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Synthesis and Characterization of 1-Amino-4-methylthio-2-nitro-1,3-butadienes

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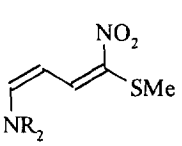
Abstract: Treatment of 3-nitrothiophene with *prim.* and *sec.* amines, followed by S-methylation leads to (*Z,Z*)-1- amino-4-methylthio-2-nitro-1,3-butadienes (**3**). Oxidation of these with LTA yields a mixture of the 2-methylthio-4-nitropyrroles (**6**) and the acetoxylated butadienes (**8**).

Introduction

2-Nitrothiophene is known to undergo facile ring-opening on treatment with *sec.* amines.[1] Subsequent S-methylation leads to 1-amino-4-nitrobutadienes (**1**). On the other hand, 3,4-dinitrothiophene undergoes desulfurization on treatment with *sec.* amines; the product (**2**) contains two nitroenamine units coupled to each other at C-2.[2] Interestingly, it has been reported that 3-nitrothiophene reacts with N-lithiopiperidide to give low yields of 3-nitro-2-piperidinothiophene and 3,3'-dinitro-2,2'-bithienyl;[3] no ring-opened products have been observed in this reaction.



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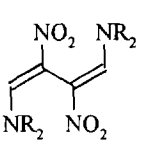

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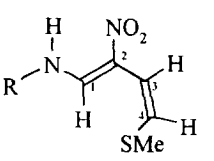
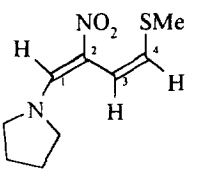


3(*Z,Z*)



4(*E,Z*)

We now record the facile ring-opening of 3-nitrothiophene with *primary* and *sec.* amines; subsequent S-methylation leads to 1-amino-4-methylthio-2-nitro-1,3-butadienes[4]. The structure and configuration about the double bonds in these nitroenamines have been established by NMR spectroscopy. In addition, the structure of one of the products has been firmly secured by X-ray crystallography; this has, however, also revealed an unexpected twisting of the butadiene moiety about the central single bond, thereby leading to a

disruption of the conjugation.

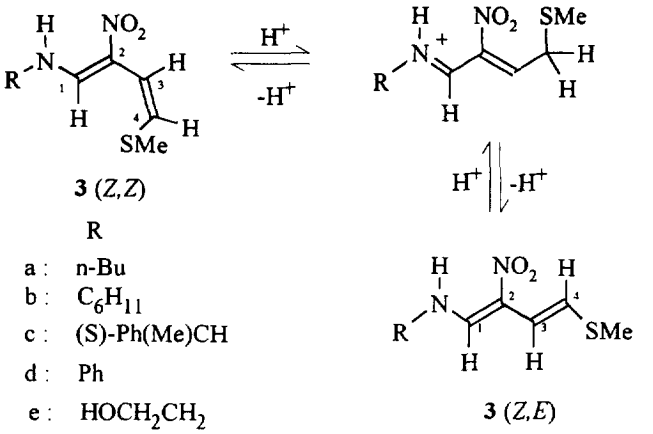
Results and discussion

Synthesis.- Treatment of 3-nitrothiophene[5] in ethanol with *n*-butylamine and $AgNO_3$ at 25° C for 30h gave the silver salt of the mercaptobutadiene. This was methylated at 0° C with excess methyl iodide to give 1-*n*-butylamino-4-methylthio-2-nitro-1,3butadiene **(3a)** in 57% yield as a yellow gum. The compound exhibited uv maximum at 392nm(ε 9350) in ethanol solution. Other primary amines reacted similarly with 3-nitrothiophene to give the corresponding ring-opened products **(3 b-e)**. Replacement of the primary amines by the *sec.* amine, pyrrolidine, in the above reaction led to the product **(4)** in 24% yield.

Double-bond configuration.- The ^1H NMR spectrum of 1-*n*-butylamino-4-methylthio-2-nitro-1,3-butadiene **(3a)** as obtained in this reaction, showed the presence of a major species together with traces of a second isomer. The major compound (see numbering in **3**) was assigned the *Z,Z* configuration on the following grounds : It had been conclusively established earlier that nitroenamines possessing an NH group existed almost exclusively in the intramolecularly hydrogen-bonded *Z*-configuration.[6] This was further confirmed in the present case by the chemical shift value of 7.45 δ for H-1, indicating that this was *trans* to the NO_2 group. The H-3, H-4 coupling constant of 10Hz proved that they are *cis* related. The second isomer present in very small amounts, was subsequently shown to have the *E*-geometry about the C-3, C-4 double bond (see below).

4-Methylthio-2-nitro-1-pyrrolidino-1,3-butadiene **(4)** exhibited the typical magnetic non-equivalence of the α-CH_2 groups characteristic of 1-nitro-2-pyrrolidinoethylenes.[7] This was evident both in the ^1H (3.15, 3.70 δ) and ^{13}C (48.80, 54.53 δ) NMR spectra. The significant difference between this compound and the butylamino analog **(3a)** lay in the configuration about the nitroenamine double bond. The preference for *E*-configuration in nitroenamines in which intramolecular hydrogen bond is not possible, is well-documented[6]. The *E*-geometry around C-1, C-2 in **(4)** was further confirmed by the far downfield shift of H-1 to 8.35δ; this proton is now deshielded by the *cis*-NO_2. The coupling constant for H-3, H-4 is 10Hz, suggestive of a *cis*-relationship ; the C-3, C-4 double bond is therefore presumed to have the (*Z*) configuration as in **(3a)**.

Equilibration and transamination studies.- Acid-catalysed equilibration of **3a** (*Z,Z*) (CH_2Cl_2, 25°C, a catalytic amount of PTSA, 24h) gave a product consisting of **3a** (*Z,Z*) and **3a**(*Z,E*) in the ratio 3:1. The newly generated isomer corresponded to the trace component present in the original sample of **(3a)**. The most significant difference between this and **3a**(*Z,Z*) was in the coupling constant $J_{H3, H4}$ which was 15Hz. This clearly indicated *E*-geometry around C_3-C_4. The preference for the (*Z,Z*) isomer over the (*Z,E*) isomer by a factor of 3 even after equilibration is intriguing. The acid catalysed change of the C-3, C-4 double bond configuration must have occurred by initial protonation at C-4, followed by rotation about the single bond and final deprotonation (Scheme1). Reaction of 4-methylthio-2-nitro-1-pyrrolidino-1,3-butadiene **(4)** with *n*-butylamine in benzene at 25°C for 18h in the presence of a catalytic amount of PTSA resulted in smooth transamination. The product **(3a)** obtained in 61% yield was once again a 3:1 mixture of the (*Z,Z*) and (*Z,E*) isomers



3 (*Z,Z*)

R

a : n-Bu
b : C_6H_{11}
c : (S)-Ph(Me)CH
d : Ph
e : $HOCH_2CH_2$

3 (*Z,E*)

Scheme 1

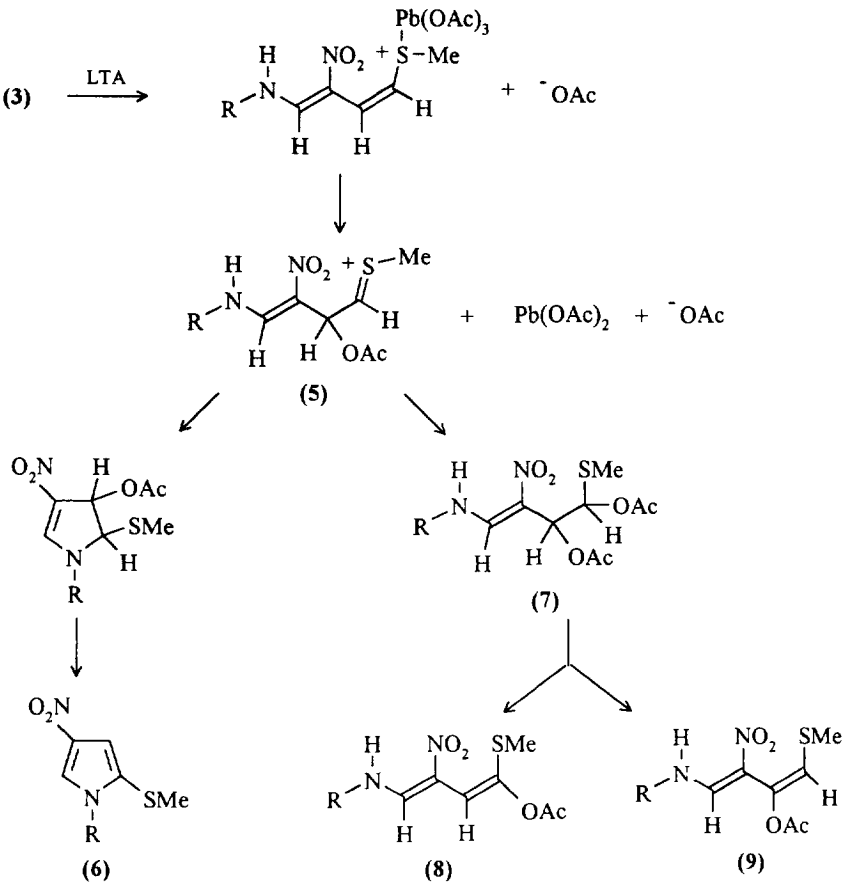
Mass spectral fragmentation.- The major fragment ion peak in the electron-impact mass spectra of **3(a, b, d, e)** and **4** occurred at *m/z* = (M-106). It is likely that this corresponds to the aminocyclopropenium ion $[R^1R^2NC_3H_2]^+$. This has relevance to the determination of the structure of the acetoxy derivative (see below).

LTA oxidation of 1-amino-4-methylthio-2-nitro-1,3-butadienes **(3)**.- Oxidation of **(3a)** with LTA (1.4eqvt) in refluxing benzene under argon for 4.5h gave two products, along with unreacted starting material (6%). The products were isolated pure by column chromatography. The first product, (14% yield), was shown to be the pyrrole **(6a)**. The molecular ion peak at *m/z* 214 was the strongest peak in the mass spectrum. In the ^{1}H NMR spectrum the two aromatic protons were seen at 6.85 and 7.60δ, coupled to each other (J = 2Hz) as expected for a 2,4-disubstituted pyrrole.

The second oxidation product (51% yield) had resulted by acetoxylation of the substrate. Such a reaction on enol thioethers of ketones had been reported earlier by Trost;[8] in that study, the acetoxylation had taken place on the carbon atom β to the sulfur. However, with an aldehyde enol thioether such as **(3a)** as the substrate, the same mechanism can as well lead to α- acetoxylation (Scheme 2). As suggested by Trost, the thionium ion **(5)** is likely to be the initial product of oxidation. This could undergo intramolecular attack by the amine, followed by elimination of acetic acid to give the pyrrole **(6)**. Alternatively, attack by $^-$OAc on the thionium ion could lead to **(7)** which can lose acetic acid to form either **(8)** or **(9)**.

The choice between **(8a)** and **(9a)** for the major oxidation product of **(3a)** could be made on the basis of NOE experiments. Irradiation of H-1 (7.55δ) gave a 3.7% NOE on the other olefinic proton at 6.5 δ, while irradiation of the methyl group of the acetoxy (2.20 or 2.25 δ) produced a 0.7% NOE on the same olefinic proton (6.5δ). Together these two results strongly suggest that the product has the structure **(8a)**. This received further confirmation from the mass spectral fagmentation of this compound, which produced the base

peak at *m/z* 110, just as the starting material **(3a)** did. If this stable fragment ion is the cyclopropenium ion



a : R = *n*-C_4H_9
b : R = C_6H_{11}
c : R = (S)-Ph(Me)CH

(Scheme 2)

$(C_4H_9NH.C_3H_2)^+$, it is obvious the acetoxy group cannot be located on C-3 of the butadiene. The correct structure therefore appears to be the one in which the acetoxy is located on C-4, *viz.*, **(8a)**.

Similar LTA oxidation of **(3b)** and **(3c)** gave the pyrroles (**6b**, 11%; **6c**, 8%) and the corresponding acetoxy compounds (**8b**, 54%; **8c**, 47%).

Crystal structure of 1-(2-hydroxyethyl)amino-4-methylthio-2-nitro-1,3-butadiene **(3e)**.-The product **(3e)** obtained by the action of ethanolamine on 3-nitrothiophene was crystalline. The X-ray crystal structure of this compound is shown in Fig. 1, and the bond lengths and bond angles are given in Table 1. The C-C bond lengths of the butadiene chain are 1.385, 1.458 and 1.315Å respectively for C_3-C_4, C_4-C_5 and C_5-C_6.[9] The butadiene

moiety has assumed a configuration close to *cisoid*; but it is not completely planar as would be expected if the two double bonds were fully conjugated. The most surprising feature of the structure is that the dihedral angle

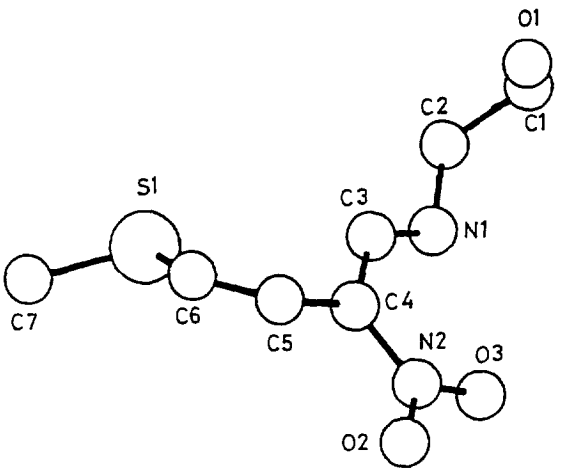


Fig.1

Table1. Bond lengths [Å] and angles [deg] for **(3e)**.

S(1)-C(6)	1.744(3)
S(1)-C(7)	1.794(3)
O(1)-C(1)	1.423(3)
N(1)-C(3)	1.302(3)
N(1)-C(2)	1.464(3)
O(2)-N(2)	1.251(3)
O(3)-N(2)	1.250(3)
C(5)-C(6)	1.315(4)
C(5)-C(4)	1.458(4)
C(4)-C(3)	1.385(4)
C(4)-N(2)	1.396(3)
C(2)-C(1)	1.500(4)
O(1)-HO1	0.83(4)
N(1)-HN1	0.85(3)
C(2)-H(2A)	1.02(3)
C(2)-H(2B)	0.89(3)
C(5)-H(5)	0.92(3)
C(3)-H(3)	0.96(2)
C(1)-H(1A)	1.00(3)
C(1)-H(1B)	0.98(3)
C(6)-H(6)	0.93(3)
C(7)-H(7A)	0.94(4)
C(7)-H(7B)	0.97(4)
C(7)-H(7C)	0.92(4)

C(6)-S(1)-C(7)	100.6(2)
C(3)-N(1)-C(2)	121.7(2)
C(6)-C(5)-C(4)	126.2(3)
C(3)-C(4)-N(2)	119.3(3)
C(3)-C(4)-C(5)	122.9(2)
N(2)-C(4)-C(5)	117.7(2)
N(1)-C(2)-C(1)	112.4(2)
N(1)-C(3)-C(4)	131.0(3)
O(1)-C(1)-C(2)	113.1(2)
O(3)-N(2)-O(2)	120.7(2)
O(3)-N(2)-C(4)	120.8(2)
O(2)-N(2)-C(4)	118.5(3)
C(5)-C(6)-S(1)	125.4(2)
C(1)-O(1)-HO1	104(3)
N(1)-C(2)-H(2A)	106.2(13)
C(3)-N(1)-HN1	121(2)
C(2)-N(1)-HN1	117(2)
C(1)-C(2)-H(2A)	112.1(13)
N(1)-C(2)-H(2B)	107(2)
C(1)-C(2)-H(2B)	108(2)
C(6)-C(5)-H(5)	119(2)
C(4)-C(5)-H(5)	114(2)
H(2A)-C(2)-H(2B)	111(2)
N(1)-C(3)-H(3)	114.4(13)
C(4)-C(3)-H(3)	114.6(13)
O(1)-C(1)-H(1A)	108(2)
C(2)-C(1)-H(1A)	108.6(14)
O(1)-C(1)-H(1B)	104(2)
C(2)-C(1)-H(1B)	112.3(14)
H(1A)-C(1)-H(1B)	112(2)
C(5)-C(6)-H(6)	121(2)
S(1)-C(6)-H(6)	113.7(14)
S(1)-C(7)-H(7A)	109(2)
S(1)-C(7)-H(7B)	114(2)
H(7A)-C(7)-H(7B)	106(3)
S(1)-C(7)-H(7C)	110(2)
H(7A)-C(7)-H(7C)	109(3)
H(7B)-C(7)-H(7C)	109(3)

between the nitroenamine plane (N-1, C-3, C-4, N-2 of Fig.1) and the vinyl thioether plane (C-4, C-5, C-6, S-1 of Fig.1) is 44^0. Theoretical calculations are currently being carried out to find out the reasons for this distortion.

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Experimental

General.- Melting points were determined with a microscope hot stage apparatus, and are uncorrected. Ir spectra were determined on a Perkin-Elmer-Infracord spectrometer. ^1H and ^{13}C NMR spectra were recorded on a Bruker-AC-200, or a Bruker-MSL-300 instrument in $CDCl_3$ solution with tetramethylsilane as internal standard. Coupling constants J are given in Hz. Uv spectra were recorded on a Shimadzu UV-240 spectrometer. Mass spectra were determined on a Finnigan-MAT-102B spectrometer. Microanalyses were performed at the Organic Chemistry Division, NCL.

General procedure for the preparation of 1-amino-4-methylthio-2-nitro-1,3-butadienes **(3)** *and* **(4).**- The amine (34.3 mmol) was added dropwise to a stirred solution of $AgNO_3$ (700mg, 4.1 mmol) in EtOH (20 ml). A small amount of black precipitate was formed, which was filtered off. To the filtrate was added 3-nitrothiophene (500mg, 3.8 mmol) in EtOH (7.0 ml). The solution was stirred at 25°C for 30h to give the silver salt of the mercaptobutadiene. This was filtered, washed with EtOH, ether and dried. The dried silver salt was coold to 0°C and treated with excess methyl iodide (5-10 ml) and stirred. The mixture was slowly allowed to come to 25°C (1.5h). It was then extracted with acetone, the acetone layer was concentrated and the residue purified by silicagel column chromatography using pet. ether and EtOAc as eluent to give **(3)** and **(4)**.

(Z,Z) 1-n-Butylamino-4-methylthio-2-nitro-1,3-butadiene **(3a).** Yield 57%, dark orange gum. ν_{max} ($CHCl_3$)/cm^{-1} : 3340, 1630, 1350, 1200; δH ($CDCl_3$) : 0.95 (3H, t, J = 7.3, CH_3), 1.45 (2H, m, CH_2), 1.7 (2H, m, CH_2), 2.35 (3H, s, SMe), 3.4 (2H, q, J = 6.6, CH_2), 5.9 (1H, d, J = 10, =CH), 6.5 (1H, d, J = 10, =CH), 7.45 (1H, d, J = 14, =CH, collapsing to a singlet on exchange of NH with D_2O.), 9.6 (1H, brs, NH); δC ($CDCl_3$) : 13.29, 17.92, 19.29, 32.32, 49.54, 117.69, 118.75, 123.04, 148.25; *m/z* : 216(M^+), 169, 152, 126, 110(100%), 97, 85, 80, 68, 57. Analysis calcd. for $C_9H_{16}N_2O_2S$: C, 49.97; H, 7.45; N, 12.95. Found : C, 49.66; H, 7.34; N, 13.22.

1-Cyclohexylamino-4-methylthio-2-nitro-1,3-butadiene **(3b)**. 35%, yellow solid, m.p. 80°-81°C (pet. ether), ν_{max} ($CHCl_3$)/cm^{-1} : 2920, 1640,1370,1220; δH ($CDCl_3$) : 1.2-2.25 (10H, m, CH_2), 2.35 (3H, s, SMe), 3.35 (1H, m, CH), 5.9 (1H, d, J = 10, =CH), 6.55 (1H, d, J = 10, =CH), 7.5 (1H, d, J = 13, =CH), 9.6 (1H, brs, NH), δC ($CDCl_3$) : 17.95, 24.20, 24.77, 33.34, 57.93, 117.80, 118.65, 122.88, 146.25; *m/z* : 242(M^+), 195, 136, 113, 97, 83, 71, 67, 55(100%). Anal. calcd. for $C_{11}H_{18}N_2O_2S$: C, 54.52; H, 7.49; N, 11.56. Found : C, 54.83; H, 7.44; N, 11.78.

1-(S)-α-Methylbenzylamino-4-methylthio-2-nitro-1,3-butadiene **(3c)**.- 20%, gum, $[\alpha]_D$ = +135.9° (c, 1.23 in $CHCl_3$); ν_{max} (Neat)/cm^{-1} : 3260, 1630, 1350, 1200; δH ($CDCl_3$) : 1.7 (3H, d, J = 6.5, CH_3), 2.3 (3H, s, SMe), 4.7 (1H, m, J = 6.5, CH), 5.85 (1H, d, J =9.6, =CH), 6.5 (1H, d, J = 9.6, =CH), 7.3-7.5 (6H, m, aromatic and =CH), 9.75 (1H, brs, NH); δC ($CDCl_3$) : 18.10, 22.44, 58.41, 117.74, 119.43, 123.58, 126.29, 128.21, 129.05, 141.03, 146.36; *m/z* : 264(M^+), 217, 172, 144, 113, 105(100%), 77. Anal. calcd. for $C_{13}H_{16}N_2O_2S$: C, 59.07; H, 6.10; N, 10.60. Found : C, 58.78; H, 6.49; N, 10.60.

1-Anilino-4-methylthio-2-nitro-1,3-butadiene **(3d)**.- 15%, red solid, m.p. 106°-107°C, ν_{max} (Nujol)/cm^{-1} : 3240, 1640,1600,1450, 1350; δH ($CDCl_3$) : 2.45 (3H, s SMe), 6,1 (1H, d, J = 10, =CH), 6.6 (1H, d, J =10, =CH), 7.15-7.5 (5H, m, aromatic), 7.95 (1H, d, J = 13, =CH), 11.05 (1H, brs, NH); δC ($CDCl_3$) : 18.47, 116.98, 117.47, 122.17, 125.01, 125.61, 129.98, 138.77, 138.97; *m/z* : 236(M^+), 189, 172, 159, 143, 130(100%), 115, 104, 97, 77, 57. Anal. calcd. for $C_{11}H_{12}N_2O_2S$: C, 55.92; H, 5.12; N, 11.86. Found : C, 55.74; H, 5.10; N, 11.79.

1-(2-Hydroxyethyl)amino-4-methylthio-2-nitro-1,3-butadiene **(3e)**.- 52%, crystalline yellow solid, m.p.. 114°-115°C (C_6H_6). ν_{max} (Nujol)/cm^{-1} : 3420, 3220, 1630, 1450, 1380, 1320, 1200; λ_{max} /nm : 395 (ε7163), 283 (ε13918); δH ($CDCl_3$ + DMSO-d_6) : 2.3 (3H, s, SMe), 3.45 (2H, m, J = 5.4, CH_2), 3.65 (2H, m, J = 5.4, CH_2), 4.9 (1H, t, OH), 5.85 (1H, d, J = 10, =CH), 6.35 (1H,d, J = 10, =CH), 7.45 (1H, d, J = 14, =CH), 9.7 (1H, brs, NH); δC ($CDCl_3$ -DMSO-d_6) : 18.02, 52.49, 60.90, 118.08, 118.37, 123.68, 149.59; *m/z* : 204(M^+), 157, 127, 112, 98(100%), 80, 72. Anal. calcd. for $C_7H_{12}N_2O_3S$: C, 41.12, H, 5.92; N, 13.71. Found : C, 41.29; H, 5.95; N, 13.89.

4-Methylthio-2-nitro-1-pyrrolidino-1,3-butadiene **(4)**.- 24%, m.p. 80°-81°C, ν_{max} (Nujol)/cm^{-1} : 1600, 1450, 1380, 1270, 1220; δH ($CDCl_3$) : 1.95 (4H, m, CH_2), 2.3 (3H, s, SMe), 3.15 (2H, brs, CH_2), 3.7 (2H, brs, CH_2), 6.2 (1H, d, J = 10, =CH), 6.3 (1H, d, J = 10, =CH), 8.35 (1H, s, =CH); δC ($CDCl_3$) : 16.66, 24.15, 25.49, 48.80, 54.53, 115.96, 119.68, 131.80, 145.30. *m/z* : 214(M^+), 167, 152, 137, 120, 108(100%), 93, 84, 70, 55. Anal. calcd. for $C_9H_{14}N_2O_2S$: C, 50.45; H, 6.58; N, 13.07. Found : C, 50.75; H, 6.02; N, 13.07.

Transamination of **(4)**.- The pyrrolidino compound **(4)** (150mg, 0.7mmol) was taken in dry benzene (5ml). To that was added a catalytic amount of PTSA and *n*-butylamine (52mg, 0.7mmol). The reation mixture was stirred at 25°C for 18h. After completion of the reation (tlc), the solvent was removed *in vacuo* to give a mixture of (*Z,Z*) and (*Z,E*) isomers of **(3a)**. The two isomers were separated by silicagel column chromatography using pet. ether and EtOAc as eluent. Yield 15%, gum. ν_{max} ($CHCl_3$)/cm^{-1} : 3260, 1640, 1370, 1220; δH ($CDCl_3$) : 0.95 (3H, t, CH_3), 1.45 (2H, m, CH_2), 1.7 (2H, m, CH_2); 2.35 (3H, s, SMe), 3.45 (2H, q, CH_2), 6.2 (1H,d, J = 15, =CH); 6.45 (1H, d, J = 15, =CH), 7.15 (1H, d, J = 14, =CH collapsing to a singlet on exchange of NH with D_2O), 9.65 (1H, brs, NH).

General procedure for LTA oxidation of **(3)**.- 1-Amino-4-methylthio-2-nitro-1,3-butadiene **(3)** (1 eqv.) was taken in dry benzene. To this was added freshly crystallized $Pb(OAc)_4$ (1.4 eqv.) and the reaction mixture was refluxed under argon for 4.5h. After completion of the reaction (tlc), lead oxide was filtered off and washed with benzene (3×5 ml). The filtrate along with the washings were concentrated *in vacuo* and the residue thus formed was dissolved in EtOAc (20 ml). The EtOAc layer was washed with brine and dried on sodiumsulphate. Removal of EtOAc *in vacuo* afforded a mixture of **(6)** and **(8)**, which were separated by silicagel column chromatography using pet. ether and EtOAc as eluent.

N-n-Butyl-2-methylthio-4-nitropyrrole **(6a)**.- 14%, gum. ν_{max} ($CHCl_3$)/cm^{-1} : 1530, 1490, 1420, 1300, 1220; δH ($CDCl_3$) : 1.0 (3H, t, J = 7.3, CH_3), 1.4 (2H, m, CH_2), 1.8 (2H,m, CH_2), 2.35 (3H, s, SMe), 4.0 (2H, t, J = 7.3, CH_2), 6.85 (1H, d, J = 2, =CH), 7.6 (1H, d, J = 2, =CH); δC ($CDCl_3$) : 13.72, 19.86,20.65,33.17,47.81,110.67, 123.29, 127.07, 136.0. *m/z* : 214(M^+, 100%), 199, 172, 157, 139, 126, 85, 57. Anal. calcd. for $C_9H_{14}N_2O_2S$: C, 50.45; H, 6.60; N, 13.07. Found : C, 50.88; H, 6.76; N, 12.82.

N-Cyclohexyl-2-methylthio-4-nitro pyrrole **(6b)**.- 11%, gum. ν_{max} ($CHCl_3$)/cm^{-1} : 1630, 1500, 1340, 1300, 1220; δH ($CDCl_3$) : 1.2-2.25 (10H, m, CH_2), 2.35 (3H, s, SMe), 4.3 (1H, m, CH), 6.85 (1H, d, J = 2, =CH), 7.65 (1H, d, J = 2, =CH); δC ($CDCl_3$) : 20.54, 25.09, 25.55, 34.36, 56.33, 110.11, 120.44, 126.21, 136.25 ; *m z* : 240(M^+) 158, 141, 83, 67, 55(100%). Analysis calcd. for $C_{11}H_{16}N_2O_2S$: C, 54.98; H, 6.71; N, 11.65. Found : C,55.23; H, 6.95; N, 11.44.

N-(S)-α-Methylbenzyl-2-methylthio-4-nitropyrrole **(6c)**.- 8%, gum, $[\alpha]_D$ +163.3 (c, 0.54, $CHCl_3$); ν_{max} $CHCl_3$/cm^{-1} : 1540, 1500, 1420, 1360, 1290, 1220; δH ($CDCl_3$) : 1.8 (3H, d, CH_3), 2.1 (3H, s, SMe), 5.85 (1H, q, CH), 6.9 (1H, d, J = 2, =CH), 7.1-7.45 (5H, m, Ph), 7.7 (1H, d, J = 2, =CH). Anal. calcd. for $C_{13}H_{14}N_2O_2S$: C, 59.52; H, 5.38; N, 10.68. Found : C, 59.86; H, 4.71; N,10.33.

1-n-Butylamino-4-acetoxy-4-methylthio-2-nitro-1,3-butadiene **(8a)**.- 51%, gum.ν_{max} ($CHCl_3$)/cm^{-1} :1750, 1630, 1360, 1200, 1050; δH ($CDCl_3$) : 1.0 (3H, t, J = 7, CH_3), 1.45 (2H, m, CH_2), 1.70 (2H, m, CH_2), 2.20 (3H, s, Me), 2.25 (3H, s, Me), 3.45 (2H, q, J = 6.7, CH_2), 6.5 (1H, s, =CH), 7.55 (1H, d, J = 14, =CH), 9.6 (1H, brs, NH); δC ($CDCl_3$) : 13.46, 15.23, 19.44, 20.45, 32.50, 49.78, 115.70, 117.29, 140.12, 149.45, 168.82; *m/z* : 274(M^+), 232, 227, 215, 185, 167, 157, 128, 110(100%), 57.Anal. calcd. for $C_{11}H_{18}N_2O_4S$: C, 48.16; H, 6.61; N, 10.21. Found : C, 48.19; H, 6.65; N, 10.13.

1-Cyclohexylamino-4-acetoxy-4-methylthio-2-nitro-1,3-butadiene **(8b)**.- 54%, solid, m.p. 96°-97°C. ν_{max} ($CHCl_3$)/cm^{-1} : 2920, 1750, 1640, 1360, 1200, 1070; δH ($CDCl_3$) : 1.15-2.25 (10H, m, CH_2), 2.05 (3H, s, CH_3), 2.1 (3H, s, CH_3), 3.35 (1H, m, CH), 6.55 (1H, s, =CH), 7.6 (1H, d, J = 16, =CH), 9.7 (1H, brs, NH); δC ($CDCl_3$) : 15.15, 20.34, 24.26, 24.79, 33.46, 58.24, 115.49, 117.23, 139.79, 147.32, 168.69; *m z* : 300(M^+), 183, 158, 136, 129, 111, 97, 91, 83(100%), 67. Anal. calcd. for $C_{13}H_{20}N_2O_4S$: C, 52.0; H, 6.71; N, 9.32. Found : C, 52.15; H, 6.81; N, 9.27.

1-(S)-Methylbenzylamino-4-acetoxy-4-methylthio-2-nitro-1,3-butadiene **(8c)**.- 47%, gum; ν_{max} ($CHCl_3$)/cm^{-1} : 1750, 1640, 1360, 1210; δH ($CDCl_3$) : 1.75 (3H, d, CH_3), 2.15 (3H, s, CH_3), 2.2 (3H, s, CH_3), 4.75 (1H,m, CH), 6.55 (1H, s, =CH), 7.35 (5H, m, aromatic), 7.6 (1H, d, J = 16, =CH), 9.85 (1H, brs, NH), δC ($CDCl_3$) : 15.12, 20.38, 22.40, 58.45, 116.19, 117.21, 126.34, 128.24, 129.01, 140.15, 140.82, 147.40, 168.71; *m/z* : 322(M^+), 280, 263, 205, 158, 147, 129(100%). Anal. calcd. for $C_{15}H_{18}N_2O_4S$: C, 55.88; H, 5.62; N, 8.68. Found : C, 55.35; H, 6.01; N, 8.73.

Crystal data and structure refinement for **(3e)**.- $C_7H_{12}N_2O_3S$, M=214.28, monoclinic, space group P21/a, a =

13.5900(10), b = 5.272(2), C = 13.6510(10)Å, β = 99.46^0, V = 964.7(4)Å^3, Z = 4, D_C = 1.406 Mg m^{-3}, crystal dimension 0.2 × 0.1 × 0.2 mm, μ(Mo-Kα) = 0.276 mm^{-1}, F(000) = 432. λ(Mo-Kα) = 0.71073Å, 2θ-ω scans, $2\theta_{max}$ = 41^0. The structure was refined by full matrix least squares on F^2 with weight W = 1/ [σ^2Fo^2 + $(0.0340P)^2$ + o.2698P], P = (Fo^2+2Fc^2) / 3 and secondary extinsion coefficient, 0.0106(23). Final refinement converged at R=0.0240, Rw = 0.0630 for 763 observed [I > 2σ(I)] from 904 data.

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