Tetrahedron Letters,Vol.24,No.6,pp 539-542,1983 0040-4039/83/060539-04$03.00/0
Printed in Great Britain

CONDUCTING SALTS OF (TELLUROPYRANYL)TELLUROPYRANS

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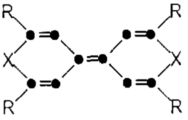
Summary: Conducting complexes of (telluropyranyl)telluropyran donors with tetracyanoquinodimethane (TCNQ) and the closed-shell anions tetrafluoroborate and perchlorate were prepared.

Since Syper and Sucharda-Sobczyk[1] discovered that (pyranyl)pyrans (**1**) form electrically conductive complexes with electron acceptors, there have been a number of studies on both the preparation and the physical characterization of new members of this class, including the recent syntheses of selenium analogues.[2-8] Extension of this class to tellurium analogues has been reported only recently.[9] In this paper we present the preparation and properties of (telluropyranyl)telluropyrans, their complexes with TCNQ and other anions, and some preliminary electrical data.

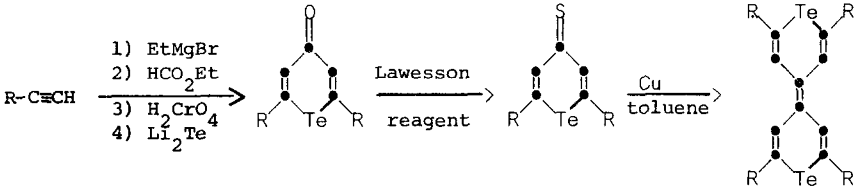


X = O, S, Se, Te

1

The preparation of (telluropyranyl)telluropyrans **2** is shown in Scheme I. The telluropyranones were prepared from the corresponding acetylenes by methods previously reported.[10,11] The telluropyran-4-thiones were prepared by treating the pyranones with the Lawesson reagent[12] in boiling toluene for 5 min and purifying the product on a short column of silica gel eluted with methylene chloride.

Scheme I



2a, R = Ph
2b, R = CH$_3$
2c, R = *tert*-Bu

The (telluropyranyl)telluropyrans were prepared by boiling a mixture of telluropyran-4-thione and an equal weight of copper powder in toluene (5 mL of toluene per millimole of thione) for 1.5 h. The reaction mixture was filtered while hot through a 5 cm pad of Celite. The filter pad was washed with methylene chloride, and the combined organic filtrates were concentrated. The products were much less soluble than the starting thiones in hot acetonitrile and were isolated by fractional crystallization from this solvent. Physical and spectral properties of the (telluropyranyl)telluropyrans are compiled in Table I.

Table I. Physical and Spectral Properties of $\Delta^{4,4'}$-4-(Telluropyranyl)-4*H*-telluropyrans

Compd	Yield,[a] %	mp, °C	λ_{max} (CH_2Cl_2), nm	log ϵ
2a	66	273-274	520	4.64
2b	32	212-217	420	4.51
2c	22	275-277	435	4.69

[a] Isolated yield.

(Telluropyranyl)telluropyran 2a formed a 1:1 complex with TCNQ when an acetonitrile solution of TCNQ (0.1 M, 1.5 equiv) was added to a hot methylene chloride solution of 2a (0.002 M). Under similar conditions, 2b gave a 2:3 complex with TCNQ. However, when 2 equiv of the 0.1 M TCNQ in acetonitrile solution was added to a 0.04 M solution of 2b, a 1:2 complex was isolated. Compound 2c gave emerald-green solutions with TCNQ, but no complexes were isolated.

Interestingly, attempts to prepare 1:1 salts of 2a, 2b, and 2c with closed-shell anions failed. Instead, when donor dications were mixed with neutral donor, complex salts were isolated containing the dication-(radical-cation) state.

Table II presents the electrochemical data for the donors as well as the electrical data for the complexes. A comparison with the oxygen, sulfur, and selenium analogues is also given.

Comparing the first oxidation potentials, E_1, for R = Ph, the general trend of increasing oxidation potential with increasing size of the heteroatom is maintained throughout the series. Effects of substituents on E_1 are still quite dramatic for Te as for O and S (and presumably Se), with the same 12 mV decrease in E_1 occurring when CH_3 is substituted for phenyl throughout the series. Interestingly, the gap between E_1 and E_2 narrows as the size of the heteroatom increases.

In the absence of X-ray structural data, the electrical properties are difficult to assess. The conductivity of the 1:2 complex with X = Te and R = CH_3 is high enough to require a segregated stack structure. The X-ray structure for the 2:3 complex with X = S and R = H is a mixed stack material with $\sigma = 0.1\ \Omega^{-1}cm^{-1}$. The analogous Te heterocycle has not been studied, but the low conductivity for the 2:3 complex with X = Te and R = CH_3 may suggest a mixed stacked behavior. Further work on single crystal growth and X-ray structural analysis would be desirable.

Table II. Oxidation Potentials of (Pyranyl)pyranylidene Donors 1 and Electrical Conductivity (σ) of Their Complexes at 25 °C

		Stoich. of	Donor Oxidation Potentials (V)[b]		σ,[c]	
X	R	TCNQ Complexes[a]	E_1	E_2	$\Omega^{-1}cm^{-1}$	Ref.
O	H	1:1	+0.21	+0.50	0.06	2,13
O	CH_3	1:1	+0.03	+0.42	10^{-6}	1,13
O	Ph	1:1	+0.15	+0.47	1.7(40)	2,4,13
S	H	1:1	+0.20	+0.46	1-4(30)	5,7,13
S	H	1:2			8	5
S	H	2:3			0.05-0.1	7
S	CH_3	1:1	+0.09	+0.34	$10^{-4}(10^{-3})$	5,13
S	CH_3	1:2			0.5	5
S	Ph	1:1	+0.22	+0.41	10(250)	4,6,13
Se	Ph	1:1	+0.33	+0.51	0.5	8
Te	CH_3	1:2	+0.22	+0.38	4	
Te	CH_3	2:3			0.4	
Te	Ph	1:1	+0.34	+0.49	0.5	
Te	*tert*-Bu	2:3 ClO_4	+0.14	+0.31	4×10^{-4}	
Te	Ph	2:3 ClO_4			10^{-4}	
Te	CH_3	2:3 BF_4			10^{-4}	

[a] Analytical: For X = Te, R = CH_3, 1:2, Calcd.: C, 53.8; H, 2.9; N, 13.2. Found: C, 53.1; H, 2.9; N, 12.7. For X = Te, R = CH_3, 2:3, Calcd.: C, 51.5; H, 3.0; N, 11.3. Found: C, 51.7; H, 2.9; N, 11.8. For X = Te, R = Ph, Calcd.: C, 61.9; H, 3.2; N, 6.3. Found: C, 61.2; H, 3.1; N, 6.6. For R = *tert*-Bu, ClO_4, salt, Calcd.: C, 41.3; H, 5.3. Found: C, 41.4; H, 5.7. For R = Ph, ClO_4 salt, Calcd.: C, 53.5; H, 3.2. Found: C, 53.9; H, 3.2. For BF_4 salt, Calcd.: C, 29.5; H, 2.8. Found: C, 30.0; H, 2.6. [b] Versus SCE or Ag/AgCl reference; solvent is CH_2Cl_2 in this work and X = Se, R = Ph; all others, acetonitrile. [c] Compressed-pellet measurement (single crystal in parentheses).

Acknowledgment

We thank Bruce Henne for help with the conductivity measurements.

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(Received in USA 22 June 1982)