

Preparation of Methyl Chalcogenated Derivatives of 1,4,5,8-Tetrathiatetralin

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Tetrakis(methylthio)-1,4,5,8-tetrathiatetralin **4** and tetrakis(methylseleno)-1,4,5,8-tetrathiatetralin **6** is successfully prepared by the reaction of tetrathiatetralin (TTT) **2** with lithium diisopropylamide and MeSSMe or MeSeSeMe in diethyl ether and a remarkable solvent effect is observed in the analogous reaction in tetrahydrofuran to give tetrakis(methylthio)tetrathiafulvalene **5** by a novel rearrangement.

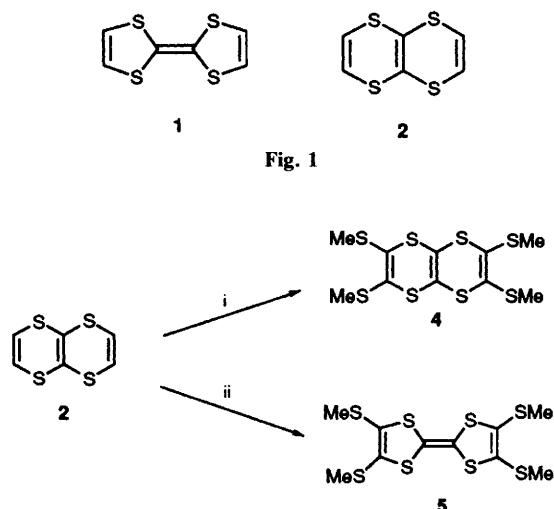
Although the charge-transfer complexes derived from TTF **1** and its derivatives are undoubtedly the most important class of highly conducting organic materials and their physical properties have been studied intensively. Developing new organic donors besides TTF and its derivatives may enrich further the field of synthetic metals. We have now studied tetrathiatetralin (TTT) derivatives, which are isomeric with the TTF series; only limited studies have been carried out on TTT

previously.^{2,3} The only known 1,4,5,8-TTT **2** was prepared and studied by Cava *et al.* but so far no study on the preparation of its derivatives has been reported. Although the first oxidation and ionization potential of **2** were not so low as **1**,^{2,3} We expected that substituents such as a methylthio group would lower the first oxidation as well as the ionization potentials. Moreover, derivatives with such substituents were also expected to have favourable intra- or inter-stack interactions *via* chalcogen atoms (*e.g.* S–S contact) compared with **2** to give charge-transfer complexes with suitable acceptors. We report in this paper the preparation of tetrakis(methylthio)- and tetrakis(methylseleno)-TTT derivatives (**4** and **6**) and a novel intramolecular rearrangement of the lithio derivative of **2**, based on a remarkable solvent effect forming tetrakis(methylthio)-TTF **5**, as well as their redox properties and the formation of an I₃⁻ complex of **4**.

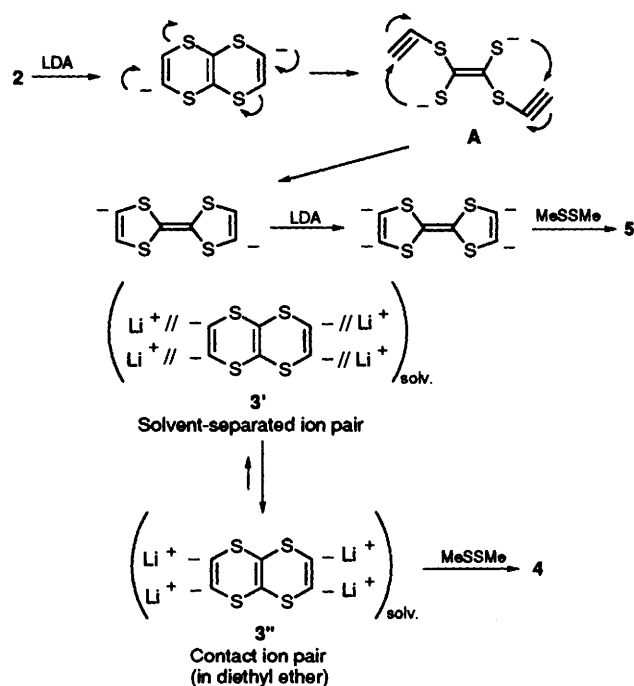
When tetralithio derivative of TTT **3** generated from unsubstituted TTT **2** *in situ* by using LDA (lithium diisopropylamide (>4 equiv.) in diethyl ether was treated with dimethyl disulfide, the desired tetrakis(methylthio)tetrathiatetralin **4** was obtained in 21–26% isolated yield. On the other hand, when the lithiation reaction was carried out in THF, an unexpected, smooth intramolecular rearrangement occurred giving tetrakis(methylthio)tetrathiafulvalene **5**[†] in moderate isolated yield (38%) (Scheme 1).

Although the mechanism of the novel rearrangement is not exactly clear,⁵ a plausible one is proposed as follows, *i.e.* the solvent-separated carbanion in THF rearranges, possibly through the dianion **A**, to form acetylenic bonds and then the intramolecular recyclization gives first the thermally more stable TTF skeleton with five-membered rings and then finally **5** (Scheme 2).[‡] Such intramolecular rearrangement is considered to be interrupted in diethyl ether because of the formation of a contact ion pair between the carbanion and lithium ion (*i.e.* **3**^{''}) as shown in the same Scheme.⁶

Tetrakis(methylseleno)tetrathiatetralin **6** was prepared in 39% isolated yield from **2**, LDA and dimethyl diselenide in diethyl ether similarly to **4**. The redox behaviour of **4** and **6** proved to be quite similar to **2** having irreversible redox waves and showing higher oxidation potentials than TTF derivatives (**1** and **5**), see Table 1. In spite of the relatively high oxidation potentials of **4**, its black I₃⁻ complex[§] was successfully prepared. Resistivity was measured on a polycrystalline sample of the complex at room temp. in a Bridgman anvil at 0.25–8 GPa with values of *ca.* 10⁴–10² Ω cm. Conductivity of



Scheme 1 Reagents and conditions: i, LDA, MeSSMe, diethyl ether, -78 °C; ii, LDA, MeSSMe, THF, -78 °C



Scheme 2

Table 1 Cyclic voltammetric data^a for **1**, **2**, **4**, **5** and **6**

Compound	MeCN			CH ₂ Cl ₂		
	E ₁ ^{ox}	E ₂ ^{ox}	ΔE ^b	E ₁ ^{ox}	E ₂ ^{ox}	ΔE ^b
1	0.42	0.78	0.36	0.49	0.80	0.31
2	1.02	1.42	0.41	1.15	1.51	0.36
4	1.05	1.30	0.25	1.14	1.38	0.24
5	0.54	0.77	0.23	0.61	0.87	0.26
6	1.05	1.30	0.25	1.10	1.38	0.28

^a Oxidation potentials given in V vs. SCE and were determined in MeCN or in CH₂Cl₂ with 0.1 mol dm⁻³ Bu₄NClO₄ at room temp. (scan rate: 50 mV s⁻¹). ^b ΔE = E₂^{ox} - E₁^{ox}.

the CT complex from **4** is less than that of the TTF complexes but interesting to study nevertheless.

We thank Dr J. Yamada of the Himeji Institute of Technology for his helpful discussion.

Received, 13th January 1994; Com. 4/00211C

Footnotes

† Compound **5** was isolated as yellow crystals, mp 91–92 °C (lit.^{4a} 94–96 °C).

‡ When TTT **2** was treated with LDA in THF, a similar rearrangement occurred to give TTF **1** in 70% yield.

§ The complex was isolated as black crystals, mp > ca. 170 °C (decomp.) and elemental analyses indicated that the D:A composition of the complex was 5:3. So far, any attempt to prepare a single crystal has been unsuccessful.

References

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