Tetrathiafulvalene: a catalyst for sequential radical–polar reactions

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The reaction between tetrathiafulvalene (TTF) and suitable arenediazonium salts leads to products arising from an ordered sequence of reactions featuring electron transfer, loss of nitrogen, radical cyclisation and nucleophilic substitution. The tetrathiafulvalenium salt **6** is shown to be an intermediate in the reaction, with substitution of TTF occurring *via* an S_N1 mechanism. The reactions are catalytic in TTF and the final substitution can be achieved by several nucleophiles. Extension of the reaction to the synthesis of bi- and tricyclic ring systems has been investigated.

Electron transfer chemistry of diazonium salts

Arenediazonium salts are versatile intermediates. The reactions of diazonium salts which involve free radical intermediates include both carbon–carbon (*e.g.* Meerwein, Pschorr, Gomberg reactions) and carbon–heteroatom (*e.g.* Sandmeyer) bond formations.[1] These reactions are well established in the literature and it is timely to review the scope and problems associated with these reactions.

In the Sandmeyer reaction, an aqueous solution of the diazonium salt is added to a solution of copper(I) chloride in hydrochloric acid. The $CuCl_2^-$ anion donates an electron to the diazonium salt so forming copper(II) chloride, nitrogen is evolved and the aryl radical then abstracts a chlorine atom from copper(II) chloride:

Sandmeyer Reaction:

$$ArN_2^+ Cl^- + CuCl_2^- \longrightarrow ArCl + N_2 + CuCl_2$$

Aryl bromides may be formed in a similar way from copper(I) bromide, but aryl iodides do not require the presence of copper intermediates as the iodide ion has a suitably low oxidation potential to permit direct electron transfer to the diazonium salt. The formation of an aryl iodide may then proceed *via* the following steps:[2]

$$ArN_2^+ + I^- \longrightarrow ArN_2^{\bullet} + I^{\bullet}$$
$$ArN_2^{\bullet} \longrightarrow Ar^{\bullet} + N_2$$
$$Ar^{\bullet} + I_3^- \longrightarrow ArI + I_2^{\bullet -}$$
$$Ar^{\bullet} + I_2 \longrightarrow ArI + I^{\bullet}$$
$$I^{\bullet} + I^- \longrightarrow I_2^{\bullet -}$$
$$2\,I^{\bullet} \longrightarrow I_2$$
$$I^- + I_2 \longrightarrow I_3^-$$
$$ArN_2^+ + I_2^{\bullet -} \longrightarrow Ar^{\bullet} + N_2 + I_2$$

Replacement of the diazonium group by a nitro group can be achieved using a number of procedures. One employs diazonium cobaltinitrites $\{[ArN_2^+]_3[Co(NO_2)_6^{3-}]\}$. Decomposition of such complexes in the presence of both copper(I) oxide and copper(II) sulfate yield the product nitroarenes.[3] Carbon–nitrogen bond formation also results from treatment of a diazonium salt with sodium azide.[4]

Carbon–sulfur bond formation can be easily effected with sulfur anions as the electron donors. For example, thiolates and xanthate anions ($ROCS_2^-$) function in this way.[5] With arenethiolates,[6] initial formation of diazosulfides has been demonstrated; these spontaneously homolyse to afford aryl radicals which then combine with thiolate anions; the resulting radical anions are excellent electron donors and propagate the chain process by electron donation to another molecule of diazosulfide.

$$ArN_2^+ + PhS^- \longrightarrow ArN{=}NSPh$$
$$ArN{=}NSPh \longrightarrow Ar^{\bullet} + N_2 + PhS^{\bullet}$$
$$Ar^{\bullet} + PhS^- \longrightarrow ArSPh^{\bullet -}$$
$$ArN{=}NSPh \xrightarrow{ArSPh^{\bullet -}} N_2 + PhS^- + ArSPh + Ar^{\bullet}$$

Reduction of the diazonium salt to form an aryl radical followed by hydrogen atom transfer can be effected in two principal ways. Phosphinic acid (hypophosphorous acid)[7] can donate an electron to the diazonium cation and the aryl radical that results can then abstract a hydrogen atom[1b] from the H_3PO_2.

$$ArN_2^+ + H_2PO_2H \longrightarrow Ar^{\bullet} + HP^{\bullet}O_2H + N_2 + H^+$$
$$Ar^{\bullet} + H_2PO_2H \longrightarrow ArH + HP^{\bullet}O_2H$$
$$ArN_2^+ + HP^{\bullet}O_2H \longrightarrow Ar^{\bullet} + H_3PO_3$$

Alternatively, an alcohol (such as ethanol[8]) can be used as the source for hydrogen atom abstraction. In this case, it is not apparent what initiates the reaction, but once initiated, a chain reaction can ensue since the hydroxyethyl radical $HOC^{\bullet}HMe$ functions as an electron donor to another diazonium cation.

The simplest carbon–carbon bond formation *via* radical intermediates using diazonium salts is the nitrile formation using copper(I) cyanide–potassium cyanide. The formation of biaryls from diazonium salts can be effected in a number of ways. Treatment of a diazonium salt with aqueous base affords the diazohydroxide which decomposes to give an aryl radical. These short-lived aryl radicals react with arenes to afford a biaryl product.[9] Sodium acetate can replace the alkali; the diazoacetates behave similarly to the diazohydroxides above. These reactions frequently do not afford very high yields of product. An alternative procedure utilises *N*-acetyl-*N*-nitrosoarylamines, which also react with arenes. During the reaction, the nitroso compounds isomerise to aryldiazoacetates.[10]

Gomberg–Bachman Reaction:

$$ArN_2^+ + OH^- \longrightarrow ArN{=}NOH \text{ (or } ArN{=}NON{=}NAr)$$

$$ArN{=}NOH \text{ (or } ArN{=}NON{=}NAr) \longrightarrow Ar^{\bullet} + N_2 + {}^{\bullet}OH \text{ (or } {}^{\bullet}ON{=}NAr)$$

$$Ar^{\bullet} + Ar'H \xrightarrow{-e^-} ArAr' + H^+$$

The Hey Variation:

$$ArN_2^+ + AcO^- \longrightarrow ArN{=}NOAc$$

$$ArN{=}NOAc \longrightarrow Ar^\bullet + N_2 + {}^\bullet OAc$$

$$Ar^\bullet + Ar'H \xrightarrow{-e^-} ArAr' + H^+$$

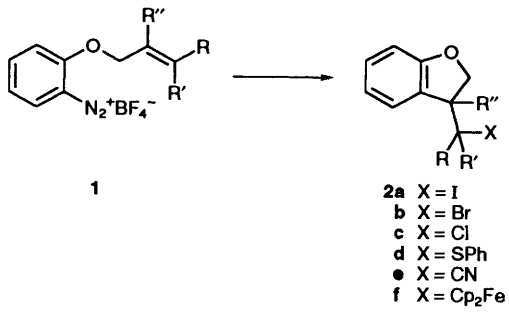
The Pschorr reaction[11] is an intramolecular arylation; however, unlike the Gomberg–Bachman and related reactions, it is not conducted under alkaline conditions, and can be highly efficient.

Of immediate relevance to our interests is the Meerwein reaction. Here, a catalytic amount of copper(I) chloride reacts with the diazonium salt to form the aryl radical; this then attacks an alkene to afford a new radical which then quenches either by chloride atom abstraction or by elimination. The mechanism of elimination has not been determined.

The Meerwein Reaction:

$$ArN_2^+Cl^- + H_2C{=}CHR \xrightarrow{CuCl} ArCH{=}CHR + ArCH_2CHClR$$

Beckwith considerably extended the usefulness of diazonium salts by performing intramolecular Meerwein reactions. In these cases, he demonstrated that many electron donors could form the aryl radical, which then cyclised in good yield. Further, he established that the clean 5-*exo* cyclisation was a hallmark of radical cyclisation; the alternative cationic cyclisation was both very slow and very unclean. Cyclisations to form the alkyl iodide[2] (**2a**, X = I) with sodium iodide as the electron transfer agent, to the alkyl bromide (**2b**, X = Br) and the chloride (**2c**, X = Cl) with the appropriate copper halide,[12] to the alkyl phenyl sulfide (**2d**, X = SPh) with benzenethiolate,[4,12] to the alkyl cyanide (**2e**, X = CN) with copper cyanide[12] and to the alkyl ferrocene[13] (**2f**, X = Cp_2Fe) with ferrocene were demonstrated (Scheme 1). Fukunishi *et al.*[14] observed cyclisation to the corresponding alcohol **5** when the diazonium salt was treated with cyclodextrin and air with an as yet unidentified initiator. Labelling studies indicated that dioxygen was the source of the oxygen atom in the alcohol. This reaction presumably involves an initial coupling of alkylperoxyl radicals



Scheme 1

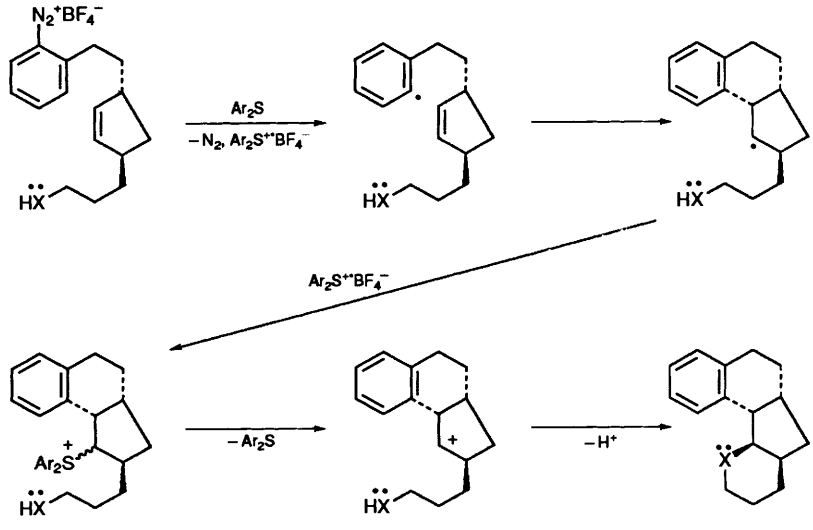
to yield a tetraoxide, followed by either a Russell fragmentation[15] or a homolytic fragmentation[16] to yield the alcohol.

Our investigations were directed to extending the possibilities for terminating such reactions and to discover the scope of such chemistry in the synthesis of complex products. In the first instance we wished to terminate the radical chemistry with the formation of a diarylsulfonium salt, and so sought a diarylsulfide which would readily effect electron transfer to an arenediazonium salt. The resulting $Ar_2S^{\bullet+}$ radical cation might then couple with the carbon radical resulting after cyclisation. The formation of such sulfonium salts might be useful for synthetic transformations. In particular, unimolecular solvolysis of diarylsulfonium salts proceeds at reasonable rates.[17] In our studies, this would afford a crossover from radical reactions to reactions of cations in a single pot; an understanding of the rates of such processes should allow predictions to be made concerning applications to synthesis. In particular, it was envisaged that following radical cyclisation(s), conversion into a cation would permit stereospecific trapping by intramolecular nucleophiles (see Scheme 2).

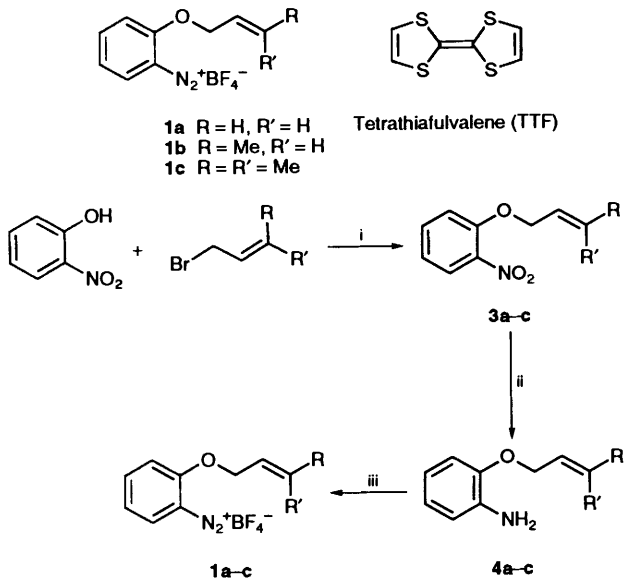
These are exciting prospects for the future. However, this paper outlines the initial results relating to the ordered sequential combination of radical and polar reactions in one pot.[18]

Results and discussion

The arenediazonium tetrafluoroborate salts, **1a–c**, were prepared using established procedures (Scheme 3). Hence, 2-nitrophenol was treated with the allyl bromides and potassium hydroxide in dimethyl sulfoxide (DMSO)[19] to give the 2-allyloxynitrobenzenes **3a–c** in good yields. Reduction, using sodium boranuide, with copper(II) acetylacetonate catalysis,



Scheme 2



Scheme 3 *Reagents and conditions:* i, DMSO, KOH, 25 °C, 2 h: **3a** 83%, **3b** 90%, **3c**, 46%; ii, $NaBH_4$, $Cu(acac)_2$, EtOH, 25 °C, 3 h: **4a** 88%, **4b** 99%, **4c** 74%; iii, $NOBF_4$, CCl_4, −5 °C, 1 h: **1a** 53%, **1b** 66%; or $NaNO_2$, HBF_4, H_2O, 30 min: **1c** 64%

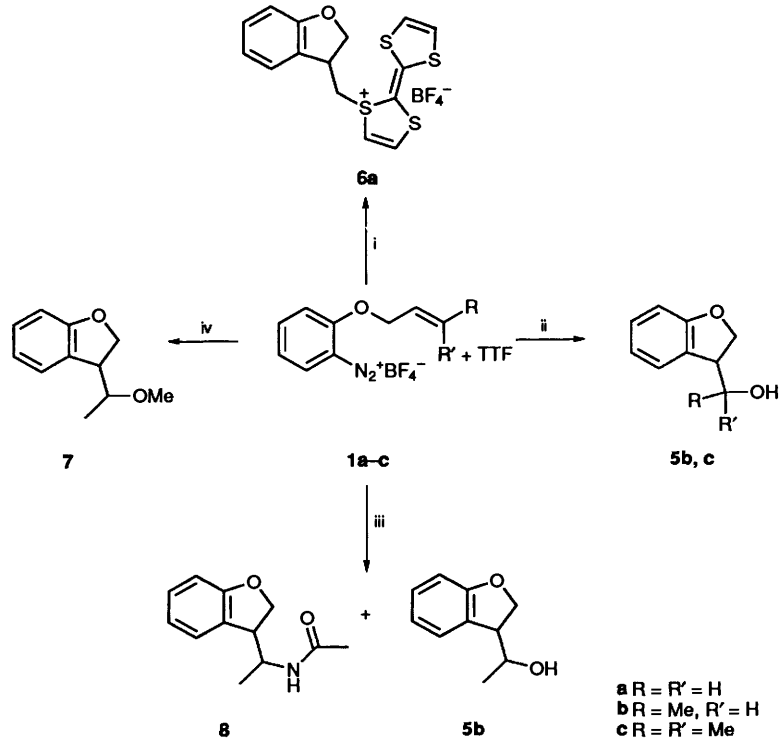
in ethanol,[20] yielded the 2-allyloxyanilines **4a–c** in excellent yields. Diazotisation with either nitrosonium tetrafluoroborate in carbon tetrachloride,[21] or with sodium nitrite in dilute tetrafluoroboric acid,[22] furnished the desired arenediazonium salts **1a–c** in good yields. The salts were purified by precipitation from an acetone solution by addition of diethyl ether and were obtained as microanalytically pure, crystalline solids.

Initial attempts to induce the reaction of these compounds with diaryl sulfides met with little success. For example, diphenyl sulfide afforded only starting materials. Accordingly, our attention was directed to sulfides with low oxidation potentials, and particularly to tetrathiafulvalene.

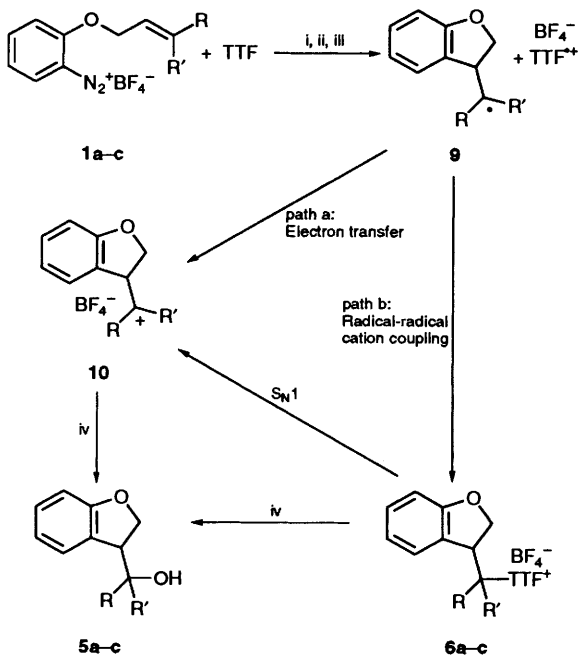
Tetrathiafulvalene (TTF) and related compounds have been the subject of intense interest in materials chemistry because of the semi-conduction and superconduction of derivatives.[23] To our knowledge, TTF has not been employed in organic synthesis.[24] Its radical cation [25] can be formed extremely easily, presumably from the favourable structure of the radical cation that incorporates an aromatic disulfonium salt and a very delocalised radical. With the delocalisation implicit in these structures, it might be questioned whether carbon–sulfur bond formation would occur in preference to carbon–carbon bond formation. Calculations have been performed on the location of spin density in $TTF^{\bullet+}$, and these show that the spin density is greatest on the sulfur atom. The fact that the organic chemistry of its radical cation has been so little explored led us to investigate [26] its reactions with arenediazonium salts.

The 2-allyloxybenzenediazonium salts **1b–c** reacted with TTF in acetone at room temperature to furnish the alcohols **5b–c** (Scheme 4). No other products were isolated from the reaction mixtures. Similarly, the arenediazonium salt **1b** reacted with TTF in methanol to give the methyl ether **7** and in acetonitrile, to give the amide **8**. However, the diazonium salt **1a** reacted with TTF in acetone to give the sulfonium salt **6a** as a mixture of two diastereoisomers, as witnessed by the presence of double the expected number of resonances in the ^{13}C NMR spectrum. The presence of the two diastereoisomers indicated that the cationic sulfur was tetrahedral, and that there was a discrete pair of compounds instead of a π-complex. Surprisingly, it was not possible to effect conversion of this compound into the alcohol **5a** (*vide infra*).

Possible mechanisms for the reactions are outlined in Scheme 5. Initial single electron transfer (SET), nitrogen expulsion and 5-*exo*-*trig* cyclisation leads to the intermediate alkyl radical **9** and tetrathiafulvalenium radical-cation. Two possibilities then



Scheme 4 *Reagents and conditions:* i, Me_2CO, room temp., 30 min: 75%; ii, Me_2CO, room temp., 30 min: **b** 73%, **c** 58%; iii, MeCN, room temp., 2 d: **8** 54%, **5b** 17%; iv, MeOH, room temp., 2 d: 54%



Scheme 5 i, Electron transfer; ii, loss of N_2; iii, 5-*exo*-*trig* cyclisation; iv, addition of H_2O or Me_2CO followed by hydrolysis

exist. In path a, one electron oxidation of the alkyl radical leads to carbocation **10**, the oxidation occurring by SET to another molecule of the diazonium salt or, less likely, to the TTF radical-cation. The resultant carbocation **10** could react with residual moisture in the acetone to give the observed alcohols directly, or acetone itself could react to give an intermediate which, on hydrolytic work-up, afforded the alcohols **5**.

If direct oxidation of the intermediate radical did not occur, then the alkyl radical and the TTF radical-cation could couple (path b) to give the intermediate salt **6**. Substitution of this compound would then yield the product alcohols **5**.

The isolation of the stable salt **6a** (which does not react with residual moisture in the acetone, even after extended reaction times) showed that tetrathiafulvalenium cation salts (as opposed to radical cation salts), which were previously unknown, do indeed form.[27] Additionally, the sulfonium salt **6b** was precipitated from the reaction of the benzenediazonium salt **1b** and TTF in acetonitrile by pouring the reaction mixture into diethyl ether as soon as the reactants had been mixed. The salt **6b** proved to be enormously more reactive than **6a**, a fact that hindered the full characterisation of the compound. However, the ^1H NMR and IR spectra of the salt **6b** compared very favourably with those of the salt **6a**, the structure of which had been confirmed. High resolution mass spectrometry of compound **6b** gave a molecular ion whose mass fitted the proposed structure [*m*/*z* (FAB): found M^+ 351.0015; $C_{16}H_{15}OS_4$ requires *M* 351.0006].

When water (0.10 cm^3) was added to a solution of the salt **6b** in [$^2H_6$]acetone, complete and rapid conversion into alcohol **5b** occurred (only very slight traces of the alcohol **5b** were visible in the ^1H NMR spectrum prior to the addition of water). The reaction was followed by ^1H NMR spectroscopy, in which the peaks belonging to **6b** disappeared and were replaced by those of **5b**. When this reaction was repeated on a preparative scale, 63% of the alcohol **5b** was obtained.

To confirm the intermediacy of the salt **6b** in the reaction, acetone solutions of the diazonium salt **1b** and TTF were mixed and then immediately poured into diethyl ether. The orange precipitate was filtered off and confirmed by ^1H NMR spectrometry (in [$^2H_3$]acetonitrile) to be the sulfonium salt **6b**. No trace of the diazonium salt **1b** was present in this spectrum. When a second spectrum of this same solution was taken after 3 h, it was found that all of the salt **6b** had been consumed, and the deuteriated analogue of amide [$^2H_3$]-**8** was isolated.

These observations showed that the sulfonium salt **6b** was an intermediate in the reaction of the diazonium salt **1b** and TTF. That the salt **6a** was so stable compared to its analogue **6b** suggested that the intermediate sulfonium salt reacts *via* an S_N1 mechanism.[28] Hence, compound **6b** dissociates to give the cation **10** (see Scheme 5) which then reacts with residual moisture in the acetone, or acetone itself followed by hydrolysis, to give the product. This means that the TTF leaving group has an astonishing selectivity for unimolecular reactions.

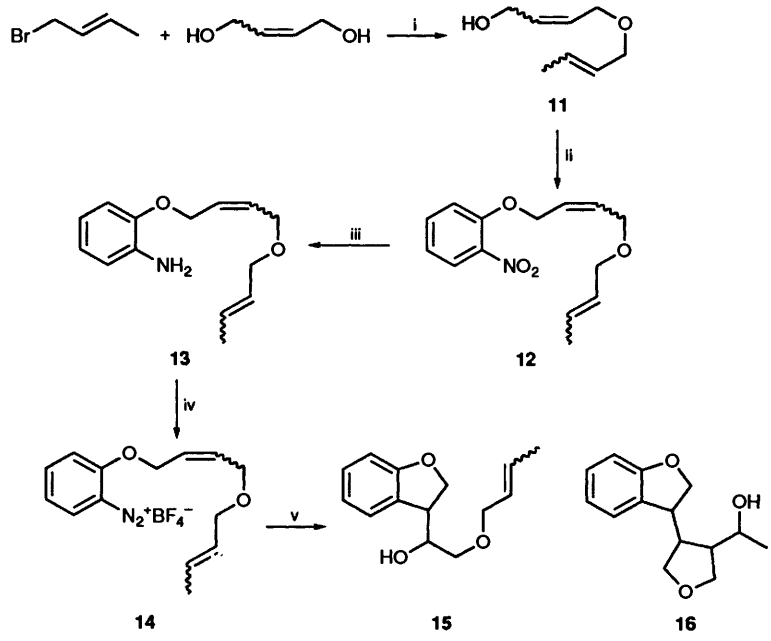
The proposed mechanism implies that TTF should act as a catalyst. This is indeed the case, as has been shown by reaction of the diazonium salt **1b** with 0.2 molar equivalents of TTF in [$^2H_6$]acetone. The reaction was followed by ^1H NMR spectroscopy which showed the clean conversion of the salt **1b** into the alcohol **5b** in 4 h. Notably, there is no signal corresponding to TTF in the final spectrum. With 0.1 molar equivalents of TTF, the reaction proceeded more slowly and halted when the ratio of **1b**:**5b** was 35:65. These observations showed that TTF was being consumed during the reaction. It is possible that tetrafluoroboric acid, a side product of the reaction, could cause the decomposition of TTF into low molecular weight molecules. However, no side products were observed in either of the catalytic experiments. Also, an attempt to decompose TTF in 40% aqueous tetrafluoroboric acid and acetone resulted in the quantitative recovery of TTF. However, these conditions do not exactly mimic those of the real reactions. The fate of TTF in these reactions is still being studied.

To determine the scope of these reactions, we investigated whether tandem radical cyclisations would be possible. Hence, the arenediazonium salts **14** and **20** were prepared. The relative amounts of the bi- and tri-cyclic products obtained in the reaction with TTF would give an indication of the rates of trapping of the intermediate carbon radicals, which would be useful for planning syntheses using diazonium salts.

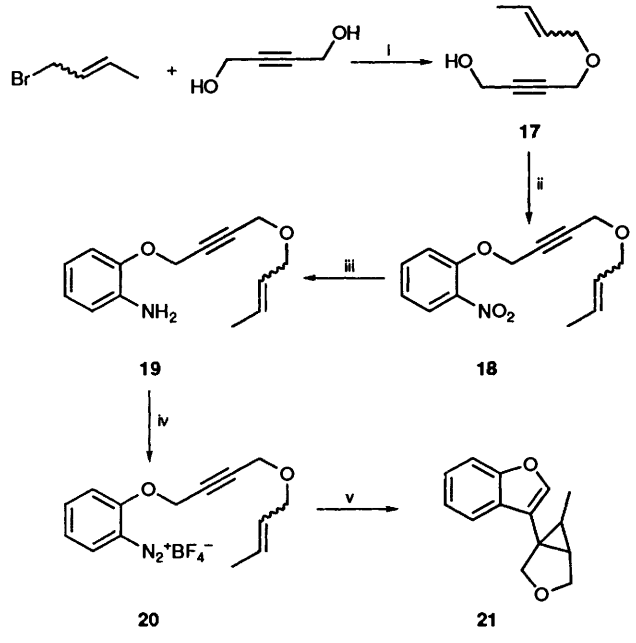
The desired arenediazonium salts were prepared using standard procedures. For compound **14**, bromobut-2-ene and but-2-ene-1,4-diol were allowed to react in DMSO in the presence of potassium hydroxide[19] to give the dienol **11** (Scheme 6). This was coupled to 2-nitrophenol using standard Mitsunobu conditions[29] to give **12**, which was then reduced to aniline **13** with sodium boranuide in ethanol, using a copper(II) catalyst.[20] Diazotisation of the aniline **13** was effected in aqueous tetrafluoroboric acid with sodium nitrite.[22] The diazonium salt **14** was initially obtained as a brown oil, but subsequent repeated precipitation from acetone–diethyl ether eventually gave the salt **14** as a powder.

Reaction of the diazonium salt **14** with TTF gave mixtures of the bicyclic alcohol **15** and the tricyclic alcohol **16**, each as a mixture of diastereoisomers. No other materials were isolated from the reaction mixture.

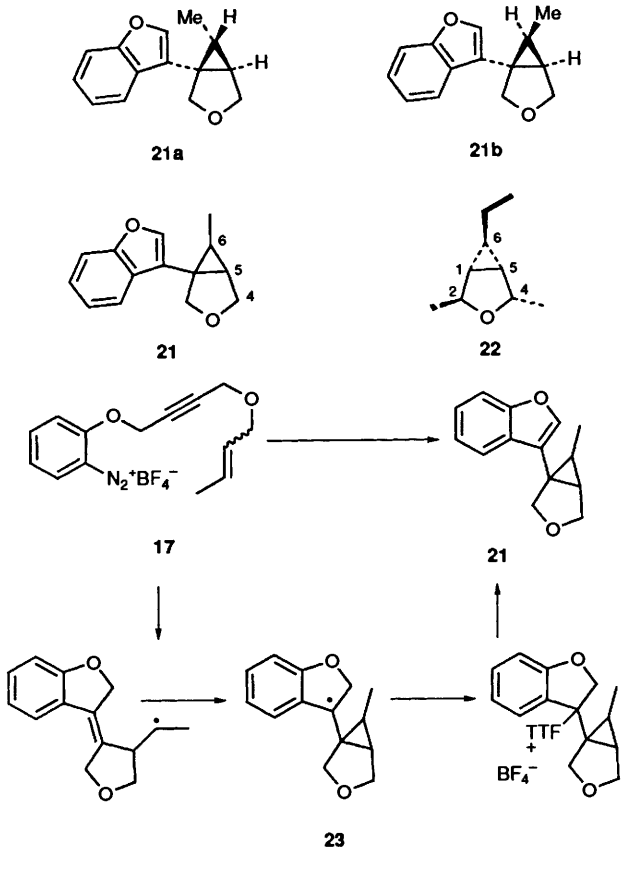
The alkenyne **20** was approached in a similar manner. Hence, coupling of bromobut-2-ene and but-2-yne-1,4-diol gave **17** (Scheme 7). This was coupled to 2-nitrophenol using Mitsunobu conditions to give the nitroarene **18**. When **18** was reduced using sodium boranuide and copper(II) acetylacetonate in ethanol, a mixture of two compounds was produced. Although one appeared to be the desired aniline **19**, the sample was contaminated with large amounts of the analogous diene compound **13**, presumably produced by the reduction of the alkyne **18**. Reduction of the nitrobenzene **18** to give pure aniline **19** was achieved using tin(II) chloride in concentrated hydrochloric acid.[22] No trace of diene **13** was found, but the yield of this reaction was low compared to the sodium boranuide



Scheme 6 *Reactions and conditions:* i, KOH, DMSO, 0.5 h: 53%; ii, 2-Nitrophenol, DEAD, Ph_3P, THF, 16 h: 56%; iii, $NaBH_4$, $Cu(acac)_2$, EtOH, 2 h: 91%; iv, $NaNO_2$, HBF_4. H_2O, 10 min: 52%; v, TTF, Me_2CO, H_2O, 4 d: **15** 41%, **16** 15%



Scheme 7 *Reagents and conditions:* i, KOH, DMSO, 0.5 h: 75%; ii, 2-nitrophenol, DEAD, Ph_3P, THF, 16 h: 68%; iii, $SnCl_2$·2 H_2O, HCl, EtOH, 16 h: 31%; iv, $NaNO_2$, HBF_4, H_2O, 10 min: 65%; v, TTF, Me_2CO, H_2O, 4 d: 64%



Scheme 8

conditions. Diazotisation of the aniline **19** with sodium nitrite, *vide supra*, gave the diazonium salt **20** as a brown, viscous oil, which could not be obtained as a solid, despite repeated attempts at precipitation.

The reaction of the diazonium salt **20** with TTF did not give the expected products, but instead afforded the substituted 3-oxabicyclo[3.1.0]hexane **21** (64%). This compound was produced as an 84:16 mixture of two diastereoisomers, **21a** and **21b**, which were separated by HPLC. The relative stereochemistry of these stereoisomers was assigned by comparison with known oxabicyclohexane **22**.[30] In compound **22**, the coupling constant between the protons of C-6 and C-5 or C-1 was 3.4 Hz. In the isomer **21a**, the coupling constant between the protons of C-6 and C-5 was 4.0 Hz, while in **21b** it was 8.2 Hz. This suggested that compound **21a** has the same relative stereochemistry as compound **22**, while **21b** has the diastereoisomeric configuration. Hence, in compound **21a** (the major isomer) the methyl group is directed away from the oxygen atom of the tetrahydrofuran, while in **21b**, the methyl group is directed towards the oxygen atom.

The fused cyclopropane of compound **21** must be formed *via* a 3-*exo-trig* intramolecular radical cyclisation, to give the benzylic radical intermediate **23** (Scheme 8). Trapping of this

intermediate by $TTF^{\bullet+}$, and subsequent elimination of TTF and a proton gives the observed product (we cannot rule out a conversion of **23** by direct electron transfer into a diazonium cation, followed by proton loss). Normally, the equilibrium between the cyclopropylmethyl radical and the ring opened but-3-enyl radical lies in favour of the latter species. However, in a number of cases[31,32] the cyclopropylmethyl radical has been found to predominate. In the case presented here, it appears that benzylic stabilisation of the cyclopropylmethyl radical is sufficient for compound **21** to become the only product of the reaction.

These experiments have shown that under the conditions used, the trapping of the TTF radical cation is slower than the aryl radical and vinyl radical cyclisations, but competes with the alkyl radical cyclisation. Although we have not performed a quantitative determination of rate constants (this is currently being pursued) these experiments gave guidance on the synthetic potential and limitations of TTF chemistry.

In summary, TTF and suitable arenediazonium salts react to give products arising from an ordered sequence of reactions featuring an initial electron transfer, then radical cyclisation followed by polar substitution. This chemistry, which starts with aryl radicals and after cyclisation to an alkyl radical leads to functionalisation, extends what is possible by current organocobalt[33] methodology. The final functionalisation with TTF occurs by a polar mechanism. We are currently applying this radical–polar crossover sequence to more complex synthetic problems.

Experimental

General information

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 FX90Q, 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. Chemical shifts (δ) are quoted in parts per million and coupling constants (J) are reported in Hz. In several cases mixtures of isomers were obtained. Where these could be distinguished in the ^{1}H NMR spectrum, the word 'minor' has been used to denote a less prevalent isomer. 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. Preparative HPLC was performed on a Waters YMC-INC 20 × 250 mm S-15 column.

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 otherwise stated all light petroleum was of boiling range 40–60 °C and was redistilled before use. Chromatography was performed using Sorbisil C60 (May and Baker), Kieselgel 60 (Art 9385) or Kieselgel HF_{254} silica gels.

2-Allyloxynitrobenzene 3a

Powdered potassium hydroxide (3.36 g, 60 mmol) was added to dimethylsulfoxide (DMSO) (30 cm^3), and the suspension was stirred for 5 min. To this, 2-nitrophenol (2.09 g, 15 mmol) and 3-bromoprop-2-ene (2.60 cm^3, 30 mmol) were added and the solution stirred for 1.5 h. The reaction mixture was poured into water (300 cm^3) and extracted with dichloromethane (3 × 150 cm^3). The combined dichloromethane extracts were washed with water (5 × 300 cm^3), dried over sodium sulfate, filtered and evaporated to dryness to give a brown oil, which was distilled (bp 116 °C/1 mmHg) to give the title nitrobenzene **3a**[20] (2.25 g, 83%) as a yellow oil (Found: C, 60.8; H, 5.2; N, 7.8. $C_9H_9NO_3$ requires C, 60.33; H, 5.06; N, 7.82%); ν_{max}(film)/cm^{-1} 3082, 2872, 1649, 1608, 1524, 1352, 1280, 934, 859 and 745; λ_{max}(EtOH)/nm 213 (ε/dm^3 mol^{-1} cm^{-1} 13 215), 258 (3222) and 320 (2353); δ_H(250 MHz; $CDCl_3$) 4.67 (2 H, ddd, J 4.9, 1.5 and 1.5, CH_2), 5.30 (1 H, ddt, J 10.7, 1.5 and 1.5, CH=CH_2), 5.49 (1 H, ddt, J 17.3, 1.5 and 1.5, CH=CH_2), 6.50 (1 H, ddt, J 17.3, 10.7 and 4.9, CH=CH_2), 6.99–7.05 (1 H, m, ArH), 7.08 (1 H, dd, J 8.4 and 1.1, ArH), 7.47–7.54 (1 H, m, ArH) and 7.82 (1 H, dd, J 8.1 and 1.7, ArH); m/z (EI$^+$) 179 (M$^+$, 6%), 123 (35) and 106 (14).

(*E*)-2-(3-Methylallyloxy)nitrobenzene 3b

In a procedure identical to that for compound **3a**, powdered potassium hydroxide (6.73 g, 120 mmol), 2-nitrophenol (4.17 g, 30 mmol) and bromobut-2-ene (6.18 cm^3, 60 mmol) were allowed to react in DMSO (60 cm^3) to give a brown oil. Distillation (bp 132 °C/1 mmHg) gave the title nitrobenzene **3b** (5.21 g, 90%)[13] as a yellow oil (Found C, 62.4; H, 5.8; N, 7.0. $C_{10}H_{11}NO_3$ requires C, 62.17; H, 5.74; N, 7.25%); ν_{max}(film)/cm^{-1} 3027, 2919, 1676, 1607, 1524, 1352, 1166, 856 and 744; λ_{max}(EtOH)/nm 214 (ε/dm^3 mol^{-1} cm^{-1} 11 995), 258 (2408) and 321 (2166); δ_H(250 MHz; $CDCl_3$) 1.73 (3 H, d, J 6.5, Me), 4.60 (2 H, dd, J 5.8 and 1.2, CH_2), 4.74 [2 H (minor), dd, J 6.2 and 0.9, CH_2], 5.65–5.94 (2 H, m, CH=CH), 6.97–7.10 (1 H, m, ArH), 7.47–7.52 (2 H, m, ArH) and 7.80 (1 H, dd, J 8.1 and 1.7, ArH); δ_C(100 MHz; $CDCl_3$) 13.36 (minor), 17.77, 65.37 (minor), 70.05, 114.97, 120.20, 120.26 (minor), 124.34 (minor), 124.69, 125.44, 129.56 (minor), 131.04, 133.97, 140.04 and 152.00; m/z (EI$^+$) 193 (M$^+$, 1%), 139 (72), 93 (5), 72 (2) and 55 (100).

2-(3,3-Dimethylallyloxy)nitrobenzene 3c

In a procedure identical to that for compound **3a**, powdered potassium hydroxide (4.48 g, 80 mmol), 2-nitrophenol (2.78 g, 20 mmol) and 1-bromo-3-methylbut-2-ene (4.0 cm^3, 40 mmol) were allowed to react in DMSO (40 cm^3) to give a brown oil. Distillation (bp 153 °C/1 mmHg) gave the *title nitrobenzene* **3c** (1.92 g, 46%) as a yellow oil (Found C, 63.7; H, 6.6; N, 6.45. $C_{11}H_{13}NO_3$ requires C, 63.75; H, 6.32; N, 6.76%); ν_{max}(film)/cm^{-1} 2974, 1674, 1606, 1582, 1525, 1353, 979, 856 and 744; λ_{max}(EtOH)/nm 205 (ε/dm^3 mol^{-1} cm^{-1} 12 514), 258 (3243) and 317 (2304); δ_H(250 MHz; $CDCl_3$) 1.74 (3 H, s, Me), 1.78 (3 H, s, Me), 4.67 (2 H, d, J 6.6, CH_2), 5.44–5.50 (1 H, t, J 6.6, CH=), 6.97–7.10 (2 H, m, ArH), 7.47–7.54 (1 H, ddd, J 8.2, 8.2 and 1.7, ArH) and 7.89–7.82 (1 H, dd, J 1.7 and 8.0, ArH); δ_C(100 MHz; $CDCl_3$) 18.36, 25.81, 66.63, 115.14, 118.65, 120.21, 125.59, 133.93, 139.18, 140.37 and 152.68; m/z (EI$^+$) 207 (M$^+$, 1%), 139 (9) and 123 (10).

2-Allyloxyaniline 4a

Under nitrogen, copper(II) acetylacetonate (1.15 g, 4.4 mmol) was added to ethanol (40 cm^3). To the suspension sodium boranuide (833 mg, 22 mmol) was flushed in using ethanol (40 cm^3). The mixture was stirred until the solution was no longer cloudy, a 'clumpy' solid being formed, and hydrogen evolution had decreased. To this, a solution of the nitrobenzene **3a** (3.94 g,

22 mmol) in ethanol (40 cm^3) was added, followed by further sodium boranuide (1.66 g, 44 mmol), again flushed in with ethanol (40 cm^3). The reaction was then stirred for 3 h, carefully poured into water (200 cm^3) and evaporated to one quarter of its original volume. More water (50 cm^3) was added and the solution was extracted with ethyl acetate (3 × 100 cm^3). The combined ethyl acetate extracts were dried over sodium sulfate, filtered and evaporated to dryness to give the title aniline **4a**[21] (2.90 g, 88%) as a clear oil, that did not require further purification (Found: M^+, 149.0813. $C_9H_{11}NO$ requires *M*, 149.0841); ν_{max}(film)/cm^{-1} 3466, 3374, 3060, 2922, 1615, 1506, 1219, 928, 847 and 741; λ_{max}(EtOH)/nm 210 (ε/dm^3 mol^{-1} cm^{-1} 13 935), 236 (6989) and 288 (2914); δ_H(400 MHz; $CDCl_3$) 3.74 (2 H, s, NH_2), 4.54 (2 H, d, *J* 5.2, CH_2), 5.26 (1 H, d, *J* 10.5, CH=C*H*$_2$), 5.38 (1 H, d, *J* 17.3, CH=C*H*$_2$), 6.01–6.12 (1 H, m, C*H*=CH_2) and 6.66–6.79 (4 H, m, ArH); δ_C(100 MHz; $CDCl_3$) 69.29, 112.14, 115.29, 117.47, 118.45, 121.45, 133.64, 136.53 and 146.32; *m*/*z* (EI^+) 149 (M^+, 42%) and 108 (100).

2-(3-Methylallyloxy)aniline 4b

In a procedure identical with that for the aniline **4a**, copper(II) acetylacetonate (1.36 g, 5.2 mmol), sodium boranuide (2.95 g, 78 mmol) and 2-(3-methylallyloxy)nitrobenzene **3b** (5.00 g, 26 mmol) were allowed to react in ethanol (200 cm^3) to give the title aniline **4b**[21] (4.20 g, 99%) as a clear oil that did not require further purification (Found: M^+, 163.0953. $C_{10}H_{13}NO$ requires *M*, 163.0997); ν_{max}(film)/cm^{-1} 3466, 3375, 3027, 2917, 1615, 1606, 1216, 967, 846 and 740; λ_{max}(EtOH)/nm 213 (ε/dm^3 mol^{-1} cm^{-1} 8439), 233 (7033) and 287 (2979); δ_H(250 MHz; $CDCl_3$) 1.76 (3 H, dd, *J* 1.0 and 5.9, Me), 3.69 (2 H, s, NH_2), 4.46 (2 H, d, *J* 5.1, CH_2), 4.61 [2 H (minor), d, *J* 6.3, CH_2], 5.72–5.83 (2 H, m, C*H*=CH) and 6.68–6.82 (4 H, m, ArH); δ_C(100 MHz; $CDCl_3$) 13.39 (minor), 17.87, 64.18 (minor), 69.15, 111.95 (minor), 112.08, 115.21, 118.43, 121.23, 126.00 (minor), 126.46, 128.32 (minor), 130.09, 136.47 and 146.50; *m*/*z* (EI^+) 163 (M^+, 23%) and 109 (100).

2-(3,3-Dimethylallyloxy)aniline 4c

In a procedure identical with that for compound **4a**, copper(II) acetylacetonate (485 mg, 1.85 mmol), sodium boranuide (1.51 g, 27.8 mmol) and the nitrobenzene **3c** (1.92 g, 9.27 mmol) were allowed to react in ethanol (80 cm^3) to give the *title aniline* **4c** (1.22 g, 74%) as a clear oil that did not require further purification (Found: M^+, 177.1173. $C_{11}H_{15}NO$ requires *M*, 177.1154); ν_{max}(film)/cm^{-1} 3450, 3379, 3059, 2971, 1614, 1505, 1459, 1214, 860 and 738; λ_{max}(EtOH)/nm 205 (ε/dm^3 mol^{-1} cm^{-1} 35 395), 237 (6794) and 289 (3172); δ_H(400 MHz; $CDCl_3$) 1.70 (3 H, s, Me), 1.75 (3 H, s, Me), 3.71 (2 H, s, NH_2), 4.49 (2 H, d, *J* 6.3, CH_2), 5.48 (1 H, t, *J* 6.3, CH=), 6.65–6.70 (2 H, m, ArH) and 6.73–6.78 (2 H, m, ArH); δ_C(100 MHz; $CDCl_3$) 18.02, 25.61, 65.05, 111.81, 115.04, 118.25, 120.05, 120.97, 136.34, 137.29 and 146.45; *m*/*z* (EI^+) 177 (M^+, 12%), 109 (100) and 69 (25).

2-Allyloxybenzenediazonium tetrafluoroborate 1a

A suspension of nitrosonium tetrafluoroborate (893 mg, 7.67 mmol) in carbon tetrachloride (20 cm^3), under nitrogen, was cooled to −5 °C. To this, a solution of the aniline **4a** (760 mg, 5.11 mmol) in carbon tetrachloride (20 cm^3) was added dropwise over 0.5 h, ensuring that the solution temperature never rose above 0 °C. Once the addition was complete, the solution was filtered to give a brown gelatinous solid, which was recrystallised (cold) from acetone by the addition of diethyl ether, to give the title diazonium tetrafluoroborate **1a**[21] (680 mg, 53%) as a white solid; mp 77–78 °C (acetone–diethyl ether) (Found: C, 43.2; H, 3.6; N, 11.3. $C_9H_9N_2O{\cdot}BF_4$ requires C, 43.59; H, 3.66; N, 11.30%); ν_{max}(KBr disc)/cm^{-1} 2255, 1591, 1569, 1300, 1263, 983 and 762; λ_{max}(EtOH)/nm 208 (ε/dm^3 mol^{-1} cm^{-1} 12 813), 266 (7476) and 354 (3581); δ_H(250 MHz; [$^2H_6$]acetone) 5.16 (2 H, ddd, *J* 5.5, 1.3 and 1.3, CH_2), 5.43 (1 H, ddt, *J* 10.6, 1.3 and 1.3, CH=C*H*$_2$), 5.61 (1 H, ddt, *J* 17.3, 1.3 and 1.3, CH=C*H*$_2$), 6.10–6.26 (1 H, ddt, *J* 17.3, 10.6 and 5.5, C*H*=CH_2), 7.51 (1 H, ddd, *J* 8.2, 8.2 and 0.6, ArH), 7.74 (1 H, d, *J* 8.2, ArH), 8.26–8.33 (1 H, m, ArH) and 8.61 (1 H, dd, *J* 8.9 and 1.6, ArH); δ_C(100 MHz; [$^2H_6$]acetone) 72.91, 102.77, 116.52, 120.29, 123.96, 131.75, 133.18, 145.01 and 163.03; *m*/*z* (EI^+) 161 [M^+, (*i.e.*, ArN_2)$^+$, 17%], 133 (15) and 92 (26).

2-(3-Methylallyloxy)benzenediazonium tetrafluoroborate 1b

In a procedure identical with that for the diazonium salt **1a**, nitrosonium tetrafluoroborate (3.21 g, 27.6 mmol) was treated with the aniline **4b** (3.00 g, 18.4 mmol) in carbon tetrachloride (80 cm^3) to give the title benzenediazonium tetrafluoroborate **1b**[21] (3.21 g, 67%) as a white solid, mp 85–86 °C (acetone–diethyl ether) (Found: C, 45.8; H, 4.2; N, 10.7. $C_{10}H_{11}N_2O{\cdot}BF_4$ requires C, 45.84; H, 4.23; N, 10.69%); ν_{max}(KBr disc)/cm^{-1} 2253, 1625, 1591, 1260, 1084 and 762; λ_{max}(EtOH)/nm 208 (ε/dm^3 mol^{-1} cm^{-1} 14 045), 265 (7404) and 355 (3736); δ_H(250 MHz; [$^2H_6$]acetone) 1.78 (3 H, d, *J* 6.5, Me), 5.05 (2 H, d, *J* 6.4, CH_2), 5.21 [2 H (minor), d, *J* 6.4, CH_2], 5.76–5.88 (1 H, m, CH=), 6.05–6.16 (1 H, m, CH=), 7.45–7.50 (1 H, m, ArH), 7.75 (1 H, d, *J* 8.8, ArH), 8.23–8.31 (1 H, m, ArH) and 8.59 (1 H, ddd, *J* 8.5, 8.5 and 1.6, ArH); δ_C(100 MHz; [$^2H_6$]DMSO) 13.46 (minor), 17.89, 68.32 (minor), 73.10, 102.52, 116.43 (minor), 116.53, 123.60 (minor), 123.73, 124.43, 132.35 (minor), 133.07, 134.23, 144.97 and 163.27; *m*/*z* (EI^+) 175 [M^+, $(ArN_2)^+$, 8%], 147 (5) and 92 (36).

2-(3,3-Dimethylallyloxy)benzenediazonium tetrafluoroborate 1c

The aniline **4c** (885 mg, 5 mmol) was dissolved in an aqueous solution of tetrafluoroboric acid (40%, 4 cm^3) and cooled to −10 °C. A solution of sodium nitrite (338 mg, 4.9 mmol) in water (1.25 cm^3) was added dropwise to it over 10 min. The mixture was stirred for a further 20 min and then filtered and washed with ice cold water to give the *title benzenediazonium tetrafluoroborate* **1c** (0.89 g, 64%) as a white solid; mp 82–83 °C (dec.) (acetone–diethyl ether) (Found: C, 47.5; H, 4.8; N, 9.8. $C_{11}H_{13}N_2O{\cdot}BF_4$ requires C, 47.86; H, 4.75; N, 10.15%); ν_{max}(KBr disc)/cm^{-1} 3061, 2980, 2247, 1589, 1564, 1484, 1293, 945 and 768; λ_{max}(EtOH)/nm 204 (ε/dm^3 mol^{-1} cm^{-1} 20 537), 266 (7729) and 357 (3809); δ_H(250 MHz; [$^2H_6$]acetone) 1.81 (3 H, s, Me), 1.82 (3 H, s, Me), 5.12 (2 H, d, *J* 7.0, CH_2), 5.55–5.61 (1 H, t, *J* 7.0, CH=), 7.44–7.51 (1 H, m, ArH), 7.74 (1 H, d, *J* 9.0, ArH), 8.24–8.31 (1 H, m, ArH) and 8.57 (1 H, dd, *J* 8.4 and 1.5, ArH); δ_C(67.5 MHz; [$^2H_6$]DMSO) 18.32, 25.79, 69.55, 102.41, 116.50, 117.72, 123.65, 133.07, 142.29, 145.00 and 163.49; *m*/*z* (FAB) 189 (M^+, 43%) and 161 (39).

1-(2,3-Dihydrobenzofuran-3-yl)ethanol 5b

The diazonium salt **1b** (130 mg, 0.5 mmol) was dissolved in degassed acetone (2.5 cm^3) and to this, a solution of TTF (122 mg, 0.6 mmol) in degassed acetone (2.5 cm^3) was added. Rapid nitrogen evolution occurred. The reaction was stirred for 0.5 h and then evaporated to dryness to give a solid that was dissolved in a mixture of ethyl acetate (20 cm^3) and water (20 cm^3). The layers were separated and the aqueous phase was extracted with ethyl acetate (2 × 20 cm^3). The combined organic layers were dried over sodium sulfate, filtered and evaporated to dryness to give a yellow solid. This was absorbed onto silica gel from dichloromethane, and was purified by column chromatography on silica gel (petrol–ethyl acetate, 4:1). Kugelrohr distillation gave the *title alcohol* **5b** (60 mg, 73%) as a clear oil (Found: C, 72.8; H, 7.6. $C_{10}H_{12}O_2$ requires C, 73.15; H, 7.37%); ν_{max}(film)/cm^{-1} 3415, 3047, 2971, 1609 and 1595; λ_{max}(EtOH)/nm 205 (ε/dm^3 mol^{-1} cm^{-1} 8625), 217 (4408)

and 282 (3142); δ_H(250 MHz; $CDCl_3$) 1.18 [3 H (minor), d, *J* 6.3, Me], 1.24 (3 H, d, *J* 6.4, Me), 1.79 (1 H, s, OH), 3.45–3.49 (1 H, m, CHAr), 3.93 [1 H (minor), quintet, *J* 6.3, C*H*OH], 4.06 (1 H, qd, *J* 6.4 and 4.7, C*H*OH), 4.24–4.65 (2 H, m, CH_2), 6.78–6.90 (2 H, m, ArH) and 7.11–7.30 (2 H, m, ArH); δ_C(100 MHz; $CDCl_3$) 19.96 (minor), 20.43, 49.13 (minor), 49.35, 68.86, 69.93 (minor), 72.30, 73.13 (minor), 109.71, 120.35, 124.51, 125.51 (minor), 126.93, 127.24 (minor), 128.85 (minor), 128.91, 160.49 (minor) and 160.81; *m/z* (EI^+) 164 (M^+, 30%), 120 (94), 119 (80) and 91 (100).

2-(2,3-Dihydrobenzofuran-3-yl)-2-propan-2-ol 5c

Using the procedure outlined for the formation of the alcohol **5b**, the diazonium salt **1c** (130 mg, 0.5 mmol) and TTF (122 mg, 0.6 mmol) were allowed to react in degassed acetone (5 cm^3) to give the *title alcohol* **5c** (52 mg, 58%) as a clear oil (Found: M^+, 178.1011. $C_{11}H_{14}O_2$ requires *M*, 178.0994); ν_{max}(film)/cm^{-1} 3425, 3046, 2974, 1609, 1593, 1484, 1235 and 750; λ_{max}(EtOH)/nm 203 (ε/dm^3 mol^{-1} cm^{-1} 14 069), 224 (5352) and 284 (4153); δ_H(250 MHz; $CDCl_3$) 1.32 (3 H, s, Me), 1.34 (3 H, s, Me), 1.75 (1 H, s, OH), 4.66 (1 H, X of ABX, J_{BX} and J_{AX} 13.3, C*H*Ar), 4.59–4.73 (2 H, A and B of ABX, J_{AB} 9.5, J_{BX} 8.6 and J_{AX} 4.7, CH_2O), 6.70–7.00 (2 H, m, ArH) and 7.24–7.27 (2 H, m, ArH); δ_C(100 MHz; $CDCl_3$) 26.61, 26.71, 53.26, 72.00, 73.41, 109.69, 120.17, 126.06, 127.19, 128.84 and 160.87; *m/z* (EI^+) 178 (M^+, 3%), 120 (100) and 91 (44).

1-[(2,3-Dihydrobenzofuran-3-yl)methyl]tetrathiafulvalen-1-ium tetrafluoroborate 6a

To the diazonium salt **1a** (124 mg, 0.5 mmol) in degassed acetone (2.5 cm^3) was added a solution of TTF (122 mg, 0.6 mmol), also in acetone (2.5 cm^3). The solution was stirred for 0.5 h and then poured into diethyl ether (250 cm^3) to give the *title tetrathiafulvalenium tetrafluoroborate* **6a** (161 mg, 75%) as a yellow solid, obtained by filtration, mp 72–73 °C (acetone–diethyl ether) (Found: M^+, 336.9863. $C_{15}H_{13}OS_4$ requires *M*, 336.9849); ν_{max}(KBr disc)/cm^{-1} 3079, 1480, 1367, 1233, 1124, 1083, 1035 and 754; δ_H(400 MHz; [$^2H_6$]acetone) 3.82 [1 H (minor), dd, *J* 10.6 and 12.9, CH_2S], 3.91–3.96 [2 H (+ 1 H minor), m, CH_2S], 4.13–4.24 (1 H, m, C*H*Ar), 4.58 [1 H (minor), dd, *J* 9.5 and 6.3, CH_2O], 4.70 (1 H, dd, *J* 5.5 and 9.5, CH_2O), 4.79–4.82 (2 H, m, CH_2O), 6.78 (1 H, d, *J* 7.3, =CH), 6.82 [1 H (minor), d, *J* 7.3, =CH], 6.86–6.91 (2 H, m, ArH and =CH), 6.69 [1 H (minor), d, *J* 5.3, ArH], 7.15–7.29 (3 H, m, ArH), 7.39 (1 H, d, *J* 7.4, =CH), 7.46 [1 H (minor), d, *J* 7.4, =CH], 8.23 (1 H, d, *J* 4.9, =CH) and 8.25 [1 H (minor), d, *J* 4.9, =CH]; δ_C(100 MHz; [$^2H_6$]acetone) 39.00, 39.27, 52.85, 53.33, 75.48, 75.80, 84.94, 85.22, 110.67, 110.89, 111.09, 112.22, 121.73, 122.53, 122.68, 123.37, 123.73, 125.88, 125.96, 126.99, 127.22, 130.32, 130.49, 145.27, 145.56, 160.46, 160.65, 162.65 and 163.67; *m/z* (FAB) 337 (M^+, 37%), 204 (100) and 133 (34).

2,3-Dihydro-3-(1-methoxyethyl)benzofuran 7

The diazonium salt **1b** (78.6 mg, 0.3 mmol) was dissolved in dry methanol (1.5 cm^3) and to this, a solution of TTF (61.2 mg, 0.3 mmol) in dry methanol (1.5 cm^3) was added. Rapid nitrogen evolution occurred. The reaction was stirred for 2 d, poured into water (50 cm^3) and extracted with ethyl acetate (3 × 50 cm^3). The combined organic extracts were washed with water (150 cm^3), dried over sodium sulfate, filtered and evaporated to dryness to give an oily residue. This was purified by column chromatography on silica gel (light petroleum–dichloromethane, 1:1), to give the *title benzofuran* **7** (29.3 mg, 54%) as a clear oil (Found: C, 74.1; H, 8.1. $C_{11}H_{14}O_2$ requires C, 74.13; H, 7.92%); ν_{max}(KBr film)/cm^{-1} 2976, 1595, 1483, 1233 and 751; δ_H(250 MHz; $CDCl_3$) 0.97 (3 H, d, *J* 6.2, Me), 1.11 [3 H (minor), d, *J* 6.0, Me], 3.27 (3 H, s, OMe), 3.31 [3 H (minor), s, OMe], 3.32–3.67 (2 H, m, MeC*H*C*H*Ar), 4.35–4.52 (2 H, m, CH_2), 6.70–6.80 (2 H, m, ArH) and 7.03–7.18 (2 H, m, ArH); δ_C(100 MHz; [$^2H_6$]acetone) 15.06 (minor), 16.15, 47.03 (minor), 48.16, 56.00, 56.05 (minor), 72.66 (minor), 73.75, 78.78, 79.01 (minor), 109.75 (minor), 109.80, 120.60 (minor), 120.79, 126.11, 126.34 (minor), 129.48 (minor), 129.00, 129.30, 161.53 and 161.83 (minor); *m/z* (EI^+) 178 (M^+, 14%), 119 (27) and 91 (47).

N-[1-(2,3-Dihydrobenzofuran-3-yl)ethyl]acetamide 8 and the alcohol 5b

To the diazonium tetrafluoroborate **1b** (78.6 mg, 0.3 mmol) in acetonitrile (1.5 cm^3), TTF (61.2 mg, 0.3 mmol) in acetonitrile (1.5 cm^3) was added. The mixture was stirred for 2 d, diluted with water (50 cm^3) and extracted into ethyl acetate (3 × 50 cm^3). The combined organic extracts were washed with water (150 cm^3), dried over sodium sulfate, filtered and evaporated to dryness to give solid residue. This was purified by column chromatography on silica gel (light petroleum–ethyl acetate, 4:1) to give the title alcohol **5b** (8.3 mg, 17%), identical to an authentic sample, and the *title acetamide* **8** (33 mg, 54%) as a waxy solid, mp 85.5–86.5 °C (ethyl acetate–light petroleum) as a mixture of isomers (Found: C, 70.65; H, 7.7; N, 6.6. $C_{12}H_{15}NO_2$ requires C, 70.22; H, 7.37; N, 6.82%); ν_{max}(KBr disc)/cm^{-1} 3432, 3279, 3083, 2926, 1642, 1552, 1481, 1226 and 753; δ_H([$^2H_3$]MeCN) 1.02 (3 H, d, *J* 6.9, Me), 1.82 and 1.83 (3 H, 2 × s, MeCO), 3.53–3.62 (1 H, m, C*H*Ar), 4.03–4.14 (1 H, m, C*H*NH), 4.35–4.52 (2 H, m, CH_2), 6.39 (1 H, br s, NH), 6.74 (1 H, d, *J* 8, ArH), 6.84 (1 H, br t, *J* 7.4, ArH), 7.13 (1 H, 2 × t, *J* 7.4 and 7.9, ArH) and 7.25 (1 H, d, *J* 7.4, ArH); δ_C(67.5 MHz; $CDCl_3$) 16.64, 17.50, 17.65, 23.58, 23.69, 23.78, 46.54, 46.65, 46.74, 47.89, 47.92, 48.05, 48.14, 74.02, 74.14, 74.23, 109.90, 109.99, 110.03, 110.14, 120.67, 120.77, 120.83, 125.50, 125.55, 125.73, 125.84, 126.61, 126.95, 127.03, 129.15, 129.25, 129.31, 129.42, 161.02, 161.13, 170.06, 170.33 and 170.40; *m/z* (EI^+) 206 (MH^+, 2%), 146 (54) and 131 (12).

1-[1-(2,3-Dihydrobenzofuran-3-yl)ethyl]tetrathiafulvalen-1-ium tetrafluoroborate 6b

To the diazonium tetrafluoroborate **1b** (78.6 mg, 0.3 mmol) in degassed acetonitrile (1.5 cm^3) was added a solution of TTF (61.2 mg, 0.3 mmol) also in acetonitrile (1.5 cm^3). The solution was stirred for 2 min and then poured into diethyl ether (250 cm^3) to give the title *tetrathiafulvalenium tetrafluoroborate* **6b** (89.3 mg, 68%) as a yellow solid, obtained by filtration, mp 78–79 °C (acetonitrile–diethyl ether). (This compound was found to be unstable in solution) (Found: M^+, 351.0015. $C_{16}H_{15}OS_4$ requires *M*, 351.0006); ν_{max}(KBr disc)/cm^{-1} 3077, 1482, 1365, 1236, 1125, 1084 and 753; δ_H(400 MHz; [$^2H_3$]MeCN) 1.25–1.41 (3 H, 4 × d, Me), 3.35–3.62 (2 H, m), 4.38–4.79 (2 H, m), 6.02–6.57 (1 H, 4 × d, CH=C*H*), 6.7–7.6 (6 H, m, 2 × CH=C*H* and 4 × ArH), 7.82–7.97 (1 H, 4 × d, CH=C*H*); *m/z* (FAB) 351 (M^+, 25%), 249 (75) and 204 (100).

Reaction of the tetrathiafulvalenium tetrafluoroborate 6b to give the alcohol 5b

The tetrathiafulvalenium tetrafluoroborate **6b** (88 mg, 0.20 mmol) was dissolved in degassed acetone (1.0 cm^3) and the mixture was stirred, under nitrogen gas, for 1 h. The mixture was diluted with water (50 cm^3) and extracted with ethyl acetate (3 × 50 cm^3), dried over sodium sulfate, filtered and evaporated to dryness. The oily residue was purified by column chromatography on silica gel (light petroleum–ethyl acetate, 4:1) to give the title alcohol **5b** (20.8 mg, 63%) as a clear oil, and tetrathiafulvalene (10.6 mg, 25%). Both products were identical to authentic samples.

Formation of the tetrathiafulvalenium tetrafluoroborate 6b and conversion into *N*-[1-(2,3-Dihydrobenzofuran-3-yl)ethyl][$^2H_3$]-acetamide [$^2H_3$]8

The diazonium tetrafluoroborate **1b** (50 mg, 0.19 mmol) was dissolved in degassed acetone (5 cm^3) and to this was added TTF (39 mg, 0.19 mmol), also in degassed acetone (1 cm^3). The mixture was vigorously stirred and immediately poured into diethyl ether (100 cm^3). Filtration under nitrogen gave the title tetrathiafulvalenium tetrafluoroborate **6b** as an orange solid. This was dissolved in [$^2H_3$]acetonitrile in an NMR tube. The solution was allowed to react for 3 h, after which time NMR spectroscopy showed that all of the tetrathiafulvalenium tetrafluoroborate **6b** had been consumed. The solution was evaporated to dryness and purified by column chromatography on silica gel (light petroleum–ethyl acetate, 1:1) to give the title labelled acetamide [$^2H_3$]**8** (17 mg, 43%) as a viscous brown oil; δ_H([$^2H_3$]MeCN) 1.02 (3 H, d, *J* 6.9, Me), 3.53–3.62 (1 H, m, C*H*Ar), 4.03–4.14 (1 H, m, C*H*NH), 4.35–4.52 (2 H, m, CH_2), 6.39 (1 H, br s, NH), 6.74 (1 H, d, *J* 8, ArH), 6.84 (1 H, br t, *J* 7.4, ArH), 7.13 (1 H, 2 × t, *J* 7.4 and 7.9, ArH) and 7.25 (1 H, d, *J* 7.4, ArH).

Attempted decomposition of tetrathiafulvalene in aqueous tetrafluoroboric acid and acetone

Tetrathiafulvalene (102 mg, 0.5 mmol) was dissolved in 40% tetrafluoroboric acid (110 mg, 0.5 mmol) and acetone (3 cm^3) and the mixture was stirred under nitrogen for 5 h. The solution was poured into water and extracted into dichloromethane (3 × 50 cm^3) and dried over magnesium sulfate, filtered and evaporated to dryness to give tetrathiafulvalene (100 mg, 98%).

5-Oxanona-2,7-dien-1-ol 11

To a suspension of potassium hydroxide (3.36 g, 60 mmol) in DMSO (30 cm^3), bromobut-2-ene (3.09 cm^3, 30 mmol) and but-2-ene-1,4-diol were added. The mixture was stirred for 30 min, poured into water and extracted with dichloromethane (3 × 150 cm^3). The aqueous phase was acidified with aqueous hydrochloric acid (200 cm^3, 2 mol dm^{-3}) and extracted with further dichloromethane (2 × 150 cm^3). The combined organic phases were washed with water (5 × 300 cm^3), dried over sodium sulfate, filtered and evaporated to dryness. Distillation (bp 82–84 °C/1 mmHg) gave the *title dienol* **11** (2.25 g, 53%) as a clear oil (Found: MH^+, 143.1062. $C_8H_{14}O_2$ requires *M*H, 143.1072); ν_{max}(KBr disc)/cm^{-1} 3396, 2918, 2856, 1449 and 1041; δ_H(250 MHz; $CDCl_3$) 1.20 [3 H (minor), d, *J* 6.4, Me], 1.59–1.64 [3 H (minor), m, Me], 1.66 (3 H, dd, *J* 6.1 and 1.2, Me), 2.65 (1 H, s, OH), 2.83–2.87 (2 H, m, CH_2), 3.97 (2 H, dd, *J* 0.8 and 6.1, CH_2), 4.10–4.13 (2 H, m, CH_2) and 5.51–5.78 (4 H, m, 2 × C*H*=C*H*); δ_C(67.5 MHz; $CDCl_3$) 13.00, 17.56, 21.10, 58.15, 63.42, 65.09, 65.18, 65.30, 65.37, 70.69, 70.87, 116.19, 126.22, 127.15, 127.73, 127.98, 128.18, 129.15, 129.67, 129.88, 131.95, 132.13, 132.24 and 139.68; *m*/*z* (CI) 143 (MH^+, 60%).

2-(5-Oxanona-2,7-dien-1-yloxy)nitrobenzene 12

2-Nitrophenol (3.10 g, 22.3 mmol), the dienol **11** (2.25 g, 15.15 mmol) and triphenylphosphane (3.85 g, 22.3 mmol) were dissolved in tetrahydrofuran (44 cm^3) and cooled to 0 °C. Diethyl diazodicarboxylate (DEAD) (3.5 cm^3, 22.3 mmol) was added dropwise over 30 min. The mixture was stirred for a further 16 h, during which time it was allowed to warm to room temperature. The mixture was evaporated to dryness, redissolved in dichloromethane and washed with aqueous sodium hydroxide (100 cm^3, 2 mol dm^{-3}), aqueous hydrochloric acid (100 cm^3, 2 mol dm^{-3}), aqueous sodium carbonate (saturated, 100 cm^3) and water (2 × 100 cm^3). Drying over sodium sulfate, followed by filtration and removal of the solvent under reduced pressure gave a brown oil. This was purified by column chromatography on silica gel (light petroleum–ethyl acetate, 9:1) and gave the *title nitrobenzene* **12** (2.24 g, 56%) as a clear oil that was a mixture of isomers (Found: MH^+, 264.1224. $C_{14}H_{17}N_2O_4$ requires *M*H, 264.1236); ν_{max}(film)/cm^{-1} 3022, 2917, 2855, 1671, 1607, 1525, 1280 and 745; δ_H(250 MHz; $CDCl_3$) 1.22 [3 H (minor), d, *J* 6.4, Me], 1.63–1.68 (3 H, m, Me), 3.86–4.00 (2 H, m, CH_2), 4.01–4.09 (2 H, m, CH_2), 4.74–4.76 (2 H, m, CH_2), 5.47–5.81 (4 H, m, 2 × C*H*=C*H*), 6.94–7.07 (2 H, m, ArH), 7.43–7.50 (1 H, m, ArH) and 7.76–7.78 (1 H, dd, *J* 1.7 and 8.1, ArH); δ_C(67.5 MHz; $CDCl_3$) 12.94, 17.52, 65.46, 65.70, 70.91, 114.63, 120.23, 125.27, 126.06, 126.20, 126.30, 126.33, 127.03, 128.03, 129.70, 130.66, 133.80, 139.84 and 151.52; *m*/*z* (CI) 264 (MH^+, 8%).

2-(5-Oxanona-2,7-dien-1-yloxy)aniline 13

In a procedure identical to that given for the amine **4a**, sodium boranuide (908 mg, 24 mmol) and copper(II) acetylacetonate (419 mg, 1.6 mmol) in ethanol (80 cm^3), were used to reduce the nitrobenzene **12** (2.10 g, 8 mmol) to give the *title aniline* **13** (1.7 g, 91%) as a clear oil that was a mixture of isomers (Found: M^+, 233.1416. $C_{14}H_{19}NO_2$ requires *M*, 233.1416); ν_{max}(film)/cm^{-1} 3468, 3364, 2916, 2854, 1672, 1614, 1504 and 738; δ_H(250 MHz; $CDCl_3$) 1.25 [3 H (minor), d, *J* 6.4, Me], 1.63–1.71 (3 H, m, Me), 3.84 (2 H, s, NH_2), 3.88–3.92 (2 H, m, CH_2), 4.04–4.07 (2 H, m, CH_2), 4.60 (2 H, m, CH_2), 5.60–5.86 (4 H, m, 2 × C*H*=C*H*) and 6.68–6.78 (4 H, m, ArH); δ_C(67.5 MHz; $CDCl_3$) 17.68, 64.28, 65.43, 65.52, 65.66, 70.98, 111.75, 115.06, 118.20, 121.33, 127.24, 128.07, 129.75, 129.85, 136.38 and 146.05; *m*/*z* (EI^+) 233 (M^+, 48%), 148 (17), 125 (16) and 109 (100).

2-(5-Oxanona-2,7-dien-1-yloxy)benzenediazonium tetrafluoroborate 14

Using a procedure identical to that for the diazonium tetrafluoroborate **1c**, sodium nitrite (32 mg, 0.45 mmol) in water (0.5 cm^3) was used to diazotise the aniline **13**, in aqueous tetrafluoroboric acid (20%, 0.4 cm^3). The *title diazonium tetrafluoroborate* **14** (1.02 g, 52%) was obtained as a powdery brown solid, mp 44–47 °C (acetone–diethyl ether) (Found: M^+, 245.1267. $C_{14}H_{17}N_2O_2$ requires *M*, 245.1290); ν_{max}(KBr disc)/cm^{-1} 3017, 2918, 2251, 1617, 1590, 1296, 831 and 761; δ_H(250 MHz; $CDCl_3$) 1.19 [3 H (minor), d, *J* 6.4, Me], 1.64 (3 H, dd, *J* 6.2 and 1.0, Me), 3.89–3.93 (2 H, m, CH_2), 4.05–4.19 (2 H, m, CH_2), 5.20–5.25 (2 H, m, CH_2), 5.49–5.74 (2 H, m, C*H*=CH), 5.83–5.95 (2 H, m, CH=C*H*), 7.45 (1 H, dd, *J* 7.9 and 7.9, ArH), 7.70 (1 H, d, *J* 8.6, ArH), 8.20–8.27 (1 H, m, ArH) and 8.50–8.54 (1 H, m, ArH); δ_C(100 MHz; [$^2H_6$]acetone) 13.18, 17.75, 66.26, 68.70, 71.46, 102.66, 116.40, 123.91, 125.01, 128.62, 129.35, 133.18, 133.71, 144.99 and 163.09; *m*/*z* (FAB) 245 (M^+, 57%), 154 (20) and 136 (14).

Reaction of the benzenediazonium tetrafluoroborate 14 with tetrathiafulvalene

The benzenediazonium tetrafluoroborate **14** (166 mg, 0.5 mmol) was dissolved in acetone (2.5 cm^3) and deoxygenated by a stream of nitrogen. To this, tetrathiafulvalene (102 mg, 0.5 mmol) in similarly treated acetone (2.5 cm^3) was added under a nitrogen atmosphere. Once nitrogen evolution had ceased, sodium hydrogen carbonate (84 mg, 1 mmol) in water (0.25 cm^3) was added, and the mixture was stirred for 4 d. After this time, the mixture was poured into water (50 cm^3) and extracted with ethyl acetate (3 × 50 cm^3). The combined organic phases were washed with water (3 × 50 cm^3), dried over magnesium sulfate, filtered and evaporated to dryness. Purification was achieved by gradient elution column chromatography on silica gel (light petroleum–ethyl acetate, 9:1–4:1) to give 1-(2,3-*dihydrobenzo*[b]*furan*-3-*yl*)-3-*oxahept*-5-*enol* **15** (48 mg, 41%) as a clear oil (Found: M^+, 234.1262. $C_{14}H_{18}O_3$ requires *M*, 234.1256); ν_{max}(film)/cm^{-1} 3454, 2896, 1609, 1595, 1482, 1233

and 752; δ_H(400 MHz; $CDCl_3$) 1.66–1.74 (3 H, m, Me), 2.33 (1 H, s, OH), 3.44–3.68 (3 H, m, CH_2 and ArC*H*), 3.85–3.98 (3 H, m, CH_2 and C*H*OH), 4.54 (1 H, dd, *J* 9.1 and 9.1, ArOCH_2), 4.69 (1 H, dd, *J* 5.0 and 9.1, ArOCH_2), 5.51–5.78 (2 H, m, C*H*=C*H*), 6.78–6.89 (2 H, m, ArH) and 7.12–7.19 (2 H, m, ArH); δ_C(100 MHz; $CDCl_3$) 17.83, 44.97, 45.41, 71.16, 71.41, 71.61, 71.79, 72.16, 72.40, 72.86, 73.07, 109.71, 109.85, 120.42, 120.55, 125.30, 125.88, 126.41, 126.80, 127.17, 128.55, 128.92, 130.24 and 160.75; *m/z* (EI$^+$) 234 (M^+, 9%), 145 (18), 119 (100) and 55 (33).

Further elution (light petroleum–ethyl acetate, 7:3) gave 1-[4-(2,3-*dihydrobenzo*[b]*furan*-3-*yl*)*tetrahydrofuran*-3-*yl*]-*ethanol* **16** (18 mg, 15%), also as a clear oil (Found: M^+, 234.1268. $C_{14}H_{18}O_3$ requires *M*, 234.1256); ν_{max}(KBr disc)/cm^{-1} 3430, 2925, 1681, 1593, 1480, 1456, 1229 and 753; δ_H(250 MHz; $CDCl_3$) 1.07–1.29 (3 H, m, Me), 1.59 (1 H, s, OH), 2.03–2.63 (2 H, m, C*H*C*H*CHOH), 3.56–4.72 (8 H, m, 3 × CH_2, C*H*Ar and C*H*OH), 6.79–7.08 (2 H, m, ArH) and 7.13–7.23 (2 H, m, ArH); δ_C(100 MHz; $CDCl_3$) 21.62, 22.09, 22.23, 22.29, 22.78, 23.23, 23.34, 23.74, 41.29, 41.54, 44.75, 44.87, 45.15, 45.36, 45.51, 45.92, 46.25, 47.10, 47.51, 47.80, 49.09, 49.82, 50.20, 50.47, 66.26, 66.91, 68.33, 68.85, 69.10, 69.48, 69.96, 70.18, 70.26, 70.64, 70.78, 71.06, 71.17, 71.24, 71.47, 72.33, 74.33, 74.71, 75.10, 76.13, 109.86, 109.99, 110.71, 120.38, 120.65, 124.12, 124.71, 124.87, 124.90, 125.02, 125.21, 128.62, 128.87, 129.02, 129.59, 129.74, 159.78, 160.46 and 160.550; *m/z* (EI$^+$) 234 (M^+, 15%), 146 (10), 132 (6) and 119 (100).

5-Oxanon-7-en-2-yn-1-ol 17

Using a procedure identical to that for the dienol **11**, but-2-yne-1,4-diol (19.37 g, 225 mmol) was treated with bromobut-2-ene (4.64 cm^3, 45 mmol) and potassium hydroxide (5.04 g, 225 mmol) for 30 min in DMSO (45 cm^3) to give the *title alcohol* **17** (4.77 g, 75%) as a clear oil [Found: $(M + NH_4)^+$, 158.1181. $C_8H_{12}O_2$ requires $(M + NH_4)^+$, 158.1181]; ν_{max}(KBr disc)/cm^{-1} 3395, 2917, 2856, 1664, 1440, 1351 and 1122; δ_H(250 MHz; $CDCl_3$) 1.21 [3 H (minor), d, *J* 6.4, Me], 1.66 (3 H, d, *J* 6.4, Me), 2.81 (1 H, s, OH), 3.92 (2 H, d, *J* 6.3, =CHCH_2), 4.03–4.13 (2 H, m, CH_2), 4.24 (2 H, m, CH_2) and 5.43–5.77 (2 H, m, C*H*=C*H*); δ_C(67.5 MHz; $CDCl_3$) 17.52, 20.85, 50.35, 55.16, 56.73, 56.95, 64.64, 70.12, 80.95, 84.60, 126.31 and 130.60; *m/z* (CI) 158 [$(M + NH_4)^+$, 100%].

2-(5-Oxanon-7-en-2-yn-1-yloxy)nitrobenzene 18

Using the same procedure as for the nitrobenzene **12**, compound **17** (2.00 g, 14.3 mmol) was treated with 2-nitrophenol (2.98 g, 21.45 mmol), DEAD (3.37 cm^3, 21.45 mmol) and triphenylphosphane (3.70 g, 21.45 mmol) in tetrahydrofuran (40 cm^3) to give the *title nitrobenzene* **18** as a clear oil [Found: $(M + NH_4)^+$, 279.1334. $C_{14}H_{15}NO_4$ requires $(M + NH_4)^+$, 279.1345]; ν_{max}(film)/cm^{-1} 3018, 2937, 2854, 1606, 1584, 1526, 1281, 1232 and 745; δ_H(250 MHz; $CDCl_3$) 1.22–1.33 [3 H (minor), m, Me], 1.61–1.72 (3 H, m, Me), 3.91–3.95 (2 H, m, CH_2), 4.06–4.22 (2 H, m, CH_2), 4.89–4.91 (2 H, m, CH_2), 5.49–5.78 (2 H, m, C*H*=C*H*), 7.08 (1 H, ddd, *J* 8.4, 8.4 and 1.0, ArH), 7.21 (1 H, dd, *J* 8.4 and 1.0, ArH), 7.55 (1 H, ddd, *J* 8.0, 8.0 and 1.7, ArH) and 7.85 (1 H, dd, *J* 8.0 and 1.7, ArH); δ_C(67.5 MHz; $CDCl_3$) 17.59, 20.91, 56.61, 56.82, 57.25, 64.73, 70.26, 79.46, 84.99, 115.27, 121.04, 125.49, 126.31, 129.00, 130.69, 133.80 and 150.64; *m/z* (CI) 279 [$(M + NH_4)^+$, 100%].

2-(5-Oxanon-7-en-2-yn-1-yloxy)aniline 19

The nitrobenzene **18** (2.61 g, 10 mmol) was dissolved in a mixture of concentrated hydrochloric acid (10 cm^3) and ethanol (10 cm^3). To this, a solution of tin(II) chloride (4.5 g, 20 mmol) in ethanol (10 cm^3) was added dropwise over 20 min. The mixture was stirred for 16 h, poured into water (200 cm^3) and washed with dichloromethane (2 × 50 cm^3). Aqueous sodium hydrogen carbonate (saturated) was added to the aqueous phase until it was alkaline and then dichloromethane (3 × 50 cm^3) was used to extract the aqueous portion. The combined organic extracts were dried over sodium sulfate, filtered and evaporated to dryness to give *the aniline* **19** (720 mg, 31%) as a brown oil, that did not require further purification (Found: M^+, 231.1260. $C_{14}H_{17}NO_2$ requires *M*, 231.1259); ν_{max}(film)/cm^{-1} 3465, 3368, 2916, 2853, 1615, 1504, 1200 and 738; δ_H(250 MHz; $CDCl_3$) 1.62–1.70 (3 H, m, Me), 3.74 (2 H, s, NH_2), 3.93 (2 H, d, *J* 6.25, =CHCH_2), 4.13–4.15 (2 H, m, CH_2), 4.73–4.75 (2 H, m, CH_2), 5.46–5.77 (2 H, m, C*H*=C*H*) and 6.66–6.86 (4 H, m, ArH); δ_C(67.5 MHz; $CDCl_3$) 17.36, 56.07, 56.44, 69.86, 81.03, 83.09, 112.13, 115.02, 117.74, 121.65, 126.27, 130.23, 136.35 and 144.88; *m/z* (EI$^+$) 231 (M^+, 65%), 159 (16), 108 (100) and 80 (45).

2-(5-Oxanon-7-en-2-yn-1-yloxy)benzenediazonium tetrafluoroborate 20

Using the same procedure as for the benzenediazonium tetrafluoroborate **1c**, the aniline **19** (720 mg, 3.11 mmol) was treated with sodium nitrite (207 mg, 3 mmol) in water (3.0 cm^3) and aqueous tetrafluoroboric acid (2.5 cm^3, 20%) to give the *title benzenediazonium tetrafluoroborate* **20** (650 mg, 65%) as an oil; ν_{max}(KBr disc)/cm^{-1} 3023, 2919, 2253, 1585, 1296, 833 and 740; δ_H(250 MHz; $CDCl_3$) 1.63 (3 H, d, *J* 5.7, Me), 3.91 (2 H, d, *J* 6.06, =CHCH_2), 4.16–4.20 (2 H, m, CH_2), 5.34–5.38 (2 H, m, CH_2), 5.63–5.72 (2 H, m, C*H*=C*H*), 7.54 (1 H, t, *J* 8.0, ArH), 7.79 (1 H, d, *J* 8.8, ArH), 8.26–8.33 (1 H, m, ArH) and 8.57–8.60 (1 H, m, ArH); δ_C(67.5 MHz; $CDCl_3$) 17.72, 56.93, 60.19, 70.61, 78.89, 87.55, 103.19, 116.48, 124.40, 127.78, 130.27, 133.39, 144.85 and 161.66; *m/z* (FAB) 243 (M^+, 6.1%).

Reaction of the benzenediazonium tetrafluoroborate 20 with tetrathiafulvalene

TTF (102 mg, 0.5 mmol), as a solution in acetone (2.5 cm^3), was added to a solution of the benzenediazonium tetrafluoroborate **20** (164.9 mg, 0.5 mmol) also in acetone (2.5 cm^3). Water (0.25 cm^3) was then added and the solution was stirred for 4 d and then poured into water (50 cm^3). Ethyl acetate (3 × 50 cm^3) was used to extract the product. The combined extracts were dried over magnesium sulfate, filtered and evaporated to dryness. The oily product was purified by column chromatography on silica gel (light petroleum–ethyl acetate, 9:1) to give 3-(6-*methyl*-3-*oxabicyclo*[3.1.0]*hexan*-1-*yl*)*benzofuran* **21** (69 mg, 64%), a colourless oil, formed as a mixture of two diastereoisomers, which were separated by high performance liquid chromatography: **21a** (Found: M^+, 214.1012. $C_{14}H_{14}O_2$ requires *M*, 214.0994); ν_{max}(film)/cm^{-1} 3035, 2854, 1625, 1585, 1452, 1225, 1101, 1074, 1056 and 857; δ_H(400 MHz; $CDCl_3$) 0.96 (3 H, d, *J* 6.3, Me), 1.27 (1 H, dq, *J* 6.3 and 4.0, C*H*Me), 1.60 (1 H, dd, *J* 4.0 and 2.8, CH), 3.75 (1 H, d, *J* 8.1, CH_2C), 3.97 (1 H, dd, *J* 8.3 and 2.8, CH_2CH), 4.02 (1 H, d, *J* 8.3, CH_2CH), 4.13 (1 H, d, *J* 8.1, CH_2C), 7.23–7.32 (2 H, m, ArH), 7.46–7.49 (1 H, m, ArH), 7.48 (1 H, s, CH=) and 7.56–7.58 (1 H, m, ArH); δ_C(100 MHz; $CDCl_3$) 13.13, 18.80, 28.33, 30.08, 70.11, 73.89, 111.65, 116.53, 120.08, 122.60, 124.38, 128.77, 143.30 and 155.48; *m/z* (EI$^+$) 214 (M^+, 100%), 199 (24), 184 (61) and 115 (72).

21b (Found: M^+, 214.097. $C_{14}H_{14}O_2$ requires *M*, 214.0994); δ_H(400 MHz; $CDCl_3$) 1.24 (3 H, d, *J* 6.4, Me), 1.45 (1 H, dq, *J* 8.2 and 6.4, C*H*Me), 1.94 (1 H, dd, *J* 8.2 and 3.7, CH), 4.01 (1 H, d, *J* 8.7, CH_2CH), 4.10 (1 H, d, *J* 8.6, CH_2C), 4.13 (1 H, d, *J* 8.6, CH_2C), 4.23 (1 H, dd, *J* 8.7 and 3.7, CH_2CH), 7.23–7.35 (2 H, m, ArH), 7.26 (1 H, s, CH=), 7.44–7.47 (1 H, m, ArH) and 7.54–7.56 (1 H, m, ArH); δ_C(100 MHz; $CDCl_3$) 6.09, 20.86, 27.63, 29.80, 68.23, 70.88, 111.83, 120.03, 120.96, 122.62, 124.48, 127.77, 142.02 and

155.55; *m/z* (EI$^+$) 214 (M^+, 100%), 199 (23), 184 (58) and 115 (59).

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