Tetrahedron Letters, Vol. 34, No. 21, pp. 3449-3452, 1993
Printed in Great Britain

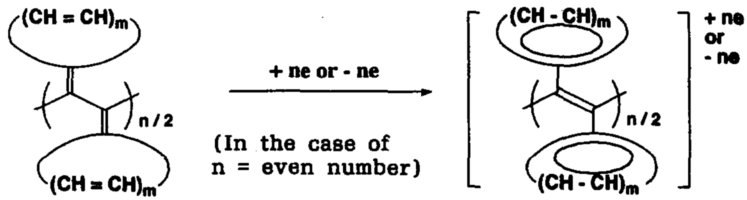
0040-4039/93 $6.00 + .00
Pergamon Press Ltd

Synthesis and Properties of Oligo-6-(2-thienyl)pentafulvenes

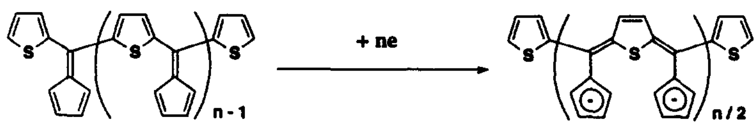
Takeshi Kawase, Hiroyuki Kurata, Tatsuya Morikawa, and Masaji Oda*
Department of Chemistry, Faculty of Science, Osaka University,
Toyonaka, Osaka 560, Japan

Abstract: Oligo-6-(2-thienyl)pentafulvenes, synthesized up to a tetramer by application of a new pentafulvene synthesis, show considerably low reduction potentials to suggest ready formation of polyanions or polyanion radicals with oligoacetylene spines.

In view of characteristic electronic properties of cross-conjugated fulvenoid compounds,[1] polymers of them at the exomethylene terminal carbons, general formula **1**, should generate poly-cations or -anions having a polyacetylene spine, **2**, upon electronic oxidation or reduction depending on their ring size. It would be of interest to examine this possibility not only as an access to novel polyacetylenes but also as a potential entry into electron-conducting polyacetylenes. However, labile properties of 6,6-bipentafulvenyl[2] and 8,8-biheptafulvenyl[3] undergoing air-oxidation and intramolecular electrocyclizations suggest synthetic difficulties for **1**. We therefore designed oligopentafulvenes inserted with 2-thienyl groups, namely oligo-6-(2-thienyl)pentafulvenes **3**, as a model system. Electronic reduction of **3** should also generate polyanions with an oligoacetylene spine. The 2-thienyl group here provides two advantages; first, its electron-donating property contributes to stabilization of the dipolar pentafulvene π-system; second, the easy metalation of thiophene at α-position furnishes sites for oligomer extension. We report here the synthesis and some properties of **3** up to the tetramer (n = 4).



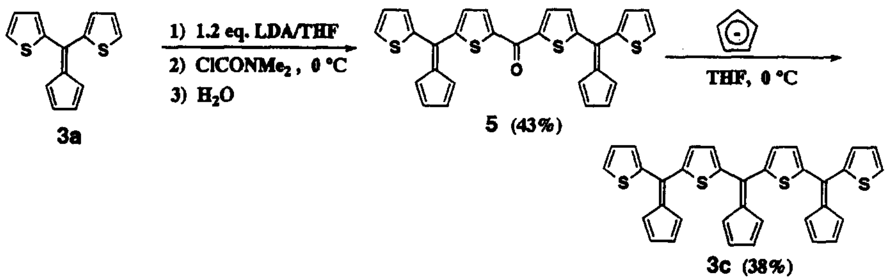
1 2



3 **4** (in case of n = even)

We examined three methods for the synthesis of series of **3**. Fisrt examined was nucleophilic substitution on 6-dimethylaminopentafulvenes.[4] This way lead to only monomer **3a** (n=1)[5] and dimer **3b** (n=2) in low yields mostly because of rather poor reactivity of 6-dimethylamino-6-(2-thienyl)pentafulvene[6] toward nulceophiles. Second examined was an application of the ketone synthesis[7] through the reaction of N,N-dialkylamides with organolithium compounds. This method requires condensation of ketones thus obtained with cyclopentadiene in the final step and was successful up to trimer **3c** via ketone **5** (Scheme 1), but suffered difficulties for higher oligomers because of the instability of the percursor ketones and the poor yield of the condensation.

Scheme 1



The most successful has been the new pentafulvene synthesis described in the accompanying paper[8] which is a modification of the second method avoiding isolation of the precursor ketones. This new method allowed one-pot synthesis of **3b**, **3c** and tetramer **3d** (Scheme 2), where selective lithiation of **3a**[5] at the thiophene x-position(s) are taken advantage of.

Scheme 2

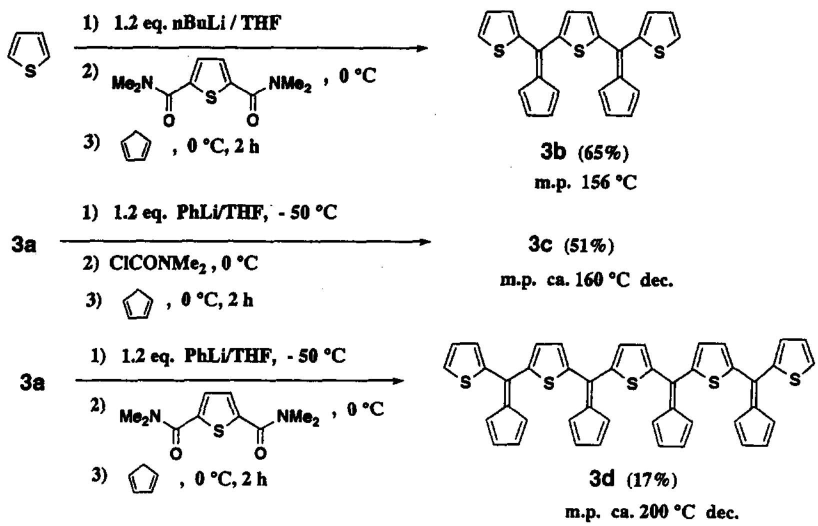


Table 1. Physical Properties of **3b** - **d** together with **3a**[4]

	Mass (m/z)	UV - Vis[a] (λ_{max} (log ε))	^{1}H - NMR[b] (δ / ppm)	Reduction Potentials[c] (V)
3a	242 (M^+) (EI)	373 (4.30) 277 (3.90)	7.52 (dd, J = 1.1, 5.5 Hz, 2H) 7.26 (dd, J = 1.1, 3.7 Hz, 2H) 7.10 (dd, J = 3.7, 5.1 Hz, 2H) 6.58 (m, 2H), 6.54 (m, 2H)	$E^1_{1/2}$ = - 1.28 $E^2_{1/2}$ = - 1.83
3b	400 (M^+) (EI)	415 (4.36) 368 (4.40) 287 (4.05)	7.56 (dd, J = 1.3, 5.0 Hz, 2H) 7.30 (dd, J = 1.3, 3.6 Hz, 2H) 7.27 (s, 2H) 7.13 (dd, J = 3.6, 5.0 Hz, 2H) 6.58 - 6.61 (m, 6H) 6.48 - 6.51 (m, 2H)	$E^1_{1/2}$ = - 0.93 $E^2_{1/2}$ = - 1.03
3c	559 ($(M+H)^+$) (FAB)	409 (4.62) 368 (4.57) 290 (4.26)	7.56 (dd, J = 1.0, 5.0 Hz, 2H) 7.28 - 7.31 (m, 6H) 7.14 (dd, J = 3.6, 5.0 Hz, 2H) 6.58 - 6.63 (m, 10H) 6.49 - 6.56 (m, 2H)	$E^1_{1/2}$ = - 0.81 $E^2_{1/2}$ = - 1.29 $E^3_{1/2}$ = - 1.85
3d	717 ($(M+H)^+$) (FAB)	408 (4.76) 365sh (4.67) 289 (4.38)	7.56 (dd, J = 1.0, 5.0 Hz, 2H) 7.32 - 7.25 (m, 8H) 7.13 (dd, J = 3.6, 5.0 Hz, 2H) 6.49 - 6.64 (m, 16H)	$E^1_{1/2}$ = - 0.84 $E^2_{1/2}$ = - 1.05

[a] In dichloromethane. [b] In $CDCl_3$, 270 MHz. [c] V vs Ag/AgCl, in 0.1 M nBu_4NClO_4/DMF, sweep rate 100 mV/sec.

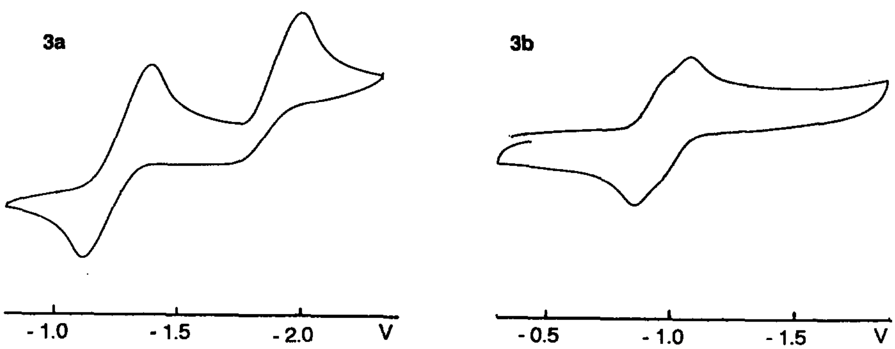


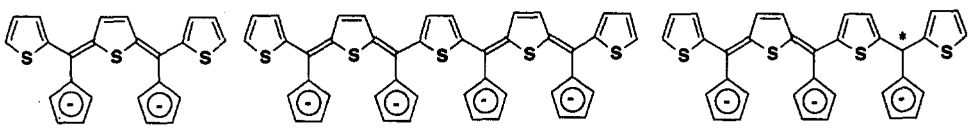
Fig. 1. Cyclic Voltammograms of **3a** and **3b**

Oligomers **3b-d** are dark red crystalline substances with fair to moderate stability. The stability, however, decreases with increase of unit number, and tetramer **3d** tends to decompose upon concentration of solutions above room temperature.[9]

Although dimer **3b** absorbs visible light at about 40 nm longer wave length (λ_{max} = 415 nm) than monomer **3a** does (373 nm), further extension of the oligomer does not appreciably affect the electronic spectra (Table 1). The lack of appreciable change may be due to the cross-conjugated structure of the pentafulvene unit and the conformational mobility of the oligomer system.[10]

The electrochemical properties of **3** are the most noticeable. While monomer **3a** shows well separated first and second reduction waves at -1.28 (E^1) and -1.83 V (E^2) in cyclic voltammetry, dimer **3b** does nearly overlapped reduction waves at appreciably lower potentials of -0.93 (E^1) and -1.03 V (E^2) (Table 1 and Figure 1) to suggest ready formation of dianion **6A**. For trimer **3c**, E^1 is even lower (-0.81 V) with almost simultaneous two electron transfer, and E^2 and E^3 correspond to the formation of trianion radical **7A** and tetraanion **7B**. Tetramer **3d** shows, similar to **3b**, only two reduction waves of here each two electron transfer to indicate easy formation of tetraanion **6B** having an oligoacetylene spine attached with cyclopentadienyl anions.

In conclusion, oligothienylpentafulvenes **3** with even unit number, **3b** and **3d**, are readily reduced electrochemically probably to polyanions with oligoacetylene spines. This may be also true for the higher oligomers and polymers. Alkali metal reductions of **3b–d** are in progress.



6A **6B** **7A** : * = •
7B : * = -

Acknowledgement: We thank to the Sumitomo Foundation and the Ministry of Education, Science and Culture of Japan for financial support.

References and Notes

1. For reviews see a) Lloyd,D. *Non-Benzenoid Conjugated Carbocyclic Compounds*, Elsevier, Amsterdam, 1984; b) Garratt,P.J., *Aromaticity*, John Wiley & Sons, New York, 1988, pp 173-194.
2. a) Sauter,H.; Prinzbach,H., *Angew. Chem. Int. Ed. Engl.*, 1972, **11**, 296; b) Sauter, H.; Gallenkamp,B.; Prinzbach,H., *Chem. Ber.*, 1977, **110**, 1382; c) Kawase,T.; Nisato,N.; Oda,M., *J. Chem. Soc., Chem. Commun.*, **1989**, 1145.
3. a) Kuroda,S.; Oda,M.; Kitahara,Y., *Angew. Chem. Int. Ed. Engl.*, 1973, **12**, 76; b) Kuroda,S.; Asao,T.; Funamizu,M.; Kurihara,H.; Kitahara,Y., *Tetrahedron Lett.*, **1976**, 251; c) Bingmann,H.; Knothe,L.; Hunkler,D.; Prinzbach,H., *ibid.*, **1979**, 4053.
4. Hafner,K.; Schmidt,F., *Tetrahedron Lett.*, **1973**, 5105, and references therein.
5. Kurata,H.; Morikawa,T.; Kumagai,T.; Kawase,T.; Oda,M., *Chemistry Express*, 1991, **6**, 853.
6. Kawase,T.; Fujino,S.; Oda,M., *Tetrahedron Lett.*, 1991, **32**, 3499.
7. For reviews see a) Wakefield,B.J., *The Chemistry of Organolithium Compounds*, Pergamon Press, Oxford, 1974; b) Wakefield,B.J., *Organolithium Methods*, Academic Press, London, 1988, pp 82-88.
8. Kurata,H.; Ekinaka,T.; Kawase,T.; Oda,M., *Tetrahedron Lett.*, the accompanying paper.
9. The decrease of stability may be due to the electron-withdrawing property of cyclopentadienylidene group (an electron-withdrawing group at the terminal methylene carbon destabilizes the pentafulvene π - system). Introduction of an alkyl group, in particular t-butyl group, in the five-membered rings should stabilize the present oligothienylpentafulvenes by steric protection.
10. Dimer **3b** shows no appreciable change down to -50 °C in ^{1}H NMR sepctra. Attempts to obtain single crystals of **3b–d** for X-ray analysis have been so far unsuccessful.

(Received in Japan 27 February 1993)