A Novel Redox Reaction of the Disulphide Dication Salt ($R_2S^+–^+SR_2 \cdot 2X^-$) with Carbanions and Alkoxides

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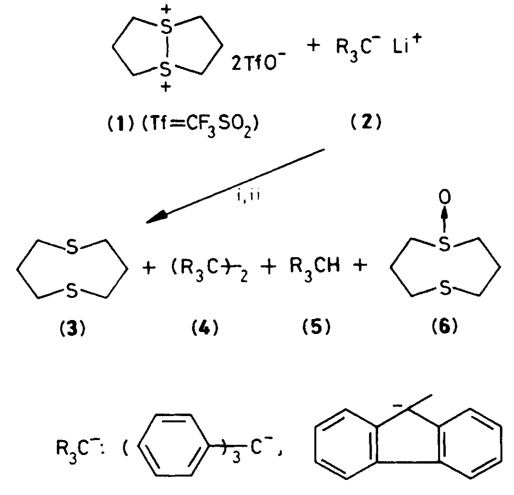
The disulphide dication salt, 1,5-dithioniabicyclo[3.3.0]octane bis(trifluoromethanesulphonate) (**1**) was reduced upon treatment with carbanions or alkoxides; it did not deprotonate.

Dications bonded by two positively charged heteroatoms have received a little attention, and investigation of their structures and reactivities is of considerable current interest.[1] Alder and co-workers reported the deprotonation of hydrazinium dication salts ($N^+–N^+$).[1a] Recently, we reported the preparation and the crystal structure of the unusually stable disulphide dication salt, 1,5-dithioniabicyclo[3.3.0]octane bis(trifluoromethanesulphonate) (**1**).[2] Surprisingly, when the disulphide dication (**1**) was treated with organolithium and Grignard reagents (RLi, RMgX) or alkoxides (RO^-), only the redox reaction took place. No hydrogen atom abstraction of (**1**) by the strong bases was observed, although normal sulphonium ion salts bearing α-protons easily undergo deprotonation to give the sulphur ylides.[3] We now report the novel redox reaction of the disulphide dication salt (**1**) with carbanions and other bases.

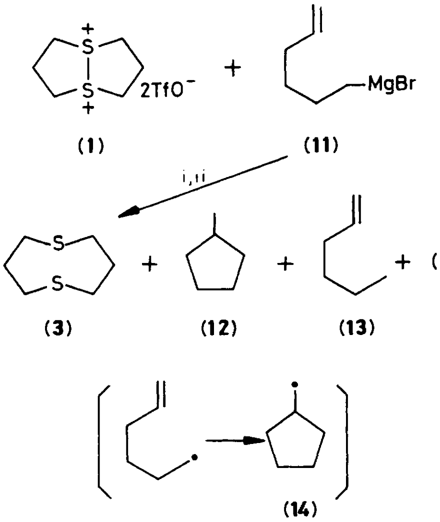
The reaction of the disulphide dication salt (**1**) (1 equiv.) with triphenylmethyl-lithium (**2a**) (1 equiv.) was carried out in anhydrous tetrahydrofuran (THF) under an Ar atmosphere at −78 °C for 3 h.† The mixture was then treated with H_2O, and after the usual work-up, the residue was chromatographed on silica gel to afford the oxidative coupling product, 1-diphenylmethylene-4-triphenylmethylcyclohexa-2,5-diene (**4a**)[4] in 31% yield, 1,5-dithiacyclo-octane (**3**) as the reduction product (40%), triphenylmethane (**5a**) (58%), and 1,5-dithiacyclooctane 1-oxide (**6**) as the hydrolysis product of (**1**) in 55% yield. Similar treatment of fluorenyl-lithium (**2b**) (1 equiv.) with dication (**1**) (1 equiv.) gave the oxidative coupling dimer, $\Delta^{9,9'}$-bifluorene (**4b**) (20%), (**3**) (42%), fluorene (**5b**) (58%), and (**6**) (46% yield). (Scheme 1).‡ Hence these carbanions (**2a**) and (**2b**) can act as one-electron donors towards the dication (**1**) to form the corresponding radicals which dimerize to produce the oxidative dimers (**4a**) and (**4b**).[4]



Scheme 1. *Reagents/conditions*: i, THF, −78 °C, Ar; ii, H_2O.

In order to verify the formation of radical intermediates in the reaction of carbanions with the dication (**1**), 9-mesitylfluorene (**7**)[5] was synthesized. When a solution of 9-mesitylfluorenyl-lithium (**8**) (1 equiv.) in anhydrous THF was added to a solution of (**1**) (1 equiv.) in anhydrous THF under an Ar atmosphere at −78 °C, the solution immediately became green. Its u.v.–visible spectrum exhibits absorptions at λ_{max} 494, 464, 338, 329, 289, and 280 nm which are consistent with the spectrum previously reported for the 9-mesitylfluorenyl radical (**9**).[5]§ This phenomenon shows that 9-mesitylfluorenide (**8**) was oxidized to its radical (**9**).¶ Treatment of this solution with H_2O gave the sulphide (**3**) as the reduction product (50%) together with (**6**) (20%), (**7**) (62%), and 9-hydroxy-9-mesitylfluorene (**10**) (9%). This result clearly indicates that the reaction of the dication (**1**) with the carbanion (**8**) proceeds *via* electron transfer as the major pathway.

Interestingly, when the Grignard reagent, hex-5-enylmagnesium bromide (**11**) and the dication (**1**) were allowed to



Scheme 2. *Reagents/conditions*: i, THF, room temp., Ar; ii, H_2O.

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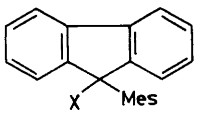
† The dication (**1**) could not be dissolved completely in anhydrous THF. However, when the carbanions were added to the solution of (**1**), the solution became homogeneous.

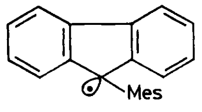
‡ The products reported herein were identified by m.p., i.r. and n.m.r. spectroscopy, and elemental analysis. The products (**5a**), (**5b**), (**7**), and (**13**) were mainly formed when the reaction mixture was treated with H_2O.

§ The corresponding radical cation derived from the dication (**1**) could not be characterized, since its absorption overlaps at 420 nm in MeCN.[1c]

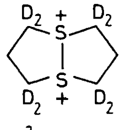
¶ The free radical (**9**) does not dimerize owing to steric hindrance.[5]



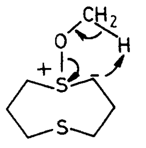
(**7**) X = H
(**8**) X = Li
(**10**) X = OH



(**9**)



$[^2H_8]$-(**1**)



(**15**)

Mes = mesityl.

react in equimolar amounts in anhydrous THF under an Ar atmosphere at room temperature for 1 h, the cyclic product, 1-methylcyclopentane (**12**) (26%), sulphide (**3**) as the reduction product (39%), hex-1-ene (**13**) (40%), and (**6**) (53%) were obtained (Scheme 2).||

The disulphide dication (**1**) could also be reduced to the sulphide (**3**) by sodium methoxide (NaOMe) in anhydrous THF. Although the mechanism of this unusual reaction can be rationally explained in terms of an electron-transfer reaction, an alternative process involving the intramolecular fragmentation[6] of the intermediate sulphur ylide such as (**15**) cannot be excluded. Accordingly, the 2,2,4,4,6,6,8,8-octadeuteriated disulphide dication $[^2H_8]$-(**1**)[7] was treated with NaOMe. However, no H–D exchange was observed in the sulphide (**3**) at all after the reaction. This result demonstrates that the mechanism involving the intermediate formation of (**15**) can be ruled out. Similarly, other bases such as KOBu^t, LiBu^t, and LiNPr$^i_2$ also act as reductants towards (**1**).

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|| Compound (**11**) has proven to be useful for detecting radical intermediates because of the cyclization of the hex-5-enyl radical to the cyclopentyl methyl radical (**14**); see a review in ref. 4. However, a referee pointed out that there have been recent doubts about its proof.

References

1 (a) R. W. Alder, R. B. Sessions, J. O. Gmünder, and C. A. Grob, *J. Chem. Soc., Perkin Trans.* 2, 1984, 411; (b) S. F. Nelsen and J. T. Ippoliti, *J. Org. Chem.*, 1986, **51**, 3169; (c) W. K. Musker, T. L. Wolford, and P. B. Roush, *J. Am. Chem. Soc.*, 1978, **100**, 6416; (d) H. Fujihara, J.-J. Chiu, and N. Furukawa, *ibid.*, 1988, **110**, 1280.

2 (a) H. Fujihara, R. Akaishi, and N. Furukawa, *J. Chem. Soc., Chem. Commun.*, 1987, 930; (b) F. Iwasaki, N. Toyoda, R. Akaishi, H. Fujihara, and N. Furukawa, *Bull. Chem. Soc. Jpn.*, 1988, **61**, 2563.

3 A. W. Johnson, 'Ylid Chemistry,' Academic Press, New York, 1966, Ch. 9.

4 Carbanions (**2a**) and (**2b**) are known to transfer electrons to suitable acceptors resulting in the formation of oxidative dimers; see: R. D. Guthrie, in 'Comprehensive Carbanion Chemistry,' Part A, eds. E. Buncel and T. Durst, Elsevier, Amsterdam, 1980, Ch. 5.

5 E. A. Chandross and C. F. Sheley, Jr., *J. Am. Chem. Soc.*, 1968, **90**, 4345. The e.s.r. spectrum of the radical (**9**) is complex.

6 C. R. Johnson and W. G. Phillips, *J. Org. Chem.*, 1967, **32**, 1926.

7 The octadeuteriated dication $[^2H_8]$-(**1**) was obtained by reaction of $(CF_3SO_2)_2O$ with the corresponding octadeuteriated monosulphoxide (N. Furukawa, A. Kawada, T. Kawai, and H. Fujihara, *J. Chem. Soc., Chem. Commun.*, 1985, 1266).