Unprecedented electrophilic behaviour of tetrathiafulvalenium salts

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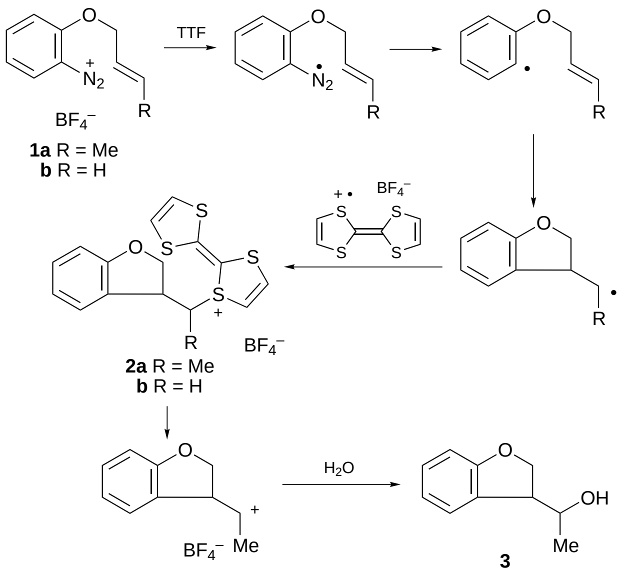
Primary tetrathiafulvalenium salts display a diverse and unprecedented reactivity towards nucleophiles.

Tetrathiafulvalene (TTF) and its derivatives have attracted widespread interest in the preparation of novel materials.[1] Recently, the synthetic value of TTF has become apparent as a result of its catalysis of 'radical-polar crossover[2] chemistry'. This leads to the formation of tetrathiafulvalenium salts **2** (Scheme 1) which have been isolated. In appropriate cases, *e.g.* **2a**, these compounds undergo facile S_N1 substitution at room temperature by such nucleophiles as water, alcohols and MeCN. Since this happens *in situ*, TTF is regenerated and so functions as a catalyst. The catalyst is effective down to a concentration of *ca*. 5 mol% but, below this level incomplete conversions are seen. It is clear that the catalyst is slowly destroyed during such reactions.

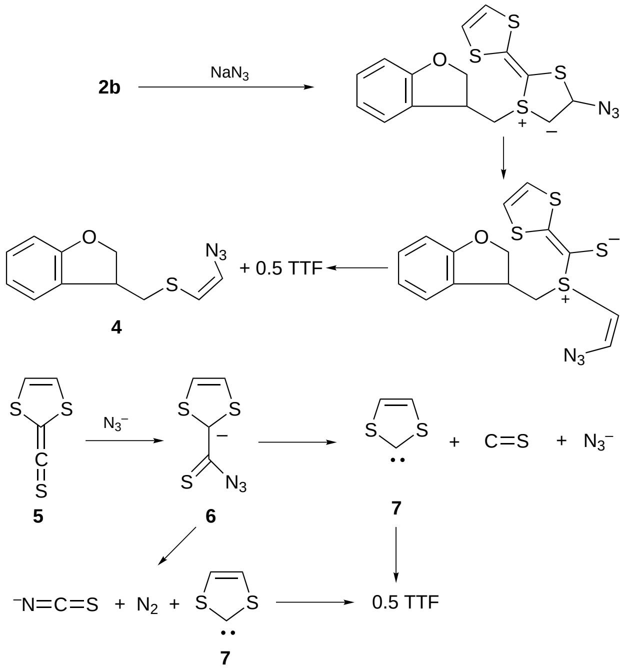
One of the goals for the future of this research is to develop catalysts with greater efficiency, *i.e.* with greater turnover numbers. To achieve this, it is necessary to develop an understanding of what processes other than substitution can occur with TTF salts. In the case of salts such as **2a**, these processes can only compete poorly with the substitution chemistry. This means that side-products are formed in very small amounts in such cases, and hence it is difficult to determine the nature of the side-reactions which ultimately limit the catalytic life of TTF.

A logical way to determine the nature of side-reactions would be to study TTF salts where S_N1 substitution reactions are inhibited. Alternative reactions observed under such conditions then provide useful information on potential side-reactions in normal radical-polar reactions. We have previously described[1] that when the TTF moiety is attached to a primary carbon, as in **2b**, no substitution was observed. It is totally reasonable that substrates such as **2b** should not undergo S_N1 substitution, and we assumed that the mildness of the nucleophiles rendered any alternative reactions too slow to observe. We now report the results of exposing primary tetrathiafulvalenium salts to various nucleophiles.



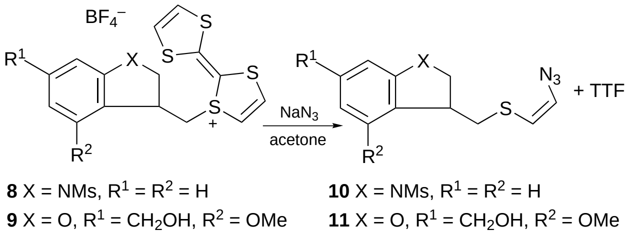
Scheme 1

The salt **2b** was subjected to attack by sodium azide in acetone (Scheme 2). The principal products from this reaction were tetrathiafulvalene (45%) and the vinyl azide **4** (46%). Although the appearance of tetrathiafulvalene initially suggested that an S_N2 substitution had occurred, this is clearly not the case. To explain the formation of these products, we propose the sequence of steps depicted in Scheme 2. The thioketene **5** has not been detected, but could suffer attack by azide, which in turn would lead to fragmentation to afford the stabilised carbene **7** together with either carbon monosulfide and azide ion or thiocyanate ion plus nitrogen gas. The carbene **7** is an established synthetic precursor of TTF in other contexts.[3]

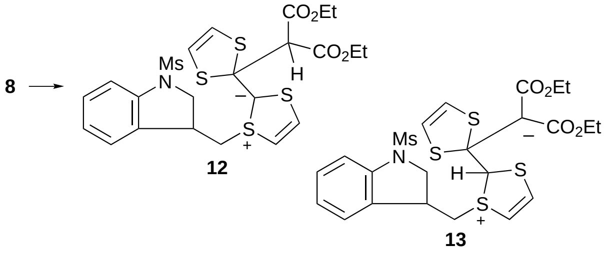


Scheme 2

To determine the generality of this process, two further primary tetrathiafulvalenium salts **8** and **9** were prepared and treated with sodium azide in acetone, producing the vinyl azides **10** (36%) and **11** (41%) respectively (Scheme 3). In both cases,



Scheme 3



Scheme 4

TTF was also produced (49 and 21%, respectively). Compound **11** was converted into its crystalline 3,5-dinitrobenzoate ester. However, attempts to produce a suitable crystal for X-ray structure determination were not successful.

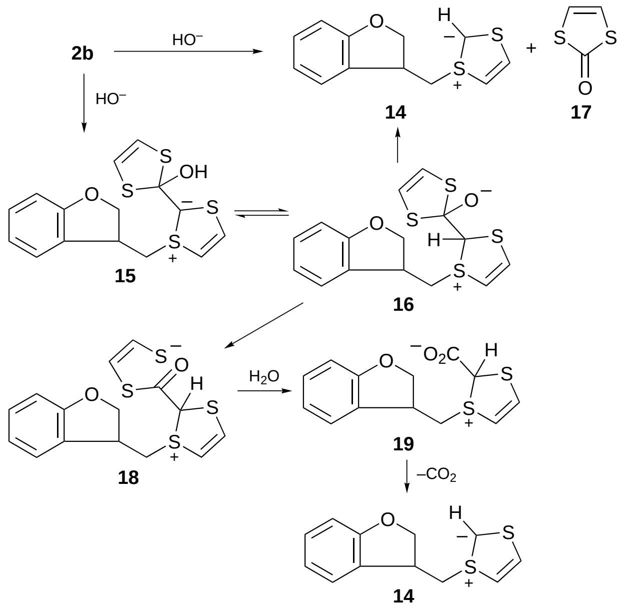
The fragmentations seen above represent a previously unseen reaction of TTF salts. However, a completely different mode of reaction was seen when **2b** was treated with the anion of diethyl malonate (Scheme 4). In this case, the product **12** (38%) resulted from reaction at the central carbon–carbon double bond of the salt. The structure **12** rather than **13** is suggested for the product, since the ^{1}H NMR spectrum exhibits a one-proton singlet at δ 3.1; this is in the expected region for a malonate proton but is considerably upfield of the expected shift for the proton in **13**. In this reaction, no attack on the peripheral double bonds of the TTF salt was observed. The reason for the complete change in selectivity for azide and malonate as nucleophiles is unknown.

Finally, the salt **2b** was treated with potassium hydroxide as base under different conditions (KOH in methanol, KOH in DMSO, KOH in acetone). In these cases, an alternative but very clean fragmentation to **14** (79% NMR yield, 66% isolated yield) was seen. Possible mechanisms for this reaction are proposed in Scheme 5. The base-sensitive dithiocarbonate **17** has not been detected, even when only 1 equiv. of base was used.

The ylide proton in **14** appeared as a singlet at δ 3.1, and this correlated with a methine carbon at δ_C 84. The chemical shift of both the carbon and the proton indicate that this structure is best viewed as an ylide *i.e.* featuring $^-$C–S$^+$ rather than a C=S π-bond. However, one interesting feature is that the ^{1}H and ^{13}C NMR spectra of **14** show no indications of the presence of diastereoisomers. This contrasts with **2b**, where signals due to diastereoisomers are clearly seen. This may indicate that inversion at the sulfonium sulfur in **14** occurs rapidly on the NMR timescale.[4]

In conclusion, primary tetrathiafulvalenium salts exhibit a rich and complex chemistry. The design of improved radical-polar crossover catalysts should take into account the observed nucleophilic attack on both the periphery and the internal alkene of these TTF salts.

These studies may also prove useful in materials chemistry.[1] A vast number of salts with intriguing electrical conductivity properties are known. These salts result from electron transfer from TTF to appropriate acceptor molecules, and hence the salts formally involve the TTF radical-cation, TTF$^{+\cdot}$. Although these



Scheme 5

cations are different from the alkylated TTF cations discussed here, it is clear that quenching of the conducting properties of these compounds could arise by attack by nucleophiles on the TTF nucleus.

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Footnote and References

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4 For rapid inversion at sulfur in a sulfur ylide, see: H. Nozaki, M. Takaku and K. Kondo, *Tetrahedron*, 1966, **22**, 2145.

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