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Reactions of Arenediazonium Salts with Diazadithiafulvalenes

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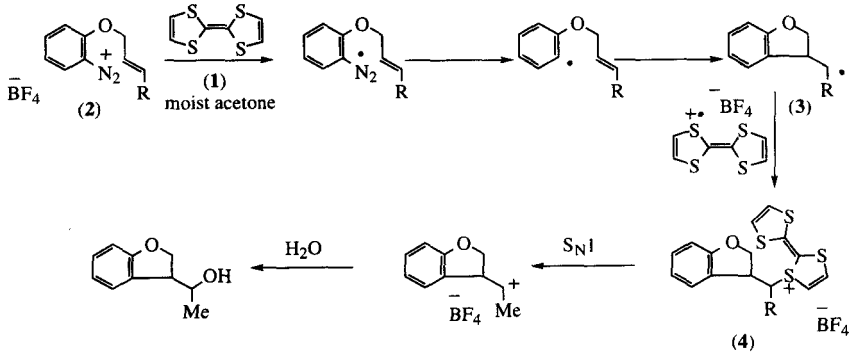
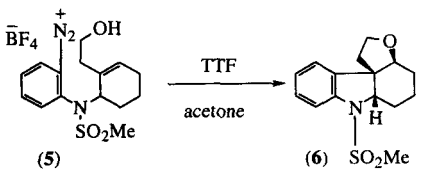
Abstract: The kinetics of coupling of carbon radicals with sulfur radical-cations in diazadithiafulvalenes is sensitive to the steric environment around sulfur. © 1997 Elsevier Science Ltd.

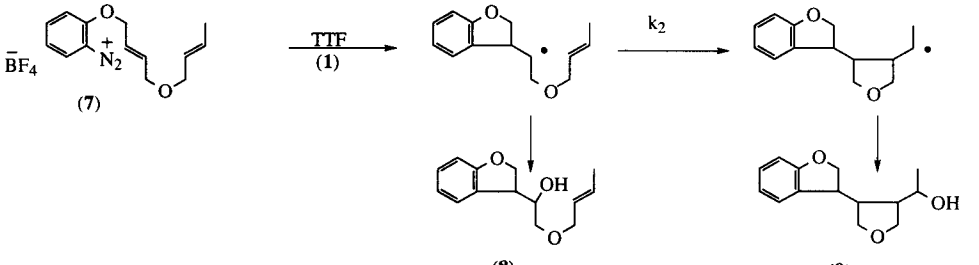
We have recently reported[1] a new chemistry utilising tetrathiafulvalene (**1**) as a catalyst which permits the ordered sequencing of radical and ionic reactions under mild conditions in a single pot, the so-called 'radical–polar crossover' reaction. The TTF transfers an electron to a diazonium cation (**2**). Nitrogen is liberated and the aryl radical so-formed cyclises to form radical (**3**) which then couples with TTF+• to form the sulfonium salt (**4**). In the final step, crossover to ionic chemistry is observed and TTF is regenerated as S_N1 substitution occurs. This chemistry has permitted the assembly of complex molecules; for example treatment of the diazonium salt (**5**) under these conditions affords[2] the tetracycle (**6**) as a single stereoisomer.

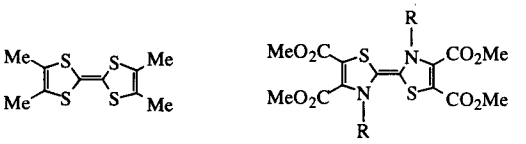




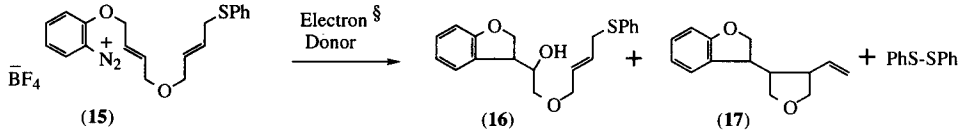
With the ground-rules now established, two important questions need to be considered: (a) Can the chemistry be extended to substrates other than arenediazonium salts? (b) Can the kinetics of interception of carbon radical intermediates by the radical cation of the donor be modulated? In this paper this second question is addressed.

Whereas quantitative kinetic studies of the radical-polar chemistry mediated by TTF have not been performed, some comparative kinetic information is available[1] from the substrates so far studied. Thus, the substrate (**7**) afforded two products when treated with TTF, monocyclised product (**8**) (41%), and bicyclised product (**9**) (15%). As the rate constant for the second cyclisation[3] can be assessed as *ca.* $5x10^6$ sec^{-1}, then, at the concentrations used, trapping with TTF+• effectively competes with cyclisations which occur at this rate. By changing from TTF+• to other radical cations which trap on sulfur, one might be able to modulate the kinetics of trapping. Decreasing the rate of trapping would allow one to perform syntheses which could incorporate slower radical cyclisations (or reactions other than cyclisations) before crossover to the ionic pathway. Ideally, a range of TTF-like catalysts would permit a broad range of rate constants for the trapping reaction.



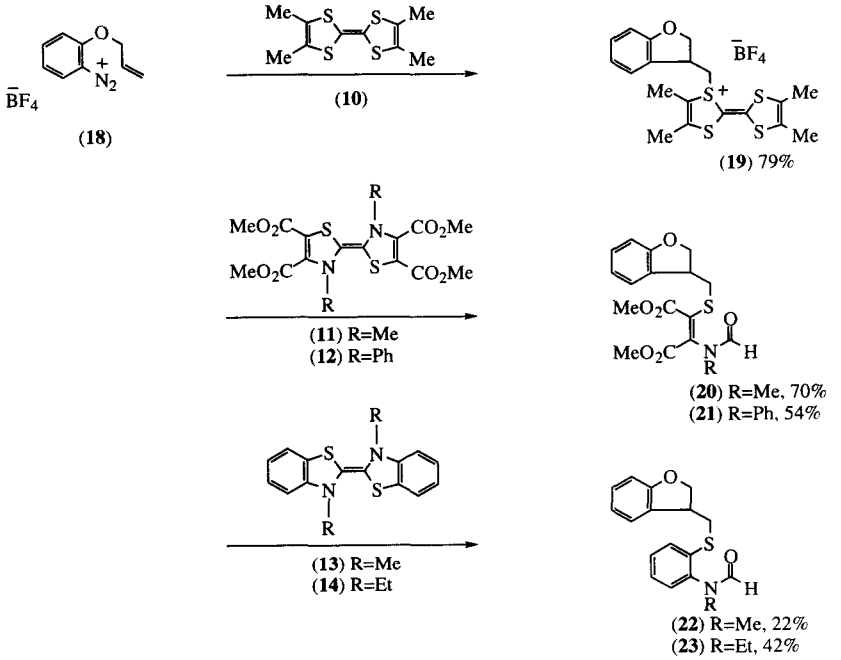


A logical way to vary the coupling rate would be to alter the steric crowding around the crucial sulfur. For these studies, five new electron donors (**10**)-(**14**) were employed. These compounds were all prepared by established routes[4-9]. The electrochemical studies previously performed guaranteed that each would be able to perform the desired reaction since all five compounds are more powerful electron donors than TTF. This is particularly noteworthy for the tetraesters (**11**) and (**12**).

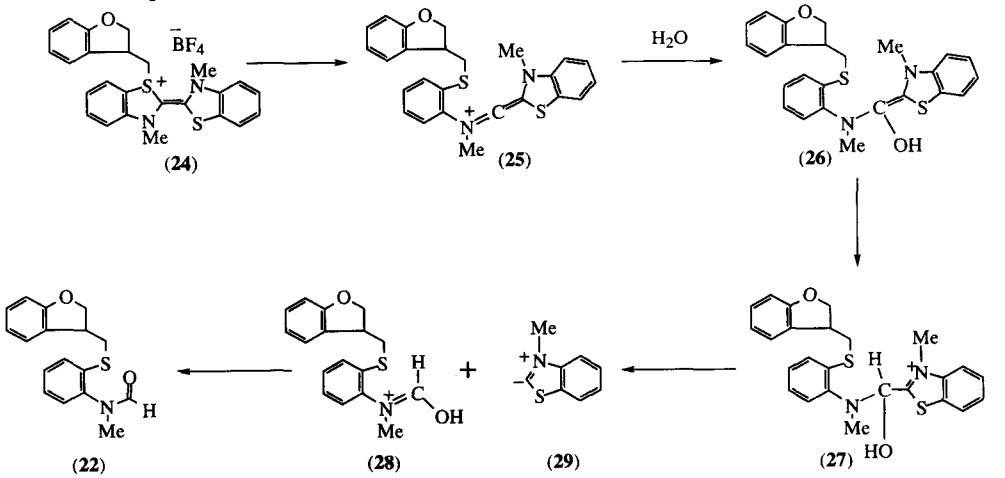


Electron Donor	(16)	(17)	PhSSPh	Electron Donor	(16)	(17)	PhSSPh
(1)	19%	48%	18%	(11)	0%	72%	31%
(10)	8%	67%	42%	(13)	0%	73%	42%

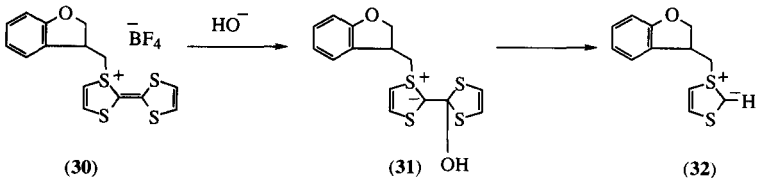
Initially substrate (**15**) was treated with electron donors (**1**), (**10**), (**11**) and (**13**). The yields of (**16**) *versus* (**17**) indicate that the radical-cation of tetramethyltetrathiafulvalene (TMTTF) (**10**) is a little slower at trapping than TTF+•, but the nitrogen heterocycles (**11**) and (**13**), which are more crowded around sulfur, permit bicyclisation to dominate completely; hence steric encumbrance of the sulfur in these compounds plays the desired rôle.



Having established the importance of steric factors, we next investigated the analogy between TTF chemistry and chemistry with these electron donors. Diazonium salt (**18**) reacted with TMTTF (**10**) to afford the expected sulfonium salt (**19**). However, on treatment with the N,S-heterocycles (**11**)-(**14**), no analogous structure was isolated or detected. In each case the isolated products (**20**)-(**23**) result from ring-opening, and we assume that the products derive from attack of water on the intermediate salts [*e.g.* (**24**)].

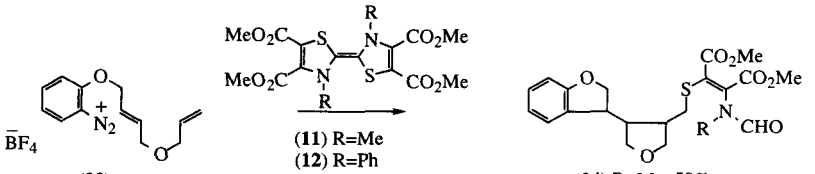


The regiochemistry of attack by water suggests that direct attack on (**24**) was not observed. Direct attack upon (**24**) should produce a sulfur ylid analogous to (**31**), the presumed intermediate in our[10] conversion of (**30**) to (**32**). We assume that the difference between the all-sulfur heterocycles and the diazadithia-counterparts is the greater ability of nitrogen to stabilise positive charge, and that this drives the formation of the ketiminium salts such as (**25**). Protonation of the resulting adduct (**26**) affording (**27**) is followed by loss of a thiazolium ylid (**29**) reminiscent of the reactions of thiamine.



(**30**) (**31**) (**32**)

A final example illustrates both the kinetic and hydrolytic results clearly. Diazonium salt (**33**) reacts with the donors (**11**) and (**12**) to afford (**34**) and (**35**) respectively. No products from trapping of carbon radicals prior to the second cyclisation were observed, and the product of ultimate carbon-radical trapping, being derived from a diazadiathia donor, undergoes facile hydrolysis and fragmentation to afford the observed products.



(**33**)

(**11**) R=Me
(**12**) R=Ph

(**34**) R=Me, 50%
(**35**) R=Ph, 55%

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§ (To facilitate internal comparison, experiments in this Table were conducted using 0.35 mmol electron donor and 0.35 mmol substrate in 8ml acetone)

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