curves with those obtained from 3-carboxy- and 3,5-dicarboxy-substituted 1,2-dithiolanes,[12c] disulfide-bridged diketopiperazines,[12b,25] and various cystine derivatives such as *cyclo*-L-cystine[14,26] and [2,7-cystine]-gramicidin S[27] makes clear that the interaction of the disulfide with peripheral groups can lead to chiroptical features significantly different from those expected for the "isolated" disulfide.

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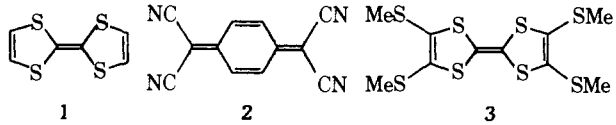
Leonard A. Neubert, Marvin Carmack*
Department of Chemistry, Indiana University
Bloomington, Indiana 47401
Received August 11, 1973

Tetrathiomethoxytetrathiofulvalene. Electrochemical Synthesis and Characterization

Sir:

The recent discovery[1,2] of highly conductive organic charge transfer complexes which are formed from derivatives of tetrathiofulvalene (**1**) and the acceptor

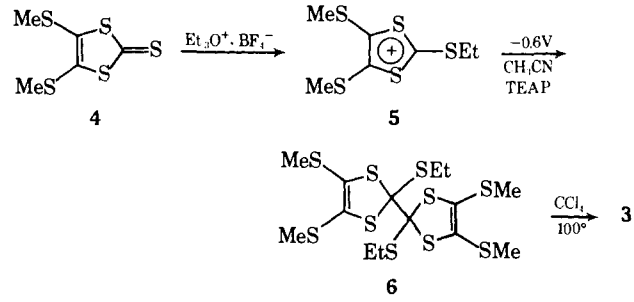


1 **2** **3**

molecule, tetracyano-*p*-quinodimethane (TCNQ) (**2**), has stirred interest in the discovery of new electron donors and acceptors which exhibit similar conductivity.[3] We wish to report the synthesis, *via* electrochemical methods, of both **1** and tetrathiomethoxytetrathiofulvalene (**3**).

The procedure reported here involves alkylation of 1,3-dithiole-2-thiones[4] to form 2-thioiethoxy-1,3-dithiolium ions, followed by electrochemical reduction to the 2,2′ dimer, an orthothiooxalate. The orthothiooxalate is isolated and pyrolyzed to the tetrathiofulvalene.[5] Good to nearly quantitative yields are obtained for each step, and, in our hands, the method has proven to be superior to the base catalyzed dimerization of 1,3-dithiolium ion, the method used by Coffen[6] initially to synthesize **1**. The method also appears to be a more general preparation of tetrathioethylenes from trithiocarbonates than desulfurization by trivalent phosphorus compounds.[7,8]

The preparation of **3** illustrates the procedure. The trithiocarbonate **4** was prepared by the method of Wawzonek and Heilman.[9] An excess of CS_2 was cathodically reduced (Pt, DMF, 0.4 *M* TBAI[10]) at −2.00 V *vs.* sce. After 0.16 F was passed, the electrolysis was stopped, excess CS_2 was removed by nitrogen purging, and 10 g of CH_3I was added. After 2 hr at room temperature, the excess CH_3I was removed, and the products were extracted with ether. The product **4** was recrystallized from ligroine as long reddish needles: mp 100–101°; nmr (δ) 2.51 (s); current yield 75%. Meerwein's reagent ethylated **4** at room temperature in CH_2Cl_2 to yield **5** which was cathodically reduced (Pt, CH_3CN, 0.2 *M* TEAP[10]) at −0.6 V *vs.* sce (1.0 F/mol). The orthothiooxalate **6** was recovered by chloroform



4 **5** **6**

extraction; crude yield: 99.5%; mp 77–79°; nmr (δ) 1.37 (t) 6 H, 2.40 (s) 6 H, 3.0 (q) 4 H; uv (CH_3CN) 307 nm, log ε 4.19. Finally, **6** was pyrolyzed in a sealed tube for 4 hr to yield **3** as a red oil in a total yield of 75% (coulometric analysis). On standing in acetonitrile, pale yellow needles formed: mp 94.5–96.0°; nmr (δ) 2.46 (s); mass spectrum (*m/e*) 388 (p), 373 ($-CH_3$), 341 ($-SCH_3$), 194 (p/2); uv see Table I. The distinctive

Table I. Spectral Data for Tetrathiomethoxytetrathiofulvalene, Its Radical Cation and Dication in Acetonitrile

3		$3^{\cdot+}$		3^{2+}	
λ, nm	log ε	λ, nm	log ε	λ, nm	log ε
370(s)	3.23	461	3.25	710	3.51
329	3.89	366	3.25	488	2.7
309	3.94	329	3.75	456	2.7
260	3.89	262	4.04		

electrochemical behavior of **3** easily permitted its analysis in the presence of other products (probably diethyl disulfide).

Cyclic voltammograms of **3** in CH_3CN at a platinum working electrode (Figure 1) exhibit two reversible one-electron couples at 0.47 and 0.71 V *vs.* sce which cor-

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(10) TBAI, tetra-*n*-butylammonium iodide; TEAP, tetraethylammonium perchlorate.

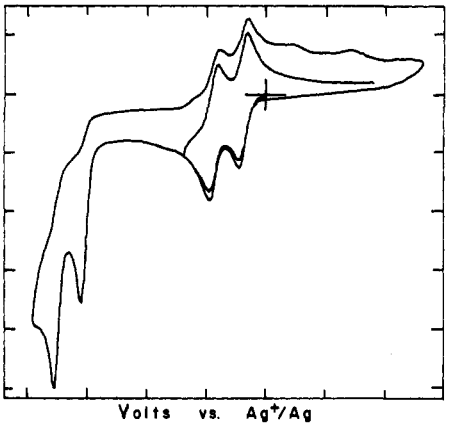

Figure 1. Cyclic voltammogram of 0.87×10^{-3} *M* **3** in 0.05 *M* TEAP, CH_3CN, Pt electrode (0.215 cm^2), 0.104 V/sec: abcissa, volts *vs.* Ag^+/Ag, 0.5 V/div; ordinate, 25 μA/div; the cross marks the (0,0) point.

respond to the formation of the radical cation and dication of **3**, respectively. The deep pink solution of the radical cation is stable for an extended period of time, while the dication, which is deep blue in solution, is stable only in the absence of oxygen and water. Spectral data are given in Table I; however, uv data below 300 nm could not be obtained for the dication since solvent impurities decomposed the dication when the solution was diluted. The esr spectrum of the radical cation exhibited unresolved hyperfine structure superimposed on an intense absorption. Seven lines could be discerned in the second derivative spectrum (splitting ≈ 0.24 G, $g = 2.00764$).

Two irreversible two-electron waves at 1.78 and 2.00 V *vs.* sce (E peak values) are observed in the voltammograms of **3** (Figure 1). No evidence of a radical trication species is present in the voltammograms at sweep rates up to 200 V/sec. The electrochemical behavior of **3** and the synthetic intermediates and the reactions of **3** with electron acceptors are under investigation and will be reported in due course.

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P. R. Moses, J. Q. Chambers*
Department of Chemistry, University of Tennessee
Knoxville, Tennessee 37916
Received October 10, 1973

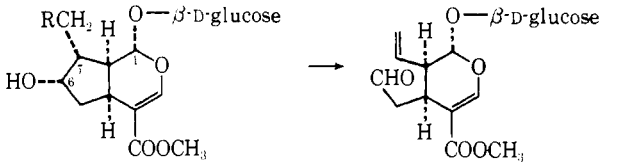
Fragmentation of Hydroxyloganin Derivatives. An Easy Access to Secologanin Type Compounds

Sir:

Secologanin (**3**), a naturally occurring monoterpene glucoside, is a key intermediate in the biogenesis of *Corynanthe*, *Aspidosperma*, and *Iboga*,[1] as well as *Ipecacuanha*[2] and *Cinchona*[3] alkaloids.

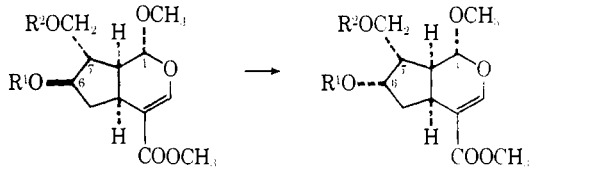
We now wish to report a simple synthesis of secologanin derivatives, which is not only fascinating from the biogenetic standpoint but also offers an easy entry to a great number of pharmacologically interesting compounds.

It has been shown by feeding experiments[1] that *in vivo* secologanin (**3**) derives from loganin (**1**) by cleavage

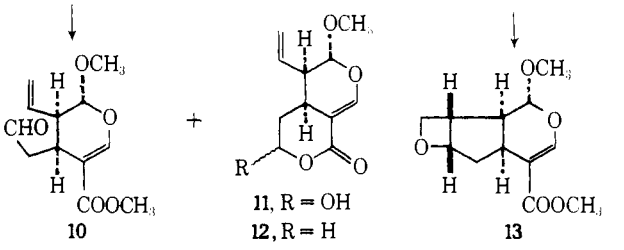


of the carbocyclic ring. Two mechanisms have been considered: (a) direct fragmentation of loganin (**1**) by hydride abstraction;[4] (b) fragmentation of the postulated intermediate hydroxyloganin (**2**). According to this, we investigated the fragmentation[5] of derivatives of hydroxyloganin, and hereby we could show that the base-catalyzed reaction of **6** leads to compounds of secologanin in high yield.

Conversion of the hydroxy acetate **4**[6] into the crystal-



4, $R^1 = COCH_3$; $R^2 = H$
5, $R^1 = COCH_3$; $R^2 = SO_2C_6H_4CH_3$-*p*
6, $R^1 = H$; $R^2 = SO_2C_6H_4CH_3$-*p*
7, $R^1 = R^2 = COCH_3$
8, $R^1 = R^2 = H$
9, $R^1 = H$; $R^2 = SO_2C_6H_4CH_3$-*p*



line *p*-toluenesulfonate **5** (mp 90–91°) (TsCl, pyridine, 20°) and hydrolysis of the acetoxy group by barium hydroxide in anhydrous methanol at 20° afforded **6** (88%). Herein the substituents at C-6 and C-7 have trans configuration. Reaction of **6** with *n*-butyllithium or potassium *tert*-butoxide did not produce any of the desired compound, whereas the reaction with sodium methylsulfinylmethide[7] in dimethyl sulfoxide at 20° gave the secologanin aglucone *O*-methyl ether (**10**) (nmr ($CDCl_3$) δ 9.78 (t, 1, J = 2 Hz, -C*H*O), 7.52 (d, 1, J = 2 Hz, C=C*H*O), 5.8–5.1 (m, 3, -C*H*=CH_2), 4.83 (d, 1, J = 4.5 Hz, OC*H*O), 3.70 (s, 3, $-CO_2CH_3$), 3.50 (s, 3, $-OCH_3$); mass spectrum *m/e* 240 (M^+)) and the lactol of the secologanic acid aglucone *O*-

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