Trapping of translocated radicals by tetrathiafulvalene radical cation

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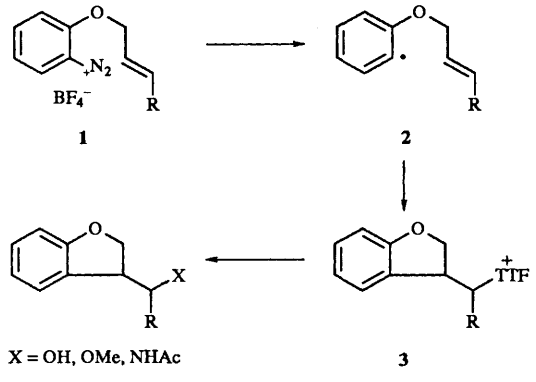
Aryl radicals are generated by electron transfer from tetrathiafulvalene to arenediazonium salts. The aryl radicals are translocated into alkyl radicals which undergo a C–S or C–C bond formation to tetrathiafulvalene radical cation, depending on the nucleophilicity/electrophilicity of the translocated carbon radical.

We have recently exploited the special properties of tetrathiafulvalene (TTF) as an electron donor. Diazonium salts **1** were converted into aryl radicals **2** which underwent cyclisation. The product alkyl radicals underwent observed (for primary and secondary alkyl radicals) C–S bond formation with tetrathiavulvalene radical cation.[1] Tertiary alkyl radicals may also have formed such salts, but these were not detected. Such salts were demonstrated to undergo a rapid unimolecular substitution in moist acetone, in methanol or in acetonitrile to afford alcohols, ethers and amides respectively. Solvolysis was so retarded for primary TTF salts **3** (where R = H) that it was not observed at all under the reaction conditions. The ease and specificity of solvolysis (no elimination products were observed)[2] permitted a useful and novel one-pot transformation linking radical cyclisation and polar substitution, a so-called 'radical-polar crossover' sequence.



Scheme 1

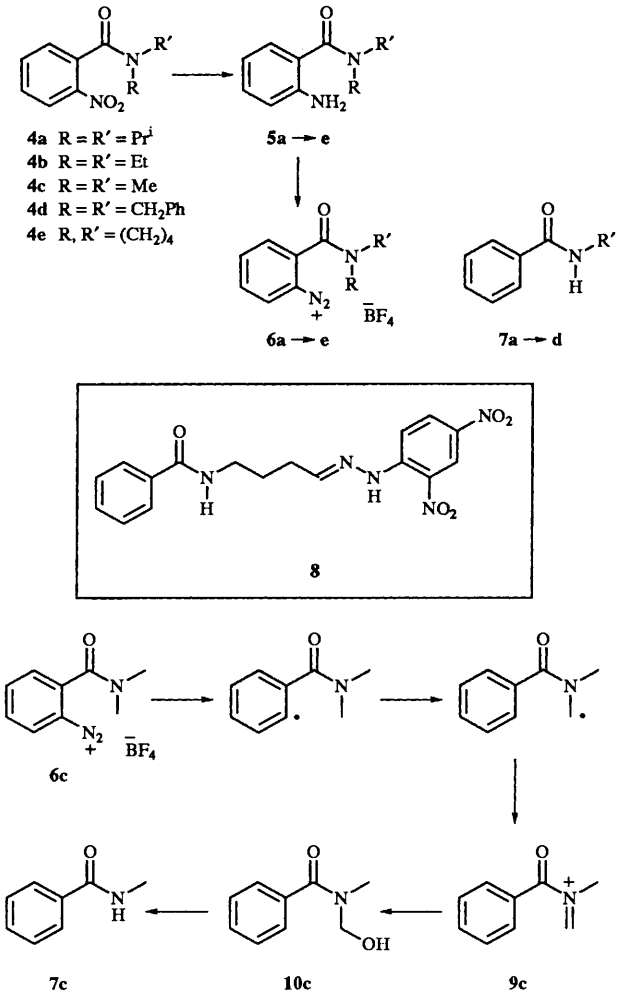
The above reports concentrated on cyclisation of the aryl radical onto an appropriate alkene followed by functionalisation. We now report the transformations of arenediazonium salts designed to undergo hydrogen atom transfer rather than cyclisation. Our aim was to investigate whether aryl radicals, formed by electron transfer from tetrathiafulvalene to diazonium salts, would conduct a tandem translocation/functionalisation sequence. Translocation of radicals has been shown to be a remarkably powerful means[3–5] of introducing functionality at unactivated sites. More recent studies[6–9] have extended the scope of this type of reaction, in particular by determining the ability of aryl and vinyl radicals to effect translocation.

The efficiency of intramolecular hydrogen atom transfer has been the subject of a number of recent studies. Among the most efficient substrates have been aryl radicals with amide[8] side-chains. The conformational rigidity of the amide can drastically affect the reaction, and so we chose for initial study aryl radicals where conformational preferences would not complicate matters.[8] Hence, a series of symmetrically *N*,*N*-disubstituted *o*-nitrobenzamides **4a** ⟶ **e** was prepared and converted *via* the corresponding amines **5** into the diazonium salts **6** which were treated with TTF. These compounds did indeed react rapidly and generally efficiently resulting in mono-*N*-alkylated products, (**7a**, 98%), (**7b**, 85%), (**7c**, 39%), (**7d**, 61%), L when the reactions were conducted in moist acetone (Scheme 2). For these reactions, aldehyde and ketone by-products were generally not isolated. However, addition of an ethanol solution of 2,4-dinitrophenylhydrazine to the crude product of the reaction of **6e** (following evaporation of acetone) afforded the 2,4-dinitrophenylhydrazone **8**, demonstrating that oxidation was indeed occurring at the translocated site. These reactions were conducted successfully both with 1 equiv. and with catalytic quantities of TTF (10 mol%). The yield of product **7c** was considerably lower than the other cases. The kinetics of hydrogen transfer have previously been demonstrated to depend on the nature of the substituents on the product radical.[6]

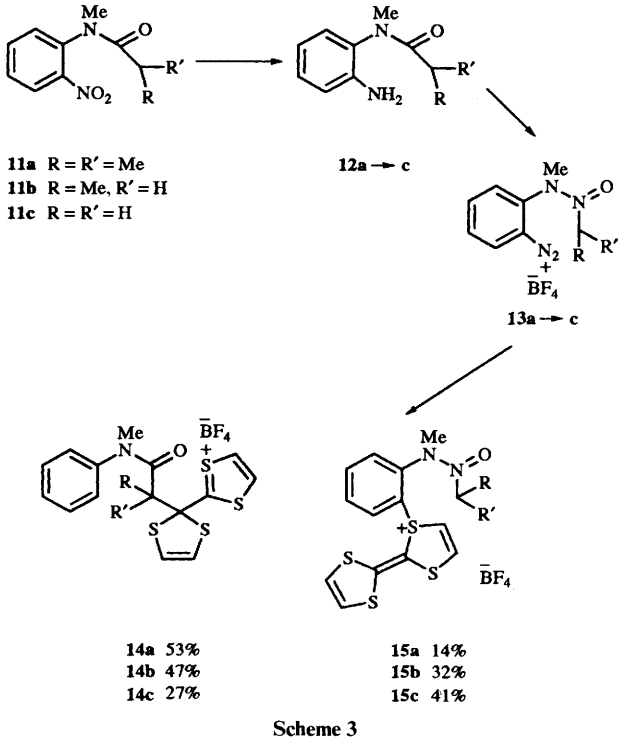
The course of the reaction for **6c** is shown in Scheme 2, and all examples will be analogous to this. The translocated radical must be converted to an aminol **10c** by (a) initial formation of the iminium salt **9c** either by direct electron transfer to another molecule of diazonium salt or by initial coupling with $TTF^{\bullet+}$ followed by loss of TTF and (b) attack of water. Whichever pathway applies, it was clear that TTF was inducing the set of reactions which ultimately led to oxidative functionalisation of the side-chain. The efficiency of the hydrogen transfer (estimates by Curran suggest $k > 10^7\ s^{-1}$) is shown by the lack of observation of products resulting from coupling of aryl radicals to $TTF^{\bullet+}$.

Dealkylation of such *N*,*N*-disubstituted amides has been observed before,[10] usually with copper powder as the reducing agent for the diazonium salt. The mechanism of the oxidation step preceding hydrolysis is not always clear. Intriguingly, Curran has recently reported oxidative transformations under reductive conditions.[8b]

The amides **13a** ⟶ **c**, which would give rise to electrophilic translocated radicals were next prepared by reducing the corresponding nitroarenes **11** to amines **12** and then diazotising them. It was immediately apparent that the reactions of **13a** ⟶ **c** with TTF had taken an unexpected course, with the isolation of the novel aromatic dithiolium salts[11] **14a** ⟶ **c**. No product arising from coupling of the translocated radical to sulfonium sulfur was observed. To rationalise this selectivity for coupling with the internal carbon of $TTF^{\bullet+}$, two facts must be considered. The first is that the alternative coupling to the sulfonium sulfur site of $TTF^{\bullet+}$ would generate an α-sulfonium amide. The presence of two strongly electron-withdrawing groups on neighbouring carbons would be expected to raise the energy of such a compound, and also that of the transition state leading to its formation. With C–S coupling retarded, the next most likely reaction would be C–C coupling. It may at first



Scheme 2



Scheme 3

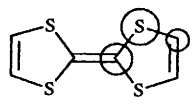
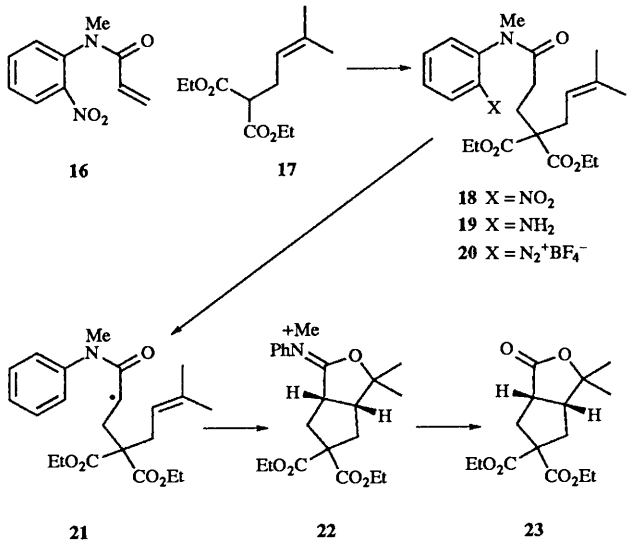


Fig. 1 Distribution of unpaired electron in $TTF^{\bullet+}$. Areas of the circles are proportional to spin density.

seem surprising that coupling to the external carbons of $TTF^{\bullet+}$ is not observed, but Zahradnik *et al.* have calculated[12] that the location of unpaired spin density follows the order: sulfonium sulfur > internal carbon > external carbon (Fig. 1).

Products **15a** (14%), **15b** (32%) and **15c** (41%) resulting from trapping of $TTF^{\bullet+}$ by the aryl radical were also observed from the above reactions; the relative yields show that the kinetics of hydrogen atom translocation was again crucially dependent on the substitution pattern of the translocated radical.[6] The observation of aryl trapped products from the anilide diazonium salts but not from the benzamide diazonium salts may suggest that the former substrates underwent a slower hydrogen atom transfer. Although definitive rate constants have not been determined, Curran *et al.* estimate[8a] that hydrogen transfer to an aryl radical in a secondary anilide (*e.g.* **13b**) occurs with $k > 5 \times 10^8$ s^{-1}, which is an extremely rapid rate. Other explanations for the observed selective trapping may exist. The formation of a product derived from the benzamide series featuring a sulfonium salt *ortho* to the amide carbonyl may be retarded if the opposing dipoles interact in the transition state as they would in the product. (This argument is analogous to that used above in the coupling of α-carbonyl radicals to $TTF^{\bullet+}$). The situation may however be more interesting. The two types of aryl radicals feature aromatic rings with very different electronic properties. The anilide ring, being electron-rich, might be expected to complex to $TTF^{\bullet+}$ forming a cation diradical, and imparting very different chemical properties to a normal aryl radical.† Coupling within this diradical might be very rapid.

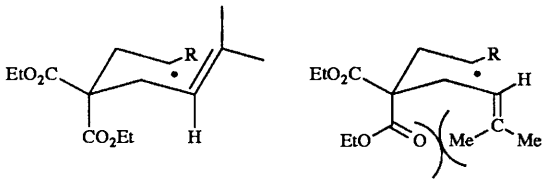
The two facts of principal interest in the anilide reactions are the rate constants for aryl C–S trapping and for alkyl C–C trapping. An initial probe of the latter was undertaken, using the diazonium salt **20** (Scheme 4) where a competition should



Scheme 4

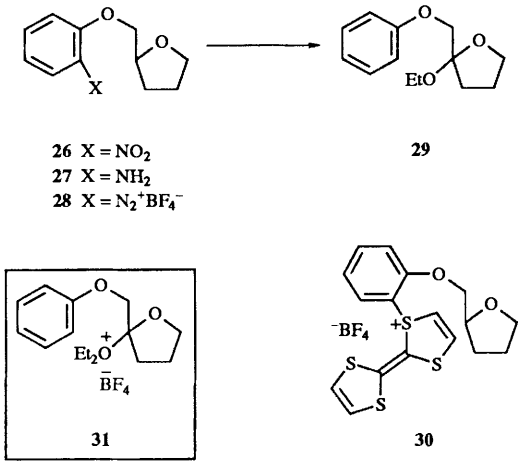
occur between cyclisation of the translocated radical and trapping with $TTF^{\bullet+}$. From analogy with compound **14b**, we should expect 47% of product to result from translocated

† We thank Dr Hendrik Zipse (Berlin) for this proposal.



24 25

Fig. 2



26 X = NO_2
27 X = NH_2
28 X = $N_2^+BF_4^-$

29 30 31

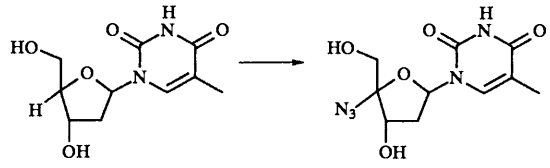
Fig. 3

radical **21**. If coupling to TTF$^{\bullet+}$ by carbon–carbon bond formation is relatively slow, then cyclised product(s) will be observed. Examination of the crude reaction mixture indicated that the iminium salt **22** was the principal product. This was not isolated, but instead was hydrolysed by base treatment and the products chromatographed to afford the lactone **23** in 45% yield. Only one diastereoisomer of the lactone is detected which we assign as the *cis*-fused product. This requires that the radical cyclisation is totally or almost totally stereoselective. We propose that this results from the presence of the *gem*-diester group. In the conformation **25** leading to the *trans* product, it is seen that the alkene adopts an 'axial' disposition. This causes steric interactions with the 'axial' ester group, which is not present in conformation **24** which leads to the *cis* product.

All of the cases studied so far have featured amide side-chains. Although less rigid side-chains can lead to less efficient radical translocation, we investigated one further case featuring an ether side-chain.[9]

Treatment of **28** with TTF in acetone at room temperature led eventually to isolation of two compounds. The product of radical translocation **29** could be isolated by treatment with diethyl ether. This caused formation of a dark precipitate, which was shown to be the salt **30** (23%) most likely formed by combination of the aryl radical with TTF$^{\bullet+}$ showing that radical translocation and direct trapping of TTF$^{\bullet+}$ compete. (The observation of aryl-trapped compound **30** is consistent with the observations reported above for anilides.) Treatment of the solution, on the other hand, with diisopropylamine then afforded the ethoxy derivative **29** (38%). It is suggested that this compound results from reaction of diisopropylamine with **31** which, in turn, is formed from attack of diethyl ether on the intermediate carbocation. If the trapping of aryl radicals with TTF$^{\bullet+}$ can be retarded, this approach may lead to a viable route from thymidine to ADRT **32**,[13] a compound with anti-HIV properties, which features a 4′-azido-2′-deoxyribose.

In summary, these studies show that in TTF/diazonium salt initiated translocations, the ultimate fate of the translocated radical depends on its nature. Nucleophilic alkyl radicals



Thymidine 32

Scheme 5

proceed to oxidised products, whereas electrophilic radicals undergo a novel carbon–carbon bond formation to TTF$^{\bullet+}$. The observation of a tandem radical translocation, cyclisation and oxidative functionalisation from **20** indicates that the diazonium salt/tetrathiafulvalene couple may have interesting applications to synthesis. Two principal limitations exist: the trapping of the aryl radical, and the C–C trapping of electrophilic radicals by TTF$^{\bullet+}$. The observed differences between benzamides and anilides suggest it may be possible to modulate the former by varying the electron richness of the aromatic ring. On the other hand, the rate constant for trapping of electrophilic radicals with the internal carbon of TTF$^{\bullet+}$ must be determined. The formation of compound **23** gives hope that the trapping may be a relatively slow reaction.

Experimental

Mps were carried out on a Kofler hot-stage apparatus and are uncorrected. Microanalyses were determined using a Perkin-Elmer 240B elemental analyser. IR spectra were obtained on a Perkin-Elmer 1720-X FTIR or a Pye-Unicam SP3-100 spectrometer. UV spectra were recorded on a Philips PU8700 series instrument. ^{1}H NMR spectra were recorded at 90 MHz on a Perkin-Elmer R32, at 250 MHz on a Bruker WM250, at 270 MHz on a JEOL EX270 or at 400 MHz on a Bruker AM400 machine. ^{13}C NMR spectra were recorded at 23 MHz on a JEOL FX290Q, at 63.5 MHz on a JEOL EX270 or at 100 MHz on a Bruker AM400 machine. NMR experiments were carried out in deuteriochloroform, [$^2H_4$]methanol, [$^2H_6$]acetone, [$^2H_3$]-acetonitrile or [$^2H_6$]dimethyl sulfoxide with tetramethylsilane as an internal reference. *J* Values are given in Hz. In several cases mixtures of isomers were obtained. In cases where superimposition of the signals of two, or more, isomers occurred, the signals have been reported as multiplets (m), unless the coupling constants of each isomer could be ascertained. Mass spectra were recorded on a VG Micromass 70E or an AEI MS902 instrument. High resolution FAB spectra were recorded at the EPSRC Mass Spectrometry Service Centre, Swansea.

Where necessary, solvents were dried and/or distilled before use. Tetrahydrofuran was distilled from sodium–benzophenone. Acetonitrile was distilled from phosphorus(v) oxide. Dichloromethane was distilled from calcium hydride. Diethyl ether, toluene and benzene were dried over sodium wire. Unless stated otherwise, light petroleum refers to the fraction with bp 40–60 °C and was distilled before use. Chromatography was performed using Sorbisil C60 (May and Baker), Kieselgel 60 (Art 9385) or Kieselgel HF254 silica gels.

N,*N*-Diisopropyl-*o*-nitrobenzamide 4a

2-Nitrobenzoyl chloride (2.29 g, 12.2 mol, 1.0 equiv.) was dissolved in dry tetrahydrofuran (20 cm^3) at 0 °C under nitrogen and a solution of diisopropylamine (2.12 g, 24.4 mol, 2.0 equiv.) in tetrahydrofuran (5.0 cm^3) was added dropwise to it, care being taken to avoid an exotherm. The mixture was stirred for 30 min after which it was evaporated to dryness and washed with water to yield, upon evaporation, the *benzamide* **4a** as cream coloured plates (2.385 g, 9.45 mol, 78.2%); mp 100–

103 °C; ν_{max}(KBr disc)/cm^{-1} 2975, 2932, 1634, 1572, 1480 and 1373; δ_H(250 MHz, CD_3OD) 1.21 (6 H, d, *J* 6.5, $CHCH_3$), 1.60 (6 H, d, *J* 6.8, $CHCH_3$), 3.66 and 3.71 (2 H, 2 × septets, *J* 6.6, CH_3CH), 7.48 (1 H, d, *J* 7.3, ArH), 7.54–7.75 (2 H, m, ArH) and 8.32 (1 H, d, *J* 7.4, ArH); δ_C(100 MHz, CD_3OD) 19.90, 20.22, 20.45, 20.63, 46.05, 51.85, 125.15, 127.85, 129.82, 135.04, 135.49, 145.70 and 166.82; *m/z* (EI$^+$) 250 (M^+, 2.4%) and 150 ($C_7H_4O_3N$, 100) (Found: M^+, 250.1294. $C_{13}H_{18}N_2O_3$ requires *M*, 250.1317).

o-Amino-*N*,*N*-diisopropylbenzamide 5a

A suspension of copper acetylacetonate (0.209 g, 0.8 mmol, 0.2 equiv.) in ethanol (200 cm^3) was stirred at room temp. to give a sky blue solution. Addition of sodium boranuide (0.151 g, 3.97 mmol, 5.0 equiv) to this formed a brown solution after an induction period of 5 s which gradually faded to a dark fawn colour with formation of a granular deposit. A solution of the nitrobenzamide **4a** (1.0 g, 4.0 mmol, 5.0 equiv.) in ethanol (10 cm^3) was then added to the mixture followed by further sodium boranuide (0.302 g, 8.0 mmol, 10.0 equiv.). The mixture was stirred at room temperature and the reaction monitored by TLC, until it was complete (2 h). The reaction mixture was quenched with water (200 cm^3), rotary evaporated to remove the ethanol and extracted with dichloromethane. The extract was evaporated to dryness to yield the *title compound* **5a** as pale yellow prisms (0.62 g, 2.82 mol, 70.5%), mp 105–106 °C (EtOAc); ν_{max}(KBr disc)/cm^{-1} 3451, 3423, 2935, 1608 and 1495; δ_H(250 MHz, $CDCl_3$) 1.35 (12 H, brs, CH_3CH), 3.72 (2 H, brs, NH_2), 4.05 (2 H, brs, CH_3CH), 6.69 (1 H, d, *J* 7.6, ArH), 6.71 (2 H, t, *J* 7.6, ArH), 6.99 (1 H, d, *J* 7.2, ArH) and 7.12 (1 H, t, *J* 7.6, ArH); δ_C(67.5 MHz, $CDCl_3$) 20.81, 21.06, 21.19, 21.60, 48.18, 116.41, 117.59, 123.74, 125.86, 129.38, 144.22 and 170.24; *m/z* (EI$^+$) 220 (M^+, 61.3%), 120 (C_7H_6ON, 100) and 100 ($C_6H_{14}N$) (Found: C, 70.7; H, 9.15; N, 12.7%; M^+, 220.1615. $C_{13}H_{20}N_2O$ requires C, 70.87; H, 9.35; N, 12.74%; *M*, 220.1576).

o-(*N*,*N*-Diisopropylcarboxamido)benzenediazonium tetrafluoroborate 6a

The benzamide **5a** (432 mg, 1.96 mmol, 1.0 equiv.) was dissolved in tetrafluoroboric acid (20%; 10 cm^3) at room temperature and the solution cooled in an ice–salt bath to *ca.* −10 °C. A solution of sodium nitrite (0.162 g, 2.35 mmol, 1.2 equiv.) in water (3.0 cm^3) was then slowly added to it and the resulting mixture stirred until a white solid precipitate was formed (*ca.* 30 min). This was filtered to give white rosettes of the *tetrafluoroborate* **6a** which were recrystallised from acetone by diethyl ether addition (455 mg, 1.427 mmol, 73%); ν_{max}(KBr disc)/cm^{-1} 2935, 2294, 1627, 1386, 1375 and 785; δ_H(250 MHz, [$^2H_6$]acetone) 1.36 [6 H, brs, $(CH_3)_2CH$], 1.51 [6 H, brs, $CH(CH_3)_2$], 3.84 (1 H, brs, CH–N), 4.15 (1 H, brs, CHN), 8.09–8.15 (2 H, m, ArH), 8.38 (1 H, t, *J* 6.8, ArH) and 8.94 (1 H, d, *J* 7.4, ArH); δ_C(67.8 MHz, [$^2H_6$]acetone) 20.70, 53.00, 116.00, 129.87, 132.98, 135.96, 141.44, 141.66 and 163.06; *m/z* (EI$^+$) 223 ($C_{13}H_{18}ONF$, 13.5%, Schiemann degradation) and 123 (C_7H_4OF, 100) (Found: C, 48.8; H, 5.8; N, 12.9. $C_{13}H_{18}N_3OBF_4$ requires C, 48.93; H, 5.69; N, 13.17).

N-Isopropylbenzamide 7a

Method 1: stoichiometric use of tetrathiafulvalene. The tetrafluoroborate **6a** (100 mg, 0.314 mmol, 1.0 equiv.) was dissolved in degassed wet acetone (10 cm^3) under nitrogen in the dark. Tetrathiafulvalene (64.1 mg, 0.314 mmol, 1.0 equiv.) was added to the solution and the mixture stirred for 2 h. It was then evaporated to dryness and the residue dissolved in dichloromethane and the solution washed with water (3 × 20 cm^3), and evaporated to dryness to give the *benzamide* **7a** as brown prisms (52 mg, 98%), mp 100–101 °C (lit.,[14] 103–104 °C); ν_{max}(KBr disc)/cm^{-1} 3298, 2971, 1633 and 1536; δ_H(400 MHz, [$^2H_6$]acetone), 1.28 (6 H, d, *J* 6.6, CH_3CH), 4.29 [1 H, m, $CH(CH_3)_2$], 7.47 (2 H, t, *J* 8.1, ArH), 7.57 (1 H, t, *J* 8.6, ArH) and 7.85 (2 H, d, *J* 6.7, ArH); δ_C(67.8 MHz, $CDCl_3$) 22.59, 41.71, 126.77, 128.27, 131.02, 134.83 and 166.65; *m/z* (EI$^+$) 163 (M^+, 55%), 105 (100) and 77 (46) (Found: M^+, 163.1056. $C_{10}H_{13}NO$ requires *M*, 163.0997).

Method 2: catalytic use of tetrathiafulvalene. A repeat of the previous reaction but using only a catalytic quantity of tetrathiafulvalene (6.4 mg, 10 mol%) also gave the benzamide **7a** (40.8 mg, 75.4%).

N,*N*-Diethyl-*o*-nitrobenzamide 4b

The general procedure used for the synthesis of **4a** was used to give the *nitrobenzamide* **4b** as yellow prisms (87.3%), mp 42–45 °C (EtOAc); ν_{max}(disc)/cm^{-1} 2985, 2939, 1641, 1577, 1524, 1486, 1346 and 747; δ_H(250 MHz, $CDCl_3$) 1.07 (3 H, t, *J* 7.1, CH_3CH), 1.31 (3 H, t, *J* 7.1, CH_3CH_2), 3.13 (2 H, q, *J* 7.2, CH_2CH_3), 3.53 (2 H, br, CH_2CH_3), 7.40 (1 H, d, *J* 7.5, ArH), 7.56 (1 H, t, *J* 8.2, ArH), 7.71 (1 H, t, *J* 7.5, ArH) and 8.20 (1 H, d, *J* 8.3, ArH); δ_C(100 MHz, [$^2H_6$]acetone) 11.90, 13.46, 38.85, 42.69, 124.64, 127.92, 129.48, 133.54, 134.31, 144.93 and 167.08; *m/z* (EI$^+$) 222 (M^+, 1.9%) 150 ($C_7H_4O_3N_2$, 100%), 72 ($C_4H_{10}N$, 97) (Found: C, 59.2; H, 6.4; N, 12.4%; M^+, 222.1029. $C_{11}H_{14}N_2O_3$ requires C, 59.45; H, 6.35; N, 12.60%; *M*, 222.1004).

o-Amino-*N*,*N*-diethylbenzamide 5b

The general procedure used for the formation of **5a** was used to give the *benzamide* **5b** as cream coloured prisms (92%), mp 44–46 °C; ν_{max}(KBr disc)/cm^{-1} 3444, 3342, 3245, 2974, 1611 and 1469; δ_H(250 MHz, $CDCl_3$) 1.19 (6 H, br, CH_3CH_2), 3.43 (2 H, br, CH_3CH_2), 3.7–4.5 (2 H, br, CH_2CH_3), 6.71 (2 H, m, NH_2), 6.71 (2 H, m, ArH) and 7.11 (2 H, m, ArH); δ_C(67.5 MHz, $CDCl_3$) 14.54, 42 (br), 116.87, 117.81, 121.98, 127.39, 130.73, 145.27 and 170.90; *m/z* (EI$^+$) 192 (M^+, 80.71%), 120 (C_6H_6ON, 100) and 72 ($C_4H_{10}N$, 100) (Found: C, 68.5; H, 8.5; N, 14.55; M^+, 192.1234. $C_{11}H_{16}N_2O$ requires C, 68.72; H, 8.39; N, 14.57%; *M*, 192.1263).

o-(*N*,*N*-Diethylcarboxamido)benzenediazonium tetrafluoroborate 6b

To a solution of the amine **5b** (2.46 g, 12.8 mmol, 1.0 equiv.) in fluoroboric acid (50%; 6.81 cm^3, 38.5 mmol, 3.0 equiv.) at 0 °C was added isopentyl nitrite (2.58 cm^3, 19.3 mmol, 1.5 equiv.) and the mixture stirred for 30 min. Dilution of the mixture with diethyl ether (20 cm^3) caused, after 10 min, the precipitation of *tetrafluoroborate* **6b** as pale cream crystals (3.4 g, 91%); ν_{max}(KBr disc)/cm^{-1} 2982, 2229, 1631 and 1562; δ_H(250 MHz, CD_3CN), 1.27 (3 H, t, *J* 7.1, CH_2CH_3), 1.32 (3 H, t, *J* 7.1, CH_2CH_3), 3.42 (2 H, q, *J* 7.1, CH_2CH_3), 3.61 (2 H, q, *J* 7.1, CH_2CH_3), 7.98 (1 H, d, *J* 7.8, ArH), 8.02 (1 H, t, *J* 8.0, ArH), 8.27 (1 H, t, *J* 7.8, ArH) and 8.66 (1 H, d, *J* 8.2, ArH); δ_C(67.8 MHz, [$^2H_6$]acetone) 12.44, 13.99, 41.00, 44.86, 116.11, 130.30, 133.21, 135.96, 140.27, 141.41 and 163.72; *m/z* (FAB) 204 [$(M - BF_4)^+$, 52%)], 176 ($M - BF_4 - N_2^+$, 28) and 105 (C_6H_5CO, 100) [Found: C, 45.4; H, 5.0; N, 14.45; M^+, 204.1125. $C_{11}H_{14}BF_4ON_3$ requires C, 45.39; H, 4.85; N, 14.44%; $(M - BF_4)^+$, 204.1137].

N-Ethylbenzamide 7b

The general reaction procedure adopted was the same as that used in preparation of **7a** (Method 1) and gave the *benzamide* **7b** as brown plates (87 mg, 85%), mp 68–69 °C (lit.,[15] 68.5 °C); ν_{max}(KBr disc)/cm^{-1} 3319, 2978, 2935, 2871, 1636 and 1549; δ_H(270 MHz, $CDCl_3$) 1.26 (3 H, t, *J* 7.3, CH_3CH_2), 3.50 (2 H, dq, *J* 7.3 and 5.7, CH_2CH_3), 6.18 (1 H, br s, NH), 7.35–7.55 (3 H, m, ArH) and 7.76 (2 H, d, *J* 8.1, ArH); δ_C(67.8 MHz, $CDCl_3$)

14.67, 34.76, 126.79, 128.25, 131.05, 134.59 and 167.48; *m/z* (EI) 149 (42%), 105 (100) and 77 (41) (Found: M^+, 149.0841. $C_9H_{11}NO$ requires *M*, 149.0841).

N,N-Dimethyl-o-nitrobenzamide 4c

Freshly ground potassium hydroxide (8.1 g, 144 mmol, 8.0 equiv.) was added to dimethyl sulfoxide (70 cm^3) and the mixture stirred for 5 min. After this *o*-nitrobenzamide (3 g, 18 mmol, 1.0 equiv.) was added to it followed immediately by methyl iodide (9.1 g, 72 mmol, 4.0 equiv.). The reaction mixture was stirred for 10 min and then poured into water (600 cm^3). The aqueous mixture was extracted with dichloromethane (3 × 300 cm^3) and the latter back-washed with water (6 × 600 cm^3), dried ($MgSO_4$) and evaporated to give the *benzamide* **4c** as yellow needles (3.18 g, 91%), mp 71–73 °C (lit.,[15] 77–78 °C); ν_{max}(KBr disc)/cm^{-1} 2937, 1636, 1576, 1529 and 1356; δ_H(250 MHz, $CDCl_3$) 2.85 (3 H, s, NCH_3), 3.18 (3 H, s, NCH_3), 7.42 (1 H, d, *J* 7.2, ArH), 7.58 (1 H, t, *J* 7.0, ArH), 7.73 (1 H, t, *J* 7.5, ArH) and 8.20 (1 H, d, *J* 7.1, ArH); δ_C(67.8 MHz, $CDCl_3$) 34.67, 38.05, 124.50, 127.93, 129.53, 133.14, 134.38 and 167.73; *m/z* (EI) 194 (M^+, 16%), 150 (100) and 76 (28) (Found: C, 55.8; H, 5.3; N, 14.7%; M^+, 194.0665. $C_9H_{10}N_2O_3$ requires C, 55.67; H, 5.19; N, 14.43%; *M*, 194.0691).

o-Amino-N,N-dimethylbenzamide 5c

The same general procedure as used in the preparation of **5a** was used to give the *benzamide* **5c** as a green oil (2.8 g, 17.1 mmol, 93%), mp 24–25 °C; ν_{max}(film)/cm^{-1} 3451, 3350, 2926, 1620, 1592, 1492, 1454 and 732; δ_H(250 MHz, $CDCl_3$) 3.07 (6 H, s, CH_3), 6.2–7.7 (2 H, br, NH_2) and 7.16–7.48 (4 H, br m, ArH); δ_C(67.8 MHz, $CDCl_3$) 35.5 (br), 38.5 (br), 116.6, 117.2, 120.1, 127.9, 130.4, 145.4 and 171.0.

o-(N,N-Dimethylcarboxamido)benzenediazonium tetrafluoroborate 6c

The same procedure as that used in preparation of **6a** was used to give the *tetrafluoroborate* **6c** as a white powder (2.7 g, 68%); ν_{max}(KBr disc)/cm^{-1} 2937, 2801, 2295, 1641, 1562 and 1504; δ_H(250 MHz, [$^2H_6$]acetone) 3.14 (3 H, s, CH_3N), 3.21 (3 H, s, CH_3N), 8.17 (1 H, t, *J* 7.0, ArH), 8.28 (1 H, d, *J* 6.9, ArH), 8.41 (1 H, t, *J* 7.3, ArH) and 9.01 (1 H, d, *J* 7.2, ArH); δ_C(100 MHz, CD_3COCD_3) 35.81, 39.68, 115.81, 131.13, 132.95, 135.63, 139.56, 140.88 and 163.64; *m/z* (FAB) 176 ($M - BF_4$)$^+$, 85%), 148 ($M - BF_4 - N_2$, 41) and 105 (C_5H_5CO, 100) [Found: C, 41.2; H, 3.8; N, 15.7%; ($M - BF_4$)$^+$, 176.0844. $C_9H_{10}N_3OBF_4$ requires C, 41.10; H, 3.83; N, 15.98%; *M* − BF_4, 176.0823].

N-Methylbenzamide 7c

The general reaction procedure used in the preparation of **7a** (Method 1) gave the benzamide **7c** as yellow plates (38 mg, 39%), mp 74–76 °C (lit.,[16] 77 °C); ν_{max}(KBr disc)/cm^{-1} 3327, 2926, 2853, 1639, 1604, 1579, 1552, 1522, 1493 and 711; δ_H(270 MHz, $CDCl_3$) 2.97 (3 H, d, *J* 3.9, CH_3NH), 6.70 (1 H, brs, NH), 7.27–7.50 (3 H, m, ArH) and 7.72–7.77 (2 H, m, ArH); δ_C(67.8 MHz, $CDCl_3$) 26.8, 127.0, 128.4, 131.2, 134.5 and 168.6; *m/z* (FAB) 136 (M^+, 100%), 105, 77, 58 and 57.

N,N-Dibenzyl-o-nitrobenzamide 4d

The general procedure as that used in preparation of **4a** was employed to give a pale yellow solid which was purified by column chromatography (15% EtOAc–light petroleum) to afford the benzamide **4d** as a white powder (2.41 g, 7.0 mmol, 80%), mp 108–109 °C (lit.,[17] 104–105 °C); ν_{max}(KBr disc)/cm^{-1} 3012, 2922, 1637, 1527 and 1496; δ_H(270 MHz, $CDCl_3$) 4.22 (4 H, s, NCH_2Ph), 7.11 (1 H, d, *J* 7.9, ArH), 7.29–7.41 (9 H, m, ArH), 7.50 (1 H, t, *J* 7.2, ArH), 7.55 (1 H, d, *J* 7.3, ArH), 7.68 (1 H, t, *J* 7.5, ArH) and 8.20 (1 H, d, *J* 6.9, ArH); δ_C(67.8 MHz, $CDCl_3$) 46.73, 51.35, 124.49, 127.10, 127.33, 127.55, 127.76, 128.28, 128.50, 128.64, 129.58, 132.51, 134.11, 134.90, 135.74, 145.52 and 168.68; *m/z* (FAB) 347 [($M + H$)$^+$, 28.7%], 196 (90%) and 150 (50%) (Found: C, 73.2; H, 5.4; N, 8.4. $C_{21}H_{18}N_2O_3$ requires C, 72.81; H, 5.51; N, 8.06%).

o-Amino-N,N-dibenzylbenzamide 5d

The general procedure used in the preparation of **5a** was used to afford the benzamide **5d** as white rosettes (1.89 g, 6.0 mmol, 77%), mp 132–134 °C (lit.,[17] 131.5–132.5 °C); ν_{max}(KBr disc)/cm^{-1} 3441, 3360, 2956, 2914, 1620 and 1494; δ_H(250 MHz, $CDCl_3$) 4.4–4.8 (4 H, br, NCH_2Ph), 6.2–6.7 (2 H, br, NH_2) and 7.2–7.5 (14 H, m, ArH); δ_C(67.8 MHz, $CDCl_3$) 47 (br), 52 (br), 117.29, 117.88, 120.49, 127.57, 127.94, 128.19, 128.84, 129.13, 131.02, 137.05, 146.00 and 172.08; *m/z* (EI) 316 (M^+, 8%), 196 (43) and 120 (100) (Found: M^+, 316.1572. $C_{21}H_{20}N_2O$ requires *M*, 316.1576).

o-(N,N-Dibenzylcarboxamido)benzenediazonium tetrafluoroborate 6d

The same procedure as that used for preparation of **6a** was used to give the *tetrafluoroborate* **6d** as pale orange prisms (1.30 g, 3.1 mmol 58%); ν_{max}(KBr disc)/cm^{-1} 3087, 3063, 2293, 1640 and 1564; δ_H(250 MHz, CD_3COCD_3) 4.78 (4 H, d, *J* 8.1, CH_2Ph), 7.42 (10 H, m, CH_2Ph), 8.17 (2 H, d + t, *J* 7.2, ArH), 8.32 (1 H, t, *J* 7.4, ArH) and 9.05 (1 H, d, *J* 7.5, ArH); δ_C(100 MHz, CD_3COCD_3) 49.53, 53.08, 116.39, 127.80, 128.27, 129.04, 129.26, 129.73, 130.00, 133.64, 136.16, 136.34, 136.45, 138.82, 141.28 and 164.97; *m/z* (FAB) 328 (M^+, 60.7%), 181 ($C_{14}H_{14}N$, 100%) (Found: $M - BF_4^+$, 328.1428. $C_{21}H_{18}N_3O$ requires $M - BF_4$, 328.1450).

N-Benzylbenzamide 7d

The general procedure used in preparation of **7a** (Method 1) was employed to give a brown oil which could be separated by column chromatography into benzaldehyde and the benzamide **7d** as a pale yellow powder (61%), mp 102–104 °C (lit.,[18] 104–106 °C); ν_{max}(KBr disc)/cm^{-1} 1642, 1577, 1544, 1490 and 729; δ_H(250 MHz, $CDCl_3$) 4.63 (2 H, d, *J* 5.7, CH_2NH), 6.53 (1 H, brs, NH), 7.3–7.6 (8 H, m, ArH) and 7.79 (2 H, d, *J* 8.0, ArH); δ_C(67.8 MHz, $CDCl_3$) 43.87, 126.47, 126.94, 127.92, 128.39, 128.55, 131.36, 134.21 and 138.19, 167.39; *m/z* (EI) 211 (M^+, 97%), 105 (100) and 77 (100) (Found: M^+, 211.0997. $C_{14}H_{13}NO$ requires *M*, 211.0997).

1-(o-Nitrobenzoyl)pyrrolidine 4e

The general procedure used for the synthesis of **4a** was employed to yield the *pyrrolidine* **4e** as yellow plates (4.4 g, 20 mmol, 88.5%), mp 86.5–88 °C; ν_{max}(disc)/cm^{-1} 2969, 2879, 1630, 1525, 1479 and 765; δ_H(80 MHz, CD_3OD) 1.97 (4 H, m, $NCH_2C_2H_4$), 3.13 (2 H, t, *J* 6.1, NCH_2), 3.75 (2 H, t, *J* 5.9, CH_2N), 7.35–7.85 (3 H, m, ArH) and 8.1–8.3 (1 H, m, ArH); δ_C(100 MHz, CD_3OD) 25.34, 26.65, 46.94, 49.00, 125.66, 129.18, 131.39, 134.26, 135.86, 146.25 and 168.28; *m/z* (EI^+) 220 (M^+, 5.0%), 70 (C_4H_8N, 100) (Found: C, 60.0; H, 5.6; N, 12.4%; M^+, 220.0804. $C_{11}H_{12}N_2O_3$ requires C, 59.99; H, 5.50; N, 12.72%, *M*, 220.0848).

1-(o-Aminobenzoyl)pyrrolidine 5e

A procedure identical with that used in the preparation of **5a** gave the *pyrrolidine* **5e** as a cream coloured solid (3.9 g, 19.3 mmol, 94%), mp 82–84 °C; ν_{max}(KBr disc)/cm^{-1} 3437, 3342, 2978, 2878, 1613, 1582, 1493 and 1582; δ_H(270 MHz, $CDCl_3$) 1.80–2.0 (4 H, m, $CH_2C_2H_4CH_2$), 3.47 (2 H, br NCH_2), 3.63 (2 H, br CH_2N), 4.32 (2 H, br, NH_2), 6.66–6.71 (2 H, m, ArH) and 7.12–7.21 (2 H, m, ArH); δ_C(67.8 MHz, $CDCl_3$), 24.44, 26.31, 45.93, 49.52, 116.67, 116.98, 120.72, 127.92, 130.62, 145.89 and 169.45; *m/z* (EI^+) 190 (M^+, 44%), 120 (100), 92 (23) and 70

(57) (Found: C, 69.4; H, 7.5; N, 14.7; M^+, 190.1087. $C_{11}H_{14}N_2O$ requires C, 69.45; H, 7.43; N, 14.73%; *M*, 190.1106).

o-Pyrrolidin-1-ylcarbonylbenzenediazonium tetrafluoroborate 6e

The general procedure used in the preparation of **6a** was employed to give the *tetrafluoroborate* **6e** as pale green needles (2.1 g, 10.3 mmol, 64%); ν_{max}(KBr disc)/cm^{-1} 3082, 3031, 2980, 2885, 2293, 1625, 1565 and 756; δ_H(250 MHz, [$^2H_6$]acetone) 1.9–2.07 (4 H, m, CH_2CH_2), 3.65 (2 H, t, *J* 6.5, NCH_2), 3.76 (2 H, t, *J* 6.1, NCH_2), 8.15 (1 H, t, *J* 8.6, ArH), 8.37 (2 H, m, ArH) and 8.97 (1 H, d, *J* 8.0, ArH); δ_C(100 MHz, [$^2H_6$]acetone) 24.7, 26.9, 47.9, 50.2, 115.9, 131.2, 133.4, 136.0, 140.3, 141.3 and 162.0; *m/z* (FAB) 202 (M^+, 53%), 120 (100) and 70 (73) (Found: C, 45.6; H, 4.2; N, 14.4. $C_{11}H_{12}N_3OBF_4$ requires C, 45.71; H, 4.18; N, 14.54%).

Reaction of the tetrafluoroborate 6e with tetrathiafulvalene

To a stirred solution of the tetrafluoroborate **6e** (200 mg, 0.77 mmol, 1.0 equiv.) in degassed acetone was added TTF (157 mg, 0.77 mmol, 1.0 equiv.) and the mixture stirred for 30 min. After this it was evaporated to dryness and the residue dissolved in methanol (5 cm^3). To this solution was added a solution of 2,4-dinitrophenylhydrazine and the mixture stirred for 10 min until a fine yellow precipitate was seen. The product was collected and recrystallised from hot ethanol to give the 2,4-*dinitrophenylhydrazone* **8** as a yellow powder (49 mg, 0.13 mmol, 17%), mp 123–125 °C; ν_{max}(KBr disc)/cm^{-1} 3301, 2934, 2877, 1638, 1618, 1593, 1537, 1520, 723, 669 and 826; δ_H(250 MHz, [$^2H_6$]acetone) 1.94–2.16 (2 H, m, NCH_2CH_2), 2.54 (2 H, dt, *J* 5.1 and 7.3, CH_2CH=N), 3.53 (2 H, dt, *J* 6.1 and 6.8, CH_2N), 7.4–7.5 (2 H, m, Ph), 7.85–7.89 (3 H, m, Ph), 8.03 (1 H, d, *J* 9.4, ArH), 8.03 (1 H, t, *J* 5.4, HC=N), 8.34 (1 H, d, *J* 9.7, ArH) and 8.96 (1 H, s, ArH).

***N*-Isobutyryl-*N*-methyl-*o*-nitroaniline 11a**

N-Methyl-*o*-nitroaniline (3.0 g, 19.74 mmol, 1.0 equiv.) was added to sodium hydride (0.95 g, 39.48 mmol, 2.0 equiv.) in dry THF (150 cm^3) and the mixture stirred for 2 h. To this mixture was added dropwise a solution of isobutyryl chloride (6.31 g, 59.22 mmol, 3.0 equiv.) and the mixture stirred for 24 h. Further isobutyryl chloride (6.31 g, 59.22 mmol, 3.0 equiv.) was added to the mixture which was then stirred for a further 48 h. The reaction mixture was then evaporated to dryness and the residue dissolved in dichloromethane (200 cm^3) and the solution washed with water (200 cm^3), and aqueous sodium hydroxide (2 mol dm^{-3}), dried ($MgSO_4$) and evaporated to dryness. Purification of the residue by column chromatography (10% diethyl ether–dichloromethane) gave the *nitroaniline* **11a** as yellow prisms (2.02 g, 9.11 mmol, 46%), mp 77–80 °C; ν_{max}(disc)/cm^{-1} 1661, 1605, 1578, 1485 and 735; δ_H(250 MHz, $CDCl_3$) (* indicates signal due to minor rotameric form) 1.00 (3 H, d, *J* 6.8, CH_3CH), 1.01 (3 H, d, *J* 6.6, CH_3CH), 1.16–1.22* [6 H, m, $(CH_3)_2CH$], 2.25 [1 H, septet, *J* 6.7, $(CH_3)_2CH$], 2.95* [1 H, septet, $(CH_3)_2CH$], 3.20 (3 H, s, NMe), 3.46* (3 H, s, NMe), 7.38 (1 H, d, *J* 7.8, ArH), 7.56 (1 H, t, *J* 7.8, ArH), 7.71 (1 H, t, *J* 7.7, ArH) and 8.01 (1 H, d, *J* 8.1, ArH); δ_C(67.8 MHz, $CDCl_3$) 18.04,* 18.74, 19.55, 30.07,* 31.38, 36.23, 37.86,* 124.56,* 125.23, 127.37,* 128.84,* 129.25, 130.62, 133.80,* 134.41, 136.80, 137.30,* 146.18, 146.31,* 176.39 and 176.62;* *m/z* (EI$^+$) 177 ($M^+ - NO_2$, 5.9%), 152 ($C_7H_7N_2O_2$, 41) and 43 [$(CH_3)_2CH$, 100] (Found: C, 59.4; H, 6.5; N, 12.8. $C_{11}H_{14}N_2O_3$ requires C, 59.45; H, 6.35; N, 12.60%).

***N*-(*o*-Aminophenyl)-*N*-methylisobutyramide 12a**

The general procedure used in the preparation of **5a** was employed to give the *butyramide* **12a** as pink plates that were recrystallised from diethyl ether by the addition of light petroleum to afford white needles (1.39 g, 7.03 mmol, 79%); mp 112–114 °C; ν_{max}(disc)/cm^{-1} 3442, 3353, 3030, 2978, 2932, 2871, 1651, 1628, 1579, 1505 and 738; δ_H(250 MHz, $CDCl_3$) 1.02 (3 H, d, *J* 6.8, CH_3CH), 1.05 (3 H, d, *J* 6.7, CH_3CH), 2.47 [1 H, septet, *J* 6.7, $(CH_3)_2CH$], 3.80 (2 H, br, NH_2), 6.37–6.81 (2 H, m, ArH), 7.01 (1 H, d, *J* 7.7, ArH) and 7.15 (1 H, t, *J* 7.5, ArH); δ_C(67.8 MHz, $CDCl_3$) 19.59, 30.84, 35.10, 116.00, 118.49, 128.05, 128.77, 129.00, 142.77 and 178.69; *m/z* (EI$^+$) 149 ($M^+ - CH(CH_3)_2$, 100%) and 122 (48) (Found: C, 68.4; H, 8.6; N, 14.9. $C_{11}H_{16}N_2O$ requires C, 68.72; H, 8.39; N, 14.57%).

***o*-(*N*-Isobutyryl-*N*-methylamino)benzenediazonium tetrafluoroborate 13a**

The general method used for the preparation of **6a** was employed to give the *tetrafluoroborate* **13a** as yellow needles (242 mg, 0.8 mmol, 80%); ν_{max}(KBr disc)/cm^{-1} 3107, 2974, 2287, 1660, 1588, 1566, 1475 and 766; δ_H(250 MHz, [$^2H_6$]acetone) 1.23 [6 H, d, *J* 6.7, $(CH_3)_2CH$], 3.29 [1 H, septet, *J* 6.7, $(CH_3)_2CH$], 3.78 (3 H, s, NMe), 7.85 (1 H, t, *J* 8.0, ArH), 8.02 (1 H, d, *J* 8.5, ArH), 8.40 (1 H, t, *J* 8.0, ArH) and 8.74 (1 H, d, *J* 8.4, ArH); δ_C(67.8 MHz, [$^2H_6$]acetone) 19.1, 31.9, 38.7, 128.1, 128.8, 133.4, 143.6, 146.7 and 178.5; *m/z* (FAB) 204 ($M - BF_4$)$^+$, (45%), 176 (100), 105 (11) and 71 (13) [Found: 204.1129. $C_{11}H_{14}N_3OBF_4$ requires $(M - BF_4)^+$, 204.1137].

Reaction of tetrathiafulvalene with the tetrafluoroborate 13a

To a stirred solution of the tetrafluoroborate **13a** (200 mg, 0.69 mmol, 1.0 equiv.) in degassed acetone (50 cm^3) was added tetrathiafulvalene (140 mg, 0.69 mmol, 1.0 equiv.) in one portion and the mixture stirred for 30 min. The mixture was then evaporated to dryness and the residue purified by column chromatography (10% acetone–dichloromethane to 20% acetone–dichloromethane) with mixed fractions being purified by recrystallisation (acetone–diethyl ether) to give the following two compounds. 2-{2-[2-(N-*Methylanilinocarbonyl*)*propan*-2-*yl*]-1,3-*dithiol*-2-*yl*}-1,3-*dithiolium tetrafluoroborate* **14a** as red crystals (169 mg, 0.36 mmol, 53%), mp 133–137 °C (decomp.); ν_{max}(KBr disc)/cm^{-1} 3079, 3012, 1612, 1591, 1496, 1084, 779 and 740; λ_{max}(EtOH)/nm 205.6 (ε/dm^3 mol^{-1} cm^{-1} 53 700), 310sh and 490.4 (ε 1737); δ_H(250 MHz, [$^2H_6$]acetone) 1.45 [6 H, br s, $(CH_3)_2C$], 3.31 (3 H, s, NMe), 6.41 (2 H, s, SC*H*C*H*S), 7.43–7.46 (5 H, m, ArH) and 9.34 (2 H, s, C*H*C*H*S$^+$); δ_C(100 MHz, CD_3CN), 25.9, 41.6, 56.0, 116.5, 128.2, 128.6, 129.5, 143.4, 143.8, 172.9 and 212.5; *m/z* (FAB) 380 (M^+, 57%), 278 (100), 204 (59), 176 (16), 134 (64), 106 (22), 103 (10) and 77 (43) (Found: $M^+ - BF_4$, 380.0282. $C_{17}H_{18}NOS_4$ requires $M - BF_4$, 380.0271). 1-{2-[o-(N-*Isobutyryl*-N-*methylamino*)-*phenyl*]}-2-(1,3-*dithiol*-2-*ylidene*)-1,3-*dithiolium tetrafluoroborate* **15a** as yellow crystals (51 mg, 0.10 mmol, 14%), mp 147–148 °C; ν_{max}(KBr disc)/cm^{-1} 2970, 2931, 1637, 1582, 1470, 1084, 1062 and 744; λ_{max}(EtOH)/nm 248.0 (ε/dm^3 mol^{-1} cm^{-1} 2814) and 338.4 (3146); δ_H(250 MHz, [$^2H_6$]acetone) 1.17 (3 H, d, *J* 6.6, CH_3CH), 1.37 (3 H, d, *J* 6.8, CH_3CH), 3.35 [1 H, septet, *J* 6.7, $CH(CH_3)_2$], 3.87 (3 H, s, NMe), 6.93 (1 H, d, *J* 5.9, CHS), 7.12 (1 H, d, *J* 6.3, SCHC*H* S), 7.28 (1 H, d, *J* 6.3, SC*H*CHS), 7.63–7.70 (2 H, m, ArH), 7.84–7.88 (2 H, m, ArH) and 8.38 (1 H, d, *J* 5.9, CHS); δ_C(100 MHz, CD_3CN) 17.6, 18.7, 30.7, 37.6, 89.9, 112.3, 121.6, 123.3, 125.3, 126.8, 128.2, 129.6, 136.2, 142.8, 143.4, 155.7 and 179.4; *m/z* (FAB) 380 [($M - BF_4$)$^+$, 4.6%], 93 (17), 71 (31) and 43 (84) (Found: $M^+ - BF_4$, 380.0283. $C_{17}H_{18}NOS_4$ requires $M - BF_4$, 380.0271).

***N*-Methyl-*N*-propionyl-*o*-nitroaniline 11b**

N-Methyl-*o*-nitroaniline was added to a suspension of THF-washed sodium hydride (0.47 g, 19.74 mmol, 1.0 equiv.) in dry THF (150 cm^3) and the mixture was stirred for 1 h. To this mixture was carefully added a solution of propionyl chloride (5.48 g, 59.22 mmol, 3.0 equiv.) in THF (150 cm^3) and the whole

stirred for 60 h. The mixture was then evaporated to dryness and the residue dissolved in dichloromethane (100 cm^3). The resulting solution was washed with water (3 × 100 cm^3), aqueous sodium hydroxide (2 mol dm^{-3}; 3 × 100 cm^3), and hydrochloric acid (2 mol dm^{-3}; 100 cm^3) and then dried ($MgSO_4$) and evaporated to dryness to give the *nitroaniline* **11b** as a yellow oil (3.60 g, 17.31 mmol, 88%); ν_{max}(thin film)/cm^{-1} 2981, 2941, 1671, 1604, 1580, 1487, 761 and 707; δ_H(250 MHz, $CDCl_3$) (signals due the minor rotameric form are designated by *) 1.05 (3 H, t, *J* 7.4, CH_3CH_2), 1.15* (3 H, t, *J* 7.4, CH_3CH_2), 1.98 (2 H, q, *J* 7.4, CH_3CH_2), 2.52* (2 H, q, *J* 7.4, CH_3CH_2), 3.22 (3 H, s, NMe), 3.43* (3 H, s, NMe), 7.39 (1 H, d, *J* 7.8, ArH), 7.57 (1 H, t, *J* 7.7, ArH), 7.71 (1 H, t, *J* 7.7, ArH) and 8.01 (1 H, d, *J* 8.1, ArH); δ_C(67.8 MHz, $CDCl_3$) (signals due to the minor rotameric form are designated by *) 8.4,* 9.1, 26.7,* 27.2, 36.6, 38.1,* 124.8,* 125.4, 127.6,* 129.1,* 129.3, 130.9, 133.9,* 134.4, 137.0, 146.6, 173.0 and 173.9;* *m*/*z* (FAB) 209 [(M + H)$^+$, 100%], 162 (22%), 153 (75) and 57 (64) (Found: C, 57.75; H, 5.8; N, 13.4. $C_{10}H_{12}N_2O_3$ requires C, 57.69; H, 5.81; N, 13.45%).

N-(*o*-Aminophenyl)-*N*-methylpropionamide 12b

The same general procedure as that used in the preparation of **5a** was employed. After removal of ethanol from the reaction mixture by rotary evaporation the product was extracted into dichloromethane and purified by extraction into hydrochloric acid (2 mol dm^{-3}), basification by aqueous sodium hydroxide and re-extraction into dichloromethane. Evaporation of the extract gave the *propionamide* **12b** as a pink powder (2.17 g, 12.2 mmol, 73%), mp 99–101 °C; ν_{max}(KBr disc)/cm^{-1} 3473, 3343, 3206, 2982, 2941, 1656, 1628, 1578, 1504, 1459 and 770; δ_H(250 MHz, $CDCl_3$) 1.06 (3 H, t, *J* 7.4, CH_2CH_3), 1.98–2.19 (2 H, m, CH_2CH_3), 3.20 (3 H, s, NMe), 6.73–6.81 (2 H, m, ArH), 7.00 (1 H, d, *J* 7.7, ArH) and 7.16 (1 H, t, *J* 8.0, ArH); δ_C(67.8 MHz, $CDCl_3$) 10.60, 27.96, 36.25, 117.29, 119.84, 129.42, 130.05, 130.30, 144.04 and 176.23; *m*/*z* (EI$^+$) 178 (M$^+$, 17%), 160 (73), 149 (24) and 121 (19) (Found: M$^+$, 178.1122. $C_{10}H_{14}N_2O$ requires *M*, 178.1106).

o-(*N*-Methyl-*N*-propionylamino)benzenediazonium tetrafluoroborate 13b

The isopentyl nitrite method used for preparation of **6b** was employed here to give the *tetrafluoroborate* **13b** as a yellow powder (269 mg, 0.97 mmol, 87%); ν_{max}(KBr disc)/cm^{-1} 3107, 2924, 2275, 1661, 1587, 1566, 1484 and 769; δ_H(250 MHz, CD_3OD) 1.32 (3 H, t, *J* 7.3, CH_3CH_2), 2.87 (2 H, q, *J* 7.3, CH_3CH_2), 3.74 (3 H, s, NMe), 7.85 (1 H, t, *J* 8.0, ArH), 7.97 (1 H, d, *J* 8.5, ArH), 8.41 (1 H, t, *J* 7.9, ArH), 8.65 (1 H, d, *J* 8.4, ArH); δ_C(67.8 MHz, $CDCl_3$) 8.8, 27.8, 38.4, 112.7, 127.6, 128.5, 133.3, 143.4, 146.7 and 175.4; *m*/*z* (FAB) 467 [(M_2 − BF_4)$^+$, 14%], 190 (48), 162 (100), 154 (30), 124 (4), 107 (20) and 57 (18) (Found: M$^+$ − BF_4, 190.0890. $C_{10}H_{12}N_3O$ requires *M* − BF_4, 190.0980).

Reaction of tetrathiafulvalene with the tetrafluoroborate 13b

To tetrathiafulvalene (147 mg, 0.72 mmol, 1.0 equiv.) in degassed acetone (50 cm^3) containing 3 Å molecular sieves in the dark was added the *tetrafluoroborate* **13b** (200 mg, 0.72 mmol, 1.0 equiv.) and the mixture stirred for 5 min. Evaporation of the mixture to dryness gave a brown glass-like solid which was purified by column chromatography (20% acetone–dichloromethane) to give two major fractions: 2-{2-[1-(*N*-*methylanilinocarbonyl*)*ethyl*]-1,3-*dithiol*-2-*yl*}-1,3-*dithiolium tetrafluoroborate* **14b** as red prisms (151 mg, 47%), mp 72–74 °C; ν_{max}(KBr disc)/cm^{-1} 2923, 2852, 1641, 1593, 1495, 1057, 760 and 705; λ_{max}(EtOH)/nm 211.2 (ε/dm^3 mol^{-1} cm^{-1} 62 300), 290sh and 489.6 (6992.0); δ_H(250 MHz, $CDCl_3$) 1.52 (3 H, d, *J* 6.8, CH_3CH), 3.17 (3 H, s, NMe), 3.69 (1 H, q, *J* 6.8, $CHCH_3$), 6.04 [1 H, d, *J* 6.5, 1 × (SCH=CHS)], 6.26 [1 H, d, *J* 6.5, 1 × (SCH=CHS)], 7.27 (2 H, d, *J* 7.4, ArH), 7.47 (1 H, t, *J* 7.4, ArH), 7.59 (2 H, t, *J* 7.6, ArH) and 9.24 (2 H, s, CH=CHS$^+$); δ_C(100 MHz, CD_2Cl_2) 18.54, 38.42, 48.51, 76.41, 115.00, 118.48, 127.67, 129.52, 131.06, 142.21, 143.70, 171.11 and 214.55; *m*/*z* (FAB) 366 [(M − BF_4)$^+$, 20%], 307 (15), 289 (14), 264 (37) and 154 (100) [Found: M − BF_4, 366.0096. $C_{16}H_{16}NOS_4BF_4$ requires (*M* − BF_4), 366.0115].

1-{2-[o-(N-*Methyl*-N-*propionylamino*)*phenyl*]}-2-(1,3-*dithiol*-2-*ylidene*)-1,3-*dithiolium tetrafluoroborate* **15b** as a yellow solid (102 mg, 32%), mp 112–117 °C; ν_{max}(KBr disc)/cm^{-1} 3103, 3087, 2926, 1642, 1583, 1481, 1125, 1084 and 760; λ_{max}(EtOH)/nm 246.9 (ε/dm^3 mol^{-1} cm^{-1} 12 636) and 337.2 (13 828); δ_H(250 MHz, CD_3CN), 1.17 (3 H, t, *J* 7.3, CH_2CH_3), 2.64–2.75 (2 H, m, CH_2CH_3), 3.62 (3 H, s, NMe), 6.66 (1 H, d, *J* 5.9, S^+CHCHS), 6.84 (1 H, d, *J* 6.2, CHS), 6.99 (1 H, d, *J* 6.2, CHS), 7.46 (1 H, d, *J* 7.5, ArH), 7.52 (1 H, t, *J* 7.4, ArH), 7.70 (1 H, d, *J* 7.4, ArH), 7.79 (1 H, t, *J* 7.4, ArH) and 7.98 (1 H, d, *J* 6.0, CHS); δ_C(100 MHz, CD_3CN) 9.2, 27.8, 38.6, 89.9, 113.3, 122.8, 124.5, 126.3, 127.6, 129.3, 130.7, 137.2, 143.9, 144.7, 155.8 and 177.5; *m*/*z* (FAB) 366 (M$^+$ − BF_4, 100%), 323 (33), 204 (72), 162 (41), 77 (51), 76 (11) and 57 (82) (Found: [M − BF_4]$^+$, 366.0105. $C_{16}H_{16}NOS_4$ requires *M* − BF_4, 366.0115).

N-Acetyl-*N*-methyl-*o*-nitroaniline 11c

To a stirred suspension of sodium hydride (0.946 g, 39.4 mmol, 2.0 equiv.) in dry THF (300 cm^3) was added the amine (3.0 g, 19.7 mmol, 1.0 equiv.) and the mixture stirred for 1 h. A solution of acetyl chloride (4.64 g, 59.1 mmol, 3.0 equiv.) in dry THF (50 cm^3) was added dropwise to the mixture which was then stirred under reflux for 16 h and then evaporated to dryness. The residue was purified by column chromatography to give the *aniline* **11c** as yellow prisms (3.60 g, 18.57 mmol, 94%), mp 62–65 °C; ν_{max}(KBr disc)/cm^{-1} 2936, 1665, 1603, 1578, 1526 and 762; δ_H(250 MHz, $CDCl_3$) 1.83 (3 H, s, $COCH_3$), 2.25 (3 H, s, $COCH_3$), 3.22 (3 H, s, NMe), 3.44 (3 H, s, NMe), 7.40 (1 H, d, *J* 7.8, ArH), 7.57 (1 H, t, *J* 7.8, ArH), 7.72 (1 H, t, *J* 7.7, ArH) and 8.01 (1 H, d, *J* 8.1, ArH); δ_C(67.8 MHz, $CDCl_3$), 22.3, 36.9, 39.5,* 125.3,* 125.8, 128.3,* 129.5,* 129.9, 131.3, 134.5,* 134.9, 137.5,* 137.8, 146.9, 170.1 and 171.4; * *m*/*z* (FAB) 195 [(M + H)$^+$, 90%], 153 (77), 148 (24) and 43 (100) (Found: M + H$^+$, 195.0770. $C_9H_{10}N_2O_3$ requires *M* + H, 195.0770).

N-(*o*-Aminophenyl)-*N*-methylacetamide 12c

The same procedure as that used in the preparation of **5a** was employed to give the *acetamide* **12c** as white needles (2.43 g, 14.8 mmol, 82%), mp (sublimes) 114–120 °C; ν_{max}(KBr disc)/cm^{-1} 3435, 3351, 3238, 3030, 1636, 1600, 1580, 1505 and 737; δ_H(250 MHz, $CDCl_3$) 1.87 (3 H, s, $COCH_3$), 3.19 (3 H, s, NMe), 3.83 (2 H, br, NH_2), 6.73–6.82 (2 H, m, ArH), 7.01 (1 H, d, *J* 7.9, ArH) and 7.15 (1 H, t, *J* 7.7, ArH); δ_C(67.8 MHz, $CDCl_3$) 21.55, 34.79, 116.03, 118.44, 127.91, 129.02, 142.68 and 171.64; *m*/*z* (EI$^+$) 164 (M$^+$, 82%), 147 (100), 149 (40) and 121 (71) (Found: M$^+$, 164.0978. $C_9H_{12}N_2O$ requires *M*, 164.0949).

o-(*N*-Acetyl-*N*-methylamino)benzenediazonium tetrafluoroborate 13c

The isopentyl nitrite method used in the preparation of **6b** was employed to give the *tetrafluoroborate* **13c** as yellow crystals (1.77 g, 6.7 mmol, 81%); ν_{max}(KBr disc)/cm^{-1} 3085, 2267, 1673, 1587, 1565, 1484 and 769; δ_H(250 MHz, [$^2H_6$]acetone) 2.43 (3 H, s, $COCH_3$), 3.71 (3 H, s, NCH_3), 7.82 (1 H, t, *J* 7.8, ArH), 7.96 (1 H, d, *J* 8.0, ArH), 8.38 (1 H, t, *J* 8.0, ArH) and 8.70 (1 H, d, *J* 8.4, ArH); δ_C(67.8 MHz, [$^2H_6$]acetone) 22.6, 39.3, 112.0, 127.6, 128.61, 133.4, 143.4, 146.1 and 172.4; *m*/*z* (FAB) 176 (M$^+$ − BF_4, 44%), 148 (100%), 106 (13), 105 (11) and 77 (17).

Reaction of the tetrafluoroborate 13c with tetrathiafulvalene

To tetrathiafulvalene (155 mg, 0.76 mmol, 1.0 equiv.) in degassed acetone (50 cm^3) containing 3 Å molecular sieves in the dark was added the tetrafluoroborate **13c** (200 mg, 0.76 mmol, 1.0 equiv.) and the mixture stirred for 5 min. The mixture was evaporated to dryness to give a brown glass-like residue which was purified by column chromatography (20% acetone–dichloromethane) to give two major fractions.

2-[2-(N-*Methylanilinocarbonyl*)*methyl*-1,3-*dithiol*-2-*yl*]-1,3-*dithiolium tetrafluoroborate* **14c** as a red powder (67 mg, 0.21 mmol, 27%), mp 48–50 °C; ν_{max}(KBr disc)/cm^{-1} 3073, 2925, 1643, 1593, 1495, 1395, 1057 and 752; δ_H(400 MHz, [$^2H_3$]-acetonitrile) 3.16 (3 H, s, NMe), 3.74 (2 H, s, $COCH_2$), 6.27 (2 H, s, SCH=CHS), 7.30 (2 H, d, *J* 7.5, ArH), 7.43–7.53 (3 H, m, ArH) and 8.89 (2 H, s, S^+CH=CH); *m*/*z* (FAB) 352 (42%) $(M - BF_4)^+$ and 250 (100) [Found: $(M - BF_4)^+$, 351.9956. $C_{15}H_{14}NOS_4BF_4$ requires M − BF_4, 351.9958].

1-{2-[o-N-*Acetyl*-N-*methylamino*)*phenyl*]}-2-(1,3-*dithiol*-2-*ylidene*)-1,3-*dithiolium tetrafluoroborate* **15c** as a yellow powder (102 mg, 0.3 mmol, 41%), mp 115–120 °C; ν_{max}(KBr disc)/cm^{-1} 2925, 1650, 1470, 1383, 1057 and 760; λ_{max}(EtOH)/nm 204.9 (ε/dm^3 mol^{-1} cm^{-1} 3666) and 335.8 (824); δ_H(250 MHz, CD_3CN) 2.38 (3 H, s, $COCH_3$), 3.65 (3 H, s, NCH_3), 6.67 (1 H, d, *J* 5.9, SCH=CHS), 6.86 (1 H, d, *J* 6.4, SCH=CH), 7.02 (1 H, d, *J* 6.3, SCH=CHS), 7.47–7.58 (2 H, m, ArH), 7.73 (1 H, d, *J* 8.5, ArH), 7.81 (1 H, t, *J* 8.2, ArH) and 7.89 (1 H, d, *J* 6.0, S^+CH); δ_C(100 MHz, [$^2H_6$]acetone) 22.5, 39.5, 113.5, 123.0, 124.4, 126.1, 127.7, 129.1, 130.7, 137.1, 143.7, 144.7 and 174.1; *m*/*z* (FAB) 352 $(M - BF_4)^+$, (17%), 204 (14), 149 (14) and 148 (13) [Found: $(M - BF_4)^+$, 351.9956; $C_{15}H_{14}NOS_4BF_4$ requires *M* − BF_4, 351.9958].

***N*-Methyl-*N*-acryloyl-*o*-nitroaniline 16**

To a mechanically stirred solution of *N*-methyl-*o*-nitroaniline (3.0 g, 19.7 mmol, 1.0 equiv.) in dry tetrahydrofuran (50 cm^3) was added acryloyl chloride (8.92 g, 98.5 mmol, 5.0 equiv.) and pyridine (4.67 g, 59.1 mmol, 3.0 equiv.) and the mixture stirred at 50 °C for 3 h, then evaporated to dryness, the residue dissolved in dichloromethane (200 cm^3). The resulting solution was washed with water (200 cm^3), saturated aqueous sodium hydrogen carbonate (200 cm^3), aqueous hydroxide (2 mol dm^{-3}; 200 cm^3), aqueous copper sulfate (2 mol dm^{-3}; 2 × 200 cm^3) and water (200 cm^3) and then evaporated to dryness. The residue was subjected to column chromatography (20% EtOAc–light petroleum) to give the *nitroaniline* **16** as yellow prisms (2.48 g, 12.04 mmol, 61%), mp 38–41 °C; ν_{max}(KBr disc)/cm^{-1} 2939, 1664, 1602, 1578, 1527, 1351, 980 and 788; δ_H(250 MHz, $CDCl_3$) 3.32 (3 H, s, NMe), 5.53 (1 H, dd, *J* 10.3 and 1.6, $COCHCH_2$), 5.86 (1 H, dd, *J* 16.6 and 10.4, $COCHCH_2$), 6.37 (1 H, dd, *J* 16.7 and 1.6, $COCHCH_2$), 7.39 (1 H, d, *J* 7.8, ArH), 7.57 (1 H, t, *J* 7.7, ArH), 7.71 (1 H, t, 7.2, ArH) and 8.02 (1 H, d, *J* 8.1, ArH); δ_C(67.8 MHz, $CDCl_3$) 36.9, 125.5, 127.0, 128.8, 129.3, 131.1, 134.4, 136.5, 146.6 and 165.1; *m*/*z* (FAB) 229 (M + H, 41%), 160 (8), 156 (4), 71 (26) and 57 (50) (Found: M + H^+, 207.0768. $C_{10}H_{10}N_2O_3$ requires *M* + H, 207.0770).

Diethyl 3-methylbut-2-enylmalonate 17

To a stirred slurry of tetrahydrofuran-rinsed sodium hydride (0.72 g, 30 mmol, 1.2 equiv.) in dry tetrahydrofuran (100 cm^3) under nitrogen was added dropwise diethyl malonate (4.0 g, 25 mmol, 1.0 equiv.). The resulting solution was stirred for 1 h after the effervescence had subsided and then 4-bromo-2-methylbut-2-ene (3.73 g, 25 mmol, 1.0 equiv.) was added dropwise to it as a solution in dry tetrahydrofuran (70 cm^3). After 34 h the mixture was evaporated to dryness and the residue dissolved in diethyl ether (100 cm^3). The solution was washed with water (2 × 100 cm^3), dried ($MgSO_4$) and evaporated to dryness to afford a yellow liquid which was purified by column chromatography (5% diethyl ether–light petroleum) to give the *ester* **17** as a clear oil (4.28 g, 18.75 mmol, 75%); ν_{max}(KBr disc)/cm^{-1} 2982, 2935, 1735, 1447, 1370 and 1332; δ_H(250 MHz, $CDCl_3$) 1.25 (6 H, t, *J* 7.1, CH_3CH_2), 1.62 (3 H, s, CCH_3), 1.67 (3 H, d, *J* 1.0, CCH_3), 2.58 (2 H, t, *J* 7.5, $CHCH_2CH$), 3.32 [1 H, t, *J* 7.7, $CH(CO_2Et)_2$], 4.18 (4 H, q, *J* 7.1, CH_3CH_2) and 5.05 (1 H, t, *J* 7.3, CH=CMe_2); δ_C(67.8 MHz, $CDCl_3$) 13.9, 17.6, 25.6, 27.4, 52.1, 61.1, 119.6, 134.6 and 169.1.

Diethyl 7-methyl-4-(*N*-methyl-*o*-nitroanilino)-1-oxooct-6-ene-4,4-dicarboxylate 18

To sodium (145 mg, 6.31 mmol, 1.0 equiv.) was added super dry ethanol (50 cm^3). When the sodium had reacted completely a solution of the ester **17** (1.582 g, 6.94 mmol, 1.1 equiv.) in super dry ethanol (10 cm^3) was added to it and the mixture stirred for 30 min. The nitroaniline **16** (1.299 g, 6.31 mmol, 1.0 equiv.) was then added dropwise as a solution in ethanol (100 cm^3). After 3 h the solution was neutralised with conc. HCl and evaporated to dryness. The residue was dissolved in dichloromethane (100 cm^3) and the solution washed with water (100 cm^3), dried ($MgSO_4$) and evaporated to dryness to give the crude product. This was purified by column chromatography (60% diethyl ether–light petroleum) to give *nitroaniline* **18** as a yellow oil (1.61 g, 3.72 mmol, 59%); ν_{max}(film)/cm^{-1} 2983, 2934, 1733, 1674, 1606 and 1533; δ_H (peaks due to minor rotameric form are indicated *) (250 MHz, $CDCl_3$) 1.14 (3 H, t, *J* 7.1, CH_2CH_3), 1.16 (3 H, t, *J* 7.1, CH_2CH_3), 1.29* (3 H, t, *J* 7.1, CH_2CH_3), 1.49 (3 H, s, CCH_3), 1.63 (3 H, d, *J* 0.7, CCH_3), 1.68* (3 H, s, CCH_3), 1.88–2.01 (2 H, m, $COCH_2CH_2$), 2.04–2.27 (2 H, m, CH_2CH), 2.42 (2 H, d, *J* 7.5, $COCH_2$), 2.63* (2 H, d, *J* 7.5, CH_2CH), 3.18 (3 H, s, NMe), 3.39* (3 H, s, NMe), 4.05 (2 H, q, *J* 7.1, CH_2CH_3), 4.05 (2 H, q, *J* 7.1, CH_2CH_3), 4.06* (2 H, q, *J* 7.1, CH_2CH_3), 4.19* (2 H, q, *J* 7.0, CH_2CH_3), 4.86 (1 H, tq, *J* 6.1 and 1.4, $CHCH_2$), 7.35 (1 H, t, *J* 7.7, ArH), 7.38 (1 H, d, *J* 7.7, ArH), 7.69 (1 H, t, *J* 7.6, ArH) and 7.98 (1 H, d, *J* 7.4, ArH); δ_C(67.8 MHz, $CDCl_3$) 13.7 (q), 17.5 (q), 17.7 (q),* 25.6 (q), 25.7 (q),* 27.4 (t),* 27.5 (t), 28.8 (t),* 28.9 (t),* 31.5 (t), 32.1 (t),* 36.5 (q), 38.0 (q)* 56.5 (s), 56.7 (s),* 60.8 (t), 60.9 (t),* 117.2 (d), 124.8 (d),* 125.3 (d), 127.7 (d),* 129.0 (d),* 129.3 (d), 130.9 (d), 133.9 (d),* 134.3 (d),* 135.1 (s), 135.4 (s),* 136.7 (s), 137.2 (s),* 146.5 (s), 170.7 (s) and 171.2 (s);* *m*/*z* (FAB) 435 [$(M + H)^+$, 90%], 389 (32), 283 (24) and 105 (16) (Found: M^+, 435.2124. $C_{22}H_{30}N_2O_7$ requires *M*, 435.2131).

Diethyl 7-methyl-4-(*o*-amino-*N*-methylanilino)-1-oxooct-6-ene-4,4-dicarboxylate 19

Copper acetylacetonate (0.6 g, 2.168 mmol, 1.2 equiv.) was stirred as a suspension in ethanol (100 cm^3) at room temperature to give a sky blue solution to which sodium boranuide (105 mg, 1.81 mmol, 1.0 equiv.) was added. This formed a brown solution after an induction period of 5 s which gradually faded to a dark fawn colour with deposition of a granular deposit. A solution of nitroaniline **18** (784 mg, 1.81 mmol, 1.0 equiv.) in ethanol (10 cm^3) was then added to the mixture followed by the further sodium boranuide (0.210 g, 3.61 mmol, 2.0 equiv.). The mixture was stirred at room temperature for 2 h and then poured into water (100 cm^3). The mixture was filtered and evaporated to remove ethanol after which the residue was stirred with saturated aqueous sodium carbonate for 1 h before extraction with chloroform (3 × 100 cm^3). The combined chloroform extracts were washed with water (2 × 100 cm^3), aqueous ammonia (32%; 5 × 200 cm^3), again with water (3 × 100 cm^3) and then dried ($MgSO_4$) and evaporated to afford the *ester* **19** as a yellow oil (718 mg, 1.78 mmol, 98%); ν_{max}(film)/cm^{-1} 3462, 3357, 2982, 2933, 1728, 1652, 1504 and 756; δ_H(250 MHz, $CDCl_3$) 1.16 (6 H, t, *J* 7.1, CH_3CH_2), 1.49 (3 H, s, Me), 1.63 (3 H, s, Me), 2.0–2.23 (4 H, m,

CH_2CH_2), 2.46 (2 H, d, *J* 7.5, CH_2CH), 3.16 (3 H, s, NMe), 4.07 (4 H, q, *J* 7.1, CH_2O), 4.84 (1 H, t, *J* 7.6, $CHCH_2$), 6.73 (1 H, t, *J* 7.5, ArH), 6.77 (1 H, d, *J* 7.2, ArH), 6.96 (1 H, d, *J* 7.8, ArH) and 7.12 (1 H, t, *J* 7.6, ArH); δ_C(67.8 MHz, $CDCl_3$) 14.3, 18.1, 26.3, 28.3, 29.0, 31.7, 35.4, 57.2, 61.5, 116.6, 117.8, 119.1, 125.6, 129.0, 129.6, 135.7, 143.2, 171.7 and 173.5; *m/z* (FAB) 405 [$(M + H)^+$, 43%], 359 (13), 209 (10) and 169 (22) [Found: (M + H), 405.2383. $C_{22}H_{32}N_2O_5$ requires (*M* + H), 405.2389].

o-[*N*-(3,3-Diethoxycarbonyl-6-methylhept-5-enylcarbonyl)-*N*-methylamino]benzenediazonium tetrafluoroborate 20

The isopentyl nitrite method for preparation of **6b** was employed here to give the *tetrafluoroborate* **20** as a white powder (407 mg, 0.81 mmol, 58%); ν_{max}(KBr disc)/cm^{-1} 3103, 2992, 2928, 2274, 1727, 1678, 1586, 1569, 1481 and 747; δ_H(250 MHz, [$^2H_6$]acetone) 1.21 (6 H, t, *J* 7.1, CH_3CH_2O), 1.63 (3 H, s, MeC), 1.67 (3 H, s, MeC), 2.23–2.30 (2 H, m, $COCH_2CH_2$), 2.64 (2 H, d, *J* 7.4, CCH_2CH), 2.79 (2 H, t, *J* 8.5, $COCH_2$), 3.73 (3 H, s, NMe), 4.17 (4 H, q, *J* 7.1, OCH_2), 5.04 (1 H, t, *J* 7.3, HC=C), 7.87 (1 H, t, *J* 8.5, ArH), 7.99 (1 H, d, *J* 7.9, ArH), 8.43 (1 H, t, *J* 8.1, ArH) and 8.76 (1 H, d, *J* 8.1, ArH); δ_C(67.8 MHz, [$^2H_6$]acetone) 14.5, 18.0, 26.2, 28.0, 32.4, 38.5, 57.8, 61.8, 112.8, 118.7, 127.8, 128.7, 133.5, 136.0, 143.5, 146.3, 171.6 and 174.0; *m/z* (EI^+) 388 ($M^+ - N_2$, 2.2%), 387 (7), 161 (60), 160 (100) and 147 (32) [Found: $(M - N_2BF_4)^+$, 388.2026. $C_{22}H_{30}NO_5BF_4$ requires *M* − N_2BF_4, 388.2124].

Diethyl 4,4-dimethyl-2-oxo-3-oxabicyclo[3.3.0]octane-7,7-dicarboxylate 23

To a solution of the tetrafluoroborate **20** (300 mg, 0.75 mmol, 1.0 equiv.) in acetone (50 cm^3) was added TTF (153 mg, 0.75 mmol, 1.0 equiv.) and the mixture stirred for 2 h. It was then evaporated to dryness and the residue dissolved in chloroform (50 cm^3). The resulting solution was washed with aqueous sodium hydroxide (2 mol dm^{-3}; 3 × 50 cm^3). The combined extracts were dried ($MgSO_4$) and evaporated to dryness and the residue purified by column chromatography (40% diethyl ether–light petroleum) to give the *bicyclooctane* **23** as a yellow oil (74 mg, 0.27 mmol, 45%); ν_{max}(thin film)/cm^{-1} 2960, 2925, 2852, 1763, 1730, 1390 and 1369; δ_H(400 MHz, $CDCl_3$) 1.25 (3 H, t, *J* 7.1, CH_3CH_2O), 1.27 (3 H, t, *J* 7.2, CH_3CH_2), 1.41 (3 H, s, MeC), 1.43 (3 H, s, Me), 2.10 (1 H, dd, *J* 13.3 and 11.8, CH_2CHC), 2.34 (1 H, br dd, *J* 13.2 and 6.83, CH_2CHC), 2.43 (1 H, dd, *J* 14.5 and 4.4, CH_2CHCO), 2.65 (1 H, ddd, *J* 15.6, 11.1 and 6.64, $CHCMe_2$), 2.82 (1 H, ddd, *J* 14.6, 7.0 and 1.7, CH_2CHCO), 3.32 (1 H, m, CHCO) and 4.18 (4 H, 2 × q, *J* 7.0, CH_3CH_2); δ_C(100 MHz, $CDCl_3$) 13.9 (q), 23.3 (d), 29.1 (d), 35.0 (t), 35.3 (t), 45.5 (q), 49.5 (q), 61.5 (s), 61.8 (t), 61.9 (t), 83.4 (s), 170.3 (s), 171.5 (s) and 178.7 (s); *m/z* (FAB) 299 ($M + H^+$, 6%), 284 (6), 253 (8) and 207 (11) [Found: $(M + H)^+$, 299.1493. $C_{15}H_{22}O_6$ requires (*M* + H), 299.1495].

o-Nitrophenyl tetrahydro-2-furfuryl ether 26

o-Nitrophenol (3.15 g, 22 mmol, 1.0 equiv.) and triphenylphosphine (5.87 g, 22.4 mmol, 1.2 equiv.) were dissolved in tetrahydrofuran (100 cm^3) and tetrahydrofurfuryl alcohol (2.29 g, 22.4 mmol, 1.2 equiv.) was added to the mixture which was then cooled to 0 °C. Diethyl azodicarboxylate (3.7 cm^3, 22.4 mmol, 1.2 equiv.) was then slowly added dropwise to the mixture over 15 min. After the mixture had been stirred overnight, it was evaporated to dryness to give a yellow solid which was taken up in dichloromethane. The resulting solution was washed with aqueous sodium hydroxide (2 mol dm^{-3}), hydrochloric acid (2 mol dm^{-3}), saturated aqueous sodium hydrogen carbonate and saturated brine and then evaporated to dryness. The residue was purified by column chromatography (100% dichloromethane) to give the *furfuryl ether* **26** as a yellow oil (2.74 g, 54%); ν_{max}(thin film)/cm^{-1} 2959, 2892 and 1530; δ_H(270 MHz, $CDCl_3$) 1.85–2.13 (4 H, m, $CH_2C_2H_4CH_2$), 3.82–3.95 (2 H, m, OCH_2CH_2), 4.15 (2 H, d, *J* 4.0, OCH_2CH), 4.32 (1 H, m, CH_2CH–O), 7.04 (1 H, t, *J* 7.6, ArH), 7.15 (1 H, d, *J* 8.0, ArH), 7.54 (1 H, t, *J* 8.1, ArH) and 7.84 (1 H, d, *J* 8.2, ArH); δ_C(67.5 MHz, $CDCl_3$) 25.63, 27.48, 68.57, 71.12, 76.35, 114.47, 120.18, 125.27, 133.94, 139.57 and 152.09; *m/z* (EI^+) 223 (M^+, 12%), 85 ($M^+ - NO_2C_6H_4O$, 4.37) and 71 ($M^+ - NO_2C_6H_4OCH_2$, 100) (Found: C, 58.5; H, 5.9; N, 6.4%; M^+, 223.0872. $C_{11}H_{13}O_4N$ requires C, 59.19; H, 5.87; N, 6.27%; *M*, 223.0845).

o-Aminophenyl tetrahydro-2-furfuryl ether 27

A method identical with that for the reduction of **5a** was employed to yield the *furfuryl ether* **27** as a colourless oil which solidified under high vacuum to give a cream coloured solid (2.15 g, 98%), mp 64–65 °C; ν_{max}(disc)/cm^{-1} 3500, 3400, 1618, 1508 and 1356; δ_H(250 MHz, $CDCl_3$) 1.74–2.16 (4 H, m, $CH_2C_2H_4CH$), 3.73 (2 H, br s, NH_2), 3.80–4.01 (4 H, m, 2 × OCH_2), 4.30 (1 H, q, *J* 5.6, CH_2CH) and 6.67–6.82 (4 H, m, ArH); δ_C(67.5 MHz, $CDCl_3$) 27.10, 29.53, 69.59, 72.67, 78.45, 113.97, 116.29, 118.21, 122.83, 138.13 and 147.59; *m/z* (EI^+) 193 (M^+, 19.6%), 109 (100), 108 (36) and 85 (8) (Found: C, 68.7; H, 8.1; N, 7.2%; M^+, 193.108. $C_{11}H_{15}NO_2$ requires C, 68.40; H, 7.80; N, 7.30%; *M*, 193.110).

o-Tetrahydro-2-furfuryloxybenzenediazonium tetrafluoroborate 28

To a solution of the furfuryl ether **27** (200 mg, 1.0 mmol, 1.0 equiv.) in ethanol (0.5 cm^3) was added fluoroboric acid (40%; 0.7 cm^3, 3.0 mmol, 3.0 equiv.) and the mixture was cooled to below 0 °C. It was then treated with small quantities of isopentyl nitrite (0.13 cm^3, 1.2 mmol, 1.2 equiv.) and stirred for 0.5 h. Diethyl ether (150 cm^3) was added to the reaction mixture which was then kept in the cold for 12 h until a brown crystalline product was formed. This was filtered off, washed with cold diethyl ether and recrystallised from acetone by addition of diethyl ether to give the *tetrafluoroborate* **28** as pale brown prisms (209 mg, 0.72 mmol, 72%); ν_{max}(KBr disc)/cm^{-1} 2981, 2865, 2266, 1567 and 1494; δ_H(250 MHz, $CDCl_3$) 2.0–2.35 (4 H, m, CH_2CH_2CH), 3.85–4.03 (2 H, m, OCH_2CH_2), 4.49 (1 H, m, CH), 4.71 (2 H, m, OCH_2CH), 7.63 (1 H, t, *J* 7.6, ArH), 7.94 (1 H, d, *J* 7.7, ArH), 8.44 (1 H, t, *J* 7.5, ArH) and 8.73 (1 H, d, *J* 7.9, ArH); δ_C(100 MHz, [$^2H_6$]acetone) 25.90, 27.63, 68.48, 74.28, 76.59, 102.20, 116.16, 123.51, 132.56, 144.60 and 163.28; *m/z* (FAB) 497 [$(M_2 - BF_4)^+$, 22%], 205 (100%), 154 (26), 121 (18), 85 (29) [Found: $(M - BF_4)^+$, 205.0975. $C_{11}H_{13}N_2O_2$-BF_4 requires *M* − BF_4, 205.0977].

2-Ethoxy-2-phenoxymethyltetrahydrofuran 29

To a stirred solution of the tetrafluoroborate **28** (200 mg, 0.98 mmol, 1.0 equiv.) in acetone (20 cm^3) was added tetrathiafulvalene (199 mg, 0.98 mmol, 1.0 equiv.) causing evolution of nitrogen. The mixture was stirred for 30 min and then diluted with diethyl ether (100 cm^3) to precipitate a black solid. The mixture was filtered, with retention of both the solid portion and the filtrate. To the filtrate was added diisopropylamine (0.99 g, 9.8 mmol, 10.0 equiv.) and the mixture stirred for 17 h. The mixture was then evaporated to dryness and the residue dissolved in chloroform (100 cm^3). The resulting solution was washed with hydrochloric acid (1 mol dm^{-3}; 3 × 100 cm^3), dried ($MgSO_4$) and evaporated to dryness. The crude brown residue was purified by column chromatography (2% diethyl ether–light petroleum) to give the *tetrahydrofuran* **29** as a pale yellow oil (69 mg, 0.31 mmol, 32%); ν_{max}(film)/cm^{-1} 2976, 2933, 2883, 1601, 1588, 1498 and 755; δ_H(250 MHz, $CDCl_3$) 1.21 (3 H, t, *J* 6.9, CH_3CH_2O), 1.88–2.17 (4 H, m, CH_2CH_2), 3.48–3.73 (2 H, m, CH_3CH_2O), 3.91–4.05 (3 H, m, OCH_2), 4.18 (1 H, d, *J* 9.8, OCH_2), 6.97 (3 H, m, ArH) and 7.30 (2 H, m, ArH); δ_C(67.8

MHz, $CDCl_3$) 15.73, 24.76, 34.40, 56.84, 68.54, 68.72, 77.20, 107.31, 114.63, 121.37, 129.34 and 158.71; *m/z* (EI) 177 (M^+ − OEt, 6.1%), 115 (94), 107 (12), 94 (12), 87 (100), 77 (25) and 45 (22).

The solid portion from the filtration was recrystallised from acetone by the addition of diethyl ether to give 2-(1,3-*dithiol*-2-*ylidene*)-1-(o-*tetrahydro*-2-*furfuryloxyphenyl*)-1,3-*dithiolium tetrafluoroborate* **30** as olive crystals comprising a mixture of diastereoisomers (28 mg, 23%); ν_{max}(KBr disc)/cm^{-1} 3427 and 1084; δ_H(400 MHz, [$^2H_6$]acetone) 1.85–2.25 (4 H, m, CH_2CH_2), 3.82 (1 H, m, OCH_2CH_2), 3.90 (1 H, m, OCH_2CH_2), 4.30 (1 H, m, $OCHCH_2$), 4.37–4.50 (2 H, m, OCH_2CH), 7.01 (1 H, d, *J* 6.0, CHS), 7.09 (1 H, d, *J* 6.0, CHS), 7.24 (1 H, d, *J* 6.0, CHS), 7.27–7.31 (2 H, m, CHS and ArH), 7.48 (1 H, m, ArH), 7.67 (1 H, t, *J* 7.5, ArH), 7.77 (1 H, t, *J* 7.5, ArH) and 8.35 (1 H, m, S^+–CH); δ_C(100 MHz, $CDCl_3$) 26.00, 28.14, 28.35, 68.53, 72.87, 73.28, 77.05, 77.19, 110.01, 110.61, 114.35, 115.56, 115.64, 123.03, 123.40, 123.50, 129.31, 129.79, 137.15, 137.25, 145.17, 145.43, 157.93 and 206.00; *m/z* (FAB) 381 (M − BF_4^+, 84%), 296 (2) and 95 (11) (Found: M^+ − BF_4, 381.0098. $C_{17}H_{17}O_2S_4$ requires *M* − BF_4, 381.0111). The complexity observed in proton and carbon spectra is due to the diastereoisomeric mixture of products.

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