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SYNTHESIS OF 1,3-DITELLUROLE AND DITELLUROLYLIUM CATIONS

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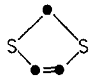
Summary: 1,3-Ditellurole was synthesized and shown to oxidize to the 1,3-ditellurolylium ion, which rearranges to a 1,2-ditellurolylium ion.

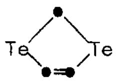
Within the considerable amount of literature on the syntheses of substituted 1,3-dithioles, 1,3-dithiolylium cations, and related heterocycles there are only a few methods for preparing the parent compounds of the series I-V.[1] Syntheses of the 1,3-dithiolylium cation (II)[2] and the 1,3-diseleno analogue (III)[3] have appeared, but preparations of 1,3-ditellurole (IV) and the corresponding 1,3-ditellurolylium cation (V) have not been reported. We present here an efficient synthesis of IV, its oxidation to V, and evidence for a novel rearrangement of V to a 1,2-ditellurolylium cation.



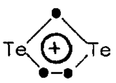
I

II

III

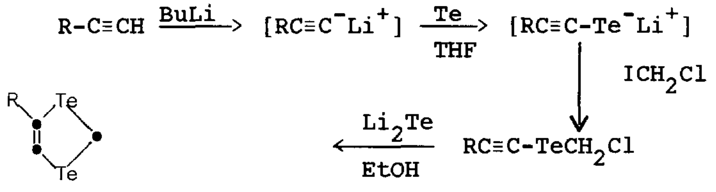


IV



V

Our method for preparing the parent 1,3-ditellurole (IV) and some derivatives of IV is shown in Scheme 1.



IVa, $R = H$
IVb, $R = CH_3$
IVc, $R = CH_3(CH_2)_3$
IVd, $R = C_6H_5$

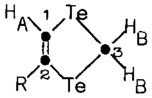
VIa, $R = (CH_3)_3Si$
VIb, $R = CH_3$
VIc, $R = CH_3(CH_2)_3$
VId, $R = C_6H_5$

Scheme 1

The alkynetellurolates were readily prepared from the corresponding alkynes (all commercially available) via their lithio salts and 1 equiv of tellurium metal at 30°C in THF.[4] Between -40 and -60°C, the alkynetellurolate slurry was treated with 1.1 equiv of iodochloromethane in THF and allowed to warm to room temperature.[5] Dilution with 50% Et_2O/pentane, filtration through a pad of Celite, and water extraction gave an organic layer of VI sometimes contaminated with $RC{\equiv}C\text{-}TeCH_2Te\text{-}C{\equiv}CR$.[6] Evaporation of the solvents followed by distillation or chromatography on silica gel gave pure VI.

Ring closure of VI to the 1,3-ditelluroles IVa-d required the use of dilithium telluride prepared from tellurium shot and 2 equiv of lithium triethyl borohydride (1 M in THF, "Superhydride," Aldrich Chemical Company). After the tellurium shot was consumed, slightly more than 2 equiv (relative to Te) of 1 M NaOEt in ethanol was added to the Li_2Te under argon.[7] The chloromethyltellurolalkyne was dissolved in DMF (volume equal to amount of ethanol added) and added to the Li_2Te solution. The resulting mixture was stirred 16-24 h at ambient temperature and then filtered through a pad of Celite to remove Te metal. The filtrate was diluted with water, extracted with CH_2Cl_2, dried ($MgSO_4$), and evaporated. The 1,3-ditelluroles were purified by recrystallization from methanol or chromatography on activity II alumina eluting with 3:1 hexane/CH_2Cl_2. Table 1 lists pertinent physical properties of IV and some derivatives prepared by the above method.

Table 1. Physical and NMR (^1H, ^{13}C) Spectral Properties of IV



IV

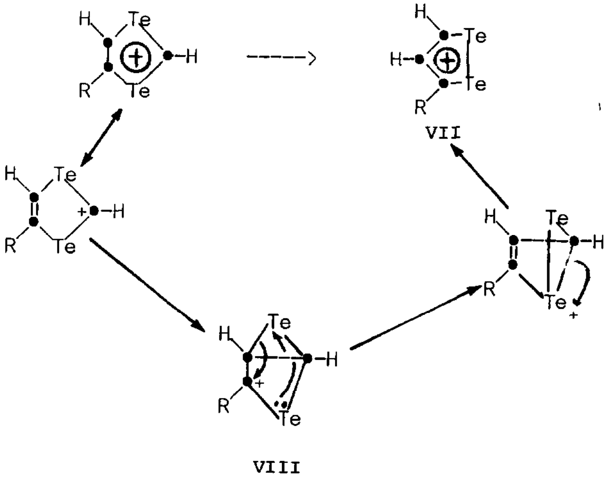
R	Yield,[a] %	mp,[b] °C	δC_1, ppm[c]	δC_2, ppm	δC_3, ppm	δH_A, ppm	δH_B, ppm
IVa H	65	83-85	120.0	120.0	-39.0	8.83	4.70
IVb CH_3	4	53-56	112.4	136.1	-40.6	8.07	4.73
IVc $CH_3(CH_2)_3$	11	37.5-40	110.7	143.7	-41.9	8.10	4.65
IVd Ph	49	80.5-82.5	141.6	143.1	-20.7	8.57	4.73

[a] Isolated yield. [b] All compounds gave satisfactory elemental analyses. For R = H, Calcd. for $C_3H_4Te_2$: C, 12.2; H, 1.4. Found: C, 12.2; H, 1.4. For R = CH_3, Calcd. for $C_4H_6Te_2$: C, 15.5; H, 2.0. Found: C, 15.4; H, 2.0. For R = $CH_3(CH_2)_3$, Calcd. for $C_7H_{12}Te_2$; C, 23.9; H, 3.4. Found: C, 24.0; H, 3.4. For R = Ph, Calcd. for $C_9H_8Te_2$: C, 29.2; H, 2.2; Te, 68.9. Found: C, 29.0; H, 2.2; Te, 69.0.
[c] $CDCl_3$ as solvent.

Treatment of 1,3-ditellurole (IVa) in acetonitrile at -30°C with 1 equiv of triphenylcarbenium (trityl) tetrafluoroborate gave a dark-purple solution. Examination of the reaction mixture by ^1H NMR at ambient temperature in CD_3CN showed the presence of a 1,3-ditellurolylium salt: a two-proton doublet at 11.81 δ, J = 1.2 Hz, and a one-proton triplet at 15.0 δ, J = 1.2 Hz. The unusual downfield shifts are notable but expected from the trend set by compounds II and III (11.3 δ and 13.4 δ, respectively, for the 2H-proton).[3] Apparently, substitution of tellurium for selenium or sulfur as in IV places a higher degree of positive charge on the 2 carbon atom, resulting in a remarkable downfield shift of 4 ppm relative to sulfur.

However, the spectrum quickly changed at ambient probe temperature (~30°C), being replaced by another two-proton doublet at 13.8 δ, J = 6.9 Hz, and a one-proton triplet at 10.3 δ, J = 6.9 Hz. Note that the latter doublet is now downfield of the triplet absorption; also, the coupling constants have increased. Similar treatment of IVb-d with trityl tetrafluoroborate gave spectra consistent only with this final product (see Table 3); no intermediate 1,3-ditellurolyliums were detected.[8] Finally, the above spectrum disappeared upon precipitation of tellurium metal.

We explain the above spectral changes by proposing an initial hydride abstraction from IV, forming the 1,3-ditellurolylium cation V, followed by a rapid rearrangement of V to a 1,2-ditellurolylium ion VII, as depicted in Scheme 2. The 1,2-ditellurolylium cations were quite unstable; they rapidly deposited tellurium metal. The mechanism (Scheme 2) is reminiscent of a homoallyl-cyclopropylcarbinyl rearrangement. The activation parameters listed in Scheme 2 are consistent with a facile process involving significant ordering in the transition state. This ordering is probably due to a puckering in the ring, allowing the initial homoallyl-cyclopropylcarbinyl-like rearrangement to proceed. Apparently, the rate-determining step is the formation of intermediate VII, since alkyl and aryl substituents accelerate the rearrangement (we have not observed any 1,3-ditellurolylium



For R = H, by ^{1}H NMR

$k_{283} = 1.38 \times 10^{-4}\ \text{sec}^{-1}$

$k_{298} = 2.97 \times 10^{-4}\ \text{sec}^{-1}$

$\Delta H^{\neq} = 8.00$ kcal/mole

$\Delta S^{\neq} = -47$ e.u.

$\Delta G^{\neq}_{298} = 22.3$ kcal/mole

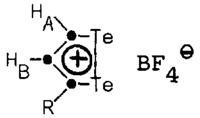
$E = 8.56$ kcal

$\log A = 2.75$

Scheme 2

ions when R ≠ H; only the 1,2-ditellurolylium ions were seen). The rearrangement appears to be regiospecific, since only cations with a terminal substituent were observed. This is consistent with the proposed mechanism. Finally, the ^1H NMR coupling constants for the 1,2-ditellurolylium ions VIIa-d are similar to those of their 1,2-dithiolylium analogues (~5 Hz) (see Table 2). The ^1H NMR multiplicities of VIIa-d are also similar to those of the sulfur analogues.[1c] We are currently investigating methods for stabilizing cation V and studying its chemistry.

Table 2. ^1H NMR Spectral Data of 1,2-Ditellurolylium Salts

	R	δH_A,[a] ppm	δH_B, ppm	*J*, Hz
	H	13.83	10.31	6.9
	CH_3	13.40	10.20	6.6
	$CH_3(CH_2)_3$	13.25	10.15	6.6
	Ph	13.30	10.61	6.9

[a] CD_3CN.

We acknowledge the assistance of J. M. Hewitt for obtaining the activation parameters for the rearrangement of V to VII. We also appreciate helpful discussions with Drs. F. R. Green III and L. H. Latimer.

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4. S. L. Bender, N. F. Haley, and H. R. Luss, Tetrahedron Lett., 1495 (1981).
5. This procedure is similar to Brandsma's preparation of chloromethylthioalkynes but modified specifically for tellurium chemistry (i.e., Na_2Te gave no IV); R. S. Sukhai, W. Verboom, J. Meijer, M.J.M. Schoufs, and L. Brandsma, Recl. Trav. Chim. Pays-Bas, 100(1), 10 (1981).
6. The correct chloromethyltellurole ether can be differentiated from the ditellurole ether by measuring the ratio of NMR peaks between the singlet methylene and its tellurium split doublet.
7. M. R. Detty, B. J. Murray, and M. D. Seidler, J. Org. Chem., submitted.
8. In all three substituted 1,3-ditelluroles only the 1,2-ditellurolylium cation was observed (Table 2); at 0°C, rearrangement of the corresponding 1,3-ditellurolylium cation had already occurred.

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