Radical-nucleophilic substitution ($S_{RN}1$) reactions. Part 7.[1] Reactions of aliphatic α-substituted nitro compounds.

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α-Nitrothiocyanates $R_2C(SCN)NO_2$ have been prepared by oxidative addition of thiocyanate anion to nitronate anions and undergo $S_{RN}1$ substitution reactions by loss of thiocyanate with nitronate anions, phenylsulfinate, azide and *p*-nitro- and *p*-chloro-benzenethiolates in dipolar aprotic solvents. 2-Nitro-2-thiocyanatopropane and other 2-substituted-2-nitropropanes [$Me_2C(X)NO_2$ with X = I, Br, Cl, NO_2, $PhSO_2$] react with thiolates by $S_{RN}1$ reactions and/or redox reactions to give disulfides by a polar abstraction or chain SET ($S_{ET}2$) mechanisms. The products are dependent on the nucleophilicity of the thiolates, the polarisability of the α-substituent, the solvent and the presence of light catalysis, radical traps or strong electron acceptors. 2-Substituted-2-nitropropanes [$Me_2C(X)NO_2$ with X = N_3, NO_2, CN, *p*-NO_2–C_6H_4–N=N] undergo $S_{RN}1$ substitutions with thiolates by loss of nitrite. 2-Substituted-2-nitropropanes $Me_2C(X)NO_2$ and thiolates only yield disulfides in methanol due to solvation of the nitro groups.

Introduction

Aliphatic α-substituted nitro compounds undergo a variety of interesting single electron transfer (SET) and radical reactions and have been the subject of extensive study.[2] In our contribution to this study, we have been interested over some time in the SET mechanisms of the reactions between α-substituted nitro compounds and nucleophiles.[1–9] We have also studied the synthesis and the SET mechanisms of reactions of new α-substituted nitro compounds[1–10] which include α-nitrosulfides,[3] α-nitrothiocyanates,[4] α-nitroazides[5] and ω-alkenyl-α-halogeno-nitroalkanes.[6] Coupled with these studies, we have also investigated the SET mechanisms of targeted nucleophiles (thiolates[7,8] and *N*-anions of nitroimidazoles[9] and other nitrodiazoles[1]) with α-substituted nitro compounds. Our interest has extended to the biological activity of these compounds which act as antibacterial and antifungal agents, several of which are used as commercial preservatives.[10] The mode of action is due to inhibition of enzymes by oxidation of thiol groups in the active sites.[10] This mode of action has focused much of our studies on the reactions between α-substituted nitro compounds and thiolates.[1–9] In this paper we report the synthesis and reactions of α-nitrothiocyanates which have been reported in a preliminary communication.[4] We also report the related and continuing study of the mechanisms of reaction between α-substituted nitro compounds and thiolates,[3–6] some of which have also been published in preliminary communications.[7,8]

Two routes have been observed for the $S_{RN}1$ reactions between α-substituted nitro compounds [$R_2C(X)NO_2$] and nucleophiles as shown in Scheme 1. Most of these $S_{RN}1$ reactions are initiated by light-induced SET in a charge-transfer complex between the nitro compound and the nucleophile (Nu^-).[2] Depending on the nature of the α-substituent, either the α-substituent (X) (Route A) or the nitro group (Route B) leaves from the intermediate radical anions. The route of dissociation of the radical anions depends on the bond strength, leaving group ability and overlap of the nitro π*-molecular orbital (MO) holding the unpaired electron of the radical anion with the C–X σ*-MO. Evidence for these steps in the mechanism is commonly obtained from inhibition of the propagation steps using radical traps [*e.g.* di-*tert*-butylaminoxyl (DTBN) or oxygen] or strong electron acceptors [*e.g.* oxygen or *p*-dinitrobenzene (DNB)].[1–9]

We have also obtained strong evidence for much of the mechanism by using EPR spectroscopy to study the structure and reactivity of the intermediate radical anions trapped in solid matrices at low temperature.[5,9,11,12] The nitro compounds efficiently undergo electron capture to give rise to radical anions which undergo dissociation by either route A or route B to yield the intermediate radicals [$R_2C^{\bullet}$)–NO_2 or $R_2C^{\bullet}$)–X]. Addition of nucleophiles to these radicals to yield new radical anions has also been observed for Route A [eqn. (2b)].[12] We used the EPR spectroscopic technique to predict that α-nitrothiocyanates would react by Route A because dissociation of the radical anions $[Me_2C(SCN)NO_2]^{-\bullet}$ to yield 2-nitro-2-propyl radicals was observed [eqn. (2a)].[4,11] $S_{RN}1$ reactions of α-nitrothiocyanates were carried out to prove the accuracy of the EPR spectroscopic conclusion.

Results and discussion

Mechanisms in the synthesis of α-nitrothiocyanates

We first attempted the synthesis using normal conditions for $S_{RN}1$ reactions between 2-bromo-2-nitropropane and thiocyanate anions (Scheme 1 with R = Me, X = Br and Nu = SCN). No traces of the desired product could be detected and unaltered 2-bromo-2-nitropropane (100%) was recovered. Even the use of entrainment with a good electron donating nucleophile, such as the anion of 2-nitropropane, failed.[2] This technique uses the good electron-donator to initiate the reaction [eqn. (1) in Scheme 1] to yield the required radical anion $[Me_2C(SCN)NO_2]^{-\bullet}$ which then enters the propagation steps [eqns. (2a)–(2c) with $Nu^- = {}^-SCN$]. Only 2,3-dimethyl-2,3-dinitrobutane, the normal product from $S_{RN}1$ reaction between 2-bromo-2-nitropropane and the anion of 2-nitropropane, was obtained as a product, indicating that the anion of 2-nitropropane adds much faster than thiocyanate anions to the intermediate 2-nitro-2-propyl radical. Thiocyanate adds easily to the 2-nitro-2-propyl radical, as evidenced from the oxidative

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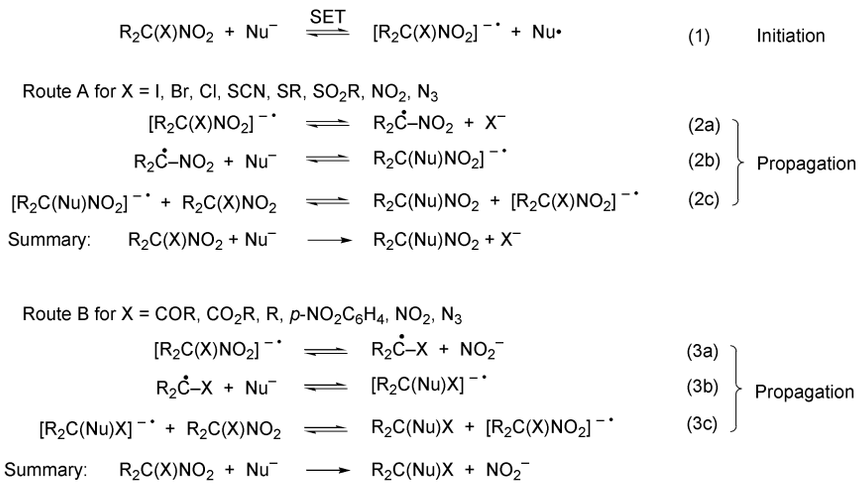
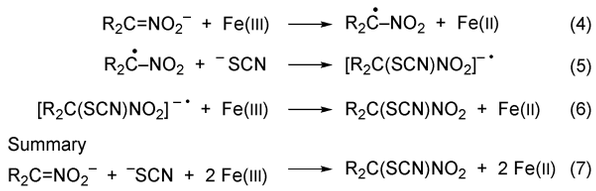


Scheme 1 $S_{RN}1$ mechanisms for α-substituted nitro compounds.



Scheme 2 Oxidative addition of thiocyanate and nitronate anions **1**, R = Me (40%) and **2**, R_2C = *c*-C_6H_{10} (43%).

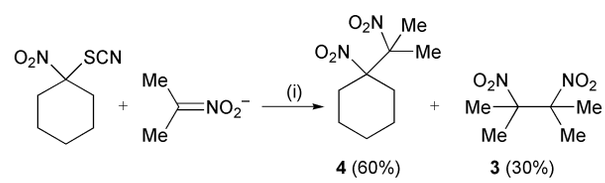
addition reactions shown in Scheme 2. The results suggest that SET between thiocyanate anions and 2-bromo-2-nitropropane is poor. The EPR spectroscopic studies show that the radical anion of 2-thiocyanato-2-nitropropane dissociates rapidly [eqn. (2a) with R = Me and Nu = SCN], suggesting that dissociation is faster than SET to the starting material [eqn. (2c) with R = Me and Nu = SCN], thereby inhibiting the propagation steps of the $S_{RN}1$ reaction. Similarly, bromide and chloride anions have not been observed to undergo $S_{RN}1$ reactions. Similar lack of reactivity for thiocyanate in $S_{RN}1$ reactions has been observed in reactions between thiocyanate and halogenoquinolines.[13]

Two α-nitrothiocyanates, 2-nitro-2-thiocyanatopropane **1** and 1-nitro-1-thiocyanatocyclohexane **2**, were successfully prepared using oxidative addition (Scheme 2). Normally in this synthetic procedure,[1–5,14] a solution of potassium ferricyanide is added to a solution of the nitronate anion and the nucleophile. However, this procedure gave large amounts of 2,3-dimethyl-2,3-dinitrobutane from the oxidative addition of the nitronate anion of 2-nitropropane to the 2-nitro-2-propyl radical. This indicates that the addition of nitronate anion to the intermediate α-nitroalkyl radical is faster than the addition of thiocyanate, which concurs with the findings from the above attempted $S_{RN}1$ reactions. In order to overcome this problem, a solution of the nitronate anion was added to a stirred solution of thiocyanate and ferricyanide. The synthesis of 1-nitro-1-thiocyanatocyclohexane **2** also yielded cyclohexanone (5%) as an impurity. Ketones are common impurities in the oxidative addition reactions. Thiocyanate is an ambident anion but no signs of addition *via* the *N*-anion (isothiocyanate) were observed. We have shown that nucleophile addition to 2-nitro-2-propyl radicals is under kinetic control and that the more nucleophilic centre in ambident anions reacts fastest.[3,9]

$S_{RN}1$ reactions of α-nitrothiocyanates

2-Nitro-2-thiocyanatopropane **1** was reacted with a range of anions known to undergo $S_{RN}1$ reactions (Table 1). All gave the expected substitution of thiocyanate anion by the nucleophile, as indicated by EPR spectroscopic studies. Alternative routes of dissociation of the intermediate radical anion of **1** by loss of nitrite or cyanide were not observed by EPR spectroscopy or in the liquid phase $S_{RN}1$ reactions. The $S_{RN}1$ reaction using the anion of 2-nitropropane gave a good yield of the expected 2,3-dimethyl-2,3-dinitrobutane **3**. The use of the normal diagnostic studies (absence of light or inhibition by an atmosphere of oxygen or the addition of sub-stoichiometric amounts of DNB or DTBN) gave reduction in the yield of **3** but not as much as normally observed. This lower than predicted inhibition can be explained by alternative SET non-chain mechanisms which are common for reactions involving the anion of 2-nitropropane.[2] The formation of the substitution product from phenylsulfinate ($PhSO_2^-$) was completely inhibited with a good yield of unaltered 2-nitro-2-thiocyanatopropane **1** indicating clearly only an $S_{RN}1$ mechanism. The reaction with azide anions was troublesome and a low yield could be observed when using HMPA as solvent. The low yield is probably explained by the lack of stability of 2-azido-2-nitropropane.

1-Nitro-1-thiocyanatocyclohexane **2** was also reacted with the anion of 2-nitropropane to give a good yield of the corresponding $S_{RN}1$ product (60%) as well as 2,3-dimethyl-2,3-dinitrobutane **3** (30%) (Scheme 3). Again, loss of thiocyanate



Scheme 3 *Reaction conditions*: i. DMSO, 4 h, light catalysis, nitrogen atmosphere.

was observed. The $S_{RN}1$ mechanism shown in Scheme 1 (Route A) explains the substitution reactions observed for these reactions.

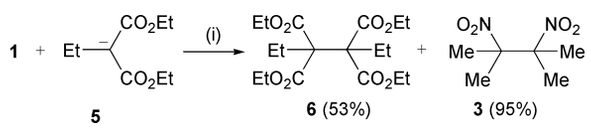
Reaction between 2-nitro-2-thiocyanatopropane **1** and thiolates gave a more complex mixture of products. The thiolate anions of *p*-chlorobenzenethiol and *p*-nitrobenzenethiol both gave the corresponding 2-nitro-2-(phenylsulfanyl)propane as the major product with loss of thiocyanate. The yield of 1-methyl-1-nitroethyl *p*-chlorophenyl sulfide was reduced and the yield of 1-methyl-1-nitroethyl *p*-nitrophenyl sulfide was almost reduced to zero when inhibitors were added (see Table 1). The yield of unaltered **1** also increased when inhibitors were used, indicating an $S_{RN}1$ reaction. Notably, the yield of disulfide increased, indicating an alternative non-chain mechanism of formation which is discussed more fully in the next section.

Table 1 Reactions: $Me_2C(SCN)NO_2 + Nu^- \rightarrow Me_2C(Nu)NO_2 + {}^-SCN$

Nucleophile	Conditions[a]	% Yield $Me_2C(Nu)NO_2$	% Yield $Me_2C(SCN)NO_2$	% Yield Other
$Me_2C{=}NO_2^-$	2 h; 2 h, DMF	72; 51	0; 0	
	2 h, dark; 2 h, O_2	42; 38	0; 0	
	2 h, DNB (5 mol%)	34	0	
	2 h, DTBN (10 mol%)	34	0	
$PhSO_2^-$	2 h	49	0	
	2 h, dark; 2 h, O_2	0; 0	40; 37	
	2 h, DNB (5 mol%)	0	40	
	2 h, DTBN (10 mol%)	0	35	
N_3^-	HMPA, 90 min; 5 h	8; 8	39; 27	
p-$ClC_6H_4S^-$	2 h	37	0	14[b], 16[c]
	2 h, dark; 2 h, O_2	20; 12	10; 41	16[b], 26[c]; 4[b], 10[c]
	2 h, DNB (40 mol%)	17	34	26[b], 8[c]
	2 h, DTBN (40 mol%)	26	11	0[b], 0[c]
p-$NO_2C_6H_4S^-$	15 min	17	18	9[b], 3[c]
	15 min, O_2	0	62	15[b], 4[c]
	15 min, DNB (20 mol%)	5	36	20[b], 4[c]
	15 min, DTBN (20 mol%)	0	36	15[b], 3[c]

[a] All reactions were carried out in DMSO, photolysed with tungsten 'white light' (350 nm, 2 × 150 W), under an atmosphere of nitrogen, unless otherwise stated. 'Dark' refers to reactions carried out without light catalysis and the reactions flask was wrapped in aluminium foil to further exclude light. [b] % Yield of corresponding disulfide. [c] % Yield of 2,3-dimethyl-2,3-dinitrobutane.

Reaction between 2-nitro-2-thiocyanatopropane **1** and the anion of diethyl 2-ethylmalonate **5** gave an efficient redox reaction with the formation of dimeric products **3** and **6** (Scheme 4).



Scheme 4 *Reaction conditions*: i. DMSO, 5 h, photolysis by tungsten 'white light' lamps (2 × 150 W), nitrogen atmosphere.

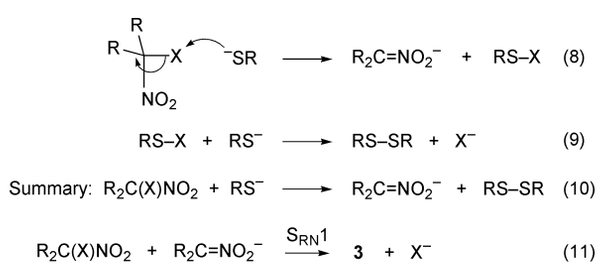
We propose a non-SET mechanism in which **5** abstracts thiocyanate from **1** to yield the anion of 2-nitropropane and diethyl 2-ethyl-2-thiocyanatomalonate. The anion of 2-nitropropane and **1** undergo an $S_{RN}1$ reaction to yield **3** (Table 1) and diethyl 2-ethyl-2-thiocyanatomalonate and the anion of diethyl 2-ethylmalonate **5** also undergo SET by either an $S_{RN}1$ or a non-chain mechanism. Attempts to prepare diethyl 2-ethyl-2-thiocyanatomalonate from **5** gave only the dimer **6**, indicating that it is easily formed. Reactions of the anion of diethyl 2-ethylmalonate **5** have been reported to give similar results as well as $S_{RN}1$ reactions with other α-substituted nitro compounds.[2,3a,15] An attempted $S_{RN}1$ reaction between **1** and the anion of diethyl phosphite, a commonly used anion in $S_{RN}1$ reactions, failed and gave intractable products.

Reactions between 2-substituted-2-nitropropanes and thiolate anions

The reaction between 2-nitro-2-thiocyanatopropane and more weakly nucleophilic thiolates, *p*-chloro- and *p*-nitrobenzenethiolates, yielded both 1-methyl-1-nitroethyl sulfides and disulfides, whereas the more nucleophilic benzenethiolate anion only gave disulfide (36–52%). The yield of disulfide was unchanged when inhibitors were added and no $S_{RN}1$ product was formed, *i.e.* a non-chain reaction. In order to explain these reactions for 2-nitro-2-thiocyanatopropane, a comparison with other unpublished or preliminary results is instructive. The reactions between 2-substituted-2-nitropropanes and thiolates of heterocyclic thiols, pyridine-2-thiol, pyrimidine-2-thiol, benzothiazole-2-thiol, 1-methylimidazole-2-thiol and 4,5-dihydro-1,3-thiazole-2-thiol have been reported in full.[3b]

We have proposed three mechanisms for these reactions which have been reported in full papers[3–6] or in preliminary communications.[7,8] Distinguishing features are summarised below:

1. $S_{RN}1$ mechanism. (Scheme 1, Route A with R = Me and Nu = RS): 1-Methyl-1-nitroethyl sulfide products [$Me_2C(SR)NO_2$], chain reaction, light catalysed, inhibited by radical traps and strong electron acceptors, only in dipolar aprotic solvents, no reaction in protic solvents, favoured by weakly nucleophilic thiolates, favoured by poor leaving groups (non-polarisable).



Scheme 5 Non-chain non-SET abstraction mechanism.

2. Non-SET abstraction mechanism. (Scheme 5), also termed X-philic: Disulfide products, non-chain reaction, not light catalysed, not inhibited by radical traps and strong electron acceptors, best in protic solvents, favoured by strongly nucleophilic thiolates, favoured by α-substituents which are strongly polarisable and have weaker bond strengths. The nitronate anion formed reacts further by an $S_{RN}1$ mechanism [eqn. (11)] to yield 2,3-dimethyl-2,3-dinitrobutane **3** which is inhibited by radical traps and strong electron acceptors and is less favoured in protic solvents.

3. SET redox mechanism. (Scheme 6), termed $S_{ET}2$ (substitution, electron transfer, bimolecular[16]): Disulfide products, chain reaction, light catalysed, inhibited by radical traps and strong electron acceptors, takes places in dipolar aprotic or protic solvents, favoured by strongly nucleophilic thiolates in protic solvents and unclear in dipolar aprotic solvents, favoured by poor leaving groups (non-polarisable). The nitronate anion also reacts as detailed in mechanism 2 above.

A similar disparity of mechanism has been reported for the reactions between α-substituted nitro compounds and tributyltin hydride (Bu_3SnH). In these radical reactions, the difficulty is determining whether there is SET between the tributyltin radicals ($Bu_3Sn^{\bullet}$) and α-substituted nitro compounds to yield the tributyltin cations (Bu_3Sn^+) and the radical anions

Table 2 Reactions between 2-substituted-2-nitropropanes and thiolates in dipolar aprotic solvents

$$Me_2C(X)NO_2 + RS^- \rightarrow Me_2C(SR)NO_2 + RSSR + \mathbf{3} + X^-$$

X	R (of RS^-)	Conditions[a]	% Yields			
			$Me_2C(SR)NO_2$	RSSR	'dimer' **3**	$Me_2C(X)NO_2$
I	*o*-$NO_2C_6H_4$	DMF, 30 min	0	97	98	[b]
	p-ClC_6H_4	DMF, 4 h[c]	0	75	79	[b]
	p-MeC_6H_4	DMF, 30 min[c]	0	78	76	0
Br	*p*-$NO_2C_6H_4$	DMF, 4 h[cd]	89	0	[b]	[b]
	p-ClC_6H_4	DMF, 2 h[c]	0	70	[b]	0
	Ph	DMF, 2 h[c]	0	87	97	0
	p-MeC_6H_4	DMF, 4 h[c]	0	90	47	0
	Bn	DMF, 4 h[c]	0	86	86	0
SCN	Ph	DMSO, 10 min, 2 h	0, 0	36, 52	35, 50	10, 0
		DMSO, 10 min, dark	0	38	41	0
		DMSO, 10 min, O_2	0	26	11	25
		DMSO, 10 min, DNB[e]	0	38	12	9
		DMSO, 10 min, DTBN[e]	0	37	13	6
	Bn	DMSO, 2 h	0	30	22	15 (15)[f]
		DMSO, 2 h, dark, O_2	0	3	3	31, 0
		DMSO, 2 h, dark, DNB[e]	0	3	3	18 (22)[f]
		DMSO, 2 h, dark, DTBN[e]	0	<2	3	39 (19)[f]
Cl	*o*-$NO_2C_6H_4$	DMF, 5 h	34	14	[b]	57
	p-ClC_6H_4	DMF, 20 min, 4 h	17, 35	44, 32	[b]	0, 0
	Ph	DMF, 4 h	0	52	13	0
	Bn	DMF, 4 h	0	87	28	0
NO_2	*o*-$NO_2C_6H_4$	DMF, 24 h, 3 h	55, 36	0	0	0
	p-ClC_6H_4	DMF, 18 h[c]	69	0	[b]	[b]
		DMF, 18 h, O_2	0	30	[b]	[b]
	Ph	DMF, 2 h, 16 h[c]	32, 0	29, 92	10,[b]	6,[b]
		DMF, 2 h, dark, O_2	18	33	4	23
		DMF, 2 h, dark, DNB[e]	26	36	6	16
		DMF, 2 h, dark, DTBN[e]	<2	50	<2	50
	Bn	DMF, 4 h[c]	0	91	15	0
SO_2Ph	*p*-ClC_6H_4	DMF, 4 h	59	0	[b]	[b]
	Ph	DMF, 4 h,[c] 5 h	0, 0	48, 23	[b], 12	38, 38
		DMF, 5 h, dark, O_2	0	12	0	56
		DMF, 5 h, dark, DNB[e]	0	43	8	9
		DMF, 5 h, dark, DTBN[e]	0	18	0	78
	Bn	DMF, 4 h, [c]	0	58	[b]	54

[a] All reactions were photolysed with tungsten 'white light' (350 nm, 2 × 150 W) under an atmosphere of nitrogen unless otherwise stated. The molar ratio of thiolate anions : $Me_2C(X)NO_2$ = 2 : 1 unless otherwise stated. 'Dark' refers to reactions carried out without light catalysis and the reactions flask was wrapped in aluminium foil to further exclude light. [b] % Yield was not measured. [c] The molar ratio of thiolate anions : $Me_2C(X)NO_2$ = 1 : 1. [d] Ref. 3*a*. [e] 20% Molar equiv. [f] Polymer.

$[R_2C(X)NO_2]^{-\bullet}$ or abstraction of the α-substituent by $Bu_3Sn^\bullet$ *via* an S_H2 mechanism.[17] In the Bu_3SnH reactions there is abstraction of the α-substituent by the $Bu_3Sn^\bullet$ radical (S_H2) instead of nucleophile polar abstraction as reported in this present study (S_N2 on X).

Reactions between 2-substituted-2-nitropropanes and thiolate anions in dipolar aprotic solvents

The results of reactions between a range of 2-substituted-2-nitropropanes and thiolates in dipolar aprotic solvents are presented in Table 1 (2-thiocyanato-2-nitropropanes) and Table 2. The general trend of the mechanism and reactivity is clear. Disulfide formation is favoured as the thiolate becomes more nucleophilic (RS^- with R = Bn > Ph > *p*-ClC_6H_4 > *o*- or *p*-$NO_2C_6H_4$) and as the α-substituent becomes more polarisable and/or has weaker C–X bond strength (I > Br > SCN > Cl > NO_2 > SO_2Ph). We have shown that formation of $Me_2C(SR)NO_2$ by the $S_{RN}1$ reactions is catalysed by light and inhibited by radical traps and strong electron acceptors (Table 1 and ref. 3).

The formation of disulfide is not inhibited by radical traps or strong electron acceptors nor light catalysed when the α-substituent is strongly polarisable and the thiolate strongly nucleophilic, *e.g.* reactions between benzenethiolate and $Me_2C(SCN)NO_2$ or $Me_2C(NO_2)_2$. The yields of disulfide in reactions between 2-bromo-2-nitropropane and benzene-, phenylmethane- and *p*-chlorobenzenethiolates were unaltered within experimental error when carried out under nitrogen and oxygen. These results indicate that these redox reactions proceed by the non-SET abstraction mechanism (Scheme 5). However, when either the α-substituent is less polarisable (and/or

$$R_2C(X)NO_2 + RS^- \overset{SET}{\rightleftharpoons} [R_2C(X)NO_2]^{-\bullet} + RS\bullet \quad (12)\ \text{Initiation}$$

$$[R_2C(X)NO_2]^{-\bullet} + RS^- \overset{SET}{\rightleftharpoons} [R_2C{=}NO_2^- + X^- + RS\bullet]_{\text{solv. cage}} \overset{\text{diffusion}}{\rightleftharpoons} R_2C{=}NO_2^- + X^- + RS\bullet \quad (13)$$

$$RS\bullet + RS^- \rightleftharpoons [RS{-}SR]^{-\bullet} \quad (14)$$

$$R_2C(X)NO_2 + [RS{-}SR]^{-\bullet} \rightleftharpoons [R_2C(X)NO_2]^{-\bullet} + RS{-}SR \quad (15)$$

(13)–(15) Propagation

$$\text{Summary:}\quad R_2C(X)NO_2 + RS^- \longrightarrow R_2C{=}NO_2^- + RS{-}SR \quad (16)$$

Scheme 6 Chain SET redox mechanism.

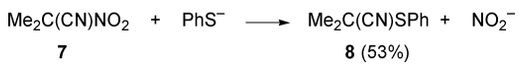
has a stronger C–X bond strength), *e.g.* SO_2Ph, or the nucleophile is strongly nucleophilic, *e.g.* phenylmethanethiolate, there is some inhibition, *e.g.* reactions between phenylmethanethiolate and $Me_2C(SCN)NO_2$, thereby indicating a chain SET redox mechanism $S_{ET}2$ (Scheme 6). Other reactions are less clear, *e.g.* the reaction between $Me_2C(SO_2Ph)NO_2$ and benzenethiolate, which possibly suggests a mixture of mechanisms.

This third mechanism, the chain SET redox $S_{ET}2$ mechanism (Scheme 6), was first proposed by Russell and co-workers for the reactions between α-substituted nitroalkanes and enolate anions which gave dimers of the enolates.[16] We also proposed this mechanism in a preliminary communication[8] to explain the formation of disulfide. The SET shown in eqn. (13) should be favoured when the leaving group X is poor, thereby increasing the lifetime of the intermediate $[Me_2C(X)NO_2]^{-\bullet}$ radical anion. Likewise, a strongly nucleophilic thiolate will react much faster and thereby intercept the radical anion before it has had time to dissociate [eqn. (13)]. Thiyl radicals ($RS^{\bullet}$) are known to add to thiolate anions to form detectable disulfide radical anions $[(RSSR)^{-\bullet}]$ [eqn. (14)] and have been observed by EPR spectroscopy.[18] Evidence for the intermediacy of radical anions of disulfides in redox reactions between thiolate anions and 1-benzyl-1,4-dihydropyridine-3-carboxamide (BNAH) has also been reported.[19] The chain reaction is completed by SET between the disulfide radical anion and the starting $Me_2C(X)NO_2$ [eqn. (15)].

Blank reactions show that the oxidation of thiolate to disulfide in an atmosphere of oxygen is very slow and not significant in inhibition reactions. However, certain factors cloud the analysis of results, *e.g.* *p*-dinitrobenzene is a slow oxidant of thiolates to disulfide and gives higher yields of disulfide than expected. Some of the 2-substituted-2-nitropropanes react to yield the corresponding $S_{RN}1$ product $Me_2C(SR)NO_2$ which reacts with further thiolate to yield disulfide, *e.g.* reaction between $Me_2C(NO_2)_2$ and benzenethiolate. In most reactions, some of the 'dimer', 2,3-dimethyl-2,3-dinitrobutane **3** was formed. This formation resulted from reaction between the starting 2-substituted-2-nitropropane and the nitronate anion, by abstraction of the α-substituent (Scheme 5). Formation of the dimer **3** was largely inhibited when radical traps or strong electron acceptors were used, indicating the $S_{RN}1$ mechanism for its formation.

In the non-SET abstraction mechanism we have assumed the arylsulfanyl derivatives (ArS–X) formed by abstraction react rapidly with a second equivalent of thiolate to yield disulfides. Sulfanyl iodides (RSI), bromides (RSBr), chlorides (RSCl), nitrites ($RSNO_2$) and sulfonates ($RS–SO_2Ph$) are all known to react rapidly with thiolate to yield disulfides. In the reaction between 2-thiocyanato-2-nitropropane and phenylmethanethiolate the intermediate sulfanylthiocyanate (BnS–SCN) is known to eliminate thiocyanic acid (HSCN) to yield thiobenzaldehyde.[20] Attempts to isolate thiobenzaldehyde have been generally unsuccessful; it either polymerises or can be trapped by suitable dienes.[20] We isolated a polymer in each reaction which we assume results from thiobenzaldehyde (Table 1). Our mechanistic proposal for the non-chain non-SET mechanism (Scheme 5) is supported by evidence in the literature which indicates that thiolates react by polar abstraction of the α-substituent by a non-SET mechanism with a range of activated halogeno compounds to yield disulfides, *e.g.* α-nitrobenzyl halides,[21] α-halogenoketones,[22] α-halogenosulfones[23] and halogenoalkynes.[24]

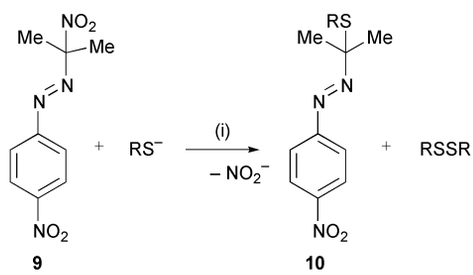
We also determined the reactions between thiolates and 2-substituted-2-nitropropanes for which the intermediate radical anions in $S_{RN}1$ reactions are known to dissociate with loss of nitrite (Scheme 1, Route B). Reactions of 2,2-dinitropropane can be regarded as loss of the α-substituent or nitrite. We have previously shown that the reactions between 2-azido-2-nitropropane and 2-azido-2-nitrocyclohexane and *p*-chorobenzenethiolate gave $S_{RN}1$ substitutions with loss of nitrite to yield 1-azido-1-methylethyl *p*-chlorophenyl sulfide (70%) and 1-(1-azidocyclohexyl) *p*-chlorophenyl sulfide (53%) respectively.[5] The reaction between *p*-chlorobenzenethiolate and the α-nitro-ketone, 3-methyl-3-nitrobutan-2-one [$Me_2C(NO_2)COMe$] gave an intractable mixture of products and was not further investigated. However, reaction between 2-cyano-2-nitropropane **7** and benzenethiolate gave a good yield (53%) of the $S_{RN}1$ product **8** with the expected loss of nitrite (Scheme 7).



Scheme 7 *Reagents and conditions*: HMPA, 3 h, photolysis by tungsten 'white light' lamps (2 × 150 W), nitrogen atmosphere.

No reaction was obtained with the less nucleophilic *p*-chlorobenzenethiolate.

Reactions between (1-methyl-1-nitroethyl)(*p*-nitrophenyl)-diazene **9** and thiolates also gave good yields of $S_{RN}1$ substitution products **10** with loss of nitrite (Scheme 8). The results



R = Ph; **10** (54%), RSSR (0%), unaltered **9** (19%)
R = *o*-NO_2-C_6H_4; **10** (16%), RSSR (0%), unaltered **9** (84%)
R = *p*-Cl-C_6H_4; **10** (25%), RSSR (46%), unaltered **9** (0%)
R = Bn; **10** (0%), RSSR (44%), unaltered **9** (45%)

Scheme 8 *Reagents and conditions*: i. DMF, 18 h, photolysis by tungsten 'white light' lamps (2 × 150 W), nitrogen atmosphere.

did not appear to follow the trend of nucleophilicity of the thiolates. However, reaction with the more nucleophilic phenylmethanethiolate yielded only disulfide and the *p*-nitrophenylhydrazone of acetone (20%). Interestingly, the attempted $S_{RN}1$ reaction between **9** and the anion of 2-nitropropane reported in the literature[25] gave no $S_{RN}1$ substitution product but instead gave a redox reaction to yield the 'dimer' of nitropropane **3**. Reactions between 2-methyl-2-nitropropane (Me_3CNO_2) and thiolates gave only disulfide products with no $S_{RN}1$ substitution [*p*-chlorobenzenethiolate (24 h), RSSR (34%); benzenethiolate (16 h), RSSR (55%); phenylmethanethiolate (8 h), RSSR (77%)]. The yields of these redox reactions reflect the nucleophilicity (or reduction ability) of the thiolates. No products resulting from the 2-methyl-2-nitropropane were detected. We propose that the mechanism is probably a non-chain SET reaction [Scheme 6, eqns. (12), (14) and (15)].

Reactions between 2-substituted-2-nitropropanes and thiolate anions in protic solvents

In sharp contrast to the reactions in dipolar aprotic solvents, only disulfide products, and no $S_{RN}1$ products, were obtained in protic solvents (MeOH or MeOH–water) (Table 3). With the polarisable α-substituents (I, Br, SCN), high yields of disulfide were obtained even with weakly nucleophilic thiolates such as *p*-nitro- and *p*-chloro-benzenethiolate. These reactions were not light catalysed nor inhibited by radical traps and strong electron acceptors, *e.g.* $Me_2C(Br)NO_2$ and *p*-nitrobenzenethiolate or *p*-chlorobenzenethiolate and $Me_2C(SCN)NO_2$ and *p*-nitrobenzenethiolate or *p*-chlorobenzenethiolate. All of these reactions gave major amounts of the $S_{RN}1$ products in dipolar aprotic solvents (ref. 3*a* and Table 1).

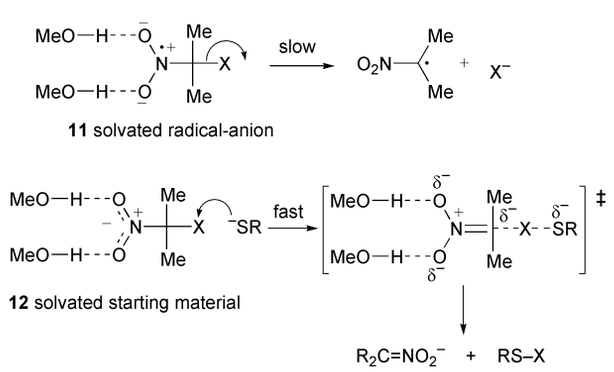
Table 3 Reactions between 2-substituted-2-nitropropanes and thiolates in MeOH $Me_2C(X)NO_2 + RS^- \rightarrow RSSR + Me_2C{=}NO_2^- + X^-$

X	R (of RS^-)	Conditions[a]	% Yield RSSR	% Yield $Me_2C(X)NO_2$
I	*p*-ClC_6H_4	5 min	94	0
Br	*p*-$NO_2C_6H_4$	MeOH–H_2O (85 : 15), 48 h	98	0
		15 min	74, 75	0, 0
		15 min, dark; 15 min, O_2	77; 67	0; 0
		15 min, DNB[b]	85	0
		15 min, DTBN[b]	59, 69	0, 0
	p-ClC_6H_4	MeOH–H_2O (85 : 15), 5 min	95	0
		20 min	71	0
		20 min, DNB[b]	70	0
		20 min, DTBN[b]	68	0
	Ph	5 min	96	0
SCN	*p*-$NO_2C_6H_4$	MeOH–H_2O (85 : 15), 20 min	39, 60	0, 0
		15 min	77	0
		15 min, dark; 15 min, O_2	69, 73; 72	0, 0; 0
		15 min, DNB[b]	78	0
		15 min, DTBN[b]	55	0
	p-ClC_6H_4	20 min	60	0
		20 min, dark; 20 min, O_2	55; 53	0; 0
		20 min, DNB[b]	55	0
		20 min, DTBN[b]	56	0
Cl	*p*-ClC_6H_4	4 h	45	0
		4 h, dark; 4 h, O_2	32, 33	0, 0
		4 h, DNB[b]	26	0
		4 h, DTBN[b]	28	0
		20 min	36	6
		20 min, O_2	21	12
		20 min, DNB[b]	18	22
		20 min, DTBN[b]	30	0
NO_2	*p*-ClC_6H_4	2 h	44	39
		2 h, dark; 2 h, dark, O_2	12; 7	55; 70
		2 h, DNB[b]; 2 h, dark, DNB[b]	6	55
		1 h	34	31
		1 h, dark; 2 h, O_2	6; 23	47; 43
		1 h, DTBN	33	47
	Ph	4 h	38, 28	62, 53
		4 h, dark, O_2	11	50
		4 h, dark, DNB[b]	50	50
		4 h, dark, DTBN[b]	28	32

[a] All reactions were carried out in MeOH, photolysed with tungsten 'white light' (350 nm, 2 × 150 W), under an atmosphere of nitrogen and with a molar ratio of RS^- : $Me_2C(X)NO_2$ = 2 : 1, unless otherwise stated. 'Dark' refers to reactions carried out without light catalysis and the reactions flask was wrapped in aluminium foil to further exclude light. [b] DTBN or DNB at 20% molar equiv.

With less polarisable α-substituents with stronger C–X bonds (*e.g.* Cl, NO_2), the reactions were much slower and unaltered starting 2-substituted-2-nitropropanes were also measured, *e.g.* $Me_2C(Cl)NO_2$ or $Me_2C(NO_2)_2$ and *p*-chlorobenzenethiolate. These reactions also showed inhibition and light catalysis, suggesting that a chain redox $S_{ET}2$ mechanism (Scheme 6) was predominant. The inhibition of the reaction between $Me_2C(NO_2)_2$ and benzenethiolate was less clear.

We have explained this clear difference in mechanism by solvation of the nitro group.[3b,8] $S_{RN}1$ reactions have been reported largely for dipolar aprotic solvents.[2] The effect of solvation on nucleophiles in $S_{RN}1$ reactions has been shown to be significant.[26] However, the solvation of thiolates is similar in protic and dipolar aprotic solvents because of the size and polarisability of the large sulfur atom,[27,28] and therefore, the effect of solvation must lie with the nitro compounds. Similarly, the nucleophilicity of thiolates is almost the same in protic and dipolar aprotic solvents.[28] The rate of dissociation of protonated radical anions of *p*-nitrobenzyl halides is slower than that of the non-protonated radical anion, *e.g.* the dissociation of the protonated radical anion of *p*-nitrobenzyl bromide is 60 times slower.[29] We have predicted that H-bonding should have similar effects and have suggested that the effect of protic solvation is two-fold.[8] Firstly, the methanol solvates the intermediate radical anion **11** in the $S_{RN}1$ or $S_{ET}2$ mechanisms as shown in Scheme 9. The H-bonding draws electron density from the nitro group and hence from the σ* MO of the C–X bond and thereby



Scheme 9 Solvated species in $S_{RN}1$ and abstraction mechanisms.

slows the rate of dissociation. For dissociation to occur, a transition state needs rearrangement of the molecular orbitals to give higher electron density in the C–X bond to facilitate dissociation by loss of X^-. Secondly, as shown in Scheme 9, for the non-SET abstraction reaction, solvation of the nitro group in the starting material, and more significantly in the transition state where charge on the oxygen atoms is higher, will strongly lower transition state energy for abstraction of the α-substituent by thiolate. Further evidence for our initially proposed mechanism has been reported for the reactions between α-bromo nitro compounds and thiolates in a synthetic protocol.[30]

Experimental

General

DMF and DMSO were distilled at reduced pressure from calcium hydride and stored over molecular sieves. Methanol was dried using magnesium and iodine. Light petroleum refers to the bp 40–60 °C fraction. Mps were determined on a Koffler block melting point apparatus and are uncorrected. Elemental analyses were determined on a Perkin-Elmer 2400 CHN Elemental Analyser in conjunction with a Perkin-Elmer AD-4 Autobalance. IR spectra were recorded as solutions of $CDCl_3$ with tetramethylsilane (TMS) as the internal standard on a Perkin-Elmer 177 spectrophotometer on NaCl plates. NMR spectra were recorded at 90 MHz on a Perkin-Elmer R32 spectrometer or at 60 MHz on a Varian EM 360A spectrometer. Chemical shifts are given in parts per million (ppm) and *J* values in hertz (Hz). Analyses of reaction mixtures using ^{1}H NMR spectroscopy were carried out using *p*-dinitrobenzene or *p*-dimethoxybenzene as internal standards. TLC using silica gel as absorbent was carried out with aluminium backed plates coated with silica gel (Merck Kieselgel 60 F254). Silica gel (Merck Kieselgel 60 H silica) was used for column chromatography unless otherwise specified. Photolysis of reactions was carried out using tungsten 'white light' lamps (2 × 150 W) or fluorescent desk lamps (2 × 15 W) which were positioned on either side of the reaction at a distance of 15 cm. The procedures for carrying out diagnostic inhibition studies and reactions in the absence of light for $S_{RN}1$ reactions are fully described in previous papers.[2–9]

Materials

Literature procedures were used for the synthesis of 2-bromo-2-nitropropane,[31] 2-chloro-2-nitropropane,[31] 2-iodo-2-nitropropane,[31] 2,2-dinitropropane,[14] 1-methyl-1-nitroethyl phenyl sulfone,[3a] 2-azido-2-nitropropane,[5] 2-cyano-2-nitropropane,[14] (1-methyl-1-nitroethyl)(*p*-nitrophenyl)diazene **9**,[25] and the sodium salts of 2-nitropropane,[3a] diethyl 2-ethylmalonate[3a] and all the thiolates.[3] The following were synthesised for comparison as authentic samples: 2,3-dimethyl-2,3-dinitrobutane **3**,[3a] 2,3-bis(ethoxycarbonyl)-2,3-diethylsuccinic acid diethyl ester **6**,[25] 1-(1-methyl-1-nitroethyl)-1-nitrocyclohexane,[3a] 1-methyl-1-nitroethyl *p*-nitrophenyl sulfide,[3a] 1-methyl-1-nitroethyl *o*-nitrophenyl sulfide,[3a] 1-methyl-1-nitroethyl *p*-chlorophenyl sulfide,[3a] 1-methyl-1-nitroethyl phenyl sulfide[3a] and all the disulfides.[3a]

Oxidative addition reactions

2-Nitro-2-thiocyanatopropane 1. Freshly distilled 2-nitropropane (4.45 g, 0.05 mol) was dissolved in a solution of sodium hydroxide (2.2 g, 1.1 molar equiv.) in water (30 cm^3). The solution was added dropwise to a two phase solution of sodium thiocyanate (8.10 g, 0.01 mol, 2 equiv.) and potassium ferricyanide (32.90 g, 0.01 mol, 2 equiv.) in water (30 cm^3) and dichloromethane (70 cm^3) at a rate such that the temperature remained between 20 and 25 °C. The reaction mixture was stirred for 20 min. The ethereal layer was separated and the aqueous layer extracted with diethyl ether. The ether extracts were combined, washed with water, dried and evaporated to dryness to yield a yellow liquid. Fractional distillation gave a yellow oil of **1** (2.46 g, 40%), bp 66–68 °C (1.5 mm Hg) (Found: C, 32.7; H, 4.3; N, 19.4; S, 22.1. $C_6H_6N_2SO_2$ requires C, 32.86; H, 4.14; N, 19.20; S, 21.94%); ν_{max}(neat)/cm^{-1} 2880, 2170 and 1550; δ_H (60 MHz) 2.10 (s, Me); *m*/*z* (EI) 100 ($M^+ - NO_2$, 100, 100%) and 41 (32).

1-Nitro-1-thiocyanatocyclohexane 2. The above conditions were used with nitrocyclohexane (6.45 g) to yield a crude oil of **2** which was analysed using GLC and IR and ^{1}H NMR spectroscopy which indicated cyclohexanone as a minor contaminant. Purification by preparative TLC (silica gel with carbon tetrachloride and hexane (60 : 40) as eluant) gave **2** as a yellow oil (4.02 g, 43%) (Found: C, 45.6; H, 5.6; N, 15.0; S, 16.8. $C_7H_{10}N_2SO_2$ requires C, 45.16; H, 5.37; N, 15.05; S, 17.20%); ν_{max}(neat)/cm^{-1} 2160 and 1550; δ_H (60 MHz) 1.50–1.70 (6 H, m) and 2.15–2.45 (4 H, m). A repeat reaction using diethyl ether in place of dichloromethane gave 34% of **2**.

General procedure for $S_{RN}1$ reactions between nucleophiles and 2-nitro-2-thiocyanatopropane

Sodium salt of 2-nitropropane. The anion of 2-nitropropane (1.00 g, 9 mmol) was dissolved in dry DMSO under nitrogen in a dry flask with one neck covered with a rubber septum. Nitrogen gas was passed through the solution for 30 min to complete deoxygenation. 2-Nitro-2-thiocyanatopropane **1** (550 mg, 3.7 mmol) was added *via* a syringe through the septum. The colour of the reaction turned red and remained red throughout the reaction. The reaction was illuminated by two tungsten 'white light' lamps for 2 h. Ice-cold water was poured into the reaction and extracted with diethyl ether. The ethereal extracts were combined and washed with water (7 times) to remove residual DMSO, dried and evaporated to dryness. The crude product was recrystallised with ethanol to yield pure colourless crystals of 2,3-dimethyl-2,3-dinitrobutane **3** (480 mg, 72%), mp 207–208 °C (lit.[3] 207–208 °C); ν_{max}(Nujol)/cm^{-1} 1552; δ_H (60 MHz) 1.73 (s, Me). The mp, IR and ^{1}H NMR spectra and TLC were identical to those of authentic material.

Sodium benzenesulfinate. Sodium benzenesulfinate (1.00 g, 6 mmol) gave 1-methyl-1-nitroethyl phenyl sulfone (420 mg, 49%), mp 116–118 °C (EtOH) (lit.[3a] mp 116–117 °C); ν_{max}(Nujol)/cm^{-1} 1590, 1550 and 760; δ_H (60 MHz) 1.95 (6 H, s, Me) and 7.50–7.75 (5 H, m, PhH).

Sodium azide. Sodium azide (500 mg, 7.6 mmol) was reacted with HMPA instead of DMSO for 90 min and for 5 h to yield crude products which were analysed using ^{1}H NMR spectroscopy and TLC with an internal standard.

Sodium diethyl 2-ethylmalonate. The general procedure for $S_{RN}1$ reactions using 2-nitro-2-thiocyanatopropane **1** (70 mg, 0.48 mmol) and sodium diethyl 2-ethylmalonate (100 mg, 0.48 mmol) for 5 h yielded a crude product which was leached with hexane. The solution was evaporated to yield pure 2,3-bis(ethoxycarbonyl)-2,3-diethylsuccinic acid diethyl ester **6** (47 mg, 53%). The residual crystals were recrystallised from ethanol to yield 2,3-dimethyl-2,3-dinitrobutane **3** (40 mg, 95%). Both compounds were identical to authentic material (mp, IR and ^{1}H NMR spectra).[3a]

1-(1-Methyl-1-nitroethyl)-1-nitrocyclohexane

The general procedure for $S_{RN}1$ reactions using 1-nitro-1-thiocyanatocyclohexane (550 mg, 3 mmol) and the anion of 2-nitropropane (1.00 g, 9 mmol) for 5 h yielded 2,3-dimethyl-2,3-dinitrobutane **3** (80 mg, 30%) and 1-(1-methyl-1-nitroethyl)-1-nitrocyclohexane (390 mg, 60%). Both products were identical to authentic material (mp, IR and ^{1}H NMR spectroscopy and TLC).[3a]

Reactions between 2-substituted-2-nitropropanes and thiolate anions

The procedures for the preparation of thiolate anions using sodium methoxide in methanol and for reactions between 2-substituted-2-nitropropanes and thiolate anions are fully described in reference 3. The solvents, times of reaction, molar equivalents of reagents, and other conditions are defined in the Tables. The disulfides are all known compounds and were

purchased commercially. The 1-methyl-1-nitroethyl aryl sulfides and disulfides were compared with authentic material.[3] In those studies in which yields were measured using ^{1}H NMR spectroscopy with an internal standard, products were isolated and characterised in at least one experiment in each series. A sample procedure for reactions in dipolar aprotic and protic solvents is detailed below.

Dipolar aprotic solvents. *Reaction between 2-nitro-2-thiocyanatopropane **1** and the sodium salt of p-chlorobenzenethiol.* The sodium salt of *p*-chlorobenzenethiol (500 mg, 3 mmol) was dissolved in dry DMSO under nitrogen in a dry flask with one neck covered with a rubber septum. The reaction mixture was stirred and nitrogen gas was passed through the solution for 30 min to complete deoxygenation. 2-Nitro-2-thiocyanatopropane **1** (500 mg, 3.6 mmol) was added *via* a syringe through the septum. The colour of the reaction turned red and remained red throughout the reaction. The reaction was illuminated by two tungsten 'white light' lamps for 2 h. Ice-cold water was poured into the reaction and extracted with diethyl ether. The ethereal extracts were combined and washed with water (7 times) to remove residual DMSO, dried and evaporated to dryness. The crude product was leached with hexane and the residue was recrystallised from EtOH to yield 2,3-dimethyl-2,3-dinitrobutane **3** (16%). The solution was evaporated to dryness and the residue recrystallised to yield 1-methyl-1-nitroethyl *p*-chlorophenyl sulfide (37%); mp 81–82 °C (lit.[3a] mp 82–83 °C); ν_{max}(Nujol)/cm^{-1} 1590 and 1552; δ_H (60 MHz) 1.83 (6 H, s, Me) and 7.40 (4 H, AA′BB′q, ArH). The filtrate from the recrystallisation was purified by chromatography to yield bis(*p*-chlorophenyl) disulfide (14%). All compounds were identical to authentic materials (TLC, mp, IR and ^{1}H NMR spectra).[3a]

Reaction between 2-cyano-2-nitropropane 7 and the sodium salt of benzenethiol. The general procedure for reactions between 2-substituted-2-nitropropanes and thiolate anions was used with 2-cyano-2-nitropropane (200 mg, 1.75 mmol) and the sodium salt of benzenethiolate (230 mg, 1.74 mmol) in HMPA (40 cm^3) for 3 h. The reaction gave a crude mixture which was purified by preparative TLC to yield 1-cyano-1-methylethyl phenyl sulfide **8** as a yellow oil (180 mg, 53%) (Found: C, 67.4; H, 6.1; N, 8.0; S, 18.4. $C_{10}H_{11}NS$ requires C, 67.76; H, 6.25; N, 7.90; S, 18.09%); ν_{max}(neat)/cm^{-1} 1595, 1150, 1070, 750 and 695; δ_H (60 MHz) 1.95 (6 H, s, Me) and 7.20–7.40 (5 H, m, PhH).

*Reaction between (1-methyl-1-nitroethyl)(p-nitrophenyl)diazene **9** and thiolates.* All the reactions were carried out using the standard conditions in dry DMF with fluorescent lamps (2 × 15 W) for 18 h using an equimolar ratio of **9** and the respective thiolate. All products were purified by preparative TLC using mixtures of diethyl ether and light petroleum as eluant.

a. Benzenethiolate. [1-Methyl-1-(phenylsulfanyl)ethyl](*p*-nitrophenyl)diazene **10** (R = Ph) (54%); mp 124–126 °C (from CCl_4) (Found: C, 60.0; H, 5.1; N, 13.5; S, 10.8. $C_{15}H_{15}N_3O_2S$ requires C, 59.8; H, 5.0; N, 13.9; S, 10.6%); ν_{max}(neat)/cm^{-1} 1535 and 1357; δ_H (60 MHz) 1.70 (6 H, s, Me), 7.20–7.30 (5 H, m, PhH) and 8.01 (4 H, AA′BB′q, *p*-$NO_2C_6H_4$); *m*/*z* (EI) 192, 151, 150, 146, 125, 122 and 105. Unaltered starting material **9** (19%) was also separated, mp 102–104 °C (lit.[25] 104 °C).

b. o-Nitrobenzenethiolate. [1-Methyl-1-(*o*-nitrophenylsulfanyl)ethyl](*p*-nitrophenyl)diazene **10** (R = *o*-$NO_2C_6H_4$) (16%); mp 92–93 °C (from CCl_4) (Found: C, 51.6; H, 4.0; N, 15.9; S, 9.6. $C_{15}H_{14}N_4O_4S$ requires C, 52.0; H, 4.06; N, 16.18; S, 9.2%); ν_{max}(neat)/cm^{-1} 1535 and 1354; δ_H (60 MHz) 1.69 (6 H, s, Me), 7.40–7.60 (4 H, m, *o*-$NO_2C_6H_4$) and 8.01 (4 H, AA′BB′q, *p*-$NO_2C_6H_4$); *m*/*z* (EI) 196, 192, 155 and 146. Unaltered starting material **9** (84%) was also separated.

c. p-Chlorobenzenethiolate. [1-Methyl-1-(*p*-chlorophenylsulfanyl)ethyl](*p*-nitrophenyl)diazene **10** (R = *p*-ClC_6H_4) (25%); mp 92–93 °C (from CCl_4) (Found: C, 51.6; H, 4.0; N, 15.9; S, 9.6. $C_{15}H_{14}N_4O_4S$ requires C, 52.0; H, 4.06; N, 16.18; S, 9.2%); ν_{max}(neat)/cm^{-1} 1535 and 1354; δ_H (60 MHz) 1.69 (6 H, s, Me), 7.40–7.50 (4 H, m, *p*-ClC_6H_4) and 8.01 (4 H, AA′BB′q, *p*-$NO_2C_6H_4$); *m*/*z* (EI) 196, 192, 155 and 146. Bis(*p*-chlorophenyl) disulfide (44%) was also separated and compared with authentic material (mp, TLC and IR and ^{1}H NMR spectra).

Protic solvents. *Reaction between 2-nitro-2-thiocyanatopropane **1** and the sodium salt of p-chlorobenzenethiol.* The general procedure for reactions between 2-substituted 2-nitropropanes and thiolates was used with methanol in place of the dipolar aprotic solvent. The sodium salt of *p*-chlorobenzenethiol (500 mg, 3 mmol) and 2-nitro-2-thiocyanatopropane **1** (220 mg, 1.5 mmol) yielded a crude product which was analysed by TLC and ^{1}H NMR spectroscopy using *p*-dimethoxybenzene as an internal standard to show pure bis(*p*-chlorophenyl) disulfide (60%) and no unaltered **1** or other products. The residue was recrystallised from hexane to yield pure bis(*p*-chlorophenyl) disulfide which was identical to authentic material (TLC, mp, IR and ^{1}H NMR spectra).

Acknowledgements

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