Crystal Structure of *trans*-2,3-Bis(mesitylthio)-4-nitro-2,3-dihydrothiophene and Kinetic Study of its Base-catalysed Aromatisation to 2-Mesitylthio-4-nitrothiophene in Toluene

Giovanni Petrillo,* Marino Novi, Giacomo Garbarino, and Carlo Dell'Erba
Istituto di Chimica Organica dell'Università, C.N.R. Centro di Studio sui Diariloidi e loro Applicazioni, Palazzo delle Scienze, Corso Europa, 16132 Genova, Italy
Angelo Mugnoli*
Istituto di Chimica Fisica dell'Università, Palazzo delle Scienze, Corso Europa, 16132 Genova, Italy

By means of a crystal-structure determination, the *trans*-configuration is unequivocally assigned to the 2,3-dihydrothiophene derivative (**2**), isolated as an intermediate in the *cine*-substitution of 3,4-dinitrothiophene (**1**) with mesitylenethiolate. The puckering of the 2,3-dihydrothiophene ring can be interpreted in terms of a half-chair conformation. Structural parameters establish the regiospecificity of the Bu^n_3N-induced *syn*-elimination of mesitylenethiol from (**2**) in toluene [leading to the final product (**3**)], for which a carbanionic, stepwise pathway through ion pairs is postulated from kinetic evidence. A brief discussion of the proposed mechanism of formation of (**2**) from (**1**) is also presented.

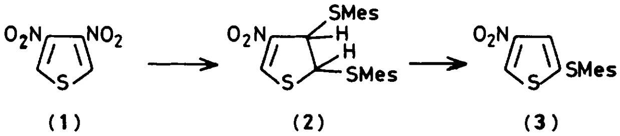
Base-promoted, alkene-forming β-elimination reactions,[1] one of the classical fields of organic chemistry, have been subjected to renewed interest since it was recognised[1d] that stepwise pathways through a carbanionic intermediate are more frequent than once believed and represent, with a number of firmly established variants,[1-3] a powerful alternative to the concerted *E*2 mechanism. Two of the most stimulating aspects of the field are, at present (*a*) the mechanistic assignment for a particular reacting system, as merging of mechanisms does not always allow unambiguous tests,[1] and (*b*) the evaluation of factors which make a system choose among the available pathways or which determine the crossover of a mechanistic borderline.[4]

The *cine*-substitution reaction between 3,4-dinitrothiophene (1) and sodium mesitylenethiolate in methanol has been shown to pass through the 2,3-dihydrothiophene (2) (Scheme 1).[5] Actually, the isolated intermediate (2) quantitatively yields 2-mesitylthio-4-nitrothiophene (3) in a base-promoted elimination, under mild conditions, in a variety of base–solvent systems. The regiospecificity of the process is, however, opposite to that displayed by recently investigated similar systems like pyrrolines (4)[6,7] or 2,3-dihalogeno-2,3-dihydrobenzofurans (5),[8,9] which undergo base-promoted HY elimination to 3-X derivatives (2-Y derivatives being formed only in acidic conditions).

This observation, coupled with the current interest in elimination reactions, led us to undertake a detailed kinetic study of the process (2) ⟶ (3). We have also performed an *X*-ray determination of the molecular geometry of the substrate, in order to assess the stereochemistry of the elimination studied herein. Actually the inter-relationship between the stereochemical course of a β-elimination and its kinetics has been well discussed;[1,10] for example, the early belief that *anti*-eliminations are concerted while the generally slower *syn*-processes are stepwise[11] has found numerous exceptions, both in acyclic and in cyclic systems,[12] and once more, very recently, it has been shown that other structural factors can become more important in determining the mechanistic outcome.[8c]

Results and Discussion

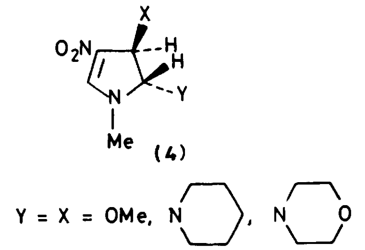
Molecular Geometry of (**2**).—The dihydrothiophene (**2**), isolated as an intermediate in the (**1**) ⟶ (**3**) *cine*-substitution reaction, showed $J_{2,3}$ 0.42 Hz (100 MHz; solvent $CDCl_3$).[5] The *trans*-configuration could be tentatively assigned from such a low value for a vicinal coupling constant[7b,13] which is known to be mainly a function of the torsion angle.[14] However, as the presence of the bulky mesitylthio groups in (**2**) could bring about sizable distortions, we felt it necessary to substantiate the attribution of configuration through a crystallographic study. The molecular structure resulting from *X*-ray diffraction and the numbering scheme adopted are shown in Figure 1 (drawn by means of the ORTEP program[15]). Hydrogen atoms have been named according to the numbering of the bonded carbon atom. Final positional and equivalent thermal parameters for heavier atoms are reported in Table 1. Selected bond lengths and bond angles are given in Tables 2 and 3; standard deviations range between 0.002 and 0.005 Å for bond lengths, and between 0.1 and 0.3° for bond angles. The *trans*-configuration of the two mesitylthio groups is unequivocally confirmed by the S(2)–C(2)–C(3)–S(3) torsion angle [−157.5(1)°, antiperiplanar[16]]; the value of the H(2)–C(2)–C(3)–H(3) torsion angle (88°) is in fair agreement with the value of 83°, calculated[14] from the experimental value of $J_{2,3}$. The value of the H(2)–C(2)–C(3)–S(3) torsion angle (−33°) places the elimination (to be discussed below) at the borderline between a *syn*-periplanar and a *syn*-clinal process.[1g]



(1) (2) (3)

Mes = mesityl

Scheme 1.



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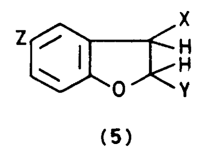

(5)

X, Y = F, Cl, Br
Z = H, Cl

The dihydrothiophene ring is puckered, the torsion angles along the ring ranging between −28 and +23°. Referring to the treatment by Duax *et al.*[17] the asymmetry parameters $\Delta C_2[C(5)] = 4.0°$ and $\Delta C_s[C(2)] = 8.9°$ can be calculated for a

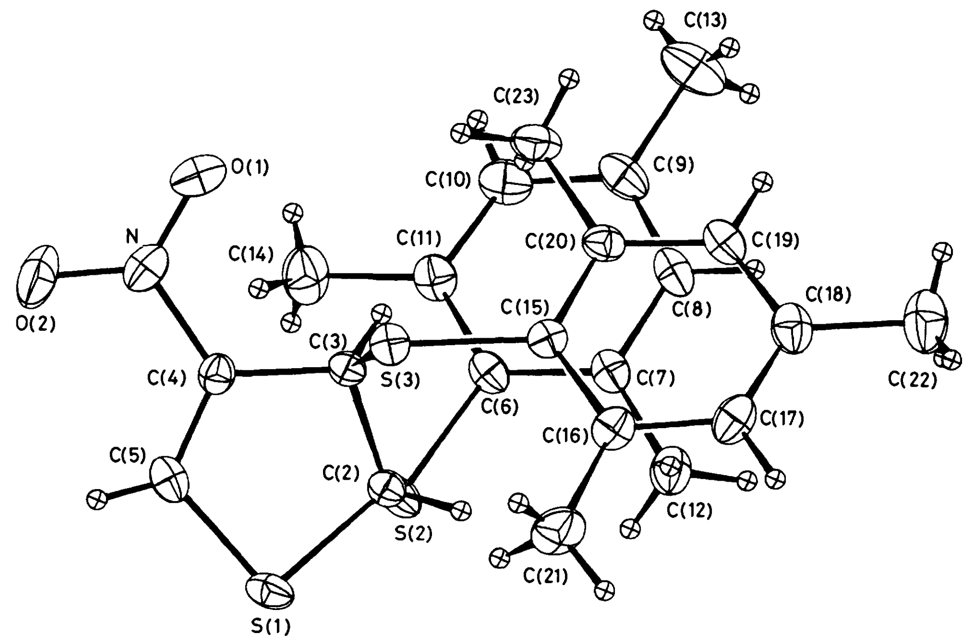

Figure 1. Molecular structure and atom-numbering scheme of (**2**) with temperature ellipsoids at 0.20 probability. Hydrogen atoms, treated as isotropic, are on an arbitrary scale

Table 1. Fractional co-ordinates (× 10^4) and equivalent thermal vibration parameters ($Å^2$ × 10^3) of non-hydrogen atoms

	x	y	z	U_{eq}
S(1)	2 643(1)	124(0)	5 256(0)	58(0)
S(2)	5 007(1)	1 173(0)	6 120(0)	54(0)
S(3)	−354(1)	580(0)	6 759(0)	49(0)
C(2)	2 988(3)	606(1)	6 195(1)	44(1)
C(3)	1 406(3)	1 135(1)	6 317(1)	41(1)
C(4)	789(3)	1 354(1)	5 523(1)	47(1)
C(5)	1 249(3)	872(2)	4 964(1)	55(1)
C(6)	4 990(3)	1 798(2)	6 953(1)	49(1)
C(7)	5 314(3)	1 478(2)	7 697(1)	51(1)
C(8)	5 291(4)	2 001(2)	8 321(2)	64(1)
C(9)	4 980(4)	2 808(2)	8 236(2)	70(1)
C(10)	4 695(4)	3 099(2)	7 502(2)	73(1)
C(11)	4 693(4)	2 615(2)	6 848(2)	60(1)
C(12)	5 646(4)	613(2)	7 838(2)	67(1)
C(13)	4 923(6)	3 364(3)	8 925(2)	112(2)
C(14)	4 344(6)	2 980(2)	6 061(2)	91(1)
C(15)	554(3)	365(1)	7 699(1)	45(1)
C(16)	912(3)	−438(2)	7 893(2)	55(1)
C(17)	1 538(4)	−600(2)	8 638(2)	65(1)
C(18)	1 836(4)	−11(2)	9 182(2)	64(1)
C(19)	1 467(4)	770(2)	8 974(2)	60(1)
C(20)	797(3)	976(2)	8 248(1)	51(1)
C(21)	621(5)	−1 121(2)	7 338(2)	83(1)
C(22)	2 493(5)	−216(3)	9 988(2)	96(2)
C(23)	356(4)	1 838(2)	8 077(2)	68(1)
N	−395(3)	2 020(2)	5 399(2)	71(1)
O(1)	−795(4)	2 406(2)	5 957(2)	106(1)
O(2)	−947(4)	2 152(2)	4 737(2)	110(1)

Table 2. Selected bond lengths (Å)

S(1)–C(2)	1.824(2)	S(2)–C(6)	1.780(2)
C(2)–C(3)	1.527(3)	C(3)–S(3)	1.835(2)
C(3)–C(4)	1.484(3)	S(3)–C(15)	1.784(2)
C(4)–C(5)	1.319(3)	C(4)–N	1.449(4)
C(5)–S(1)	1.710(3)	N–O(1)	1.211(5)
C(2)–S(2)	1.832(2)	N–O(2)	1.228(5)

Table 3. Selected bond angles (°)

S(1)–C(2)–C(3)	106.6(1)	C(5)–C(4)–N	123.0(2)
C(2)–C(3)–C(4)	104.2(2)	C(4)–N–O(1)	117.8(3)
C(3)–C(4)–C(5)	116.4(2)	C(4)–N–O(2)	118.1(3)
C(4)–C(5)–S(1)	114.2(2)	O(1)–N–O(2)	124.1(3)
C(5)–S(1)–C(2)	90.7(1)	C(2)–S(2)–C(6)	102.3(1)
S(1)–C(2)–S(2)	105.1(1)	S(2)–C(6)–C(7)	120.9(3)
C(3)–C(2)–S(2)	113.6(1)	S(2)–C(6)–C(11)	118.2(2)
C(2)–C(3)–S(3)	112.1(1)	C(3)–S(3)–C(15)	102.1(1)
C(4)–C(3)–S(3)	107.1(2)	S(3)–C(15)–C(16)	118.5(2)
C(3)–C(4)–N	120.4(2)	S(3)–C(15)–C(20)	120.7(2)

half-chair and an envelope conformation respectively. Therefore the conformation of the ring can be better described as a half-chair with a pseudo-two-fold axis running through atom C(5) and the midpoint of the C(2)–C(3) bond (Figure 2).

To our knowledge, very few crystal-structure determinations have been performed so far on comparable 2,3-dihydrothiophene derivatives. In 2,5-dimethyl-*trans*-2,3-dimorpholino-4-nitro-2,3-dihydrothiophene[18] the puckering of the thiophene ring is somewhat less remarkable, the torsion angles ranging between +20 and −24°; anyway, the conformation of the ring can be described as a half-chair within an asymmetry parameter ΔC_2 = 4.0°, identical with that found for (**2**). An analogous result (half-chair within a ΔC_2 asymmetry parameter of 3.9°) has been found in a spiro-2,3-dihydrothiophene derivative,[19] thus further substantiating a fairly constant conformation of the 2,3-dihydrothiophene ring.*

However, for compound (**2**) the whole nitroethylene system C(3),C(4),C(5),S(1),N,O(1),O(2), is not far from planarity,

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* As expected on the basis of its *ortho*-quinonoid structure, the dihydrothiophene ring in 2-(diethylamino)-5-(t-butylimino)-4-(*p*-tolylsulphonylimino)-3-methyl-4,5-dihydrothiophene is planar (deviations within 0.013 Å).[20]

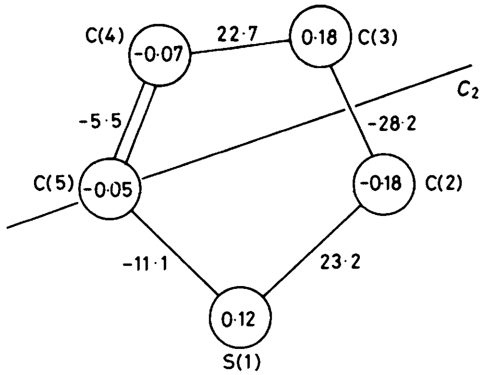


Figure 2. The puckering of the 2,3-dihydrothiophene ring. Figures in the circles give the distance (Å) from the least-squares plane calculated for the five atoms. Values of torsion angles (°) along the ring are also reported

the deviations of each of the defining atoms from the corresponding least-squares plane being within 0.034 Å.* This structural result, even if it cannot be taken for granted in the free molecule, is in agreement with an effective conjugation between the nitro group and the cyclic sulphur atom. This conjugative effect, which contributes to the enhancement of the acidity of H(2), is further substantiated by an examination of the length of the various C–S bonds present in the molecule. Whereas C(2)–S(1), C(2)–S(2), and C(3)–S(3) (average bond length 1.830 Å) show some stretching with respect to the accepted C–S single-bond distance of 1.80—1.81 Å,[21,22] the C(6)–S(2) and C(15)–S(3) bonds (average length 1.782 Å) display a noticeable shortening, which is far more evident for the C(5)–S(1) bond (1.710 Å). According to an early proposal[23] the mobile bond order is 0.20 for C(6)–S(2) and C(15)–S(3), and 0.64 for C(5)–S(1).

Bond distances and angles in the nitro group and in both mesitylthio groups are normal. Oxygen and methyl carbon atoms are remarkably affected by anisotropic vibration. With respect to the mean plane of the nitroethylene moiety, the two phenyl groups (which are planar within 0.008 and 0.015 Å) form a dihedral angle of 28.0 and −31.2°, respectively.

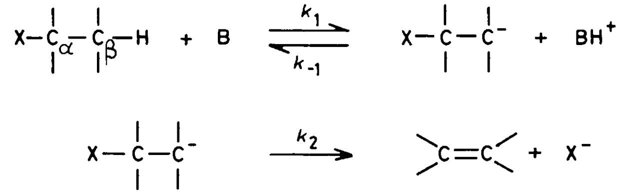
Intermolecular contacts are in the normal range. There are only four contacts shorter by 0.1 Å or more than the sum of van der Waals radii (S 1.85, C 1.7, CH_3 2.0, N 1.5, O 1.4, H 1.2 Å):[24]

Atom in x, y, z	To atom	In position	Distance (Å)
S(1)	C(5)	$-x, -y, 1 - z$	3.44
S(1)	C(13)	$1 - x, -\frac{1}{2} + y, \frac{3}{2} - z$	3.74
S(3)	C(12)	$-1 + x, y, z$	3.67
C(21)	C(23)	$-x, -\frac{1}{2} + y, \frac{3}{2} - z$	3.55

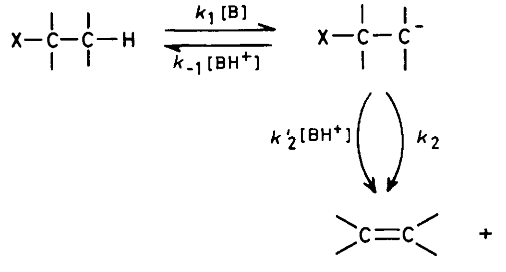
Most structural calculations were performed using the SHELX 76 program.[25]

Kinetic Investigation.—Kinetic data for the Bu^n_3N-promoted elimination from (**2**) in toluene are collected in Tables 4 and 5. The choice of a sterically hindered tertiary amine in a non-hydroxylic solvent was due mainly to the need to minimize the competitive nucleophilic attack to the activated C(4)–C(5) double bond of (**2**), although the relatively low reactivity of this system forced us to employ high amine concentrations.

The reaction is first-order with respect to (**2**), and the overall second-order rate constant (k_{II}/ l mol^{-1} s^{-1}), obtained as the ratio between the experimental pseudo-first-order rate constant



Scheme 2.



Scheme 3.

(k_{obs}/s^{-1}) and amine concentration ([B]/M), shows a slight dependence on [B] in the concentration range explored

$$k_{II} = k_o + k_c[B] \qquad \text{(i)}$$

[equation (i)]. However, the low ($\leqslant 1$ l mol^{-1}) $k_c:k_o$ values (a criterion generally accepted for the exclusion of catalysis in, for example, nucleophilic aromatic substitutions[26]), the aprotic apolar nature of the solvent, and the relatively high amine concentrations employed suggest a medium effect for such a mild rate enhancement.†

The stepwise nature of the present *syn*-elimination is revealed by the very weak dependence of the rate constant on the temperature and by the absence of any appreciable substrate kinetic isotope effect in the whole [B] range explored (Table 4). The former result, which is brought about by a very low activation energy (E_a 1.8 kcal mol^{-1}), can be readily rationalised on the grounds of a complex rate constant for a mechanism in which the slow step is preceded by at least one fast equilibrium.[28] The latter result would, at least in principle, be compatible with a very early or a very late transition state[1e,29] for the concerted *E*2 process, but it is most easily explained by a pre-equilibrium deprotonation, with the primary kinetic isotope effect corresponding to the equilibrium isotope effect for such deprotonation.[1e,30] It must be pointed out that the kinetic isotope effect reported herein is actually a combination of both a primary (β-D) and a secondary (α-D) effect; anyway, as secondary deuterium isotope effects are known to be small,[31] the presence of any such effect in our system would entail at most a small primary effect, well within the range of equilibrium isotope effects.[1e] It should be clear that the above results likewise disfavour, among the recognised variants of the carbanionic, stepwise, elimination process,[1-3] the ($E1cB)_I$ pathway {Scheme 2, $k_{-1}[BH^+] \ll k_2$, and equation (ii)}, whose

$$k_{obs} = k_1[B] \qquad \text{(ii)}$$

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* Accordingly, the C(4)–C(5)–H(5) bond angle assumes the large value of 130° to allow a normal H(5) ••• O(2) non-bonding distance (2.64 Å).

† Fractional (higher than one) orders in base have already been observed for both *syn*- and *anti*-eliminations from 2,3-dihalogeno-2,3-dihydrobenzofurans (**5**)[8] and 1,2-dihalogenoacenaphthenes[27] promoted by potassium alkoxide in EtOH or Bu^tOH; such orders have been attributed to the formation of more effective catalytic species (contact ion pairs or ionic aggregates) at high alkoxide concentrations.

Table 4. Kinetic data for the reaction between (**2**) and $Bu^n{}_3N$ in toluene[a]

T 25.0 °C

$[Bu^n{}_3N]$/M	0.25	0.25[b]	0.49	0.74	0.82	0.82[c]	0.99	1.23	1.23[b]	1.23[d]
10^4k_{II}/l mol^{-1} s^{-1}	1.06	1.05	1.36	1.54	1.68	1.67	1.73	1.96	2.04	2.03

$k_{II} = 0.88 \times 10^{-4} + 0.89 \times 10^{-4}[Bu^n{}_3N]$ (n = 6; r = 0.990)

T 34.5 °C[e]

$[Bu^n{}_3N]$/M	0.49	0.82	1.23
10^4k_{II}/l mol^{-1} s^{-1}	1.38	1.68	2.05

$k_{II} = 0.94 \times 10^{-4} + 0.91 \times 10^{-4}[Bu^n{}_3N]$ (n = 3; r = 1.0)

T 50.0 °C[e]

$[Bu^n{}_3N]$/M	0.49	0.82	1.23
10^4k_{II}/l mol^{-1} s^{-1}	1.49	1.79	2.08

$k_{II} = 1.11 \times 10^{-4} + 0.79 \times 10^{-4}[Bu^n{}_3N]$ (n = 3; r = 0.997)

E_a 1.8 kcal mol^{-1}
$\Delta H^{\ddagger}{}_{25\,°C}$ 1.2 kcal mol^{-1}
$\Delta S^{\ddagger}{}_{25\,°C}$ −73.04 cal mol^{-1} K^{-1}

[a] [(**2**)] 1.10×10^{-4}M if not otherwise stated. [b] [2,3,5-trideuterio-(**2**)] 1.30×10^{-4}M. [c] [(**2**)] 0.90×10^{-4}M. [d] [(**2**)] 3.37×10^{-4}M. [e] Rate values not corrected for solvent expansion.

Table 5. Effect of added $Bu^n{}_3NH^+Cl^-$ on the rate of the reaction between (**2**) and $Bu^n{}_3N$ in toluene at 25 °C[a]

$10^4[Bu^n{}_3NH^+Cl^-]$/M	0	2.45	6.10	12.00
10^4k_{II}/l mol^{-1} s^{-1}	1.96	1.97	1.95	1.84

[a] [(**2**)] 1.10×10^{-4}M; $[Bu^n{}_3N]$ 1.23M.

main feature is represented by a sizable substrate primary kinetic isotope effect.[1]

As for the $(E1cB)_R$ mechanism {Scheme 2, $k_{-1}[BH^+] \gg k_2$, and equation (iii)} we must consider the absence of any

$$k_{obs} = \frac{k_1[B]}{k_{-1}[BH^+]}k_2 \qquad \text{(iii)}$$

appreciable effect of BH^+ on the reaction rate: good pseudo-first-order plots (see Experimental section) are obtained for every single kinetic run and added $Bu^n{}_3NH^+Cl^-$ has only a minor retarding effect, hardly outside experimental error (Table 5). These results could still be reconciled with an $(E1cB)_R$ mechanism through free ions under the assumption that an acid-catalysed route to leaving-group departure overcomes the uncatalysed one (Scheme 3, $k'_2[BH^+] \gg k_2$). Such an assumption, not unreasonable from the nature of both the solvent and the leaving group, would lead to equation (iv), thus justifying

$$k_{obs} = \frac{k_1[B]}{k_{-1}}k'_2 \qquad \text{(iv)}$$

the absence of any BH^+ effect. Anyway, the failure to detect any D–H exchange in the unchanged substrate when the deuteriated substrate reacts with amine in the presence of $Bu^n{}_3NH^+$ Cl^- (see Experimental section) seems definitely to rule out the formation of a free carbanion.

Therefore we believe that the most likely pathway for the present system is represented by an $(E1cB)_{ip}$ mechanism (Scheme 4) with pre-equilibrium ion-pair formation ($k'_{-1} \gg k''_2$) and extensive internal return ($k''_2 \gg k_{exch}[BH^+]$) [equation (v)].

$$k_{obs} = \frac{k'_1[B]}{k'_{-1}}k''_2 \qquad \text{(v)}$$

Although not very common, the carbanion mechanism *via* ion pairs or tightly solvated anions (either irreversibly or reversibly formed[32a]) is today well recognised[1] both in protic solvents[32] and in media of low polarity.[33] Further substantiation of the proposed mechanism comes from the activation entropy, whose highly negative value (Table 4) is responsible for the low reactivity of the system: similar values are generally explained, in an aprotic medium, with the pre-equilibrium formation of highly polar intermediates from neutral reactants.[34]

The regiospecificity of the present elimination may find, in our opinion, a reasonable explanation in the different acidities of H(2) and H(3). Carbanion (**6**), formed along the reaction coordinate as an ion pair with $Bu^n{}_3NH^+$, is a dithioacetal anion, further stabilised by direct conjugation of the cyclic sulphur atom with the nitro group. The stability of such anions is well known,[35] and most likely overcomes that of a carbanion like (**7**), stabilised by the interaction with only one adjacent sulphur atom[35] and by the proximity of a nitro group which is, however, already engaged in conjugation. Furthermore, it seems likely that the acidity of H(2) in (**2**) is also a factor in the opposite regiospecificity of our system with respect to (**4**)[6,7] and (**5**).[8,9]

Finally, the acidity of H(2), together with the nature of the leaving group,[*] bears upon the mechanistic choice (stepwise carbanionic pathway) of our system.[1,37] Current views of chemical reactivity attribute a fundamental role to the lifetime of possible intermediates for the pathway chosen;[4,38] applied to alkene-forming eliminations such views foresee a shift towards the right of the mechanistic spectrum in Scheme 5 with

$$\begin{matrix}\text{carbocationic}\\ \text{pathways}\end{matrix} - E2 - (E1cB)_I - (E1cB)_{ip} - (E1cB)_R - (E1)_{anion}$$

Scheme 5.

increasing carbanion stability. Accordingly, the stability of (**6**) with respect to both reprotonation and leaving-group expulsion makes a concerted process unnecessary and allows (**6**) a lifetime

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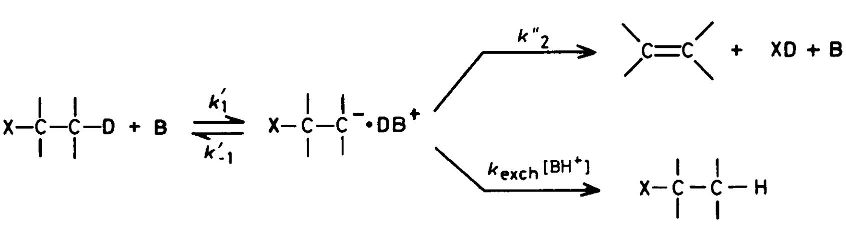
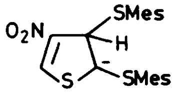
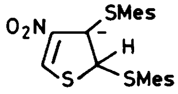
[*] Arylthio groups are generally regarded not to be very good leaving groups in alkene-forming eliminations as compared, for example, to halogens or 'onium groups.[1,36]



Scheme 4.



(6)



(7)

long enough for its equilibration with the substate ($k'_{-1} \gg k''_2$) but not with the medium ($k''_2 \gg k_{exch}[BH^+]$).

Experimental

^{1}H N.m.r. spectra were obtained on a Varian XL 100 instrument (solvent $CDCl_3$; standard Me_4Si). Kinetic experiments were carried out using a Perkin-Elmer 554 spectrophotometer.

Material.—3,4-Dinitrothiophene (**1**), 2,5-dideuterio-3,4-dinitrothiophene (96% deuteriated), 2,3-bis(mesitylthio)-4-nitro-2,3-dihydrothiophene (**2**), 2-(mesitylthio)-4-nitrothiophene (**3**), and mesitylenethiol were prepared as previously reported.[5] Tributylammonium chloride was prepared according to a literature method.[39] CH_3OD was a commercial (Merck) product. Tributylamine (Schuchardt) was fractionally distilled from KOH and successively from CaH_2, b.p. 90—91 °C at 10 mmHg (lit.,[40] 91—92 °C at 9 mmHg), and stored over KOH. Toluene (Hoechst) was refluxed over sodium and distilled before use.

2,3,5-*Trideuterio*-2,3-*bis*(*mesitylthio*)-4-*nitro*-2,3-*dihydrothiophene* [2,3,5-*Trideuterio*-(**2**)].—A solution of sodium mesitylenethiolate (3.6 mmol) in CH_3OD (6 ml) was added to a solution of 2,5-dideuterio-3,4-dinitrothiophene (1.25 g, 7.1 mmol) in the same solvent (18 ml). After 1 h at room temperature the solution was cooled in acetone–CO_2 and most unchanged substrate (0.7 g) was recovered by filtration. The filtered solution was evaporated at room temperature. The residue was treated with CH_2Cl_2 (2 ml), $NaNO_2$ was filtered off, and the solution chromatographed on silica gel with CH_2Cl_2–light petroleum (b.p. 40—70 °C) (1:2.5) as eluant to give 2,3,5-trideuterio-(**2**) (0.4 g, 51%), uncorrected m.p. 129—130 °C [from benzine (b.p. 80—100 °C)], identical with that of the undeuteriated compound (**2**).[5] Deuteriation at C(2) was 88% (^{1}H n.m.r.).

X-*Ray Crystallography.*—A crystal of (**2**) was ground in a sphere (*r* 0.24 mm) and sealed in a thin glass capillary. Intensities were measured on a CAD4 diffractometer equipped with graphite monochromator.

Crystal data. $C_{22}H_{25}NO_2S_3$, $M = 431.6$. Monoclinic, $a = 7.722(1)$, $b = 16.665(2)$, $c = 17.318(2)$ Å, $\beta = 92.13(1)°$, $V = 2\,227$ Å^3 (by least-squares refinement on diffractometer angles for 25 automatically centred reflections, $\lambda = 0.710\,69$ Å), space group $P2_1/c$, $Z = 4$, $D_x = 1.29$ g cm^{-3}, μ(Mo-K_α) = 3.42 cm^{-1}.

Intensities of 5 065 independent reflections [2 990 with $F > 3\sigma(F)$] were collected in the range $3 \leqslant \theta \leqslant 27.5°$ in the ω—θ scan mode, scan width 0.80°, scan speed 1.8—10° min^{-1}. One reference reflection was monitored periodically to test the crystal stability, and three to test the crystal orientation. The data were corrected for Lorentz and polarization effects.

Structure solution and refinement. The structure was solved by direct methods using the SHELX 76 system of programs.[25] The 'best' *E*-map showed unambiguously all but six non-hydrogen atoms; the six lacking atoms were located by means of a difference synthesis.

Refinement was accomplished by full-matrix isotropic, and then anisotropic least squares[25] on C, N, O, and S atoms. Four hydrogen atoms belonging to methyl groups were set in calculated positions; all the other hydrogen atoms were recognised on difference maps. They were not refined, but included in the structure factor calculations with an isotropic temperature factor equal to the $U_{equivalent}$ value for the bonded carbon atom. The weighting function was of the form $w = [\sigma^2(F_0) + g\,F_0{}^2]^{-1}$. Zero weight was given to the very strong 200 and -202 reflections, as presumably affected by extinction. In the last cycle (2 988 observations, 253 parameters) the highest shift was less than 0.5σ, most shifts being less than 0.2σ. The factor R converged to 0.037, with $g = 0.0060$. A final difference map showed no significant features, the electron density values ranging between $+0.25$ and -0.26 e Å^{-3}.

Tables of hydrogen atom co-ordinates, anisotropic thermal parameters, and additional bond distances and angles have been deposited as Supplementary Publication No. SUP 56241 (6 pp.).*

Kinetics.—Kinetic runs were initiated by the addition of a negligible volume of a stock solution of substrate in toluene to base solution (2 ml) in a cell placed in the thermostatted compartment of a spectrophotometer. The reaction was followed by recording the absorbance (*A*) decrease at λ 340 nm (reference air). Pseudo-first-order conditions were always employed and pseudo-first-order rate constants (k_{obs}/s^{-1}) were obtained from $\lg(A_t - A_\infty)$ *versus t* plots (which always showed good linearity up to at least three half-lives). The u.v. spectrum of the final mixture was always identical, within experimental error, with that expected for a 100% conversion into (**3**). Each value reported in Tables 4 and 5 is the mean of at least two independent runs, reproducibility always being within ±2%.

D–H *Exchange Experiment.*—The experiment was performed in conditions similar to those used for the kinetic runs, with [2,3,5-trideuterio-(**2**)] 0.64×10^{-2}M, [$Bu^n{}_3NH^+Cl^-$] 1.31M, and [$Bu^n{}_3N$] 0.84M. The reaction was quenched after *ca.* 13% conversion of substrate (u.v.) with 10% HCl. The organic layer was washed with water, dried (Na_2SO_4), and evaporated, and the residue was chromatographed on silica gel with CH_2Cl_2–light petroleum (b.p. 40—70 °C) (1:2.5) as eluant. The recovered substrate showed (^{1}H n.m.r.) the same deuteriation as the starting material.

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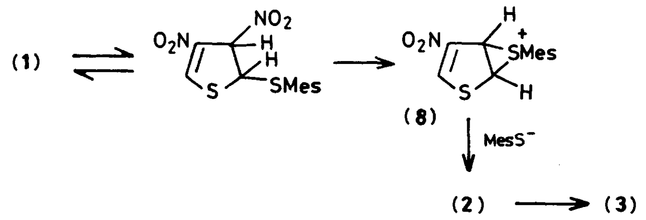
* For details, see Instructions for Authors, *J. Chem. Soc., Perkin Trans. 2*, 1985, Issue 1.

Appendix

Proposed Mechanism of Formation of (**2**) *from* (**1**).—For the overall (**1**) ⟶ (**3**) *cine*-substitution reaction we proposed[5] a complex pathway through successive addition and elimination steps. A relatively simpler alternative route [addition–substitution–elimination (ASE) mechanism[41]] (Scheme 6) could involve the formation of the episulphonium ion (**8**)[42] as precursor of (**2**) and would perhaps better justify its exclusive *trans*-configuration. In such a pathway, the saturated diastereoisomeric 2,3,5-tris(mesitylthio)-4-nitrotetrahydrothiophenes, isolated in the presence of excess of MesSH,[5] would be side products equilibrated with (**2**). What remains firm in the (**1**) ⟶ (**3**) process, however, is the intermediacy of (**2**),[5] while doubts have been raised on the intermediacy of pyrrolines (**4**; X = Y = piperidino or morpholino) in the *cine*-substitution reaction between 1-methyl-3,4-dinitropyrrole and piperidine or morpholine in acetonitrile.[7b]



Scheme 6.

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