

## Reaction of 2,4-Dinitrobenzenediazonium Ions with Thiophens. Part 2.<sup>1</sup> Coupling Reactions, Involving Unexpected Reactions with Electron-rich Methyl Groups in Addition to the Expected Ring Attack

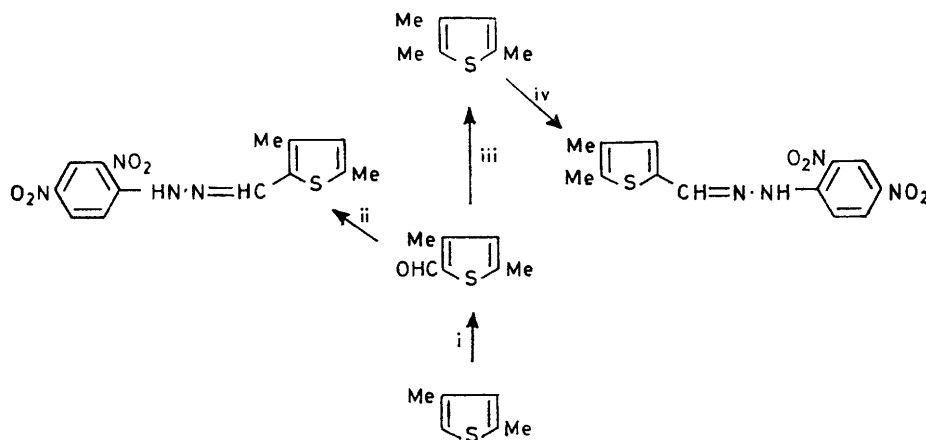
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2,4-Dinitrobenzenediazonium ions couple with 2-phenylthiophen, 2-t-butylthiophen, 2,4-dimethylthiophen, and 2-methyl- and 3-methyl-benzo[*b*]thiophen to give the expected dinitrophenylazothiophens. 2,5-Dimethylthiophen yields in addition to the 3-(2,4-dinitrophenylazo)thiophen an almost equal proportion of the 2,4-dinitrophenylhydrazone of 5-methylthiophen-2-carbaldehyde. 2,3,5-Trimethylthiophen and tetramethylthiophen, treated with the diazonium salt, give exclusively the 2,4-dinitrophenylhydrazone formed by coupling with the  $\alpha$ -methyl group. 2,3-Dimethylbenzo[*b*]thiophen does not react.

THE preceding paper<sup>1</sup> describes the reaction of thiophen and monomethylthiophens with 2,4-dinitrobenzenediazonium ions in acid solution. No coupling was observed; instead nitrogen was evolved with concomitant arylation. When 2,5-dimethylthiophen was treated in the same manner, no nitrogen was evolved and instead two coloured products were isolated. The more soluble (m.p. 137 °C), eluted first from a chromatography column, gave analytical figures as expected for 3-(2,4-dinitrophenylazo)-2,5-dimethylthiophen, and its

that the product was the result of coupling through an  $\alpha$ -methyl group. That coupling was through the 5- and not the 2-methyl group was established by comparison with the 2,4-dinitrophenylhydrazone of 3,5-dimethylthiophen-2-carbaldehyde (Scheme 1).

Tetramethylthiophen coupled extremely rapidly with the acidic 2,4-dinitrobenzenediazonium solution. The product was established as the 2,4-dinitrophenylhydrazone of 3,4,5-trimethylthiophen-2-carbaldehyde by comparison with the 2,4-dinitrophenylhydrazone of



SCHEME 1 Reagents: i,  $\text{Bu}^{\text{t}}\text{Li}-\text{HCO}-\text{NMe}_2$ <sup>a</sup>; ii,  $2,4-(\text{NO}_2)_2\text{C}_6\text{H}_3-\text{NH}\cdot\text{NH}_2$ ; iii,  $\text{NH}_2\cdot\text{NH}_2-\text{KOH}$ <sup>b</sup>; iv,  $2,4-(\text{NO}_2)_2\text{C}_6\text{H}_3\text{N}_3^{\oplus}\text{N}^-$   
<sup>a</sup> J. Sicé, *J. Org. Chem.*, 1954, **19**, 70. <sup>b</sup> W. J. King and F. F. Nord, *J. Org. Chem.*, 1949, **14**, 638.

spectra (n.m.r., i.r., and u.v.) were consistent with this structure. The second product (m.p. 233°) had the same analytical figures and molecular weight (high resolution mass spectrum) as the first. However, unlike the lower melting compound, this second product had i.r. absorption at 3 300  $\text{cm}^{-1}$ . This was attributed to N-H stretching, and the second product was identified as the 2,4-dinitrophenylhydrazone of 5-methylthiophen-2-carbaldehyde. This was confirmed by synthesis.

2,3,5-Trimethylthiophen was synthesised from 2,4-dimethylthiophen *via* the Vilsmeier reaction (to give 3,5-dimethylthiophen-2-carbaldehyde), followed by Wolff-Kishner reduction (Scheme 1). Coupling occurred rapidly with the acidic 2,4-dinitrobenzenediazonium salt solution to give a phenylhydrazone derivative (NH absorption in the i.r.). The n.m.r. spectrum established

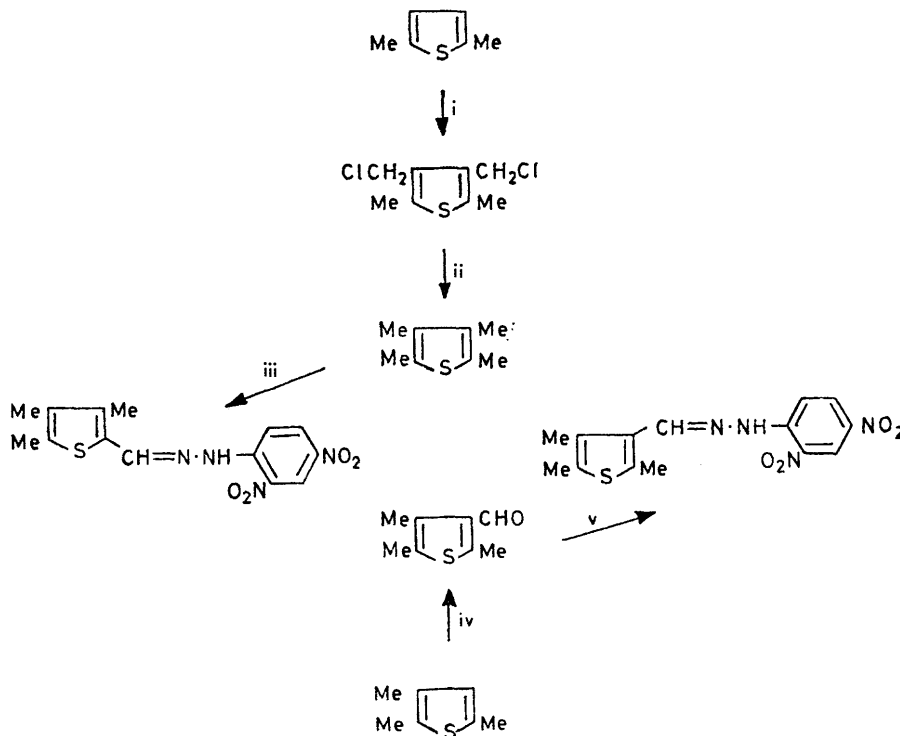
2,4,5-trimethylthiophen-3-carbaldehyde, synthesised by an unambiguous route (Scheme 2).

The preceding paper describes how 2,4-dinitrobenzenediazonium ions react with thiophen and with 2- and 3-methylthiophens with evolution of nitrogen to yield arylation products. So far the thiophens we have described which couple have both  $\alpha$ -positions blocked. 2,4-Dimethylthiophen couples rapidly with the acidic diazonium salt solution and the product, which shows no NH i.r. absorption, proved to be 2-(2,4-dinitrophenylazo)-3,5-dimethylthiophen. Subsequently two mono-substituted thiophens, 2-t-butyl- and 2-phenyl-, were found to couple readily to give the corresponding azo-dyes, coupling occurring in the  $\alpha$  position of the thiophen

<sup>1</sup> Part 1, M. Bartle, S. T. Gore, R. K. Mackie, and J. M. Tedder, preceding paper.

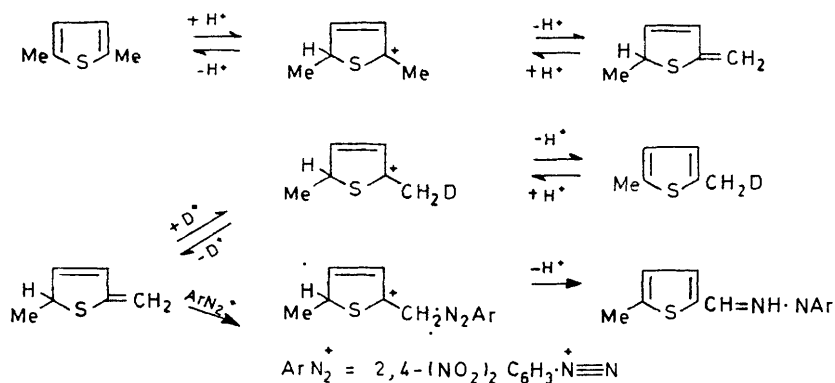
ring. Similarly both 2-methyl- and 3-methyl-benzo[*b*]thiophen couple to yield azo-dyes, but 2,3-dimethyl-benzo[*b*]thiophen does not react with the diazonium salt in marked contrast to tetramethylthiophen.

involve similar mechanisms. Eaborn and Wright have studied hydrogen exchange in 2-methyl-, 3-methyl-, and 2,3-dimethyl-benzo[*b*]thiophen, quantitatively.<sup>2</sup> The exchange of protons from the methyl group is *ca.* 10<sup>4</sup>



SCHEME 2 Reagents: i,  $(\text{CH}_2\text{O})_6\text{-HCl}$ ; ii,  $\text{LiAlH}_4$ ; iii,  $2,4\text{-(NO}_2)_2\text{C}_6\text{H}_3\text{-N}\equiv\text{N}^+$ ; iv,  $\text{PhNMe-CHO-POCl}_3$ ; v,  $2,4\text{-(NO}_2)_2\text{-C}_6\text{H}_3\text{-NH-NH}_2$

<sup>a</sup> R. Garetner and R. G. Tonkyn, *J. Amer. Chem. Soc.*, 1951, **73**, 5872. <sup>b</sup> J. E. Johnson, R. H. Blizzard, and H. W. Carhart, *J. Amer. Chem. Soc.*, 1948, **70**, 3664.



The <sup>1</sup>H n.m.r. spectrum of 2,5-dimethylthiophen in trifluoroacetic [<sup>2</sup>H]acid shows that the ring protons at positions 3 and 4 exchange extremely rapidly. The methyl protons exchange less rapidly but sufficiently so for this process to be associated with the coupling at the methyl group. Similar studies were made with 2,3,5-trimethyl- and tetramethyl-thiophen, and again rapid exchange of the methyl protons was observed. The exchange process and the coupling almost certainly

times slower than exchange of protons from the thiophen ring. This is consistent with our qualitative observations for 2,5-dimethylthiophen.

The coupling of reactive diazonium salts with acidic (electron-deficient) methyl or methylene groups is well known.<sup>3</sup> *p*-Nitrobenzenediazonium ions are reported to

<sup>2</sup> C. Eaborn and G. J. Wright, *J. Chem. Soc. (B)*, 1971, 2262.

<sup>3</sup> K. H. Saunders, *The Aromatic Diazo-compounds and their Technical Applications*, Arnold, London, 2nd edn., 1949, pp. 209-217.

couple with the methyl groups in 2,4,6-trinitrotoluene,<sup>4</sup> but prior to the preliminary report of the present work the coupling of diazonium ions with methyl groups in electron-rich sites appeared to be without precedent. Since then a report, predating our publication, which describes the coupling of 2,3-dimethylindole with 2-methoxy-4-nitrobenzenediazonium ions has appeared.<sup>5</sup> The coupling occurred in aqueous solutions of moderately high pH. Electrophilic substitution at the 2-methyl group of 2,3-dimethylbenzo[*b*]thiophen has been reported by Bordwell,<sup>6</sup> and electrophilic attack on methyl groups attached to hexamethylbenzene and polyalkyl-naphthalenes has also been described.<sup>7</sup> The striking feature of the present work is that electrophilic substitution occurs at a methyl group even when reactive 'aromatic' sites are available (*cf.* 2,5-dimethyl- and 2,3,5-trimethyl-thiophen). It is possible to acylate thiophen with acetic acid dissolved in trifluoroacetic anhydride.<sup>8</sup> When this reaction was tried with 2,3,5-trimethylthiophen, acylation occurred readily to yield 3-acetyl-2,4,5-trimethylthiophen, *i.e.* attack occurred at the 'aromatic' 3-position rather than at a side chain methyl group. This means that side-chain attack depends not only on the acidity of the medium, but also on the nature of the electrophile.

The complete series of thiophens investigated is listed in the Table.

Reactions of 2,4-dinitrobenzenediazonium ions with thiophens

Thiophen	Yield of arylation product (%)	Yield of azo-dye (%)	Yield of aldehyde 2,4-dinitrophenylhydrazone (%)
Thiophen	20		
2-Methylthiophen	27		
3-Methylthiophen	30		
2- <i>t</i> -Butylthiophen		20	
2-Phenylthiophen		13	
2,4-Dimethylthiophen		60	
2,5-Dimethylthiophen		13.5	13.5
2,3,5-Trimethylthiophen			93
Tetramethylthiophen			93
Benzo[ <i>b</i> ]thiophen	50		
2-Methylbenzo[ <i>b</i> ]thiophen		62	
3-Methylbenzo[ <i>b</i> ]thiophen		25	

#### EXPERIMENTAL

For the diazotisation of 2,4-dinitroaniline, see preceding paper.

**Reaction with 2,5-Dimethylthiophen.**—The thiophen (0.672 g, 0.006 mol) in glacial acetic acid (24 cm<sup>3</sup>) was added to the diazonium salt solution (0.01 mol) and the mixture was stirred at 0 °C for 68 h. A red precipitate was filtered off, washed, dried, and chromatographed on silica. Elution with benzene gave 3-(2,4-dinitrophenylazo)-2,5-dimethylthiophen, as yellow crystals from benzene-petroleum (0.25

g, 13.5%), m.p. 137° (Found: C, 47.1; H, 3.45; N, 17.85%;  $M^+$ , 306.041 565.  $C_{12}H_{10}N_4O_4S$  requires C, 47.65; H, 3.25; N, 18.3%;  $M^+$ , 306.042 272);  $\nu_{max}$  1 600, 1 530, and 1 350 (NO<sub>2</sub>), 1 190, 920, 850, 840, and 750 cm<sup>-1</sup>;  $\lambda_{max}$  378 ( $\epsilon$  1.601  $\times$  10<sup>4</sup>) and 218 nm (2.26  $\times$  10<sup>4</sup>). Further elution with benzene gave the 2,4-dinitrophenylhydrazone of 5-methylthiophen-2-carbaldehyde as red needles (from chloroform-petroleum) (0.25 g, 13.5%), m.p. 233° (alone or in admixture with an authentic specimen) (Found: C, 46.7; H, 3.3; N, 18.3%;  $M^+$ , 306.042 357.  $C_{12}H_{10}N_4O_4S$  requires C, 47.65; H, 3.25; N, 18.3%;  $M^+$ , 306.042 272);  $\nu_{max}$  3 295 (NH), 1 618, 1 598, 1 500, 1 335 (NO<sub>2</sub>), 1 145, 830, and 805 cm<sup>-1</sup>;  $\lambda_{max}$  395 ( $\epsilon$  2.72  $\times$  10<sup>4</sup>), 309 (6.35  $\times$  10<sup>3</sup>), and 223 nm (1.54  $\times$  10<sup>4</sup>). Further elution with chloroform followed by chloroform-methanol yielded a red glassy solid (0.675 g) which t.l.c. showed to contain many components; it was not investigated further.

**Reaction with 2,3,5-Trimethylthiophen.**—Trimethylthiophen was prepared as shown in Scheme 1. The thiophen (0.63 g, 0.005 mol) in glacial acetic acid (40 cm<sup>3</sup>) was added to a stirred solution of diazonium salt (0.0083 mol) at room temperature. A red precipitate formed immediately and after 15 min the solution was diluted with ice-water and the precipitate was filtered off. Recrystallisation from glacial acetic acid gave the 2,4-dinitrophenylhydrazone of 4,5-dimethylthiophen-2-carbaldehyde as red needles (1.49 g, 93%), m.p. 252° (Found: C, 48.65; H, 4.0; N, 17.35%;  $M^+$ , 320.058 860.  $C_{13}H_{12}N_4O_4S$  requires C, 48.75; H, 3.75; N, 17.5%;  $M^+$ , 320.057 922);  $\nu_{max}$  3 300 (NH), 1 615, 1 600, 1 500, 1 335 (NO<sub>2</sub>), 1 140, 845, and 750 cm<sup>-1</sup>;  $\lambda_{max}$  396 nm ( $\epsilon$  3.2  $\times$  10<sup>4</sup>);  $\delta$ (C<sub>5</sub>D<sub>5</sub>N at 90 °C) 1.88 (3 H, s), 2.14 (3 H, s), 6.95 (1 H, s), 7.84 (1 H, d, *J* 9.5 Hz), 8.14 (1 H, dd), 8.36 (1 H, s), and 8.87 (1 H, d, *J* 2 Hz), which differed from the 2,4-dinitrophenylhydrazones of 2,5-dimethylthiophen-3-carbaldehyde and 3,5-dimethylthiophen-2-carbaldehyde (mixed m.p.).

**Reaction with 2,4-Dimethylthiophen.**—The thiophen (0.672 g, 0.006 mol) in glacial acetic acid (24 cm<sup>3</sup>) was added to the diazonium salt solution (0.01 mol) at room temperature. After stirring for 5 min the solution was filtered to remove an orange-red precipitate (1.54 g). A portion of this product was purified by chromatography on silica (benzene as eluant). Recrystallisation from methanol gave 2-(2,4-dinitrophenylazo)-3,5-dimethylthiophen as red crystals (equivalent to 72%), m.p. 176° (Found: C, 46.9; H, 3.2; N, 17.95%;  $M^+$ , 306.043 031.  $C_{12}H_{10}N_4O_4S$  requires C, 47.65; H, 3.25; N, 17.95%;  $M^+$ , 306.042 272);  $\nu_{max}$  1 610, 1 590, 1 520, 1 340, and 1 200 cm<sup>-1</sup>;  $\lambda_{max}$  418 nm ( $\epsilon$  2.45  $\times$  10<sup>4</sup>).

**Reaction with Tetramethylthiophen.**—Tetramethylthiophen was prepared as shown in Scheme 2. A solution of the thiophen (0.56 g, 0.004 mol) in glacial acetic acid (16 cm<sup>3</sup>) was added to the diazonium solution (0.006 mol). The mixture was stirred at room temperature for 10 min, before dilution with ice-water. A red precipitate was filtered off. Recrystallisation from aqueous dimethylformamide gave the 2,4-dinitrophenylhydrazone of 3,4,5-trimethylthiophen-2-carbaldehyde as red needles (1.25 g, 93%), m.p. 247–248° (Found: C, 49.95; H, 4.35; N,

<sup>4</sup> A. A. Kharkharov, *J. Gen. Chem. (U.S.S.R.)*, 1953, **23**, 1175; but see also H. G. Gunter quoted by R. Huisgen and H. Nakaten, (*Annalen*, 1954, **586**, 84).

<sup>5</sup> T. F. Spande and G. G. Glenner, *J. Amer. Chem. Soc.*, 1973, **95**, 3400.

<sup>6</sup> F. G. Bordwell and T. W. Cutshall, *J. Org. Chem.*, 1964, **29**, 2020.

<sup>7</sup> L. J. Andrews and R. M. Keefer, *J. Amer. Chem. Soc.*, 1964, **86**, 4158; D. J. Blackstock, A. Fischer, K. E. Richards, and G. J. Wright, *Austral. J. Chem.*, 1973, **26**, 775; A. Fischer and A. L. Wilkinson, *Canad. J. Chem.*, 1972, **50**, 3988.

<sup>8</sup> E. J. Bourne, M. Stacey, J. C. Tatlow, and J. M. Tedder, *J. Chem. Soc.*, 1951, 718.

16.55.  $C_{14}H_{14}N_2O_4S$  requires C, 50.3; H, 4.2; N, 16.75%;  $m/e$  334 ( $M^+$ );  $\nu_{\max}$  3 290  $cm^{-1}$  (NH);  $\lambda_{\max}$  406 nm ( $\epsilon$   $3.5 \times 10^4$ );  $\delta(C_5D_5N$  at 90 °C) 1.76 (3 H, s), 1.99 (3 H, s), 2.14 (3 H, s), 7.85 (1 H, d,  $J$  10 Hz), 8.14 (1 H, dd,  $J$  10 and 2 Hz), 8.60 (1 H, s), and 8.88 (1 H, d,  $J$  2 Hz), which differed from the 2,4-dinitrophenylhydrazone of 2,4,5-trimethylthiophen-3-carbaldehyde (i.r. and u.v. spectra; m.p. and mixed m.p.).

*Reaction with 2-t-Butylthiophen.*—A solution of the thiophen (0.280 g, 0.002 mol) in glacial acetic acid (16  $cm^3$ ) was added to the diazonium salt solution (0.0033 mol) and the mixture was stirred at 0 °C for 62 h, then extracted with chloroform. The extract was washed (NaHCO<sub>3</sub> and H<sub>2</sub>O), dried, and evaporated to leave a black oil which was chromatographed on a silica column. Elution with benzene gave a small amount of t-butylthiophen, followed by a purple band which gave a trace of a minor component (see below). Further elution yielded 2-(2,4-dinitrophenylazo)-2-t-butylthiophen, which formed red crystals (0.14 g), m.p. 136° (from petroleum) (Found: C, 50.75; H, 4.15; N, 16.5%;  $M^+$ , 334.073 51.  $C_{14}H_{14}N_2O_4S$  requires C, 50.3; H, 4.2; N, 16.75%;  $M$ , 334.073 57);  $\nu_{\max}$  1 600, 1 525, 1 345 (NO<sub>2</sub>), 1 185, and 1 065  $cm^{-1}$ ;  $\lambda_{\max}$  412 ( $\epsilon$   $2.505 \times 10^4$ ) and 330 nm ( $7.5 \times 10^3$ );  $\delta(C_6D_6)$  1.19 (9 H, s), 6.60 (1 H, d,  $J$  4 Hz), 7.19 (1 H, d,  $J$  9 Hz), 7.55 (1 H, d,  $J$  4 Hz), 7.65 (1 H, dd,  $J$  9 and 2 Hz), and 8.07 (1 H, d,  $J$  2 Hz). The trace product from the purple band separated as a red-green solid from petroleum; m.p. 220°;  $\lambda_{\max}$  526 nm ( $\epsilon$   $2.094 \times 10^5$ ) (Found:  $M^+$ , 472.124 48.  $C_{22}H_{24}N_4O_4S_2$  requires  $M$ , 472.154 68); tentatively identified as 2-(2,4-dinitrophenylazo)-5-t-butyl-3-(5-t-butyl-2-thienyl)thiophen.

*Reaction with 2-Phenylthiophen.*—2-Phenylthiophen was prepared from thiophen via 2-thienyl-lithium and 2-cyclohexenylthiophen.<sup>9,10</sup> A solution of the thiophen (0.320 g, 0.002 mol) in glacial acetic acid (20  $cm^3$ ) was added to the diazonium salt solution (0.002 mol). The solution was stirred for 40 h at 0 °C, and the precipitate was then filtered off. The product was chromatographed on silica; elution with benzene-carbon tetrachloride gave a trace of 2-phenylthiophen, followed by an orange fraction which was further purified on a second silica column. 2-(2,4-Dinitrophenylazo)-5-phenylthiophen crystallised from methanol as purple crystals (0.095 g, 13%), m.p. 183° (Found: C, 54.45; H, 2.7; N, 15.75.  $C_{16}H_{10}N_4O_4S$  requires C, 54.25; H, 2.85; N, 15.8%);  $\lambda_{\max}$  453 nm ( $\epsilon$   $2.478 \times 10^4$ ).

*Reaction with 2-Methylbenzo[b]thiophen.*<sup>11</sup>—The diazonium salt solution (0.003 3 mol) was added to a solution of the benzo[b]thiophen (0.296 g, 0.002 mol) in glacial acetic acid (8  $cm^3$ ). The mixture was stirred for 58 h at 0 °C. The red precipitate was filtered off and dissolved in chloroform. The solution was washed (NaHCO<sub>3</sub> and H<sub>2</sub>O) and evaporated. The residue was chromatographed on silica. Elution with benzene gave, after recrystallisation from benzene-petroleum, 3-(2,4-dinitrophenylazo)-2-methylbenzo[b]thiophen as red needles (0.425 g, 62%), m.p. 182° (Found: C, 52.55; H, 2.85; N, 16.7.  $C_{15}H_{10}N_4O_4S$  requires C, 52.65; H, 2.9;

N, 16.35%);  $m/e$  342 ( $M^+$ );  $\nu_{\max}$  1 600, 1 520, 1 340 (NO<sub>2</sub>), 1 180, 1 060, and 750  $cm^{-1}$ ;  $\lambda_{\max}$  408 nm ( $\epsilon$   $1.71 \times 10^4$ ), 288 ( $1.47 \times 10^4$ ), and 222 nm ( $2.414 \times 10^4$ ).

*Reaction with 3-Methylbenzo[b]thiophen.*<sup>12</sup>—A solution of 3-methylbenzo[b]thiophen (0.269 g, 0.002 mol) in glacial acetic acid (8  $cm^3$ ) was added to the diazonium salt solution (0.003 3 mol) and the mixture was stirred at 0 °C for 68 h. The red precipitate was filtered off and dissolved in chloroform. The solution was washed (NaHCO<sub>3</sub> and H<sub>2</sub>O), dried, and evaporated. The residue was chromatographed on silica. Elution with benzene yielded 2-(2,4-dinitrophenylazo)-3-methylbenzo[b]thiophen as orange needles (0.170 g, 25%), m.p. 190° (from benzene-petroleum) (Found: C, 52.3; H, 2.85; N, 16.1.  $C_{15}H_{10}N_4O_4S$  requires C, 52.65; H, 2.9; N, 16.35%);  $m/e$  342 ( $M^+$ );  $\nu_{\max}$  1 520, 1 340 (NO<sub>2</sub>), and 840  $cm^{-1}$ ;  $\lambda_{\max}$  406 ( $\epsilon$   $3.106 \times 10^4$ ), 277 ( $1.04 \times 10^4$ ), and 217 nm ( $3.591 \times 10^4$ ).

*2,4-Dinitrophenylhydrazones from Thiophencarbaldehydes for Characterisation.*—The 2,4-dinitrophenylhydrazine of 5-methylthiophen-2-carbaldehyde formed red needles, m.p. and mixed m.p. 233–234° (Found: C, 47.4; H, 3.25; N, 18.6. Calc. for  $C_{12}H_{10}N_4O_4S$ : C, 47.65; H, 3.25; N, 18.3%);  $m/e$  306 ( $M^+$ );  $\nu_{\max}$  3 290  $cm^{-1}$  (NH);  $\lambda_{\max}$  394 ( $\epsilon$   $2.77 \times 10^4$ ), 309 ( $6.44 \times 10^3$ ), and 223 nm ( $1.48 \times 10^4$ ).

The 2,4-dinitrophenylhydrazone of 4-methylthiophen-2-carbaldehyde formed red needles, m.p. 235–236° (Found: C, 46.95; H, 3.35; N, 18.15.  $C_{12}H_{10}N_4O_4S$  requires C, 47.65; H, 3.25; N, 18.3%);  $m/e$  306 ( $M^+$ );  $\nu_{\max}$  3 290  $cm^{-1}$  (NH);  $\lambda_{\max}$  393 nm ( $\epsilon$   $2.47 \times 10^4$ );  $\delta(C_5D_5N$ ; 90 °C) 2.02 (3 H, s), 6.98–7.04 (2 H, m), 7.83 (1 H, d,  $J$  10 Hz), 8.11 (1 H, dd,  $J$  10 and 2 Hz), 8.43 (1 H, s), and 8.86 (1 H, d,  $J$  2 Hz).

The 2,4-dinitrophenylhydrazone of 3,5-dimethylthiophen-2-carbaldehyde formed red needles, m.p. 253–254° (Found: C, 48.3; H, 3.75; N, 17.5.  $C_{13}H_{12}N_4O_4S$  requires C, 48.75; H, 3.75; N, 17.5%);  $m/e$  320 ( $M^+$ );  $\nu_{\max}$  3 280  $cm^{-1}$  (NH);  $\lambda_{\max}$  402 nm ( $\epsilon$   $2.7 \times 10^4$ ).

The 2,4-dinitrophenylhydrazone of 2,5-dimethylthiophen-3-carbaldehyde formed red needles, m.p. 248–249° (Found: C, 48.3; H, 3.65; N, 17.3.  $C_{13}H_{12}N_4O_4S$  requires C, 48.75; H, 3.75; N, 17.5%);  $m/e$  320 ( $M^+$ );  $\nu_{\max}$  3 290  $cm^{-1}$  (NH);  $\lambda_{\max}$  388 nm ( $\epsilon$   $1.9 \times 10^4$ );  $\delta(C_5D_5N$ ; 88 °C) 2.21 (3 H, s), 2.30 (3 H, s), 7–7.08 (1 H, m), 7.90 (1 H, d,  $J$  10 Hz), 8.18 (1 H, dd,  $J$  10 and 2 Hz), 8.36 (1 H, s), 8.90 (1 H, d,  $J$  2 Hz), and 3.8–4.4br (1 H).

The 2,4-dinitrophenylhydrazone of 2,4,5-trimethylthiophen-3-carbaldehyde formed red needles, m.p. 236° (Found: C, 50.15; H, 4.25; N, 16.8.  $C_{14}H_{14}N_4O_4S$  requires C, 50.3; H, 4.2; N, 16.75%);  $m/e$  334 ( $M^+$ );  $\nu_{\max}$  3 290  $cm^{-1}$  (NH);  $\lambda_{\max}$  390 nm ( $\epsilon$   $2.15 \times 10^4$ );  $\delta(C_5D_5N$ ; 88 °C) 2.08 (3 H, s), 2.13 (3 H, s), 2.38 (3 H, s), 3.6–4.0br (1 H), 7.75 (1 H, d,  $J$  9 Hz), 8.15 (1 H, dd,  $J$  9 and 2 Hz), 8.41 (1 H, s), and 8.90 (1 H,  $J$  2 Hz).

We thank Dr. N. R. Clark and the Midland Tar Distillers Ltd., for a gift of 2,4-dimethylthiophen.

[5/2499 Received, 22nd December, 1975]

<sup>9</sup> H. Gilman and D. A. Shirley, *J. Amer. Chem. Soc.*, 1949, **71**, 1870.

<sup>10</sup> A. I. Kosak, R. J. F. Palchak, W. A. Steele, and C. M. Selwitz, *J. Amer. Chem. Soc.*, 1954, **76**, 4450.

<sup>11</sup> D. A. Shirley and M. D. Cameron, *J. Amer. Chem. Soc.*, 1952, **74**, 664.

<sup>12</sup> E. Campagne and E. S. Neiss, *J. Heterocyclic Chem.*, 1965, **2**, 231.