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Acid Mediated Intramolecular Cyclization of π-Donors Bearing Two Vicinal "cis"-Branched, 1,4-Dithiafulven-6-yl Substituents on a C=C Bond

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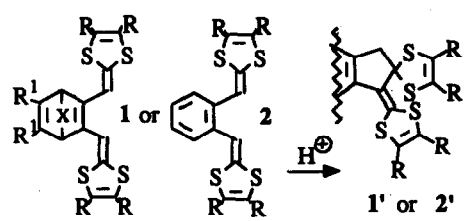
Abstract : *Cis-ethylenic analogues 1 and ortho-benzenic analogues 2 of TTF undergo a rapid acid mediated intramolecular cyclization into the corresponding cycloisomers 1' and 2' whose structures are confirmed by X-ray diffraction; as shown by cyclic voltammetry, compounds 1 may act as convenient precursors of organic metals.*

Modifications of the tetrathiafulvalene (TTF) framework[1] are still being intensively studied in search for new molecular conductors and superconductors.[2,3] Most of them consist of increasing the dimensionality of the corresponding radical cation salts (RCSs) in order to avoid the breakdown of their electroconductive properties at low temperature, due to the arising of crystalline transitions (Peierls distorsions) when these materials possess a pronounced monodimensional character. One modification involves replacement of the central ethylenic linkage of TTF by larger conjugated spacers,[4-8] leading to highly extended analogues of TTF that may favour intra- and inter-chains contacts between the new donors, due to the lowering of their charge density and an increase of π-interactions. Moreover, this spatial extension should decrease the coulombic repulsions in the di- (or poly-) cationic states of the donors.

In this context, we have developed the study of some TTF vinylogues **1** in which two vicinal 1,4-dithiafulven-6-yl substituents are "cis"-linked on a C=C bond.[9] We report here that such new compounds, as well as the parent *ortho*-disubstituted benzenic TTF analogues **2**[5,10] undergo an easy acid mediated intramolecular cyclization into **1'** and **2'** (Scheme 1).



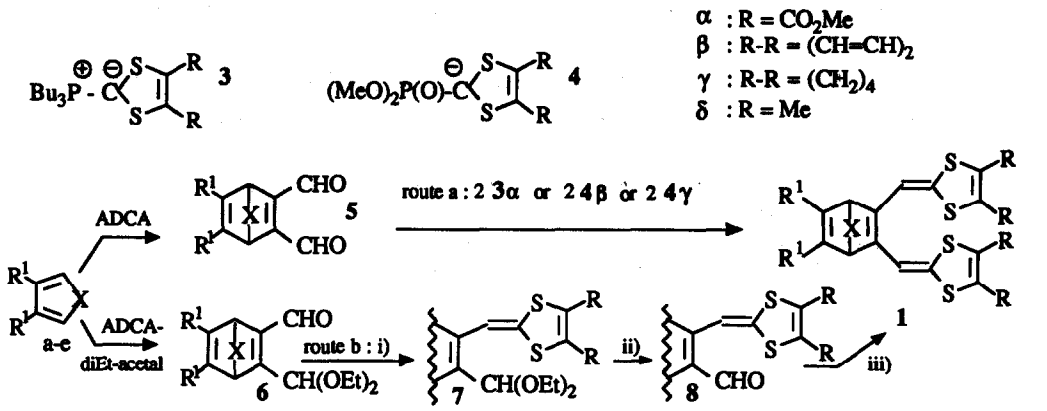
Scheme 1

Preparation of **1** and **2** (*)

As previously described in the benzenic series,[5] the general synthesis involves bis-Wittig(-Horner) olefinations of the corresponding dialdehydes with the P-reagents **3** or **4** bearing the 1,3-dithiol-2-ylidene moiety. Experimental conditions depended mainly on the nature of the R substituents. Thus for **3α**, an equilibrated deprotonation of the corresponding phosphonium tetrafluoroborate with Et_3N (20°C, acetonitrile) was used, whereas for all other reagents, a quantitative deprotonation with *n*-BuLi (-80°C, THF) was required. With **4γ**, good yields could only be obtained using the unconventional procedure we recently reported,[11] by

dropping *n*-BuLi into a THF solution of the corresponding phosphonate and dialdehyde at 0-10°C.

For the "cis"-ethylenic series, the starting materials were the Diels-Alder adducts **5** or **6** derived from acetylenedicarbaldehyde (ADCA) or its mono-di-Et-acetal.[12] Thus compounds **1** could be obtained in one or three steps (routes a and b, Scheme 2). In all cases, the target compounds **1** (Table 1) were isolated from the mixture by precipitation with methanol and crystallization.



i) 4β, THF removed *in vacuo*, CH_2Cl_2 dilution, washing with water, drying over Na_2SO_4, **7** were characterized and submitted to ii) filtration on SiO_2 (CH_2Cl_2) on which they soon hydrolyse into **8**, iii) 4β, THF removed *in vacuo*, addition of MeOH.

Scheme 2

Table 1 : Preparation of **1** via route a or b (Scheme 2)

a-e	R^1 or R^1-R^1	X	1	route	% yield	mp°C	(solvent)
a cyclohexadiene	H	CH_2-CH_2	1aα	(a)	70	133 dec.	$CHCl_3$-MeOH
"	"	"	1aβ	(b)	(90,71,74)[ii]	160 dec.	MeOH
"	"	"	1aγ	(a[i])	56	174 dec.	MeOH
b 6,6-diPh-fulvene	H	CPh_2	1bα	(a)	73	210	Toluene-pentane
c anthracene	(CH=CH)2	*o*-phenylene	1cα	(a)	75	110	CH_2Cl_2-MeOH
d butadiene	H	2H	1dβ	(b)	(93,61,54)[ii]	152-4	acetonitrile
e 2,3-diMe-butadiene	Me	2H	1eβ	(b)	(93,70,51)[ii]	210-2	THF

[i] unconventional procedure, see text; [ii] the three values are related to steps i, ii and iii of route b in Scheme 2.

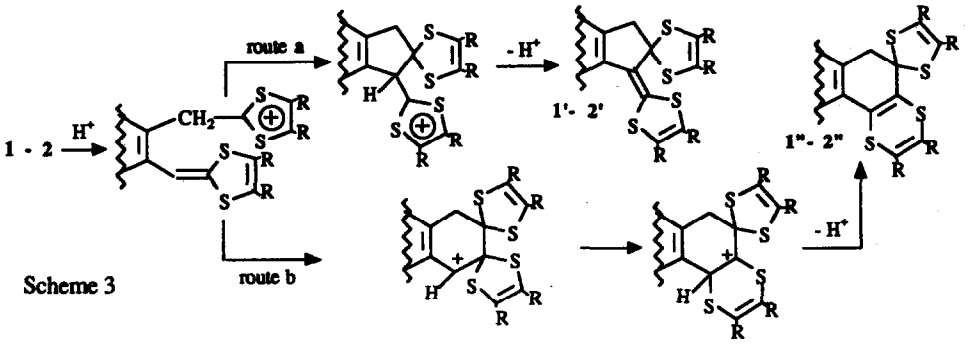
For derivatives **2**, *ortho*-phthalaldehyde was used as the starting material, the choice of the experimental conditions being also dependent upon the nature of R : Et_3N, r.t., for 3α (2α,[5,10a] 90% yield), *n*-BuLi at 0-10°C (see above the unconventional procedure) for 4β (2β,[5] 70% yield) and 4γ (2γ, 59% yield) and *n*-BuLi at -78°C for 4δ (2δ, 75% yield), all compounds **2** being also precipitated from the reaction mixture with MeOH.

Intramolecular cyclizations of **1** and **2** into **1'** and **2'**(*)

Compounds **1** and **2** are slowly converted into **1'** and **2'** on standing in chloroform solution or by chromatography over silicagel, the reaction being easily monitored by ^1H nmr spectroscopy. For example, for compound 1aβ in $CDCl_3$ (δ in ppm), the singlet at 6.10 (2C<u>H</u>=CS_2) is gradually replaced by a singlet at 3.60 (CH_2), whereas the broad singlet at 4.10 (2H, equivalent bridgeheads) is split into two multiplets at 4.00 and

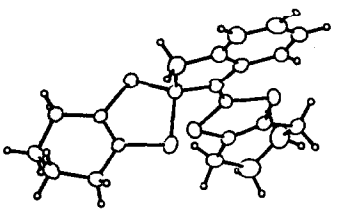
4.50 (1H and 1H, unequivalent bridgeheads). Similar observations are found in the benzenic series during the conversion of 2α–δ into 2'α–δ.

The role of protons is clearly shown by the absence of cyclisation in acid-free solvents [e.g. after addition of a base] and, in contrast, by the dramatic increase of the cyclization rate in presence of acids such as HCl, HCO_2H, SiO_2-H_2SO_4. Since the stronger the electron-releasing effect of R, the greater the cyclization rate [2γ>2β>2α], a mechanism involving a protonation of a $CH{=}CS_2$ as the rate determining step, followed by an internal 1,5-addition [route a, Scheme 3], can be anticipated.



Scheme 3

An alternative mechanism (route b) involving a possible, but unlikely 1,6-intramolecular addition followed by a S-C 1,2-shift[10b] could also yield structures 1"- 2". ^1H and ^{13}C nmr spectra could not distinguish between the two possible isomers.[13] X-ray diffraction analysis on a single crystal of 2'γ proved the structures to be 1'- 2' (Figure 1).[14]



X-Ray molecular structure of 2'γ

Figure 1

π-donating ability

Likewise their trans-ethylenic analogues,[6] compounds 1 can be regarded as convenient precursors of synthetic metals since their cyclovoltammograms (CH_2Cl_2) exhibit one 2e⁻ reversible oxidation peak. The coalescence of both 1e⁻ peaks results from a decrease of the coulombic repulsion in 1^{++} [e.g. 1aγ, see (*)]. Such a behaviour is in sharp contrast with that of compounds 2 whose oxidation is irreversible.[5] This difference can be explained by comparing the canonical forms of the oxidized states of 1 and 2, the latter, only, lossing their aromatic character.[4]

Conclusion

Although the acid mediated internal cyclization of 1 and 2 is of obvious synthetic interest, i.e. the access to unprecedented 1' and 2', this process constitutes a severe drawback for the preparation of the RCSs of 1. Consequently, the synthesis of such materials through chemical or electrochemical oxidation of 1 must be carried out under rigorously proton-free conditions; related results will be soon presented.[10c,11b]

Acknowledgments :

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(9) For another preceding example of cis-blocked ethylenic analog of TTF, see Sato, M.; Gonnella, N.C.; Cava, M.P. *J. Org. Chem.*, 1979, 44, 930-934.
(10) a) Lakshmikantham M.V.; Cava M.P.; Caroll P.J. *J. Org. Chem.*, 1984, 49, 726-728; b) in this paper, the conversion of 2α into a tetracyclic derivative through bromine oxidation is reported; among the putative mechanistic steps, such a C-S 1,2-shift is proposed; c) our preliminary results of chemical and electrochemical oxidations of 2α, which finally lead to the tetracyclic derivative invoked above, clearly show that 2'α is an intermediate in the bromine oxidation of 2α (see ref.11b).
(11) a) Benahmed-Gasmi, A.S.; Frère, P.; Garrigues, B.; Gorgues, A.; Jubault, M. *Tetrahedron Lett.* 1992, 43, 6457-6460; b) Frère, P.; Thèse de Doctorat, Angers, Jan. 13th, 1993.
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(13) We thank Dr I. Johannsen who suggested structures 1''- 2''.
(14) Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Cristallographic Data Centre.
(*) All new compounds gave satisfactory analytical data. We thank the CNRS for elemental analyses and the CRMPO (Rennes) for m.s. Selected examples :

1aγ, orange powder, m.p.174-8°C (dec.); m.s.($C_{24}H_{26}S_4$) calcd 442.09173, found 442.0925 and (M-C_2H_4) calcd 414.06043, found 414.0625; ^{1}H nmr (CS_2+C_6D_6), 6.22 (m, 2H, CH=CH), 5.86 (s, 2H, CH=CS_2), 3.89 (s wide, 2H, bridge head), 2.14 (m, 8H, CH_2-CS=), 1.72 (m, 8H, CH_2CH_2), 1.27 (m, 4H, CH_2CH_2 bridge); cyclic voltam. (CH_2Cl_2, Bu_4NPF_6, 0.1M, scan rate 0.2 V.s^{-1}) 1 reversible peak at 0.21 V.SCE.

1'aγ, yellow powder, m.p.151°C (dec.); m.s.($C_{24}H_{26}S_4$), calcd for (M-C_2H_4) 414.06043, found 414.0626; ^{1}H nmr ($CDCl_3$), 6.33 (m, 2H, CH=CH), 4.33 (m, 1H, bridge head), 3.47 (m, 1H, bridge head), 3.46 and 3.50 (AB system, very close to A_2, 2H, ^{2}J=18.5 Hz, CH_2CS_2), 2.17-2.30 (m, 8H, CH_2-CS=), 1.74 (m, 8H, CH_2CH_2), 1.37 (m, 4H, CH_2CH_2 bridge).

2γ, orange needles, m.p.164°C; m.s.($C_{22}H_{22}S_4$) calcd 414.06043, found 414.0625; anal. calcd (found) C 63.72 (63.53), H 5.34 (5.31), S 30.93 (30.02); ^{1}H nmr (CS_2+C_6D_6) 7.26 and 6.98 (2m, 4H, arom.), 6.26 (s, 2H, CH=CS_2), 2.16 (m, 8H, CH_2-CS=), 1.71 (m, 8H, CH_2-CH_2); ^{13}C nmr (CS_2+ C_6D_6) 126.20 and 126.38 (CH arom.), 134.92 (C arom.), 110.32 (CH=CS_2), 136.71 (CS_2), 123.98 and 124.2 (SC=CS), 26.00 and 26.08 (CH_2-CS=), 23.45 and 23.50 (CH_2CH_2); cyclic voltam. (THF, Bu_4NPF_6 0.1M, scan rate 0.2 V.s^{-1}), 1 irreversible peak at 0.69V.SCE.

2'γ, orange plates from MeOH, m.p. 170°C; m.s. ($C_{22}H_{22}S_4$) calcd 414.06043, found 414.0606, anal. calcd (found) C 63.72 (63.52), H 5.34 (5.17), S 30.93 (30.67); ^{1}H nmr ($CDCl_3$) 7.52, 7.28 and 7.12 (3m, 4H, arom.), 4.06 (s, 2H, CH_2CS_2), 2.43 (m, 4H, SCCH$_2$), 2.25 (m, 4H, SCCH$_2$), 1.80 (m, 8H, CH_2CH_2); ^{13}C nmr (C_6D_6+ CS_2) 121.98, 122.88, 123.80 and 125.57 (CH arom.),139.40, 135.54, 127.82, 127.07, 124.08 and 140.02 (all quatern. sp^{2}C), 71.77 (SCS), 58.86 (CH_2CS_2), 25.95 and 25.07 (CH_2CS=), 22.87 and 22.55 (CH_2CH_2).

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