NONCLASSICAL CONDENSED THIOPHENES. THE SELENOLO[3,4-\(\tau\)]THIOPHENE SYSTEM

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The first nonclassical selenolothiophenes, namely 1,3-dimethylselenolo[3,4-\(\tau\)]thiophene (1a) and 1,3-dicarbomethoxyselenolo[3,4-\(\tau\)]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-\(\tau\)]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-\(\tau\)]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.\textsuperscript{3)} We now report the generation and characterization of the first derivatives (1\textsubscript{a} and 1\textsubscript{b}) of the mixed selenium-sulfur system, selenolo[3,4-c]thiophene.

Reaction of the known halides 2\textsubscript{a}\textsuperscript{4)} and 2\textsubscript{b}\textsuperscript{5)} with aqueous sodium hydrogen selenide in dioxane afforded mixtures of 3\textsubscript{a} (60\%, mp 66-67\textdegree)\textsuperscript{6)} and 4\textsubscript{a} (mp 165-166\textdegree) and of 3\textsubscript{b} (88\%, mp 182-183\textdegree) and 4\textsubscript{b} (mp 216-220\textdegree). Monomers and dimers were separated by sublimation.

Hydrogen peroxide oxidation of 3\textsubscript{a} and 3\textsubscript{b} in THF at -15\textdegree gave the selenoxides 5\textsubscript{a} (99\%, mp 108-110\textdegree) and 5\textsubscript{b} (85.6\%, mp > 110\textdegree dec), while bromination in CCl\textsubscript{4} or CH\textsubscript{2}Cl\textsubscript{2} gave the corresponding dibromides 5c (92\%, mp 133-135\textdegree) and 5d (43\%, mp 180\textdegree). Selenoxides 5\textsubscript{a} and 5\textsubscript{b} decompose readily and were used directly in subsequent reactions.

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

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

\[ R = CH_3 \]
\[ R = CO_2CH_3 \]

(2)

\[ R = CH_3 \]
\[ X = Cl \]
\[ R = CO_2CH_3 \]
\[ X = Br \]

(3)

\[ R = CH_3 \]
\[ R = CO_2CH_3 \]

(4)

\[ R = CH_3 \]
\[ R = CO_2CH_3 \]
in the same solvent, while the selenoloselenophene \( 7d \) shows \( \lambda_{\text{max}} \) 563 nm in hexane. Generation of \( 1b \) could also be effected in CDCl\(_3\) by the action of Et\(_3\)N on dibromide \( 5d \);\(^{10}\) the aromatic singlet of \( 1b \) at \( \delta \) 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\(^\circ\)) 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 \( 7d \).

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(5)
\[ R \text{, } R \]

a, \( R = \text{CH}_3 \) \( X = \text{O} \)
b, \( R = \text{CO}_2\text{CH}_3 \) \( X = \text{O} \)
c, \( R = \text{CH}_3 \) \( X = \text{Br}_2 \)
d, \( R = \text{CO}_2\text{CH}_3 \) \( X = \text{Br}_2 \)

(6)

(7)

a, \( R = \text{CH}_3 \) \( X = \text{S} \)
b, \( R = \text{CO}_2\text{CH}_3 \) \( X = \text{S} \)
c, \( R = \text{CH}_3 \) \( X = \text{Se} \)
d, \( R = \text{CO}_2\text{CH}_3 \) \( X = \text{Se} \)
e, \( R = \text{H} \) \( X = \text{S} \)

(8)

(9)
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6) All melting points are uncorrected. Satisfactory spectral analyses were obtained for all new compounds reported.
7) Exo adduct, $\alpha_a$, nmr (CDCl$_3$): $\delta$ 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, $\beta_b$, nmr (CDCl$_3$): $\delta$ 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).
10) This represents the first synthesis of a selenophene via dehydrobromination.

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