

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.

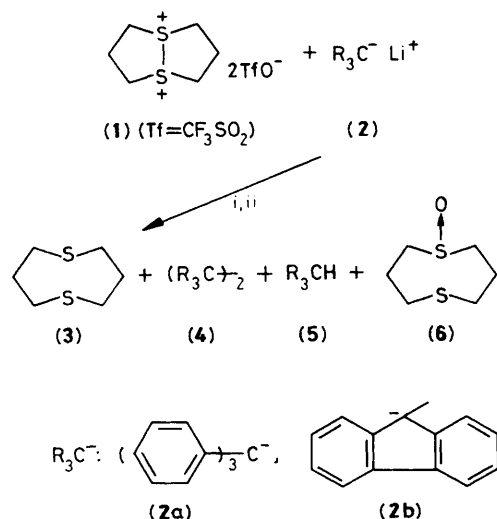
Dications bonded by two positively charged heteroatoms have received a little attention, and investigation of their structures and reactivities is of considerable current interest.¹ Alder and co-workers reported the deprotonation of hydrazinium dication salts ($N^{+}-N^{+}$).^{1a} Recently, we reported 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 $-78^{\circ}C$ 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-dithiacyclo-octane 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

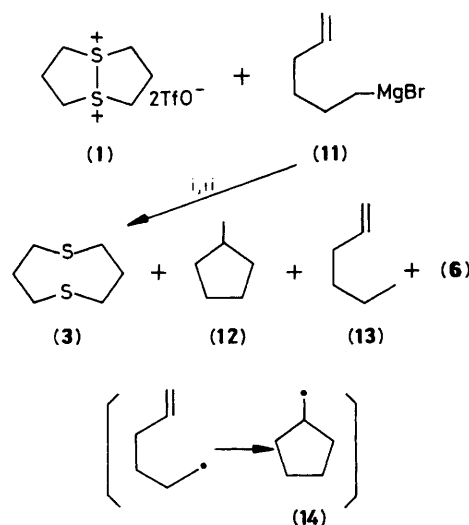
In order to verify the formation of radical intermediates in the reaction of carbanions with the dication (**1**), 9-mesitylfluorene (**7**) was synthesized. When a solution of 9-mesitylfluorenyl-lithium (**8**) (1 equiv.) in anhydrous THF was added to a solution of (**1**) (1 equiv.) in anhydrous THF under an Ar atmosphere at $-78^{\circ}C$, 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-mesitylfluorenyl-lithium (**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 1. Reagents/conditions: i, THF, $-78^{\circ}C$, Ar; ii, H_2O .

[†] 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.

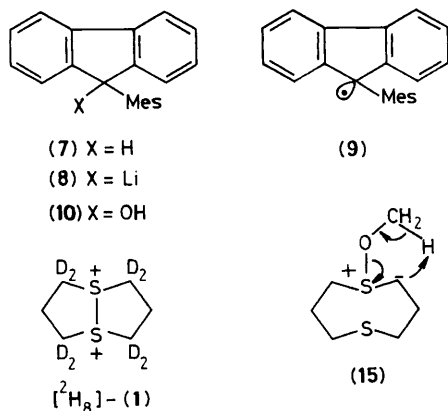


Scheme 2. Reagents/conditions: i, THF, room temp., Ar; ii, H_2O .

[‡] 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



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,

|| 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.

an alternative process involving the intramolecular fragmentation⁶ of the intermediate sulphur ylide such as (**15**) cannot be excluded. Accordingly, the 2,2,4,4,6,6,8,8-octadeuteriated disulphide dication [2H₈]-(**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 LiNPri₂ also act as reductants towards (**1**).

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