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Electrochemically Induced Intramolecular Cyclization of 1,2-bis(1,4-dithiafulven-6-yl)benzenes

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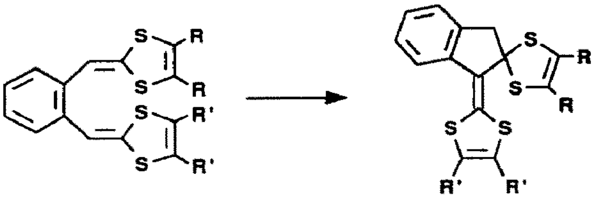
Abstract : *Potentiostatic oxidation of the title compounds 1 induces their intramolecular cyclization in 2. A mechanism involving a protonic catalysis as determining step is proposed.*

The molecular design of new π-donors of the TTF series in view of achieving the improvement of the (super)conducting properties of the resulting cation radical salts together with a better understanding of the structural variables which control these properties has attracted strong interest.[1] However, besides the accomplishment of such objectives, the manipulation of the molecular structure of the TTF precursor can considerably affect the fate of the cationic species resulting from its oxidation and hence the nature of the resulting product.

We have recently shown that ortho-bis(1,4-dithiafulven-6-yl)benzenes **1** can be readily converted with good yields into type **2** compounds by acid-catalyzed intramolecular cyclization.[2] Such compounds constitute interesting starting materials for the synthesis of new π-donors.[3]



1 **2**

aa: R = R' = CO_2Me
ab: R - R = $(CH{=}CH)_2$, R' = CO_2Me
bb: R- R = R'- R' = $(CH{=}CH)_2$

As a further step we report here an analysis of the electrochemical behavior of compounds **1**. We show that the intramolecular cyclization can be electrochemically induced with complete conversion. This process is interpreted by a mechanism involving as determining step, the catalysis of the cyclization by the protons released during the electrolysis of **1**.

Cyclic voltammetry (CV) and preparative electrolyses were performed in a three-compartment cell equipped with a 1.5 mm^2 area Pt anode for CV and a 0.75 cm^2 one for preparative electrolyses. All potentials refer to the saturated calomel reference electrode (SCE). The electrolytic medium involved 1.2 10^{-3} M substrate and 0.1 M Bu_4NPF_6. The solvent (CH_2Cl_2, SDS spectrosol grade) was purified by filtration on basic Al_2O_3. Solutions were degassed by N_2 bubbling and experiments were run under an N_2 atmosphere.

Fig. 1a shows as a typical example the CV of **1bb**. Whatever scan rate (0.10 to 10 V s^{-1}) an irreversible oxidation peak is observed at 0.84 V (Epa_1). After exhaustive potentiostatic electrolysis at Epa_1 the initial anodic peak disappears while a new oxidation wave occurs at 1.00 V which exactly matches that of authentic compound **2bb** (Fig. 1b).

Fig. 2 shows the variation of the logarithm of the oxidation current (I_{ox}) corresponding to the potentiostatic electrolysis of **1bb** at Epa_1. Contrary to what could be expected, the logI_{ox}(t) curve doest not fit a linear decay but exhibits a sharp current decrease, indicative of fast consumption of substrate.[4,5] Coulometric measurements show that the number faradays per mol (*n*) required to achieve complete conversion in **2bb** amounts only to 0.05 (Table 1). Similar results are obtained with **1aa** and **1ab**,[6] the latter being converted in **2ab** whose structure,[7] and in particular the position of R and R', was fully ascertained by X-ray diffraction.[8] A preparative electrolysis was carried out with the most soluble compound (**1aa**) and **2aa** isolated in 73% yield after recrystallization.

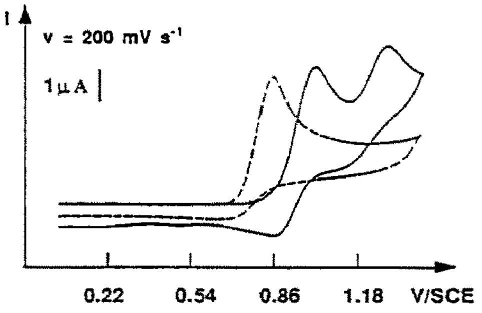


Figure 1: CV of (a)(-----) **1bb**, (b)(———)**2bb**

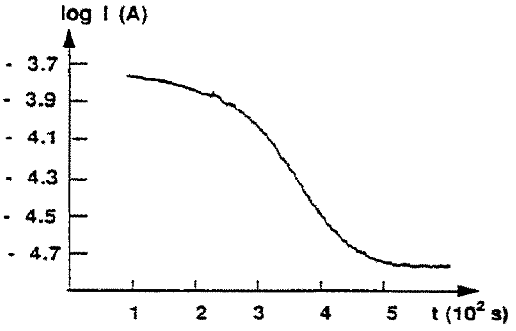


Figure 2 : logI_{ox} = f(t) for **1bb**

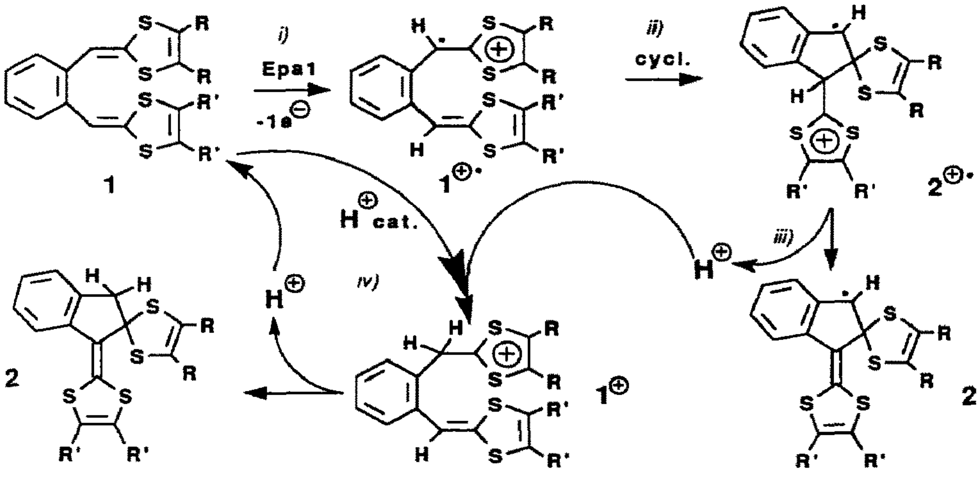
These results are consistent with a fast chemical reaction following the initial electrochemical step. Furthermore, the fast decrease of I_{OX} and the surprising low *n* values strongly suggest that the overall cyclization process involves a catalytic step.

Table 1

		Epa_1 (V/SCE)	*n* (F mol^{-1})
1aa	R = R' = CO_2Me	1.00	0.14
1ab	R' = CO_2Me, R-R = $(CH{=}CH)_2$	0.90	0.04
1bb	R-R = R'-R' = $(CH{=}CH)_2$	0.84	0.05

Our previous results on the acid-catalyzed cyclization of compounds **1**[2] led us to suspect that protons could be also responsible for the present catalytic step. This hypothesis is supported by the inhibited conversion of **1** when electrooxidized in the presence of a non nucleophilic base such as 2,4,6-collidine. On the other hand, the higher *n* value obtained with **1aa** agrees with the slower conversion rate previously observed in the case of acid-catalyzed cyclization.[2]

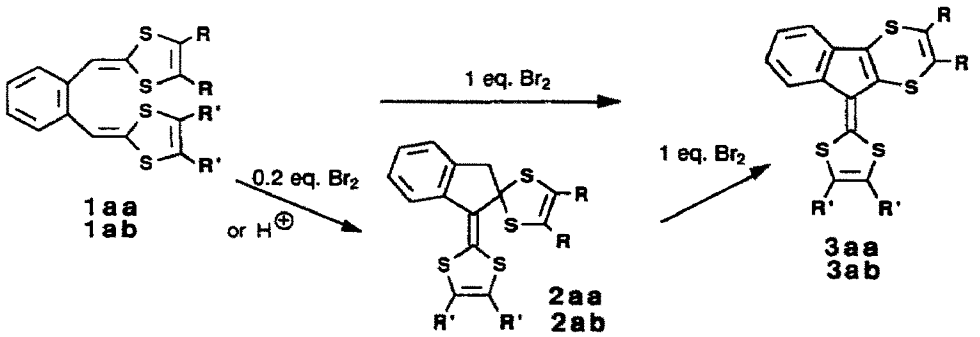
The overall process can thus be explained by an ECC mechanism [9] involving an electrochemical step (E) and two subsequent chemical reactions (C) according to the following pathway (Scheme I): *i)* one-electron oxidation of **1** in $\mathbf{1}^{+\cdot}$, *ii)* intramolecular cyclization of $\mathbf{1}^{+\cdot}$ in $\mathbf{2}^{+\cdot}$, *iii)* decomposition of $\mathbf{2}^{+\cdot}$ in $\mathbf{2}^{\cdot}$ with release of H^+ and *iv)* proton-catalyzed conversion of **1** in **2** via $\mathbf{1}^{+}$ according to the previously reported mechanism.[2]



Scheme 1

Preliminary UV-vis. studies performed in the presence of Na_2CO_3 suggest that $\mathbf{2}^{\cdot}$ *i.e.* the radical resulting from the deprotonation of $\mathbf{2}^{+\cdot}$ is subject to further evolution, leading to the formation of other compounds whose identification is presently under investigation.

Chemical oxidation of **1aa** by Br_2 with formation of another cyclized compound (**3aa**) has already been reported and a mechanism involving cyclization of the initially formed cation radical $\mathbf{1aa}^{+\cdot}$ proposed.[10] A detailed analysis of the effects of Br_2 on **1aa** allowed us to confirm the formation of **3aa** by reaction of **1aa** with 1 eq. Br_2 in CCl_4.



Scheme II

However, reaction of **1aa** with only 0.2 eq. Br_2 leads to the exclusive formation of **2aa** whereas **3aa** is produced by further oxidation with an excess of Br_2 (Scheme II). Similary, **3ab**[11] can be selectively obtained from either **1ab** or **2ab**. These last results clearly show that **2** in fact represents an intermediate compound between **1** and **3**.

In the specific case of $\mathbf{1ab}^{+\cdot}$ it seems reasonable to assume that the mechanism involves merely the more stable cation radical with the positive charge on the dithiolium moiety bearing the $(CH{=}CH)_2$ substituent and not on that with the electron-withdrawing CO_2Me groups.

Preliminary investigations on other vicinal dithiafulvenyl arenes or heteroarenes indicate that this reaction seems to be general and the corresponding results will be presented in the full paper.

References and notes

(1) The Physics and Chemistry of Organic Superconductors, ed.Saito, G.; Kagoshima, S. Springer-Verlag, London (1990). b) Bryce, M.R. *Chem. Soc. Rev.* **1991**, *20*, 355.

(2) a) Benhamed-Gasmi, A.S.; Frère, P.; Belyasmine, A.; Melik, K.M.A.; Hursthouse, M.B.; Moore, A.J.; Bryce, M.R.; Jubault, M.; Gorgues, A. *Tetrahedron Lett.* **1993**, *34*, 2131-2134. b) Frère, P. *New π-donors from Ethylenic Tetrathiafulvalene Analogs*, PhD Thesis, University of Angers 1993.

(3) a) By hydrolysis of 2 [(a)] and subsequent olefination by Akiba's reagents [(b)]; (a) Doad, G.J.S. *J. Chem. Res. (S)* **1987**, 370. (b) Akiba, K.; Ishikawa, K.; Inamoto, N. *Bull. Chem. Soc. Japan* **1978**, *51*, 2674

(4) In the absence of applied potential compounds **1** are stable in the electrolytic medium.

(5) This reaction was also monitored by UV-vis spectroscopy and HPLC. UV-Vis, λmax (nm) (logε): **1bb** 329 (4.21), 368 (4.25); **2bb** 362 (4.20), 375 (4.23). HPLC, column C18, reverse phase, MeOH, UV-Vis detn. 370 nm.

(6) Prepared according to (1) by a one pot bis-Wittig olefination of orthophthaldehyde, by reacting first the $(CH{=}CH)_2$ substituted P-ylid (Et_3N, MeCN, rt, 15 min., and then 1.5 eq. of the CO_2Me substituted P-ylid (12 hrs), 64% overall yield after crystn. from THF-EtOH. Orange crystals, m.p. 127°C (dec.) satisfactory m.s. and elemental analysis. ^1H nmr ($CDCl_3$): 7.50 and 7.33(2d, 2H, arom.), 7.20 (m, 4H, arom.), 7.09 (m 2H, arom), 6.48 and 6.47 (2s, 2H, H-C=), 3.85 and 3.80 (2s, 6H, CO_2Me).

7) Orange crystals, m.p. 174°C, satisfactory m.s. and elemental analysis. ^1H nmr ($CDCl_3$): 7.58 (d, 1H, arom.), 7.29 (s, 1H, arom.), 7.29 (m, 4H, arom.), 7.10 (m, 2H, arom), 4.18 (s, 2H, CH_2), 3.93 and 3.89 (2s, 6H, CO_2Me).

(8) Crystal data for **2ab** : $C_{22}H_{16}O_4S_4$, Mr 472.63; monoclinic, space group $P2_1/c$ (Z=4); a= 8.494(7)Å, b= 23.56(4)Å, c= 10.47(2)Å, $\beta = 93.02(9)$; μ (MoKα) = 4.61 cm^{-1}; F(000) = 976; data collected at 120 K using graphite monochromated MoKα radiation ($\lambda = 0.7173$ Å) and an Enraf- Nonius CAD4-F diffractometer. The crystal structure was solved by direct methods and refined by full-matrix least-squares techniques, 3179 unique reflections (Rint = 0.068) of which 1575 with $I > 3\sigma(I)$ were used. R = 0.082; Rw = 0.074.

(9) Tallec, A. *Electrochimie Organique*, Masson, Paris, 1985, p. 97.

(10) Lakshmikanthan, M.V.; Cava, M.P.; Caroll, P.J. *J. Org. Chem.* **1984**, *49*, 726-728.

(11) Red powder, m.p. 210°C (dec.); satisfactory m.s. and elemental analysis. ^1H nmr ($CDCl_3$): 7.55-7.20 (m, 8H, arom.), 3.96 and 3.92 (2s, 6H, CO_2Me).

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