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NONCLASSICAL CONDENSED THIOPHENES. THE SELENOLO[3,4-*c*]THIOPHENE SYSTEM

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The first nonclassical selenolothiophenes, namely 1,3-dimethylselenolo[3,4-*c*]thiophene (**1a**) and 1,3-dicarbomethoxyselenolo[3,4-*c*]thiophene (**1b**), have been generated from appropriate precursors and characterized as trapping products with 1,3-dipolarophiles. These selenolothiophenes are similar to the corresponding thienothiophenes (**7a** and **7b**) in their high reactivity, and consequently less stable than their recently reported selenoloselenophene analogs **7c** and **7d**.

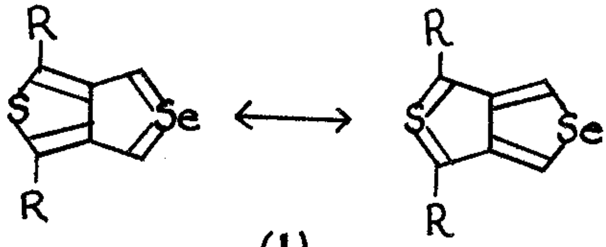
We have been interested for some years in the chemistry of thieno[3,4-*c*]thiophene (**7e**), a system which is nonclassical in the sense that its only uncharged resonance contributors are structures containing a tetracovalent sulfur atom.(1) As part of our study of this system, we generated the 1,3-dimethyl and 1,3-dicarbomethoxy derivatives (**7a** and **7b**) and found that N-phenylmaleimide (NPM) added to them exclusively at the ring of highest electron density; compound **7a** was too reactive to be directly observable visually, but **7b** formed orange solutions of marginal stability.(2) Very recently, Gronowitz and Konar reported the generation of the selenolo[3,4-*c*]selenophene analogs (**7c** and **7d**) of these compounds; these purple selenoloselenophenes, while not isolable, were clearly far more stable in solution than their thienothiophene counterparts.3) We now report the generation and characterization of the first derivatives (1a and 1b) of the mixed selenium-sulfur system, selenolo[3,4-c]thiophene.

Reaction of the known halides 2a4) and 2b5) with aqueous sodium hydrogen selenide in dioxane afforded mixtures of 3a (60%, mp 66-67°)6) and 4a (mp 165-166°) and of 3b (88%, mp 182-183°) and 4b (mp 216-220°). Monomers and dimers were separated by sublimation.

Hydrogen peroxide oxidation of 3a and 3b in THF at -15° gave the selenoxides 5a (99%, mp 108-110°) and 5b (85.6%, mp > 110° dec), while bromination in CCl_4 or CH_2Cl_2 gave the corresponding dibromides 5c (92%, mp 133-135°) and 5d (43%, mp 180°). Selenoxides 5a and 5b decompose readily and were used directly in subsequent reactions.

Dehydration of selenoxide 5a in refluxing acetic anhydride (nitrogen, 3.5 hr) in the presence of NPM brought about the generation and trapping of selenolothiophene 1a and the formation of *exo* adduct 8a (57%, mp 231-232°), along with a lesser amount (9%) of *endo* adduct 8b;7) addition of NPM thus was observed only at the alkyl-bearing thiophene ring. Attempts to generate 1a by stirring the selenide dibromide 5c or 5a with benzene and 40% aqueous NaOH 8) gave a yellow organic layer from which diselenide 6 9) (39%, mp 144-145°) and selenide 3a (29%) were isolated; heating 5a alone with acetic anhydride afforded, after aqueous work-up, a similar mixture of 6 and 3a.

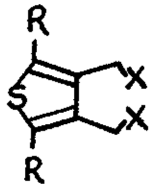
Selenoxide 5b dissolves slowly in acetic anhydride at room temperature with the production of a reddish-pink color, which we attribute to the selenolothiophene 1b. This color, which remains for about 3 hr under nitrogen at room temperature, corresponds to an observable band (EtOH) of λ_{max} 536 nm; the related thienothiophene 7b shows λ_{max} 500 nm



(1)

a, R = CH_3

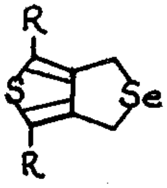
b, R = CO_2CH_3



(2)

a, R = CH_3 X = Cl

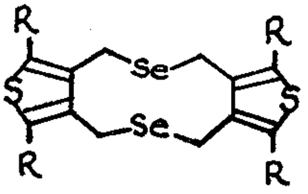
b, R = CO_2CH_3 X = Br



(3)

a, R = CH_3

b, R = CO_2CH_3



(4)

a, R = CH_3

b, R = CO_2CH_3

in the same solvent, while the selenoloselenophene **7d** shows λ_{max} 563 nm in hexane. Generation of **1b** could also be effected in $CDCl_3$ by the action of Et_3N on dibromide **5d**;10) the aromatic singlet of **1b** at δ 10.00 (as compared to 10.04 for **7d**) slowly decreased as the red color faded.

Although **1b** could not be isolated as such, it was trapped as the aromatized adduct **9** (16%, mp 180-181°) when selenoxide **5b** was heated in acetic anhydride (nitrogen, 3.5 hr) with dimethyl acetylenedicarboxylate. The same adduct **9** was obtained (62%) by the trapping of thienothiophene **7b** under similar conditions; addition of the alkyne to **1b** thus took place at the ring of higher electron density.

In conclusion, the selenolothiophenes **1a** and **1b** resemble their thienothiophene counterparts **7a** and **7b** in their high reactivity and in their reactions with dipolarophiles. They are, in contrast, less stable than the recently reported selenoloselenophenes **7c** and **7d**.

ACKNOWLEDGMENT

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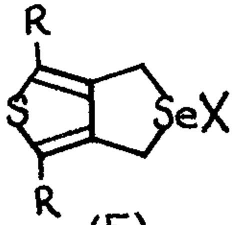


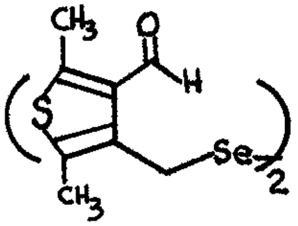
(5)

a, $R = CH_3$ $X = O$

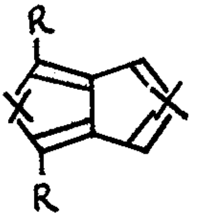
b, $R = CO_2CH_3$ $X = O$

c, $R = CH_3$ $X = Br_2$

d, $R = CO_2CH_3$ $X = Br_2$



(6)



(7)

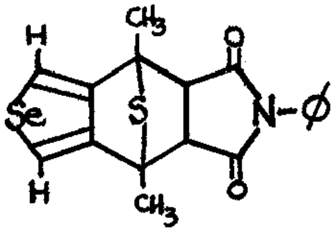
a, $R = CH_3$ $X = S$

b, $R = CO_2CH_3$ $X = S$

c, $R = CH_3$ $X = Se$

d, $R = CO_2CH_3$ $X = Se$

e, $R = H$ $X = S$



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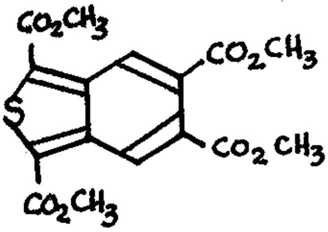

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3) S. Gronowitz and A. Konar, *J.C.S. Chem. Comm.*, 1977, 163.

4) K. Dimroth, G. Pohl and H. Follman, *Chem. Ber.*, 1966, **99**, 634.

5) H. Wynberg and D. J. Zwanenburg, *J. Org. Chem.*, 1964, **29**, 1919.

6) All melting points are uncorrected. Satisfactory spectral analyses were obtained for all new compounds reported.

7) Exo adduct, **8a**, nmr ($CDCl_3$) δ 2.05 (s, 6 H), 3.27 (s, 2 H), 7.18-7.53 (m, 5 H) superimposed on aromatic singlet 7.37 (2 H).

Endo adduct, **8b**, nmr ($CDCl_3$) δ 2.03 (s 6 H), 3.93 (s 2 H), 6.7-6.9 (m, 2 H), 7.23-7.5 (m, 3 H) superimposed on aromatic singlet 7.41 (2 H).

8) L. E. Saris and M. P. Cava, *J. Am. Chem. Soc.*, 1976, **98**, 867.

9) For a similar result see B. E. Norcross, J. M. Lansinger and R. L. Martin, *J. Org. Chem.*, 1977, **42**, 369.

10) This represents the first synthesis of a selenophene via dehydrobromination.

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