interesting aspects of 2-nitroenamines is represented by their reactivity with carbon nucleophiles.[6-10] In order to verify the possible extension of such behaviour to compounds **3**, we have firstly examined the reactions of **3b** with various Grignard reagents and butyl lithium in THF.



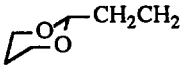
3b M = MgBr, Li **4a-k**

The results obtained (Table 3) show that the treatment of **3b** with 2.2 molar equivalents of a number of Grignards in THF at 0°C, followed by quenching into 3% HCl, represents an excellent access to hitherto unknown 2,3-dinitrobutadienes **4**. Furthermore, the successful synthesis of 6,7-dinitro-5,7-dodecadiene **4i** by reaction of **3b** with butyllithium in the same conditions suggests that, as for simple nitroenamines,[6] the method can be conveniently extended also to lithium reagents.

The reaction proved to be of quite general applicability as far as substrates are concerned, although yields do not always reach the high values of Table 3; for instance, **3d** and **3e** led, by reaction with PhMgBr in the usual conditions, to **4a** in 30% and 67% yield respectively. The choice of the bis(diethylamino)derivative **3b** as a model substrate for the reaction under examination was thus obviously dictated by its apparently being the best compromise between accessibility (75% yield from **1**) and reactivity towards organometals.

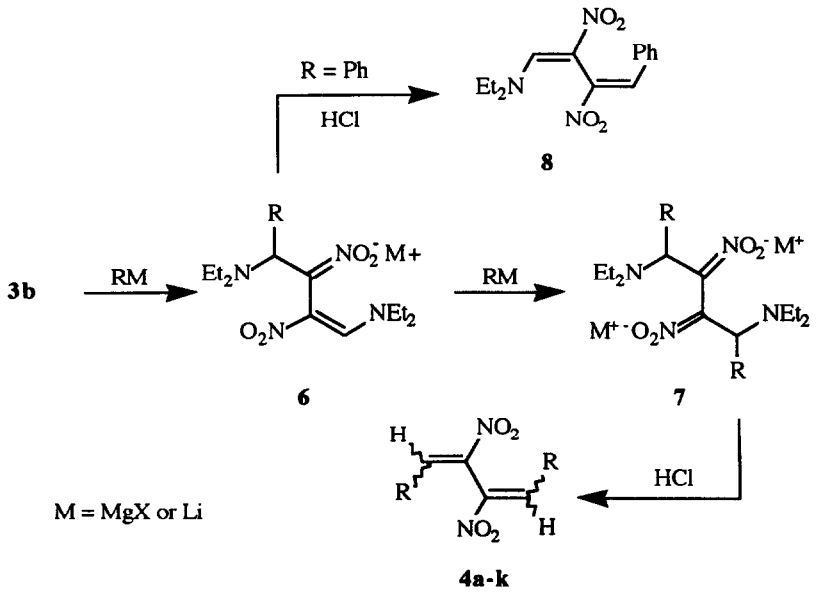
The transformation of substrates **3** into the 2,3-dinitro-1,3-butadienes **4** parallels the behaviour of simple nitroenamines in the same kind of processes.[4-6] Accordingly, it is likely that the reactions proceed *via* two successive 1,4-additions of the organometallic reagent to the nitro-vinyl systems of **3**, followed by elimination of two amine molecules as a result of acidic quenching of the reaction. In agreement with the steps sketched in Scheme 1, the reaction of **3b** with only 1.1 moles of phenylmagnesium bromide gave, besides unreacted **3b** (30%) and the bis-substituted product **4a** (38%), (*E,E*)-1-diethylamino-4-phenyl-2,3-dinitro-1,3-butadiene **8**

Table 3. Yields of isolated 1,4-diaryl- and 1,4-dialkyl-2,3-dinitro-1,3-butadienes **4a-k** in the reactions of **3b** with Grignard reagents and butyllithium. [a]

Compd.	R =	Yield (%) [b]
4a	phenyl	88 [c]
4b	1-naphthyl	87
4c	2-thienyl	86
4d	2-MeC_6H_4	87
4e	4-MeC_6H_4	95
4f	4-$MeOC_6H_4$	90
4g	Me	73 [d]
4h	Et	94 [c]
4i	Bu^n	97 [e]
4j	c-C_6H_{11}	90 [c]
4k		83

a) Unless otherwise stated, freshly prepared RMgBr (2.2 mol. equiv. in THF) was reacted with **3b** in THF at 0 °C for 30-45 min; quenching was performed by pouring the reaction mixture into ice/3% HCl.b) Yields of isolated mixtures of stereoisomers (see text) from which the main (*E,E*)-component could be isolated by crystallization (60-85% overall yield from **3b**).c) Data from ref.11.d) Commercial MeMgBr (nominally 3.0 M in Et_2O) was used. e) Commercial butyllithium (nominally 1.6 M in hexane) was used.

Scheme 1



(31%) evidently deriving from acidic quenching of the intermediate mono-adduct (**6**, R=Ph). A computer simulated kinetics of the two consecutive addition steps of Scheme 1 indicates that the obtained relative percentages of unreacted **3b**, of **4a** and of **8** are consistent with a ratio of 0.8 between the rates of the first and the second addition reaction.

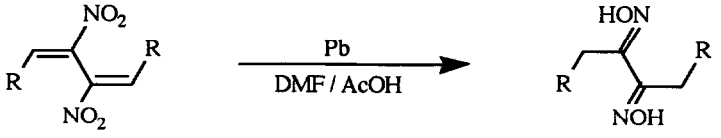
As regards the stereochemistry of the isolated dinitrobutadienes **4a-k**, the ^{1}H NMR analysis of the crude reaction products showed that the formation of the (*E,E*) isomers was always predominant.

However, while in the reactions leading to **4a-f** the formation of (*E,E*)-isomers appeared exclusive, variable percentages of the (*E,Z*)-form were detected in the crude reaction mixtures of the alkyl substituted products **4g-k**. In the case of the bis-cyclohexyl derivative **4j**, portions of the dichloromethane extracts of the reaction were evaporated at different times and the residues checked by ^{1}H NMR; such analysis showed, besides traces of the (*Z,Z*)-**4j** in the earlier worked-up portion, that the original diastereomeric ratio varied with time to give a mixture more and more enriched in the (*E,E*)-form of **4j**. Such a kind of stereomutation was also observed, although slower, in the $CDCl_3$ solutions used to record spectra.

Therefore it is likely that in all the experiments of Table 3 the reaction gives a mixture of diastereoisomers of **4** whose composition varies, in solution, with a rate depending on the nature of the solvent and of the R groups. Actually, on a preparative point of view, allowing the reaction extracts to stand overnight, the above stereomutation furnishes a mixture enriched in (*E,E*)-**4a-k** [from 85% (R = c-C_6H_{11}) to 100% (R = aryl)], from which such major component is obtained in pure form by crystallization. No attempt of separation of other stereoisomers was tried.

Synthesis of 1,4-Diaryl- and 1,4-Dialkyl-2,3-butanedione Dioximes 5.

Selective reductions of conjugated nitroalkenes have been extensively studied[23-25] as their conversion to compounds such as, e.g., nitroalkanes, carbonyl compounds, amines, substituted hydroxylamines and oximes is of particular interest. As a further step of a sequence aimed at exploiting the high functionality of our system for synthetically useful processes, we investigated the potential utility of dinitrobutadienes **4** for the synthesis of substituted 2,3-butanedione dioximes.



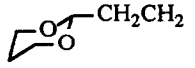
4a-k **5a-k**

Thus,by means of a procedure which has been successfully applied to simple nitroalkenes,[26] the reduction of compounds **4a-k**, with lead powder in an acetic acid-DMF mixture and at room temperature, gave good yields (Table 4) of 1,4-disubstituted 2,3-butanedione dioximes **5a-k**. The latter products represent in turn interesting target molecules as *vic* -dioximes find utilization, *e.g.* , as chelating agents in photographic materials[27] and as synthetic precursors of 1,2,5-oxadiazoles[28] and of heteromacrocyclic compounds.[29]

From a stereochemical point of view, although traces of isomers sometimes show up in the spectra of crude reaction products, the (*E,E*) configuration can be confidently attributed to pure crystalline **5** on the grounds of the single absorption and of the chemical shift values observed for the NOH protons in DMSO-d_6.

Such chemical shifts, in fact,closely match those reported for the (*E,E*) form of similar dioximes[29] and, in the case where our compound coincides with an already synthesized one (namely **5h** herein), reproducibility of the whole spectrum with that of the (*E,E*) isomer occurs.

Table 4. Reduction of dinitrobutadienes **4a-k** to butanedione dioximes **5a-k.**

Compd.	R =	Yield (%) [b]	time (h)
5a	phenyl	81	2.0
5b	1-naphthyl	72	2.0
5c	2-thienyl	89	1.0
5d	2-MeC_6H_4	68	3.0
5e	4-MeC_6H_4	75	2.0
5f	4-$MeOC_6H_4$	80	2.0
5g	Me	80	2.0
5h	Et	72	1.3
5i	Bu^n	85	2.0
5j	c-C_6H_{11}	84	2.0
5k		69	4.0

a) Yields of isolated and purified dioximes **5** to which the (*E,E*)-configuration can be confidently attributed (see Experimental Section).

Conclusions

The results presented herein appear to open a number of novel and useful synthetic pathways. Actually, the four-carbon skeleton of 3,4-dinitrothiophene, made available through the initial opening of the aromatic ring, can be regarded as a building block amenable to further manipulation by conveniently modifying its functionality: the reported syntheses of dinitrobutadienes **4** and dioximes **5** only scratch the surface of an area in which deeper investigation is in progress.

EXPERIMENTAL

Melting points were determined on a Büchi 535 apparatus and are uncorrected. ^1H 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

Light petroleum and petroleum ether 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 before use. 3,4-Dinitrothiophene was synthesized as reported.[30] Amines were all commercial samples used as received with the exception of cyclohexylamine and 4-methylaniline which were distilled before use. Ethylamine was a 70% solution in water. Grignard reagents (*ca.* 1.1 M in THF) were prepared from the corresponding bromoderivatives (commercial samples dried over 4 Å molecular sieves) using standard procedures.

Methylmagnesium bromide (nominally 3.0 M in Et_2O) and butyllithium (nominally 1.6 M in hexanes) were commercial products. All the solutions of organometallic reagents were titrated just before use, using a reported procedure.[31]

Ring-opening Reactions of 3,4-Dinitrothiophene with Primary and Secondary Amines

In an Erlenmeyer flask, 3,4-dinitrothiophene (1 g, 5.75 mmol) was suspended in 20 ml of EtOH and cooled at 0 °C with an external ice bath. Under magnetic stirring, 4 molar equivalents of amine were slowly syringed into the reaction mixture which became in a short time a homogeneous orange/red solution. Reaction temperatures and times are reported in Table 1: during such period hydrogen sulfide evolution and precipitation of diaminobutadienes **2** or **3** occurred. The solid was filtered, washed with little EtOH and crystallized.

1,4-Bis(alkylamino)- and 1,4-bis(arylamino)-2,3-dinitro-1,3-butadienes 2a-h

As mentioned in the text, solutions of crude **2a-h** appear as mixtures of (*Z,Z*), (*Z,E*) and (*E,E*) forms, whose composition depends on the nature of the solvent (Table 2). The ^1H NMR absorptions relevant to the various stereoisomers are collected in Table 5.

1,4-Bis(ethylamino)-2,3-dinitro-1,3-butadiene **2a**: mp 142.6-143.0 °C (dec.) (EtOH) (Found: C, 41.6; H, 6.1; N, 24.2. $C_8H_{14}N_4O_4$ requires: C, 41.7; H, 6.1; N, 24.3%).

1,4-Bis(butylamino)-2,3-dinitro-1,3-butadiene **2b**: mp 131.6-131.9 °C (dec.) (EtOH-dioxane) (lit.,[2] mp 134 °C).

1,4-Bis(tert-butylamino)-2,3-dinitro-1,3-butadiene **2c**: mp 173.2 °C (dec.) (EtOH-dioxane) (Found: C, 50.2; H, 7.6; N, 19.3. $C_{12}H_{22}N_4O_4$ requires: C, 50.3; H, 7.7; N, 19.6%).

1,4-Bis(cyclohexylamino)-2,3-dinitro-1,3-butadiene **2d**: mp 156.0-156.3 °C (dec.) (EtOH-dioxane) (Found: C, 56.4; H, 7.6; N, 16.4. $C_{16}H_{26}N_4O_4$ requires: C, 56.8; H, 7.7; N, 16.6%).

1,4-Bis(benzylamino)-2,3-dinitro-1,3-butadiene **2e**: mp 151.6-152.3 °C (dec.) (dioxane) (Found: C, 59.9; H, 5.2; N, 15.5. $C_{18}H_{18}N_4O_4$ requires: C, 61.0; H, 5.1; N, 15.8%).

1,4-Bis(phenylamino)-2,3-dinitro-1,3-butadiene **2f**: mp 181.3-181.7 °C (dec.) (dioxane) (lit.,[2] mp 194 °C) (Found: C, 58.7; H, 4.2; N, 17.0. $C_{16}H_{14}N_4O_4$ requires: C, 58.9; H, 4.3; N, 17.2%).

1,4-Bis(3-methylphenylamino)-2,3-dinitro-1,3-butadiene **2g**: mp 199.0-199.5 °C (dec.) (dioxane) (lit.,[2] mp 200 °C).

1,4-Bis(4-methylphenylamino)-2,3-dinitro-1,3-butadiene **2h**: mp 199.8 °C (dec.) (dioxane) (lit.,[2] mp 200 °C).

(E,E)-1,4-Bis(dialkylamino)-2,3-dinitro-1,3-butadienes 3a-f

The yields reported in Table 1 refer to pure (crystallized) derivatives. In no case the ^1H NMR spectrum of the crude reaction product revealed the presence of stereoisomers different from the (*E,E*) forms hereinafter described. The bis(diethylamino)derivative **3b** has been already described in our previous communication.[11]

(E,E)-1,4-Bis(dimethylamino)-2,3-dinitro-1,3-butadiene **3a**: mp 208 °C (dec.) (EtOH-dioxane) (lit.,[3] 207 °C); ^1H NMR ($CDCl_3$) δ 2.99 (6H, br s), 3.27 (6H, br s) and 8.54 (2H, s).

(E,E)-1,4-Bis(dipropylamino)-2,3-dinitro-1,3-butadiene **3c**: mp 119.7-120.5 °C (EtOH-dioxane) (lit.,[3] 127 °C); ^1H NMR ($CDCl_3$) δ 0.83 (6H, X_3 of ABM_2X_3, J_{MX} 7.4 Hz), 0.98 (6H, t, *J* 7.4 Hz), 1.48 (4H, M_2 of ABM_2X_3, *J* 7.4 Hz), 1.71 (4H, app. sextect), 3.17 (4H, qt, AB of ABM_2X_3, J_{AB} 14.0 Hz, $J_{AX} = J_{BX}$ 8.1 Hz), 3.34 (4H, t, *J* 7.4 Hz) and 8.56 (2H, s).

(E,E)-1,4-Dipyrrolidino-2,3-dinitro-1,3-butadiene **3d**: mp 245.5 °C (dec.) (EtOH-dioxane) (Found: C, 51.2; H, 6.5; N, 19.9. $C_{12}H_{18}N_4O_4$ requires: C, 51.1; H, 6.4; N, 19.85%); ^1H NMR ($CDCl_3$) δ 1.96 (8H, m), 3.34 (4H, m), 3.70 (4H, m) and 8.70 (2H, s).

(E,E)-1,4-Dipiperidino-2,3-dinitro-1,3-butadiene **3e**: mp 196.3-197.6 °C (dec.) (lit.,[3] mp 200 °C); ^1H NMR ($CDCl_3$) δ 1.68 (12H, m), 3.50 (8H, m) and 8.53 (2H, s).

(E,E)-1,4-Dimorpholino-2,3-dinitro-1,3-butadiene **3f**: mp 251.4-251.9 °C (dec.) (EtOH-dioxane) (lit.,[3] mp 260 °C); ^1H NMR ($CDCl_3$) δ 3.56 and 3.75 (16H in all, two partly overlapped multiplets) and 8.50 (2H, s).

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

In a flame-dried flask, equipped with an argon inlet, a rubber septum and a magnetic stirring bar, **3b** (2 mmol) was suspended in 50 ml of THF and cooled to ca. 0 °C with an external ice bath. By means of a syringe, 4.4 mmol of the organometallic reagent (1-1.5 M in THF) was slowly added under magnetic stirring. The reaction mixture was kept at the same temperature for 30-45 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. Evaporation of the solvent under reduced pressure gave essentially pure

compounds **4a-k** in good yields (Table 3). The ^{1}H NMR spectrum of the crude reaction product revealed, in some cases, the presence of minor amounts of (*E,Z*)-**4** beside the main (*E,E*)-**4** component. The latter was then obtained in pure form *via* a single crystallization from a suitable solvent or, in the case of **4i**, by column chromatography on silica gel. No isolation of the (*E,Z*)-isomers was attempted.

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

1,4-Diphenyl- **4a**, 1,4-diethyl- **4h** and 1,4-dicyclohexyl- **4j** derivatives have already been described in our previous communication.[11]

(E,E)-1,4-Bis(1-naphthyl)-2,3-dinitro-1,3-butadiene **4b**: mp 211.5-212.0 °C (light petroleum-toluene) (Found: C, 72.9, H, 4.1; N, 6.9. $C_{24}H_{16}N_2O_4$ requires: C, 72.7; H, 4.1; N, 7.1%); ^{1}H NMR ($CDCl_3$) δ 6.82 (2H, m), 7.18 (8H, m), 7.48 (4H, m) and 8.62 (2H, s).

(E,E)-1,4-Bis(2-thienyl)-2,3-dinitro-1,3-butadiene **4c**: mp 188.1-189.3 °C (dec.) (light petroleum-toluene) (Found: C, 47.0, H, 2.6; N, 9.2. $C_{12}H_8N_2O_4S_2$ requires: C, 46.7; H, 2.6; N, 9.1%); ^{1}H NMR ($CDCl_3$) δ 7.16 (2H, dd, *J* 3.8 and 5.0 Hz), 7.63 (4H, m) and 8.80 (2H, s).

(E,E)-1,4-Bis(2-methylphenyl)-2,3-dinitro-1,3-butadiene **4d**: mp 185.2-186.6 °C (toluene) (Found: C, 66.8, H, 4.9; N, 8.7. $C_{18}H_{16}N_2O_4$ requires: C, 66.7; H, 5.0; N, 8.6%); ^{1}H NMR ($CDCl_3$) δ 1.62 (6H, s), 7.12 (8H, m) and 8.30 (2H, s).

(E,E)-1,4-Bis(4-methylphenyl)-2,3-dinitro-1,3-butadiene **4e**: mp 139.2-140.1 °C (petroleum ether-toluene) (Found: C, 66.6, H, 4.9; N, 8.6. $C_{18}H_{16}N_2O_4$ requires: C, 66.7; H, 5.0; N, 8.6%); ^{1}H NMR ($CDCl_3$) δ 2.33 (6H, s), 7.15 and 7.34 (4H each, AA'BB' system, *J* 8.2 Hz) and 8.50 (2H, s).

(E,E)-1,4-Bis(4-methoxyphenyl)-2,3-dinitro-1,3-butadiene **4f**: mp 171.0-172.4 °C (light petroleum-toluene) (Found: C, 60.5, H, 4.5; N, 7.8. $C_{18}H_{16}N_2O_6$ requires: C, 60.7; H, 4.5; N, 7.9%); ^{1}H NMR ($CDCl_3$) δ 3.80 (6H, s), 6.85 and 7.45 (4H each, AA'BB' system, *J* 9.0 Hz) and 8.51 (2H, s).

(E,E)-3,4-Dinitro-2,4-hexadiene **4g**: mp 60.5-62.0 °C (petroleum ether-toluene) (Found: C, 41.7, H, 4.5; N, 16.2. $C_6H_8N_2O_4$ requires: C, 41.9; H, 4.7; N, 16.3%); ^{1}H NMR ($CDCl_3$) δ 1.93 (6H, d, *J* 7.5 Hz) and 7.76 (2H, q, *J* 7.5 Hz).

(E,E)-6,7-Dinitro-5,7-dodecadiene **4i**: yellow oil (Found: C, 56.0, H, 7.8; N, 10.8. $C_{12}H_{20}N_2O_4$ requires: C, 56.2; H, 7.9; N, 10.9%); ^{1}H NMR ($CDCl_3$) δ 0.91 (6H, t, *J* 7.1 Hz), 1.43 (8H, m), 2.18 (4H, m) and 7.67 (2H, t, *J* 8.0 Hz).

(E,E)-1,8-Bis(1,3-dioxan-2-yl)-4,5-dinitro-3,5-octadiene **4k**: mp 71.7-72.5 °C (MeOH-petroleum ether) (Found: C, 50.5, H, 6.4; N, 7.4. $C_{16}H_{24}N_2O_8$ requires: C, 51.6; H, 6.5; N, 7.5%); ^{1}H NMR ($CDCl_3$) δ 1.28 (2H, m), 1.83 (4H, dt, *J* 4.8 and 7.1 Hz), 2.02 (2H,m), 2.31 (4H, dt, *J* 7.1 and 8.1 Hz), 3.70 (4H, m), 4.05 (4H, m), 4.50 (2H, t, *J* 4.8 Hz) and 7.68 (2H, t, *J* 8.1 Hz).

Isolation of compound 8 from the reaction of 3b with phenylmagnesium bromide

Following the general procedure reported above, 2 mmol of **3b** were reacted with 2.2 mmol of phenylmagnesium bromide in THF. The residue obtained by evaporation of the dichloromethane extracts of the reaction was chromatographed on a silica gel column. Eluting with dichloromethane the following fractions were collected: i) 0.76 mmol (38%) of 1,4-diphenyl-2,3-dinitro-1,3-butadiene **4a**; ii) 0.62 mmol (31%) of *1-diethylamino-4-phenyl-2,3-dinitro-1,3-butadiene* **8**, mp 104.6-105.4 °C (petroleum ether-toluene) (Found: C, 57.6, H, 5.8; N, 14.3. $C_{14}H_{17}N_3O_4$ requires: C, 57.7; H, 5.9; N, 14.4%); ^{1}H NMR ($CDCl_3$) δ 0.92 (3H, X_3 of ABX_3, $J_{AX} = J_{BX}$ 7.2 Hz), 1.19 (3H, t, *J* 7.1 Hz), 3.11 (2H, AB of ABX_3, J_{AB} 14.3 Hz and $J_{AX} = J_{BX}$ 7.2 Hz), 3.40 (2H, q, *J* 7.1 Hz), 7.45 (5H, m), 8.31 (1H, s) and 8.55 (1H, s). Unreacted **3b** (0.60 mmol, 30%) was eventually eluted using a dichloromethane-ethyl acetate gradient.

Lead Reduction of Dinitrobutadienes 4a-k to Butanedione Dioximes 5a-k [32]

In an Erlenmeyer flask, compounds **4a-k** (2 mmol) were dissolved in dimethylformamide (30 ml) and acetic acid (2 ml). Under magnetic stirring and at room temperature, lead powder (1.8 g) was added, and the mixture was stirred for the period given in Table 4. Usual workup involved pouring of the reaction mixture into water and 6-fold extraction with Et_2O, followed by washing of the combined extracts with brine. The organic layer was dried (Na_2SO_4) and the solvent removed under reduced pressure to give essentially pure (TLC, ^{1}H NMR) dioximes **5** in more than 90% yield. The residue was either taken up with little CH_2Cl_2 (**5a-e**) or light petroleum (**5h,j**) or crystallized from a proper solvent (**5f,g,i,k**). The resulting pure dioximes were thus obtained as a single configurational isomer in the yields reported in Table 4.

1,4-Disubstituted 2,3-butanedione dioximes 5a-k

As mentioned in the text, to pure and crystallized dioximes **5a-k** the (*E,E*) configuration can be confidently attributed on the grounds of the single absorption and on the chemical shift values observed for the NOH protons in CD_3SOCD_3 [δ_{NOH}(DMSO)]. The ^{1}H NMR spectrum of (*E,E*)-**5h** closely matches that

previously reported.[29]

1,4-Diphenyl-2,3-butanedione dioxime **5a**: mp 191.4-192.5 °C (toluene) (lit.,[33] mp 193 °C); ^{1}H NMR (CD_3COCD_3) δ 4.02 (4H, s), 7.16 (10H, m) and 10.78 (2H, s); δ_{NOH}(DMSO) 11.64.

1,4-Bis(1-naphthyl)-2,3-butanedione dioxime **5b**: mp 189.7-191.0 °C (toluene) (Found: C, 78.6, H, 5.6; N, 7.7. $C_{24}H_{20}N_2O_2$ requires: C, 78.2; H, 5.5; N, 7.6%); ^{1}H NMR (CD_3COCD_3) δ 4.56 (4H, s), 7.13 (2H, dd, *J* 1.1 and 7.1 Hz), 7.29 (2H, t, *J* 7.7 Hz), 7.52 (4H, m), 7.74 (2H, d, *J* 8.3 Hz), 7.90 (2H, m), 8.26 (2H, m) and 10.78 (2H, s); δ_{NOH}(DMSO) 11.64.

1,4-Bis(2-thienyl)-2,3-butanedione dioxime **5c**: mp 185.0-186.0 °C (light petroleum-toluene) (Found: C, 51.6, H, 4.2; N, 9.8. $C_{12}H_{12}N_2O_2S_2$ requires: C, 51.4; H, 4.3; N, 10.0%); ^{1}H NMR (CD_3COCD_3) δ 4.16 (4H, s), 6.84 (4H, m), 7.15 (2H, m) and 10.99 (2H, s); δ_{NOH}(DMSO) 11.85.

1,4-Bis(2-methylphenyl)-2,3-butanedione dioxime **5d**: mp 182.4-183.3 °C (toluene) (Found: C, 73.0, H, 6.9; N, 9.5. $C_{18}H_{20}N_2O_2$ requires: C, 72.95; H, 6.8; N, 9.45%); ^{1}H NMR (CD_3COCD_3) δ 2.33 (6H, s), 4.00 (4H, s), 7.03 (8H, m) and 10.67 (2H, s); δ_{NOH}(DMSO) 11.55.

1,4-Bis(4-methylphenyl)-2,3-butanedione dioxime **5e**: mp 214.6-216.0 °C (toluene) (Found: C, 72.9, H, 6.7; N, 9.4. $C_{18}H_{20}N_2O_2$ requires: C, 72.95; H, 6.8; N, 9.45%); ^{1}H NMR (CD_3COCD_3) δ 2.24 (6H, s), 3.96 (4H,s), 6.99 and 7.11 (4H each, AA'BB' system, *J* 8.1 Hz) and 10.71 (2H, s); δ_{NOH}(DMSO) 11.57.

1,4-Bis(4-methoxyphenyl)-2,3-butanedione dioxime **5f**: mp 192.4-193.6 °C (toluene) (Found: C, 66.0, H, 6.1; N, 8.6. $C_{18}H_{20}N_2O_4$ requires: C, 65.8; H, 6.1; N, 8.5%); ^{1}H NMR (CD_3COCD_3) δ 3.72 (6H,s), 3.93 (4H,s), 6.74 and 7.15 (4H each, AA'BB' system, *J* 8.8 Hz) and 10.71 (2H, s); δ_{NOH}(DMSO) 11.56.

3,4-Hexanedione dioxime **5g**: mp 191.5-193.3 °C (toluene) (lit.: mp 196-197.5 °C,[34] mp 185 °C[35]), ^{1}H NMR (CD_3COCD_3) δ 1.06 (6H, t, *J* 7.5 Hz), 2.59 (4H, q, *J* 7.5 Hz) and 10.37 (2H, s); δ_{NOH}(DMSO) 11.29.

4,5-Octanedione dioxime **5h**: mp 181.0-182.4 °C (benzene) (lit.,[36] mp 181-182 °C); ^{1}H NMR in CD_3SOCD_3 in agreement with that reported.[29]

6,7-Dodecanedione dioxime **5i**: mp 179.3-180.3 °C (toluene) (lit,[37] mp 185 °C); ^{1}H NMR (CD_3COCD_3) δ 0.87 (6H, t, *J* 6.9 Hz), 1.40 (12H, m), 2.60 (4H, t, *J* 7.6 Hz) and 10.36 (2H, s); δ_{NOH}(DMSO) 11.27.

1,4-Dicyclohexyl-2,3-butanedione dioxime **5j**: mp 239.0-240.7 °C (toluene) (Found: C, 68.7, H, 10.3; N, 10.0. $C_{16}H_{28}N_2O_2$ requires: C, 68.5; H, 10.1; N, 10.0%); ^{1}H NMR (CD_3COCD_3) δ 1.10 (10H, m), 1.65 (12H, m), 2.54 (4H, d, *J* 7.1 Hz) and 10.35 (2H, s); δ_{NOH}(DMSO) 11.24.

1,8-Bis(1,3-dioxan-2-yl)-4,5-octanedione dioxime **5k**: mp 143.0-144.0 °C (petroleum ether-toluene) (Found: C, 55.9, H, 8.1; N, 8.0. $C_{16}H_{28}N_2O_6$ requires: C, 55.8; H, 8.2; N, 8.1%); ^{1}H NMR ($CDCl_3$) δ 1.33 (2H, m), 1.60 (8H, m), 2.07 (2H, m), 2.60 (4H, t, *J* 7.2 Hz), 3.75 (4H,m), 4.09 (4H, m), 4.53 (2H, t, *J* 4.6 Hz) and 7.74 (2H, br s); δ_{NOH}(DMSO) 11.32.

Table 5. ^{1}H NMR data for diaminodinitrobutadienes **2a-h** in $CDCl_3$ and/or CD_3SOCD_3.[a]

Compd.	Solv.	Config.	δ(NH)	δ(CH)	others [b]
2a	$CDCl_3$	(*E*,*Z*)	(*E*): 5.47 (br s)	8.40 (d, *J* 14.9 Hz)	3.45 (m, CH_2CH_3) and
			(*Z*): 9.62 (br s)	7.09 (d, *J* 14.4 Hz)	1.33 (m, CH_2CH_3)
		(*Z*,*Z*)	9.33 (br s)	7.05 (d, *J* 14.2 Hz)	
		(*E*,*E*)	*c*	8.39 (d, *J* 15.2 Hz)	
	DMSO	(*E*,*Z*)	(*E*): 8.40 (m)	8.56 (d, *J* 14.6 Hz)	3.45 (m, CH_2CH_3) and
			(*Z*): 9.90 (m)	7.47 (d, *J* 14.7 Hz)	1.33 (m, CH_2CH_3)
		(*Z*,*Z*)	9.71 (m)	7.64 (d, *J* 14.7 Hz)	
		(*E*,*E*)	8.02 (m)	8.43 (d, *J* 14.8 Hz)	
2b	$CDCl_3$	(*E*,*Z*)	(*E*): 5.35 (br s)	8.38 (d, *J* 15.0 Hz)	3.40, 1.65 and 1.38 [m, $(CH_2)_3CH_3$]
			(*Z*): 9.67 (br s)	7.07 (d, *J* 15.1 Hz)	and 0.94 [m, $(CH_2)_3CH_3$]
		(*Z*,*Z*)	9.38 (m)	7.03 (d, *J* 14.2 Hz)	
		(*E*,*E*)	*c*	*c*	

Compd.	Solv.	Config.	δ(NH)	δ(CH)	others [b]
2b	DMSO	(*E*,*Z*)	(*E*): 8.30 (m)	8.54 (d, *J* 15.0 Hz)	3.40, 1.65 and 1.38 [m, $(CH_2)_3CH_3$]
		(*Z*,*Z*)	9.75 (m)	7.62 (d, *J* 14.6 Hz)	
		(*E*,*E*)	8.08 (m)	8.43 (d, *J* 15.0 Hz)	
2c	$CDCl_3$	(*E*,*Z*)	(*E*): 5.30 (m)	8.52 (d, *J* 15.3 Hz)	1.46 and 1.38 [s, $C(CH_3)_3$]
			(*Z*): 10.08 (d, *J* 14.8 Hz)	7.19 (d, *J* 14.8 Hz)	
		(*Z*,*Z*)	9.75 (d, *J* 14.6 Hz)	7.14 (d, *J* 14.6 Hz)	
		(*E*,*E*)	*c*	8.50 (d, *J* 15.6 Hz)	
	DMSO	(*E*,*Z*)	(*E*): 8.39 (m)	8.48 (d, *J* 15.2 Hz)	1.45 and 1.36 [s, $C(CH_3)_3$]
			(*Z*): 9.83 (d, *J* 14.6 Hz)	7.55 (d, *J* 14.6 Hz)	
		(*Z*,*Z*)	9.75 (d, *J* 14.6 Hz)	7.74 (d, *J* 14.6 Hz)	
		(*E*,*E*)	7.95 (d, *J* 15.5 Hz)	8.37 (d, *J* 15.5 Hz)	
2d	$CDCl_3$	(*E*,*Z*)	(*E*): 5.25 (br s)	8.45 (d, *J* 15.1 Hz)	3.29 [m, c-$(CH_2)_5CH$] and
			(*Z*): 9.77 (br s)	7.14 (d, *J* 14.3 Hz)	2.10-1.10 [m, c-$(CH_2)_5CH$]
		(*Z*,*Z*)	9.40 (m)	7.04 (d, *J* 14.3 Hz)	
		(*E*,*E*)	*c*	8.41 (d, *J* 15.4 Hz)	
	DMSO	(*E*,*Z*)	(*E*): 8.37 (m)	8.54 (d, *J* 15.0 Hz)	3.42 [m, c-$(CH_2)_5CH$] and
			(*Z*): 9.77 (dd, *J* 8.3 and 14.5 Hz)	7.50 (d, *J* 14.5 Hz)	2.00-1.00 [m, c-$(CH_2)_5CH$]
		(*Z*,*Z*)	9.58 (dd, *J* 8.3 and 14.5 Hz)	7.64 (d, *J* 14.5 Hz)	
		(*E*,*E*)	7.92 (dd, *J* 7.6 and 15.0 Hz)	8.37 (d, *J* 15.0 Hz)	
2e	DMSO	(*E*,*Z*)	(*E*): *d*	*d*	7.42-7.25 (m, $C_6H_5CH_2$)
			(*Z*): 10.02 (m)	7.57 (d, *J* 14.7 Hz)	4.50 (m, $C_6H_5CH_2$)
		(*Z*,*Z*)	9.83 (m)	7.72 (d, *J* 14.4 Hz)	
		(*E*,*E*)	*d*	*d*	
2f	DMSO	(*E*,*Z*)	(*E*): 10.17 (d, *J* 14.2 Hz)	8.86 (d, *J* 14.2 Hz)	7.56, 7.37 and 7.15 (m, C_6H_5)
			(*Z*): 11.23 (d, *J* 13.9 Hz)	8.15 (d, *J* 13.9 Hz)	
		(*Z*,*Z*)	11.01 (d, *J* 14.3 Hz)	8.26 (d, *J* 14.3 Hz)	
		(*E*,*E*)	9.93 (d, *J* 14.3 Hz)	8.78 (d, *J* 14.3 Hz)	
2g	DMSO	(*E*,*Z*)	(*E*): 10.11 (d, *J* 14.2 Hz)	8.86 (d, *J* 14.2 Hz)	7.26-6.93 (m, 3-$CH_3C_6H_4$) and
			(*Z*): 11.17 (d, *J* 14.1 Hz)	8.15 (d, *J* 14.1 Hz)	2.30 (s, 3-$CH_3C_6H_4$)
		(*Z*,*Z*)	10.98 (d, *J* 13.8 Hz)	8.25 (d, *J* 13.8 Hz)	
		(*E*,*E*)	9.87 (d, *J* 14.6 Hz)	8.77 (d, *J* 14.6 Hz)	
2h	DMSO	(*E*,*Z*)	(*E*): 10.13 (d, *J* 14.2 Hz)	8.82 (d, *J* 14.2 Hz)	7.50-7.14 (m, 4-$CH_3C_6H_4$) and
			(*Z*): 11.22 (d, *J* 14.0 Hz)	8.10 (d, *J* 14.0 Hz)	2.26 (s, 4-$CH_3C_6H_4$)
		(*Z*,*Z*)	11.01 (d, *J* 14.2 Hz)	8.21 (d, *J* 14.2 Hz)	
		(*E*,*E*)	9.88 (d, *J* 14.5 Hz)	8.73 (d, *J* 14.5 Hz)	

a) Concentrations: 18 mM in $CDCl_3$ and 37 mM in CD_3SOCD_3. b) Diaminodinitrobutadienes **2** appear, in solution, as mixtures of the three possible stereoisomers (*E*,*E*), (*E*,*Z*) and (*Z*,*Z*) whose relative percentages depend on the solvent used (see text and Table 2); in every case the overall integration of the signals of the 1,4-diaryl or 1,4-dialkyl portion of the molecule is consistent with the sum of integrations of peaks relevant to the NH and vinylic CH absorptions. c) Undetectable signal because of too low concentration of the stereoisomer. d) Reliable attributions cannot be done as overlapped multiplets of low intensity fall in the same spectral range of a main signal (δ 8.48) attributable to both NH and CH absorptions of the (*E*,*E*) isomer.

Acknowledgment. Financial support by M.U.R.S.T. (Roma) is gratefully acknowledged.

REFERENCES AND NOTES

1. Spinelli, D.; Consiglio, G.; Dell'Erba, C.; Novi, M. Nucleophilic Substitution of Thiophene Derivatives. In *The Chemistry of Heterocyclic Compounds, Thiophene and its Derivatives,* Part IV, Gronowitz, S. Ed; John Wiley and Sons, Inc.: New York, 1991, Chapter 2.
2. Dell'Erba, C.; Spinelli, D. *Boll. Sci. Fac. Chim. Ind. Bologna* **1968**, *26*, 97 (*Chem. Abstr.* **1968**, *69*, 106381q).
3. Dell'Erba, C.; Spinelli, D.; Leandri, G. *J. Chem. Soc., Chem. Commun.* **1969**, 549.
4. Rajappa, S. *Tetrahedron* **1981**, *37*, 1453.

5. Fuji, K.; Node, M. *Synlett* **1991**, 603.
6. Severin, T.; Scheel, D.; Adhikary, P. *Chem. Ber.* **1969**, *102*, 2966.
7. Büchi, G.; Mak, C.-P. *J. Org. Chem.* **1977**, *42*, 1784.
8. Fuji, K.; Node, M.; Nagasawa, H.; Naniwa, Y.; Terada, S. *J. Am. Chem. Soc.* **1986**, *108*, 3855.
9. Node, M.; Nagasawa, H.; Naniwa, Y.; Fuji, K. *Synthesis* **1987**, 729.
10. Severin, T.; Ipach, I. *Chem. Ber.* **1978**, *111*, 692 and preceding papers in the series.
11. Dell'Erba, C.; Mele, A.; Novi, M.; Petrillo, G.; Stagnaro, P. *Tetrahedron Lett.* **1990**, *31*, 4933.
12. Kamimura, A.: Ono, N. *Synthesis* **1988**, 921.
13. Relevant examples of nucleophilic cleavage of a (2-nitrovinyl)-sulfur bond are also represented by the reactions of amines with 1,1-bismercapto-2-nitroethylene derivatives leading to nitroketene aminals: Gompper, R.; Schaefer, H. *Chem. Ber.* **1967**, *100*, 591; Rajappa, S.; Sreenivasan, R.; Advani, B.G.; Summerville, R.H.; Hoffmann, R. *Indian J. Chem.* **1977**, *15B*, 297; Schäfer, H.; Batho, B.; Gewald, K. *J. Prakt. Chem.* **1977**, *319*, 149.
14. In the experiments reported in Table 1, the use of 4 mol. equiv. of amine, instead of the two required by the reaction stoicheiometry, is a compromise between short reaction times and satisfactory yields.
15. Gate, E.N.; Meek, M.A.; Schwalbe, C.H.; Stevens, M.F.G.; Threadgill, M.D. *J. Chem. Soc., Perkin Trans. 2* **1985**, 251.
16. Büchi, G.; Wüest, H. *J. Org. Chem.* **1979**, *44*, 4116.
17. According to previous results[16] the 2-nitroimine proton signals would fall in an uncrowded spectral region (5-6 ppm *vs.* TMS) and would thus be easily detectable in the spectra of **2**.
18. Fetell, A.I.; Feuer, H. *J. Org. Chem.* **1978**, *43*, 497.
19. Fetell, A.I.; Feuer, H. *J. Org. Chem.* **1978**, *43*, 1238.
20. Krowczynski, A.; Kozerski, L. *Synthesis* **1983**, 489.
21. The identification of the various configurational isomers of **2** and **3** was achieved by comparison with the reported[4, 15, 18-20, 22] spectral data of related simple 2-nitroenamines and on the marked deshielding (ca. 1 ppm) of the nitrovinylic proton in the *E* (*i.e. cis* to the nitro group) with respect to the *Z* configuration.
22. Faulques, M.; Rene, L.; Royer, R. *Synthesis* **1982**, 260.
23. Barrett, A.G.; Graboski, G.G. *Chem. Rev.* **1986**, *86*, 751.
24. Rosini, G.; Ballini, R. *Synthesis* **1988**, 833.
25 Kabalka, G.W.; Guindi, L.H.M. *Tetrahedron* **1990**, *46*, 7443.
26. Sera, A.; Yamauchi, H.; Yamada, H.; Itoh, K. *Synlett* **1990**, 477.
27. Ricoh Co., Ltd. *Jpn. Korai Tokkyo Koho* **JP 81,106,242** (*Chem. Abstr.* **1982**, *96* , 94992g). Ishikawa, T.; Fujimoto, H.; Naruse, H.; Ando, K. *Jpn. Korai Tokkyo Koho* **JP 63 56,654 [88 56,654]** (*Chem. Abstr.* **1988**, *109* , 83297v). Naruse, H.; Yagihara, M. *Jpn. Korai Tokkyo Koho* **JP 63,148,258 [88,148,258]** (*Chem. Abstr.* **1990**, *112* , 66562x).
28. Paton, R.M. 1,2,5-Oxadiazoles and their Benzo Derivatives. In *Comprehensive Heterocyclic Chemistry* ; Katritsky, A.R.; Rees, C.W. Eds.; Pergamon Press: Oxford, 1984; Vol. 6, pp 415, 416 and 420.
29. Hosokawa, T.; Ohta, T.; Okamoto, Y.; Murahashi, S.-I. *Bull. Chem. Soc. Jpn.*, **1985**, *58*, 194 and references therein.
30. Blatt, A.H.; Gross, N. *J. Org. Chem.* **1957**, *22*, 1588.
31. Bergbreiter, D.E.; Pendergrass, E. *J. Org. Chem.* **1981**, *46*, 219.
32. The method is an adaptation of the procedure already reported for the reduction of 1-nitro-1-alkenes.[26]
33. Ruggli, P.; Zeller, P. *Helv. Chim. Acta* **1945**, *28*, 741.
34. Freeman, J.P.; Emmons, W.D. *J. Am. Chem. Soc.* **1957**, *79*, 1712.
35. Urion, E. *C. R. Hebd. Seances Acad. Sci.* **1930**, *191*, 263.
36. Blaise, E.E. *C. R. Hebd. Seances Acad. Sci.* **1923**, *176*, 1148.
37. Bouveault, L.; Locquin, R. *C. R. Hebd. Seances Acad. Sci.* **1909**, *148*, 1595.