

NONCLASSICAL CONDENSED THIOPHENES. THE SELENOLO[3,4-c]THIOPHENE SYSTEMLydia E. Saris and Michael P. Cava*Department of Chemistry, University of PennsylvaniaPhiladelphia, Pennsylvania 19104, U. S. A.

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 tetravalent 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

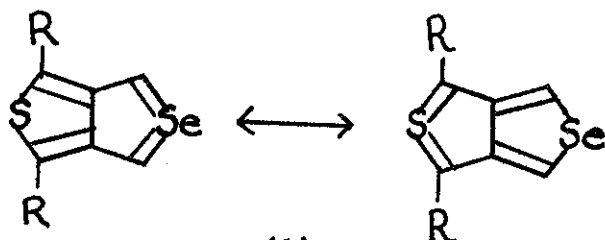
than their thienothiophene counterparts.³⁾ We now report the generation and characterization of the first derivatives (1a and 1b) of the mixed selenium-sulfur system, selenolo[3,4-c]thiophene.

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 CCl₄ or CH₂Cl₂ 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.

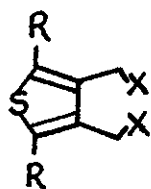
Selenoxide 5b dissolves slowly in acetic anhydride at room temperature with the production of a reddish-pink color, which we attribute to the selenolothiophene 1b. This color, which remains for about 3 hr under nitrogen at room temperature, corresponds to an observable band (EtOH) of λ_{\max} 536 nm;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



(1)

a, $R = \text{CH}_3$

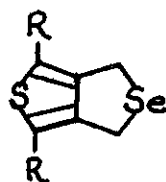
b, $R = \text{CO}_2\text{CH}_3$



(2)

a, $R = \text{CH}_3$ $X = \text{Cl}$

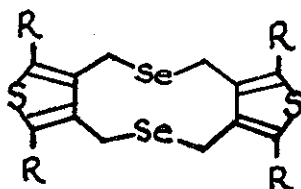
b, $R = \text{CO}_2\text{CH}_3$ $X = \text{Br}$



(3)

a, $R = \text{CH}_3$

b, $R = \text{CO}_2\text{CH}_3$



(4)

a, $R = \text{CH}_3$

b, $R = \text{CO}_2\text{CH}_3$

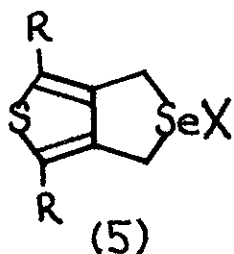
in the same solvent, while the selenoloselenophene 7d shows λ_{max} 563 nm in hexane. Generation of 1b could also be effected in CDCl_3 by the action of Et_3N on dibromide 5d; ¹⁰) the aromatic singlet of 1b at δ 10.00 (as compared to 10.04 for 7d) slowly decreased as the red color faded.

Although 1b could not be isolated as such, it was trapped as the aromatized adduct 9 (16%, mp 180-181^o) 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.

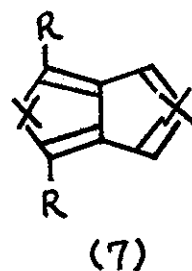
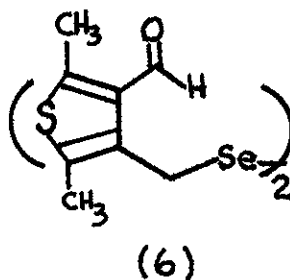
In conclusion, the selenolothiophenes 1a and 1b resemble their thienothiophene counterparts 7a and 7b in their high reactivity and in their reactions with dipolarophiles. They are, in contrast, less stable than the recently reported selenoloselenophenes 7c and 7d.

ACKNOWLEDGMENT

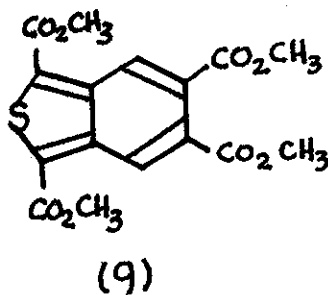
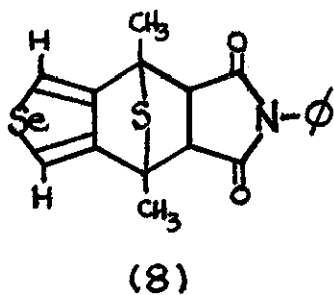
We thank the National Science Foundation for a grant (MPS 74-03279 A01) in support of this research.



- a, R = CH₃ X = O
- b, R = CO₂CH₃ X = O
- c, R = CH₃ X = Br₂
- d, R = CO₂CH₃ X = Br₂



- a, R = CH₃ X = S
- b, R = CO₂CH₃ X = S
- c, R = CH₃ X = Se
- d, R = CO₂CH₃ X = Se
- e, R = H X = S



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- 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 (CDCl₃) 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 (CDCl₃) 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.

Received, 13th June, 1977