cine-Substitution in the Thiophen Series. Mechanism of the Reaction of 3,4-Dinitrothiophen with Sodium Arenethiolates in Methanol

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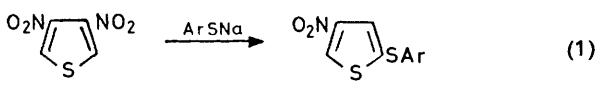
The mechanism of *cine*-substitution of 3,4-dinitrothiophen (1) with sodium arenethiolates in methanol, which yields 2-arylthio-4-nitrothiophens (2), has been studied. By t.l.c. and ^{1}H n.m.r. techniques it was found that, besides the final sulphide (2), 3-nitrothiophen, diaryl disulphide, and three other compounds were present in amounts depending on the molar ratio of the reactants and on the experimental conditions. Using sodium 2,4,6-trimethylbenzenethiolate as nucleophile it was possible to isolate the other three components of the mixture, which were identified as two stereoisomers [(3) and (4)] of 4-nitro-2,3,5-tris-(2,4,6-trimethylphenylthio)tetrahydrothiophen and as 4-nitro-2,3-bis-(2,4,6-trimethylphenylthio)-2,3-dihydrothiophen (5). Evidence was found that compounds (3)—(5) are intermediates in the transformation of the substrate (1) into the final product. A mechanism involving a set of consecutive addition–elimination steps is suggested to account for the *cine*-substitution process.

THE *cine*-substitution reaction, in which the entering group takes an *ortho*-position with respect to that vacated by the leaving group, is by far the most usual among aromatic nucleophilic substitutions proceeding with rearrangement.[1,2] Two mechanisms are generally operative, *viz.* elimination–addition (*EA*) and anomalous addition–elimination (AE_a).[1e,f]

Continuing previous research in the field of thiophen derivatives,[3] we have further investigated the reaction[3a] of 3,4-dinitrothiophen (1) with sodium arenethiolates in



(1) (2) a; Ar = 2,4,6−$Me_3C_6H_2$ (1)

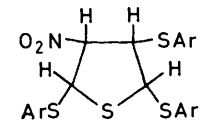
methanol, which affords 2-arylthio-4-nitrothiophen (2) [equation (1)], in order to establish the mechanism of this *cine*-substitution.

The thiol used for this investigation was, for practical reasons, 2,4,6-trimethylbenzenethiol (TMBT). Experiments with other arenethiols gave similar results with the only disadvantage that the compounds formed were generally unstable and/or oils difficult to purify.

RESULTS AND DISCUSSION

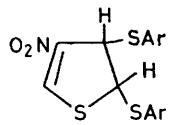
When a methanol solution of equimolar amounts of dinitrothiophen (1), sodium 2,4,6-trimethylbenzenethiolate (Na-TMBT), and TMBT was heated under reflux for 8 h and the reaction mixture worked up as previously reported,[3a] 4-nitro-2-(2,4,6-trimethylphenylthio)thiophen (2a) was obtained in 75% yield together with small amounts (<10%) of 3-nitrothiophen (see later). The presence of free TMBT was essential to improve the yield of sulphide (2a) as the reagent was destroyed by the formation of some bis-(2,4,6-trimethylphenyl) disulphide even under nitrogen.

If the above reaction was carried out at room temperture, the formation of sulphide (2a) was very slow and a small quantity of oil separated. From this oil it was possible to isolate a crystalline material, formulated as 4-nitro-2,3,5-tris-(2,4,6-trimethylphenylthio)tetrahydrothiophen (3) on the basis of analytical and ^{1}H n.m.r. data.† The ^{1}H n.m.r. spectrum of the crude oil



(3) and (4)

Ar = 2,4,6−$Me_3C_6H_2$



(5)

showed also the presence of a minor amount of compound (4), subsequently identified (see below) as a stereoisomer of the tetrahydrothiophen (3). The ratio (3) : (4) was 5.7 : 1. T.l.c. of the reaction mother-liquor revealed a large quantity of the starting material (1), and traces of bis-(2,4,6-trimethylphenyl) disulphide, the sulphide (2a), and another yellow compound (see later).

Other experiments (all at room temperature) were performed with different molar ratios of the reactants. Use of a substrate : Na-TMBT molar ratio of 1 : 1 and a 10-fold excess of free TMBT gave a larger amount of the oil and hence the yield of compounds (3) and (4) was improved. In contrast, when the reaction was performed in the absence of free TMBT and with a substrate : Na-TMBT molar ratio of 2 : 1 no separation of oil occurred. T.l.c. of the reaction mixture showed the formation of the same yellow compound observed in the

† The structure of (3) and of the other compounds reported was established by comparison of ^{1}H n.m.r. spectra of ordinary and deuteriated products (see Experimental section).

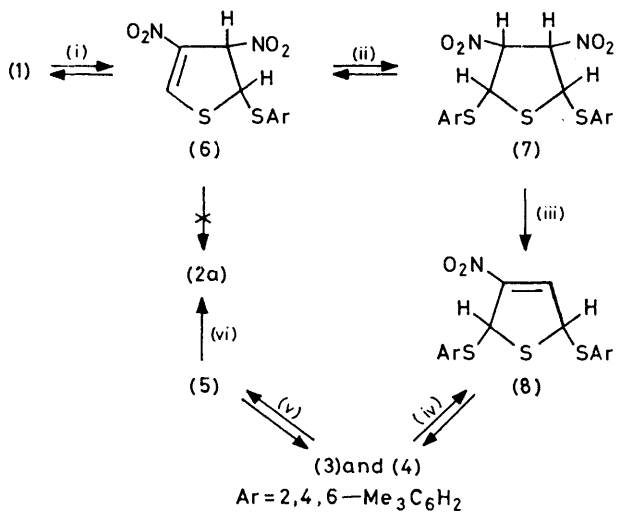
[1] (*a*) J. F. Bunnett and R. E. Zahler, *Chem. Rev.*, 1951, **49**, 273; (*b*) J. F. Bunnett, *Quart. Rev.*, 1958, **12**, 1; (*c*) H. Heaney, *Chem. Rev.*, 1962, **62**, 81; (*d*) G. Wittig, *Angew. Chem. Internat. Edn.*, 1965, **4**, 731; (*e*) T. Kauffmann, *ibid.*, p. 543; (*f*) F. Pietra, *Quart. Rev.*, 1969, **23**, 504.

[2] (*a*) R. W. Hoffmann, 'Dehydrobenzene and Cycloalkynes,' Academic Press, New York, 1967; (*b*) J. Miller, 'Aromatic Nucleophilic Substitution,' Elsevier, Amsterdam, 1968; (*c*) H. J. Shine, 'Aromatic Rearrangements,' Elsevier, Amsterdam, 1967.

[3] (*a*) C. Dell'Erba, D. Spinelli, and G. Leandri, *Gazzetta*, 1969, **99**, 535; (*b*) M. Novi, G. Guanti, C. Dell'Erba, and D. Spinelli, *J.C.S. Perkin I*, 1976, 2264; (*c*) F. Sancassan, M. Novi, G. Guanti, and C. Dell'Erba, *J. Heterocyclic Chem.*, 1975, **12**, 1083, and previous papers in the series.

preceding experiments, which at short reaction times was the only product and later vanished as the amount of sulphide (2a) increased [only a faint spot attributable to the compounds (3) and/or (4) was observed after some time]. By stopping the reaction after 1 h the yellow compound was isolated by column chromatography and identified, on the basis of analytical and ^{1}H n.m.r. data, as 4-nitro-2,3-bis-(2,4,6-trimethylphenylthio)-2,3-dihydrothiophen (5). The yield of compound (5) based on reacted substrate was practically quantitative.

Finally we repeated reaction (1) at reflux (1 : 1 : 1 substrate : Na-TMBT : TMBT molar ratio), stopping it before completion. Column chromatography gave [together with bis-(2,4,6-trimethylphenyl) disulphide, the sulphide (2a), the dihydrothiophen (5), and unchanged starting material] a mixture of compounds (3) and (4)



SCHEME 1

[from which the main component (4) could be isolated and identified as a stereoisomer of (3) (mixed m.p. depressed, identical t.l.c. R_F value and analytical data, and a similar ^{1}H n.m.r. pattern with different chemical shifts and coupling constants)] and 3-nitrothiophen. The formation of this last compound is probably due to thermal decomposition of the dihydrothiophen (5); in fact, as observed separately, compound (5), when refluxed in methanol, decomposed to give 3-nitrothiophen and bis-(2,4,6-trimethylphenyl) disulphide.

Experiments on the influence of light and azobenzene [4] on reaction (1) were also carried out in order to test the occurrence of electron-transfer processes, but no significant effect on the yield and on the rates of formation of the various compounds was detected.

A reasonable mechanism is shown in Scheme 1. The substrate (1) first undergoes a reversible addition of one molecule of TMBT to the 2,3 double bond to give the intermediate (6) [step (i)], which by successive addition of a second molecule of thiol gives the tetrahydrothiophen (7) [step (ii)]. This compound, can then undergo an irreversible elimination of nitrous acid [step (iii)] (a standard reaction of *vic*-dinitroalkanes [5a]) to furnish the 2,5-dihydrothiophen (8), which by fast addition of a third molecule of TMBT may be reversibly transformed into isomers (3) and (4) [step (iv)]. These eventually, by successive elimination of two molecules of TMBT, yield the sulphide (2a) through the dihydrothiophen (5) [steps (v) and (vi)].

In principle the addition product (6) might undergo either a nitrous acid elimination to give the sulphide (2a) directly (according to an AE_a mechanism) [1e,f] or a TMBT addition to the 4,5 double bond to furnish tetrahydrothiophen (7) (a standard reaction of nitroalkenes [5b,6]). The occurrence of the second pathway is supported by the isolation of compounds (3)—(5), which are not by-products of a side-reaction but precursors of the sulphide (2a) as supported by their irreversible * and quantitative transformation into (2a) when refluxed separately in methanol with traces of Na-TMBT. Moreover the fact that, under certain conditions, the total transformation of substrate (1) into dihydrothiophen (5) without traces of sulphide (2a) was observed, seems to suggest that the AE_a mechanism does not contribute significantly to formation of the *cine*-substitution product (2a), and that the only operative mechanism proceeds through the steps (i)—(vi). As found for Michael and Michael-type addition reactions to activated cycloalkenes,[7] it is most likely that the steps leading to compounds (3) and (4) are subject either to kinetic or thermodynamic control. The different values observed for (3) : (4) ratios as the experimental conditions are varied, are consistent with a larger stability and a lower rate of formation of the isomer (4) with respect to (3). To test this point the reactions of compounds (3)—(5) were studied separately with an excess of TMBT and a catalytic amount of Na-TMBT in methanol † at room temperature. In all three cases a mixture of compounds (3) and (4) was obtained in which the latter was always the main component. In the proposed scheme the configurations of the chiral centres in the various intermediates are not specified. However, among the various possible stereoisomers which can form in the course of the reaction, only one compound corresponding to the 4-nitro-2,3-bis-(2,4,6-trimethylphenylthio)-2,3-dihydrothiophen structure and only two corresponding to

* The irreversibility of the formation of compound (2a) was confirmed by the fact that if it was allowed to stand (or even refluxed) for a long period in methanol with Na-TMBT and TMBT, it was recovered practically unchanged (as previously reported,[3b] only a slight decomposition caused by the heating and by the basic medium was detected).

† Addition of dioxan (see Experimental section) was necessary in the case of the reaction of compounds (3) and (4) owing to their low solubility in methanol.

[4] J. A. Soltewicz and T. M. Oestreich, *J. Amer. Chem. Soc.*, 1973, **93**, 6863 and references cited therein.

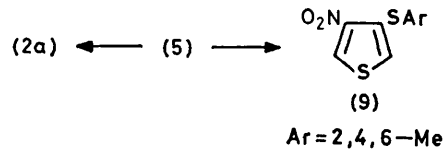
[5] V. V. Perekalin, ' Unsaturated Nitro Compounds,' ed. Israel Program for Scientific Translation, Jerusalem, 1964, (*a*) ch. 4; (*b*) ch. 5.

[6] H. H. Baer and L. Urbas, ' The Chemistry of the Nitro and Nitroso Group,' ed. H. Fuer, Wiley, New York, 1970, p. 181.

[7] R. A. Abramovitch, M. M. Rogic, S. S. Singer, and N. Venkatesvaran, *J. Org. Chem.*, 1972, **37**, 3577 and references cited therein.

the 4-nitro-2,3,5-tris-(2,4,6-trimethylphenylthio)tetrahydrothiophen structure were revealed by the analytical techniques used (^{1}H n.m.r. and t.l.c.).

From the dihydrothiophen (5) two different eliminations of TMBT are in principle possible, leading respectively to the sulphide (2a) and to 3-(2,4,6-trimethylphenylthio)-4-nitrothiophen (9) (Scheme 2). The fact



SCHEME 2

that in all experiments no trace of the sulphide (9) was detected means that only one type of elimination actually occurs with (5),* for reasons which are currently not completely clear.

We conclude that the proposed reaction sequence is the most reasonable mechanism which can explain the formation of compounds (3)—(5) and their transformation into the final product. The most striking feature of this mechanism is the route followed by the addition product (6) to give the sulphide (2a). Surprisingly this intermediate is converted into the *cine*-substitution product through a complex and unusual pathway involving a set of consecutive addition–elimination steps rather than through the simpler route expected on the basis of the AE_a mechanism (nitrous acid elimination).† An alternative route involving a heteroaryne intermediate (*EA* mechanism) seems unlikely for the following reasons: (*a*) it does not explain the formation of compounds (3)—(5); (*b*) the nitro-group is not a good leaving group for aryne formation;[1b,8] (*c*) arynes in five-membered rings[9] and in methanol solvent[10] are generated with difficulty and; (*d*) no trace of methoxy-derivatives, which could form by attack of methanol on the heteroaryne intermediate, was found.

EXPERIMENTAL

Light petroleum refers to the fraction of b.p. 30—50 °C. Organic extracts were dried over sodium sulphate and solvents were removed under reduced pressure below 50 °C. Known products were identified by comparison of their m.p.s, chromatographic data, and ^{1}H n.m.r. spectra with those of authentic samples. ^{1}H N.m.r. spectra of solutions in $CDCl_3$ were obtained on a Varian XL 100 instrument ($SiMe_4$ as internal reference). ^{1}H N.m.r. identification of all the new compounds was performed with the aid of products derived from reactions between deuteriated reagents: run A refers to the reaction of 2,5-dideuterio-3,4-dinitrothiophen with sodium 2,4,6-trimethylbenzenethiolate (Na-TMBT) and 2,4,6-trimethylbenzenethiol (TMBT) in MeOH, and run B to the reaction of 3,4-dinitrothiophen with Na-TMBT and *S*-deuteriated TMBT in MeOD.

Materials.—3,4-Dinitrothiophen[11] and TMBT[12] were prepared as reported in the literature. Deuteriated solvents were commercial (Merck) products.

2,5-Dideuterio-3,4-dinitrothiophen.— 2,5-Dibromo-3,4-dinitrothiophen[13] (5 g, 15 mmol) was dissolved in CH_3CO_2D (20 ml) and copper powder (4 g, 63 mg atom) was added in portions with stirring. The mixture was heated under reflux for 30 min. The solvent was distilled off and the residue extracted (Soxhlet) with benzene (100 ml) for 5 h. The benzene solution was filtered through a silica gel column (15 × 2 cm); addition of light petroleum gave, *2,5-dideuterio-3,4-dinitrothiophen*, m.p. 95 °C (lit.,[11] 94—95 °C for non-deuteriated material). The ^{1}H n.m.r. spectrum, in the presence of 0.5 mol. equiv. of αα′-dichloro-*p*-xylene as an unlabelled reference, showed that only traces of non-deuteriated compound were present.

Reactions of 3,4-Dinitrothiophen (1) *with* Na-*TMBT.*—(a) *At room temperature in the presence of free TMBT and stopped before completion.* A solution of dinitrothiophen (1) (1 g, 5.75 mmol), Na-TMBT (5.75 mmol), and TMBT (57.5 mmol) in methanol (15 ml) was kept at room temperature. An insoluble oil which separated after 6 h was isolated by decantation, washed with methanol (4 × 4 ml), and dissolved in hot light petroleum. From this solution, by cooling and scratching, a white crude solid crystallized. Two crystallizations from methanol–dioxan afforded pure *4-nitro-2,3,5-tris-(2,4,6-trimethylphenylthio)tetrahydrothiophen* (3) (0.98 g, 29%), m.p. 140—142 °C (Found: C, 63.8; H, 6.3; N, 2.45; S, 21.8. $C_{31}H_{37}NO_2S_4$ requires C, 63.8; H, 6.35; N, 2.4; S, 21.95%); τ 3.13br, 3.25br, and 3.28br (each 2 H, s, $Me_3C_6H_2S$), 4.77 (1 H, d, *J* 7.0 Hz, 5-H), 5.16 (1 H, dd, *J* 7.0 and 4.9 Hz, 4-H), 5.70 (1 H, d, *J* 3.6 Hz, 2-H), 5.91 (1 H, dd, *J* 4.9 and 3.6 Hz, 3-H), 7.55br and 7.67br (each 6 H, s, 2 × CH_3), and 7.7br (15 H, s, 5 × CH_3).

The ^{1}H n.m.r. spectrum of the crude oil showed the presence of a minor amount of compound (4), subsequently identified (see below) as a stereoisomer of (3) [ratio (3) : (4) *ca.* 1 : 5.7].

The same experiment, repeated with equimolar amounts of the reactants, gave results similar to those described above but with a lower yield of compound (3).

Run A afforded the corresponding dideuteriated product (deuteriation >90%) as shown by the ^{1}H n.m.r. spectrum, where the τ 4.77 and 5.70 resonances could hardly be detected and the τ 5.16 and 5.91 ones were sharp doublets. This result shows that the τ 4.77 and 5.70 resonances are due to protons bonded to two carbon atoms α to the ring

* Independent experiments established that compound (9) does not isomerize to the sulphide (2a) under typical reaction conditions.

† Preliminary results show that a mechanism similar to the one proposed here also probably operates in the *cine*-substitution of 4-nitro-3-thienyl phenyl sulphone with sodium arenethiolates.[3b]

[8] Ref. 2*a*, p. 66; P. Buck, *Angew. Chem. Internat. Edn.*, 1969, **8**, 120.

[9] Ref. 2*a*, p. 293; G. Witting and M. Rings, *Annalen*, 1968, **719**, 127; M. G. Reinecke and H. W. Adickes, *J. Amer. Chem. Soc.*, 1968, **90**, 511; D. A. de Bie, H. C. van der Plas, and G. Geurtsen, *Rec. Trav. chim.*, 1971, **90**, 594; M. G. Reinecke and T. A. Hollingworth, *J. Org. Chem.*, 1972, **37**, 4257; D. A. de Bie, H. C. van der Plas, G. Guertsen, and K. Nijdam, *Rec. Trav. chim.*, 1973, **92**, 245; M. G. Reinecke, W. B. Mohr, H. W. Adickes, D. A. de Bie, H. C. van der Plas, and K. Nijdam, *J. Org. Chem.*, 1973, **38**, 1365; M. G. Reinecke and R. H. Walter, *J.C.S. Chem. Comm.*, 1974, 1044.

[10] T. Kauffmann, J. Hansen, K. Udluft, and R. Wirtwein, *Angew. Chem. Internat. Edn.*, 1964, **3**, 650; T. Kauffmann, R. Nurnberg, and K. Udluft, *Chem. Ber.*, 1969, **102**, 1177.

[11] A. H. Blatt, N. Gross, and E. W. Tristram, *J. Org. Chem.*, 1957, **22**, 1588.

[12] Chi Hua Wang and S. G. Cohen, *J. Amer. Chem. Soc.*, 1957, **79**, 1924.

[13] R. Mozingo, S. A. Harris, D. E. Wolf, C. E. Hoffhine, N. R. Easton, and K. Folkers, *J. Amer. Chem. Soc.*, 1945, **67**, 2092.

sulphur. The observed pattern of multiplets of the spectrum of the undeuteriated compound can thus be explained only if the two protons with resonances at τ 5.16 and 5.91 are bonded to the two carbon atoms β with respect to the ring sulphur.

In agreement with the proposed structure, run B afforded a corresponding dideuteriated product exhibiting a ^{1}H n.m.r. spectrum where the τ 5.16 and 5.91 resonances could hardly be detected and the τ 4.77 and 5.70 ones appeared as sharp singlets.

(b) *At room temperature in the absence of free TMBT and stopped before completion.* A solution of Na-TMBT (1.43 mmol) in methanol (5 ml) was added to a solution of the dinitrothiophen (1) (0.5 g, 2.86 mmol) in the same solvent (7.5 ml). After 1 h at room temperature the mixture was poured into ice–water (100 ml), containing concentrated HCl (1 ml), and extracted with benzene. The extracts were washed with water, dried, concentrated, and chromatographed on a silica gel column [eluant light petroleum–dichloromethane (3 : 1)] to give: (i) TMBT (0.056 g) containing traces of the corresponding disulphide; (ii) 4-*nitro*-2,3-*bis*-(2,4,6-*trimethylphenylthio*)-2,3-*dihydrothiophen* (5) (0.215 g, 0.5 mmol; 98% based on reacted substrate), m.p. 130 °C [from petroleum (b.p. 80—100 °C)] (Found: C, 61.6; H, 5.85; N, 3.2; S, 22.1. $C_{22}H_{25}NO_2S_3$ requires C, 61.25; H, 5.8; N, 3.25; S, 22.25%); τ 2.02 (1 H, d, *J* 1.22 Hz, 5-H), 3.25 (4 H, m, 2 × $Me_3C_6H_2S$), 5.53 (1 H, d, *J* 0.42 Hz, 3-H), 5.62 (1 H, dd, *J* 1.22 and 0.42 Hz, 2-H), and 7.71br, 7.76br, and 7.92br (each 6 H, s, 2 × CH_3); * and (iii) 0.41 g (2.35 mmol) of unchanged starting material (1).

(c) *At reflux in the presence of free TMBT and stopped before completion.* A solution of the dinitrothiophen (1) (2 g, 11.5 mmol), Na-TMBT (11.5 mmol), and TMBT (11.5 mmol) in methanol (50 ml) was heated under reflux for 2 h. The solvent was evaporated off and the residue extracted with benzene. The extracts were washed with water, concentrated, and chromatographed on a silica gel column. The first fraction, eluted by light petroleum, contained traces of bis-(2,4,6-trimethylphenyl) disulphide. Further elution by light petroleum–dichloromethane (3 : 1) gave (i) a mixture of compounds (3) and (4) (ratio *ca.* 1 : 9) from which, by crystallization from methanol dioxan, the main component (4) (0.225 g, 3.4%) could be isolated and identified as a stereoisomer of (3) (mixed m.p. depressed, identical analytical data, similar ^{1}H n.m.r. pattern but different chemical shifts and coupling constants). The *tetrahydrothiophen* (4) had m.p. 142—144 °C (Found: C, 64.1; H, 6.4; N, 2.3; S, 21.8%), τ 3.04br, 3.27br, and 3.32br (each 2 H, s, $Me_3C_6H_2S$), 4.23 (1 H, dd, *J* 9.40 and 5.31 Hz, 4-H), 4.63 (1 H, d, *J* 9.40 Hz, 5-H), 5.93 (1 H, d, *J* 1.52 Hz, 2-H), 6.24 (1 H, dd, *J* 5.31 and 1.52 Hz, 3-H), 7.47br (6 H, s, 2 × CH_3), 7.74br (15 H, s, 5 × CH_3), and 7.90 (6 H, s, 2 × CH_3). (ii) 4-Nitro-2-(2,4,6-trimethylphenylthio)-thiophen (2a) (1.07 g, 33.5%), m.p. 71 °C (lit.,[3a] 71 °C); τ 1.99 (1 H, d, *J* 1.65 Hz, 5-H), 2.69 (1 H, d, *J* 1.65 Hz, 3-H), 3.01br (2 H, s, $Me_3C_6H_2S$), 7.52br (6 H, s, 2 × CH_3), and 7.70br (3 H, s, CH_3). (iii) 3-Nitrothiophen (0.06 g, 4.1%), m.p. 78—79 °C (lit.,[14] 74—76 °C). (*iv*) Dihydrothiophen (5) (0.9 g, 18.2%). (*v*) Unchanged starting material (0.41 g, 14.7%). Some uninvestigated tarry material was then eluted by methanol.

* The ^{1}H n.m.r. assignments were made on the basis of spectra of deuteriated analogues of compound (5).

[14] H. Burton and W. A. Davy, *J. Chem. Soc.*, 1948, 525.

In agreement with the proposed structures, run A afforded: a deuteriated analogue of (4) the ^{1}H n.m.r. spectrum of which showed almost no signal at τ 4.63 and 5.93 and sharp doublets at τ 4.23 and 6.24; a deuteriated analogue of (5) with an n.m.r. spectrum showing 60% deuteriation of the proton at τ 2.02 and 80% deuteriation of the one at τ 5.62 [this result allowed us to establish that the τ 2.02 and 5.62 absorptions are due to protons bonded to α-carbon atoms, thus confirming structure (5) and ruling out the isomeric structure (8), where the lower-field absorption should be generated by a β-proton]; 5-deuterio-4-nitro-2-(2,4,6-trimethylphenylthio)thiophen (55% deuteriation); and starting material which was no longer deuteriated.

Run B afforded: a deuteriated analogue of compound (4) showing >90% deuteriation of the β-protons and 60% deuteriation of the α-protons; a deuteriated analogue of (5) exhibiting 90% deuteriation of the proton at τ 5.53 and 75% deuteriation of the protons at τ 2.02 and 5.62; a deuteriated analogue of the sulphide (2a) having 90% deuteriation of the proton at τ 2.69 and 40% deuteriation of the one at τ 1.99; and starting material (90% deuteriated).

Experiments on the Influence of Light and Azobenzene on Reaction Rate and on Relative Yields.—A set of four independent runs was carried out at reflux using equimolar amounts (1.15 mmol) of dinitrothiophen (1), TMBT, and Na-TMBT, 5 ml of methanol, and a reaction time of 30 min. Three experiments were a repetition of a standard one (conducted under conditions identical with those for the reaction of 3,4-dinitrothiophen at reflux) except that the first of these was carried out in total darkness, the second in the presence of 0.5 mmol of azobenzene, and the third under illumination by a 300 W lamp. In each case work-up involved pouring the reaction mixture into 100 ml of ice–water (acidified with 1 ml of concentrated HCl), extracting with benzene, washing the extracts with water, and drying. Removal of the benzene under reduced pressure gave a residue which was dissolved in $CDCl_3$ (1 ml), and 0.5M-1,3,5-trinitrobenzene in $CDCl_3$ was added as internal standard. ^{1}H N.m.r. analysis showed that in all four experiments the same quantity of the dihydrothiophen (5), corrected for the presence of 3-nitrothiophen (see text), and of the sulphide (2a) was present within acceptable experimental error. It was impossible to determine the amounts of tetrahydrothiophens (3) and (4) owing to their low concentration.

Transformation of Compounds (3)—(5) *into the Sulphide* (2a).—A solution of the compound (0.5 mmol) in methanol (150 ml), containing traces of Na-TMBT, was refluxed for 15 min. The solvent was removed *in vacuo* and the residue, dissolved in dichloromethane, was chromatographed on a silica gel column. The first fraction, eluted by light petroleum, contained TMBT with traces of bis-(2,4,6-trimethylphenyl) disulphide. Further elution by light petroleum–dichloromethane (3 : 1) gave the sulphide (2a) almost quantitatively.

Addition of TMBT to the Dihydrothiophen (5).—A solution of the dihydrothiophen (5) (0.5 mmol), TMBT (2.5 mmol), and a catalytic amount of Na-TMBT in methanol (10 ml), was kept at room temperature for 36 h. The white solid which precipitated (0.2 g) was filtered off and washed with a little methanol. The ^{1}H n.m.r. spectrum showed that this was essentially the tetrahydrothiophen (4) and some (<10%) of the isomer (3). Crystallization from methanol–dioxan afforded pure (4), as shown by ^{1}H n.m.r. and mixed m.p.

Transformation of the Pure Compounds (3) *and* (4) *into a Mixture of the Two Isomers.*—To a solution of compound (3) or (4) (0.2 mmol) in methanol–dioxan (1 : 2; 6 ml) a solution of TMBT (1 mmol), containing traces of Na-TMBT, in methanol (1 ml) was added. After 4 d at room temperature, the solvent was evaporated off and the residue taken up in methanol. The ^{1}H n.m.r. spectrum of this crude material showed that from both the isomers (3) and (4) the same mixture [(3) : (4) 1 : 3] was obtained.

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